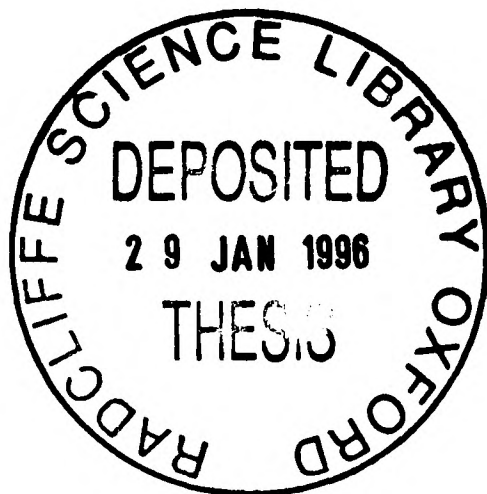


# **High Resolution Infrared Spectroscopy of Jet-Cooled Molecules**



**A thesis submitted for the degree of Doctor of Philosophy  
at the University of Oxford**

**Matthew Daniel Brookes  
Lady Margaret Hall  
Trinity 1995**



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The development and implementation of a high resolution, direct absorption, rapid-scanning infrared diode laser spectrometer incorporating a supersonic jet expansion source is described. High sensitivity is achieved by directly modulating absorption signals at frequencies in excess of 50 kHz, enabling their separation from lower frequency mechanical and diode  $1/f$  noise. This is accomplished by rapidly scanning the diode laser across a small frequency window ( $\sim 0.5 - 1.5 \text{ cm}^{-1}$ ) synchronously with a pulsed supersonic expansion in a time period of 1 or 2 ms. Absorptions appear as small attenuations in the overall variation of the laser mode power across the scan window. This background profile is removed by recording the laser power without gas pulsing and subtracting. Relative frequency calibration is effected by simultaneously recording the spectrum of a reference gas and the interference fringes of an etalon. Absorption signals are recorded by means of a fast 12-bit analog-to-digital converter operating at 1 MHz. This is housed within a dedicated PC microprocessor which performs spectrometer control, data co-addition, signal processing and spectrum calibration functions.

The spectrometer has been used to measure the infrared spectra of two weakly bound complexes, CO-OCS and Ne-SiH<sub>4</sub>. The infrared absorption spectrum of CO-OCS was measured in the  $5 \mu\text{m}$  region of the OCS  $\nu_3$  asymmetric stretch. In addition microwave spectra of CO-OCS and two isotopomers <sup>13</sup>CO-OCS and CO-OC<sup>34</sup>S have been recorded using a pulsed nozzle microwave Fourier transform spectrometer. The lines have been fitted to a Watson  $S$  reduction Hamiltonian yielding rotational, quartic and (for the ground states) sextic centrifugal distortion constants. A  $T$ -shaped structure is determined and this is rationalised by a simple potential model incorporating a distributed multipole analysis of the electrostatic charge distribution, distributed dispersion contribution and a cylindrical hard-core repulsion.

The infrared spectrum of Ne-SiH<sub>4</sub> was recorded in the vicinity of the SiH<sub>4</sub>  $\nu_3$  triply degenerate stretching vibration centred at  $2189.19 \text{ cm}^{-1}$ . Ne-SiH<sub>4</sub> is only the second atom-spherical top complex to be successfully recorded and analysed. The complex exhibits an intermolecular potential with considerably smaller anisotropy than its argon analogue Ar-SiH<sub>4</sub>. Consequently the SiH<sub>4</sub> unit is almost free to rotate within the complex, resulting in novel Coriolis interaction between the angular momentum of the SiH<sub>4</sub> unit and that of the overall complex. Individual bands are fitted to Coriolis interaction Hamiltonians, and the band centres for all the transitions of the complex are fitted to an anisotropic intermolecular potential.

Finally, applications of the spectrometer to the study of air sensitive compounds and species generated by electric discharge sources are considered.

# Preface

Amongst the synonyms for ‘enthusiasm’ offered by the thesaurus are words such as eagerness, warmth, zest— and mania. Dr Brian Howard, like no-one else I have met, combines all that is best in this characteristic *without* the negative aspects which may often accompany it. His energy and ingenuity are matched only by his aptitude for difficult mental arithmetic, and each new discovery is met with an excitement and exhilaration which is infectious. It is a privilege to have spent five years under his supervision (albeit unofficially for the last four), and I would like to take this opportunity to thank him for his friendship, guidance and patient explanations. And sense of humour (but don’t give up the day job). Without him this thesis would be considerably shorter (by some two hundred pages).

My thanks are due also to Dr John Brown, a valued tutor throughout my undergraduate course, who has allowed me the freedom to pursue fields of study outside his usual realm. He generously provided my funding for this doctorate via the European Community Molecular Ions Twinning Project (whatever *did* happen to those ions?) and a PC to ease the strain on the limited Howard group computing facilities. Prof. John Simons kindly provided additional financial support from PTCL funds during the fourth year.

Many others have contributed to the work in this thesis. Dr James Connelly sacrificed much of his time adapting his microwave software for the prototype rapid scanning spectrometer, and Andrew ‘C’ Barber provided invaluable help in interfacing the FLASH-12 card for the current version of the experiment.

Danny Clift injected his own unique methodology (not to say character) to the CO-OCS work, and was in part responsible for various enterprises (such as driving to Barcelona and back in four days and dressing up as spacemen (though not at the same time)) which can only be defended in retrospect by the flimsy excuse of ‘it seemed like a good idea at the time’. They were good times, Danny, notwithstanding the traumas (and no, it’s still not a Fourier transform spectrometer).

Danny Hughes has worked tirelessly during the last month to add a fitting routine to his potential program, despite being on the other side of the atlantic. He was there at the start with Ne-SiH<sub>4</sub>, and during the initial analysis of the  $R(0)$  transition. The memory of running fits an hour before his Part 2 thesis deadline still makes me shudder.

Dr Andrew Auty provided the impetus for the air sensitive compound work, in addition to valued help and guidance. Russell Low’s expertise on the microwave apparatus is responsible for the CO-OCS pure rotational transitions (bought any more microwave salads, Russell?) and Dimitris Skouteris wrote the Coriolis intensity prediction program used in figure 4.6. Chris Dennis generously loaned a desk to accommodate thesis related clutter, and Neville Baker ensured the smooth running of all the electronic bits and pieces. I would like to thank the group as a whole for a friendly and (except when Russell is word-processing) relaxed working environment.

Education without enthusiasm is lifeless and dull, and I wish to thank Simon Caspell and Dr Michael Cox, both former teachers at Poole Grammar School, for communicating science with excitement and making it fun. Without that perspective I would never have made it this far.

Over the last four years, 25 Wren Road has been a hotbed of domestic chaos, hoovering challenge and barbecues (in the summer). Thanks to all who made it so memorable, especially Barney and Leena— congratulations on your engagement!

The love and support of my family and friends remains very precious. I am doubly blessed in having parents who love each other and love me, and who have always believed in me but never pushed me. Mum and Dad, thank you. And Edward and Catherine, I'm proud to be your brother. I would also like to express my gratitude to my grandparents, Mr and Mrs F. G. Rowe, for their love, support and encouragement.

It's hard to single out individual friends for special thanks, but my love and appreciation go particularly to Alistair Cumberford, Danny Clift and Julie Chad. And to Mark and Viola Goodacre for their constant friendship and the privilege of being Godfather to Emily Jane.

Jacqueline Clare Fradin— thank you for your patient, enduring and unselfish love. This one's for you, Jack.

MDB July 1995.

It was with great shock and sadness that all of us in Oxford learnt of the tragic and premature death of Danny Hughes in Stanford, California on 23<sup>rd</sup> August this year. We were in close touch right up until the submission of this thesis, and his contribution to the Ne-SiH<sub>4</sub> work continued well beyond his Oxford days. He gave freely of his time and energy to help me with the potential fitting in the final stages, so characteristic of his warm and generous spirit. There is little doubt that he would have made a significant impact within the world of science, but far greater is the loss to his family and friends of a loved, respected and very excellent person. I would like to dedicate the Ne-SiH<sub>4</sub> work to Danny's memory.

MDB September 1995.



‘Mighty God!

Creator unbegun, unending!

Your works, when I think that they are yours, dazzle me to silence and to awe and awful prayer.

For I may know some little something of the sun, may take its temperature, may track its travels relative to other stars, may date its age, may predict its death, observe the windy rage of its digestion in the time between. But what do such solar figures do to the size of me? And what are my own travels and my age and my death beside this brutal fire in the universe? Tiny, tiny, insignificant. My God, the little that I know of your sun, and this but one among a sea of suns, belittles me. How is it that you love me?

For who can say, of those who did not see it, how first you bulged that sun into its place, and hammered its brazen face, and shocked it at the heart and set it afire? Who knows the word wherewith you commanded the sun to be? But when I can say with courage that I know I do not know; when I admit that I stand with my back to a void, that I am indeed blind to the beginning of things, then I am silenced. Then I am chilled by my own triviality—some dust at the edge of a desert. Nevertheless, you kneel down, and find me, and tell me that you love me.

And even as I am dust in space, so I am but an instant in time—always an instant, never more than this particular instant. Yet it is me. And behold! You enter from the other side of time; you stride from timelessness to this sole moment, to the ragged stretch of my existence, to me, to love me. How can such kindness be?

For you are wonderful beyond describing it. And yet you love me. And still you choose to notice me. And nonetheless, you bend you boundless being, your infinity, into space and time, into things and into history, to find me, to preserve my life.

Eternal God, such thoughts are too wonderful for me. They are high: I cannot attain unto them.’

Walter Wangerin Jr, from *‘Meditation on a New Year’s Day’*<sup>†</sup>

Καὶ ὁ λόγος σὰρξ ἐγένετο καὶ ἐσκήνωσεν ἐν ἡμῖν  
καὶ ἐθεασάμεθα τὴν δόξαν αὐτοῦ

‘And the Word became flesh and dwelt among us  
and we beheld His glory’

John 1.14

---

<sup>†</sup> Taken from *‘Ragman and other cries of faith’*, copyright © 1984 by Walter Wangerin Jr.

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# Chapter 1

## Introduction

### 1.1 Spectroscopy of molecular beams

The combination of high resolution spectroscopic methods with molecular beam sources has resulted in the development of extremely powerful techniques for the investigation of molecular systems across the electromagnetic spectrum from the radiofrequency region to the ultraviolet. The use of supersonic beams (or jets, if uncollimated) provides a sample characterised by a narrow velocity distribution in addition to a number of advantages specific to the individual spectroscopic technique employed. Broadly speaking these include the elimination of pressure broadening as a result of the collision free environment, the high degree of rotational and translational cooling undergone by species in the jet and, importantly, the ability to produce high concentrations of unstable species such as Van der Waals molecules (see § 1.2). An overview of the practical considerations pertaining to the spectroscopy of molecular beams is provided by Gough [1]. The following sections briefly review the history and current state-of-the-art in rotational, ro-vibrational and electronic spectroscopy of jet-cooled molecules.

#### 1.1.1 Pure rotational spectroscopy

Molecular beam electric resonance spectroscopy (MBER), developed by Rabi [2] and Hughes [3], utilises the Stark effect to probe molecules with permanent dipoles. By means of an inhomogeneous electric field the Stark effect is used to select molecules in a particular rotational state. Microwave or radiofrequency radiation is then tuned to match a transition between two states, and quadrupolar fields focus molecules in defined states

onto a detector [4, 5]. The linewidth is in principle determined only by the lifetime of the states in the radiation field, which for electronic ground states corresponds to the times of flight of the molecules through the radiation field. Sensitivity is independent of the transition frequency, and MBER spectra have been recorded from  $10^4$  to  $10^{15}$  Hz.

Van der Waals molecules have been extensively studied using MBER [6], most notably  $(\text{HF})_2$  [7,8], and electrical discharge sources have been used to create high vibrational temperatures [9] and generate rotationally cold free radicals [10, 11]. A recent modification of the technique using only one refocussing region combined with bolometric detection has observed rotational tunnelling transitions in  $(\text{H}_2\text{O})_2$  [12].

MBER has been superseded in sensitivity and resolution (though not in operating range) by pulsed nozzle Fourier transform microwave (FTMW) spectroscopy developed by Balle and Flygare [13] for the study of weakly bound molecular complexes. A supersonic expansion of gas is pulsed into an evacuated microwave cavity and polarized by a narrow bandwidth of microwave frequencies from a coherent source. Coherent emission is detected using superheterodyne detection and Fourier transformed to give spectra covering the polarizing bandwidth of a few MHz. The high sensitivity of the instrument and larger concentrations of Van der Waals complexes generated in pulsed as opposed to continuous expansions has enabled the study of even very weakly polar complexes such as  $\text{Ar-N}_2$  [14] as well as trimers and larger complexes such as  $\text{Ar}_n\text{-HF}$  ( $n \geq 4$ ) [15] and  $(\text{HCN})_2\text{-X}$  ( $\text{X} = \text{HF}, \text{H}_2\text{O}, \text{HCN}$  etc.) [16]. Hydrogen bonded interactions have been well studied using this technique (e.g.  $(\text{H}_2\text{O})_2$  [12] and  $\text{HCN-HF}$  [17]), and tunnelling motions of the nitrogen molecule have been studied in  $\text{N}_2\text{-OCS}$ ,  $\text{N}_2\text{-O}_3$  and  $\text{N}_2\text{-SO}_2$  [18]. More recently spectra of open shell species such as  $\text{Ar-NO}_2$  [19] and  $\text{Ar-OH}$  [20] (the latter generated in an electric discharge nozzle) have been reported.

The technique has also been extended to the study of diatomic molecules containing transition metals [21, 22], work greatly facilitated by the development of laser ablation methods [23, 24]. For example, rotational hyperfine structure has been observed in  $\text{CuCl}$  and  $\text{CuBr}$ , produced by ablating target rods of compressed  $\text{CuCl}$  or  $\text{CuBr}$  in the throat of a pulsed argon jet [25].

The rotational constants provided by microwave studies can be used to determine precise vibrationally averaged structures, and both MBER and FTMW experiments resolve

hyperfine structure resulting from nuclear quadrupole and magnetic dipole interactions [16] in addition to internal motion and tunnelling effects to a few kHz [18].

### 1.1.2 Infrared spectroscopy

Infrared spectroscopy is an extremely versatile technique, since practically all molecules (with the exception of homonuclear diatomics) possess one or more infrared active vibrational mode; microwave techniques are limited to polar species. It also provides information on the excited vibrational states of systems. Miller has reviewed the field of infrared laser-molecular beam experiments in a recent article [26].

Doppler broadening, which is a major limitation in the infrared region of the spectrum, is substantially reduced by the use of supersonic jets (particularly from slit sources), and ro-vibrational spectra are considerably simplified by the rotational cooling which occurs. Most infrared spectroscopy of molecular beams has centred around the study of Van der Waals complexes, although by no means exclusively. The first reported direct absorption infrared spectra utilising free jet expansions were obtained by Travis *et al.* [27] who studied systems such as CO<sub>2</sub>, SF<sub>6</sub>, WF<sub>6</sub> and UF<sub>6</sub> at rotational temperatures of  $\sim 20$  K.

The integration of Fourier transform infrared (FTIR) spectrometers with molecular beam sources is extremely difficult, though not impossible [28]. Therefore tunable laser sources are most widely used, in conjunction with one of several available detection methods. Direct absorption experiments are currently in the ascendency, with a variety of noise discriminating modulation techniques and slit expansion sources [29] enabling high sensitivities to be achieved. Pulsed nozzle sources not only increase the optical density of expansions but also allow the use of phase sensitive detection [30, 31, 32] or rapid scanning techniques to reduce the spectral bandwidth of the noise [33].

A variety of laser sources may be used. Diode lasers provide the best overall coverage of the infrared region, but suffer from low power output. The diode laser spectrometer in Oxford has been used to study many Van der Waals complexes, including rare gas-CO<sub>2</sub> complexes [34], Ar-SiH<sub>4</sub> [35] and Ne-CO [36]. The latter two are examples of non-rigid systems whose spectra yield significant dynamical information. Muentert and co-workers have used a colour centre laser to record absorption spectra of



HCCH complexes, including  $(\text{HCCH})_2$  [37], and Lovejoy *et al.* have studied  $\text{CO}_2$ -HF using a difference-frequency laser source [38].

The other main technique used is that of optothermal detection, where the laser induced change in the internal energy of molecules in the beam is measured by a liquid helium cooled bolometer [39]. The resolution of the spectra can be sub-Doppler if the molecular beam is skimmed. In addition, dynamical information is obtained from rates of predissociation. If the molecule of interest dissociates before it reaches the detector, the photofragments recoil from the beam resulting in a decrease in the overall energy delivered to the detector. Van der Waals and hydrogen bonded complexes typically display this behaviour [40]. By positioning the bolometer at an angle to the beam axis, the angular distribution of the fragments can be measured. These data can be correlated to their quantum states which can be determined by using a second laser to observe rotational transitions in the fragments. Such methodology has been used very effectively by Miller and co-workers to measure the internal state distributions of vibrational predissociation fragments from  $(\text{HF})_2$ , HF-DF and DF-HF [41].

Mass spectrometric detection can be used in a similar way to study molecules undergoing laser-induced photodissociation in the beam [42], although unlike bolometric detection this method cannot be used to obtain spectra of stable molecules since laser excitation does not change the molecular density in the ioniser. However, an adaptation of MBER to the infrared (by simply replacing the microwave field with an infrared laser) has enabled stable molecules to be studied [43].

Laser induced fluorescence lacks sufficient sensitivity in the infrared region for general high resolution work where detectors are much less sensitive than in the visible or ultraviolet. However, studies using this method have contributed to an understanding of intramolecular vibrational relaxation dynamics associated with the excitation of fundamental C-H stretching vibrations [44]. It has also been used in conjunction with efficient White cell [45] collection systems to study collisional energy transfer processes in selected systems [46].

The Van der Waals bond of weakly bound complexes can be probed directly by the use of tunable far infrared laser (FIR) sources. Saykally and co-workers have developed a tunable microwave-FIR sideband spectrometer and recorded zero electric field spectra of Ar-HCl [47].



### 1.1.3 Visible and ultraviolet spectroscopy

The absence of collisions in the free molecular flow region of molecular beams results in a quantum efficiency of 1 for the fluorescence of a molecule excited by the absorption of a laser photon, and therefore ultra-high sensitivity for excitation spectroscopy in the visible and UV regions. Still higher sensitivity can be achieved by the technique of two-photon ionisation. A second laser is used to ionise the excited molecules, and the ions are coupled into an ion-multiplier by an electric field.

The use of supersonic jets to simplify complex electronic spectra was pioneered by Levy and Wharton [48], who have used laser induced fluorescence to successfully elucidate the electronic spectra of large molecules such as tetrazine,  $\text{H}_2\text{C}_2\text{N}_4$  [49]. Levy *et al.* have in addition studied the structure and predissociation dynamics of complexes based on tetrazine and similar aromatics with rare gas atoms, such as  $\text{Ar}_n$ -aminotetrazine [50]. The number of available chromophores tends to limit visible/ UV studies of Van der Waals complexes, but complexes such as  $\text{I}_2\text{He}_n$ ,  $\text{I}_2\text{Ne}_n$  and  $\text{NaAr}$  have been studied [51]. Janda *et al.* have used two laser pump-probe techniques to investigate rare gas dihalogen complexes [52]. Radical and ion complexes such as  $\text{Ne-OH}$  [53] and  $\text{Ne-N}_2\text{O}^+$  [54] have also been investigated using electronic spectroscopy, and state-to state dynamics of predissociation in  $\text{Ar-OH}$  have been elucidated by Lester *et al.* [55].

In his review of the area, Demtröder considers an additional number of special techniques available to the electronic spectroscopist in conjunction with molecular beams which are outside the scope of this brief overview [56].

## 1.2 Van der Waals complexes

A perfect gas is described by the equation of state

$$\frac{p}{\rho kT} = 1 \quad (1.1)$$

where  $\rho = N/V$ , the number density. For a real gas,

$$\frac{p}{\rho kT} = Z \quad (1.2)$$

where  $Z$  is the compression factor. The deviation of  $Z$  from unity at non-zero pressure is a consequence of intermolecular forces, which are ultimately electrostatic in nature. Repulsive forces between atoms or molecules are a consequence of the exchange effect, and operate at very short range. According to the Pauli exclusion principle, two electrons cannot possess the same quantum numbers [57]. In the case of two discrete (filled shell) atomic or molecular units approaching such that there is overlap of electron clouds, this prohibits some electrons from occupying the region of overlap, and thus reduces the shielding between respective nuclei. Attractive forces, on the other hand, have a relatively long range, and comprise dispersion forces (e.g. Ar-Ar), induction forces (e.g. Ar-HCl), and dipole-dipole interactions (e.g. HCl-HCl). This latter category includes hydrogen bonding. Van der Waals complexes are weakly bound associations of atomic or molecular units (which may be charged) arising from such interactions rather than formal chemical bonds. They are characterised by long bond lengths (typically 3 - 4 Å) and low binding energies ( $\sim kT$  at room temperature).

These weak intermolecular forces play important roles in a variety of fundamental physical and chemical phenomena, from condensed phases to reaction dynamics and collisional energy transfer. Equation (1.2) can be rewritten as a power series in  $V_m$ , the molar volume, to give the virial equation:

$$pV_m = RT \left\{ 1 + B/V_m + C/V_m^2 + \dots \right\} \quad (1.3)$$

The second virial coefficient can be expressed in terms of the intermolecular pair potential  $U(\mathbf{r})$ ,

$$B(T) = - \frac{1}{2} \int d\mathbf{r} \left\{ \exp\left(- \frac{U(\mathbf{r})}{kT}\right) - 1 \right\} \quad (1.4)$$

forging a direct link between  $B(T)$ , a measurable macroscopic property, and  $U(\mathbf{r})$ . Measurements of  $B(T)$  provided early information on intermolecular potentials, although for bulk properties these are averaged over orientation, velocity distribution and many body interactions, giving radial information only. Experimental methods for extracting potential information from bulk properties are reviewed by Maitland *et al.* [58].

For molecular complexes, the intermolecular potential is a function of both separation and orientation, reflecting the electronic distributions and polarisabilities of the participating molecules. Spectroscopic studies therefore offer much greater insight into the nature of the interactions, which can then be extended to describe bulk properties. Molecular beam scattering experiments also provide information on the potential surface, but are somewhat confined to collisions involving one very small, light partner such as a rare gas atom or  $H_2$  [59].

The first spectroscopic studies of Van der Waals complexes were undertaken in low temperature static gas cells by Welsh and co-workers [60]. Although largely superseded by jet techniques, equilibrium methods offer the advantage of higher rotational states for the complexes formed than can be achieved in the low rotational temperature environment of a jet, and hence a higher information content. Very long absorption paths can be achieved, and the cells are readily integrated with high resolution infrared Fourier transform spectrometers. McKellar has used such a set-up to successfully record spectra of many Van der Waals molecules, including rare gas- $H_2$  complexes [61], CO- $H_2$  and CO-rare gas complexes [62], the latter in collaboration with groups measuring direct absorption spectra of the complexes in a jet [36, 63].

The development of molecular beam methods has revolutionised the study of weakly bound complexes by providing (once free molecular flow has been achieved) a high density of Van der Waals molecules in a rotationally cold and (almost) collision free environment. The principal spectroscopic techniques have already been discussed.

Recently, much activity has centred on the study of the dynamics of Van der Waals systems, particularly via infrared laser-induced vibrational predissociation [40]. Potential energy surfaces provide a common framework for the treatment of both structure and dynamics, and much theoretical effort has been directed towards the determination of

potential energy surfaces from high resolution spectroscopic data. The Ar-HCl system has served as one of the basic prototypes in the study of anisotropic intermolecular forces. Hutson and Howard obtained a potential by simultaneously fitting to molecular beam spectra, pressure broadening cross sections and second virial coefficients [64]. The potential correctly predicted a linear Ar-H-Cl geometry, but also indicated a secondary minimum at the alternative linear geometry Ar-Cl-H. More recently microwave and far infrared data have been used to confirm the presence of this secondary potential minimum [65]. Hutson has reviewed the general theoretical methods for the extraction of potential energy surfaces from spectroscopic data [66], and Nesbitt has evaluated the latest experimental means of probing potential energy surfaces via high resolution infrared spectroscopy [67].

The development of infrared laser-molecular beam spectroscopy has enabled both structural and dynamical information to be obtained from molecular systems [68]. The work in this thesis is primarily concerned with the development of an infrared direct absorption experiment in a supersonic jet to investigate the structure and dynamics of two previously uncharacterised (and very different) Van der Waals complexes, CO-OCS and Ne-SiH<sub>4</sub>. Chapter 2 covers the experimental development of a rapid-scanning infrared diode laser spectrometer used in conjunction with a supersonic jet expansion. Chapters 3 and 4 are concerned with the spectroscopy and analysis of CO-OCS and Ne-SiH<sub>4</sub> respectively, and the concluding chapter examines more general applications to the spectroscopy of unstable species.

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# Chapter 2

## The rapid-scanning infrared diode laser spectrometer

### 2.1 Introduction

Absorption or emission spectra arising from the ro-vibrational motions of molecules in the electronic ground state occur mostly in the infrared region. Fundamental vibrations of molecules generally occur in the mid-infrared between a few hundred and  $4000\text{ cm}^{-1}$ , and it is in this region that most infrared spectrometers operate. Combination bands and overtones can occur well into the near-infrared (up to  $15000\text{ cm}^{-1}$ ), whilst Van der Waals bonds, as a consequence of the much weaker interaction, have fundamental bands lying in the far-infrared, typically at wavenumbers of a few tens per centimetre [1].

Many different techniques have been used to study weakly bonded complexes and other unstable species in the infrared, such as Fourier transform infrared spectroscopy (FTIR) [2, 3], molecular beam bolometric techniques [4, 5], molecular beam mass spectroscopy [6] and direct absorption spectroscopy [7]. The diversity of the techniques stems from the different characteristics of the infrared laser sources used. General requirements for this region are reasonable power output (preferably of the order of mW), narrow bandwidth ( $< 10\text{ MHz}$ ), tunability and straightforward integration with supersonic jet sources.

FTIR has the broadest spectral coverage, although it lacks sensitivity at high resolution and is difficult to combine with supersonic expansions. It has however been combined successfully with cold static cells for the study of Van der Waals molecules [3]. Semiconductor diode lasers provide tunable infrared radiation of narrow linewidth across

a wide spectral range (0.4 - 34  $\mu\text{m}$ ). The power output of the ternary lead salt type diodes used in this work is much smaller than that of  $F$ -centre lasers ( $< 100 \mu\text{W}$  single mode compared with  $\sim 10 \text{ mW}$ ), and they are not as continuously tunable as difference frequency lasers over a single mode (50 GHz compared with 150 GHz). The higher power output of colour centre lasers makes them more suitable for a ‘pump’ type of experiment utilising bolometric detection of vibrationally excited species in a collimated molecular beam [8]. However, neither of these alternative sources is tunable over such a wide frequency range ( $450 - 3500 \text{ cm}^{-1}$ ) [9], and both are restricted to the spectral region above  $2500 \text{ cm}^{-1}$ . This makes them unsuitable for probing the vibrational modes of small polyatomic molecules which generally lie to lower wavenumber.

Diode lasers provide accessibility to this most important part of the infrared. Direct absorption techniques are currently the method of choice with diode laser sources; although they operate at low power, this is not in principle a problem for absorption experiments provided the laser itself is the dominant source of noise in the spectrum. In such a case the absolute power of the laser will not affect the signal to noise ratio.

## 2.2 Direct absorption infrared diode laser spectroscopy

There are a number of difficulties associated with direct absorption infrared spectroscopy. Infrared spectroscopy is intrinsically the least sensitive form of molecular spectroscopy, with small transition moments depending not upon the *absolute* dipole moment of a molecule but rather upon the small changes in dipole moment as the molecule vibrates. The dipole moment of a vibrating diatomic molecule can be written as a Taylor series which rapidly converges:

$$\mu = \mu_e + \left( \frac{d\mu}{dq} \right)_e q + \frac{1}{2} \left( \frac{d^2\mu}{dq^2} \right)_e q^2 + \dots \quad (2.1)$$

where  $\mu$  is the dipole moment,  $q$  is the vibrational coordinate and  $e$  denotes the equilibrium configuration of the molecule. The transition moment  $\mu_{nm}$  (between two states  $|m\rangle$  and  $|n\rangle$ ) is then given by

$$\mu_{nm} = \mu \langle m | n \rangle + \left( \frac{d\mu}{dq} \right)_e \langle m | q | n \rangle + \frac{1}{2} \left( \frac{d^2\mu}{dq^2} \right)_e \langle m | q^2 | n \rangle + \dots \quad (2.2)$$

where  $|m\rangle$  and  $|n\rangle$  represent the initial and final vibrational states of the molecule. The first term vanishes unless  $\Delta v = 0$  since  $\langle n | m \rangle = 0$  for  $n \neq m$ , and the infrared transition moment therefore depends upon the higher order terms. For a non zero transition probability (which is proportional to the square of the transition moment), we require (in first order)

$$\left( \frac{d\mu}{dq} \right)_e \neq 0 \quad (2.3)$$

$$\langle m | q | n \rangle \neq 0 \quad (2.4)$$

Equation (2.3) precludes homonuclear diatomics from having infrared spectra, whilst equation (2.4) gives rise to the  $\Delta v = \pm 1$  selection rule; the vibrational coordinate  $q$  can be written as a linear combination of raising and lowering operators by substituting  $y = (m\omega/\hbar)^{1/2} q$  ( $m$  is the reduced mass and  $\omega$  the angular frequency):

$$a \equiv \frac{d}{dy} + y \quad (2.5)$$

$$a^+ \equiv \frac{d}{dy} - y \quad (2.6)$$

$$q = \left( \frac{\hbar}{m\omega} \right)^{1/2} (a - a^+) \quad (2.7)$$

Overtone bands with  $\Delta v = \pm 2$  and greater arise from the second and higher order terms in the expansion (equation (2.2)), as well as vibrational anharmonicities, and are therefore correspondingly weaker.

Direct absorption experiments also suffer the attendant difficulties associated with detecting small differences in large background signals. For this reason, the principal sensitivity limitation for direct absorption infrared experiments is the amplitude noise of the laser. When the spectroscopy is concerned with molecules such as Van der Waals complexes which are unstable under normal conditions, it is therefore vital to maximise the sensitivity of the instrument as well as optimising the method of production of the species of interest. Indeed, generating sufficient concentrations of Van der Waals molecules is often the most difficult part of the experiment.

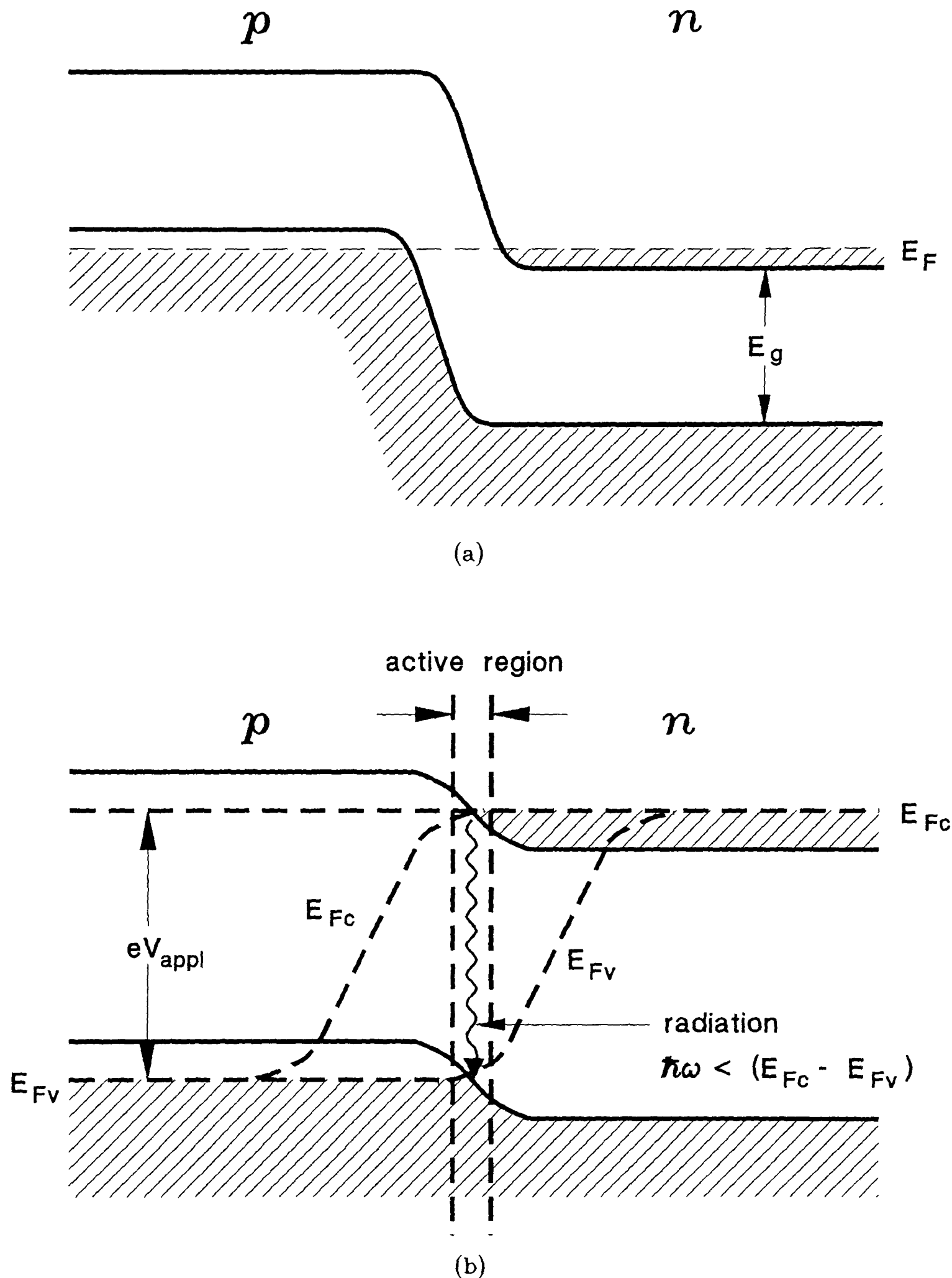
The next section outlines the theory of diode lasers, and the one following that summarises the experimental techniques which have been used to circumvent the practical difficulties associated with direct absorption infrared spectroscopy of unstable species in supersonic jets.

### 2.2.1 The diode laser

Tunable diode lasers (TDLs) have inherently low amplitude noise, particularly suiting them to direct absorption studies. The noise bandwidth can be further reduced by the use of modulation techniques such as those described in the following section. A complete account of the theory of diode lasers is documented elsewhere [10]. Those operating in the infrared are typically ternary lead salt type semiconductors ( $\text{PbS}_x\text{Se}_{1-x}$ ,  $x \approx 0.8$ ).

When a forward bias voltage is applied across a p/n junction in a diode, an ‘active’ region is produced. This has holes in its valence band and electrons in its conduction band with the result that two Fermi levels are produced. This is illustrated in **figure 2.1**. Photons with energies larger than  $E_g$ , the band gap of the semiconductor, but smaller than the difference between the two Fermi levels,  $E_{Fc} - E_{Fv}$ , can stimulate recombination of electrons and holes in the active region which results in the emission of a photon  $\hbar\omega$ . If an optical cavity is present to provide amplification, then above a certain threshold current stimulated emission can exceed spontaneous emission and lasing occurs. This cavity is provided by simply polishing the ends of the semiconductor crystal; the refractive index of most is sufficient to produce a suitable resonant cavity in this manner. Because of the band structure of the semiconductor, the gain profile for lasing is of the order of several wavenumbers. The small size of the diode laser (typically  $1 \times 1 \times 1$  mm) together with the refractive index of  $\sim 4$  results in an effective return path for the radiation of  $\approx 1$  cm; the longitudinal modes are therefore separated by approximately  $1 \text{ cm}^{-1}$ . For the purposes of this work, unwanted modes were removed by the use of a 0.5 m monochromator.

The radiation is tuned by utilising the temperature dependence of the energy separation of the two Fermi levels. Coarse tuning is achieved by varying the temperature of the diode between 10 and 90 K, depending on each diode’s individual characteristics. The very low temperatures required for the operation of infrared diodes require the use of a closed cycle helium refrigerator; the diode is mounted on a thermally insulated copper



**Figure 2.1** Schematic energy level diagram of a semiconductor diode laser  
(a) unbiased, (b) with a forward voltage bias.

block contained within an evacuated cold head. This contains the mechanical pump which drives the helium around its cooling circuit via a compressor and adsorber to maintain extremely high helium purity. Unfortunately this pump is also the source of considerable mechanical noise and therefore frustration for the spectroscopist.

Fine tuning of the laser frequency is effected by varying the current applied to the diode, which causes local heating of the active region. However, this also changes the gain profile of the laser and the length of the optical cavity through thermal expansion and changes in the refractive index. For uniform and continuous tuning these changes must be matched. ‘Mode hops’, abrupt changes in frequency, occur when the various rates lose synchronisation and a different gain profile becomes dominant. With careful tuning, modes typically extend  $0.5\text{--}2\text{ cm}^{-1}$ . Because of the dynamic nature of diode tuning characteristics with respect to the temperature, it is often possible to extend a given mode by up to  $1\text{ cm}^{-1}$  by thermally cycling the diode to room temperature and re-cooling, although this is by no means an exact science.

The intrinsic bandwidth of a diode laser is very narrow, although this is heavily dependent on the cooling system employed. Liquid helium baths can give figures as low as 22 kHz [11], but practically speaking between 1 and 50 MHz is a reasonable range for a diode cooled by a closed cycle helium compressor cold head system [12]. The 3 Hz motor of the cold head refrigerator is the main source of noise which results from two separate effects. Temperature instability is produced in the laser frequency as a result of uneven cooling rates at the beginning and end of each cycle, in addition to the mechanical shock the diode receives from the motor piston at the extremities of each cycle. This affects laser alignment, particularly through multipassing optics which are extremely sensitive to any change in the beam path, and potentially causes pressure tuning of the band gap and therefore frequency instabilities.

Recently infrared diodes have become available which lase at liquid nitrogen temperatures and higher (up to 120 K). These have many advantages over diodes requiring colder temperatures. Most notably, the cooling is achieved by the use of a liquid nitrogen dewar, which effectively eliminates all mechanical noise which plagues the helium compressor cold head system. The tunability of these diodes is also far superior, having longer modes (up to  $5\text{ cm}^{-1}$ ) which generally operate single mode with high power output ( $\sim 0.1\text{ mW}$ ). Sadly the advent of this technology was too late to benefit the work in this

thesis which was undertaken on the helium cooled system. Happily, the converse is not true and the rapid scanning system is currently being used with considerable success in conjunction with liquid nitrogen cooled diodes.

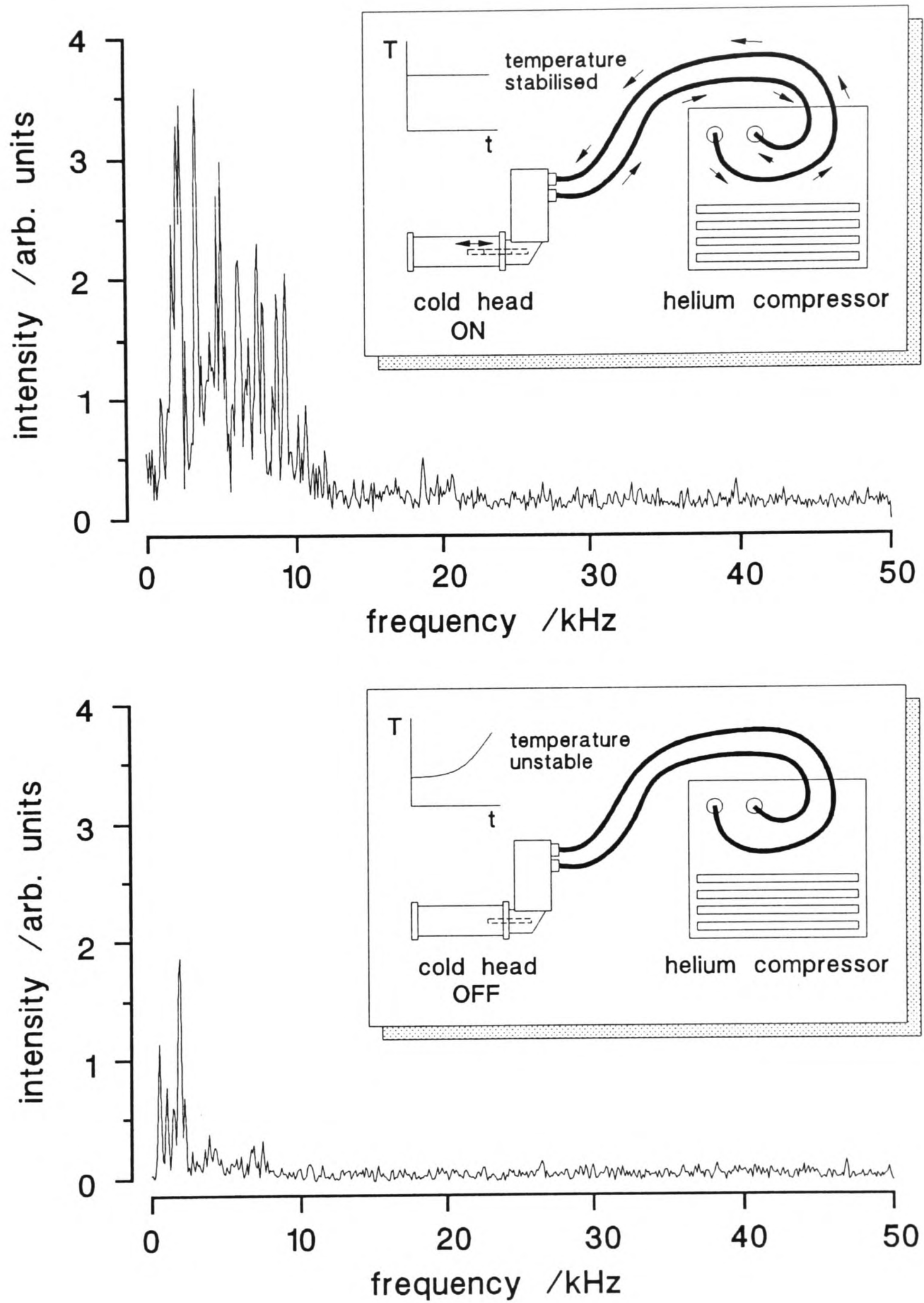
## 2.2.2 Modulation schemes

The frequency characteristics of the diode laser noise are demonstrated in **figure 2.2** which shows Fourier transformed noise spectra with and without the mechanical cold head pump in operation. These were recorded on the Oxford diode laser system by digitising at 100 kHz the laser power output at fixed laser frequency and Fourier transforming the result (see § 2.7.2). The power spectrum was then calculated from the sum of the squares of the real and imaginary components of the Fourier transform. The marked difference in the two profiles underlines the scale of the problem caused by the mechanical pumping of the cold head. Although the frequency of the pumping is ostensibly 3 Hz, the effect of residual vibration is evident in the laser noise spectrum at frequencies up to 10 kHz, and it is this smearing of the 3 Hz motor frequency over such a wide frequency range which makes it so hard to combat effectively. It is of course unfeasible to simply turn the cold head off during the course of each scan; an average scan takes ~ 5 minutes, and with the cold head off the temperature begins to rise within seconds.

There are two further sources of noise in the experiment. From **figure 2.2** it can be seen that even with the cold head off, there is low frequency noise present in the laser output. This noise has a  $1/f$  form typical of any semiconductor device, and is caused by the random spontaneous emission of photons from the diode, which occurs in addition to stimulated emission. The detectors are also semiconductor based devices with  $1/f$  noise characteristics, although as previously stated the laser noise is generally much larger than the detector noise, especially above  $1800\text{ cm}^{-1}$ , unless the laser power output is particularly low.

The detector used in this work for the jet data was an Infrared Associates liquid nitrogen cooled InSb detector; this gives an order of magnitude better sensitivity above





**Figure 2.2** Diode laser noise spectra with and without mechanical cold head pump operating.



1800 cm<sup>-1</sup> than HgCdTe detectors<sup>†</sup>, although these were used for the reference spectra where absorptions are much stronger and high sensitivity is not so important (see § 2.4). Its power output is 0.334 V (μW)<sup>-1</sup>, with a noise equivalent power (NEP) of 0.387 × 10<sup>-12</sup> W Hz<sup>-1/2</sup>. At 1 MHz laser bandwidth, the root mean square (RMS) noise is therefore 0.387 × 10<sup>-9</sup> W, with typical peak-to-peak noise of ~ 1.5 × 10<sup>-9</sup> W. For laser power of ~ 1 μW, this is only ~ 0.15 %. However, if the diode power is low (≤ 0.1 μW), the detector noise may contribute significantly such that it becomes the limiting factor in sensitivity. Whilst it is possible to effectively discriminate against the noise of the laser through modulation techniques, this is wasted effort if the diode power is so small that sensitivity is in fact detector limited. To take maximum advantage of ever improving diode laser modulation techniques, it is advantageous to have as high a diode power output as possible.

The principle behind the various modulation schemes which have been used in conjunction with diode lasers is simple. Sensitivity can be greatly enhanced by increasing the detection frequency of the signals to a region where laser noise, both 1/*f* and mechanical, is lower. The modulation schemes used can be loosely separated into two types, concentration modulation and direct laser (or source) modulation.

Concentration modulation shifts absorptions to high frequencies by directly modulating the production of the Van der Waals complexes (or other unstable species). The original pioneering work by Howard *et al.* utilised a pulsed nozzle to generate transient populations of Van der Waals complexes in a supersonic jet [13]. This technique has been progressively refined and used with great success to study a wide variety of Van der Waals complexes in the infrared including Rg-CO<sub>2</sub> complexes [14], CO<sub>2</sub> dimer [15] and Ne-CO [16].

An electronic clock provides trigger pulses at a frequency variable between 1 kHz and DC and is used to pulse the nozzle driver and, after a short delay, two boxcar integrators. The frequency of the trigger pulse is maximised without overloading the pumping system, typically 50 Hz for 250 μs gas pulses. The laser frequency is scanned very slowly, such that it is approximately constant for the duration of several gas pulses. The 250 μs pulsed jet produces transient absorption of laser power which is recorded by

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<sup>†</sup> The Ar-NO<sub>2</sub> spectra used as illustrations in this chapter fall below the 1800 cm<sup>-1</sup> threshold and therefore in these cases a HgCdTe detector was employed.

an InSb detector as already described. The effective modulation of the signals is at  $\sim 5$  kHz.

The detector signal is processed by a high pass filter which removes much of the low frequency noise, and also has the effect of differentiating the absorption signal. The two gates of the boxcar are positioned over the positive and negative halves of this derivative signal; each gate is  $\sim 100\ \mu\text{s}$  long with a time constant of about  $500\ \mu\text{s}$ , so that each gate is averaged over several gas pulses. The outputs of the two gates are then subtracted and averaged over a further time constant of 3 s. The purpose of this subtraction step is to remove more of the low frequency noise of the cold head, which has approximately equal amplitude over the two gates. However, any phase differences between the gates results in imperfect subtraction, and there is in any case a bandpass of frequencies around 5 kHz. **Figure 2.2** demonstrates that there is still substantial noise at this frequency, and this remains unfiltered. The final signal is recorded on a computer together with reference spectra for calibration purposes. Using this method it is possible to achieve an ultimate sensitivity of  $\sim 3$  parts in  $10^5$  corresponding to a signal to noise ratio of about 3000:1 for a 10 % absorption [17]. The technique can be further refined by acoustic monitoring of the cold head; if the pulsing of the nozzle is inhibited at either end of the pumping cycle when the noise is greatest, signals are only recorded during ‘quiet’ periods. However, as **figure 2.2** illustrates, the noise is distributed much more evenly over the cycle than the pure 3 Hz pumping frequency would suggest, and the improvement in signal to noise is a factor of 2 or 3 at best.

This limitations of this method lie in the threshold modulation rate imposed by the mechanical operation of the pulsed nozzle. In order to modulate at higher frequencies, the pulse length must be reduced, and even using a piezo-electric nozzle valve,  $150\ \mu\text{s}$  is the shortest pulse width possible. However, shortening the pulse width results in poorer complexation and therefore sensitivity is lost by virtue of a depletion in the numbers of Van der Waals complexes generated.

Recently a concentration modulation technique utilising a continuous jet with an AC discharge has been developed and used to study CO containing Van der Waals complexes [18]. An AC discharge perpendicular to the jet operating at 3 kHz destroys Van der Waals complexes, creating transient populations whilst leaving stable species relatively unaffected. Signals are recorded in conjunction with frequency modulation of

the diode laser. However, despite enthusiastic advocates, the technique remains unconvincing and offers no significant improvement in signal to noise over the gated detection scheme described above.

Direct modulation of the laser frequency is simple to achieve with diode lasers. One of their main advantages is the ease of tunability; the laser frequency can be rapidly tuned across a single mode simply by the application of a voltage ramp. Second derivative spectroscopy has been used with pulsed nozzles and involves the rapid ‘dithering’ of the laser frequency over a narrow region whilst the central frequency is slowly ramped under computer control [19]. In this way the infrared absorption signals are shifted to the 10 kHz region.

The rapid-scanning technique described in this thesis is in many ways the simplest of all, and enables absorptions to be modulated at 50 kHz. It is described in the next section.

## 2.3 The spectrometer

The rapid-scanning infrared diode laser spectrometer was first described by DePiante *et al.* [20] and has subsequently been used by Sharpe *et al.* to study CO<sub>2</sub>-hydrogen halide complexes [21] and Ar-N<sub>2</sub>O [22]. By rapidly scanning the laser across a small frequency window ( $\sim 1\text{ cm}^{-1}$ ), it is possible to record the entire spectrum across this window during a single gas pulse by means of fast digitisers. Thus the absorption signals are modulated directly by the scanning laser. By repeating the process over the same scan window, and co-adding of scans, sensitivity is improved through signal averaging.

At a scan rate of  $0.5\text{ cm}^{-1}\text{ ms}^{-1}$ , a typical absorption feature  $0.005\text{ cm}^{-1}$  FWHM (full width at half maximum) is modulated at a frequency in excess of 50 kHz.  $1/f$  noise in this region is an order of magnitude lower than at 5 kHz, resulting in a theoretical factor of 10 improvement in sensitivity over the gated detection scheme. Furthermore, low frequency cold head noise can easily be removed by the use of a high pass filter. The rapid-scanning technique emphasises the distinguishability of the signal from the noise. An absorption modulated at 50 kHz is readily distinguishable from 5 kHz noise at the same amplitude

because the latter is spread out in time and will appear as baseline undulation. The 50 kHz noise which is indistinguishable from the absorption signal is a factor of 10 smaller.

There are three main practical problems to be overcome. The first is simply acquiring the data rapidly enough and with sufficient digital resolution to record even small absorptions. This difficulty is exacerbated by the non-linearity of diode laser power output. Within individual modes the power may vary by an order of magnitude; the digitiser must have sufficient vertical resolution to record the power profile of the mode without missing small absorptions on the mode structure because they fall below the quantisation step of the digitiser.

Equally, a sufficient number of points must be collected during the opening of the nozzle and scanning of the laser. Increasing the pulse rate of the nozzle enables more scans to be recorded in a fixed time and hence better signal to noise per unit time. Faster pulse rates are achieved by using shorter pulses, and this requires faster digitisation. The scan rate is also limited by the time constants of the detectors used,  $\sim 2 \mu\text{s}$ . For an absorption feature to be described accurately, without distortion, it should take no less than two and ideally four or more time constants to scan through. This condition sets an upper limit on the scan rate of  $\sim 1.25 \text{ cm}^{-1} \text{ ms}^{-1}$ . For practical purposes, therefore, pulse widths of  $\sim 1 - 2 \text{ ms}$  with scan rates of  $\leq 1 \text{ cm}^{-1} \text{ ms}^{-1}$  yield the optimum repetition rate for scanning. This in turn requires an acquisition rate of  $\sim 1 \text{ MHz}$  in order to achieve a sufficient number of data points per line ( $\geq 5$ ). The requirement for the data collection is therefore a fast A/D which combines sufficient dynamic range with fast acquisition of data. Furthermore, the data must be quickly transferred from the A/D card to the PC controlling the experiment for processing, thus easy interfacing is also preferable.

The second and third practical requirements have already been mentioned in the above discussion, namely scanning the laser at a sufficient rate and with adequate repeatability, and pulsing the gas efficiently and generating optimum concentrations of Van der Waals complexes in the jet. Diode lasers are particularly suited to rapid frequency modulation, and have good stability characteristics over the duration of typical scan periods ( $\sim 15$  minutes). It is in principle a simple matter to coordinate the pulsing of the jet with the application of an adjustable voltage ramp to the laser control module. The pulsed nozzle must have good mechanical damping attributes which ensure it remains open throughout the  $1 - 2 \text{ ms}$  of the scan time. Any ‘bouncing’ of the nozzle during this period

would lead to perturbed gas flow and uneven concentrations of Van der Waals complexes across the scan window.

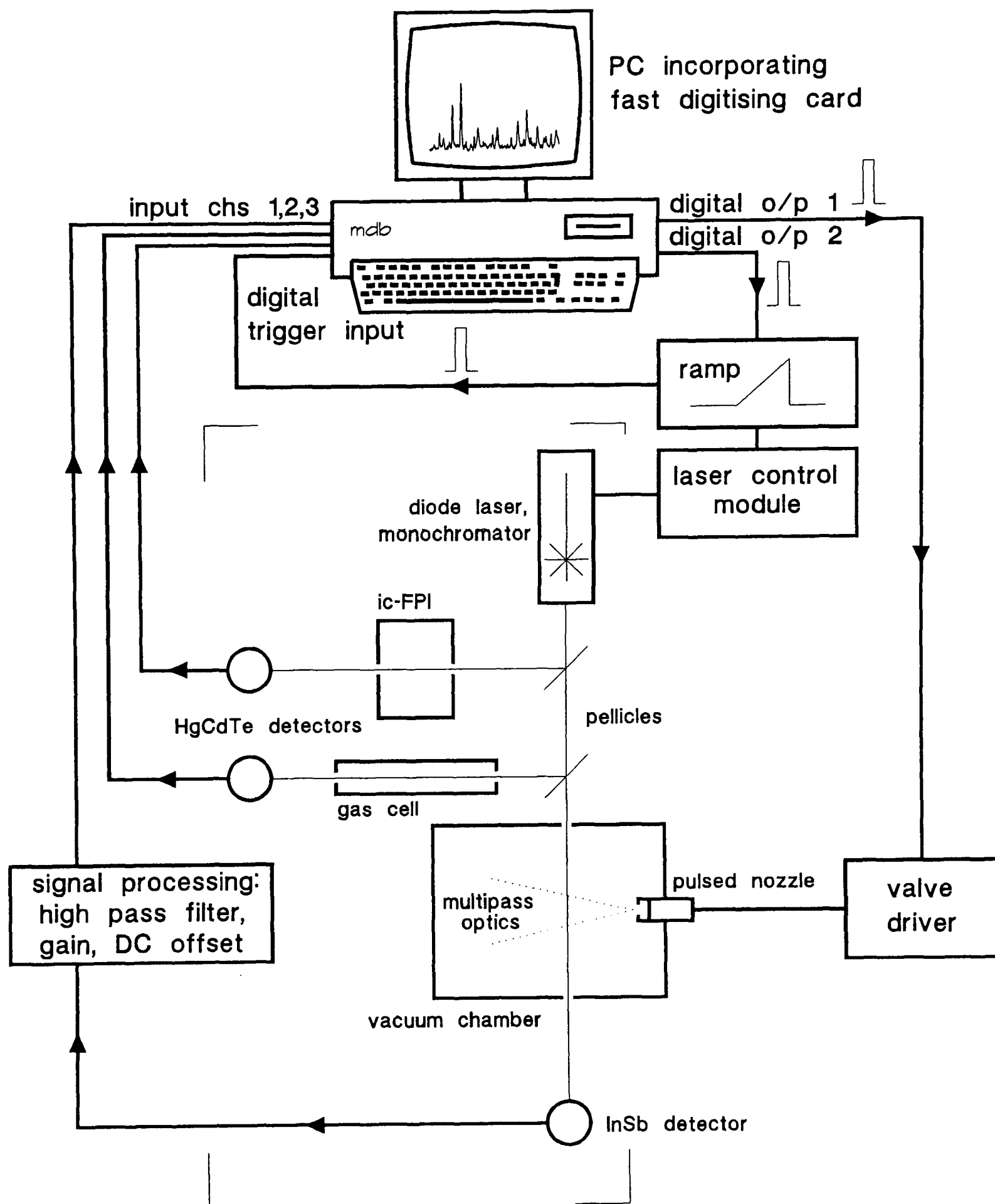
During its development the spectrometer has utilised two acquisition systems, based upon two different fast digitising cards. The two differ only in minor respects, the first using an 8-bit resolution card collecting on two channels, and the second (current) system employing a 12-bit single channel card; both operated at 1 MHz. The system configuration for the experiment is shown in **figure 2.3**. The spectrometer can be divided into three sections for discussion: the laser configuration, the supersonic jet, and the control and acquisition system.

## 2.4 The laser configuration

The cold head, containing up to four diodes, is fixed onto the optical table of a Laser Analytics LS-3 laser source spectrometer. Radiation emerges from the diode in a very divergent ( $f/1$ ) cone due to the very short resonant cavity. It passes from vacuum into air through a BaF<sub>2</sub> window and is focused into a parallel beam by a KBr lens, mounted on an xyz translatable stage for precise alignment. A 0.5 m Czerny Turner monochromator then removes unwanted modes, and the beam emerges onto the optical table.

An arrangement of two flat mirrors, one above the other, translates the horizontal movement of the laser beam resulting from the monochromator into a vertical plane. This is an important step in the reduction of the laser noise; the precise alignment of the beam through the multipass cell, which consists of two off parallel vertical mirrors in an horizontal plane, is unaffected by vertical movement of the beam. An horizontal displacement, however, would result in the beam clipping the edge of either the facing or reverse facing mirror (or both), with consequent noise problems.

**Figure 2.3** illustrates schematically the path of the beam once it has emerged from the monochromator. The tuning rate of a laser mode is not constant with the applied current, and therefore frequency calibration is very important. Absolute calibration, either by use of a wavemeter or by heterodyning the diode laser with a fixed frequency gas laser, is impractical. The procedure adopted is to simultaneously record the known absorption



**Figure 2.3** Schematic configuration of the rapid-scanning diode laser spectrometer.

spectrum of a well-characterised molecule and the interference fringes of an etalon with the supersonic jet absorption spectrum. Suitable calibrant gases must have several absorption lines in the scan frequency window and a spectrum measured to high accuracy. Linear triatomics generally meet these criteria, and spectra and line listings are available in reference texts such as those by Guelachvili and Rao [23] and Maki and Wells [24]. The former used FTIR spectroscopy giving line positions to an accuracy of 5 MHz, the latter heterodyne techniques with significantly better accuracy.

Two nitrocellulose pellicle beam splitters therefore each remove 5 % of the laser power, directing it through a gas cell in one case and an etalon with well defined spectral range in the other. Two etalons were used in this work. The preferred instrument is an internally coupled, confocal Fabry-Pérot etalon. This has the advantage that the free spectral range is almost independent of alignment (see § 3.3 and equations (3.1a) and (3.1b) in footnote). However, for weak laser modes a germanium etalon was used as it had better peak-to-trough fringe characteristics. The free spectral range of the germanium etalon is slightly larger ( $0.016\text{ cm}^{-1}$  compared with  $0.01\text{ cm}^{-1}$ ). The fringes of the etalon are used to interpolate between gas cell lines in order to measure the frequencies of transitions in the jet. The calibration spectra are recorded by two liquid nitrogen cooled Santa Barbara Research Center photovoltaic HgCdTe detectors. These are approximately a factor of 10 noisier than the InSb detector used for the jet (§ 2.2.2) above  $1800\text{ cm}^{-1}$ , but the calibration data are averaged over many ( $\sim 2000$ ) scans and the signals are usually sufficiently strong to be observed on a single scan.

The remaining 90 % of the laser power is guided into the vacuum chamber through a sodium chloride window and is incident on the multipass cell. This is a very simple arrangement consisting of two slightly off parallel mirrors. The radiation is made to ‘walk’ down and back up the mirrors, crossing the jet at between 0 and  $5^\circ$  from the normal. With an axisymmetric (pinhole) source, the major contribution to the Doppler broadening is from the jet itself and the components of the velocity perpendicular to the direction of flow. Up to about 25 passes are possible, though each reflection reduces the power of the incident radiation by  $\sim 5\%$ . A compromise between path length and laser power is therefore necessary. In fact, a larger number of passes can be disadvantageous because of the much lower number density of Van der Waals species further downstream (see § 2.5.1) where the majority of the passes must take place in order to accommodate the



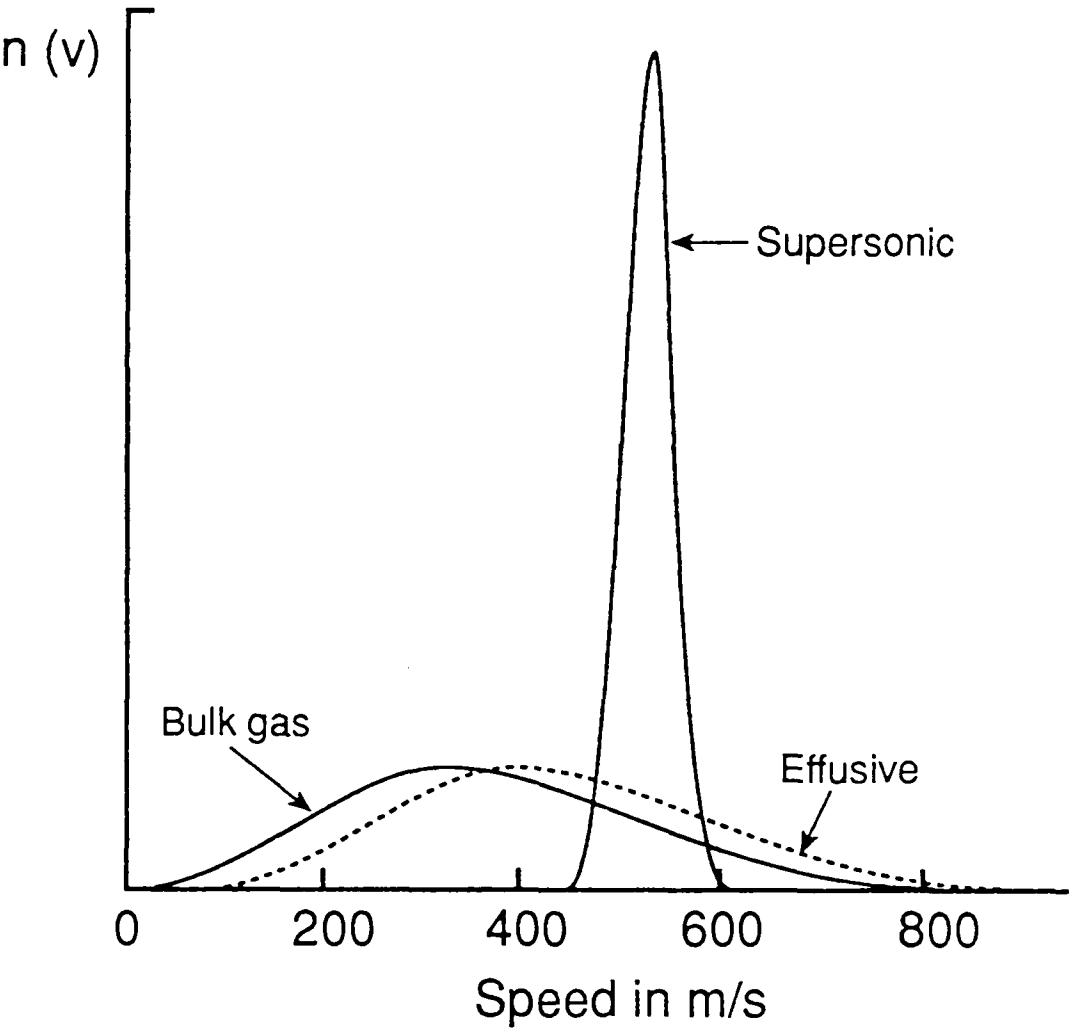
greater number of reflections. Typically 15 passes are made between 30 and 100 nozzle diameters (1 cm and 3.5 cm for a 0.35 mm nozzle) downstream in the expansion. The laser beam emerges from the chamber through a NaCl window and is focused onto a liquid nitrogen cooled Infrared Associates InSb detector, as described in § 2.2.2.

## 2.5 The supersonic jet

The term ‘molecular beam’ is commonly applied to the expansions used in these types of study, but since they are generally uncollimated a more accurate description is a ‘free jet’. The use of supersonic expansions allows the formation of internally cold, isolated species without the disadvantage of unwanted intermolecular perturbations which occur in solid state and matrix isolation studies. The low rotational temperatures obtained produce simplified, decongested spectra (with minimal monomer interference) in which line patterns are more readily recognised and thus bands more easily identified. Conversely, the lack of higher  $J$  transitions can make the determination of higher order rotational distortion terms difficult.

When a gas expands through an orifice from a high pressure to a low pressure region, the mean free path of the gas molecules in the region of the nozzle determine whether an effusive or a supersonic beam will be produced. In an effusive beam the gas molecules have independent dynamic properties, and this results from no collisions occurring in the region of the nozzle. Hence for an effusive beam,  $\lambda \gg D$ , where  $\lambda$  is the mean free path of the molecules at source pressure and  $D$  is the diameter of the nozzle. A supersonic jet occurs when  $\lambda \ll D$ . The gas molecules will then undergo many collisions as they travel through the nozzle aperture resulting in significant velocity collimation and reduction in translational temperature as the internal energy is converted into directed mass flow. At a nozzle backing pressure (i.e. source pressure) of 1.5 atm  $\lambda \sim 10^{-7} - 10^{-8}$  m, compared to the nozzle diameter of 0.35 mm. Simulated velocity distributions are shown in **figure 2.4**. As the gas expands the number density and hence the collision rate drops. The expansion density falls as  $x^{-i}$ , where  $i = 1$  for a plane jet and  $i = 2$  for an axisymmetric (pinhole) source. At a certain distance downstream from the





**Figure 2.4** Molecular speed distributions for argon in the bulk gas, effusive and supersonic expansions.

nozzle the collisions effectively stop and the velocity distribution is ‘frozen’. No further cooling occurs and the terminal Mach number  $M_T$  is reached; the Mach number  $M$  is defined as the ratio of the flow velocity  $V$  to the local speed of sound  $c$  [25]:

$$V = Mc = M \left\{ \frac{\gamma k T}{m} \right\}^{1/2} \quad (2.8)$$

where  $\gamma$  is the ratio of the specific heat capacities  $C_p/C_v$ ,  $m$  is the mass of the gas atom or molecule,  $T$  is the local temperature and  $k$  is the Boltzmann constant. For an adiabatic and isentropic expansion of a perfect gas, the thermodynamic properties of a supersonic expansion can be determined from  $\gamma$  and  $M$  [26]:

$$\left( \frac{T}{T_0} \right) = \left( \frac{\rho}{\rho_0} \right)^{\gamma-1} = \left( \frac{p}{p_0} \right)^{\frac{\gamma-1}{\gamma}} = \left( 1 + \frac{(\gamma-1)}{2} M^2 \right)^{-1} \quad (2.9)$$

where  $T$ ,  $\rho$  and  $p$  are the temperature, density and pressure respectively with the subscript zero indicating conditions behind the nozzle. The flow velocity is then given by

$$V = \left[ \frac{k T_0}{m} \left( \frac{2\gamma}{\gamma-1} \right) \left( 1 - \frac{T}{T_0} \right) \right]^{1/2} \quad (2.10)$$

For a continuum gas flow (i.e. before the terminal Mach number is reached) at a distance  $x$  downstream from a pinhole nozzle, the Mach number is a function of the ratio  $x/D$  where  $D$  is the nozzle diameter (provided  $x$  is greater than a few nozzle diameters) [27]:

$$M = A \left( \frac{x-x_0}{D} \right)^{\gamma-1} - \frac{1}{2A} \left( \frac{\gamma+1}{\gamma-1} \right) \left( \frac{x-x_0}{D} \right)^{1-\gamma} \quad (2.11)$$

$x_0$  is an ‘effective’ source for the nozzle and  $A$  is a function of  $\gamma$  and is equal to 3.20 for a monatomic gas. The terminal Mach number is determined by the source pressure  $p_0$  and the nozzle diameter, and for an argon expansion is given by [28]

$$M_T = 133 (p_0 D)^{0.4} \quad (2.12)$$

for  $p_0/\text{atm}$  and  $D/\text{cm}$ . Thus for a pure argon expansion from a 0.35 mm axisymmetric nozzle with a 2.5 atm backing pressure, equation (2.12) gives  $M_T \approx 50$ , equation (2.9) yields  $T = 0.35 \text{ K}$  (if  $T_0 = 298 \text{ K}$ ) and equation (2.10) gives  $V = 556 \text{ m s}^{-1}$ .

Formation of clusters in the jet result in slightly higher temperatures than predicted, and seeding the expansion increases  $T$  as a result both of mixed clustering and having to cool more internal degrees of freedom in the case of molecular species. Provided the

mixtures are dilute, the seeded molecule will attain approximately the same velocity distribution as the rare gas carrier. The internal degrees of freedom of the seeding molecule are cooled by the refrigerant effect of the cold translational bath provided by the rare gas carrier. Small quanta of energy are removed more efficiently, resulting in higher vibrational temperatures than rotational; the rotational temperature tends to follow the translational temperature quite closely. The final state of the system is kinetically determined, since the seeding molecules are only in collisional contact with the rare gas carrier for a finite period of time<sup>†</sup>.

Pulsing the nozzle has the advantage of ensuring low background chamber pressure during the expansion of the gas. The chamber is pumped by an Edwards E 09 unbaffled oil diffusion pump ( $2400 \text{ l s}^{-1}$  of air at  $10^{-4}$  Torr) backed by a Leybold Trivac D 40 B; the background chamber pressure is typically  $10^{-7}$  Torr which rises to  $10^{-4}$  Torr when the nozzle is pulsing. A low chamber pressure minimises problems with shock waves, which are caused by the fast moving gas beam striking the ‘stationary’ background gas. The use of longer gas pulses can result in jet molecules being reflected back from the end wall of the chamber and causing scattering effects; a 2 ms gas pulse travelling at  $600 \text{ m s}^{-1}$  has a length of 1.2 m, compared to a chamber length of  $\sim 1$  m. However, any such effects occur well beyond the region of the expansion close to the nozzle which the laser probes.

## 2.5.1 Cluster formation

Van der Waals molecules are formed by three body collisions occurring in the initial, high number density region of the expansion, provided the mean thermal energy of the expansion is lower than the Van der Waals binding energy. Subsequent two body collisions result in either further cooling or higher order cluster formation until the collision free environment of free molecular flow is achieved. Provided the Van der Waals molecules are formed in the bound state they cannot dissociate by tunnelling, and only collisional fragmentation can occur; the rate of destruction thus falls with the number density.

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<sup>†</sup> During the course of this study evidence has been found of quasi-equilibration within the bimolecular collision region of the expansion resulting in preferential forming of more stable complex isotopomers (see § 4.5.2).

Hagena [29] has comprehensively reviewed the experimental and theoretical aspects of cluster formation in molecular beams. A few nozzle widths  $D$  downstream is the so-called hypersonic flow regime, where the streamlines are almost straight and the flow velocity is approaching its maximum value. The centreline flow properties can be written in terms of the reduced source distance  $\delta = x/D$ . For a monatomic gas expansion, the density ratio is given by

$$\frac{n}{n_0} = 0.150 \delta^{-i} \quad (2.13)$$

and the temperature ratio by

$$\frac{T}{T_0} = 0.282 \delta^{-(2/3)i} \quad (2.14)$$

where the subscript zeros refer to initial (behind the nozzle) conditions and  $i = 1$  for a plane jet and 2 for an axisymmetric jet. The (termolecular) rate of formation of bimolecular complexes for an axisymmetric jet is proportional to the density cubed or  $\delta^{-6}$ ; the density of the expansion falls more rapidly than the temperature, resulting in too high a temperature in the early stages of the expansion to stabilise complexes formed in the high density region. There is a rapid increase in complex formation once the mean thermal energy has fallen below the Van der Waals dissociation threshold ( $\sim 100 \text{ cm}^{-1}$  or  $< 144 \text{ K}$ ), but this quickly falls off as the density decreases. Further downstream the bimolecular removal of dimer to give trimers and higher clusters (with rate proportional to  $\delta^{-4}$ ) becomes dominant.

The slower temperature and density reduction in a plane jet results in greater clustering, although the clusters formed may be of higher order than desired. The other benefits of plane (or slit) expansions are the extremely long path length and significant reduction in Doppler width of the transitions,  $\sim 20 \text{ MHz}$  [22] compared with  $\sim 150 \text{ MHz}$  for axisymmetric expansions; only those gas molecules at the very edge of the slit have significant velocity components perpendicular to the direction of gas flow. The much higher throughput of gas necessitates much slower pulse rates, and pulsed slit nozzles are very difficult to seal effectively. Despite this, the immense sensitivity and resolution enhancement have resulted in pulsed slit nozzles [30] becoming widely used in infrared absorption spectroscopy [20, 21, 22].

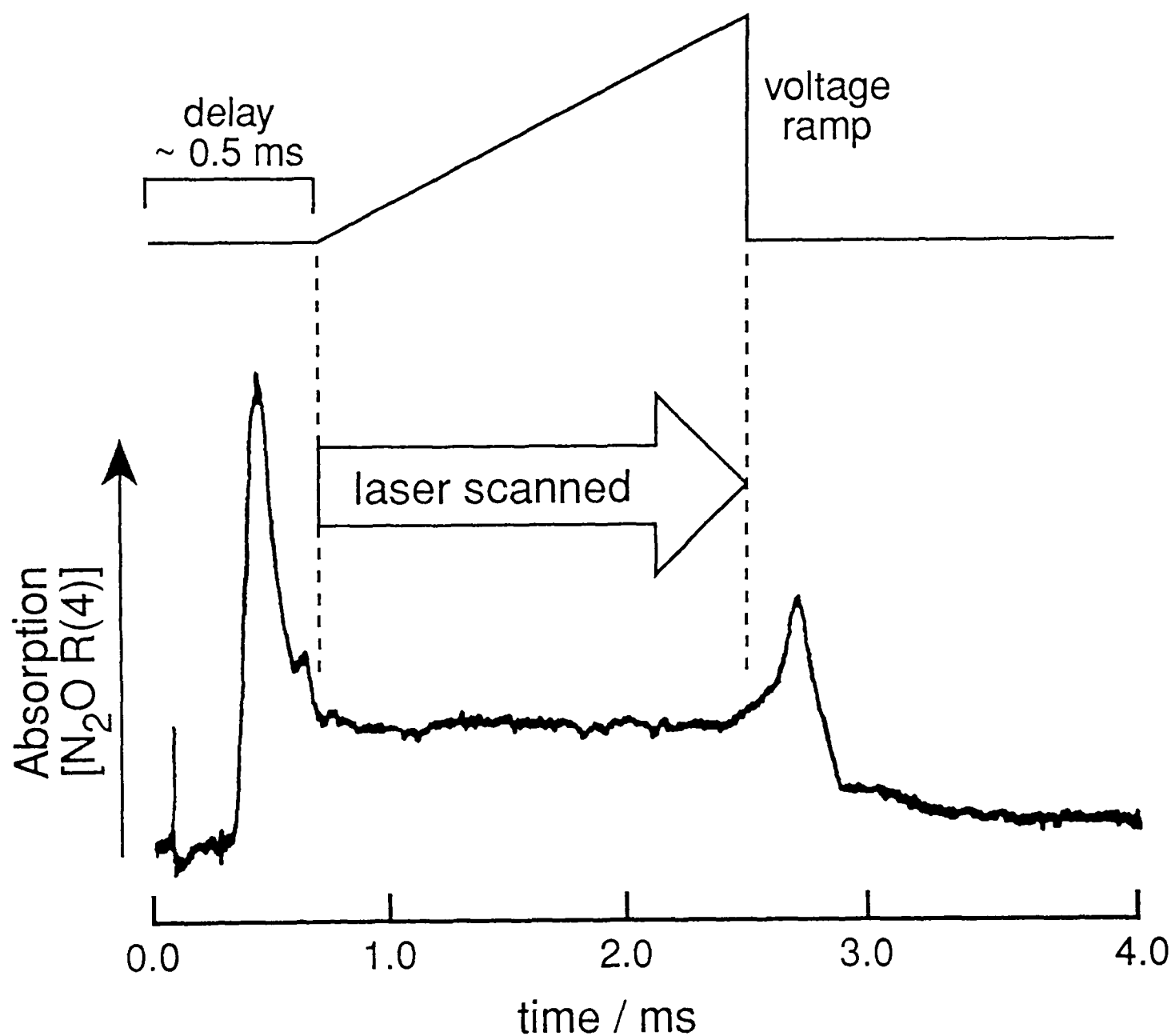
An axisymmetric expansion was used in this work, which enabled a faster scan repetition rate. The previous pulsed nozzle system used in conjunction with the gated detection scheme utilised a piezo-electric Lasertechnics valve, but this was found to be unsuitable for producing smooth pulses longer than  $\sim 500\ \mu\text{s}$  because of poor damping characteristics; the sealing plunger tended to bounce shut producing unstable gas flow. For this work, a General Valve Corporation Series 9 solenoid operated nozzle was used, with a specially built driver unit to minimise electrical noise<sup>†</sup>. This produced smooth pulses of the required length (1 - 2 ms). The opening characteristics of a nozzle can be monitored by locking the laser frequency to a low- $J$  monomer transition and recording the transient absorption with time as the nozzle is pulsed. This is illustrated in **figure 2.5**, which shows the synchronisation of the laser scan with the nozzle opening. The absorption is strongest at the beginning and end of the pulse, where the movement of the sealing poppet causes perturbed gas flow and a much lower effective backing pressure, minimising complexation. Once the nozzle is fully open, the depletion in the monomer intensity reflects the greater cooling and complexation occurring. In order to achieve 2 ms of stable gas flow, a pulse width of  $\sim 3$  ms is necessary. A 0.35 mm diameter nozzle<sup>††</sup> fitting was machined for use with the valve.

Typical gas mixtures are  $\sim 1\%$  molecular species in a rare gas for Rg-molecule complexes, with higher molecular concentrations used for the formation of molecular dimers or mixed molecule complexes. In these cases it is normal to use neon as the carrier gas. Its smaller polarisability results in lower Van der Waals binding energies in its complexes and therefore preferential formation of the desired non-neon complex. Both studies presented in this work utilise neon expansions. Neon is more efficient in cooling vibrations because of its shorter collision time scale than argon (and hence higher frequency energy transfer) [31], resulting in lower temperature expansions. Typical rotational temperatures for neon expansions are  $\sim 1$  K (see § 3.4 and § 4.5.2) compared with 5 K for argon expansions [31]. Higher backing pressures are generally required to ensure

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<sup>†</sup> There are three high voltage noise spikes associated with each operation of the nozzle. The first and last relate to the opening and closing of the nozzle respectively. The second spike results from a 'sustaining' pulse which the driver delivers to the solenoid  $\sim 200\ \mu\text{s}$  after opening to prevent the plunger bouncing shut. The commercially produced 'Iota One' driver unit was found to produce such large RF noise at these points that the induced voltages in the experimental system were causing laser instability. A custom built noise shielded driver was therefore constructed by Mr K. Valentine of the PTCL electronics workshop.

<sup>††</sup> Constructed by Mr L. Hill of the PTCL mechanical workshop.



**Figure 2.5** Synchronisation of the laser scan with the gas pulse. The depletion of the monomer absorption in the central region of the gas pulse is due to rotational cooling and the formation of Van der Waals complexes.

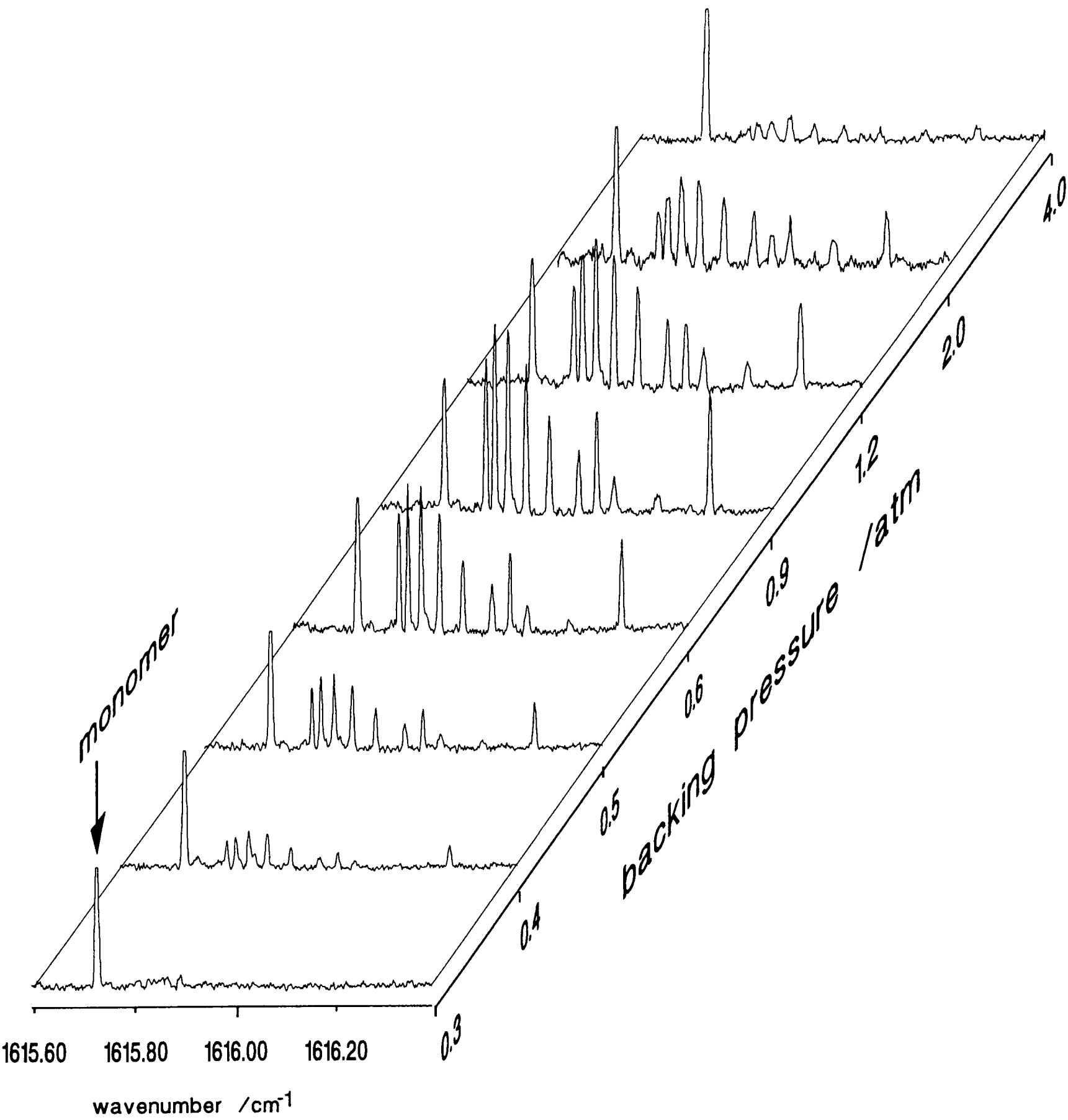


Figure 2.6 Variation in Ar-NO<sub>2</sub> concentration with backing pressure (0.5 % NO<sub>2</sub> in Ar).



there are sufficient collisions early in the expansion to facilitate fast cooling. However, the generation of complexes in the jet depends upon many factors including the nature of the molecules involved, and in practice the optimum conditions are determined largely by informed trial and error. **Figure 2.6** shows the dependence of complex formation upon backing pressure for the Ar-NO<sub>2</sub> complex, the  $^RQ_0$  band of which is shown. (The labelled monomer absorption is due to multimoding of the diode and should not in fact appear at the frequency indicated by the scale.) At high backing pressures the peaks begin to show a broader doublet structure due to the formation of higher clusters. The line broadening and central dip are due to the greater collision rate along the axis of the beam than off axis; the Ar-NO<sub>2</sub> is thus mainly present in the ‘wings’ of the expansion, with higher clusters forming along the axis. In these experiments the spectral linewidth is due solely to the factors of Doppler and laser broadening, already discussed. The other general source of line broadening in experiments of this type is vibrational predissociation; the energy of an infrared photon is in general much larger than the binding energy of a Van der Waals molecule, and if a dissociation channel exists then very short lifetimes may result.

## 2.6 The control and acquisition system

Once the diode laser has been tuned to a suitable mode, the entire operation of the spectrometer is under computer control. Four separate data samples are required for each cycle of the experiment. In addition to the absorption spectrum in the jet and the two calibration spectra (gas cell and etalon), a background signal is required from the jet detector (i.e. the detector signal when no gas is pulsing) to enable subtraction of the baseline to give a normalised absorption spectrum. A timing scheme for a single cycle of acquisition is illustrated in **figure 2.7**. (The timing scheme applies to the most recent acquisition system, but differs from the previous system only in that it operates on a single channel and therefore requires four separate acquisitions per cycle rather than the 2 × 2 ‘parallel’ acquisition possible on the dual channel card.)



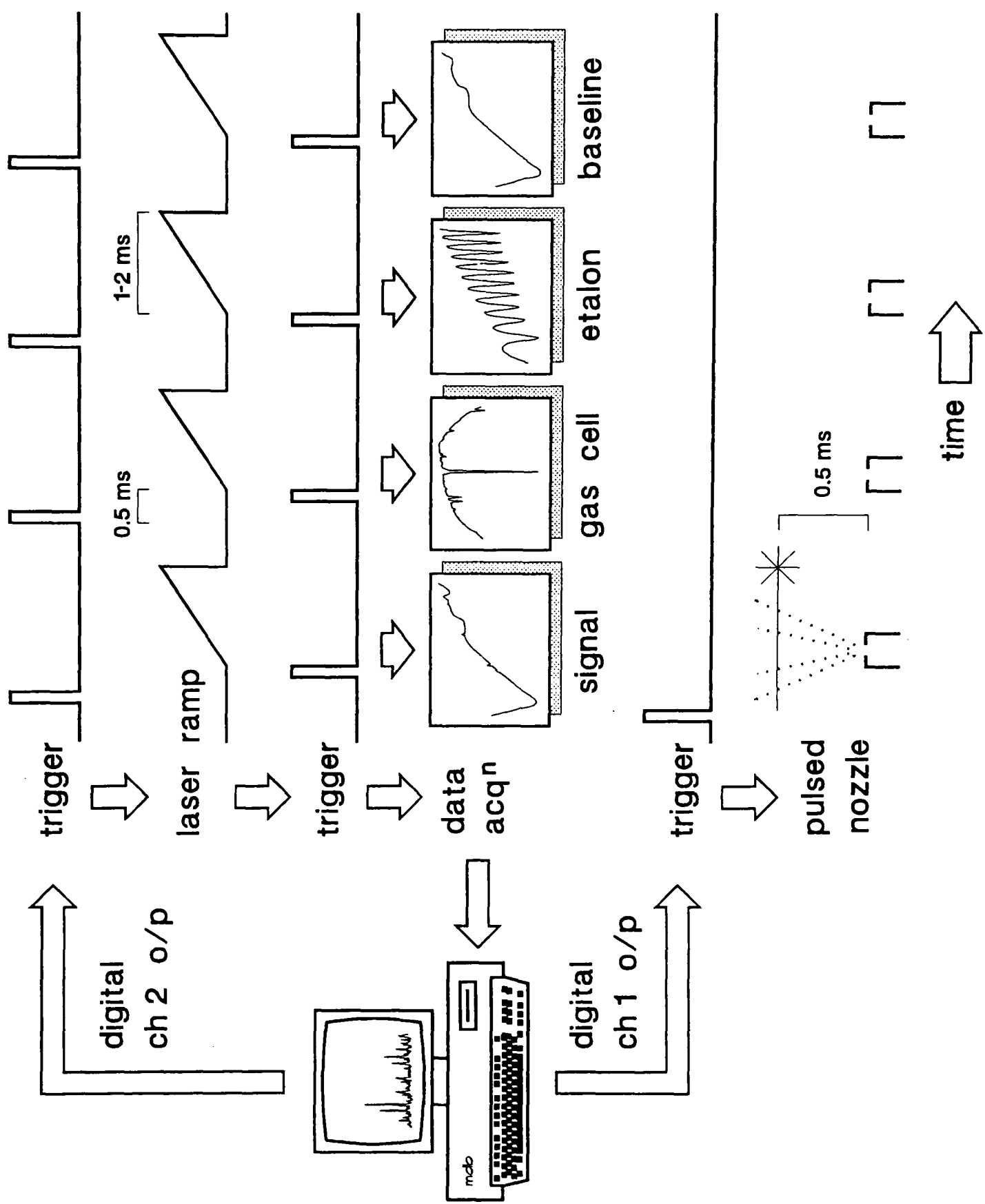


Figure 2.7 Timing schematic showing one cycle of data acquisition.

Two fast A/D based acquisition systems have been used. The initial prototype spectrometer utilised an 8-bit resolution Markenrich WAAG (waveform acquisition and arbitrary generation) board, which operates at a maximum of 20 MHz with 16 kbytes of onboard memory. A PC-30 card was also required in this configuration to provide output pulses to scan the laser and open the nozzle valve. The WAAG card was capable of operating on two channels simultaneously; the gas cell and etalon detector outputs were multiplexed to channel two whilst the jet detector was monitored by channel one. The valve was pulsed every other laser scan, and data recorded in the parallel fashion described above: {jet + gas cell}, followed by {background + etalon} (see also § 3.3). The card was used at 1 MHz per channel to collect 2048 data points per scan. The interfacing software was adapted from that used in a pulsed nozzle Fourier transform microwave spectrometer (see § 3.2.1) by its author, James Connelly [32].

The nature of the experiment results in a direct correlation between the ultimate sensitivity of the instrument and the digital resolution of the A/D converter. It was found that 8-bit resolution was insufficient to detect very small absorptions (see footnote and discussion on p. 64) and a higher resolution digitiser was sought. The twin requirements of resolution and speed are hard to find together, most available hardware concentrating on only one; thus many 16-bit cards are available but with kHz acquisition rates, and the WAAG card itself is an example of a high speed board with limited resolution. The current system, shown in **figures 2.3** and **2.7**, incorporates a 'FLASH-12' 12-bit 1 MHz single channel A/D converter manufactured by Strawberry Tree Inc. This was found to be the best compromise between speed and sensitivity. Digital oscilloscopes are the acquisition instruments of choice, providing 12-bit resolution at 5 MHz collection rates [21], but were unfortunately prohibitively expensive.

The FLASH-12 is automatically self-calibrating, with a bipolar full scale range of  $\pm 5$  V and therefore 2.44 mV resolution, with  $\pm 0.05$  % accuracy. Typical internal rms noise is 2.5 mV. It has the additional advantage of digital input/output channels for triggering the laser scan and valve driver, and a 64 kbyte on-board memory buffer for storage of data before it is transferred to the operating PC. The FLASH-12 is fully software controlled by dedicated code written in 'C', and user options allow the collection of either 1 or 2 kbytes of data (1024 or 2048 data points corresponding to  $\sim 1$  ms or  $\sim 2$  ms scans), and a variable number of scans.

Each acquisition cycle consists of four separate data acquisitions, but only one gas pulse. Referring to **figures 2.3** and **2.7**: the digital output channels 1 and 2 are synchronised such that at the start of each cycle both channels output a pulse simultaneously. Digital o/p 1 triggers the pulsed valve, whilst o/p 2 triggers the linear voltage ramp to scan the laser. There is a delay of  $\sim 500 \mu\text{s}$  before the laser is scanned to allow the nozzle time to open fully and the gas to reach the interaction area ( $\sim 1 - 3.5 \text{ cm}$  from the nozzle) as illustrated in **figure 2.5**. At the beginning of the laser ramp a digital trigger is sent by the ramp controller to the FLASH-12, and 1 MHz data collection is initiated on input channel 1. The electronically filtered InSb detector signal from the jet is thus digitised in 1024 or 2048 data points as the laser frequency is scanned. Digital o/p 1 then remains silent for the rest of the cycle. Digital o/p 2 pulses three more times and the input channel on the FLASH-12 is cycled through channels 2 and 3 to record the gas cell and etalon traces, back to channel 1 to record the background spectrum. The four sets of data are then read into the PC memory, the FLASH-12 buffer is cleared and the cycle is repeated, typically 2000 times for a standard spectrum. The rate of data collection is limited by the speed of the PC's 386 processor to  $\sim 8 \text{ cycles s}^{-1}$  for 1 k scans, and  $\sim 4 \text{ cycles s}^{-1}$  for 2 k scans.

The signal/noise improvement factor for  $n$  coadditions is  $\sqrt{n}$ , since noise adds with random phase, thus doubling the number of scans results in a  $\sqrt{2}$  sensitivity enhancement. Laser stability is crucial for the duration of the data collection. The internal temperature stabiliser in the Laser Photonics Laser Control Module provided sufficient stability for typical scans of  $\sim 10$  minutes without the need for additional frequency stabilisation. This can be accomplished by monitoring the zero crossing of an etalon fringe using a gated integrator and feeding the voltage recorded over a suitable time constant back to the temperature stabiliser [20].

## 2.7 Signal processing

The InSb detector signal is electronically processed before it reaches the FLASH-12 card in order to match the measured signal to the input requirements of the digitiser, and also to remove low frequency cold head noise. The InSb detector has a +2 V DC offset on its

signal which must be removed so that the laser mode can occupy all the available 12-bit dynamic range of the card. This is accomplished by use of a variable high pass filter<sup>†</sup>, which may be set at 2.0 kHz, 1.5 kHz, 1.0 kHz, 0.5 kHz or 0.0 kHz. At this lowest setting the filter works as an AC couple, removing the 0 kHz DC component but not filtering any frequencies >0 kHz. The bandpass of the filter is ~ 1 MHz. The resulting AC coupled signal is then amplified such that it occupies the full  $\pm 5$  V input range. To facilitate this there is a variable DC offset which can be used to ‘centre’ the laser mode profile at zero volts.

The high pass filter not only removes much of the low frequency noise apparent in **figure 2.2**, but also has the effect of ‘compressing’ any variations in the laser mode power output. This enables greater amplification of the signal resulting in better signal to noise, as illustrated in **figure 2.8** for a single cycle of data collection. However, the high pass filter also has the effect of phase-shifting signals at frequencies higher than the 3 dB point<sup>††</sup> indicated by the filter frequency setting. Precisely this effect was used with the gated detection scheme to ‘differentiate’ the transient absorption signals. For the rapid-scanning scheme it is extremely undesirable, resulting in baseline distortion (especially for very strong monomer absorptions) and small changes in line position. The effects of the high pass filter are shown in **figure 2.9**. Note the increasing signal to noise ratio of the complex transitions with higher frequency filter setting as low frequency noise is removed and gain maximised, but also the increasing baseline distortion occurring, affecting not only the intense NO<sub>2</sub> *P*(2) line but also the Ar-NO<sub>2</sub> <sup>*R*</sup>*Q*<sub>0</sub> branch.

## 2.7.1 Phase correction

The effect of the high pass filter can be reversed by considering AC circuit theory. **Figure 2.10a** shows a simplified circuit diagram of a high pass filter. The voltage is given by

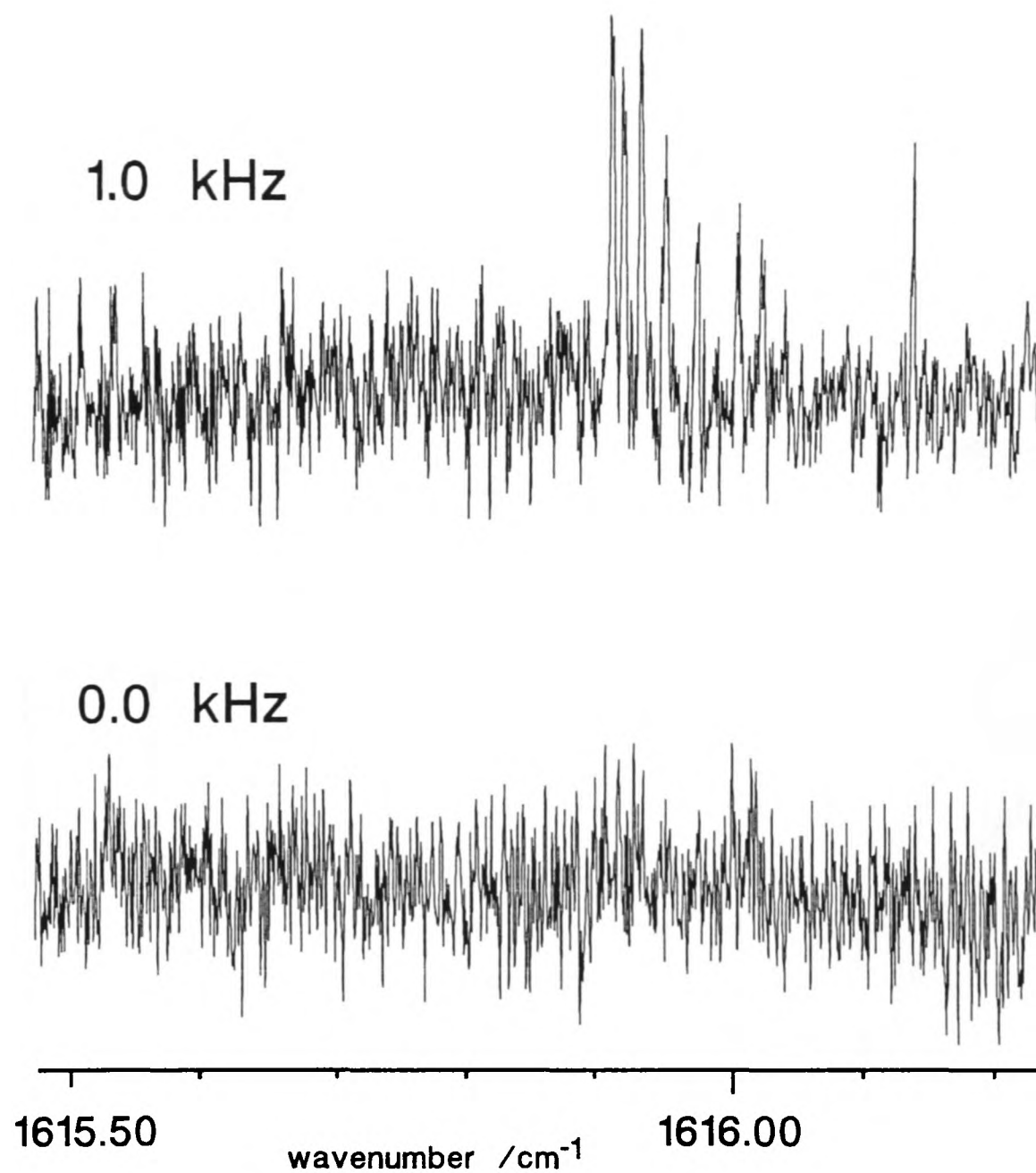
$$V = V_0 e^{i\omega t} \quad (2.15)$$

and the corresponding current by

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<sup>†</sup> Built by Mr N. Baker of the PTCL electronics workshop.

<sup>††</sup> The 3 dB point is where the amplitude of a signal of certain frequency is reduced by a factor of 2. Thus at the 1.0 kHz setting, signals of 1 kHz are attenuated by half.



**Figure 2.8** The effect of the high pass filter on sensitivity. The higher gain possible for the 1.0 kHz filtered signal enables the Ar-NO<sub>2</sub> <sup>R</sup>Q<sub>0</sub> branch to be observed on a single scan.

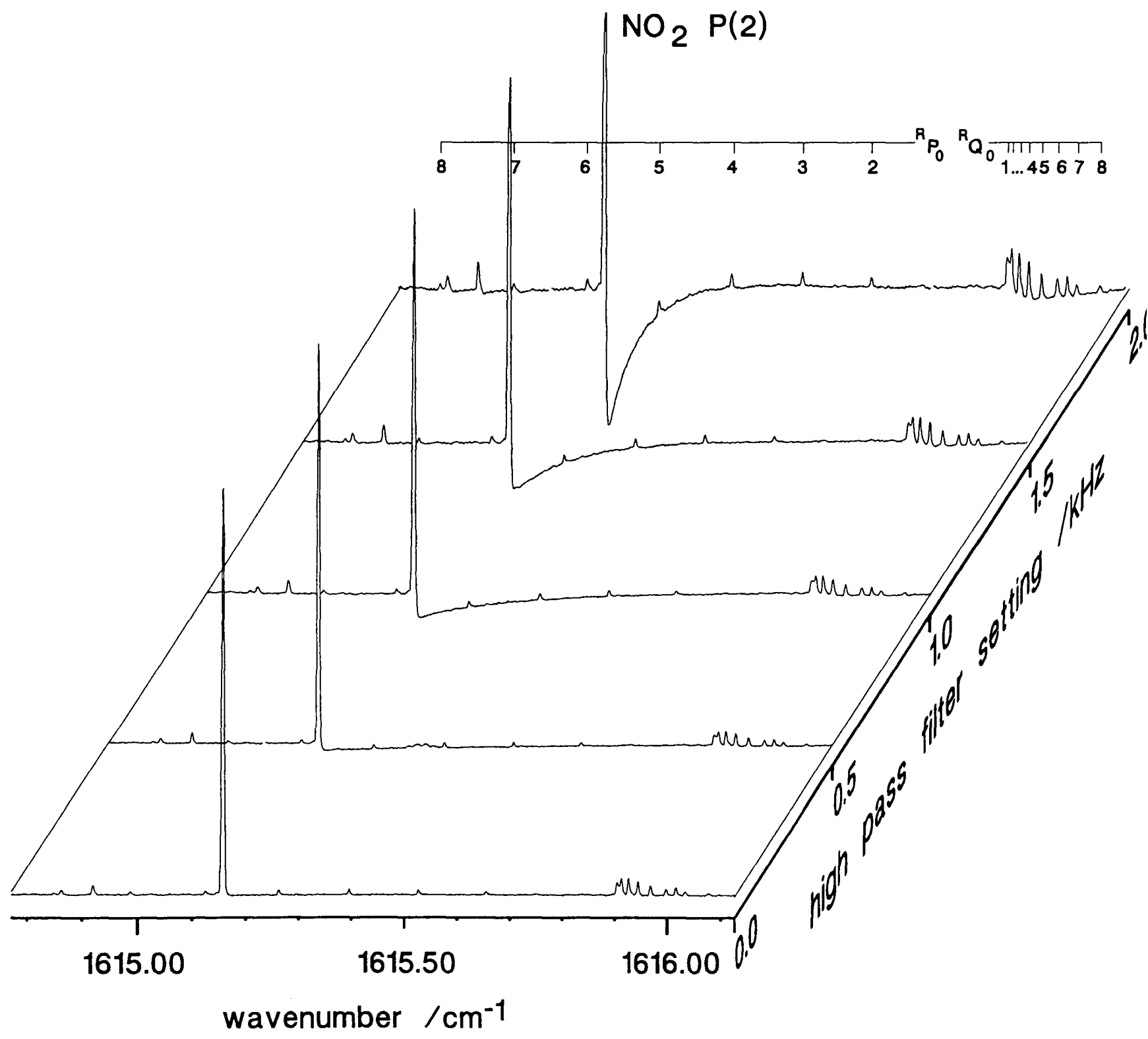
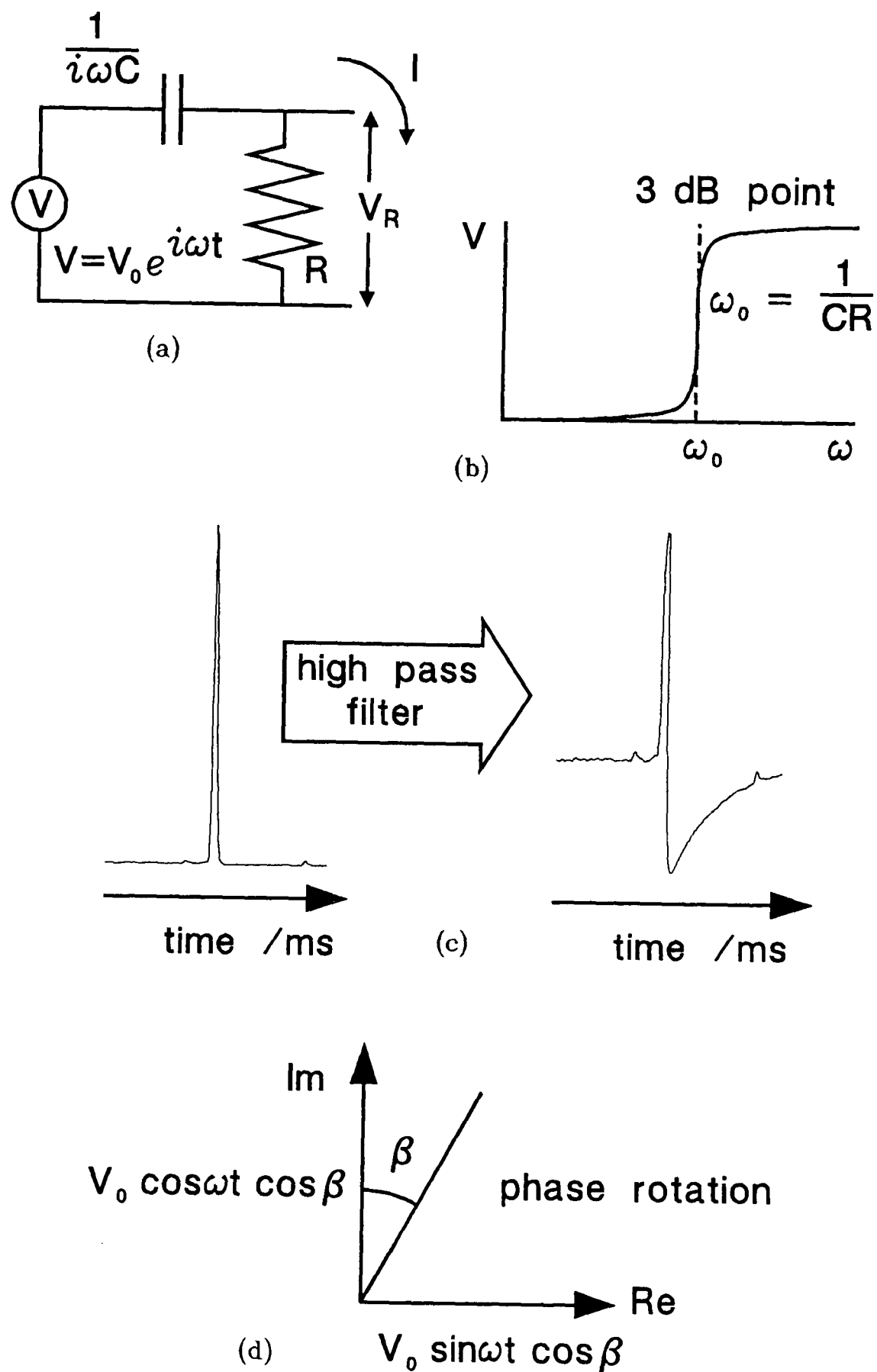


Figure 2.9 Effect of the high pass filter on lineshapes for Ar- $\text{NO}_2$ .



**Figure 2.10** The high pass filter: (a) Simplified circuit diagram; (b) Characteristic frequency; (c) Effect on time domain signal; (d) Phase rotation of complex voltage.



$$I = \frac{V}{Z} = \frac{V_0 e^{i\omega t}}{\left\{ R + \frac{1}{i\omega C} \right\}} \quad (2.16)$$

where  $Z$  is the complex impedance, the sum of the resistance  $R$ , and the impedance  $(i\omega C)^{-1}$  of the capacitor. The output of the high pass filter is the voltage across the resistor,  $V_R$ , which is then given by

$$V_R = IR = V_0 e^{i\omega t} \left\{ \frac{1}{1 + (i\omega CR)^{-1}} \right\} \quad (2.17)$$

The characteristic frequency of the filter  $\omega_0$  (**figure 2.10b**) can be defined as

$$\omega_0 = \frac{1}{CR} \quad (2.18)$$

Equation (2.17) can then be rewritten

$$\begin{aligned} V_R &= V_0 e^{i\omega t} \left\{ \frac{1}{1 - i\omega_0/\omega} \right\} \\ &= V_0 e^{i\omega t} \left\{ \frac{1 + i\omega_0/\omega}{1 + (\omega_0/\omega)^2} \right\} \end{aligned} \quad (2.19)$$

This may be written in terms of an angle  $\beta$ , where  $\tan\beta = \omega_0/\omega$ , thus:

$$\begin{aligned} V_R &= V_0 e^{i\omega t} \left\{ \frac{1 + i \tan\beta}{(\cos\beta)^{-2}} \right\} \\ &= V_0 e^{i\omega t} e^{i\beta} \cos\beta \end{aligned} \quad (2.20)$$

where

$$\cos\beta = \frac{1}{\sqrt{1 + (\omega_0/\omega)^2}} \quad (2.21)$$

Hence the effect of the high pass filter is to introduce a phase rotation of  $\beta = \tan^{-1}(\omega_0/\omega)$ , where  $\omega_0$  is the characteristic frequency of the filter and  $\omega$  is the angular frequency of the signal. The real and imaginary parts of the signal can be expanded separately using the sine and cosine addition formulae (**figure 2.10d**). From equation (2.20),



$$\begin{aligned}
V_R &= V_0 e^{i\omega t} e^{i\beta} \cos\beta \\
&= (V_0 \cos\beta) e^{i(\omega t + \beta)} \\
&= V_0 \cos\beta \{ \cos(\omega t + \beta) + i \sin(\omega t + \beta) \}
\end{aligned} \tag{2.22}$$

Thus the effects of the high pass filter upon the real and imaginary parts of the signal can be summarised as follows:

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p><b>REAL PART:</b> <math>V_{Re} = V_0 \cos \omega t \rightarrow V_0 \cos \beta \cos (\omega t + \beta)</math> <span style="float: right;">(2.23)</span></p> <p style="text-align: right;"><math>= V_0 \cos \beta (\cos \omega t \cos \beta - \sin \omega t \sin \beta) = V'_{Re}</math></p> <p><b>IMAGINARY PART:</b> <math>V_{Im} = V_0 \sin \omega t \rightarrow V_0 \cos \beta \sin (\omega t + \beta)</math> <span style="float: right;">(2.24)</span></p> <p style="text-align: right;"><math>= V_0 \cos \beta (\sin \omega t \cos \beta + \cos \omega t \sin \beta) = V'_{Im}</math></p> |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

The original phase of the signal can be regenerated by taking linear combinations of the real and imaginary parts of the phase-shifted signals. Thus to restore the phase of the real component, the appropriate linear combination is

$$\begin{aligned}
V''_{Re} &= V'_{Re} \cos\beta + V'_{Im} \sin\beta = V_0 \cos\beta \{ \cos\omega t \cos^2\beta - \sin\omega t \sin\beta \cos\beta \} \\
&\quad + V_0 \cos\beta \{ \sin\omega t \cos\beta \sin\beta + \cos\omega t \sin^2\beta \} \\
&= V_0 \cos\beta \{ \cos\omega t (\cos^2\beta + \sin^2\beta) \} \\
&= V_0 \cos\beta \cos\omega t
\end{aligned} \tag{2.25}$$

and for the imaginary component the transformation is

$$\begin{aligned}
V''_{Im} &= V'_{Im} \cos\beta - V'_{Re} \sin\beta = V_0 \cos\beta \{ \sin\omega t \cos^2\beta + \sin\omega t \sin\beta \cos\beta \} \\
&\quad - V_0 \cos\beta \{ \sin\omega t \cos\beta \sin\beta - \sin\omega t \sin^2\beta \} \\
&= V_0 \cos\beta \{ \sin\omega t (\cos^2\beta + \sin^2\beta) \} \\
&= V_0 \cos\beta \sin\omega t
\end{aligned} \tag{2.26}$$

For the purposes of this discussion it is important to note that we are referring to the *modulation* frequency of the detected signal and not the spectral frequency of the transition. The signals are recorded in the time domain (**figure 2.10c**) by the rapid-scanning of the diode laser, and it is therefore possible to access the frequency components of the signal and perform the operations in equations (2.25) and (2.26) by the method of Fourier transformation.

## 2.7.2 Fourier transform and data processing

A physical process may be measured either in the time domain as  $h(t)$  where  $t$  is time, or in the frequency domain as  $H(f)$  (generally a complex number including phase information) where  $f$  is frequency.  $h(t)$  and  $H(f)$  can be considered as two different representations of the same function. The Fourier transform equations are the means of interconversion between these two representations:

$$H(f) = \int_{-\infty}^{\infty} h(t) e^{2\pi i f t} dt \quad (2.27)$$

$$h(t) = \int_{-\infty}^{\infty} H(f) e^{-2\pi i f t} df \quad (2.28)$$

Fourier transform techniques are well established in NMR and ESR [33], as well as FTIR and pulsed nozzle microwave Fourier transform spectroscopy [32]. The discrete Fourier transform [34],

$$F_n = \sum_{k=0}^{N-1} f_k \exp\left(\frac{2\pi i k n}{N}\right) \quad (2.29)$$

maps  $N$  data points in the time domain,  $f_k$ , to  $N$  points in the frequency domain,  $F_n$ , the number of data points  $N$  defining the resolution. The discrete Fourier transform is analogous to the continuous infinite transform, with the same symmetry properties, except that the transform function,  $F_n$  or  $f_k$ , sampled between convenient limits, is treated as a periodically repeating function. The formula for the discrete inverse Fourier transform, which recovers the set of  $f_k$ 's exactly from the  $F_n$ 's is

$$f_k = \frac{1}{N} \sum_{n=0}^{N-1} F_n \exp\left(\frac{-2\pi i k n}{N}\right) \quad (2.30)$$

The method used is based upon the Cooley-Tukey algorithm [34], whereby the discrete Fourier transform is successively rewritten as the sum of two discrete FTs formed from the even and odd numbered points of the previous transform. By recursion the problem is ultimately reduced to  $N$  transforms of length 1, which are the identity operations which copy the input number onto its one output value, which is itself one of the input numbers

$f_k$ . The process overall requires  $N \log_2 N$  operations compared to the  $N^2$  process of the standard discrete FT.

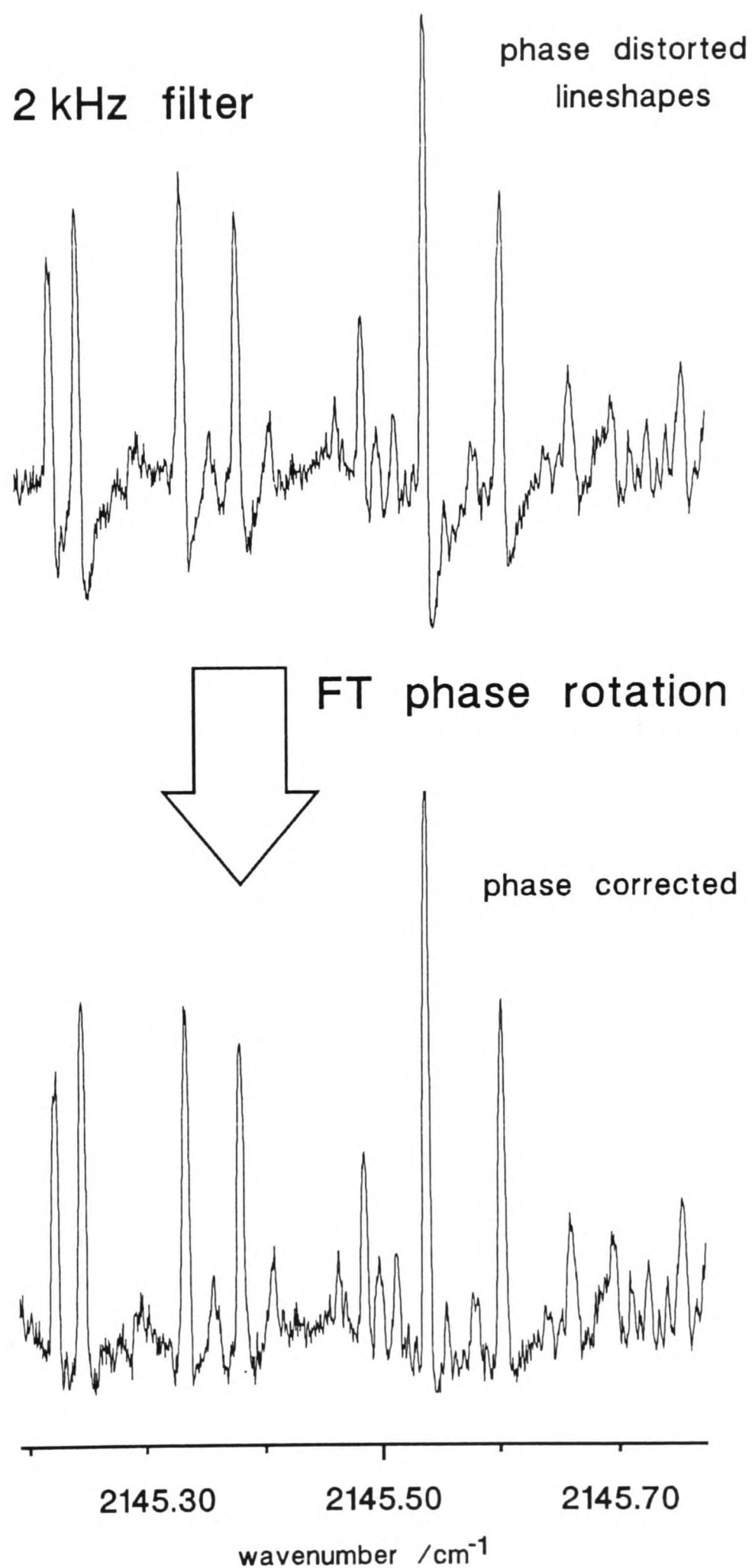
The  $N$  points in equations (2.29) and (2.30) are complex, and the standard routines circumvent the inefficiency of complex algebra by storing each complex element in two locations, DATA( $n$ ) for the real part and DATA( $n + 1$ ) for the complex part. However, the data points of the time domain signal are all real numbers, and rather than fill every other array location with zeros, it is possible to split the 1024 or 2048 point real array in half, forming two real arrays of half the size, one containing the odd numbered data points and the other the even. This is then treated as an  $N/2$  size complex array, with the odd numbered data set corresponding to the ‘real’ and the even numbered data set to the ‘imaginary’ parts. The transform  $H_n$  of the original real data set  $f_n$  can then be written in terms of the transform  $F_n$  of this effective ‘complex’ data set as

$$H_n = \frac{1}{2} \left( F_n + F_{N/2-n}^* \right) - \frac{i}{2} \left( F_n - F_{N/2-n}^* \right) \exp \left( \frac{2\pi i n}{N} \right) \quad n = 0, \dots, N-1 \quad (2.31)$$

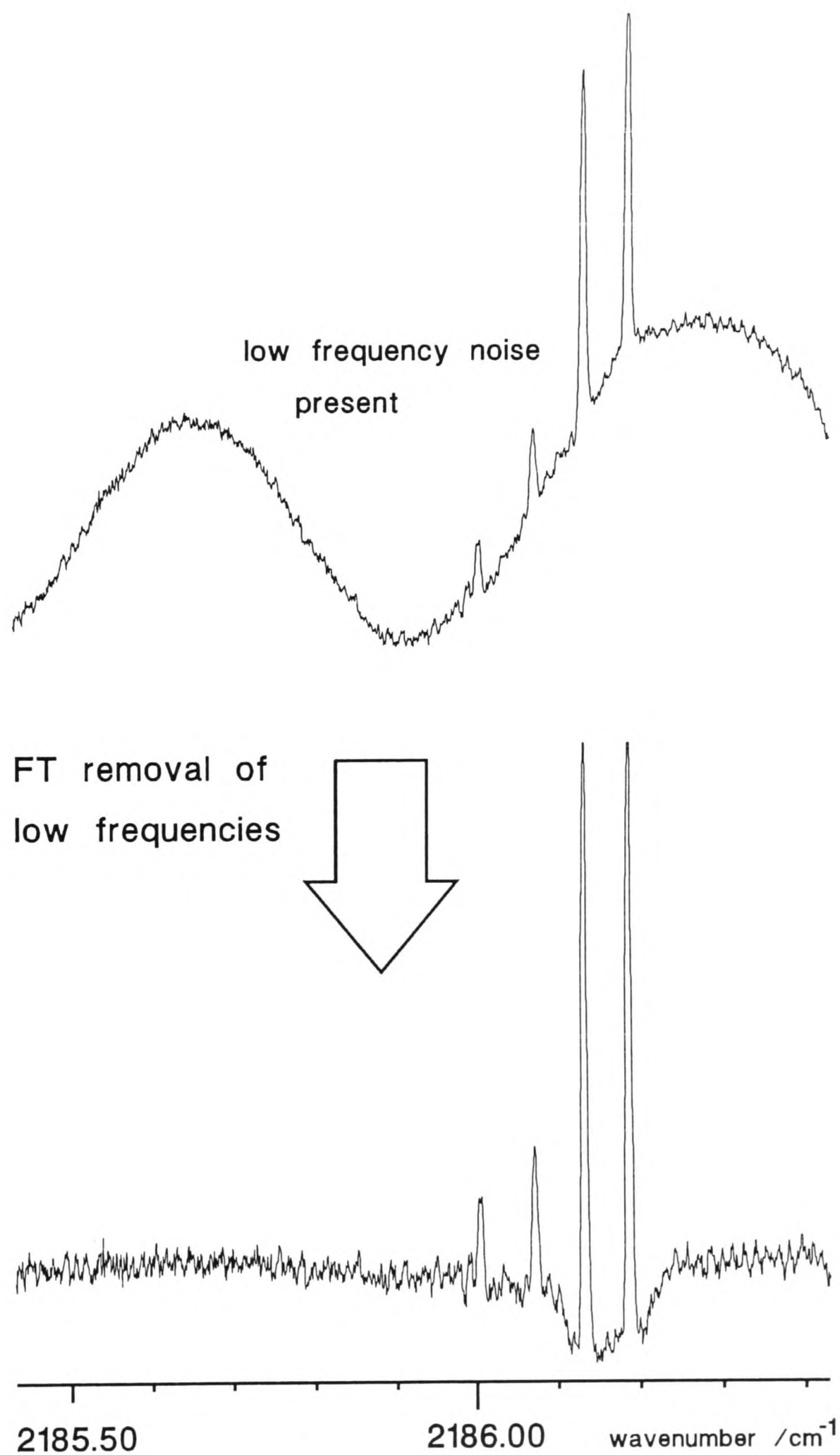
producing the required real and imaginary parts of the frequency domain spectrum.

Using this procedure it was possible to calculate the real and imaginary components of the frequency spectra for the time domain signals and remove the phase shift distortion caused by the high pass filter according to equations (2.25) and (2.26). An example of this process is illustrated in **figure 2.11**. In practice the phase angle  $\beta$  is empirically determined for each frequency setting of the high pass filter. At its maximum setting of 2 kHz line positions are shifted  $\sim 0.0005 \text{ cm}^{-1}$  to lower wavenumber with respect to the 0 kHz setting. The phase correction restores line positions to within  $\sim 0.0002 \text{ cm}^{-1}$  of this value, within the expected experimental accuracy of  $\sim 0.0004 \text{ cm}^{-1}$ .

The process has its limitations, particularly with very strong monomer transitions. These typically saturate the input range of the FLASH-12 resulting in truncated lineshapes which do not respond well to the method. An additional problem is encountered when the beginning and end of the scan have significantly different  $y$  coordinates. The discrete Fourier transform assumes the scan to be an infinite repeat unit, and this creates a discontinuity in the ‘wrap around’. In such a case the beginning and end of the re-transformed scan exhibit considerable distortion. However, such a situation only arises in the case of extreme low frequency noise causing baseline undulations.



**Figure 2.11** Fourier transform phase correction (unassigned CO dimer lines).



**Figure 2.12** Low frequency noise filtering using Fourier transform technique. (Unidentified lines in neon/silane expansion- see Chapter 4.)

The Fourier transform technique is also useful as a final stage noise filter. High and low frequency noise components can be removed in the Fourier transform resulting in smoothing and baseline flattening respectively. The latter case is illustrated in **figure 2.12**. Smoothing of high frequency noise is a feature of the derivative calculation routine used to determine line positions and is therefore not usually accomplished via the FT. This is described in the final section of this chapter.

## 2.8 Calibration of spectra

The PC based calibration program written for the rapid-scanning spectrometer incorporates the signal processing techniques described above in addition to spectrum measuring software. The method used to determine transition frequencies is based upon linear interpolation between fringes of an etalon of well characterised free spectral range. The etalon fringes are calibrated by the spectrum of the reference gas. Each reference line is used to calculate an origin for the etalon fringes which corresponds to the position of the first etalon fringe. The mean origin value is then used to calculate the position of each fringe of the etalon grid. This process is equivalent to least squares fitting the etalon fringes to the reference spectrum. As many reference lines as possible are used to minimise the possibility of statistical errors and increase the overall precision of the fit.

In order to determine the position of the reference, etalon and jet spectrum lines, the first derivative of the signal is calculated and the zero crossing determined. The least squares convolution (or filter) function method of Savitzky and Golay [34, 35] is used for the derivative calculation incorporated in code written by J.P. Connelly [32] for the measurement of microwave transitions. A variable size cubic fit first derivative convoluting polynomial based on coefficients operating over 5 to 25 data points is stepped through the data point by point. The function consists of weighting coefficients calculated to least squares fit the central data point to the first derivative of the polynomial when convoluted with an equal number of data points either side of the central point [36]. Some smoothing results since the function will not fit all features precisely; the number of points in the function is determined by width at half height of the feature to be differentiated.

A straight line is then least squares fitted to data points in the linear region about the zero crossing (corresponding to the transition maximum).

In the case of reference lines, the transition wavenumber is entered into the computer. Once this process is complete, the positions of the etalon fringes are calculated automatically by a routine which searches for zero crossings a minimum separation from the previous location; this prevents very weak fringes from close lying modes interfering with the calibration. The standard deviation of the fringe origin calculation is displayed to indicate any errors in reference spectrum wavenumbers. The jet spectrum may then be calibrated. The overall accuracy of this method is  $\sim 12$  MHz ( $\sim 0.0004\text{ cm}^{-1}$ ), with significantly better precision. The software also incorporates a linearisation routine to enable scans to be plotted with the same linear wavenumber scale whatever the frequency window or modulation rate. The measured line positions are then stored in calibration files which include the relevant reference data.

Spectra are stored in directories and an option allows on-screen comparison of different scans, as well as subtraction of one scan from another. This is useful in cases where spectra are congested by low- $J$  monomer transitions which can often be subtracted out by varying the expansion conditions to produce a ‘monomer only’ spectrum. The calibration and data processing program is menu driven, and written in fortran and assembly language. The assembly routines supporting the menu and graphics functions were written by J. P. Connelly, whose advice and assistance is gratefully acknowledged.



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# Chapter 3

## The structure of CO-OCS from infrared and microwave spectra

### 3.1 Introduction

Recent developments in both microwave and infrared spectroscopy have made these techniques powerful and complementary tools for the experimental study of Van der Waals molecules [1, 2]. Such studies provide a direct method of probing the intermolecular potential in the attractive region, and yield much information on the structure and dynamics of these species.

Infrared spectroscopy has been applied to both polar and nonpolar complexes in a variety of forms [3, 4, 5]. Direct absorption, tunable diode laser techniques in conjunction with supersonic jets have provided a key, non-intrusive method of probing Van der Waals molecules; detection by other means (such as mass spectrometry) is often hampered by their small binding energies. A variety of modulation techniques has been employed [6], most recently rapid scanning of the diode laser, modulating signals directly [7]. The sensitivity enhancement achieved by effectively shifting absorption signals to higher frequency regions where laser  $1/f$  noise is lower has been described in detail in the previous chapter. Pulsed nozzle microwave Fourier transform spectroscopy [8, 9] has been adopted by a number of groups and used to study many polar complexes, including those of radical species [10, 11, 12].

The CO-OCS complex has not previously been studied either in the infrared or microwave region. It was therefore considered a suitable candidate with which to test the performance of the newly commissioned rapid scanning diode laser spectrometer. The

source modulation/ gated detection technique had previously been used to measure the spectrum of the iso-electronic N<sub>2</sub>-OCS complex [13]. This indicated a planar *T*-shaped structure, with the nitrogen axis oriented towards the electropositive carbon in OCS. The structure was confirmed by electrostatic distributed multipole analysis (DMA) calculations where the dominant interaction was found to be that between the molecular quadrupole moments. Additional work in the microwave region [14] failed to determine the tilt of the N<sub>2</sub> axis unambiguously because of insufficient isotopic substitution data; a hard cylinder repulsion model of the Van der Waals radii, however, favoured a structure with the N<sub>2</sub> tilted towards the oxygen atom (and away from the larger sulphur) at an angle of 69.9°. The CO-CO<sub>2</sub> complex has also been studied in the infrared at Oxford using the previous technique [15], and was similarly found to have a *T*-shaped structure.

It was therefore with the primary aim of assessing the performance of the spectrometer that this study was undertaken, rather than any expectation of unusual effects in the complex. In all respects CO-OCS should behave as a conventional semi-rigid molecule, and is likely to be *T*-shaped.

The infrared spectrum was recorded first, and used to obtain ground and excited state constants. Isotopic substitution experiments were then performed using pulsed nozzle microwave Fourier transform spectroscopy to determine the ground state constants more precisely and deduce the geometry of the complex. A potential surface was also calculated using a simple model to account for the observed structure in terms of the dispersive and electrostatic contributions to the intermolecular potential function.

Throughout this chapter, ‘CO-OCS’ will always refer to the most abundant isotopomer, <sup>12</sup>CO-O<sup>12</sup>C<sup>32</sup>S (‘O’ will always mean <sup>16</sup>O). Other isotopomers are distinguished from this by labelling only the differing isotope, as in <sup>13</sup>CO-OCS and CO-OC<sup>34</sup>S.

## 3.2 Asymmetric rotors

The important features of asymmetric top theory are reviewed here, with particular reference to Van der Waals molecules and the interpretation of their spectra. For a full discussion see any standard texts on the subject such as Refs. 16 or 20.

### 3.2.1 The rigid rotor Hamiltonian

The Hamiltonian for a rigid molecule rotating about its axes is given by

$$H_{\text{rigid}} = A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2 \quad (3.1)$$

where  $A$ ,  $B$  and  $C$  are the rotational constants about the principal axes of the complex (related to the moments of inertia  $I$  about these axes by  $A = \hbar^2/(2I_a)$  etc.), and  $\hat{J}_a$ ,  $\hat{J}_b$ ,  $\hat{J}_c$  are the components of the total angular momentum (in units of  $\hbar$ ) referred to the principal axes.

The three rotational constants of an asymmetric rotor are unequal and labelled by convention such that  $A \geq B \geq C$ . The two limiting cases which arise correspond to symmetric tops; a prolate symmetric top has  $A > B = C$ , and an oblate symmetric top  $A = B > C$ . The degree of asymmetry has been quantified by Ray [17] in terms of an asymmetry parameter  $\kappa$ :

$$\kappa = \frac{2B - A - C}{A - C} \quad (3.2)$$

In the prolate and oblate limits  $\kappa = -1$  and  $+1$  respectively. Binary Van der Waals complexes involving simple molecules are close to the prolate limit because of the large intermolecular separation of the two monomer units. They may therefore be considered as near prolate tops, with the  $A$  axis coinciding closely with the intermolecular axis of the complex. The general Hamiltonian of equation (3.1) can then be rewritten in terms of an effective rotational constant  $\bar{B} = (B + C)/2$  as follows:

$$H_{\text{rigid}} = \bar{B} \hat{J}^2 + (A - \bar{B}) \hat{J}_a^2 + \left( \frac{B - C}{4} \right) (\hat{J}_+^2 + \hat{J}_-^2) \quad (3.3)$$

where  $\hat{J}^2 = \hat{J}_a^2 + \hat{J}_b^2 + \hat{J}_c^2$  and  $\hat{J}_{\pm} = \hat{J}_b \mp i\hat{J}_c$ . The asymmetry is contained within the third term, and this has the effect of removing the two fold degeneracy of the  $+K$  and  $-K$  symmetric top states, giving  $2J + 1$  states with different energies for a given value of  $J$ . These states are labelled  $J_{K_a, K_c}$  where the two subscripts refer to the value of  $K$  in the prolate and oblate limits respectively. In a symmetric top basis set  $|J, K\rangle$ , no matrix elements connect the odd and even  $K$  states; the non-zero matrix elements of the Hamiltonian are given by

$$\langle J,K | \mathbf{H}_{\text{rigid}} | J,K \rangle = \bar{B}J(J+1) + (A - \bar{B})K^2 \quad (3.4)$$

$$\begin{aligned} \langle J,K\pm 2 | \mathbf{H}_{\text{rigid}} | J,K \rangle &= \left( \frac{B-C}{4} \right) [J(J+1) - K(K\pm 1)]^{1/2} \\ &\times [J(J+1) - (K\pm 1)(K\pm 2)]^{1/2} \end{aligned} \quad (3.5)$$

There is no general formula for the energy levels of an asymmetric top, and they must be found by diagonalising the matrix for each value of  $J$ . The procedure is far more efficient if a new set of basis functions is introduced by means of the Wang transformation [18]:

$$\begin{aligned} |J,0^+\rangle &= |J,0\rangle \\ |J,K^\pm\rangle &= \frac{1}{\sqrt{2}} \{ |J,K\rangle \pm |J,-K\rangle \}, \quad (K>0) \end{aligned} \quad (3.6)$$

This introduces further symmetrisation, as there are found to be no matrix elements connecting the  $|J,K^+\rangle$  and  $|J,K^-\rangle$  states. The matrix for each  $J>1$  is therefore reduced to four tridiagonal submatrices, according to whether  $K$  is even or odd and has a plus or minus combination in the Wang transformation, which are labelled  $E^+$ ,  $E^-$ ,  $O^+$  or  $O^-$ . The Hamiltonian is therefore much faster to diagonalise, reducing for example the largest matrix for  $J=20$  from  $41 \times 41$  to  $11 \times 11$  in size. However, this has become less vital as computer technology has improved over the years.

### 3.2.2 Selection rules

The Wang transformation utilises the symmetry of the Hamiltonian to achieve a simpler block diagonal matrix form. The Hamiltonian is invariant to a rotation of  $180^\circ$  about any of the principal axes of the molecule, and these operations generate the  $D_2$  point group<sup>†</sup>. The asymmetric rotor wavefunctions can be classified according to the parities of  $K_a$  and  $K_c$  under the operations of this group, giving four distinct categories labelled  $ee$ ,  $eo$ ,  $oe$  and  $oo$ , where  $e$ =even parity and  $o$ =odd parity, in the order  $K_a K_c$ .

---

<sup>†</sup> The  $x$ ,  $y$  and  $z$  axes of the  $D_2$  point group can be identified with the principal axes of the molecule in three right-handed and three left-handed representations. The right-handed  $I'$  representation is used here in which the  $a$ ,  $b$  and  $c$  principal axes of the molecule correspond to the  $z$ ,  $x$  and  $y$  axes of the  $D_2$  point group respectively.

The levels of the four sub-matrices are then given as follows:

| <i>matrix</i> | <i>levels</i>                            | <i>J even</i> | <i>J odd</i> |
|---------------|------------------------------------------|---------------|--------------|
| $E^+$         | $J_{0,J}, J_{2,J-2}, J_{4,J-4}, \dots$   | $ee$          | $eo$         |
| $E^-$         | $J_{2,J-1}, J_{4,J-3}, J_{6,J-5}, \dots$ | $eo$          | $ee$         |
| $O^+$         | $J_{1,J-1}, J_{3,J-3}, J_{5,J-5}, \dots$ | $oo$          | $oe$         |
| $O^-$         | $J_{1,J}, J_{3,J-2}, J_{5,J-4}, \dots$   | $oe$          | $oo$         |

Three distinct sets of selection rules in the  $K_a$  and  $K_c$  quantum numbers apply to vibrational transitions as the transition dipole moment may have components along any of the three principal axes. Transitions are labelled *a*-type, *b*-type or *c*-type according to the axis along which the component of the transition dipole moment lies. The selection rules for each type of transition are tabulated below (these are in addition to the usual  $\Delta J=0, \pm 1$ ):

| <i>transition</i> | <i>parity</i>                                                                                 | <i>selection rules</i>                                                   |
|-------------------|-----------------------------------------------------------------------------------------------|--------------------------------------------------------------------------|
| $a\text{-type}$   | $\left\{ \begin{array}{l} ee \leftrightarrow eo \\ oo \leftrightarrow oe \end{array} \right.$ | $\Delta K_a = 0, \pm 2, \dots$<br>$\Delta K_c = \pm 1, \pm 3, \dots$     |
| $b\text{-type}$   | $\left\{ \begin{array}{l} ee \leftrightarrow oo \\ eo \leftrightarrow oe \end{array} \right.$ | $\Delta K_a = \pm 1, \pm 3, \dots$<br>$\Delta K_c = \pm 1, \pm 3, \dots$ |
| $c\text{-type}$   | $\left\{ \begin{array}{l} ee \leftrightarrow oe \\ eo \leftrightarrow oo \end{array} \right.$ | $\Delta K_a = \pm 1, \pm 3, \dots$<br>$\Delta K_c = 0, \pm 2, \dots$     |

Symmetric top notation is used to identify the transitions of a near prolate rotor:

$$J'_{K'_a, K'_c} \leftarrow J''_{K''_a, K''_c} \Leftrightarrow {}^{\Delta K_a} \Delta J_{K''_a}(J'') \tag{3.7}$$

where *P*, *Q* or *R* are used for  $\Delta J$  and  $\Delta K_a$ . Thus  ${}^P R_1(1)$  indicates  $2_{0,2} \leftarrow 1_{1,1}$ .



3.2.3 Intensities

Intensities are given by the expression

$$I \propto A_{JK} \times \exp\left(\frac{-E_{\text{rot}}(J,K)}{kT}\right) \tag{3.8}$$

where the Boltzmann factor is given by the exponential term and  $A_{JK}$  is the square of the transition dipole moment matrix elements linking the two asymmetric top wavefunctions. For a symmetric top these are the Hönl-London factors [19], which are tabulated below:

| $\Delta K = 0$                                                 | $\Delta K = \pm 1$                                                               |
|----------------------------------------------------------------|----------------------------------------------------------------------------------|
| $P(J'') \quad A_{JK} = \frac{(J''+K'')(J''-K'')}{J''}$         | $P(J'') \quad A_{JK} = \frac{(J''-1 \mp K'')(J'' \mp K'')}{4J''}$                |
| $Q(J'') \quad A_{JK} = \frac{(2J''+1)K''^2}{J''(J''+1)}$       | $Q(J'') \quad A_{JK} = \frac{(J''+1 \pm K'')(J'' \mp K'')(2J''+1)}{4J''(J''+1)}$ |
| $R(J'') \quad A_{JK} = \frac{(J''+1+K'')(J''+1-K'')}{(J''+1)}$ | $R(J'') \quad A_{JK} = \frac{(J''+2 \pm K'')(J''+1 \pm K'')}{4(J''+1)}$          |

The eigenfunctions of an asymmetric top are linear combinations of the symmetric top basis functions; thus the transition dipole matrix elements must be calculated by summing the contributions from each symmetric top basis function in the lower and upper states:

$$A_{JK} = \left[ \sum_{K'} \sum_{K''} \mu_{K''K'} c_{J'K'} c_{J''K''}^* \right]^2 \tag{3.9}$$

where  $\mu_{K''K'}$  is the transition dipole matrix element connecting each pair of basis states, which when squared gives the Hönl-London factors.  $c$  represents the symmetric top eigenvector elements labelled by  $J$  and  $K$ .

Generally only  $a$  and  $b$ -type transitions are observed because most Van der Waals complexes containing linear molecules (such as CO-OCS) are planar. Strongly allowed



transitions for near prolate tops have  $\Delta K_a = 0$  or  $\pm 1$ , and at high  $K_a$  the strongest transitions have  $\Delta K_a = \Delta J$ .

### 3.2.4 Centrifugal distortion

Particularly for large  $J$ , centrifugal forces cause a molecule to distort, and hence the rotational constants are dependent on the angular momentum of the molecule. The rigid rotor Hamiltonian is therefore inadequate, and the distortion is described by the addition of higher terms as a power series in the components of  $J$ .

At first sight there appear to be six quartic distortion terms, corresponding to the coefficients of  $\hat{J}_a^4$ ,  $\hat{J}_b^4$ ,  $\hat{J}_c^4$ ,  $\hat{J}_a^2\hat{J}_b^2$ ,  $\hat{J}_b^2\hat{J}_c^2$  and  $\hat{J}_a^2\hat{J}_c^2$ . However, any two of these are further correlated; only five of the six are independent. Watson [20] has shown that the number of terms may be reduced to five distinct quartic and seven (rather than ten) distinct sextic centrifugal distortion terms for an asymmetric rotor. He has developed two asymmetric top Hamiltonians, the  $A$  (asymmetric) reduction and the  $S$  (symmetric) reduction. The advantage of the  $A$  reduction is that it eliminates matrix elements off diagonal in  $K$  by more than two, resulting in simple tridiagonal matrices. However, a more important drawback is that it blows up for an accidental symmetric top; it has terms depending upon the asymmetry parameter  $\sigma = (2A - B - C)/(B - C)$  which becomes infinite for a prolate symmetric top.

In the  $S$  reduction all  $\hat{J}_z$  dependent terms which mix  $K$  are eliminated; however, terms off diagonal in  $K$  by  $\pm 4$  are present in the Hamiltonian. The reduction also has the advantage of lower correlation between the constants than the  $A$  reduction. The  $S$  reduced Hamiltonian has the form (up to the quartic centrifugal distortion terms):

$$\begin{aligned}
 H = & \bar{B}\hat{J}^2 + (A - \bar{B})\hat{J}_a^2 + \left(\frac{B-C}{2}\right)(\hat{J}_b^2 - \hat{J}_c^2) \\
 & - D_J\hat{J}^4 - D_{JK}\hat{J}_a^2\hat{J}^2 - D_K\hat{J}_a^4 \\
 & + d_1\hat{J}^2(\hat{J}_+^2 + \hat{J}_-^2) + d_2(\hat{J}_+^4 + \hat{J}_-^4)
 \end{aligned} \tag{3.10}$$

where  $D_J$ ,  $D_{JK}$ ,  $D_K$ ,  $d_1$  and  $d_2$  are the quartic centrifugal distortion constants. The matrix elements of the  $S$  reduced Hamiltonian are as follows:

$$\begin{aligned} \langle J, K | \mathbf{H}_{\text{rot}}^S | J, K \rangle = & \bar{B}J(J+1) + (A - \bar{B})K^2 \\ & - D_J J^2(J+1)^2 - D_{JK}J(J+1)K^2 - D_K K^4 \end{aligned} \quad (3.11)$$

$$\begin{aligned} \langle J, K \pm 2 | \mathbf{H}_{\text{rot}}^S | J, K \rangle = & \left[ \left( \frac{B - C}{4} \right) + d_1 J(J+1) \right] \\ & \times [J(J+1) - K(K \pm 1)]^{1/2} \\ & \times [J(J+1) - (K \pm 1)(K \pm 2)]^{1/2} \end{aligned} \quad (3.12)$$

$$\begin{aligned} \langle J, K \pm 4 | \mathbf{H}_{\text{rot}}^S | J, K \rangle = & d_2 [J(J+1) - K(K \pm 1)]^{1/2} \\ & \times [J(J+1) - (K \pm 1)(K \pm 2)]^{1/2} \\ & \times [J(J+1) - (K \pm 2)(K \pm 3)]^{1/2} \\ & \times [J(J+1) - (K \pm 3)(K \pm 4)]^{1/2} \end{aligned} \quad (3.13)$$

The vibrational and rotational motions of the complex are separated according to the Born-Oppenheimer approximation; the difference due to the vibrational part of the Hamiltonian is represented by a pure vibrational transition frequency,  $\nu_0$ , the vibrational band origin. A computer program is used to calculate the rotational energies which are used to predict the frequencies and calculated intensities of transitions. A least squares routine is used to fit the various constants to the data, and these may be floated separately in the ground and first excited vibrational states or tied together. In addition, the program is able to fit pure rotational transitions simultaneously with the ro-vibrational transitions.

### 3.3 Experimental details

These measurements employed the first version of the spectrometer described in the previous chapter (§ 2.6); data collection was secured by an 8 bit resolution fast A/D card operating at a maximum speed of 20 MHz (10 MHz on each channel) with 16 kbytes of onboard memory (Markenrich WAAG board). The onboard memory maps directly onto

the PC system memory giving fast access. For this configuration, each cycle consists of two data acquisitions, each on two channels. The first records the jet spectrum on channel one and a calibration gas cell spectrum on channel two, and the second records the laser power mode profile (i.e. the signal on the jet InSb detector without the nozzle pulsing, to facilitate baseline subtraction) on channel one and a calibration etalon signal on channel two. 0.2 Torr OCS was used as the reference spectrum [21], and a  $0.016\text{ cm}^{-1}$  free spectral range germanium etalon was used to interpolate between gas cell lines (the free spectral range was first determined by a least squares analysis of the calibration data). A germanium etalon was used in preference to the confocal Fabry-Perot interferometer normally used because it gave better peak/trough characteristics at the low power output of the diode used. The disadvantage of the germanium etalon is that it is a plane interferometer and therefore its free spectral range is more dependent on the angle at which the radiation enters the cavity<sup>†</sup>. It is possible that this may result in an overall lower precision for the data.

The CO-OCS was formed by expanding a mixture of 2 % CO and 0.5 % OCS in Ne with a backing pressure of between 2 and 3 atm from a 0.35 mm diameter axisymmetric nozzle. Pulse lengths of  $\sim 3$  ms were synchronised with a laser scan time of 2 ms (over the stable region of the expansion). Data collection and timing pulses were under direct PC control. A repetition rate of 20 Hz was possible, the nozzle pulsing every other scan to enable a background signal to be recorded and subsequently subtracted to yield a flat baseline. Calibration signals were multiplexed and recorded on one channel, the jet data on the other. 2048 points were sampled per channel per scan at 1 MHz, with a scan range of between 0.5 and  $0.8\text{ cm}^{-1}$ . Typical linewidths resulting from an axisymmetric (pin hole) expansion are 150 MHz full width at half maximum (FWHM). Signals from the InSb

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<sup>†</sup> For a confocal Fabry-Perot etalon, the free spectral range  $\delta\nu$  is given by

$$\delta\nu = \frac{c}{4r + \rho^4/r^3} \quad (3.1a)$$

where  $r$  is the separation of the two spherical mirrors (also of curvature radius  $r$ ),  $\rho^2 = \rho_1\rho_2$  (where  $\rho_1$  and  $\rho_2$  are the offset distances of the rays from the axes of the two mirrors) and  $c$  is the velocity of light ( $\rho \ll r$ ). The expression for a plane etalon is

$$\delta\nu = \frac{c}{2d\sqrt{n^2 - \sin^2\alpha}} \quad (3.1b)$$

where  $\alpha$  is the angle of incidence of the radiation and  $n$  is the refractive index of the medium (in this case germanium). In the first case (equation (3.1a)),  $\delta\nu$  is approximately constant for small off-axis alignments; for the plane etalon (equation (3.1b)),  $\delta\nu$  depends more directly upon the angle of incidence  $\alpha$ . For more information see '*Laser Spectroscopy*' by W. Demtröder (Springer-Verlag 1981), pp.152-176.

detector were AC coupled to remove a 2 V DC shift and the gain adjusted (bandpass > 1 MHz) to bring the signal within the full input voltage range of the card ( $\pm 0.64$  V).

The high density of strong OCS monomer lines in the jet ( $\sim 0.4 \text{ cm}^{-1}$  spacing) prevented the use of the high pass filter; such strong lines produce severe baseline distortion as described in § 2.7. One of the main benefits of the high pass filter is to ‘compress’ the variation in the InSb detector signal. This allows greater amplification of the signal and therefore greater sensitivity. With only the DC frequency shift of the detector removed, the detector signal may vary by as much as the input range of the acquisition card ( $\pm 0.64$  V). This prevents amplification of the signal and may result in complex absorptions falling below the level required to register on the digital scale<sup>†</sup>. A smaller scan window often reduces the variation in detector output voltage sufficiently to considerably improve the sensitivity of the instrument.

Real-time, co-addition of many scans (up to 5000) yields the signal averaged spectrum. A much greater path length is achieved in slit expansions. Had a slit nozzle been used, fewer scans would have been required, but at the expense of a reduced repetition rate due to increased gas through-put. Narrower linewidths place a greater demand upon laser stability, and additional frequency stabilisation may be required [7]. This was generally not a problem in these experiments.

The infrared absorption spectrum was measured in the 5 micron wavelength region of the OCS  $\nu_3$  asymmetric stretch; the intensity of the vibration-rotation band derives from the carbonyl stretching vibration of the monomer, while the rotational structure is determined by the geometry of the complex. As presented in the discussion, these results were insufficient to pin down the geometry of the molecule, and so isotopic substitution experiments were conducted in the microwave region.

### 3.3.1 The Fourier transform microwave spectrometer

The pure rotational spectrum of CO-OCS, and its isotopomers  $^{13}\text{CO-OCS}$  and  $\text{CO-OC}^{34}\text{S}$  was recorded on a pulsed nozzle microwave Fourier transform spectrometer. C-13

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<sup>†</sup> An 8 bit card has 256 quantised steps to register an input signal. For the input range of the WAAG card,  $\pm 0.64$  V, each step therefore corresponds to 0.005 V. If the complex absorption changes the detector power output by less than this voltage, no absorption is registered. Thus there is a clear advantage in minimising the variation in the detector output voltage.

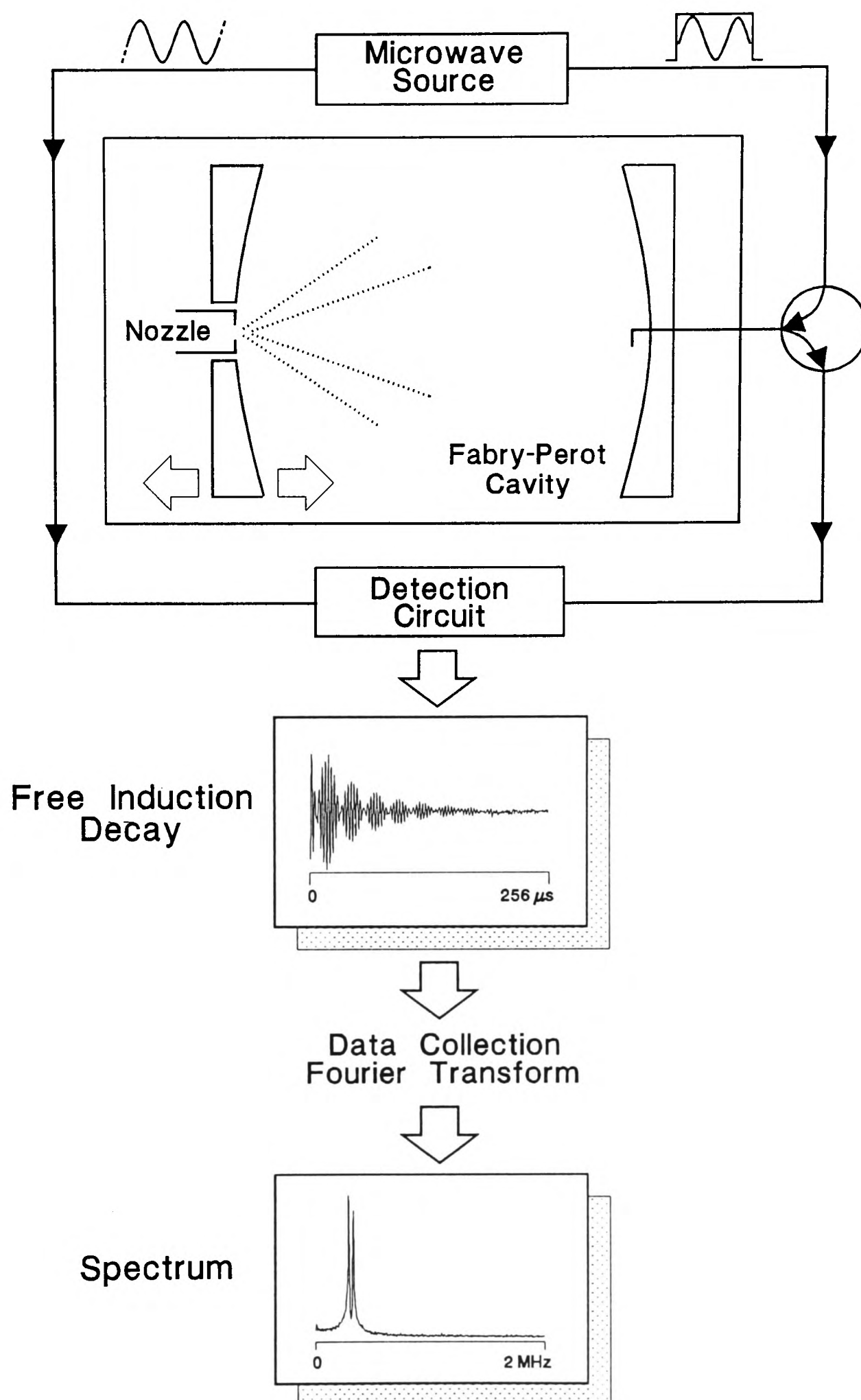
enriched CO (Sigma Chemical Co. Ltd.) was used for the first set of isotope measurements, and the high sensitivity of the instrument enabled the  $^{34}\text{S}$  signals to be recorded at the level of natural abundance (4.22 %).

The spectrometer has been described in detail elsewhere [22, 23, 24], but a brief resumé is given here. Its data acquisition system is based on the same principle of fast A/D conversion as used in the rapid scanning infrared spectrometer. Indeed the same model Markenrich WAAG card was used for the infrared experiments in this chapter, and until this was upgraded to a higher resolution card the acquisition software for the two systems was virtually identical, with the obvious exception of the Fourier transform step.

The instrument is similar in design to that described by Suenram *et al.* [25], and has a frequency range of 6 - 18 GHz with a resolution of  $\sim 1$  kHz. A schematic of the apparatus is given in **figure 3.1**. A pulse of gas is released into the Fabry-Perot cavity where it is briefly irradiated with a broad band of microwave radiation. The cavity can support a bandwidth of  $\sim 1$  MHz. The coherent spontaneous emission from the excited molecules is then detected, digitised by a fast A/D converter and Fourier transformed to give a frequency domain spectrum.

The Fabry-Perot cavity consists of a pair of concave aluminium mirrors (50 cm radius of curvature and 35 cm diameter) arranged opposite one another 60 cm apart. At the centre of one mirror is a coaxial antenna, which both transmits and detects the microwave radiation. The impedance of the antenna is matched to the input impedance of the cavity in order to dissipate incident microwave power without producing any reflected waves.

At the centre of the other mirror is the pulsed nozzle through which a parallel supersonic expansion enters the cavity. Expanding the gas coaxially into the chamber results in it travelling parallel and anti-parallel to the direction of propagation of the microwave standing wave within the cavity. The velocity of molecules parallel to the expansion have a much narrower distribution than the perpendicular components, and a parallel expansion thus results in narrower linewidths and improved resolution. One transition therefore gives rise to two peaks in the spectrum, one for each Doppler component. This splitting of the lines is related to the parallel velocity of the interacting molecules by the expression



**Figure 3.1** A schematic of the Fourier transform microwave spectrometer.

$$V = c \left( \frac{2\nu_0 + \Delta\nu}{2\nu_0} - 1 \right) \quad (3.14)$$

where  $V$  is the velocity of the molecules parallel to the expansion,  $c$  is the velocity of light,  $\nu_0$  is the irradiating frequency and  $\Delta\nu$  is the frequency separation of the Doppler components. The frequency of the transition is given by the mean of the frequencies of each component.

The cavity is tuned by adjusting the separation of the mirrors, which is effected by means of a computer controlled hydraulic stepper motor attached to the mirror containing the nozzle. Resonant frequencies for transverse modes are given by the expression

$$\nu_0 = \left( \frac{c}{2d} \right) \left[ (q+1) + \frac{1}{\pi} (m+n+1) \cos^{-1} \left( 1 - \frac{d}{R} \right) \right] \quad (3.15)$$

where  $q$  is the number of nodes in the electric field along the cavity axis,  $m$  and  $n$  are the number of radial nodes,  $c/2d$  is the fundamental frequency ( $c$  is the velocity of light and  $d$  the separation of the two mirrors) and  $R$  is the radius of curvature of the mirrors [3]. These modes correspond to Hermite-Gaussian wavefunction solutions for standing waves [26] and are labelled  $\text{TEM}_{mnq}$ ;  $q$  represents the same quantity as in equation (3.2), but  $m$  and  $n$  refer to the order of the Hermite polynomial in each of the transverse directions<sup>†</sup>.

The  $Q$  factor of the cavity is defined as the ratio of total energy stored in the cavity to the energy dissipated per cycle, and is approximately given by

$$Q = \frac{\nu_0}{\Delta\nu} \quad (3.16)$$

where  $\nu_0$  is a resonant frequency and  $\Delta\nu$  the frequency envelope around this central frequency in which the energy is stored. The cavity has a bandwidth of  $\sim 2$  MHz at a frequency of 10 GHz giving a high  $Q$  of  $2 \times 10^4$ . The narrow bandwidth requires that the cavity be retuned if a frequency range greater than  $\sim 2$  MHz is being scanned. Therefore scans over a region several GHz wide are very time consuming; it is possible to reduce the  $Q$  during searches but at the expense of resolution and sensitivity. The design of the spectrometer is biased towards better resolution, and therefore an automated scanning

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<sup>†</sup> Hermite polynomials are also solutions to the harmonic potential Schrödinger equation.



system performs the tedious process of retuning and searching for transitions. For these measurements, with the ground state rotational and distortion constants determined from the infrared data, the transitions were located quickly without the need for extensive searches. Constants were calculated for the isotopomers by assuming plausible rigid geometries and searching the relevant regions.

Microwaves are generated by a synthesizer at a frequency between 2 - 20 GHz with a maximum power of 18 dBm (60 mW). The radiation is transmitted through a low loss semi-rigid cable to a divider where it is split in half. 50 % travels to the mixing crystal where it is mixed with the *detected* microwave radiation from the spontaneous emission by the molecules in the cavity; the difference frequency generated<sup>†</sup> gives the offset of the detected radiation from the initial microwave frequency generated, and hence calibration of the spectra.

The other 50 % is directed to the Fabry-Perot cavity through a computer controlled switch enabling the microwaves to be pulsed with  $\sim 1 \mu\text{s}$  duration. In accordance with the lifetime broadening relation  $\tau \delta E \approx \hbar/2$  this produces a range of frequencies of  $\sim 1 \text{ MHz}$  bandwidth, tuned to match the bandwidth of the cavity which results in optimum power transfer. The radiation then enters the cavity, exciting rotational transitions within range; a circulator prevents reflected radiation being transmitted back along the circuit.

The excited molecules then spontaneously emit microwave radiation, the free induction decay. This is detected by the same circuitry used for the excitation. The circulator passes the radiation to a low noise amplifier, through a directional coupler and triggers a data collection timing switch. Timing is optimised at this stage to collect the maximum amount of free induction decay signal without additional noise from the remnant of the initial excitation pulse decaying in the cavity (ring down).

Having passed through a phase adjuster and isolator the signal reaches the mixing crystal where the difference frequency is generated, this being the offset of the emitted radiation from the frequency of the incident microwave pulse. There follows a process of signal amplification, filtering (to remove unwanted frequencies) and phase adjustment (to remove a DC voltage offset arising from the mixing crystal).

The final step is the digitisation of the signal which occurs at a rate of  $0.25 \mu\text{s}$  per point for 1024 points. The nozzle is pulsed every other scan in order to record and

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<sup>†</sup> The sum frequency is also generated but discarded.



subtract the background spectrum of the cavity. Several thousand cycles are performed to give the final, averaged free induction decay. This is then Fourier transformed to give a spectrum, which is measured using exactly the same procedure as described in the previous chapter, § 2.8 for the infrared data.

The amount of power required from the microwave synthesizer depends upon the size of the dipole moment of the chromophore; if necessary an amplifier may be used to boost the power output for complexes with small dipole moments. In this work, the large OCS dipole moment (0.715 D) resulted in strong, easily observed transitions, and greatly facilitated the measurement of the CO-OC<sup>34</sup>S isotopomer, present in natural abundance of 4.2 %.

## 3.4 Results

For the infrared work, the optimum gas mixture was determined by careful comparison of spectra with previously measured Ne-OCS infrared transitions [27] to ensure the lines were due to the correct species. 98 *b*-type transitions were observed near the OCS  $\nu_3$  stretch at 2062 cm<sup>-1</sup> and fitted using the  $I'$  representation of the Watson  $S$  reduction of the asymmetric top Hamiltonian presented in § 3.2.4. A representative scan is shown in **figure 3.2** (OCS monomer transitions are either explicitly labelled or marked with an asterisk).

The data were fitted to a vibrational origin,  $\nu_0$ , ground and excited state rotational constants, and a single set of quartic distortion constants ( $d_1$  and  $d_2$  were set to zero since they could not be determined with statistical significance). Residuals were typically < 0.001 cm<sup>-1</sup>, and the standard deviation of the fit was 17.3 MHz (0.00058 cm<sup>-1</sup>). The relative intensities of the infrared transitions were consistent with a rotational temperature of 0.5 - 1.0 K. The lineshape of absorptions is determined by Doppler broadening associated with an uncollimated supersonic expansion; the FWHM linewidths are approximately 150 MHz (0.005 cm<sup>-1</sup>).

In addition, 22 pure rotational transitions (*a*- and *b*-type) were observed for <sup>12</sup>CO-OCS, 31 for <sup>13</sup>CO-OCS, and 23 for CO-OC<sup>34</sup>S. **Figure 3.3** shows a free induction decay and its Fourier transform for a rotational transition of the main isotopomer CO-OCS. The

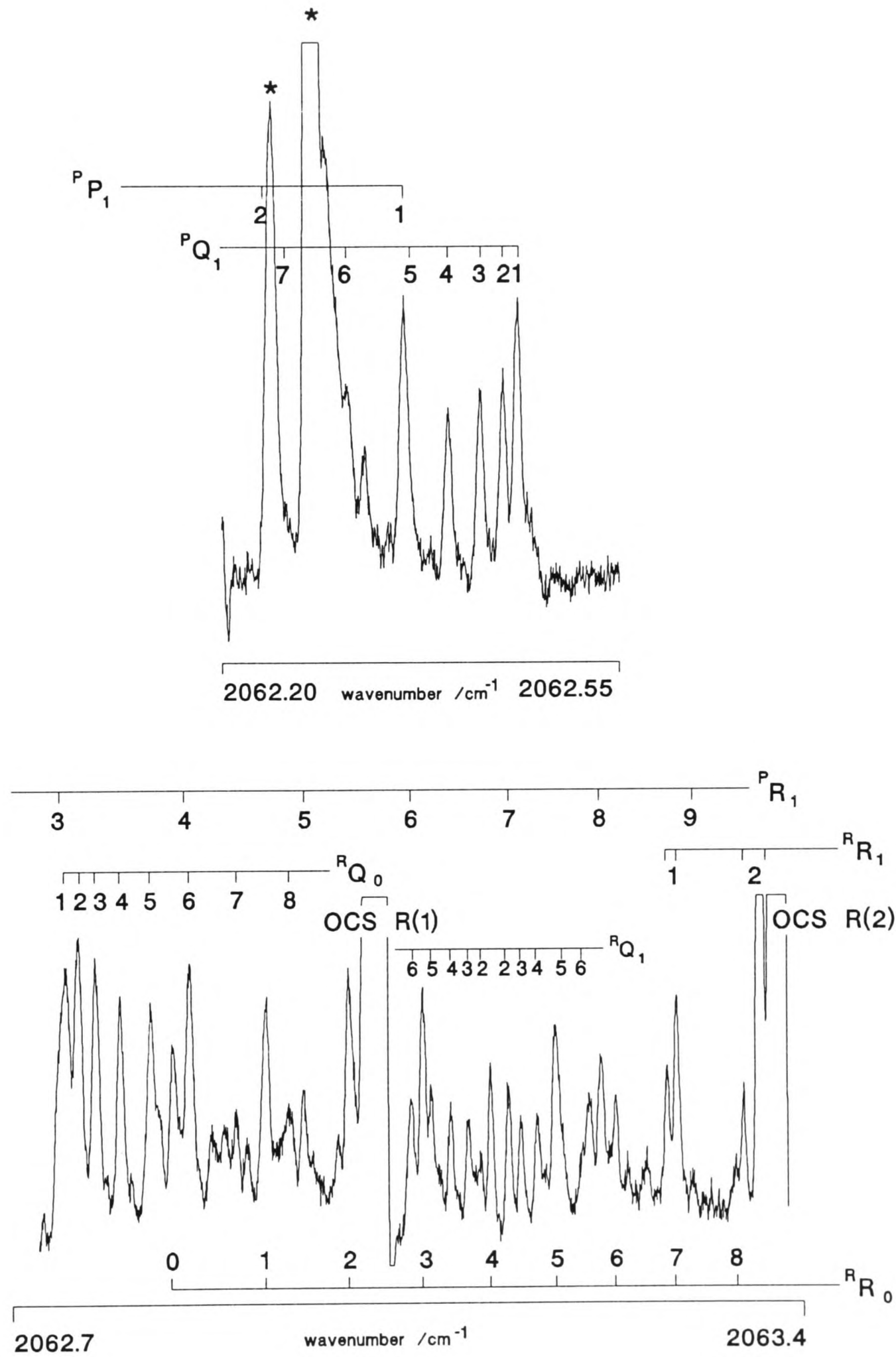
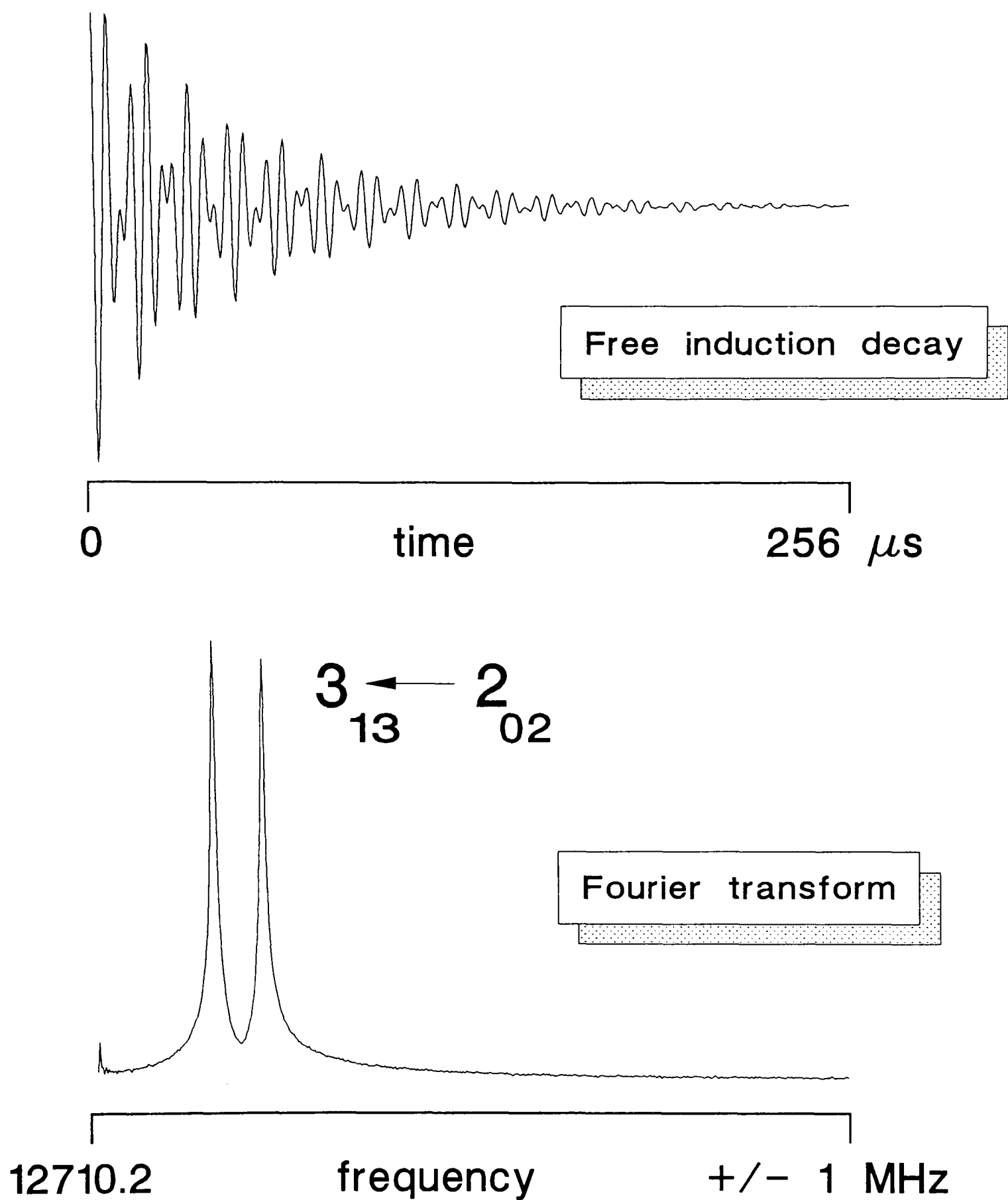


Figure 3.2 Infrared supersonic jet spectra of CO-OCS.

**Figure 3.3** Pure rotational transition of CO-OCS.

data from each were fitted to an extended Hamiltonian which included sextic distortion terms:

$$\begin{aligned}
 H = & \bar{B}\hat{J}^2 + (A - \bar{B})\hat{J}_a^2 + \left(\frac{B-C}{2}\right)(\hat{J}_b^2 - \hat{J}_c^2) \\
 & - D_J\hat{J}^4 - D_{JK}\hat{J}_a^2\hat{J}^2 - D_K\hat{J}_a^4 \\
 & + d_1\hat{J}^2(\hat{J}_+^2 + \hat{J}_-^2) + d_2(\hat{J}_+^4 + \hat{J}_-^4) \\
 & + H_J\hat{J}^6 + H_{JK}\hat{J}^4\hat{J}_a^2 + H_{KJ}\hat{J}^2\hat{J}_a^4 + H_K\hat{J}_a^6 \\
 & + h_1\hat{J}^4(\hat{J}_+^2 + \hat{J}_-^2) + h_2\hat{J}^2(\hat{J}_+^4 + \hat{J}_-^4) + h_3(\hat{J}_+^6 + \hat{J}_-^6)
 \end{aligned} \tag{3.17}$$

In addition to determining  $d_1$  and  $d_2$ , the fit yielded  $H_J$ ,  $H_{JK}$ ,  $H_{KJ}$ ,  $h_1$  and  $h_2$  ( $H_K$  and  $h_3$  were both fixed at zero). The standard deviations of the fits for  $^{12}\text{CO-OCS}$  and  $\text{CO-OC}^{34}\text{S}$  pure rotational transitions were 0.149 kHz and 0.211 kHz respectively, demonstrating the high precision of the FT microwave data. A simultaneous fit of the infrared and microwave data for  $^{12}\text{CO-OCS}$  was also performed, yielding a weighted standard deviation of 16.8 MHz. The microwave transitions were weighted at  $1.0 \times 10^9$  to reflect the higher precision of the measurements over the infrared data which were weighted 1.0 for the best determined lines. The constants are listed in **table 3.1**.

### 3.5 Analysis

For both upper and lower states of CO-OCS the inertial defect,  $\Delta = I_c - I_a - I_b$ , is small and positive ( $\Delta'' \approx 4.1 \text{ u } \text{\AA}^2$  and  $\Delta' \approx 3.8 \text{ u } \text{\AA}^2$ ), indicating a planar structure. Positive contributions to the inertial defect are due to Coriolis interactions associated with in-plane bending motions. Effective moments of inertia have been attributed to three contributions [28, 29] which can be written

$$I_{\text{effective}} = I_0 + \delta I_{\text{harmonic}} + \delta I_{\text{coriolis}} \tag{3.18}$$

$\delta I_{\text{harmonic}}$  and  $\delta I_{\text{coriolis}}$  model changes to a standard moment of inertia  $I_0$  (corresponding approximately to the equilibrium structure) due to averaging over vibrational amplitudes

Table 3.1 Spectroscopic constants of CO-OCS and its isotopomers obtained from infrared and microwave transitions.

| molecular constant                               | <sup>12</sup> CO-OCS: infrared | microwave and infrared | <sup>13</sup> CO-OCS: microwave | CO-OC <sup>34</sup> S: microwave |
|--------------------------------------------------|--------------------------------|------------------------|---------------------------------|----------------------------------|
| $\nu_0 / \text{cm}^{-1}$                         | 2 062.556 81 (17)              | 2 062.556 81 (5)       | ---                             | ---                              |
| $\Delta\nu_0 / \text{cm}^{-1} \text{ }^\ddagger$ | 0.355                          | 0.355 5                | ---                             | ---                              |
| $A'' / \text{MHz}$                               | 6 878.9 (17)                   | 6 879.613 72 (18)      | 6 874.566 50 (15)               | 6 749.517 57 (55)                |
| $B'' / \text{MHz}$                               | 1 463.1 (8)                    | 1 460.102 91 (10)      | 1 439.338 85 (6)                | 1 437.109 04 (19)                |
| $C'' / \text{MHz}$                               | 1 190.9 (9)                    | 1 192.921 17 (4)       | 1 178.977 98 (4)                | 1 173.555 13 (15)                |
| $\Delta'' / \text{u } \text{\AA}^2$              | 5.48 (53)                      | 4.062 30 (4)           | 4.025 40 (3)                    | 4.099 38 (11)                    |
| $D''_J / \text{kHz}$                             | 20 (7) <sup>§</sup>            | 9.786 (4)              | 9.480 (2)                       | 10.051 (3)                       |
| $D''_{JK} / \text{kHz}$                          | 138 (54) <sup>§</sup>          | 212.12 (2)             | 203.05 (1)                      | 183.70 (7)                       |
| $D''_K / \text{kHz}$                             | 1 220 (210) <sup>§</sup>       | 906.99 (4)             | 895.01 (4)                      | 947.34 (13)                      |
| $d''_1 / \text{kHz}$                             | ---                            | − 3.804 (3)            | − 3.617 (1)                     | − 3.881 (5)                      |
| $d''_2 / \text{kHz}$                             | ---                            | − 1.495 (1)            | − 1.402 9 (6)                   | − 1.393 (6)                      |
| $H''_J / \text{Hz}$                              | ---                            | 0.28 (9)               | 0.11 (2)                        | 0.0 <sup>¶</sup>                 |
| $H''_{JK} / \text{Hz}$                           | ---                            | 73.7 (6)               | 68.1 (2)                        | 69.3 (18)                        |
| $H''_{KJ} / \text{Hz}$                           | ---                            | − 395 (2)              | − 394 (2)                       | − 432 (15)                       |
| $h''_1 / \text{Hz}$                              | ---                            | 0.59 (7)               | 0.40 (2)                        | 0.0 <sup>¶</sup>                 |
| $h''_2 / \text{Hz}$                              | ---                            | 0.60 (4)               | 0.46 (1)                        | 0.42 (9)                         |
| $A' / \text{MHz}$                                | 6 956.9 (26)                   | 6 954.4 (13)           | ---                             | ---                              |
| $B' / \text{MHz}$                                | 1 449.4 (15)                   | 1 449.70 (81)          | ---                             | ---                              |
| $C' / \text{MHz}$                                | 1 189.7 (13)                   | 1 189.03 (48)          | ---                             | ---                              |
| $\Delta' / \text{u } \text{\AA}^2$               | 3.47 (85)                      | 3.75 (38)              | ---                             | ---                              |
| $D'_J / \text{kHz}$                              | 20 (7) <sup>§</sup>            | 18 (6)                 | ---                             | ---                              |
| $D'_{JK} / \text{kHz}$                           | 138 (54) <sup>§</sup>          | 165 (37)               | ---                             | ---                              |
| $D'_K / \text{kHz}$                              | 1 220 (210) <sup>§</sup>       | ---                    | ---                             | ---                              |
| $\sigma_{\text{fit}} / \text{MHz}$               | 17.3                           | 16.8                   | 0.000 149                       | 0.000 211                        |

<sup>†</sup> Figures in parentheses represent one standard deviation uncertainty.  
<sup>‡</sup> Based on  $\nu_{\text{monomer}} = 2062.20127 \text{ cm}^{-1}$  and  $\Delta\nu = \nu_{\text{dimer}} - \nu_{\text{monomer}}$ .  
<sup>§</sup> Centrifugal distortion coefficients were fixed to be identical for the ground and excited states and  $d_1$  and  $d_2$  were fixed at zero.  
<sup>¶</sup> Unable to be determined with statistical significance and set at zero.

and Coriolis effects respectively. Anharmonic terms cancel in calculating the inertial defect for planar species [30]. Of the harmonic contributions, only out of plane vibrations alter the inertial defect, introducing a negative change. For CO-OCS the Coriolis interactions dominate; the planar N<sub>2</sub>-OCS complex shows a positive inertial defect of similar magnitude [31].

**Figure 3.4** shows the coordinate system used to describe the effective structure of CO-OCS. The centre of mass (c.m.) to centre of mass (c.m.) distance  $R$  is determined from the  $C$  rotational constant using the relation

$$R = \left\{ \left( \frac{k}{\mu} \right) \left( \frac{1}{C} - \frac{1}{b_{\text{OCS}}} - \frac{1}{b_{\text{CO}}} \right) \right\}^{1/2} \quad (3.19)$$

where  $\mu$  is the reduced mass of the pseudodiatom formed between the CO and OCS, and  $k = 505\,379 \text{ MHz u } \text{\AA}^2$  (this assumes a planar structure). Only two of the three rotational constants are independent (because of the planar structure), which means that only the *dependence* of the two angles  $\theta_1$  and  $\theta_2$  can be deduced by solving

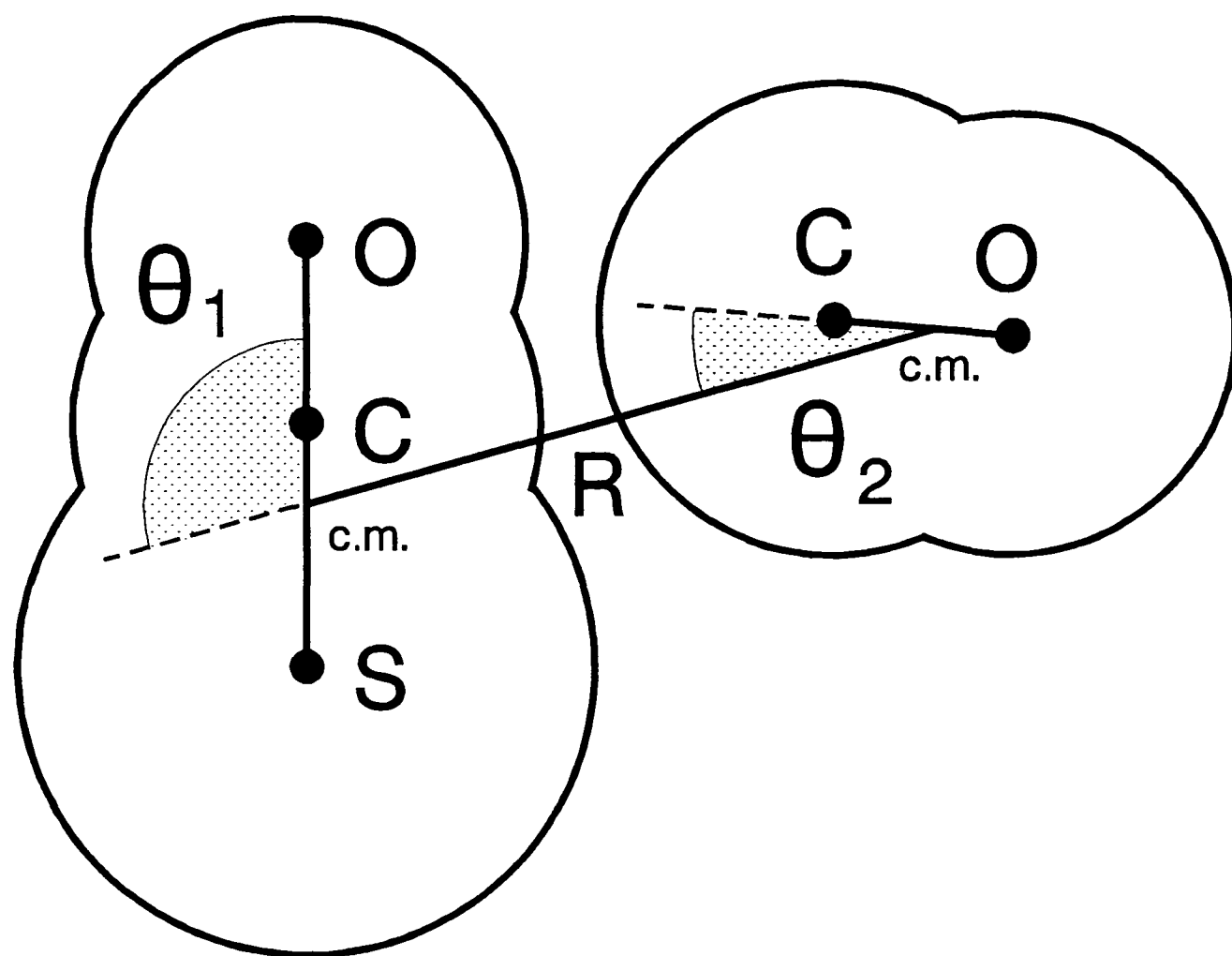
$$\begin{vmatrix} I_{xx} - I & I_{xy} \\ I_{yx} & I_{yy} - I \end{vmatrix} = 0 \quad (3.20)$$

(where  $I_{nm}$  are the elements of the inertial tensor matrix). A good indication of the value of  $\theta_1$  can readily be obtained from

$$I_{yy} = I_{\text{OCS}} \sin^2 \theta_1 + I_{\text{CO}} \sin^2 \theta_2 \quad (3.21)$$

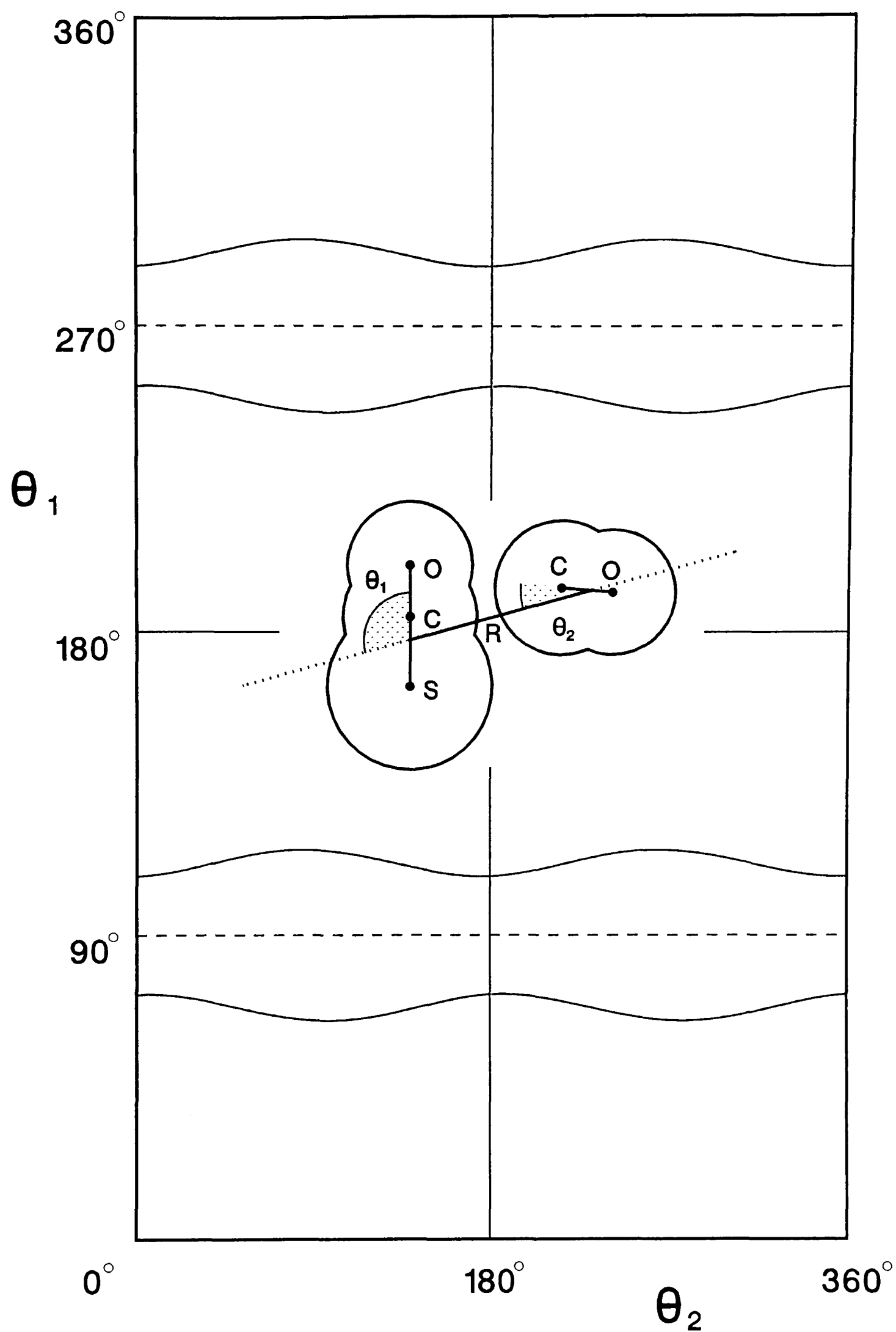
by recognising that  $I_{yy}/I_{\text{OCS}} \approx b_{\text{OCS}}/A$ , and the major contribution to  $I_{yy}$  is from  $\sin^2 \theta_1$  (since  $I_{\text{OCS}}/I_{\text{CO}} \approx 10$ ). This gives an approximate value of  $70^\circ$  or  $110^\circ$  for  $\theta_1$ . The full range of values possible for  $\theta_1$  and  $\theta_2$  are shown in **figure 3.5**. No unique set of solutions can be determined from the rotational constants because of the  $180^\circ$  periodicity of the sine and cosine functions, and although OCS is constrained to lie within a range of angles, its absolute orientation within the complex is still ambiguous. Furthermore, the CO alignment is unconstrained by the rotational constants and  $\theta_2$  may adopt any value between  $0$  and  $360^\circ$ . Hence the need for isotope data.

Upon isotopic substitution, the calculated value of  $R$  decreases from  $4.17 \text{ \AA}$  in  $^{12}\text{CO-OCS}$  to  $4.15 \text{ \AA}$  in the  $^{13}\text{CO}$  isotopomer. A shortening of the intermolecular bond



**Figure 3.4** The coordinate system used to describe the structure of CO-OCS.





**Figure 3.5** Relationship between  $\theta_1$  and  $\theta_2$  for CO-OCS from rotational constants.



indicates that the C atom is closest to the OCS c.m., and a simple calculation gives  $\theta_2 = \pm 20.50^\circ$ . (If the C atom were in fact external, the centre of mass separation would be expected to increase by at least  $0.022 \text{ \AA}$ , twice as much as the increase in this distance between the ground and first excited states.) This vibrationally averaged result does not rule out a potential minimum in which the CO internuclear axis is much closer to collinearity with the intermolecular c.m. to c.m. axis, since the majority of the terms in the diagonalisation of the inertial tensor are quadratic in sine and cosine. The off-diagonal terms

$$I_{xy} = I_{yx} = I_{\text{OCS}} \sin\theta_1 \cos\theta_1 + I_{\text{CO}} \sin\theta_2 \cos\theta_2 \quad (3.22)$$

contribute a small asymmetric factor which results in the slight ‘phase shift’ in **figure 3.5** away from symmetry about  $180^\circ$ .

An increase in  $R$  is observed for the CO-OC<sup>34</sup>S isotopomer. The effect of the <sup>34</sup>S will be to move the centre of mass of the OCS towards the S atom. A larger c.m. to c.m. distance therefore indicates that the CO is tilted away from the S end of the molecule, and of the two possible estimates for  $\theta_1$ ,  $110^\circ$  is consistent with the experimental evidence. The value calculated from the change in  $R$  and OCS c.m. position is  $105.7^\circ$ .

## 3.6 Distributed multipole analysis

**Table 3.2** summarises the structural information obtained from the combined infrared and microwave spectroscopy of CO-OCS and its isotopomers. Rotational constants for CO and OCS ( $v_3=0$  and  $v_3=1$ ) were obtained from Refs. 32 and 33 respectively. The isotope data has enabled accurate determination of an effective structure for the CO-OCS complex. However, because of the vibrational averaging the equilibrium values of  $\theta_1$  and particularly  $\theta_2$  will be smaller than the vibrationally averaged values obtained from the rotational constants.

Clearly, some indication as to the nature of the intermolecular potential would be helpful, particularly if it gave semi-quantitative information on the well-depth of the local minima in which the CO and OCS molecules find themselves. A simple model based upon the electrostatic and dispersive contributions to the intermolecular potential function

**Table 3.2** Structural parameters for CO-OCS<sup>¶</sup>.

| <i>isotopomer</i>                         | $R''/\text{\AA}$ | $R'/\text{\AA}$ | $\theta_1/^\circ$ | $\theta_2/^\circ$ | $v_{\text{vdW}}/\text{cm}^{-1}$ |
|-------------------------------------------|------------------|-----------------|-------------------|-------------------|---------------------------------|
| $^{12}\text{CO-OC}^{32}\text{S}$          | 4.169 4          | 4.178 (1)       | 105.7             | 20.50             | 32.6                            |
| $^{13}\text{CO-OC}^{32}\text{S}^\ddagger$ | 4.148 5          |                 |                   |                   | 32.5                            |
| $^{12}\text{CO-OC}^{34}\text{S}^\ddagger$ | 4.178 6          |                 |                   |                   | 31.4                            |

<sup>¶</sup> Figures in parentheses represent one standard deviation uncertainty; no parentheses indicate uncertainty less than 1 in last figure quoted.

<sup>‡</sup> Pure rotational transitions only.

can be used to calculate a potential surface for the system. The model combines a distributed multipole analysis (DMA) description of the monomer charge distribution [34, 35] and a dispersion contribution similarly distributed over the atoms. It is assumed that the induction contribution to the binding is small compared to the other terms; for (OCS)<sub>2</sub>, the induction energy has been estimated at only 5.9 cm<sup>-1</sup> [36], two orders of magnitude smaller than the corresponding dispersion energy.

Distributed multipoles for CO and OCS were already available [35, 36], and these are given in **tables 3.3** and **3.4**, together with appropriate dispersion coefficients as described below. Each monomer charge distribution is described by a charge, a dipole moment and a quadrupole moment located at each atom and at the centre of each bond: essentially a compact summary of information contained in the electronic wavefunction. The total electrostatic energy  $U_{\text{elec}}$  is then given by summing the individual interactions of all the sites on one molecule with all the sites on the other molecule:

$$U_{\text{elec}} = \sum_{a \in A} \sum_{b \in B} U_{ab} \quad (3.23)$$

where  $U_{ab}$  is the electrostatic energy for the interaction of site  $a$  in monomer  $A$  with site  $b$  in monomer  $B$ . The explicit forms for the interaction are given in Ref. 37.

For bimolecular interactions at large intermolecular separations, isotropic  $C_6$  coefficients may be used to model dispersion contributions ( $U_{\text{disp}} \approx -C_6/R^6$ ). By considering the total long range isotropic interaction for CO<sub>2</sub> ( $C_6=192.0$  au [38]) and OCS ( $C_6=402.2$  au [39]) a fraction of the total energy can be assigned to each pairwise atom-atom interaction. If the nine different pairwise interactions in (CO<sub>2</sub>)<sub>2</sub> are equally weighted, then 1/9 of  $C_6$  for CO<sub>2</sub> can be assigned to the O-O, C-O, and C-C interactions.

Table 3.3 Distributed multipoles and dispersion coefficients for CO<sup>†</sup>.

| /au   | <i>R</i> | <i>q</i> | <i>μ</i> | Θ      | γ    |
|-------|----------|----------|----------|--------|------|
| C     | 1.218    | 0.366    | −0.398   | −1.062 | 4.62 |
| C − O | 0.152    | −0.516   | −0.161   | 0.585  | 0.0  |
| O     | −0.914   | 0.150    | 0.430    | 0.128  | 4.62 |

Table 3.4 Distributed multipoles and dispersion coefficients for OCS<sup>†</sup>.

| /au   | <i>R</i> | <i>q</i> | <i>μ</i> | Θ        | γ     |
|-------|----------|----------|----------|----------|-------|
| O     | −3.179 5 | −0.055 2 | 0.273 5  | 0.375 4  | 4.62  |
| O − C | −2.083 3 | −0.892 3 | 0.034 8  | 0.337 2  | 0.0   |
| C     | −0.987 2 | 1.431 4  | −0.594 2 | −0.178 6 | 4.62  |
| C − S | 0.487 0  | −1.058 6 | 0.152 4  | 0.782 4  | 0.0   |
| S     | 1.961 2  | 0.574 7  | −0.759 2 | 1.942 8  | 10.82 |

<sup>†</sup> Positions (*R*), charges (*q*), dipole moments (*μ*), quadrupole moments (Θ), and dispersion coefficients (γ) all in atomic units (au).

Conversion factors to S.I. units are given below:

$1\,a_0 \approx 5.2918 \times 10^{-11}\,\text{m},$

$1\,e \approx 1.6022 \times 10^{-19}\,\text{C},$

$1\,e\,a_0 \approx 8.4784 \times 10^{-30}\,\text{C m},$

$1\,e\,a_0^2 \approx 4.48655 \times 10^{-40}\,\text{C m}^2.$

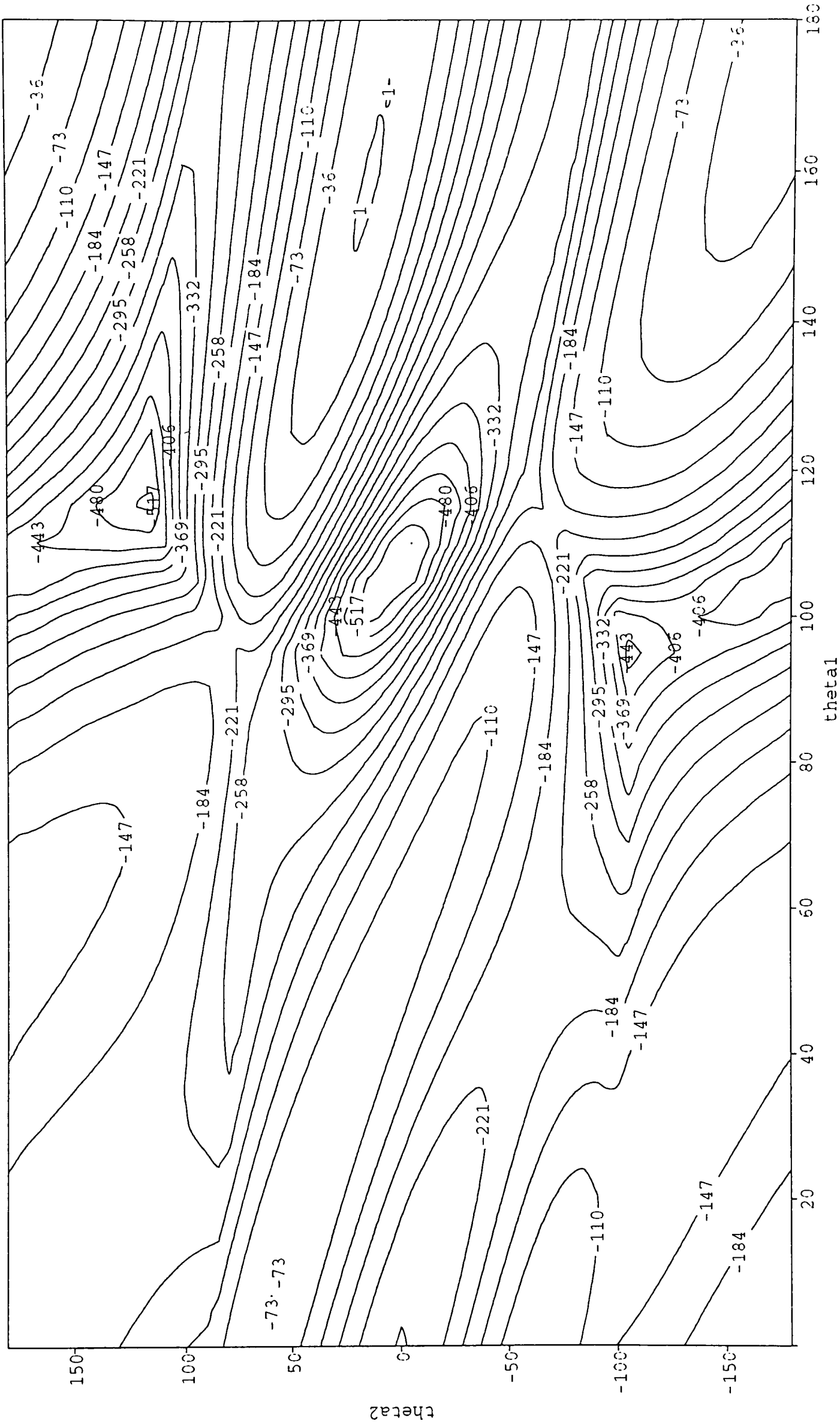
$\gamma$  is in units of  $(E_{\text{h}}\,a_0^6)^{1/2}$ ;  $1\,E_{\text{h}}\,a_0^6 \approx 9.574 \times 10^{-80}\,\text{J m}^6.$

Hence  $\gamma_C = \gamma_O = \sqrt{\{C_6/9\}}$ , where  $\gamma$  is the dispersion coefficient per atom, and  $C_6 = \sum \gamma_i \gamma_j$ , where the indices  $i$  and  $j$  run over the atoms of each monomer. This gives a value of 4.62 au for  $\gamma_C$  and  $\gamma_O$ . The procedure was repeated for OCS in order to determine  $\gamma_S$ , resulting in a value of 10.82 au. Using these coefficients,  $U_{\text{disp}} = \sum \gamma_i \gamma_j / R_{ij}^6$ . The total interaction energy for a given structure (defined by  $\theta_1$ ,  $\theta_2$ , and  $R$ ) is then the sum of the electrostatic and dispersion terms.

This methodology has previously been applied to  $(\text{OCS})_2$  [36] and  $(\text{CO}_2)_2$  [40] to choose between alternative structures with the same rotational constants. In these instances, the perpendicular separation was fixed at the experimentally determined value and a two dimensional potential constructed as a function of ‘parallel’ c.m. - c.m. displacement. To calculate the total interaction over a full range of values for  $\theta_1$  and  $\theta_2$  the molecules were treated as hard cylinders and the potential energy calculated for the closest possible in-plane approach. Each atom was assigned an effective radius corresponding approximately to the Van der Waals radius, but essentially empirically determined by reference to the  $(\text{OCS})_2$  and  $(\text{CO}_2)_2$  structures, i.e. values were chosen for the radii of the C and O atoms to correctly reproduce the observed structure of  $(\text{CO}_2)_2$ , and these in turn were used to determine an effective radius for S using the  $(\text{OCS})_2$  data.

The calculated potential surface is shown in **figure 3.6**; contour labels are in  $\text{cm}^{-1}$ . There are three potential minima. The deepest ( $U_{\text{total}} = -554 \text{ cm}^{-1}$ ) corresponds to the observed *T*-shaped geometry of the complex, with  $\theta_1 \approx 106^\circ$  and  $\theta_2 \approx 2^\circ$ . These angles define an *equilibrium* geometry. The calculated value of  $R$  for this energy (assuming a hard cylinder repulsion) is approximately 3.9 Å, too small by 5 %. This seems a fair error given the simple form attributed to the repulsion. The other two minima correspond approximately to the parallel conformers. The calculated centre of mass separations in these cases are over 15 % too small. The surprising feature of these minima is the lower energy for the parallel structure with the dipoles *aligned*, which is predicted to be 65  $\text{cm}^{-1}$  more favourable ( $U_{\text{min}} \approx -525 \text{ cm}^{-1}$ ) than its ‘anti-parallel’ analogue ( $U_{\text{min}} \approx -460 \text{ cm}^{-1}$ ). However, the small dipole moment of CO ( $\mu = 0.112 \text{ D}$  ( $3.74 \times 10^{-31} \text{ C m}$ )) results in the quadrupole moment playing the dominant role in the (electrostatic) structure determination.

Qualitative information about the dynamics of the system may also be inferred from the potential surface. The barrier to internal rotation of the CO, around 320  $\text{cm}^{-1}$ , is very high, indicating that the CO atom is not free to rotate, and undergoes a rocking motion of



significant amplitude. As has already been noted, the vibrationally averaged value of  $\pm 20.5^\circ$  for  $\theta_2$  does not preclude an equilibrium value for the angle much closer to zero, and such a rocking motion within its potential well would account for the calculated value. The OCS, though enjoying a shallower well (in the direction of change in  $\theta_2$ ) is limited by its greater inertia to much lower amplitude vibration (see **figure 3.5**). The calculated value of  $105.7^\circ$  for  $\theta_1$  is therefore a much better indication of its equilibrium value.

An estimate for the harmonic stretching frequency of the Van der Waals bond is readily obtained from  $D_J$  via  $D_J = (B + C)^3 / 2\nu^{2\dagger}$ , giving  $\nu_{\text{vdw}} = 33 \text{ cm}^{-1}$ , which compares with values of  $40 \text{ cm}^{-1}$  for  $(\text{OCS})_2$  [36] and  $47 \text{ cm}^{-1}$  for  $\text{CO}_2\text{-OCS}$  [41]. The centre of mass separation is significantly longer than for either of these species, indicative of a weaker interaction which is manifested in a smaller vibrational frequency. The potential energy minimum for  $(\text{OCS})_2$  was calculated at  $\sim 200 \text{ cm}^{-1}$  lower. A similar *T*-shaped structure is exhibited by  $\text{CO-CO}_2$ , which also has a long intermolecular bond ( $3.906 \text{ \AA}$  in the ground state). The small hypsochromic shift ( $0.356 \text{ cm}^{-1}$ ) for  $\text{CO-OCS}$  indicates a slight weakening of the Van der Waals bond upon vibrational excitation, but negligible vibrational coupling; the  $\text{CO-OCS } \nu_3$  mode is localised in the OCS monomer with little influence on the properties of the complex.

## 3.7 Conclusions

There are a number of comments which can be made concerning the rapid-scanning infrared spectrometer. As a general observation, the signal to noise ratio achieved was disappointing, although the time spent recording the data was considerably less than under the source modulation, gated detection scheme. For example, the scan reproduced in **figure 3.2** was recorded in approximately 5 minutes; the same frequency coverage would require 40 minutes using the previous system. Unfortunately, laser drift becomes a serious problem if  $> 10000$  scans are taken, and this prevents better sensitivity being achieved through longer averaging.

---

<sup>†</sup> The expression  $D = 4B^3/\nu^2$  is known as *Kratzer's Relationship*. For a derivation see '*Molecular Spectra and Molecular Structure Volume 1: Spectra of Diatomic Molecules*' p.104 by G. Herzberg, 2<sup>nd</sup> edition, Krieger Publishing Company; alternatively see A. Kratzer, *Z. Phys.*, **3**, 289 (1920).

However, the diode power output was very small ( $< 0.15 \mu\text{W}$ ), with the result that the detector noise becomes a significant factor, as explained in § 2.2.2. At this low power level, detector noise  $\sim 3$  parts in 100 for a single scan, compared to 1 part in 1000 for a more typical diode output power of  $1.5 \mu\text{W}$ . Since each absorption must be detected on every individual scan in order to average the spectrum effectively, those with less than 0.03 % absorption will tend to be lost in the detector, and thus reduce sensitivity.

Increasing the vertical resolution of the digitising card from 8 bit to 10 or 12 bit would also enhance the sensitivity, and such a measure was taken shortly after the CO-OCS measurements were completed (see § 2.3.3, and Chapter 4).

The residuals in the fit were also slightly larger than expected. The standard deviation of the fit for  $(\text{OCS})_2$  was 9.6 MHz [36], roughly half that for the CO-OCS fit. This may have been due to the poor signal to noise for some of the weaker lines combined with the density of the spectrum which resulted in many lines being blended. The process of line calibration and measurement should in principle be better protected from laser drift than previously. Any drift in the laser frequency will affect all subsequent scans and result in a concerted frequency shift manifesting as wider linewidths, and in extreme cases significant blurring and even doubling of spectral features. The previous method relied upon very slow scanning of the laser such that the frequency was approximately constant for the duration of several gas pulses. Thus a drift in the laser frequency shifted only subsequent lines by a certain amount resulting in inconsistencies in the etalon fringe/reference gas correlation.

Overall, however, the system has shown itself to be an effective and fast method of measuring high resolution infrared spectra of jet-cooled molecules.



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# Chapter 4

## The infrared spectrum and dynamics of Ne-SiH<sub>4</sub>

### 4.1 Introduction

The last few years have witnessed an awakening of interest in both the theoretical and experimental study of Van der Waals complexes involving spherical top molecules. This has largely grown out of the increasing success with which spectroscopic studies of weakly bound systems have been correlated to their dynamical behaviour via the calculation of potential energy surfaces. From initial microwave and infrared studies of Ar-H<sub>2</sub> [1] and Ar-HF [2, 3] accurate intermolecular potentials have been calculated from the experimental data [4, 5, 6] which have yielded information on the vibrational dependence of the potential as well as its anisotropy. The dynamics of such systems are now well understood, and various angular momenta coupling schemes have been identified [7].

There has been a growing effort to extend this understanding to complexes involving nonlinear molecules. Studies of complexes of light monomers such as H<sub>2</sub>O [8, 9] or NH<sub>3</sub> [10, 11] indicate the bending levels are best characterised by the internal rotation of the monomer in the complex [12], the same representation as for an atom-diatom complex where the potential anisotropy is of a similar magnitude to the monomer rotational constant.

The present understanding of complexes involving spherical tops is, however, far from complete. Scattering studies of rare gas atoms in collision with methane molecules are well established both experimentally by Buck *et al.* [13] and theoretically by Heil

and Secrest [14] and Smith and Secrest [15], though the bound state situation is obviously quite different. Microwave spectra of CH<sub>4</sub>-HCN and CH<sub>4</sub>-HX (X = Cl, F) have been recorded by Legon and co-workers [16, 17] and Ohshima and Endo have interpreted the microwave spectrum of CH<sub>4</sub>-HCl by considering the internal dynamics in the ground vibrational state [18]. However, very little dynamical information can be extracted from microwave studies since all the observed transitions occur between identical internal rotor states of the CH<sub>4</sub> molecule.

The first spectroscopic study of a rare gas-spherical top molecule was the pioneering work by Randall *et al.*, who recorded the infrared spectrum of Ar-SiH<sub>4</sub> in a supersonic jet expansion using direct absorption diode laser spectroscopy, in the region of the SiH<sub>4</sub>  $\nu_3$  vibration at  $\sim 2189\text{ cm}^{-1}$  [19]. Several groups have very recently obtained infrared spectra of rare gas-CH<sub>4</sub> complexes. Lovejoy and Nesbitt [20] and Block and Miller [21] have recorded the jet spectrum of Ar-CH<sub>4</sub> and McKellar has used a long-path low-temperature equilibrium cell to measure the infrared spectra of Ar-CH<sub>4</sub>, Kr-CH<sub>4</sub> [22] and Rg-SiH<sub>4</sub> (Rg = Ne, Ar, Kr) [23]. Theoretical advances have also been made, notably by Hutson and Thornley [24] who have used close-coupling methods to investigate vibration-rotation states of atom-spherical top complexes.

However, there has been a marked failure in attempts to combine the experimental and theoretical results, and none of the measured spectra has yet been successfully analysed, with one exception: Randall and Howard developed an anisotropic potential which successfully interpreted the hindered rotational structure of Ar-SiH<sub>4</sub> [25], and were able to fit the observed spectrum to an accuracy of  $0.03\text{ cm}^{-1}$ . The problem is simplified somewhat in Ar-SiH<sub>4</sub>, since it is a much more strongly anisotropic system than Ar-CH<sub>4</sub>, and exhibits behaviour intermediate between free rotor and rigid molecule limits, yet the potential model developed provides an important foundation upon which further studies can be based. Specifically, given a much more isotropic system, could the same model be used successfully to interpret the spectrum?

The smaller size and therefore lower polarisability of Ne results in its forming much ‘floppier’, less rigid complexes; for example the CO unit in Ne-CO [26] is much closer to the limit of nearly free internal rotation than in Ar-CO [27], demonstrated by the observation of a bending combination band in the former. Ne-SiH<sub>4</sub> should therefore

behave in a very similar fashion to Ar-CH<sub>4</sub>, and this chapter describes its infrared spectrum and the challenges faced (and overcome) in its analysis and interpretation.

## 4.2 Angular momentum coupling in atom-molecule Van der Waals complexes

Before considering the experimental details and presenting the spectra obtained for Ne-SiH<sub>4</sub>, there follows a brief discussion of the limiting behaviour of atom-molecule Van der Waals complexes in order to ascertain what behaviour might be expected for such a complex.

The intermolecular interactions which are responsible for the formation of Van der Waals complexes determine the structure and dynamical behaviour of these systems. The coupling between the various angular momenta present in the complex is a function of the intermolecular potential; the magnitude of the barrier to internal rotation of the molecule within the complex governs the extent of coupling and also therefore the energy levels of the complex. It is the magnitude of the anisotropic part of the intermolecular potential relative to the energy separation between rotational states of both the molecular component of the complex, and the complex as a whole, that determines the different angular momentum coupling schemes which can occur [28, 29].

For a fixed intermolecular separation  $R$ , the Hamiltonian for the rotational levels can be approximated to

$$H = B\hat{l}^2 + b\hat{j}^2 + V \quad (4.1)$$

where  $b$  and  $B$  are the rotational constants for the tetrahedral molecule and the diatom respectively,  $l$  is the angular momentum of the complex (operator  $\hat{l}$ ) and  $j$  is the angular momentum of the monomer unit (operator  $\hat{j}$ ) [30]. (The convention will be adopted that quantum numbers and operators written as upper case letters refer to the complex as a whole, whereas lower case letters refer to the isolated tetrahedral molecule). In general  $B \ll b$  since  $\mu > \mu_{mol}$  and  $R > r$ ; the relative magnitudes of  $B$  and  $b$  with respect to the

dominant anisotropic term in the potential,  $\Delta V$ , determines which of three major coupling schemes will occur. These are described below in order of increasing anisotropy.

#### 4.2.1 Case 1: $\Delta V \ll B \ll b$

For very low anisotropies the spherical top is almost free to rotate within the complex. Both  $j$  and  $l$  can be considered as (nearly) good quantum numbers, and the total angular momentum  $J$  is given by the vector coupling of  $j$  and  $l$ ,  $J = j + l$ . Both  $j$  and  $l$  may be considered to precess about the vector  $J$  as illustrated in **figure 4.1**, so that  $m_j$  and  $m_l$  are not individually conserved. The Hamiltonian may then be written [29]

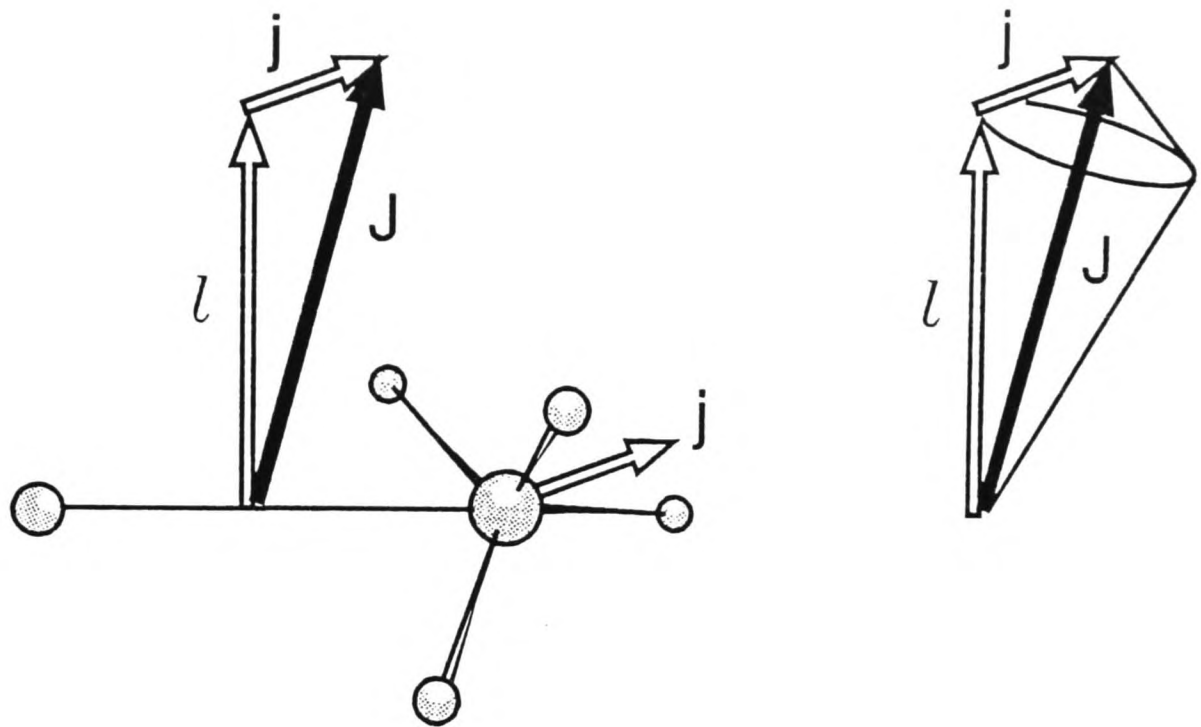
$$H = \frac{\hbar^2}{2\mu} \left( \frac{\hat{l}^2}{R^2} - \frac{\partial^2}{\partial R^2} \right) + H_{\text{mon}} + V \quad (4.2)$$

where  $l$  is the angular momentum of the pseudodiatom (with corresponding operator  $\hat{l}$ ),  $\mu$  its reduced mass ( $\mu = m_{\text{atom}} m_{\text{mol}} / \{m_{\text{atom}} + m_{\text{mol}}\}$ ), and  $R$  is the length of the vector  $R$  between the centres of mass of the neon atom and silane molecule.  $H_{\text{mon}}$  is the Hamiltonian for the isolated monomer molecule and  $V$  is the intermolecular potential. This expression is exact within the Born-Oppenheimer approximation. An approximate expression for the energy levels (at constant  $R$ ) is then

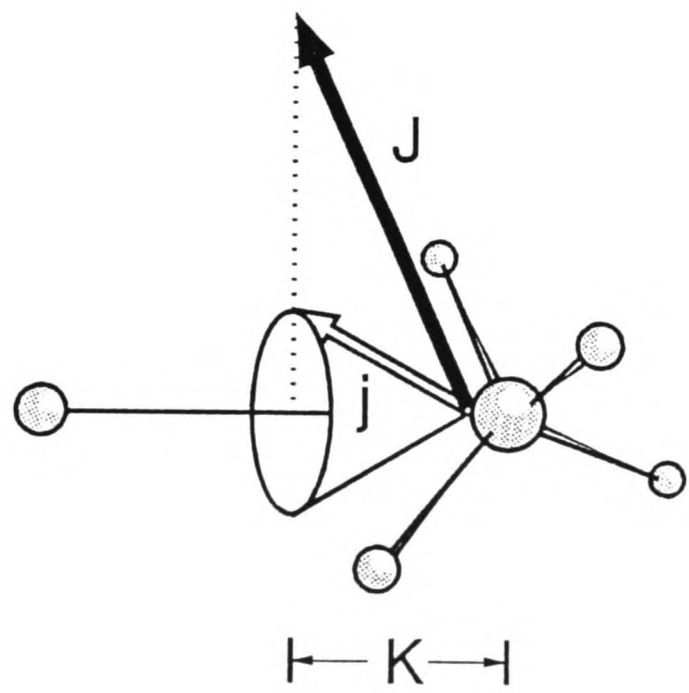
$$E(J, j, l) = b j(j+1) + B l(l+1) + \Delta V f(j, l, J) \quad (4.3)$$

where  $f(j, l, J)$  is a vector coupling term combining  $j$  and  $l$  to form  $J$ . For a given  $j$  and  $l$ ,  $J$  may take all values from  $|j-l|$  to  $|j+l|$ , therefore giving rise to groups of energy levels with a particular  $j$  and  $l$  which are split by the anisotropy of the potential into components of different  $J$ . Provided the separation between two levels of different  $l$  is much larger than the matrix elements of the anisotropic potential between these two states ( $\Delta V \ll B l$ ) this coupling scheme will be in operation.

Rare gas-H<sub>2</sub> [31] complexes are examples of atom-diatom systems where the relatively large  $B$  and small anisotropy result in this type of coupling.



**Figure 4.1** Case 1 angular momentum coupling in an atom-tetrahedral molecule complex.



**Figure 4.2** Case 2 angular momentum coupling in an atom-tetrahedral molecule complex.



### 4.2.2 Case 2: $B \ll \Delta V \ll b$

Case 2 coupling occurs when the anisotropic terms are large compared with the separation of different  $l$  levels, but remain small compared with the separation between levels of different  $j$ . Therefore  $j$  (but not  $l$ ) retains its meaning, and it is appropriate to replace  $\hat{l}$  by  $(\hat{J} - \hat{j})$  in the Hamiltonian, which becomes

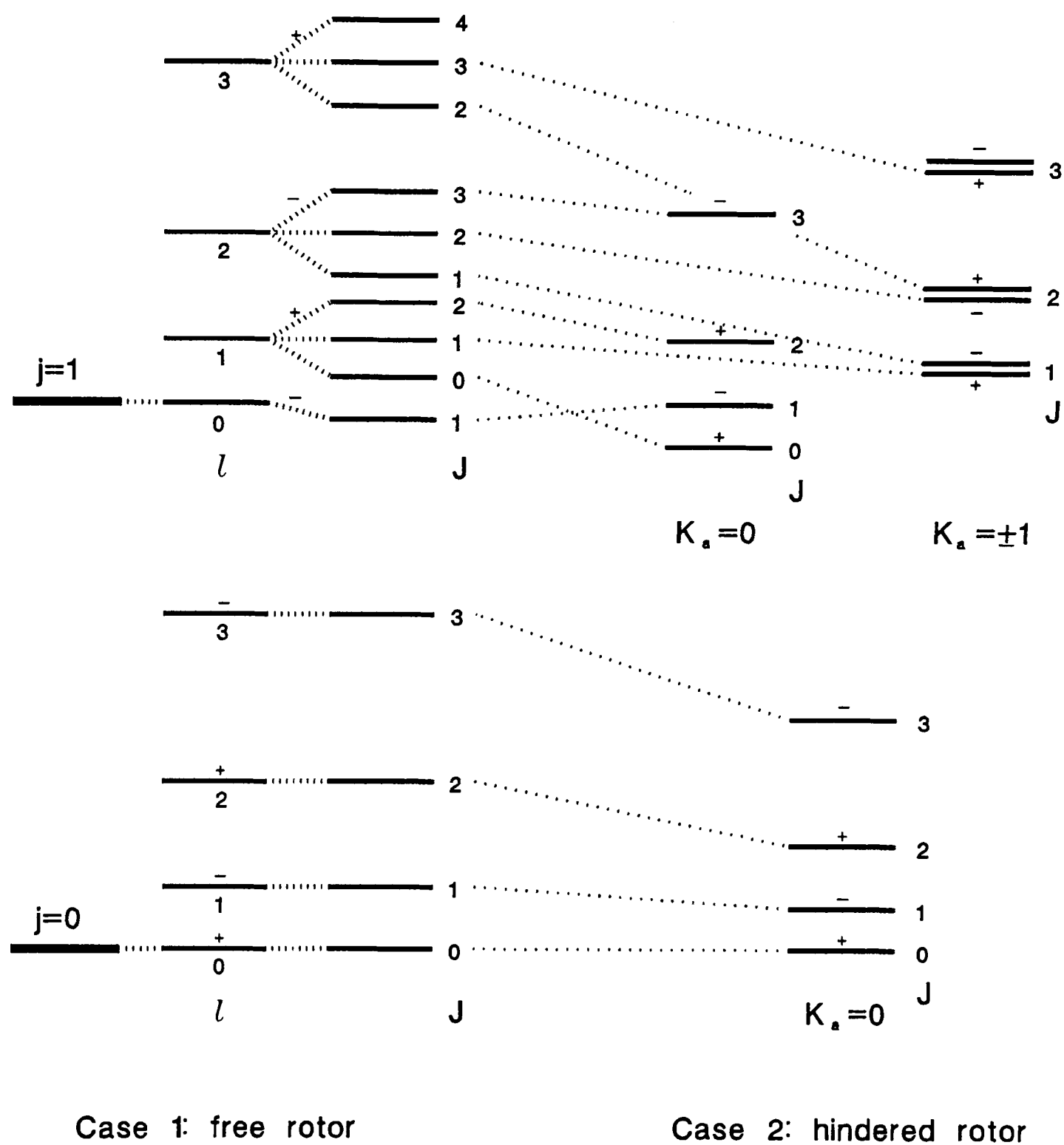
$$H = \frac{\hbar^2}{2\mu} \left\{ \frac{(\hat{J} - \hat{j})^2}{R^2} - \frac{\partial^2}{\partial R^2} \right\} + H_{\text{mon}} + V(R, \alpha, \beta, \gamma) \quad (4.4)$$

The potential  $V$  is a function of the intermolecular separation  $R$  and the orientation of the tetrahedral molecule with respect to the intermolecular axis. **Figure 4.2** shows a vector model, with  $j$  strongly coupled to the intermolecular axis, with a projection  $K$  onto this axis. The overall angular momentum is obtained by coupling  $j$  and  $l$  together.

The expansion of the  $(\hat{J} - \hat{j})^2$  term gives Coriolis matrix elements which couple states of the same  $j$  and  $J$  which have  $K$  differing by  $\pm 1$ .  $K$  is therefore no longer a perfect quantum number and the degeneracy of the  $\pm K$  levels is removed.  $K$  is however still a useful label, and the splitting is largest for the  $K = \pm 1$  states. Provided the Coriolis matrix elements remain substantially smaller than the splitting of the levels being mixed by the Coriolis interaction, this has the effect in second order of introducing slightly different rotational constants in the two levels. Coupling tends more towards case 1 when the splitting and the Coriolis interaction are of similar magnitude, either due to a decrease in the anisotropy or increase in the Coriolis term. The latter can occur without any change in the potential as  $J$  or  $j$  increase, resulting in case 2 operating at low  $J$  and case 2 at high  $J$ . The Ne-HF complex is an example of an atom-diatom system which appears to display this behaviour [32]. The magnitude of the Coriolis matrix elements for Ne-SiH<sub>4</sub> relative to the potential splittings are considered in detail in §4.11.1, and further discussion is left until then.

As well as splitting the different  $\pm K$  levels, an additional effect of the anisotropy is to mix states of differing  $j$  but the same  $K$ , with the result that levels with different values of  $K$  for a given  $j$  are not degenerate. A correlation diagram illustrating the change in energy levels with increasing anisotropy is shown in **figure 4.3**. Provided the anisotropy remains low, first order perturbation theory can be used to model the energy levels, which are given approximately by





**Figure 4.3** Correlation diagram showing transition from Case 1 to Case 2 coupling as anisotropy increases.

$$E(J,j,K) = B\{J(J+1) + j(j+1) - 2K^2\} + bj(j+1) + \Delta V f(j,K) \quad (4.5)$$

where  $f(j,K)$  gives the diagonal matrix element of the intermolecular potential in the state with quantum numbers  $j$  and  $K$ .

### 4.2.3 Case 3: $B \ll b \ll \Delta V$

If the energy spacing of the rotational states of the diatom is small compared with the anisotropy of the potential, the complex is forced to adopt a well defined equilibrium structure. This is common in atom-linear molecule and linear molecule-linear molecule complexes which typically adopt either parallel (for example OCS dimer [33]), *T*-shaped (CO-OCS [34]) or linear geometries (such as Ar-ClF [35]). The quantum numbers  $j$  and  $l$  are no longer conserved, although  $K$  is still quite good and retains its meaning (as  $K_a$ ). The internal states with different  $j$  and  $K$  then become vibrational states of a semi-rigid molecule.

Throughout this discussion the emphasis has been upon the splitting effect of the anisotropy  $\Delta V$  relative to the different rotational state separations approximated by  $b$  and  $B$ . A diagonal term in the potential (such as the  $V_4$  term introduced in § 4.8) results in energy level splittings which, depending on the magnitude of the splitting, will give rise to one of the cases above. For such a potential the appropriate quantum numbers may be summarised thus:

| case 1      | case 2      | case 3      |
|-------------|-------------|-------------|
| $j \ l \ J$ | $J \ K \ j$ | $J \ K \ v$ |

$v$  is the quantum number for the internal vibrational states of the semi-rigid case 3 molecule. However, for case 2 it has already been noted that the splitting of the  $K$  levels is accompanied by a *mixing* of the  $j$  levels. An off diagonal term in the potential (for example the  $V_3$  term introduced in § 4.8) will have a predominantly mixing effect on the energy levels. This may result in splittings appropriate to a case 2 coupling scheme, but with substantial mixing of energy levels resulting in  $j$  no longer being an appropriate

quantum number. A potential combining both diagonal and off diagonal terms may therefore produce angular momentum coupling which does not fit neatly into any one of these schemes, but they should nevertheless provide a valuable qualitative model for the treatment of such systems.

### 4.3 Experimental details

The infrared spectrum of Ne-SiH<sub>4</sub> was recorded in the vicinity of the SiH<sub>4</sub>  $\nu_3$  triply degenerate stretching vibration centred at 2189.19 cm<sup>-1</sup>. Scans were recorded using 12 bit digitisation at 1 MHz and typical scan rates of 0.5 - 1.0 cm<sup>-1</sup> ms<sup>-1</sup>. The digital resolution enhancement provided by the FLASH-12 card over the WAAG card (which had only 8 bit vertical resolution) afforded a sixteenfold improvement in amplitude resolution over the measurements of CO-OCS, and this proved invaluable for weaker areas of the spectrum. Indeed, scans recorded at the time of the Ar-SiH<sub>4</sub> measurements using mixtures of neon and silane and a range of backing pressures had failed to find any lines attributable to Van der Waals complexes [25].

The scans were calibrated by simultaneous recording of the absorption spectrum of N<sub>2</sub>O [36] in a room temperature gas cell (~0.5 Torr), and fringes of a 0.01 cm<sup>-1</sup> free spectral range (fsr) internally coupled Fabry-Perot etalon. A gas cell containing ~1 Torr pure SiH<sub>4</sub> was also available for regions of the spectrum where distinction between complex lines and monomer lines was difficult, particularly in the *Q* branch region between 2185 and 2189 cm<sup>-1</sup>. In practice, the spectrum was so congested that the only definite way to rule out ambiguous lines was by recording Ar-SiH<sub>4</sub> spectra in difficult regions and making direct comparisons. The calibration data were recorded using HgCdTe detectors.

Initially a 0.8 % mixture of SiH<sub>4</sub> in neon was used with backing pressures ranging from 2 to 5 atm (absolute) to search the region around 2192 cm<sup>-1</sup> where the strongest Ar-SiH<sub>4</sub> absorptions were detected. A cluster of closely spaced lines was observed around 2194 cm<sup>-1</sup> which did not correlate with any monomer lines, and the conditions were adjusted to optimise this signal. Optimum conditions were found to be 0.5 % SiH<sub>4</sub> in neon

with 3.5 atm (absolute) backing pressure expanding through a 350  $\mu\text{m}$  axisymmetric pulsed nozzle. This compares with a 1 % mixture and 0.75 - 1.25 atm backing pressure for Ar-CH<sub>4</sub>; harsher expansion conditions relative to argon complexes are demanded for neon because the lower binding energy of the complexes formed requires that more 3-body collisions are necessary once the jet has cooled to low rotational temperatures. However, the different pulsed nozzle source used in this work (a solenoid operated rather than piezoelectric valve opening mechanism) and the greater pulse lengths used with the rapid scanning system (1 - 2 ms rather than 250  $\mu\text{s}$ ) precludes too direct a comparison of the expansion conditions. The radiation was reflected a minimum of fifteen times through the jet before being focused onto an InSb detector, though the number of passes was increased where the mode power permitted.

An initial survey scan revealed complex lines over a broad region, from 2180 to 2205  $\text{cm}^{-1}$ , and subsequent scans were used to improve signal to noise. Typically 2000 coadditions were required for each scan of 1 - 2  $\text{cm}^{-1}$ , though regions of weak absorption (or poor laser modes) required longer averaging. Many regions were recorded several times, particularly during the process of assigning the spectra, to verify weak features or to discriminate against monomer lines by fine tuning the expansion conditions. This has the additional advantage of improving the statistical accuracy of the line measurements. Two laser diodes were employed, one of which operated sufficiently selectively in this region to be used without passing the radiation through the monochromator. Such single mode operation has the considerable advantage of maximising power at the detector (the monochromator may attenuate up to 50 % of the laser power of the selected mode) and ensuring the signals remain source rather than detector noise limited.

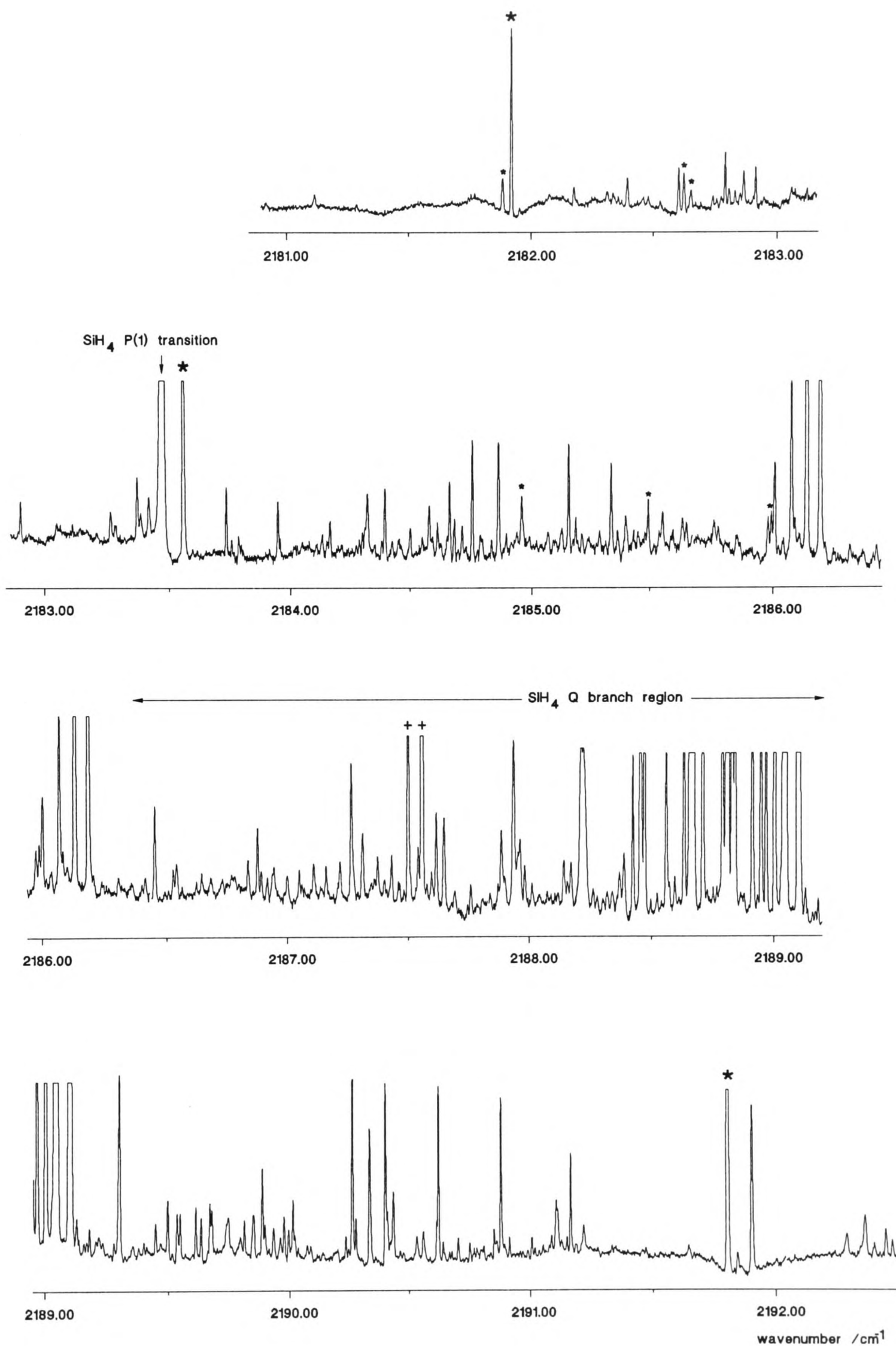
Signals were recorded using maximum high pass filtering (frequency cut-off at 2 kHz) to discriminate against low frequency noise and phase corrected using the Fourier transform technique detailed in Chapter 2. For regions where strong silane monomer absorptions appeared in the scan window (such as  $P(1)$ ,  $R(0)$ ,  $R(1)$  and the  $Q$  branch) too much distortion of the baseline occurred and the minimum setting was used (i.e. AC coupling to remove the InSb detector's 2 V DC offset). Additional filtering of low frequency noise was performed digitally using Fourier transform methods where the laser modes were particularly noisy, notably in the vicinity of the silane  $R(1)$  monomer absorption, but this was not generally necessary.

## 4.4 Preliminary results

The measured spectrum of Ne-SiH<sub>4</sub> is reproduced in full in **figures 4.4a** and **4.4b**. In common with other diode laser spectra, the intensities should not be taken to be absolute, as laser power varies across individual modes and between modes. As far as possible, however, the many discrete scans which make up the whole have been combined to preserve relative intensities within bands, though the vertical scale should not be assumed constant between different bands. Thus, the most intense complex absorptions occur in the region around 2194 cm<sup>-1</sup> near the silane *R*(0) transition; the band which appears to higher frequency of the silane *Q* branch region is displayed with expanded vertical scale for clarity, and similarly for other regions.

The task of identifying silane monomer transitions was made considerably easier by a low pressure (0.6 Torr), low temperature (98 K) static cell spectrum supplied by Dr A.R.W. McKellar of the NRC. The principal silane transitions have been labelled, and other monomer lines are marked by an asterisk. The silane *Q* branch is so dense, even in the cold environment of the jet, that individual labelling is impractical; most of the lines in the area indicated by the arrows are in fact monomer transitions. Those which are not are marked by a '+'. It is interesting that the corresponding region of the Ar-SiH<sub>4</sub> spectrum in Ref. 25 showed far fewer monomer lines, indicated either a colder jet or much more complexation by the argon.

The contrast with the recorded spectrum of Ar-SiH<sub>4</sub> is very marked. For the argon complex, most of the lines observed could easily be recognised as belonging to one of a series of *P* or *R* branches, with almost equal spacings between consecutive transitions given by approximately  $2B$ , where  $B$  is the rotational constant of Ar-SiH<sub>4</sub>. Each band in the spectrum was then fitted to within experimental accuracy using only rotational and quartic centrifugal distortion constants [25]. Slightly different  $B$  values were obtained for the different bands, which was accounted for by contributions from second order Coriolis interactions and the neglected radial dependence of the potential; an average  $B$  value of about 0.057 cm<sup>-1</sup> was obtained, giving a mean Ar-SiH<sub>4</sub> centre of mass separation  $R$  of approximately 4.04 Å. This distance can be scaled according to the smaller Van der Waals radius of Ne compared with Ar (1.55 Å and 1.88 Å respectively [37]) to calculate an expected rotational constant for Ne-SiH<sub>4</sub> (based upon the approximation of a rigid

**Figure 4.4a** Infrared supersonic jet spectrum of Ne-SiH<sub>4</sub>.

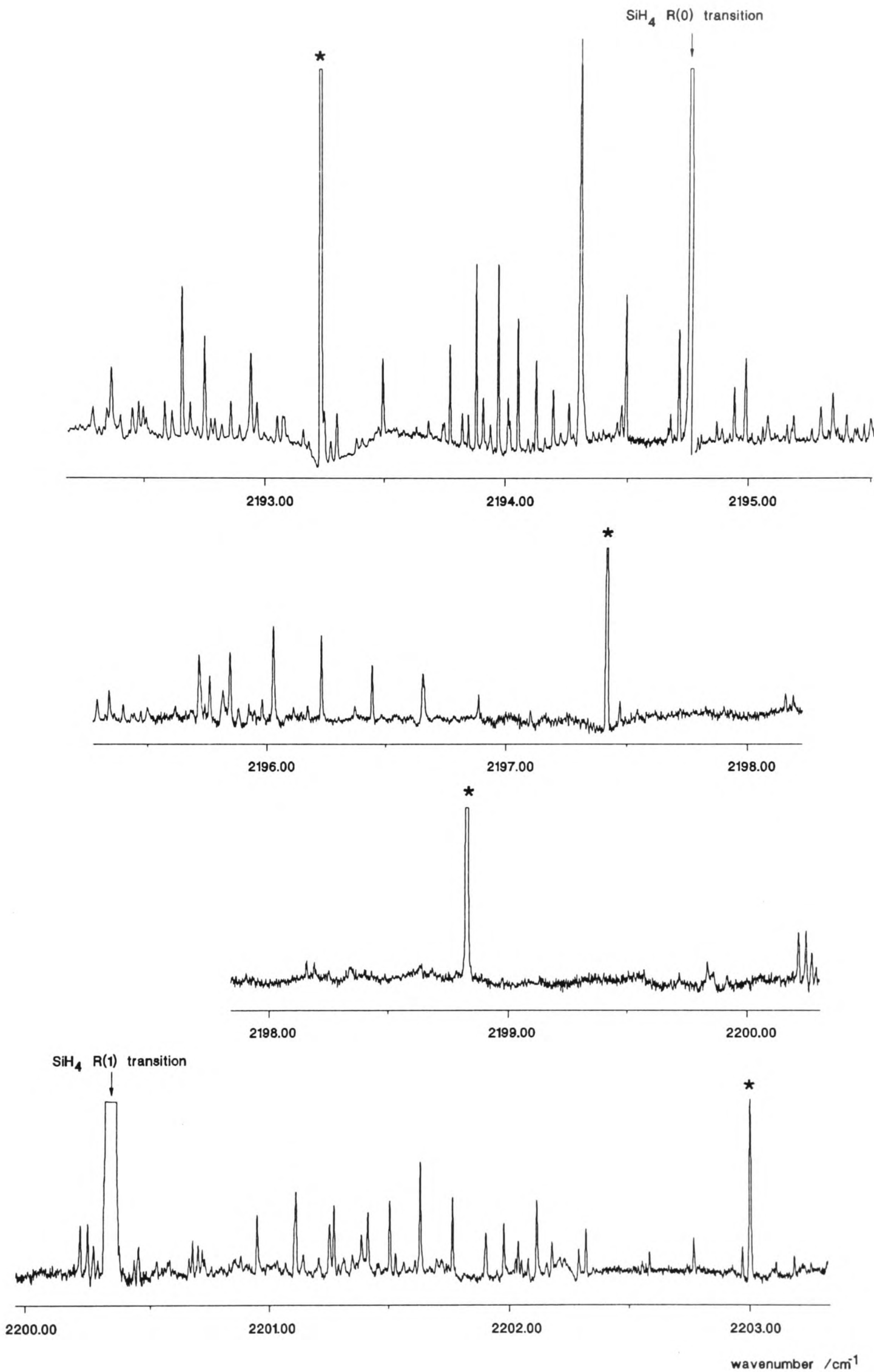


Figure 4.4b Infrared supersonic jet spectrum of Ne-SiH<sub>4</sub>.



structure). The relevant equation is

$$I_{\text{Ne-SiH}_4} = \mu R^2 + I_{\text{SiH}_4} \quad (4.6)$$

where  $\mu = m_{\text{Ne}}m_{\text{SiH}_4}/(m_{\text{Ne}} + m_{\text{SiH}_4})$  is the reduced mass of the complex,  $R$  is the centre of mass separation, and the  $I$  are the relevant moments of inertia which are related to the appropriate rotational constants (expressed in cm<sup>-1</sup>) by  $B = h/(8\pi^2cI)$  [ $h$  is Planck's constant and  $c$  the velocity of light]. This gave a predicted  $B$  value of 0.096 cm<sup>-1</sup>, and therefore line spacings within bands should be about 0.19 cm<sup>-1</sup> (i.e.  $2B$ ) if the complex behaves in an analogous manner to Ar-SiH<sub>4</sub>.

However, an examination of the spectra in **figures 4.4a** and **4.4b** revealed no obvious  $P$  and  $R$  band structure, and no constant 0.19 cm<sup>-1</sup> spacings. The three most conspicuous features of the spectrum, the series of lines around 2190.5, 2194.0 and 2196.0 cm<sup>-1</sup>, appeared to provide conflicting evidence.

The strongest absorbing 'band', around 2194.0 cm<sup>-1</sup>, consists of a single intense line at 2194.3 cm<sup>-1</sup> with a slight shoulder to high frequency, suggesting a  $Q$  branch. The spacing of the lines to lower wavenumber, suggesting a  $P$  branch, increases from 0.065 cm<sup>-1</sup> to 0.107 cm<sup>-1</sup> with decreasing wavenumber, and then abruptly stops, and there is no analogous band to higher frequency of the  $Q$  branch feature. There is, however, a series of lines of approximately the same intensity as the band to lower wavenumber, the spacings of which increase from 0.19 cm<sup>-1</sup> to 0.22 cm<sup>-1</sup>, but which rapidly lose intensity.

The other two bands, around 2190.5 and 2196.0 cm<sup>-1</sup>, show very similar structure, though the former is far stronger. Both appear to be  $R$  branches, but with no discernable  $P$  counterparts, and both exhibit increasing line spacings with higher wavenumber. The band around 2196 cm<sup>-1</sup> is superficially the most promising, with a steady increase in line spacing from 0.18 cm<sup>-1</sup> to 0.22 cm<sup>-1</sup>, whilst the series around 2190.5 cm<sup>-1</sup> shows a maximum spacing of 0.30 cm<sup>-1</sup>.

The first possibility to address was the presence of other complexes in the jet, particularly (SiH<sub>4</sub>)<sub>2</sub>. The formation of dimers and higher clusters is a common, if often unwanted, feature of neon expansions (see, for example, Ref. 26); the lower binding energy of neon complexes frequently results in their collisional destruction in favour of more stable dimers. By subtracting the Van der Waals radius of argon (1.88 Å) from the centre of mass separation in Ar-SiH<sub>4</sub>, a value for the Van der Waals radius of SiH<sub>4</sub> can be obtained, namely 2.17 Å. This is a minimum value because the equilibrium geometry of



the complex locates the argon atom over one of the faces of the SiH<sub>4</sub> tetrahedron, which behaves as a hindered rotor, and as a consequence it is able to approach slightly within the spherical Van der Waals radius. This radius gives a minimum centre of mass separation in (SiH<sub>4</sub>)<sub>2</sub> of about 4.34 Å, which corresponds to a maximum  $B$  value of approximately 0.05 cm<sup>-1</sup>. Assuming the anisotropy in silane dimer is similar to that in Ar-SiH<sub>4</sub>, line spacings within individual bands would be expected to be 0.1 cm<sup>-1</sup> or less. This cast doubt upon the identification of the lines around 2194 cm<sup>-1</sup> as arising from Ne-SiH<sub>4</sub>; given the smaller than expected spacing, perhaps they were due to the dimer, (SiH<sub>4</sub>)<sub>2</sub>. However, increasing the concentration of SiH<sub>4</sub> in the expansion mixture above 0.5 % resulted in a decrease in the intensity of these signals, rather than the increase which would be expected if the lines were indeed due to (SiH<sub>4</sub>)<sub>2</sub>. This appeared to confirm their identity as Ne-SiH<sub>4</sub> lines, and this conclusion was fully vindicated by subsequent analysis.

## 4.5 Rotational analysis

The spectrum of Ar-SiH<sub>4</sub> was successfully fitted to a model based upon a case 2 coupling scheme (see § 4.2.2), where several approximations were made to produce a viable set of equations which could be solved for the energy levels of the complex. It has already been stated that Ne-SiH<sub>4</sub> would be expected to demonstrate a lower rotational anisotropy, allowing significantly freer rotation of the tetrahedral monomer unit within the complex. In the isotropic limit of case 1 coupling, the selection rule  $\Delta l = 0$  would tend to result in transitions appearing at the same frequency, with consequent piling up of intensity, whilst the  $\Delta J = 0, \pm 1$  selection rule would produce a small splitting of each of these transitions. The overall effect therefore would be a very dense cluster of lines associated with each monomer  $j$  transition, and not the extensive band structure observed for Ne-SiH<sub>4</sub> and discussed above. It was therefore judged appropriate to investigate the rotational structure of Ne-SiH<sub>4</sub> using a case 2 basis, with particular consideration of whether the approximations made for Ar-SiH<sub>4</sub> were realistic for the more isotropic Ne-SiH<sub>4</sub> system.

The first approximation made was the assumption that the tetrahedral molecule retained its integrity upon complexation. In a more weakly bound system such as Ne-SiH<sub>4</sub>,

this is even more valid. The tetrahedral symmetry of silane is preserved and its Hamiltonian remains the same within the complex as it is for the free molecule. The Hamiltonian used is discussed in the next section (§ 4.6.2); in practice, the dominant effect of the intermolecular potential (§ 4.8) requires that only a fairly simple monomer Hamiltonian be used.

The second approximation made for Ar-SiH<sub>4</sub> was that the rotational and intramolecular stretching motions of the complex could be separated from the rest of the Hamiltonian in an adiabatic sense. That is, the energy levels of the silane monomer are perturbed only by the intermolecular potential, and the rotational and intramolecular vibrational levels of the complex can be built up on top of these levels as if the monomer rotational levels are separate librational or hindered rotational levels. In practical terms this means neglecting the Coriolis coupling between the rotation of the tetrahedral monomer unit within the complex and the end over end rotation of the complex. The term  $(\hat{J} - \hat{j})^2$  in the Hamiltonian for case 2 coupling (§ 4.2.2) can be expanded thus:

$$\begin{aligned} (\hat{J} - \hat{j})^2 &= \hat{J}^2 - 2\hat{J} \cdot \hat{j} + \hat{j}^2 \\ &= \hat{J}^2 - 2\hat{J}_x \hat{j}_x - 2\hat{J}_y \hat{j}_y - 2\hat{J}_z \hat{j}_z + \hat{j}^2 \\ &= \hat{J}^2 - 2\hat{J}_z^2 + \hat{j}^2 - (\hat{J}_+ \hat{j}_+ + \hat{J}_- \hat{j}_-) \end{aligned} \quad (4.7)$$

where the equivalence of  $\hat{J}_z$  and  $\hat{j}_z$  has been used, and  $\hat{J}_\pm$  and  $\hat{j}_\pm$  are raising and lowering operators<sup>†</sup>. The Coriolis coupling term is given by  $(\hat{J}_+ \hat{j}_+ + \hat{J}_- \hat{j}_-)$ , and has the effect of removing the degeneracy of the  $\pm K$  states.  $K$  is the ‘helicity’ quantum number, and therefore the neglect of Coriolis coupling terms off-diagonal in  $K$  is known as the helicity decoupling approximation [38].

The validity of this approximation can be judged according to a number of criteria. In general,  $K$  remains a good quantum number as long as the splitting due to the anisotropy of the potential is greater than the Coriolis matrix elements. If this is the case, the effects of the Coriolis interaction can be absorbed into the rotational constants and centrifugal distortion constants as a second order effect. A rigorous treatment of this topic is given later in § 4.11.1, but in general terms this condition for the helicity decoupling approximation can be formalised thus:

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<sup>†</sup> Note the anomalous commutation relations for the components of  $J$ , the angular momentum in the body fixed axis system:  $\hat{J}_\pm = \hat{J}_x \mp i\hat{J}_y$ . (For  $j$ ,  $\hat{j}_\pm = \hat{j}_x \pm i\hat{j}_y$ .)

$$\left\{ \frac{H_{\text{cor}}^2}{\Delta E} \right\} \ll \Delta E \quad (4.8)$$

where  $H_{\text{cor}}$  is the Coriolis matrix element between interacting  $K$  states and  $\Delta E$  is the splitting due to the potential. The Coriolis matrix elements are given by

$$\langle JjkK | H_{\text{cor}} | JjkK \pm 1 \rangle = -B [J(J+1) - K(K \pm 1)]^{1/2} \times [j(j+1) - K(K \pm 1)]^{1/2} \quad (4.9)$$

where  $B$  is the rotational constant of the complex. An important insight into the relative behaviour of the Ne-SiH<sub>4</sub> system can thus be made; it is expected to be closer to the free rotor limit than Ar-SiH<sub>4</sub>, and therefore demonstrate much lower anisotropy (giving a smaller  $\Delta E$ ), and its rotational constant is expected to be almost twice that of Ar-SiH<sub>4</sub>, giving rise to larger Coriolis matrix elements. Both these factors point towards the inadequacy of second order perturbation theory in modelling the Coriolis interaction; in contrast to Ar-SiH<sub>4</sub>, the rotational levels of the Ne-SiH<sub>4</sub> complex may be expected to experience significant perturbation due to rotation of the SiH<sub>4</sub> unit within the complex. This interaction between  $J$  and  $j$  will manifest itself in the following ways.

The major effect of the Coriolis term is to remove the degeneracy of the  $K = \pm 1$  and  $\pm 2$  levels associated with  $j = 1$  and 2. Thus  $j = 1$  gives rise to  $K = 0, \pm 1$ ; the  $|K| = 1$  levels, which are degenerate in the absence of Coriolis interaction, are the symmetric and antisymmetric combinations of the eigenstates with  $K = 1$  and  $K = -1$ :

$$\begin{aligned} |1^+\rangle &= 1/\sqrt{2} \{ |1\rangle + |-1\rangle \} \\ |1^-\rangle &= 1/\sqrt{2} \{ |1\rangle - |-1\rangle \} \end{aligned} \quad (4.10)$$

The degeneracy is lifted by the Coriolis interaction because only the symmetric combination,  $|1^+\rangle$ , has non zero matrix elements with the  $K = 0$  level  $|0\rangle$ :

$$\begin{aligned} \langle 0 | H_{\text{cor}} | 1^\pm \rangle &= \langle 0 | -B(\hat{J}_+ \hat{j}_+ + \hat{J}_- \hat{j}_-) | 1^\pm \rangle \\ &= -B/\sqrt{2} \{ \langle 0 | \hat{J}_- \hat{j}_- | 1\rangle \pm \langle 0 | \hat{J}_+ \hat{j}_+ | -1\rangle \} \\ &= -B/\sqrt{2} \{ \langle 0 | [J(J+1)j(j+1)]^{1/2} | 0\rangle \pm \langle 0 | [J(J+1)j(j+1)]^{1/2} | 0\rangle \} \\ &= -\sqrt{2} B [J(J+1)j(j+1)]^{1/2} \text{ only for } |1^+\rangle \end{aligned} \quad (4.11)$$

This has the effect of pushing the  $|0\rangle$  and  $|1^+\rangle$  levels apart whilst leaving the  $|1^-\rangle$  unperturbed. As a consequence, the  $|J 1^+\rangle$  states, i.e. the rotational levels associated with  $|1^+\rangle$ , appear further apart in energy whilst the  $|J 0\rangle$  states appear closer together. (This assumes that  $K = 0$  is lower in energy than  $K = 1$ ; the situation is reversed if the ordering

is inverted). Therefore a small interaction can be modelled by allowing different rotational and centrifugal distortion constants in each  $K$  state; a smaller  $B$  for the depressed rotational levels and a larger value for the elevated levels, with the  $|J 1^- \rangle$  levels unaffected and providing a 'true'  $B$  value reflecting the equilibrium structure of the complex.

Information on these unperturbed  $K$  states is contained within  $Q$  branch transitions associated with monomer transitions involving  $j$  levels up to  $j=1$  (in  $j=2$  perturbations can occur between  $|1^- \rangle$  and  $|2^- \rangle$  states). Only transitions with  $\Delta J=0$  can link symmetric states (i.e.  $|0 \rangle$  and  $|1^+ \rangle$ ) with antisymmetric states (i.e.  $|1^- \rangle$ )<sup>†</sup>. In the case of Ar-SiH<sub>4</sub>, no  $Q$  branches were resolved, and therefore the Coriolis corrections to the rotational constants were explicitly calculated in order to give equilibrium centre of mass separations.

The large discrepancy in line spacings in the Ne-SiH<sub>4</sub> spectrum is rationalised by this model. Spacings between adjacent lines for transitions between strongly Coriolis interacting levels would bear little or no relationship to a conventional near- $2B$  spacing expected from a second order model. Specifically, the strongest band around 2194 cm<sup>-1</sup> which has very small line spacings is easily accounted for. The two limiting cases are either transitions from an unperturbed  $K''$  level to a Coriolis depressed  $K'$  level, or transitions from a Coriolis elevated  $K''$  level to an unperturbed  $K'$  level. In either limit, spacings between  $R$  branch lines would be  $< 2B$  and become smaller as  $J$  increased, whereas spacings between  $P$  branch lines would be  $> 2B$  and become larger as  $J$  increased. The corresponding transitions involving the other Coriolis mixed level would demonstrate exactly the opposite characteristics: an  $R$  branch with large, increasing spacings and a  $P$  branch with small, decreasing spacings. The pattern of spectral lines around the 2194 cm<sup>-1</sup> region in **figure 4.4b** appeared to manifest exactly this effect.

The symmetry properties of the internal rotor states of SiH<sub>4</sub> are the subject of the next section (§ 4.6). It was, however, possible to assign and fit this and one other region of the spectrum by direct analogy with Ar-SiH<sub>4</sub> before a detailed analysis of the intermolecular potential had been undertaken, using this simple Coriolis interaction model. The symmetry labels given refer to the  $T$  point group which is discussed in detail in

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<sup>†</sup>  $P$  and  $R$  branch transitions between antisymmetric levels can occur when  $j' = j'' = 1$ , i.e. transitions associated with the monomer  $Q(1)$ .

§ 4.8<sup>†</sup>, and the transitions are labelled according to the silane monomer ro-vibrational transition upon which the complex rotational levels are built.

Except where stated, 'Ne-SiH<sub>4</sub>' refers to the most abundant isotopomer, <sup>20</sup>Ne-SiH<sub>4</sub>, and 'SiH<sub>4</sub>' will refer always to <sup>28</sup>SiH<sub>4</sub>.

### 4.5.1 $j = 1 \leftarrow 0$ $A \leftarrow A$ transitions

The strongest transitions observed in the Ar-SiH<sub>4</sub> spectrum were found to be the parallel and perpendicular bands correlating with the silane monomer  $R(0)$  transition. The anisotropy of the potential not only removes the  $2j+1$ -fold  $K$  degeneracy of each SiH<sub>4</sub> rotational level, causing splittings between states with different values of  $|K|$ , but also splits each rotational level into its symmetry components. In the ground vibrational state of silane ( $\nu_3=0$ ), the  $j=0$  level and therefore all the  $J$  levels associated with it have  $A$  symmetry. The only allowed transitions from these levels are to  $\nu_3=1$   $J$  levels with the same symmetry, which are those correlating to  $j=1$  and  $n=0$  (where  $n$  is the pure rotational angular momentum which, when coupled to the vibrational angular momentum  $l$ , gives the total angular momentum  $j=n+l$  [see § 4.6.1]). The upper state therefore consists of  $K=0$  and  $\pm 1$  states each with associated stacks of rotational levels. Given that it is the region of strongest complex absorption and the proximity to the monomer  $R(0)$  transition, the bands were assigned to the  $j = 1 \leftarrow 0$   $A \leftarrow A$  transition. This section of the spectrum with the assignments are reproduced in **figure 4.5**. Standard symmetric top notation has been used for the transitions, i.e.  ${}^{\Delta K}\Delta J_{K''}(J'')$ .

The  $K=0 \leftarrow 0$  parallel band is centred at  $2193.64\text{ cm}^{-1}$  and consists of a very intense, increasingly closely spaced  $R$  branch and a weaker increasingly widely spaced  $P$  branch which rapidly falls off in intensity. The picture is reversed for the  $K=1 \leftarrow 0$  perpendicular band centred at  $2194.30\text{ cm}^{-1}$ , where the  $R$  branch diminishes fast with increasing line spacing, and the  $P$  branch bunches up, maintaining its intensity to higher  $J$ . The perpendicular band also incorporates a  $Q$  branch (the  $|1^- \rangle \leftarrow |0 \rangle$   $\Delta J=0$  transitions) at the band centre which is not resolved.

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<sup>†</sup> The effect of complexation upon the silane monomer unit is to reduce its symmetry from  $T_d$  to  $T$ .

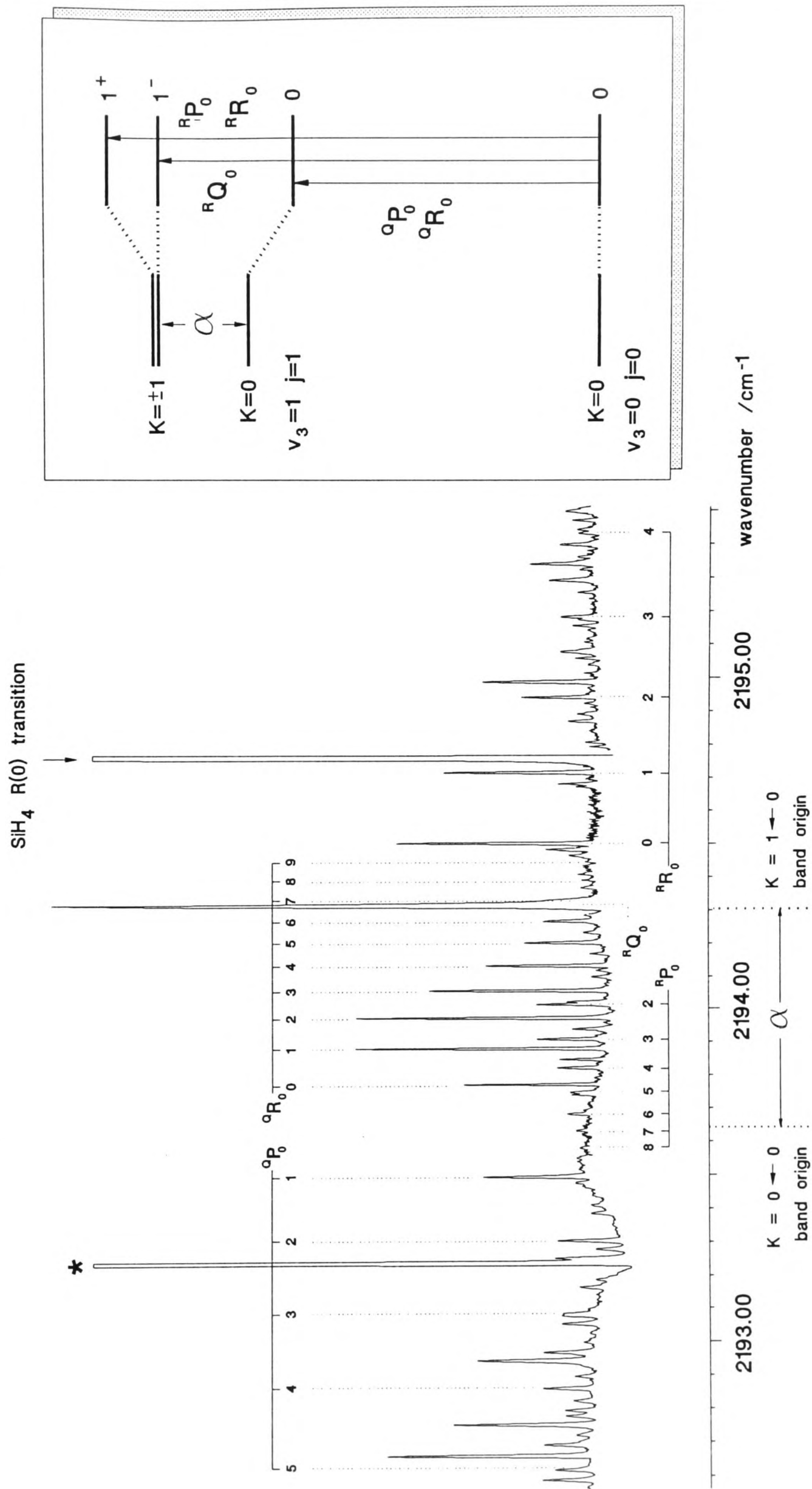


Figure 4.5 Ne-SiH<sub>4</sub> transitions correlating to SiH<sub>4</sub> R(0).

It is convenient to set the problem up using a case 2 basis set  $|JjK\rangle$ , as this most intuitively models the effect of increasing Coriolis interaction. The rotational Hamiltonian for the  $v_3 = 1$ ,  $j = 1$  levels is given by (see equation (4.7)):

$$H_{\text{rot}} = B(\hat{J} - \hat{j})^2 = B\{\hat{J}^2 - 2\hat{J}_z^2 + \hat{j}^2 - (\hat{J}_+ \hat{j}_+ + \hat{J}_- \hat{j}_-)\} \quad (4.12)$$

The Hamiltonian is diagonal in  $J$  and  $j$ ; the terms arising from  $B\{\hat{j}^2 - 2\hat{J}_z^2\}$ , namely  $\{Bj(j+1) - 2BK^2\}$ , can be included in a splitting parameter  $\alpha$  which also incorporates the effect of the potential and any vibrational terms;  $\alpha$  gives the separation of the two band origins. The energy level expression for the  $|1^- \rangle$   $J$  levels is simply

$$E_{|J1^- \rangle} = v_{K=0 \leftarrow 0} + B_{K=1}J(J+1) + \alpha \quad (4.13)$$

though since the  $Q$  branch was not resolved this was not required, and the energies of the  $v_3 = 0$ ,  $j = 0$  ( $K = 0$ ) levels are given by the usual  $BK(K+1)$  term.

The Coriolis matrix elements for the terms off diagonal in  $K$  are given in equation (4.11), resulting in a simple  $2 \times 2$  matrix, the eigenvalues of which give the energies of the rotational levels relative to the vibrational origin  $v_{K=0 \leftarrow 0}$ :

$$H = \begin{pmatrix} B_{K=0}J(J+1) & -\sqrt{2}B\{j(j+1)J(J+1)\}^{1/2} \\ -\sqrt{2}B\{j(j+1)J(J+1)\}^{1/2} & B_{K=1}J(J+1) + \alpha \end{pmatrix} \quad (4.14)$$

where  $B_{K=0}$  and  $B_{K=1}$  refer to the  $|J0\rangle$  and  $|J1^+\rangle$  states, and  $B$  is the geometric mean of these two values. The vibrational origin of the  $K = 1 \leftarrow 0$  band is given by  $v_{K=1 \leftarrow 0} = v_{K=0 \leftarrow 0} + \alpha$ . It is more appropriate to replace the  $j$  quantum number by an empirical parameter  $j^*$  given that the case 2 basis becomes increasingly invalid as the Coriolis interaction increases, and  $j$  may well no longer remain a good quantum number. The resulting energy level expression is then given by

$$E_K = v_{K=0 \leftarrow 0} + \left( \frac{B_{K=0} + B_{K=1}}{2} \right) J(J+1) + \frac{\alpha}{2} \quad (4.15)$$

$$\pm \frac{1}{2} \sqrt{\Delta B^2 J^2 (J+1)^2 + 2\alpha \Delta B J(J+1) + \alpha^2 + 8B^2 j^*(j^*+1)J(J+1)}$$

where  $\Delta B = B_{K=1} - B_{K=0}$ ; the positive root applies to the upper  $|1^+\rangle$  level and the negative root to the lower  $|0\rangle$  level of the Coriolis interacting pair. If the rotational constants in



the two interacting  $K$  states are constrained to be equal, then  $\Delta B = 0$  and equation (4.15) reduces to

$$E_K = \nu_{K=0 \leftarrow 0} + BJ(J+1) + \frac{\alpha}{2} \pm \sqrt{\left\{ \frac{\alpha^2}{4} + 2B^2j^*(j^*+1)J(J+1) \right\}} \quad (4.16)$$

The difficulty in allowing  $B_{K=0}$  and  $B_{K=1}$  to float separately is the high degree of correlation between these constants and the  $2B^2j^*(j^*+1)$  term, since both this and  $\Delta B$  are functions of  $J(J+1)$ . As  $\Delta B$  is likely to be very small, the higher order  $\Delta B^2J^2(J+1)^2$  term may not become sufficiently large to effectively distinguish between the Coriolis matrix element term and the upper vibrational state rotational constants. Two separate fits were therefore made of the data, initially to one rotational constant in  $\nu_3 = 1$  (equation (4.16)) and subsequently to separate values of  $B$  for  $K=0$  and  $K=1$  (equation (4.15)). The lines were fitted to these expressions using a Levenberg-Marquardt non-linear least squares method [39]. A quadratic centrifugal distortion term,  $-DJ^2(J+1)^2$ , constrained to be the same in both vibrational levels, was also introduced, and this improved the fit to well within experimental error. The fitted parameters for both fits are given in **table 4.1**, and the line positions and residuals are reproduced in appendix II.

As expected, the correlation matrix for fit 2 indicated very high correlation between the  $\nu_3 = 1$  rotational constants and the  $2B^2j^*(j^*+1)$  term (+0.99 for  $B_{K=0}$  and -0.99 for  $B_{K=1}$ ), although the standard deviation of fit 1 was approximately twice that of fit 2. Had higher  $J$  transitions been recorded the effects of  $\Delta B$  and the  $2B^2j^*(j^*+1)$  term would have been better separated. In view of this, the discussion below will refer to the values of fit 1, with the values from fit 2 in square brackets, except where the two values are significantly different. In fact, as can be seen from **table 4.1**, the majority of constants (with the obvious exceptions of  $B_{K=0}$  and  $B_{K=1}$ ) are relatively unchanged.

The rotational constant of Ne-SiH<sub>4</sub> for the  $A$  states was found to be  $\approx 0.016 \text{ cm}^{-1}$  smaller than anticipated at  $0.08023 \text{ cm}^{-1}$  [ $0.08000 \text{ cm}^{-1}$  for fit 2] in the ground vibrational state. In fit 1, the common  $\nu_3 = 1$   $B$  value was found to be  $0.08063 \text{ cm}^{-1}$ , whilst in fit 2 the  $B$  values showed considerable  $K$  dependence, with  $B_{K=1} = 0.08269 \text{ cm}^{-1}$  and  $B_{K=0} = 0.07817 \text{ cm}^{-1}$ . Since the interaction between the  $|0\rangle$  and  $|1^+\rangle$  states in  $j' = 1$  is the dominant Coriolis interaction in either vibrational level, these rotational constants can be thought of as ‘true’ in the sense that they are separated from the effect of Coriolis



**Table 4.1** Fitted parameters for  $j = 1 \leftarrow 0$   $A \leftarrow A$  transitions of Ne-SiH<sub>4</sub>.

| parameter                        | value <sup>¶</sup> /cm <sup>-1</sup> |                   |
|----------------------------------|--------------------------------------|-------------------|
|                                  | fit 1                                | fit 2             |
| $\nu_{K=1 \leftarrow 0}$         | 2 194.297 45 (31)                    | 2 194.297 92 (39) |
| $\nu_{K=0 \leftarrow 0}$         | 2 193.641 29 (31)                    | 2 193.640 54 (18) |
| $B'_{K=1}$                       | 0.080 625 (21)                       | 0.082 687 (70)    |
| $B'_{K=0}$                       |                                      | 0.078 170 (99)    |
| $B''$                            | 0.080 225 (19)                       | 0.080 000 (24)    |
| $\alpha$                         | 0.656 16 (35)                        | 0.657 38 (21)     |
| $\sqrt{2}B'\{j^*(j^*+1)\}^{1/2}$ | 0.103 20 (5)                         | 0.095 23 (17)     |
| $D_J$                            | 0.000 012 (3)                        | 0.000 007 4 (6)   |
| $\sigma_{\text{fit}}$            | 0.000 767                            | 0.000 363         |

<sup>¶</sup> Figures in parentheses represent one standard deviation uncertainty.

interaction, which has been treated as an off diagonal term rather than a second order correction (see Ref. 25)<sup>†</sup>. In the isotropic limit of free internal rotation, the moment of inertia of the complex is given simply by  $I = \mu R^2$ , and in the rigid (high anisotropy) limit by equation (4.6). For intermediate cases, the moment of inertia of the silane molecule in equation (4.6) is replaced by an effective contribution from the Coriolis coupling term  $-B\mathbf{J} \cdot \mathbf{j}$ , giving  $B_{\text{obs}} = B_{\text{pd}} + B_{\text{cor}}$ , unless the effects of the Coriolis interaction are sufficiently large that they must be dealt with explicitly. Assuming there are no significant second order effects from more distant  $A$  states the observed rotational constants for Ne-SiH<sub>4</sub> correspond much more closely to the free rotor limit

$$B_{\text{obs}} = \frac{h}{8\pi^2 c \mu R^2} \tag{4.17}$$

and the value of  $R$  gives the best radially averaged centre of mass separation of the complex.

<sup>†</sup> The weak Coriolis interaction with more distant  $A$  states should not be discounted, but other  $A$  states are sufficiently far away in energy to have only small second order effects on the rotational constants. Quantitative evaluation of these small corrections to the  $B$  values requires explicit evaluation of the Coriolis matrix elements for the interacting states and is dealt with in § 4.11.1.

In this limit the vibrational ground state centre of mass separation  $R'' = 4.132$  Å [4.138 Å for fit 2]. Both fits indicate a smaller centre of mass separation between neon and silane in at least one of the  $\nu_3 = 1$   $K$  states; for fit 1, the tied  $K = 0$  and  $K = 1$   $B$  value gives  $R' = 4.122$  Å, a 0.25 % shortening. A much more extreme situation is modelled by fit 2;  $R' = 4.186$  Å in the  $K = 0$  state, an increase of 1.3 %, whereas in the  $K = 1$  state  $R' = 4.070$  Å. This indicates a counter intuitive closer approach between neon and silane in the  $K = 1$  state of  $\nu_3 = 1$  with a 1.6 % shortening of the centre of mass separation. Since the  $j = 1$ ,  $K = 0, \pm 1$   $A$  states are the lowest lying  $A$  states in  $\nu_3 = 1$  ( $j = 0$  gives rise to a  $T$  state), there is no possibility of the  $K = 1$  rotational constant being elevated by weak Coriolis interactions from states below to give an artificially small value of  $R'$ ; the  $j = 1$  or 2  $A$  states could only have the opposite effect and depress the value of  $B'$ , giving an artificially large value of  $R''$ . It is possible that such an effect in the ground vibrational state results in too small a value of  $B'$  and therefore too large a value of  $R'$ . For a fuller discussion of this topic refer to § 4.11.1.

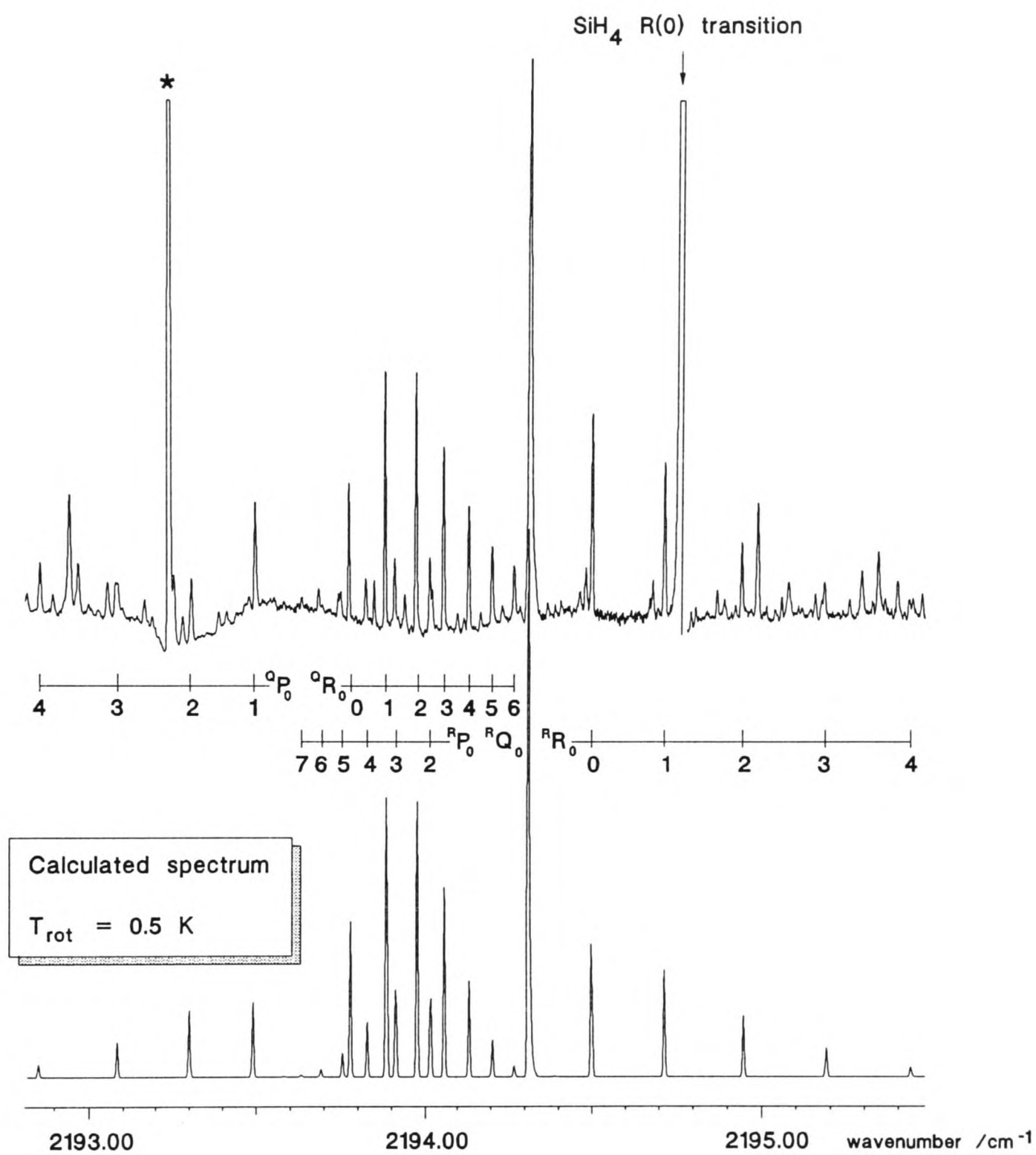
The main interest, however, of these results is that the centre of mass separation is larger in Ne-SiH<sub>4</sub> than in Ar-SiH<sub>4</sub> (the ‘corrected’ value for Ar-SiH<sub>4</sub> is 4.063 Å in the ground vibrational  $A$  state). With its larger Van der Waals radius, the argon complex would superficially be expected to have a larger  $R$  value. However, because Ar-SiH<sub>4</sub> is a more rigid structure, the argon atom is able to approach within the Van der Waals radius of SiH<sub>4</sub> (as has already been alluded to) by preferentially occupying a site on one of the faces of the SiH<sub>4</sub> tetrahedron and avoiding the protruding hydrogen electron density. The much freer rotation of the SiH<sub>4</sub> in Ne-SiH<sub>4</sub>, however, precludes such a cosy potential minimum, and the neon is forced to occupy a more distant position; it experiences a much more spherically averaged Van der Waals radius than the argon.

The discrepancy in fit 2 between the  $B'$  values for  $K = 0$  and  $K = 1$  may be due to the differing symmetries of the states.  $K = 0$  has  $j$  oriented perpendicular to the complex  $Z$  axis (the intermolecular axis) and thus has cylindrical symmetry about  $j$ . This is analogous to the spherical symmetry of the  $j = 0$   $A$  state in  $\nu_3 = 0$ ; the potential experienced by the neon is therefore isotropic provided  $R$  is constant.  $K = 1$  has  $j$  oriented at an angle to the intermolecular axis, removing the cylindrical symmetry (and therefore the angular isotropy of the potential) and perhaps resulting in a potential minimum over a face of the SiH<sub>4</sub> tetrahedron, allowing the neon to approach more closely.

The splitting,  $\alpha = 0.656 \text{ cm}^{-1}$  [ $0.657 \text{ cm}^{-1}$  for fit 2], is considerably smaller than the value of  $2.78 \text{ cm}^{-1}$  in Ar-SiH<sub>4</sub>, reflecting the much lower anisotropy in the neon complex. As the anisotropy of such a system tends to zero, so too does  $\alpha$ , and the two band origins tend towards the same value, an effective band origin, which itself tends to that of the pure monomer  $R(0)$  transition. An approximate value for this band origin,  $\nu_{\text{eff}}$ , can be calculated by taking the weighted average of the two band origins (there are twice as many  $J$  levels in  $K = 1$  as there are in  $K = 0$ ). This assumes the effects of the potential are approximately equal in both vibrational states. This yields a value of  $2194.079 \text{ cm}^{-1}$ , with the SiH<sub>4</sub>  $R(0)$  transition appearing at a frequency of  $\sim 2194.75 \text{ cm}^{-1}$  [40]. The shift in the band origin,  $\Delta\nu = \nu_{\text{eff}} - \nu_{\text{SiH}_4} \approx -0.67 \text{ cm}^{-1}$ , compares with a value for Ar-SiH<sub>4</sub> of  $-3.07 \text{ cm}^{-1}$ , indicating considerably smaller anisotropic behaviour of Ne-SiH<sub>4</sub> relative to its argon analogue.

The  $\Delta l = 0$  selection rule in the case 1 limit also explains the intensity effects observed within the bands. Reference to **figure 4.3** reveals the correlation between case 1 and case 2 coupling for a  $j = 1 \leftarrow 0$  transition. For  $K = 0 \leftarrow 0$  transitions, the  $^Q R_0$  transitions correlate to  $\Delta l = 0$  in the free rotor limit and are allowed in this limit, whereas the  $^Q P_0$  transitions (with the exception of  $^Q P_0(1)$ ) correlate to  $\Delta l = -2$ . As  $J$  increases, the off diagonal Coriolis matrix elements become larger, and the Ne-SiH<sub>4</sub> system becomes closer to the case 1 limit. Therefore the intensities of the lines reflect the case 1 selection rule, and the  $^Q P_0$  lines become forbidden and rapidly die away whereas the allowed  $^Q R_0$  transitions maintain their intensity to much higher  $J$ . The reverse situation operates for the  $K = 1 \leftarrow 0$  band; the  $^R P_0$  transitions are allowed in the free rotor limit, whilst the  $^R R_0$  transitions are forbidden, and it is the  $^R P_0$  band which maintains its intensity at higher  $J$ . The  $^R Q_0$  transitions are similarly allowed, having  $\Delta l = 0$  and would therefore be expected to show a lesser intensity reduction effect at high  $J$ ; however, this cannot be verified as the  $Q$  branch was not resolved.

The mechanism underlying this effect is the constructive and destructive interference of the transition dipole moment matrix elements between mixed states. Appendix III gives the relevant expressions for the expectation values of the transition dipole moment operators for the  $K = 0 \leftarrow 0$   $P$  and  $R$  branches and the  $K = 1 \leftarrow 0$   $P$ ,  $R$  and  $Q$  branches. **Figure 4.6** shows a calculated spectrum at  $T_{\text{rot}} = 0.5 \text{ K}$ , based on the parameters from fit 1, with the measured spectrum for comparison. The intensity effect



**Figure 4.6** Calculated and observed spectrum showing Coriolis modified intensities.

described above is convincingly reproduced, and the good overall agreement of the line intensities indicates that the rotational temperature in the jet is close to 0.5 K. An unexpected isotope effect in the jet enabled a more precise determination of  $T_{\text{rot}}$ , and this is described in the following section (§ 4.5.2). The relative intensity of the  $^R R_0$  transitions appears high in the measured spectrum, but this is likely to be due to the variation in power across the different laser modes used to cover the region. Normalisation of diode laser spectra, even within a single mode, is notoriously difficult.

This intensity loss effect at higher  $J$  for case 1 forbidden transitions is of course in addition to the normal effects due to Boltzmann populations in the cold environment of the jet and the Hönl-London factors for each  $\Delta J$  of  $-1$ ,  $0$  and  $+1$ . In the limit of completely unhindered rotation of SiH<sub>4</sub> within the complex, the allowed  $^Q R_0$ ,  $^R Q_0$  and  $^R P_0$  lines would coalesce at the band origin  $\nu_0$  where each  $\Delta l = 0$  transition would appear; the band origin itself would closely coincide with the SiH<sub>4</sub> R(0) transition. The  $J$  components of the levels would result in a small splitting of the lines, which would also gradually move away from the band origin at high  $l$  because of the different rotational constants in the upper and lower vibrational states.

The goodness of the  $j$  quantum number can be tested by evaluating the empirical parameter  $j^*$  from  $\sqrt{2B'}j^*(j^*+1)$ , which gives  $j^* \approx 0.53$ . This is indicative of the mixing of  $j = 1$  with higher states by the potential (see § 4.9 and equations (4.50) and (4.51)). The true ' $j = 1$ ' state of the complex is a linear combination of  $j$  states  $|j = 1\rangle + \lambda |j = 2\rangle + \dots$ , and the value of  $j^*$  derived from the Coriolis expression is an average reflecting contributions from higher states (with negative coefficients giving  $j^* < 1$ ). This illustrates well a coupling case which does not fall neatly into any of the cases outlined in § 4.2; the  $K$  quantum number has lost its meaning as the rotation of the SiH<sub>4</sub> becomes decoupled from the intermolecular axis of the complex at high  $J$ , but so has  $j$ , which under normal circumstances is a good quantum number in case 1. This effect is due to the off diagonal  $V_3$  term in the potential which mixes different  $j$  states; the form of the intermolecular potential is described in § 4.8 and further discussion is left until then.

The centrifugal distortion constant  $D_J$  is between one and two orders of magnitude larger for Ne-SiH<sub>4</sub> than for Ar-SiH<sub>4</sub>, indicating a considerably weaker intermolecular bond. The vibrational stretching frequency of the Van der Waals bond can be calculated from the relation  $D_J = 4B^3/\nu_0^2$  (see footnote p. 82), yielding a value of  $13.2 \text{ cm}^{-1}$  for fit 1 and

16.6 cm<sup>-1</sup> for fit 2; this compares with a value of 27.9 cm<sup>-1</sup> for Ar-SiH<sub>4</sub>. The relative bond strengths are further illustrated by calculating the stretching force constant for each complex (via  $k_s = 4\pi^2 c^2 \nu_0^2 \mu$ ); for Ne-SiH<sub>4</sub>,  $k_s = 0.126 \text{ N m}^{-1}$  [0.202 N m<sup>-1</sup> for fit 2], and for Ar-SiH<sub>4</sub>  $k_s = 0.791 \text{ N m}^{-1}$ .

No information on the  $|1^- \rangle$  state was obtained, other than that its  $B$  value is very close to that of the  $\nu_3 = 0$   $|0 \rangle$  since no  $Q$  branch structure was resolved. The perceptible shoulder to higher frequency indicates a slightly larger rotational constant in the upper vibrational state, and there is no reason to believe it is any different from the  $B$  of 0.08269 cm<sup>-1</sup> in the  $|1^+ \rangle$  state in fit 2; indeed, this value convincingly reproduces the observed  $Q$  branch lineshape. However, it is possible that weak Coriolis interactions with other antisymmetric  $A$  states could result in a slightly different rotational constant for the  $|1^- \rangle$  and  $|1^+ \rangle$  states.

### 4.5.2 <sup>22</sup>Ne-SiH<sub>4</sub> transitions and isotope enrichment

Careful examination of **figure 4.5** reveals a number of lines lying close to assigned Ne-SiH<sub>4</sub> transitions but with approximately one sixth the intensity. Neon occurs naturally in three isotopic forms: <sup>20</sup>Ne, <sup>21</sup>Ne and <sup>22</sup>Ne with isotopic abundances of 90.48 %, 0.27 % and 9.25 % respectively [41]. It may therefore be expected that for the stronger transitions, such as the  $R(0)$   $A \leftarrow A$  bands analysed in the previous section, spectra due not only to <sup>20</sup>Ne-SiH<sub>4</sub>, the most abundant species present in the jet, but also to <sup>22</sup>Ne-SiH<sub>4</sub> should be observed.

In total 12 lines were assigned and fitted as belonging to the <sup>22</sup>Ne-SiH<sub>4</sub>  $j = 1 \leftarrow 0$   $A \leftarrow A$  bands, illustrated in **figure 4.7**. The  $K = 0 \leftarrow 0$  lines were the most intense, with 7  $^2R_0$  lines and 2  $^2P_0$  transitions observed. Only 3  $^4R_0$  lines were sufficiently intense to be added to the fit from the  $K = 1 \leftarrow 0$  band, and therefore the  $\nu_3 = 1$   $j = 1$  rotational constants were tied together as for fit 1 in § 4.5.1 (i.e.  $B'_{K=0} = B'_{K=1}$ ). The results of the fit are given in **table 4.2**; line positions and residuals are listed in appendix II.

The <sup>20</sup>Ne-SiH<sub>4</sub>  $B$  values determined in fit 1 can be used to calculate anticipated <sup>22</sup>Ne-SiH<sub>4</sub> rotational constants and the Coriolis term, giving  $B'' = 0.07574 \text{ cm}^{-1}$ ,  $B' = 0.07611 \text{ cm}^{-1}$  and  $\sqrt{2}B\{j(j+1)\}^{1/2} = 0.00949 \text{ cm}^{-1}$ . The fitted parameters are reasonably close to these values, although the poorer data set used, with far fewer transitions,

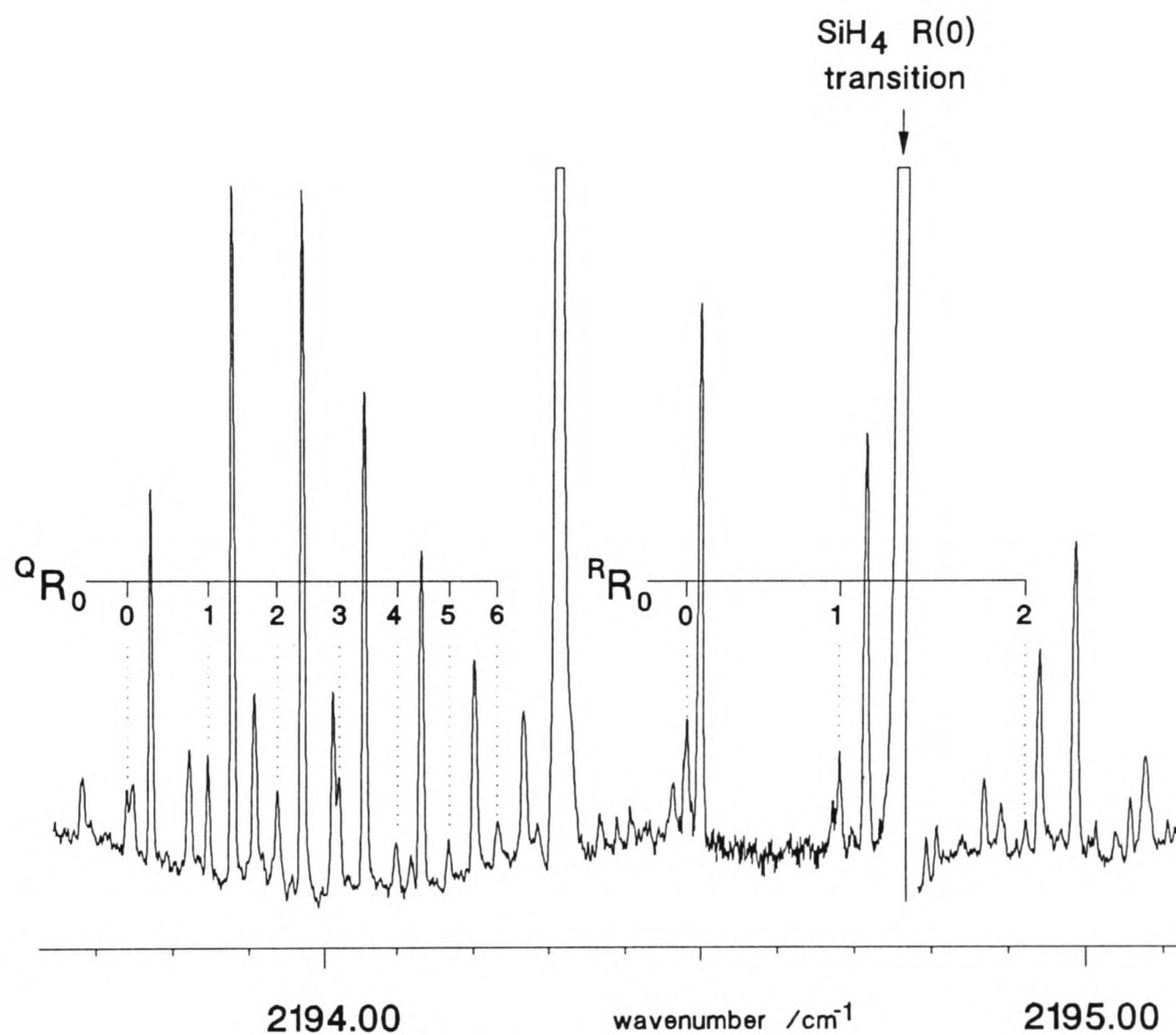


Figure 4.7 <sup>22</sup>Ne-SiH<sub>4</sub> transitions correlating to SiH<sub>4</sub> R(0).



**Table 4.2** Fitted parameters for  $j = 1 \leftarrow 0$   $A \leftarrow A$  transitions of <sup>22</sup>Ne-SiH<sub>4</sub>.

| <i>parameter</i>                 | <i>value</i> <sup>¶</sup> /cm <sup>-1</sup> |
|----------------------------------|---------------------------------------------|
| $\nu_{K=1 \leftarrow 0}$         | 2 194.284 19 (61)                           |
| $\nu_{K=0 \leftarrow 0}$         | 2 193.616 19 (61)                           |
| $B'_{K=1}$                       | } 0.078 339 (52)                            |
| $B'_{K=0}$                       |                                             |
| $B''$                            | 0.076 122 (44)                              |
| $\alpha$                         | 0.668 00 (62)                               |
| $\sqrt{2}B'\{j^*(j^*+1)\}^{1/2}$ | 0.104 32 (13)                               |
| $D_J$                            | 0.000 049 (1)                               |
| $\sigma_{\text{fit}}$            | 0.000 445                                   |

<sup>¶</sup> Figures in parentheses represent one standard deviation uncertainty.

particularly  $K = 1 \leftarrow 0$ , together with the  $B'_{K=0} = B'_{K=1}$  constraint, indicate that the fit is likely to yield parameters ambiguous in their interpretation. The extent to which the discrepancies between these and the calculated values are artefacts of the functional form of the Hamiltonian is unclear, given that constraining parameters to their calculated values results in a considerably worse fit ( $\sigma_{\text{fit}} = 0.0139 \text{ cm}^{-1}$ ).

A far more interesting and significant effect is uncovered by careful examination of the intensities of the <sup>22</sup>Ne-SiH<sub>4</sub> lines. Superficially one would expect the ratio of intensities of <sup>22</sup>Ne-SiH<sub>4</sub> lines to <sup>20</sup>Ne-SiH<sub>4</sub> lines to be simply the ratio of the natural abundances of the two isotopes, which is  $\approx 0.10$ . However, this is not the case; the mean intensity ratio obtained by comparison of the strongest <sup>22</sup>Ne-SiH<sub>4</sub> lines ( $^Q R_0(1)$ ,  $^Q R_0(2)$  and  $^R R_0(0)$ ,  $^R R_0(1)$ ) with their <sup>20</sup>Ne-SiH<sub>4</sub> analogues is  $\approx 0.16$ . The only explanation for this is a greater population of <sup>22</sup>Ne-SiH<sub>4</sub> in the jet than expected on purely statistical grounds. The Van der Waals bond of <sup>22</sup>Ne-SiH<sub>4</sub> has a slightly smaller vibrational frequency than <sup>20</sup>Ne-SiH<sub>4</sub>, and so a higher dissociation energy. If there persists in the jet sufficient binary collisions to maintain a quasi-equilibrium, collisional interconversion of the two main isotopic forms of Ne-SiH<sub>4</sub> will be allowed, favouring the formation of the more strongly bound <sup>22</sup>Ne-SiH<sub>4</sub> and increasing its population in the jet above the natural abundance of <sup>22</sup>Ne.



The effect can be considered quantitatively as follows. The equilibrium for the collisional interconversion of <sup>20</sup>Ne-SiH<sub>4</sub> and <sup>22</sup>Ne-SiH<sub>4</sub> is written



and the equilibrium constant for this process is defined as

$$K = \frac{[^{20}\text{Ne}][^{22}\text{Ne-SiH}_4]}{[^{20}\text{Ne-SiH}_4][^{22}\text{Ne}]} \quad (4.19)$$

where the square brackets denote concentrations. This can be rewritten in terms of the statistical mechanical partition functions  $q$  of the components thus

$$K = \left\{ \frac{q_{^{20}\text{Ne}} q_{^{22}\text{Ne-SiH}_4}}{q_{^{20}\text{Ne-SiH}_4} q_{^{22}\text{Ne}}} \right\} e^{\Delta D_0/kT} \quad (4.20)$$

where  $\Delta D_0$  is the difference in the binding energies  $D_0(^{20}\text{Ne-SiH}_4) - D_0(^{22}\text{Ne-SiH}_4)$ ,  $k$  is the Boltzmann constant and  $T$  is the temperature. Equations (4.19) and (4.20) can be combined to give

$$\frac{[^{22}\text{Ne-SiH}_4]}{[^{20}\text{Ne-SiH}_4]} = \frac{[^{22}\text{Ne}]}{[^{20}\text{Ne}]} \left\{ \frac{q_{^{20}\text{Ne}} q_{^{22}\text{Ne-SiH}_4}}{q_{^{20}\text{Ne-SiH}_4} q_{^{22}\text{Ne}}} \right\} e^{\Delta D_0/kT} \quad (4.21)$$

The molecular partition function  $q$  is the product of the contributions from each degree of freedom  $q = q_{\text{trans}} \times q_{\text{rot}} \times q_{\text{vib}} \times q_{\text{elec}}$ . Since the transitions in question arise from specific, well-defined ro-vibrational states of the ground electronic state of the Van der Waals molecule, the only significant contribution will be from  $q_{\text{trans}}$ , which is given by

$$q_{\text{trans}} = \frac{V}{\Lambda^3}, \quad \Lambda = \frac{h}{[2\pi mkT]^{1/2}} \quad (4.22)$$

where  $V$  is the volume,  $h$  is Planck's constant and  $m$  is the mass of the atom or molecule<sup>†</sup>. Equation (4.21) can then be reduced to

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<sup>†</sup> There will in addition be a small contribution from the rotational energy of the states. The intensity ratio has been calculated taking transitions from  $J \leq 2$ ; there is no underlying change in intensity ratio with increasing  $J$ , indicating that the effect of the rotational energy is negligible.

$$\frac{[{}^{22}\text{Ne-SiH}_4]}{[{}^{20}\text{Ne-SiH}_4]} = \frac{[{}^{22}\text{Ne}]}{[{}^{20}\text{Ne}]} \left\{ \frac{m_{{}^{20}\text{Ne}} m_{{}^{22}\text{Ne-SiH}_4}}{m_{{}^{20}\text{Ne-SiH}_4} m_{{}^{22}\text{Ne}}} \right\}^{3/2} e^{-\Delta D_0/kT} \quad (4.23)$$

where the ratio  $[{}^{22}\text{Ne}]/[{}^{20}\text{Ne}]$  is simply the ratio of the natural abundances of the isotopes (since  $[\text{Ne}] \gg [\text{Ne-SiH}_4]$ ).  $\Delta D_0$  can be calculated by scaling the vibrational frequency of the Van der Waals bond of  ${}^{20}\text{Ne-SiH}_4$ :

$$\nu_{\text{vdW}}({}^{22}\text{Ne-SiH}_4) = \nu_{\text{vdW}}({}^{20}\text{Ne-SiH}_4) \times \sqrt{\left\{ \frac{\mu_{{}^{20}\text{Ne-SiH}_4}}{\mu_{{}^{22}\text{Ne-SiH}_4}} \right\}} \quad (4.24)$$

where  $\mu$  is the reduced mass of the isotopomer. The mean of the values for  $\nu_{\text{vdW}}$  obtained from fits 1 and 2 is  $14.9 \text{ cm}^{-1}$ , giving a value of  $14.5 \text{ cm}^{-1}$  for the Van der Waals stretching frequency of  ${}^{22}\text{Ne-SiH}_4$ . The value of  $\Delta D_0$  is then given by half the difference between these values, i.e.  $\Delta D_0 = 0.20 \text{ cm}^{-1}$ . The temperature of the jet can then be calculated from equation (4.23) based upon the observed intensity ratio (and therefore population ratio) of the  ${}^{22}\text{Ne-SiH}_4$  and  ${}^{20}\text{Ne-SiH}_4$  lines. This yields a value of  $T_{\text{trans}} = 0.57 \text{ K}$ , which is thoroughly consistent with neon expansions, and close the result obtained previously for  $T_{\text{rot}}^\dagger$  by simply optimising the temperature at which the intensities were calculated in order to reproduce the observed intensities most closely (see **figure 4.6**).

The significance of this effect should not be underestimated, although its consequences are limited in scope. A supersonic expansion is typically described as a non-equilibrium method for the formation of Van der Waals complexes, depending upon kinetic factors to generate high concentrations of the species in the jet. This contrasts with static cell methods which depend upon true thermodynamic equilibria at low temperatures between the Van der Waals complexes and their constituent free monomer units. This result demonstrates a quasi-equilibration within a kinetic process, resulting in preferential conversion of  ${}^{20}\text{Ne-SiH}_4$  to  ${}^{22}\text{Ne-SiH}_4$  in the region of the jet where collisions are still occurring and facile isotopic exchange is possible. This thermodynamic selection is then frozen into the jet at the point of free molecular flow, where no further collisions occur.

There is currently much interest in the nuclear industry in the use of supersonic jets

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<sup>†</sup> Sufficiently downstream in a supersonic jet (i.e. once free molecular flow is achieved)  $T_{\text{trans}} \approx T_{\text{rot}}$ .

in conjunction with infrared lasers as a powerful uranium isotope separation technique<sup>†</sup> [42, 43]. Uranium, as UF<sub>6</sub>, is expanded through a nozzle and infrared photons are used to selectively excite and dissociate one <sup>235</sup>U-F bond; the resulting <sup>235</sup>UF<sub>5</sub> then aggregates and precipitates as a fine white solid. Although a different effect, it is interesting to see what has hitherto been a very powerful analytical tool being developed as a commercially important means of isotope purification. The efficiency of the process gives it considerable economic advantage over conventional gas centrifuging.

### 4.5.3 $j = 0 \leftarrow 1$ $T \leftarrow T$ transitions

The success with which the  $R(0)$   $A \leftarrow A$  transitions had been assigned and fitted with only an intuitive feel for the effects of the intermolecular potential encouraged a search for the Ne-SiH<sub>4</sub> transitions correlating with the silane  $P(1)$ . The ground vibrational state  $j=1$  ( $T$  symmetry) level was predicted to be analogous to the upper  $\nu_3=1$  state  $j=1$  ( $A$  symmetry) in § 4.5.1; if the splitting of the  $K=0$  and  $K=\pm 1$  states by the potential in the ground state is of a similar magnitude to that in the  $\nu_3=1$   $j=1$ , then strong Coriolis interaction would be expected, with all the accompanying effects described above, notably expanding and contracting  $P$  and  $R$  branches and intensities at high  $J$  dependent on the case 1  $\Delta l=0$  selection rule.

The pattern would be reversed relative to the  $R(0)$  bands in that transitions from the lowest lying  $j=1$  level,  $K=0$ , would appear to high frequency of the band origin and transitions from the upper levels ( $P$  and  $R$  branches from  $K=1^+$  and a  $Q$  branch from  $K=1^-$ ) to lower frequency. A difference in intensities between  $K=0 \leftarrow 0$  and  $K=0 \leftarrow 1$  would also be expected due to the split nature of the ground vibrational state; the population of the  $|JK\rangle$  states for a given  $J$  will be larger for  $K=0$  than for  $K=1$ .

The region around the SiH<sub>4</sub>  $P(1)$  line was carefully studied, and the  $K=0 \leftarrow 0$  band was identified, centred at 2185.0 cm<sup>-1</sup>. However, the  $K=0 \leftarrow 1$  band proved far more elusive; its very weak intensity (not least because of the disadvantageous Boltzmann factor) and the poor quality of the laser modes available in this region required repeated scans to be made of the region to confirm the presence of very weak features. The  $K=0 \leftarrow 1$

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<sup>†</sup> Molecular laser isotope separation (MLIS).

transitions were eventually pinpointed by the method of combination differences; the difference in frequency  $R(J) - P(J)$  for a given  $J$  must be the same for both  $K=0 \leftarrow 0$  and  $K=0 \leftarrow 1$  bands since the upper state is common to each. The assignments and energy level diagram are shown in **figure 4.8**.

Exactly the same Hamiltonian was used to describe the Coriolis interacting states, except in the ground vibrational state rather than  $\nu_3=1$ ; the splitting is given by  $\beta$ . The high  $J$  intensity loss is particularly severe in the  $^P P_1$  branch, which dies away so rapidly that only two transitions are observable. However, there is one advantage which this band has over the  $R(0)$   $A \leftarrow A$ , in that the  $^P Q_1$  branch is resolved. This has the important consequence of de-correlating  $B_{K=1}$  (and also therefore  $\Delta B$ ) from the Coriolis matrix element term  $\sqrt{2}B'j^*(j^*+1)$ , giving separate, well-determined rotational constants for  $K=0$  and  $K=1$  in  $\nu_3=0$ ,  $j=1$  deriving from equation (4.15).

The rotational constants in the  $|1^- \rangle$  and  $|1^+ \rangle$  states were tied as  $B''_{K=1}$ , and the  $j''=1$  and  $j'=0$   $|0 \rangle$  states were fitted to  $B''_{K=0}$  and  $B'$  respectively. The line positions and residuals are listed in full in appendix II, and the fitted parameters are reproduced in **table 4.3**. It is significant that even with reduced correlation between the ground vibrational state rotational constants and  $\sqrt{2}B'j^*(j^*+1)$ ,  $B_{K=0} < B_{K=1}$ . The Coriolis and splitting terms are very similar to those of the ' $R(0)$ ' band in **table 4.1**.

The  $B$  values correspond to centre of mass separations of 4.133 Å and 4.112 Å in the  $\nu_3=0$ ,  $K=0$  and 1 states respectively ( $B''_{K=0}=0.08017 \text{ cm}^{-1}$ ,  $B''_{K=1}=0.08101 \text{ cm}^{-1}$ ), and 4.142 Å in the  $\nu_3=1$ ,  $K=0$  states ( $B'_{K=0}=0.07983 \text{ cm}^{-1}$ )<sup>†</sup>. In common with fit 2 of the  $R(0)$  bands, the centre of mass separation for  $K=1$  is smaller than for  $K=0$  (although the difference is much less extreme), and for both  $P(1)$  transitions there is an increase in the value of  $R$  for  $\nu_3=1$  relative to  $\nu_3=0$ . The converse was found to be the case in Ar-SiH<sub>4</sub>, with a larger rotational constant for  $K=0$  than for  $K=1$  in the  $j=1$ ,  $\nu_3=0$   $T$  state ( $0.0580 \text{ cm}^{-1}$  and  $0.0576 \text{ cm}^{-1}$  respectively), and therefore a smaller  $R$  in  $K=0$  of 4.044 Å compared to 4.058 Å for  $K=1$ ; but in accordance with Ar-SiH<sub>4</sub>, Ne-SiH<sub>4</sub> has a larger centre of mass separation in the  $\nu_3=0$   $j=0$   $A$  state than the  $j=1$   $T$  states, despite the  $A$  state having lower energy. However, since this state correlates with the spherically

<sup>†</sup> As with the  $A$  states involved in the  $R(0)$  bands, these are the lowest lying  $T$  states and therefore the fitted rotational constants are 'maximum' values; it is likely that weaker Coriolis interactions with higher energy  $T$  states will cause a slight depression in the rotational constants. The reader is referred to § 4.11.1 for a more detailed discussion.

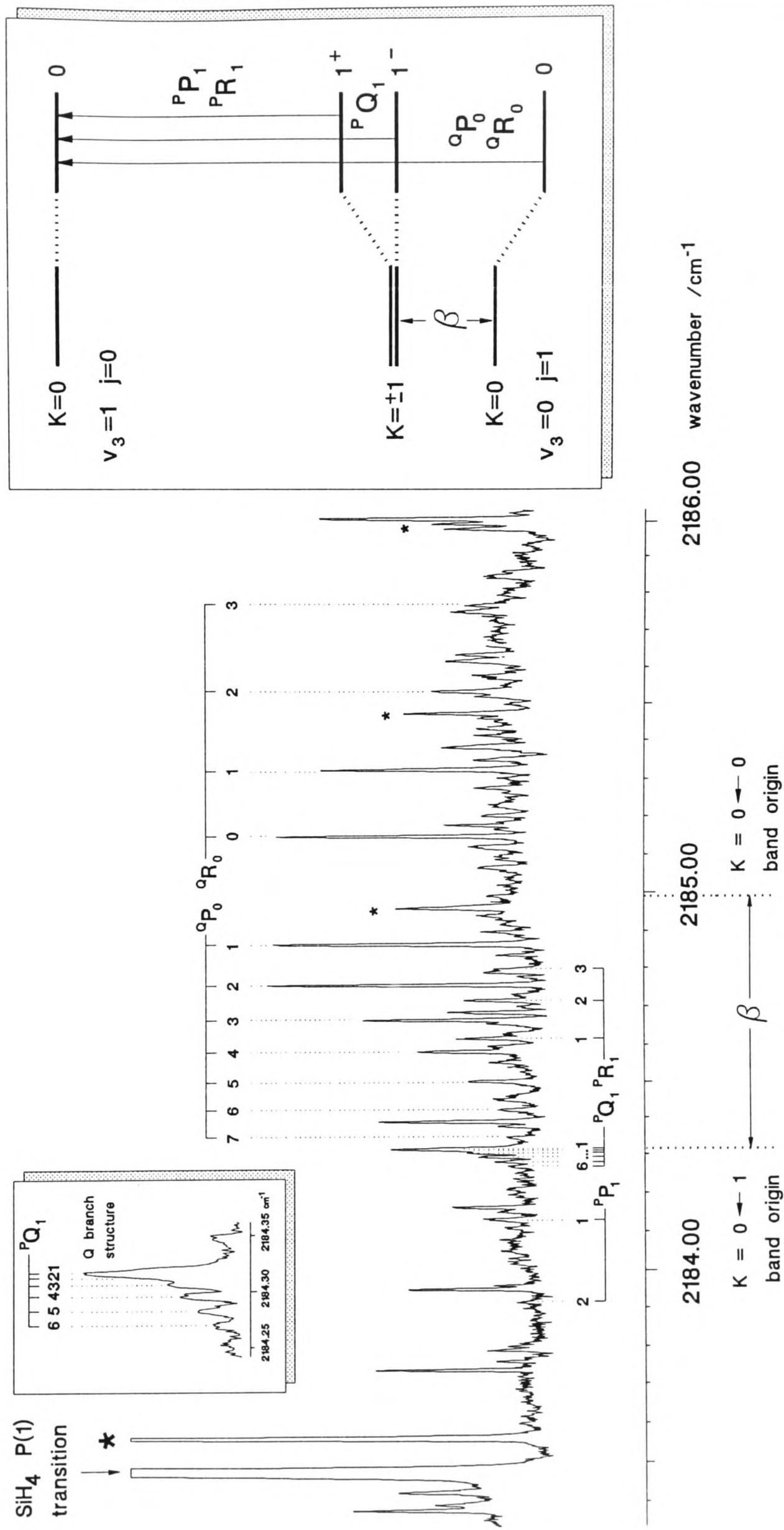


Figure 4.8 Ne-SiH<sub>4</sub> transitions correlating to SiH<sub>4</sub> P(1).

Table 4.3 Fitted parameters for  $j = 0 \leftarrow 1$   $T \leftarrow T$  transitions of Ne-SiH<sub>4</sub>.

| Parameter                         | value <sup>¶</sup> /cm <sup>-1</sup> |
|-----------------------------------|--------------------------------------|
| $\nu_{K=0 \leftarrow 0}$          | 2 184.992 55 (25)                    |
| $\nu_{K=0 \leftarrow 1}$          | 2 184.320 51 (67)                    |
| $B'$                              | 0.079 825 (43)                       |
| $B''_{K=1}$                       | 0.081 008 (47)                       |
| $B''_{K=0}$                       | 0.080 171 (71)                       |
| $\beta$                           | 0.672 04 (42)                        |
| $\sqrt{2}B''\{j^*(j^*+1)\}^{1/2}$ | 0.100 94 (14)                        |
| $D_J$                             | 0.000 012 1 (6)                      |
| $\sigma_{fit}$                    | 0.000 473                            |

<sup>¶</sup> Figures in parentheses represent one standard deviation uncertainty.

symmetric  $j = 0$ , the potential is isotropically averaged; there is no minimum corresponding to the SiH<sub>4</sub> faces and this prevents a closer approach. **Table 4.4** summarises relevant parts of the discussion for comparison purposes.

The splitting parameter  $\beta$  is only 2 % larger than  $\alpha$  for the *A* states, perhaps superficially indicating little change in the intermolecular potential between the ground and first excited vibrational levels, suggesting that there is not a significant contribution from the vibrational anisotropy arising from the triply degenerate  $\nu_3$  stretch. The  $K = 0 \leftarrow 1$  band was not observed in the Ar-SiH<sub>4</sub> spectrum, but a splitting of  $\approx 2.4$  cm<sup>-1</sup> was determined by taking other transitions from out of the  $K = 1$  levels. The value of  $j^*$  (0.517) is similar to that for the  $\nu_3 = 0, j = 1$  *A* states, and indicates a comparable mixing of  $j = 1$  with higher states.

The effective band origin (2184.545 cm<sup>-1</sup>) shows a shift of +1.07 cm<sup>-1</sup> from the silane monomer *P*(1) transition (2183.475 cm<sup>-1</sup>), approximately twice the magnitude and opposite in sign to  $\Delta\nu_0$  for the *R*(0) associated transitions. Although  $\Delta\nu_0$  for *R*(0) and *P*(1) would be expected to have the same magnitude but opposite sign (assuming the effects of the potential to be the same in the ground and first excited vibrational level), the difference may be accounted for by a positive shift in the vibrational frequency  $\nu_3$  itself due to the

Table 4.4 Band origin shifts,  $j^*$ , and centre of mass separations for  $R(0)$  and  $P(1)$  associated bands of Ne-SiH<sub>4</sub>.<sup>†</sup>

| transition:                 | $j = 1 \leftarrow 0 \quad (A \leftarrow A)$ |              | $j = 0 \leftarrow 1 \quad (T \leftarrow T)$ |
|-----------------------------|---------------------------------------------|--------------|---------------------------------------------|
| parameter                   | [fit 1]                                     | [fit 2]      |                                             |
| $\Delta v / \text{cm}^{-1}$ | $-0.671 (1)^\ddagger$                       |              | $+1.069 (6)^\ddagger$                       |
| $j^*$ (for ' $j=1$ ')       | 0.534 1 (5)                                 | 0.474 (1)    | 0.517 (1)                                   |
| $R'_{K=1} / \text{\AA}$     | 4.121 9 (5)                                 | 4.070 2 (17) | ---                                         |
| $R'_{K=0} / \text{\AA}$     |                                             | 4.186 1 (26) | 4.142 5 (11)                                |
| $R''_{K=1} / \text{\AA}$    | ---                                         | ---          | 4.112 2 (12)                                |
| $R''_{K=0} / \text{\AA}$    | 4.132 2 (5)                                 | 4.138 0 (6)  | 4.133 6 (18)                                |

<sup>†</sup> Figures in parentheses represent one standard deviation uncertainty.  
<sup>‡</sup> Monomer lines measured to 3 d.p. accuracy (see Ref. 40).

potential<sup>†</sup>.  
The centrifugal distortion constant gives a stretching frequency for the Van der Waals bond of 13.1 cm<sup>-1</sup>, indicating a slight weakening of the bond in the higher energy  $j=1$  level of  $\nu_3=1$  (the corresponding force constant is 0.126 N m<sup>-1</sup>).

4.5.4 Other transitions

Having analysed successfully the Ne-SiH<sub>4</sub> transitions associated with the monomer  $R(0)$  and  $P(1)$  using a simple Coriolis interaction model, attention was turned to the region of the spectrum around the SiH<sub>4</sub>  $R(1)$  line. The  $j=2$  level in the first excited vibrational state would be expected to demonstrate a more complicated interaction; with  $K$  taking the values 0,  $\pm 1$  and  $\pm 2$ , two separate Coriolis effects would occur. The  $K$  states with even symmetry,  $|0\rangle$ ,  $|1^+\rangle$  and  $|2^+\rangle$ , interact according to  $\Delta K = \pm 1$ , as do those with odd symmetry,  $|1^-\rangle$  and  $|2^-\rangle$ . The degeneracy of the  $K = \pm 1$  and  $\pm 2$  levels is therefore lifted and  $K=2 \leftarrow 1$  and

<sup>†</sup> The Coriolis interaction between the rotational and vibrational angular momentum in  $\nu_3=1$  results in three times as many states in this level. The interaction between these states is thus far more complicated than in the ground vibrational level, and it is hard, if not impossible, to draw any firm conclusions at this stage. The extent to which these 'pointers' are justified can be judged by reference to the later sections.



$1 \leftarrow 0$  transitions should show a doublet structure. The strong lines in the region of the spectrum around  $2201.0 \text{ cm}^{-1}$  appeared to display a gradually increasing spacing in accordance with this prediction.

Transitions from the  $\nu_3=0, j=1$   $T$  states to the relevant  $T$  state associated with  $j=2$  in  $\nu_3=1^\dagger$  must give combination differences appropriate to the  $K$  states from which the transition originates. It was thus possible to tentatively assign lines in this region by identifying combination differences and assuming that the ordering of the  $j=2$   $K$  states was  $E_{K=2} > E_{K=1} > E_{K=0}$ . The resulting assignment was then fitted to a Coriolis interaction model as described above. The matrix elements for the interaction of the symmetric  $K$  states are given in the  $3 \times 3$  Hamiltonian below:

$$\mathbf{H}^+ = \begin{pmatrix} B'_{K=0}J(J+1) & -\sqrt{\{2B'_{K=0}B'_{K=1}j(j+1)J(J+1)\}} & 0 \\ -\sqrt{\{2B'_{K=0}B'_{K=1}j(j+1)J(J+1)\}} & B'_{K=1}J(J+1) + \epsilon_1 & -\sqrt{\{B'_{K=1}B'_{K=2}[j(j+1)-2][J(J+1)-2]\}} \\ 0 & -\sqrt{\{B'_{K=1}B'_{K=2}[j(j+1)-2][J(J+1)-2]\}} & B'_{K=2}J(J+1) + \epsilon_2 \end{pmatrix} \quad (4.25)$$

The subscripts on the rotational constants indicate the  $K$  state to which they belong,  $\epsilon_1$  is the splitting term between the  $K=0$  and  $K=1$  levels and  $\epsilon_2$  the splitting between  $K=0$  and  $K=2$ . The interaction of the antisymmetric  $K$  states  $|1^- \rangle$  and  $|2^- \rangle$  is modelled by a  $2 \times 2$  Hamiltonian analogous to equation (4.14):

$$\mathbf{H}^- = \begin{pmatrix} B'_{K=1} + \epsilon_1 & -\sqrt{\{B'_{K=1}B'_{K=2}[j(j+1)-2][J(J+1)-2]\}} \\ -\sqrt{\{B'_{K=1}B'_{K=2}[j(j+1)-2][J(J+1)-2]\}} & B'_{K=2} + \epsilon_2 \end{pmatrix} \quad (4.26)$$

Centrifugal distortion constants were also added to these expressions, constrained to be the same within each  $j$  level.

However, despite apparently feasible assignments which reproduced combination differences within experimental error, the line positions could not be fitted to these expressions. In particular, the line spacings of the  $R$  branch starting at  $2202.5 \text{ cm}^{-1}$  indicated transitions to a virtually *unperturbed* (approximately constant  $B$  value) upper state

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<sup>†</sup> There are in fact five  $j'=2$  states of  $T$  symmetry- see table 4.7.



(from  $K=0$  in the  $\nu_3=0, j=1$  level). Two questions arose: first, was the assumed order of the  $K$  states,  $E_{K=2} > E_{K=1} > E_{K=0}$ , necessarily correct given the effects of the intermolecular potential; and second, is there a possibility that neighbouring states of apparently the same symmetry do *not* Coriolis interact?

In order to proceed with the analysis and interpretation of the spectrum an understanding of the intermolecular potential is required, and this is addressed in the following sections.

## 4.6 Spherical tops

This section considers the properties of spherical tops, and tetrahedral molecules in particular. The interpretation of the remaining bands in the spectrum of Ne-SiH<sub>4</sub> must be built on these principles, which have already been used successfully in the elucidation of Ar-SiH<sub>4</sub> [25]. It is assumed that the Hamiltonian for the silane monomer,  $H_{\text{mon}}$ , is unaltered on complexation, and therefore the same symmetry considerations will apply to transitions between energy levels of the complex.

### 4.6.1 Symmetry properties of tetrahedral molecules

A tetrahedral molecule such as SiH<sub>4</sub> belongs to the  $T_d$  point group; its character table is shown in **table 4.5** [44]. SiH<sub>4</sub> possesses  $(3N-6)=9$  vibrational degrees of freedom, which transform according to the irreducible representation

$$\Gamma_{\text{vib}} = A_1 + E + 2T_2 \quad (4.27)$$

The associated transitions are conventionally labelled  $\nu_1(A_1)$ ,  $\nu_2(E)$ ,  $\nu_3(T_2)$  and  $\nu_4(T_2)$ . The electric dipole selection rule allows only the vibrations of  $T_2$  symmetry (i.e.  $\nu_3$  and  $\nu_4$ ) to be infrared active (since the components of  $\mu$ , the electric dipole moment operator, span the  $T_2$  irreducible representation, and therefore give rise to the totally symmetric representation  $A_1$  in the direct product  $\Gamma_{\nu=0} \otimes \Gamma_{\mu} \otimes \Gamma_{\nu=1}$ ). The  $\nu_1$  and  $\nu_2$  bands can however be weakly observed through Coriolis interactions with the nearby triply degenerate levels

Table 4.5 Character table for the  $T_d$  point group.

| $T_d$ | $E$ | $8C_3$ | $3C_2$ | $6S_4$ | $\sigma_d$ |                                                                        |
|-------|-----|--------|--------|--------|------------|------------------------------------------------------------------------|
| $A_1$ | 1   | 1      | 1      | 1      | 1          | $x^2 + y^2 + z^2$                                                      |
| $A_2$ | 1   | 1      | 1      | -1     | -1         |                                                                        |
| $E$   | 2   | -1     | 2      | 0      | 0          | $((2z^2 - x^2 - y^2, \sqrt{3}(x^2 - y^2))$                             |
| $T_1$ | 3   | 0      | -1     | 1      | -1         | $(R_x, R_y, R_z)$                                                      |
| $T_2$ | 3   | 0      | -1     | -1     | 1          | $(x, y, z)$ <span style="float:right"><math>(xy, xz, yz)</math></span> |

[45]. Only the ground and first excited triply degenerate stretching states associated with  $\nu_3$  are considered here.

The three principal moments of inertia of a tetrahedral molecule are all equal, resulting in an infinite number of ways the molecular framework can be orientated with respect to the principal axis system. The conventional orientation adopted [46] identifies the  $z$  axis with one of the  $S_4$  axes and aligns one of the  $C_3$  axes in the  $(1, 1, 1)$  direction, such that each  $C_3$  axis form the body diagonals of a cube. However, when considering the complex formed with a rare gas atom, it will be expedient to change this orientation to produce a simpler intermolecular potential.

In the vibrational ground state, the Hamiltonian for the rotational energy levels of a rigid spherical top is given by

$$H_{\text{rot}} = \frac{\hbar^2}{2I} \hat{j}^2$$

(4.28)

where  $I$  is the moment of inertia of the molecule, and  $\hat{j}$  is the rotational angular momentum operator for the molecule. For a spherical top in the absence of external fields and centrifugal distortion,  $j$  has overall a  $(2j + 1)^2$  fold degeneracy, since both the space and molecule fixed projections of  $j$  are each  $(2j + 1)$  fold degenerate. For a tetrahedral molecule, the lower symmetry results in the molecule fixed  $(2j + 1)$  fold degeneracy being split in higher order. The rotational energy levels of SiH<sub>4</sub> can be classified by their

**Table 4.6** Symmetry labels for  $v_3=0$  rotational levels in SiH<sub>4</sub>.

| $j$ | Symmetry species      |
|-----|-----------------------|
| 0   | $A_1$                 |
| 1   | $T_1$                 |
| 2   | $E + T_2$             |
| 3   | $A_2 + T_1 + T_2$     |
| 4   | $A_1 + E + T_1 + T_2$ |
| 5   | $E + 2T_1 + T_2$      |

symmetry species in the  $T_d$  point group<sup>†</sup>. In the ground vibrational state there is no contribution from vibrational angular momentum, and the symmetries of the ro-vibrational levels for a given value of  $j$  are found simply by the reduction (by means of descent in symmetry) of the representation  $\Gamma^j$  of the full rotation group into irreducible representations of the  $T_d$  point group [47]. **Table 4.6** lists the symmetries of  $j=0$  to  $j=5$  for  $v_3=0$ .

The situation is somewhat more complicated in the first excited vibrational state due to the presence of vibrational angular momentum. **Figure 4.9** illustrates the three equivalent  $v_3$  vibrations of the SiH<sub>4</sub> molecule. Excitation of the  $v_3$  vibration induces motion which is a linear combination of each orthogonal vibration, resulting in a motion with spherical symmetry. The result is vibrational angular momentum  $\mathbf{l}$  with components  $l_x$ ,  $l_y$  and  $l_z$ . The total angular momentum  $\mathbf{j}$  is then given by the vector coupling of  $\mathbf{l}$  with  $\mathbf{n}$ , the rotational angular momentum, giving  $\mathbf{j}=\mathbf{n}+\mathbf{l}$ . Each rotational level is therefore split into three levels with values of  $j$  given by  $j=n-1$ ,  $n$ , and  $n+1$ , since for  $v_3=1$   $l=1$ . The  $3(2j+1)$  degeneracy of these ro-vibrational levels produced is lifted by Coriolis interaction between  $\mathbf{n}$  and  $\mathbf{l}$ , though the magnitude of this interaction in any one direction is small and given by  $\zeta\hbar l_x$ , etc., where  $\zeta \ll 1$  (for  $v_3$  vibration of SiH<sub>4</sub>  $\zeta \approx 0.011$  [40]). The Hamiltonian

<sup>†</sup> Strictly speaking we are using the permutation-inversion group (for the permutation of identical hydrogen atoms in SiH<sub>4</sub>) which is *isomorphic* with the  $T_d$  point group. This is discussed more fully in the footnote on p. 136.

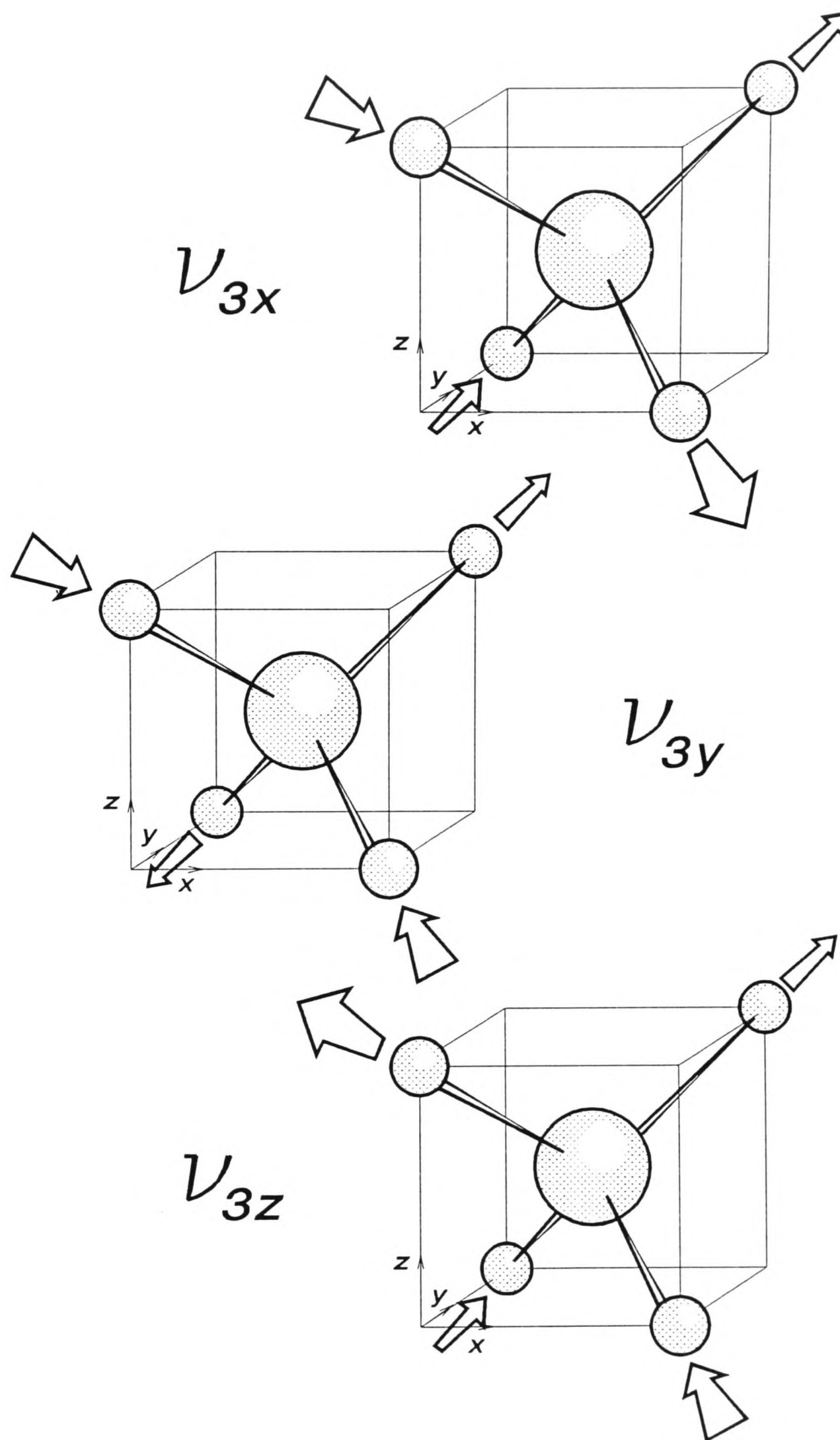


Figure 4.9 The three degenerate  $T_2$  stretching vibrations of SiH<sub>4</sub>.

Table 4.7 Symmetry of the ro-vibrational levels for  $\nu_3 = 1$  in SiH<sub>4</sub>.

| $j$ | $n=j+1$                      | $n=j$                 | $n=j-1$               |
|-----|------------------------------|-----------------------|-----------------------|
| 0   | $T_2$                        |                       |                       |
| 1   | $E + T_1$                    | $T_2$                 | $A_2$                 |
| 2   | $A_1 + T_1 + T_2$            | $E + T_1$             | $T_2$                 |
| 3   | $A_2 + E + T_1 + T_2$        | $A_1 + T_1 + T_2$     | $E + T_1$             |
| 4   | $E + T_1 + 2T_2$             | $A_2 + E + T_1 + T_2$ | $A_1 + T_1 + T_2$     |
| 5   | $A_1 + A_2 + E + 2T_1 + T_2$ | $E + T_1 + 2T_2$      | $A_2 + E + T_1 + T_2$ |

for the rotation of a rigid molecule can then be written<sup>†</sup>

$$\begin{aligned} H_{\text{rot}} &= b(\hat{j} - \zeta \hat{l})^2 \\ &= b(\hat{j}^2 - 2\zeta \hat{j} \cdot \hat{l} + \zeta^2 \hat{l}^2) \\ &= b(\hat{j}^2 + \zeta^2 \hat{l}^2 - 2\zeta \hat{j}_z \hat{l}_z - \zeta \hat{j}_+ \hat{l}_+ - \zeta \hat{j}_- \hat{l}_-) \end{aligned}$$

(4.29)

where  $b$  is the rotational constant of the molecule and  $\hat{j}_{\pm}$  and  $\hat{l}_{\pm}$  are raising and lowering operators in the molecular fixed axis system. In the basis  $|jkm;lk_l\rangle$  the non-zero matrix elements are

$$\begin{aligned} \langle jkm;lk_l | H_{\text{rot}} | jkm;lk_l \rangle &= bj(j+1) + b^2\zeta^2l(l+1) - 2b\zeta k k_l \\ \langle jk\pm 1m;lk_l\pm 1 | H_{\text{rot}} | jkm;lk_l \rangle &= -b\zeta [j(j+1) - k(k\pm 1)]^{1/2} \times [l(l+1) - k_l(k_l\pm 1)]^{1/2} \end{aligned}$$

(4.30)

The  $b^2\zeta l(l+1)$  term is constant for all rotational levels and is therefore usually included in the vibrational part of the Hamiltonian. Each of the three levels produced ( $n=j+1$ ,  $j$  and  $j-1$ ) has  $(2j+1)$  space fixed degeneracy, with the splitting between different  $n$  levels being roughly proportional to  $b\zeta j$ . The value of  $n$  best determines the symmetries of the ro-vibrational levels, which are obtained by taking the direct product  $\Gamma_j \otimes T_2$ . These are shown in **table 4.7** for the first few values of  $j$ . Although the effect of centrifugal

<sup>†</sup> It should be noted that equation (4.29) is not equivalent to writing  $H_{\text{rot}} = b\hat{n}^2$ , since  $n=j-l$ . The Coriolis coupling term  $\zeta$  appears in equation (4.29) as a result of the separation of the rotational and vibrational angular momentum. The Eckart condition chooses an axis system to minimise the vibrational angular momentum, and in practice this means the axis system rotating with the reference (equilibrium) geometry of the system. The isotropic motions of the hydrogen atoms caused by the  $T_2$  stretch give overall one unit of vibrational angular momentum about the individual rest positions of the hydrogen atoms, and *not* about the centre of mass of the SiH<sub>4</sub> molecule. The vibrational contribution to the total angular momentum about the SiH<sub>4</sub> centre of mass is therefore greatly reduced. A rigorous treatment of this topic is given in ‘Molecular Vibrations’ by E.B. Wilson, J.C. Decius and P.C. Cross (chapter 11 p. 273).

distortion is to mix levels of the same  $j$  but differing  $n$ , each value of  $n$  has the same symmetry label.

### 4.6.2 An effective Hamiltonian for tetrahedral molecules

An effective Hamiltonian allows the total Hamiltonian for the molecule to be approximated for the specific vibronic level in question, giving a numerically simpler problem. Although the constants used in an effective Hamiltonian are less physically meaningful than those of the total Hamiltonian, provided enough terms are included in it the eigenvalues obtained should be identical to those of the total Hamiltonian. Whilst many formalisms exist for the effective Hamiltonians of tetrahedral molecules [48, 49, 50, 51, 52, 53] the most appropriate here is that of Robiette *et al.* [51] since many of the terms introduced are similar to those of a symmetric top.

Operators in the effective Hamiltonian are constructed from rotational operators  $\hat{j}_\alpha$ , vibrational operators  $\hat{q}_{3\alpha}$  and their conjugate momenta  $\hat{p}_{3\alpha}$ , where  $\alpha = x, y, z$ .  $\hat{j}_\alpha$  are the usual dimensionless angular momentum operators referred to the molecular fixed axes, i.e.  $\hat{j}^2 = \hat{j}_x^2 + \hat{j}_y^2 + \hat{j}_z^2$  is the total angular momentum operator with eigenvalue  $j(j+1)$ .  $\hat{q}_{3\alpha}$  and  $\hat{p}_{3\alpha}$  are also dimensionless operators, defined in terms of the normal coordinates  $Q_{3\alpha}$  by

$$\hat{q}_{3\alpha} = (2\pi c \omega_3 / \hbar)^{1/2} Q_{3\alpha} \quad (4.31)$$

$$\hat{p}_{3\alpha} = -i\hbar \partial / \partial q_{3\alpha} \quad (4.32)$$

The effective (transformed) Hamiltonian is expressed as the sum of terms  $\tilde{H}_{mn}$  indicating  $m$  powers of vibrational operators and  $n$  powers of rotational operators [54] (the terms in the untransformed Hamiltonian are written  $H_{mn}$ ). All the operators required for the analysis of a fundamental band have the form  $\tilde{H}_{0n}$  and  $\tilde{H}_{2n}$ . Contributions from higher terms such as  $\tilde{H}_{4n}$  cannot be separated from those of  $\tilde{H}_{0n}$  and  $\tilde{H}_{2n}$  without a study of overtone bands. The symmetry properties of these terms are obtained by taking the direct products of the symmetry labels of the rotational operators (which transform as the rotational operators  $(R_x, R_y, R_z)$  i.e.  $T_1$ ) and the vibrational operators (which transform as  $(x, y, z)$  i.e.  $T_2$ ).

The symmetries of the  $j_\alpha^n$  terms are given by the symmetrised direct products  $[T_1^n]$  since the antisymmetric products can always be reduced to terms with a lower power of



$j$  by commutation relations<sup>†</sup>. A further distinction is that  $j_\alpha^n$  terms with  $n$  odd change sign upon time reversal whereas those with  $n$  even do not. This is important in constructing the effective Hamiltonian since the terms comprising it must overall be totally symmetric and invariant to time reversal. The symmetrised direct products are given below up to  $n=4$  [44]:

$$\begin{aligned} [T_1^2] &= A_1 + E + T_2 \\ [T_1^3] &= A_2 + 2T_1 + T_2 \\ [T_1^4] &= 2A_1 + 2E + T_1 + 2T_2 \end{aligned} \quad (4.33)$$

Quadratic combinations of the vibrational operators which have non-zero matrix elements in the first excited vibrational state ( $v_3=1$ ) give rise to two distinct direct products:

$$T_2 \otimes T_2 = A_1 + E + \{T_1\} + T_2 \quad (4.34)$$

$A_1$  and  $E$  are spanned by three terms of the type  $\frac{1}{2}(q_{3\alpha}^2 + p_{3\alpha}^2)$  ( $\alpha=x, y, z$ ) and  $T_2$  by terms of the type  $\frac{1}{2}(\hat{q}_{3\alpha}\hat{q}_{3\beta} + \hat{p}_{3\alpha}\hat{p}_{3\beta})$  ( $\alpha, \beta = x, y$  or  $y, z$  or  $z, x$ ). The  $T_1$  antisymmetric direct product is spanned by three terms of the type  $(\hat{q}_{3\alpha}\hat{p}_{3\beta} - \hat{p}_{3\alpha}\hat{q}_{3\beta}) \equiv \hat{l}_{3\gamma}$  ( $\alpha, \beta, \gamma = x, y, z$  and cyclic permutations). These are the dimensionless vibrational angular momentum operators; these change sign on time reversal whereas the symmetric combinations do not.

The terms which can have non-zero coefficients in the effective Hamiltonian can be determined by group theory. Combinations of powers of vibration and rotation operators must be chosen to give a resulting term  $\tilde{H}_{mn}$  which is overall totally symmetric (i.e. transforms as  $A_1$ ) and invariant to time reversal.

Terms independent of vibration are given by  $\tilde{H}_{0n}$ . Terms with  $n$  odd are ruled out by the time reversal criterion, and the number of terms for each even value of  $n$  is given by the number of times  $A_1$  appears in the  $n$ th direct product. Thus  $\tilde{H}_{02}$  contains one term and  $\tilde{H}_{04}$  two terms, and so on.

For the vibrationally dependent terms ( $v_3=1$ ), odd values of  $n$  are permitted provided they are combined with the antisymmetric vibrational combinations  $T_1$  to give an overall term invariant to time reversal. The number of these terms is therefore the number of times the  $T_1$  representation appears in the appropriate symmetrised direct product, since

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<sup>†</sup> The symmetry species of  $\hat{j}_\alpha^2$  are given by  $T_1 \otimes T_1 = A_1 + E + \{T_1\} + T_2$ ; the antisymmetric combinations transforming as  $T_1$  are  $(\hat{j}_{\alpha\beta} - \hat{j}_{\beta\alpha})$  which reduce simply to  $-i\hat{j}_\gamma$ .

$T_1 \otimes T_1$  contains  $A_1$  once (see equation (4.33)). Thus there is one  $\tilde{H}_{21}$  term and there are two  $\tilde{H}_{23}$  terms. Even values of  $n$  give one term each time  $A_1$ ,  $E$ , or  $T_2$  occurs in the direct product, since, for example, a vibrational operator with  $E$  symmetry can be combined with a rotational operator of  $E$  symmetry to give a totally symmetric product. So there are three  $\tilde{H}_{22}$  terms and six  $\tilde{H}_{24}$  terms. These terms all have zero expectation value in the ground ( $v_3=0$ ) vibrational state.

The procedure of Hecht [48] is used to construct the actual form of these terms in the effective Hamiltonian. The vibrational and rotational operators required for each term are constructed as tensor operators formed from the components of the angular momentum operators, and these are then coupled using the usual angular momentum coupling formula:

$$T_m^k(V^{k_1}, R^{k_2}) = \sum_{m_1, m_2} T_{m_1}^{k_1}(V) T_{m_2}^{k_2}(R) \langle k_1 k_2 m_1 m_2 | km \rangle \quad (4.35)$$

where  $T_m^k$  is the  $m$ th component of a tensor of rank  $k$  constructed from vibrational ( $V$ ) or rotational ( $R$ ) operators. Finally, a totally symmetric operator is obtained by taking the appropriate linear combinations of the same rank tensor with different components. These terms are analogous to the rotational wave functions of the ground vibrational state that have  $A_1$  symmetry, with the first three being given by

$$\begin{aligned} T^0(A_1) &= T_0^0 \\ T^4(A_1) &= \sqrt{70} T_0^4 + 5 T_4^4 + 5 T_{-4}^4 \\ T^6(A_1) &= \sqrt{14} T_0^6 + 7 T_4^6 + 7 T_{-4}^6 \end{aligned} \quad (4.36)$$

In the vibrational ground state ( $\tilde{H}_{0n}$  terms), only rotational operators need be considered. The appropriate rotational tensor operators are [55]

$$\begin{aligned} T_{\pm 1}^1(R) &= \pm j_{\pm} / \sqrt{2} \\ T_0^1(R) &= -j_z \end{aligned} \quad (4.37)$$

where  $j_{\pm} = j_x \mp ij_y^{\dagger}$ . Rotational tensor operators of rank greater than 1 are built up by repeated application of the angular momentum coupling formula (4.35) from the first-rank

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<sup>†</sup> Note the anomalous commutation relations of the components of total angular momentum when applied to the molecular fixed axes.



tensor<sup>†</sup>. Applying equation (4.36) to generate totally symmetric operators gives the following result for the first two terms in the vibrational ground state:

$$\tilde{H}_{02} = b\hat{j}^2 \quad (4.38)$$

$$\tilde{H}_{04} = -d_j \hat{j}^4 - d_t \left\{ \frac{1}{2} (35\hat{j}_z^4 + 5(5-6\hat{j}^2)\hat{j}_z^2 + 3(\hat{j}^2)^2 - 6\hat{j}^2) + \frac{5}{4}(\hat{j}_+^4 + \hat{j}_-^4) \right\} \quad (4.39)$$

The two possible terms  $\tilde{H}_{04}$  are the centrifugal distortion terms; the term  $d_t$  corresponds to the centrifugal distortion constants  $d_{jk}$  and  $d_k$  of a symmetric top (where lower case letters have been used to preserve the established convention with regard to the monomer molecule). The term associated with  $d_j$  acts like a centrifugal distortion constant in a symmetric top molecule, shifting the energy levels but causing no splittings. The second part of the  $\tilde{H}_{04}$  term in equation (4.39) lifts the  $(2j+1)$  fold  $k$  degeneracy of a rotational level and splits it into all the levels of different symmetry given in **table 4.6**. The effect is small for the lower rotational levels of silane, with the coefficients taking the values  $d_j = 3.69 \times 10^{-5} \text{ cm}^{-1}$  and  $d_t = 2.493 \times 10^{-6} \text{ cm}^{-1}$ .  $j=2$  is the lowest level that can be split, with the  $E$  levels lying  $1.5 \times 10^{-4} \text{ cm}^{-1}$  below the  $T$  levels.

The  $v_3 = 1$  state is more complicated since it involves the coupling of vibrational and rotational terms, but the procedure is essentially the same. The Coriolis term, with coefficient  $-2b\zeta$ , corresponds to the term  $\tilde{H}_{21}$  of the effective Hamiltonian, and a level of a given value of  $j$  is split into the three Coriolis sub-levels characterised by the value of  $n$ , which are then further split according to **table 4.7**. This splitting is larger for the  $E$  and  $T$  levels of  $n=2$  ( $\approx 0.01 \text{ cm}^{-1}$ , depending on the value of  $j$ ) than in the ground vibrational state, and is reversed for levels with  $j=2$ .

<sup>†</sup> For example the operators required for  $\tilde{H}_{04}$ ,  $T_0^4$  and  $T_{\pm 4}^4$  are given by

$$\begin{aligned} T_{\pm 4}^4(R) &= j_{\pm}^4/4, \\ T_0^4(R) &= \{35j_z^4 + 5(5-6j^2)j_z^2 + 3(j^2)^2 - 6j^2\}/2\sqrt{70} \end{aligned} \quad (4.39a)$$

## 4.7 The Hamiltonian for an atom-tetrahedral molecule complex

In constructing a suitable Hamiltonian for an atom-spherical top system, it is convenient to choose a coordinate system and form of the Hamiltonian which reflects its composition; the weakly bonded nature of Van der Waals complexes means that the constituent monomers retain their identity in the complex. Three distinct axis systems are required. The position of the rare gas atom and the tetrahedral molecule must be specified with respect to the laboratory fixed space axes, and this is achieved by describing the orientation of *two* sets of axis systems with respect to the laboratory *space fixed* axes. The orientation of the pseudodiatom axis<sup>†</sup> with respect to the laboratory fixed Z axis is described by the polar coordinates  $\theta$  and  $\phi$ . The eigenfunctions of the end over end rotation of the complex are expressed in terms of these two angles. It is further necessary to distinguish between the *body fixed* axis system, which has the intermolecular axis as its Z axis, and the *molecular fixed*<sup>††</sup> axis system. This distinction arises because the tetrahedral molecule can rotate independently of the body fixed system, and the three Euler angles  $(\alpha, \beta, \gamma)$  give the orientation of the molecular fixed axis system with respect to the body fixed axes. The z direction of the molecular fixed axis system is initially chosen to coincide with one of the  $S_4$  axes of the tetrahedral molecule. The vector from the centre of mass of the molecule to the atom is denoted  $\mathbf{R}$ , and has magnitude  $R$ .

The Hamiltonian appropriate to a case 2 coupling scheme has been given in equation (4.4) and is reproduced below:

$$H = \frac{\hbar^2}{2\mu} \left\{ \frac{(\hat{\mathbf{J}} - \hat{\mathbf{j}})^2}{R^2} - \frac{\partial^2}{\partial R^2} \right\} + H_{\text{mon}} + V(R, \alpha, \beta, \gamma). \quad (4.40)$$

The rotational and stretching motions of the complex are described by the first two terms,  $H_{\text{mon}}$  is the Hamiltonian for the tetrahedral molecule (see previous section) and  $V$  the intermolecular potential. The body fixed axes rotate with the complex, and the molecular

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<sup>†</sup> The pseudodiatom axis of a complex is the vector between the centres of mass of the constituent monomer units, in this case the neon atom and the silane molecule.

<sup>††</sup> The molecular fixed axis system can also be described as the (silane) *monomer* fixed axis system; the former was used in Ref. 25 and this convention is unchanged in the present work.

fixed axis system rotates with the tetrahedral molecule, independently of the body fixed system and is specified by  $(\alpha, \beta, \gamma)$  with respect to the body fixed axes. In such a coordinate system the intermolecular potential is just a function of the Euler angles  $(\alpha, \beta, \gamma)$  and the separation  $R^\dagger$ . The projection of  $j$ , the angular momentum of the tetrahedral molecule, along the molecular fixed  $z$  axis is  $k$ , and the projection along the body fixed  $Z$  axis is  $m$ , which is identical to  $K$ , the projection of the total angular momentum of the complex,  $J$ , along this axis.  $K$  will be used in preference to  $m$  when referring to the energy levels of the perturbed tetrahedral complex.

The approximations required to be made have already been discussed in some detail (§ 4.5). Briefly, these are as follows. The first approximation is that the tetrahedral molecule does not change upon complexation; its Hamiltonian is exactly the same within the complex as for the free molecule, with the addition of the  $Bj(j+1)$  term which derives from the expansion of the  $(\hat{J}-\hat{j})^2$  term in equation (4.7) and is due to the rotation of the complex.

The second approximation is to separate the end over end rotation of the complex from its internal motions, such as the rotational motion of the SiH<sub>4</sub> monomer unit, and assume that the rotational levels are built upon the perturbed tetrahedral molecule energy levels as if they were separate vibrational bands. It is intuitively easier to make this separation than to deal with everything at once. In equation (4.7) the  $(\hat{J}-\hat{j})^2$  term from the Hamiltonian has been expanded. The  $\hat{J}_Z^2$  term could equally be written as the SiH<sub>4</sub>  $\hat{j}_Z^2$  operator, giving

$$(\hat{J}-\hat{j})^2 = \hat{J}^2 - 2\hat{j}_Z^2 + \hat{j}^2 - (\hat{J}_+ \hat{j}_+ + \hat{J}_- \hat{j}_-) \quad (4.41)$$

In making the Born-Oppenheimer separation, the terms involving overall complex rotational operators (i.e.  $\hat{J}$  terms) are arbitrarily assigned to the rotational part, leaving the  $\hat{j}^2 - 2\hat{j}_Z^2$  terms arising from hindered internal rotation of the SiH<sub>4</sub> which are treated as a vibrational contribution to the total Hamiltonian. As has been seen in § 4.5, this separation is not entirely adequate, since the Coriolis terms which would otherwise be neglected in this approximation had to be evaluated explicitly in the rotational part of the Hamiltonian.

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<sup>†</sup> This formalism differs from that used in scattering studies of rare gas atom-tetrahedral molecule collisions where  $\alpha$ ,  $\beta$ , and  $\gamma$  define the orientation of the molecular fixed axes of the tetrahedral molecule with respect to the laboratory space fixed  $Z$  axis rather than the body fixed  $Z$  axis. The body fixed projection of  $j$  is not quantised along the complex axis but along the laboratory fixed  $Z$  axis. The potential is then a function of all five angles  $\alpha' \beta' \gamma' \theta \phi$ .

A fairly simple effective Hamiltonian is sufficient to represent the energy levels of the tetrahedral molecule in the complex because the intermolecular potential, which is of a similar form, dominates, producing corresponding effects but of much greater size.

## 4.8 The intermolecular potential

Upon complexation with a rare gas atom such as neon, much of the tetrahedral symmetry of the SiH<sub>4</sub> is preserved. All dynamically feasible permutations of SiH<sub>4</sub> within the complex which leave it (apparently) unchanged must leave the properties of the complex invariant<sup>†</sup>. These allowed permutations correspond to the pure rotations belonging to the  $T_d$  point group and the molecular symmetry group is therefore isomorphic with the  $T$  point group, which consists of just the pure rotations belonging to  $T_d$ . Its character table is given in **table 4.8** [44]. Therefore, the overall Hamiltonian for the complex must transform as the totally symmetric representation  $A_1$  of the symmetry group isomorphic with the  $T_d$  point group, whereas the Hamiltonian for the SiH<sub>4</sub> monomer and the potential function  $V$  must transform as the totally symmetric representation  $A$  of the rotational subgroup  $T$ . The overall state thus has a higher symmetry than the individual states composing it, contrary to what may be expected. This distinction has been the source of much confusion in the literature. The potential can be expanded as a series of suitable angular functions; the most convenient are the rotation matrices  $D_{ok}^j(\alpha\beta\gamma)$ . The potential must have cylindrical symmetry about the pseudodiatom axis  $\mathbf{R}$  (since the neon has no structure), therefore the

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<sup>†</sup> In the case of both the isolated SiH<sub>4</sub> molecule and its complex with a rare gas atom, we are considering the symmetry consequences of permuting identical hydrogen atoms. This *molecular symmetry group* is isomorphic with the  $T_d$  molecular point group, although there is an important difference in some of the symmetry operations. A molecule is restricted to feasible permutations, i.e. those which can occur on the experimental timescale, which generally prohibits those permutations which require overcoming (tunnelling through) a large energy barrier. Of the operations of the  $T_d$  point group, the rotations ( $C_3$  and  $C_2$ ) are feasible, whereas the rotation-reflection ( $S_4$ ) and reflection ( $\sigma_d$ ) are, in fact, not since they convert between 'left handed' and 'right handed' forms of the tetrahedral molecule and therefore must overcome a large energy barrier. However, combining these non-feasible permutations with the space inversion operation  $E_i$  (which transforms  $x, y, z$  to  $-x, -y, -z$ , and is also a symmetry operator of the Hamiltonian) results in feasible permutations which have the same characters as the non-feasible permutations. This permutation group of 24 feasible permutations (those which do not interconvert left and right handed forms of the molecule) is therefore isomorphic with the  $T_d$  point group (which contains 12 feasible ( $E$ ,  $8C_3$  and  $3C_2$ ) and 12 non-feasible ( $6S_4$  and  $6\sigma_d$ ) operations). In considering the complex, therefore, the permutation group relating to feasible permutations of SiH<sub>4</sub> *within* the complex is isomorphic with  $T$ , because only the 'rotations'  $C_3$  and  $C_2$  do not affect the position of the neon atom; use of  $E_i$  clearly does and so the 'inverted  $S_4$ ' and 'inverted  $\sigma_d$ ' are not applicable. However, in considering the end-over-end rotation of the complex, we return to using the  $T_d$  point group, with  $A$  and  $T$  rotational levels being labelled with subscript 1 or 2 according to parity of the individual  $J$  level, and  $E$  and  $E'$  levels reverting to  $E$  symmetry. For a detailed discussion of permutation vs. point groups see '*Molecular Symmetry and Spectroscopy*' by Philip R. Bunker.

Table 4.8 Character table for the  $T$  point group.

| $T$ | $E$                                                            | $4C_3$                                                                         | $4C_3^2$                                                                       | $3C_2$                                         | $\epsilon = \exp(2\pi i/3)$                                              |
|-----|----------------------------------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|------------------------------------------------|--------------------------------------------------------------------------|
| $A$ | 1                                                              | 1                                                                              | 1                                                                              | 1                                              | $x^2 + y^2 + z^2$                                                        |
| $E$ | $\begin{Bmatrix} 1 & \epsilon \\ 1 & \epsilon^* \end{Bmatrix}$ | $\begin{Bmatrix} \epsilon & \epsilon^* \\ \epsilon^* & \epsilon \end{Bmatrix}$ | $\begin{Bmatrix} \epsilon^* & \epsilon \\ \epsilon & \epsilon^* \end{Bmatrix}$ | $\begin{Bmatrix} 1 & 1 \\ 1 & 1 \end{Bmatrix}$ | $\begin{Bmatrix} \sqrt{3}(x^2 - y^2), \\ 2z^2 - x^2 - y^2 \end{Bmatrix}$ |
| $T$ | 3                                                              | 0                                                                              | 0                                                                              | -1                                             | $(x, y, z), (R_x, R_y, R_z)$<br>$(xy, xz, yz)$                           |

potential is invariant to  $\alpha$  and the first subscript is zero. There are only a small number of terms which satisfy the symmetry criterion, thus simplifying the calculation.

The reduction in the symmetry of the SiH<sub>4</sub> molecule from  $T_d$  to  $T$  when it becomes associated with a neon atom has the effect of removing any distinction between different representations of the same multiplicity. Thus ro-vibrational levels of SiH<sub>4</sub> with  $A_1$  or  $A_2$  symmetry in the free molecule become levels of  $A$  symmetry in the complex;  $T_1$  and  $T_2$  levels in free SiH<sub>4</sub> are both reduced to  $T$  symmetry in the complex. The  $E$  levels retain their original labelling, but because the  $E$  representation in the  $T$  point group is not truly doubly degenerate, the degeneracy can be lifted by the potential. The reduction in symmetry also removes any confusion due to differing symmetry labelling conventions which exist in the literature for ro-vibrational levels of tetrahedral molecules.

The effect of the potential on the ground ( $v_3 = 0$ ,  $A$  symmetry) and first excited vibrational states ( $v_3 = 1$ ,  $T$  symmetry) of SiH<sub>4</sub> within the complex will be different. The neon atom will have the effect of shifting the singly degenerate  $A$  state, which is by definition isotropic and therefore insensitive to the position of the neon atom. The three-fold degeneracy of the  $T$  vibration is lifted by the potential, which can be represented by a vibrational anisotropic term. This is readily seen by considering the limit when the internal rotation of SiH<sub>4</sub> within the complex is completely quenched; the component of  $v_3$  parallel to the complex axis would be expected to have a different frequency than either of the other two components which would be perpendicular to this axis, and would therefore remain degenerate.

The neon-SiH<sub>4</sub> potential possesses the tetrahedral symmetry of the system and must therefore be invariant under all the symmetry operations of the  $T$  point group. The

interaction potential can be separated into radial and angular parts (denoted  $V$  and  $T$  respectively), and expanded in terms of symmetry-adapted rotation operators thus [14]:

$$V(R\alpha\beta\gamma) = V_0(R) + V_3(R)T_3(\alpha\beta\gamma) + V_4(R)T_4(\alpha\beta\gamma) \quad (4.42)$$

where  $V_i(R)$  are purely radial functions and  $T_i(\alpha\beta\gamma)$  are linear combinations of rotation matrices transforming as the totally symmetric  $A$  representation of the  $T$  point group. Higher order terms are not included as their effect on the energy levels of the complex will be much smaller than that of the first two. This expression applies to the vibrational ground state, since when  $\nu_3=0$  there is no contribution from vibrational anisotropy, and so the angular form of the rotational anisotropic part of the potential is just a function of the two Euler angles  $\beta$  and  $\gamma$ . Since  $\alpha$  defines a rotation about the  $Z$  axis, which is the intermolecular axis of the complex, it has no effect on the potential, as stated earlier.  $T_3$  and  $T_4$  have been calculated by Phillips and Secrest [56] in the scattering formalism where the coordinate system is defined differently; Randall *et al.* [25] have shown that these terms can be rewritten for our coordinate system thus:

$$T_3(\alpha\beta\gamma) = i\{D_{02}^{3*}(\alpha\beta\gamma) - D_{0-2}^{3*}(\alpha\beta\gamma)\} \quad (4.43)$$

$$T_4(\alpha\beta\gamma) = \sqrt{5}D_{04}^{4*}(\alpha\beta\gamma) + \sqrt{14}D_{00}^{4*}(\alpha\beta\gamma) + \sqrt{5}D_{0-4}^{4*}(\alpha\beta\gamma) \quad (4.44)$$

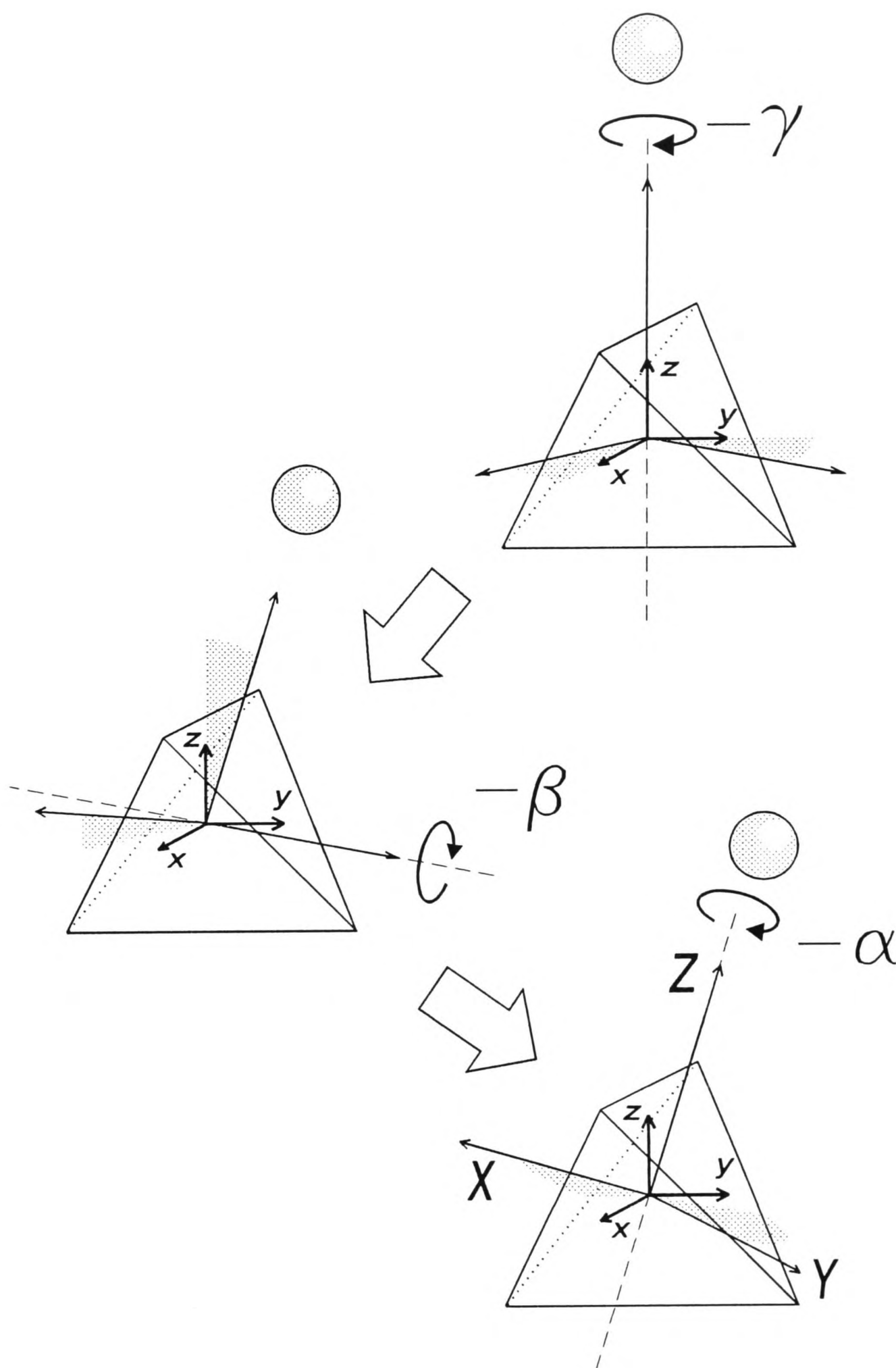
The inconvenience of the imaginary matrix elements generated by  $T_3$  is easily removed by rotating the molecular axis coordinate system so that  $\gamma$  is reduced by  $45^\circ$ , so that at  $\gamma=0$  one of the hydrogen atoms of SiH<sub>4</sub> is at  $(\sqrt{2}, 0, 1)$  rather than  $(1, 1, 1)$ . This is achieved by multiplying each term in the potential by a factor of  $\exp(-i\lambda\pi/4)$ , where  $\lambda$  is the second subscript on each rotation matrix in the potential. The terms in the potential then become

$$T_3(\alpha\beta\gamma) = D_{02}^{3*}(\alpha\beta\gamma) + D_{0-2}^{3*}(\alpha\beta\gamma) \quad (4.45)$$

$$T_4(\alpha\beta\gamma) = -\sqrt{5}D_{04}^{4*}(\alpha\beta\gamma) + \sqrt{14}D_{00}^{4*}(\alpha\beta\gamma) - \sqrt{5}D_{0-4}^{4*}(\alpha\beta\gamma) \quad (4.46)$$

The transformation of the molecule fixed axis system  $(x, y, z)$  onto the body fixed axis system  $(X, Y, Z)$  via the Euler angles  $(\alpha, \beta, \gamma)$  for this orientation of the SiH<sub>4</sub> molecule is shown in **figure 4.10**.

These terms give the rotational anisotropy in both the ground and first excited vibrational states. The vibrational anisotropy in  $\nu_3=1$  lifts the three-fold degeneracy of this



**Figure 4.10** Transformation of the molecular fixed axis system  $(x, y, z)$  onto the body fixed axis system  $(X, Y, Z)$  via the Euler angles  $(\alpha, \beta, \gamma)$ .



state, as explained earlier. Defining the vibrational coordinate as the vector  $\mathbf{Q}$ , the vibration can be written as either  $(Q_x, Q_y, Q_z)$  or  $(Q, \Theta, \Phi)$ , where  $\Theta$  and  $\Phi$  are the polar angles defining the orientation of  $\mathbf{Q}$  with respect to the body fixed  $Z$  axis of the complex. The functional form of the interaction can be deduced by considering how the magnitude of the vibrational anisotropy depends upon the angle  $\Theta$ . With the neon atom on the  $Z$  axis, the interaction must be greatest when  $\Theta=0$  and least when  $\Theta=\pi/2$ . Further, situating the neon atom at  $Z$  and  $-Z$  should have the same effect when averaged over the monomer vibrational motions. These suggest a  $\cos^n\Theta$  dependence, with only even powers in the expansion of the anisotropy in terms of spherical harmonics. The first term is therefore proportional to  $\cos^2\Theta$  and can be written as the zeroth component of a second rank spherical harmonic in the body fixed representation as

$$V(\mathbf{Q}) = V_2^v(R)T_2^v(\Theta\Phi) = V_2^v(R)Y_{20}(\Theta\Phi) \quad (4.47)$$

where the  $V_2^v(R)$  term is a purely radial function. This can be rewritten in the molecular fixed axis system as

$$T_2^v(\Theta\Phi) = \sum_{q=-2}^2 D_{0q}^{2*}(\alpha\beta\gamma)Y_{2q}(\Theta'\Phi') \quad (4.48)$$

## 4.9 Energy levels

To calculate the energy levels of the complex, the basis functions used for the internal motion of the SiH<sub>4</sub> within the complex are simply the product of the symmetric rotor eigenfunctions  $|jKk\rangle$  with the appropriate vibrational functions. For the triply degenerate  $\nu_3=1$  states these are chosen to be the eigenfunctions of  $\hat{l}^2$  and  $\hat{l}_z$ , with eigenvalues  $l(l+1)$  and  $k_l$  respectively, written  $|lk_l\rangle$  where  $l=0$  and  $l=1$  refer to  $\nu_3=0$  and  $\nu_3=1$  respectively.  $k_l$  is the component of the vibrational angular momentum along the molecule (i.e. SiH<sub>4</sub> ‘monomer’) fixed  $z$  axis. The advantage of this choice over the cartesian components of  $\mathbf{Q}$  is the greater ease of evaluation of the matrix elements. For the rotational anisotropic terms these are given by



$$\begin{aligned} \langle jKk | T_3(\alpha\beta\gamma) | j'K'k' \rangle &= (-1)^{k-K} [(2j+1)(2j'+1)]^{1/2} \\ &\times \begin{pmatrix} j & 3 & j' \\ -K & 0 & K' \end{pmatrix} \left[ \begin{pmatrix} j & 3 & j' \\ -k & 2 & k' \end{pmatrix} + \begin{pmatrix} j & 3 & j' \\ -k & -2 & k' \end{pmatrix} \right] \end{aligned} \quad (4.49)$$

$$\begin{aligned} \langle jKk | T_4(\alpha\beta\gamma) | j'K'k' \rangle &= (-1)^{k-K} [(2j+1)(2j'+1)]^{1/2} \\ &\times \begin{pmatrix} j & 4 & j' \\ -K & 0 & K' \end{pmatrix} \left[ -\sqrt{5} \begin{pmatrix} j & 4 & j' \\ -k & 4 & k' \end{pmatrix} + \sqrt{14} \begin{pmatrix} j & 4 & j' \\ -k & 0 & k' \end{pmatrix} - \sqrt{5} \begin{pmatrix} j & 4 & j' \\ -k & -4 & k' \end{pmatrix} \right] \end{aligned} \quad (4.50)$$

and for the vibrational anisotropic term by

$$\begin{aligned} \langle lk_l; jKk | T_2^v(\Theta\Phi) | l'k'_l; j'K'k' \rangle &= \sum_q \langle lk_l | Y_{2q}(\Theta\Phi) | l'k'_l \rangle \times \langle jKk | D_{0q}^{2*} | j'K'k' \rangle \\ &= (-1)^{l-k_l} \sum_q \begin{pmatrix} l & 2 & l' \\ -k_l & q & k'_l \end{pmatrix} \langle l || Y_2 || l' \rangle \\ &\times (-1)^{k-K} [(2j+1)(2j'+1)]^{1/2} \begin{pmatrix} j & 2 & j' \\ -K & 0 & K' \end{pmatrix} \begin{pmatrix} j & 2 & j' \\ -k & q & k' \end{pmatrix} \end{aligned} \quad (4.51)$$

where (:::) is a Wigner 3j-symbol [57]. The effective Hamiltonian of Robiette *et al.* [51] discussed in § 4.6.2 must undergo the same rotation of the molecular fixed axis, 45° about the (body fixed) Z axis, which was required to give a real potential. All the terms in the effective Hamiltonian must be multiplied by the same factor of  $\exp(-i\lambda\pi/4)$ , and this transforms the tensor relations in equation (4.36) thus:

$$\begin{aligned} T^0(A_1) &= T_0^0 \\ T^4(A_1) &= \sqrt{70} T_0^4 - 5 T_4^4 - 5 T_{-4}^4 \\ T^6(A_1) &= \sqrt{14} T_0^6 + 7 T_4^6 + 7 T_{-4}^6 \end{aligned} \quad (4.52)$$

### 4.9.1 Ground state

In the ground vibrational state the anisotropic potential mixes rotational levels with the same symmetry but different values of the molecule fixed projection  $k$ . A given  $j$  level is therefore split into its various symmetry components. The magnitude of the energy shift, and therefore the splittings between different  $K$  states, is dependent on the value of the body fixed projection  $K$ , and so this degeneracy is also removed. A full description

of the differing effects of the  $T_3$  and  $T_4$  anisotropic terms in the potential, including correlation diagrams, is given in Ref. 25. The main points are summarised for each term below; reference to **figure 4.10** may be helpful.

A consideration of the matrix elements in equation (4.49) and the properties of 3- $j$  symbols reveals the following features of the  $T_3$  rotational anisotropic term. In a symmetric top basis, if  $j=0$  or 1 or  $K=0$  then the  $T_3$  term can have no diagonal matrix elements<sup>†</sup>, while this is not the case for levels with non-zero values of  $K$  and  $j \geq 2$ . For example, the degeneracy of the  $j=2$   $E$  states is lifted for  $K=1$  and 2, but not for  $K=0$ . Where no diagonal matrix elements exist, the effect on the energy levels is the same for both positive and negative values of  $V_3(R)$ , whereas the splittings of states with  $K \neq 0$  are reversed when  $V_3(R)$  changes sign, although the energy levels are experimentally indistinguishable.

The rotation matrices which comprise  $T_3$  are proportional to spherical harmonics which can be written out explicitly to give the angular dependence of this term:

$$T_3 = -\sqrt{\{15/2\}} \cos\beta \sin^2\beta \cos 2\gamma \quad (4.53)$$

The maxima and minima of the potential are interchanged by changing the sign of  $V_3(R)$ ; when  $V_3(R)$  is positive the faces of the tetrahedron correspond to the minima and the corners to the maxima in the potential, and vice versa for negative values of  $V_3(R)$ . One of the minima for positive  $V_3(R)$  occurs when  $\cos\beta = 1/\sqrt{3}$  and  $\gamma = 90^\circ$ , where the potential has a value of  $-\sqrt{10/3} V_3(R)$ . Since there are four equivalent maxima and minima positions, in the limit of infinite anisotropy, when the internal motion is quenched and no tunnelling occurs between equivalent positions, the resulting energy levels will become fourfold degenerate. The lowest four rotational levels in the free rotor limit correlate with the ground and first excited states of the torsional vibration in the rigid molecule limit, and since this vibration has two equivalent modes, the overall degeneracy of the first excited state levels is eightfold in this limit. Each bending state will then contain a stack of

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<sup>†</sup> If  $K=0$  then changing the sign of all the magnetic quantum numbers must leave the value of the 3- $j$  symbol unchanged. Therefore the relation

$$\begin{pmatrix} j & 3 & j' \\ -K & 0 & K' \end{pmatrix} = (-1)^{j+3+j'} \begin{pmatrix} j & 3 & j' \\ K & 0 & -K' \end{pmatrix} \quad (4.54)$$

requires that  $j+3+j'$  must be even and  $j \neq j'$ .

associated rotational levels with spacings resembling a symmetric top, with an  $A$  rotational constant approximately the same as the rotational constant of the tetrahedral molecule.

The  $T_4$  term is capable of a much larger effect on the energies of the rotational levels if the magnitudes of  $V_3(R)$  and  $V_4(R)$  are similar, since it can have diagonal matrix elements for  $K=0$  (but only if  $j \geq 2$ ). Neglecting the  $K$  dependence of  $T_4$  by omitting the  $3-j$  symbol containing  $K$  in equation (4.50), the elements of  $T_4$  diagonal in  $j$  are directly proportional to  $D_i$ , the centrifugal distortion term of the free tetrahedral molecule [51]. The inclusion of  $D_i$  and like terms in the Hamiltonian is thus qualitatively unimportant and may be omitted. The presence of the diagonal terms results in qualitatively different effects for positive and negative values of  $V_4(R)$ . However, the  $T_4$  term cannot lift the degeneracy of the  $E$  rotational levels. The explicit angular dependence of  $T_4$  is given by

$$T_4(\alpha\beta\gamma) = \frac{\sqrt{14}}{8} \{ 35 \cos^4\beta - 30 \cos^2\beta - 5 \sin^4\beta \cos 4\gamma + 3 \} \quad (4.55)$$

The midpoints of the six edges of the tetrahedron correspond to the potential minima for negative values of  $V_4(R)$ , and thus in the rigid limit the energy levels are sixfold degenerate for negative  $V_4(R)$ , becoming 12-fold degenerate in the first excited bending state. One of these minima is given by  $\beta=0, \gamma=0$  where the potential has a value of  $\sqrt{14}V_4(R)$ . For the positive values of  $V_4(R)$  the minima correspond to the eight vectors radiating from the centre of a cube to its corners, four of which correspond to Si-H bonds. The rare gas atom is therefore situated above either an 'occupied' or 'unoccupied' corner of cube which defines the tetrahedron. The four occupied sites are minima in the  $T_3$  potential when  $V_3(R)$  is negative. The value of the potential at all eight sites is  $-2/3\sqrt{14}V_4(R)$ , and one such site is at  $\gamma=0, \sin\beta=\sqrt{2}/\sqrt{3}$ . These levels, in the limit of infinite anisotropy, will become eightfold degenerate in the lowest bending state and 16-fold degenerate in the first excited bending state.

## 4.9.2 First excited vibrational state

As well as rotational anisotropy, a further contribution from vibrational anisotropy must be included in the  $\nu_3=1$  triply degenerate levels. The effects of  $T_3$  and  $T_4$  are analogous to those in the ground state, except for the added complication of Coriolis sublevels

characterised by the quantum number  $n$ . As stated in § 4.6.1, each rotational level in the tetrahedral molecule is split by Coriolis interaction with the vibrational angular momentum associated with  $\nu_3 = 1$  into three levels<sup>†</sup>,  $n = j+1, j, j-1$ . If the matrix elements of the potential become significantly larger than those of the Coriolis coupling term the validity of  $n$  is called into question, though it may still be a useful label. Since the potential anisotropy will almost certainly be larger than the Coriolis term,  $b\zeta j$ , this is a likely scenario. In the rigid limit, there is no Coriolis term and the three  $n$  levels arising from each  $j$  level are degenerate, giving overall a 12-fold degeneracy in the ground bending state. The correlation with the isotropic limit is fairly straightforward with reference to **table 4.7**. Rotational levels giving rise to  $K=0$  states (which correlate with the 12-fold degenerate  $K=0$  in the rigid limit) are as follows: three  $T$  symmetry levels, one from  $j=0$  ( $n=1$ ) and two from  $j=1$  ( $n=2$  and  $1$ ), an  $A$  symmetry level from  $j=1$  ( $n=0$ ) and one pair of degenerate  $E$  levels from  $j=1$  ( $n=2$ ). At least  $j=1$  is required to give  $K=1$ , and the levels correlating with  $K=1$  in the rigid limit are the same as for  $K=0$  except for one  $T$  symmetry level coming from  $j=2$ ; the degeneracy of the  $E$  levels is also lifted. The symmetry levels for  $K=2$  all correlate with at least  $j=2$ . A more complicated pattern of energy levels is produced by  $T_4$ ; in the rigid limit the levels become 18-fold degenerate for negative  $V_4(R)$  and 24-fold degenerate for positive  $V_4(R)$ .

The vibrational anisotropic term  $T_2^\nu(\Theta\Phi)$  behaves similarly to the vibration-rotation Coriolis coupling term. The matrix elements in equation (4.51) require  $(k - k_l)$  to be conserved, although  $n$  itself is not preserved by the  $T_2^\nu$  term; the eigenfunctions which result from the vibrational perturbation are different linear combinations of basis functions to those which arise from the Coriolis term. The splittings depend on the amount of rotational anisotropy, and the ordering of the  $K$  sublevels upon the magnitude of  $V_2^\nu(R)$ . For large values of  $T_2^\nu$  and  $T_3$  rotational anisotropy, there are 12 energy levels which correlate with the ground state of a rigid molecule, and in the rigid limit the levels become four- and eightfold degenerate [25].

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<sup>†</sup> With the exception of  $j=0$  which can only result in one value of  $n$ , namely  $n=1$ .

## 4.10 Intensities

The infrared selection rules in the coupled basis  $n=j-l$  are  $\Delta v = \pm 1$ ,  $\Delta n = 0$  and  $\Delta k_l = 0$  [51]. The transitions are purely vibrational in character and the observed rotational structure arises from the coupling of  $n$  and  $l$  to give  $j$ . The validity of the rotational selection rules clearly depends on the ‘goodness’ of the quantum number  $n$ , which in turn is determined by the relative sizes of the potential and Coriolis matrix elements, as explained above. Mixing of levels with different  $n$  values by the tensor components of the centrifugal distortion-like terms in the effective Hamiltonian gives rise to weak transitions with  $\Delta n \neq 0$ , and these transitions will gain in intensity as the anisotropy of the intermolecular potential increases. The intensity of a transition between two states of the complex  $|i\rangle$  and  $|f\rangle$  is proportional to the square of the matrix element of the transition dipole operator between the two states and is given by

$$I_{if} \propto A \langle f | T_p^1(\mu) | i \rangle^2 \exp \left\{ \frac{-E(j, k, K)}{kT} \right\} \quad (4.56)$$

where  $T_p^1(\mu)$  is the transition dipole operator, a spherical tensor operator whose components are referred to the body fixed axes. Parallel transitions occur with  $p=0$ , and perpendicular transitions with  $p=\pm 1$ . The factor  $A$  is equal to 1/2 for parallel transitions with  $K=0$ , and equal to 1 otherwise. The tensor components of the transition dipole operator must be transformed from the body fixed to the molecule fixed axis system thus:

$$T_p^1(\mu) = \sum_q T_q^1(\mu) D_{pq}^{1*}(\alpha\beta\gamma) \quad (4.57)$$

The states  $|i\rangle$  and  $|f\rangle$  are each a linear combination of basis functions  $|jk; l k_l\rangle$  with  $l=0$ ,  $k_l=0$  and coefficients  $c_r$  for  $|i\rangle$ , and  $l=1$  and coefficients  $c_s$  for  $|f\rangle$ , for example  $|i\rangle = \sum_r c_r |j, k, K; l=0, k_l=0\rangle$ . The matrix elements in equation (4.56) are then given by

$$\begin{aligned} \langle f | T_p^1(\mu) | i \rangle &= \sum_{q,r,s} c_r c_s \langle j' k' K' | D_{pq}^{1*}(\alpha, \beta, \gamma) | j k K \rangle \\ &\quad \times \langle l'=1, k_l' | T_q^1(\mu) | l=0, k_l=0 \rangle \\ &= \sum_{q,r,s} c_r c_s (-1)^{k'-K'} [(2j'+1)(2j+1)]^{1/2} \\ &\quad \times \begin{pmatrix} j' & 1 & j \\ -K' & p & K \end{pmatrix} \begin{pmatrix} j' & 1 & l \\ -k' & q & k \end{pmatrix} \times \delta_{k_l' q} \end{aligned} \quad (4.58)$$

The selection rules resulting are  $k_l = q$  and  $k = k_l + k_{\perp}$ , which can be expressed as  $\Delta k = \Delta k_l = q$ , and  $\Delta j = 0, \pm 1$ . The symmetries of the states are contained within the eigenvector elements and therefore the symmetry selection rule is implicit in the summation over basis functions in the above expression.

### 4.10.1 Nuclear spin statistics

The nuclear spin statistics are an important factor in determining the intensities of transitions in a tetrahedral molecule. The number of nuclear spin functions for a tetrahedral molecule XY<sub>4</sub> is  $(2I_Y + 1)^4$ , where  $I_Y$  is the nuclear spin quantum number for the Y atom. For SiH<sub>4</sub>,  $I_H = 1/2$ , giving 16 nuclear spin functions, which form a basis of the permutation group of the molecule, the group of operators which interchange identical particles. For the feasible permutations of SiH<sub>4</sub>, the group is isomorphic with the  $T$  point group. Under this group the 16 nuclear spin functions transform as  $5A + E + 3T$  [58]; the  $A$  functions corresponding to  $I_{\text{total}} = 2$ , the  $E$  functions to  $I_{\text{total}} = 0$  and the  $T$  functions to  $I_{\text{total}} = 1$ . The overall wavefunction which combines vibration-rotation and spin must be totally symmetric in the  $T$  point group, since feasible operations of the permutation group must not change the sign of the wavefunction<sup>†</sup>. Therefore, the degeneracy of the allowed nuclear spin states for a  $j$  level of particular symmetry is given by the number of times the totally symmetric representation  $A$  appears in the direct product  $\Gamma(\psi_{\text{vib-rot}}) \otimes \Gamma(\psi_{\text{spin}})$ . The direct products which yield totally symmetric representations are, for each symmetry<sup>††</sup>:

$$\begin{aligned} A \otimes 5A &= 5A \\ E \otimes E &= 2A + E \\ T \otimes 3T &= 3A + 3E + 6T \end{aligned} \tag{4.59}$$

Assuming equal numbers of  $A$ ,  $E$  and  $T$  rotational levels, the expected population ratios due to nuclear spin statistics would therefore be 5:2:3 respectively. However, there are in fact three times as many  $T$  levels as  $A$  or  $E$  levels in the high temperature limit, so in

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<sup>†</sup> This is true whether the  $Y$  nuclei in XY<sub>4</sub> are fermions or bosons, since the feasible permutation group operations all involve two exchanges of identical nuclei.

<sup>††</sup> It should be noted that the degeneracy of the spin states  $A$  (1),  $E$  (2) and  $T$  (3) does not contribute to the relative populations of the states, because it is the direct product which determines 'allowed' states, i.e. those which transform as the totally symmetric representation  $A$ .

a bulk sample, the total weights of the  $A$ ,  $E$  and  $T$  forms should be 5, 2 and 9 respectively. The extremely rapid cooling which occurs in a supersonic jet prohibits any interconversion between spin states, and so this ‘high temperature’ distribution is frozen into the low temperature environment of the jet; a SiH<sub>4</sub> molecule of a given spin symmetry can only cool to the lowest rotation level of that symmetry. The Ne-SiH<sub>4</sub> complexes formed will therefore populate the lowest three SiH<sub>4</sub> rotational levels  $j=1, 2$  and  $3$  in the ratio 5:9:2, since these are the lowest levels of symmetry  $A$ ,  $T$  and  $E$  respectively.

## 4.11 Simulation of Ne-SiH<sub>4</sub> ro-vibrational energy levels

A computer program was used to predict the positions of the Ne-SiH<sub>4</sub> ro-vibrational energy levels by setting up the Hamiltonian described in the previous sections for each vibrational state and diagonalising. Although no modifications were necessary to the original code written by Randall [30], an alternative and considerably faster routine incorporating symmetry adapted basis functions written by D. J. Hughes [59] was available. However, the program by Randall has the advantage of predicting transition intensities. Both programs made the same approximation in order to simplify the problem: the potential was assumed to be independent of the centre of mass separation  $R^\dagger$ .

Although this is a severe restriction, if the different librational levels of the complex are treated separately, each may be fitted to a slightly different value of  $R$ , and this introduces a corrective factor to terms proportional to  $J(J+1)$ . The two bands already analysed have displayed slightly different rotational constants for  $K=1$  and  $K=0$  states in their respective  $j=1$  levels, and these have been loosely interpreted in terms of the effects of the symmetries of the  $K$  states upon the angular averaging of the intermolecular potential (see § 4.5.1).

This approach was used for Ar-SiH<sub>4</sub> with considerable success, although it may be expected that for a more isotropic system such as Ne-SiH<sub>4</sub> there are other significant factors not dependent upon  $J(J+1)$ , particularly coupling between the radial and angular

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<sup>†</sup> The code by Hughes sufficiently simplifies the calculation of the angular parts of the potential to make a potential with  $R$  dependence a feasible proposition. This possibility is addressed in § 4.12.



motions of the complex, which may give rise to a less good fit if the radial dependence of the potential is ignored. This model should nevertheless provide a good guide to the positions of band centres of the transitions corresponding to the monomer  $R(1)$  and  $Q(1)$  lines and their expected intensities.

The effective Hamiltonian of Robiette *et al.* [51] presented in § 4.6.2 was used to represent the energy levels of the silane molecule ( $H_{\text{mon}}$  in equation (4.40)). Compared to the perturbations caused by the potential, the higher order terms  $\tilde{H}_{mn}$  are very small; only terms up to second order in the Amat-Nielsen ordering scheme [60] were used (those up to  $\tilde{H}_{22}$  and  $\tilde{H}_{04}$ ). For the vibrationally independent terms this means just the rotational constant ( $\tilde{H}_{02}$ ) and the two quartic centrifugal distortion terms ( $\tilde{H}_{04}$ ), which for low  $j$  reproduce the dominant splittings of a given rotational level into its symmetry components (see **table 4.6**). The terms with vibrational dependence are the Coriolis term ( $\tilde{H}_{21}$ ), depending on  $\hat{j} \cdot \hat{l}$ , which is dominant, and three terms resulting from  $\tilde{H}_{22}$  which are vibrational corrections to the rotational constant.

The radial terms in the potential,  $V_3(R)$ ,  $V_4(R)$  and  $V_2^v(R)$ , are thus denoted  $V_3$ ,  $V_4$  and  $V_2^v$  to indicate fixed values. It was assumed that the rotational anisotropies were the same in both vibrational states, an approximation valid for Ar-SiH<sub>4</sub> [25], and the vibrational anisotropy was initially set to zero. Rotational constants for the silane molecule were taken from Ref. 61 for the ground vibrational state and Ref. 40 for the first excited vibrational state. An uncoupled basis set, in which the  $\hat{j} \cdot \hat{l}$  Coriolis term is not diagonal, was used since the matrix elements of the potential off diagonal in  $j$  are much larger than the matrix elements of the Coriolis term. The two vibrational states were taken to be separated by a pure vibrational transition of wavenumber  $\nu_0$ , assumed to be close to that for the silane monomer.

The values of the rotational anisotropic parameters  $V_3$  and  $V_4$  for Ar-SiH<sub>4</sub> were found to be  $91.2 \text{ cm}^{-1}$  and  $-7.8 \text{ cm}^{-1}$  respectively. The expectation from the two bands already fitted is that the anisotropy of Ne-SiH<sub>4</sub> will be considerably smaller. The cumulative evidence of smaller than expected  $B$  value and hence larger than expected intermolecular separation, close correlation between  $\nu_0$  and the monomer transition and small splitting of  $K$  states all point in that direction, confirming the intuitive assumption of much less anisotropic behaviour of SiH<sub>4</sub> when complexed with the smaller, less polarisable neon atom. Having experimentally determined the values of  $\alpha$  and  $\beta$ , the



splitting parameters, the procedure adopted was to vary  $V_3$  and  $V_4$  in a systematic way in order to obtain the closest match for the splittings and also the real, observed band origins (rather than the effective band origins used in § 4.5).

The symmetries of the ro-vibrational levels whose energies are predicted by the Hamiltonian presented for Ne-SiH<sub>4</sub> in § 4.7 are given in **tables 4.6** and **4.7**. It can be seen by reference to these that in the cases of the two bands currently assigned, unique ro-vibrational energy levels enabled unambiguous assignments to be made. For the  $j = 1 \leftarrow 0$  'R(0)' transitions, only one  $A$  state is present in each of  $j'' = 0$  and  $j' = 1$ , for the latter case correlating to  $n = j - 1 = 0$ . Similarly, for the  $j = 0 \leftarrow 1$  'P(1)' band, there is a unique  $T$  state in each of  $j'' = 1$  and  $j' = 0$  (which correlates to  $n = j + 1 = 1$ ).

However, the situation becomes somewhat more complicated for the  $T$  states in the first excited vibrational level (**table 4.7**). These levels are ro-vibrational states of the SiH<sub>4</sub> molecule within the Ne-SiH<sub>4</sub> complex, each of which has an associated stack of complex end-over-end rotational levels. Consequently, as discussed in § 4.8, the descent in symmetry from  $T_d$  to  $T$  removes the distinction between  $T_1$  and  $T_2$  states;  $j = 1$  yields two  $T$  states, correlating to  $n = 2$  and  $n = 1$ , and  $j = 2$  gives rise to five, three correlating to  $n = 2$ , and one to each of  $n = 1$  and in  $n = 0$ .

The infrared selection rules are given in § 4.10 as  $\Delta v = \pm 1$ ,  $\Delta n = 0$  and  $\Delta k_l = 0$ . Therefore the strongest transitions will be those for which  $\Delta n = 0$  (in the ground vibrational state,  $n = j$ ). For the  $j = 1 \leftarrow 0$   $A \leftarrow A$  transitions, the value of the effective quantum number  $j^*$  (i.e. ' $j' = 1$ ') was found to be 0.53, indicating that  $n$  is likely to be mixed by the potential (see § 4.9.2) and so not retain its integrity as a good quantum number. It may be expected therefore that transitions with  $\Delta n \neq 0$  will have significant intensity.

Therefore the transitions of Ne-SiH<sub>4</sub> correlating to  $Q(1)$  of the monomer must be of  $T$  symmetry and correspond to  $\Delta n$  of +1 and 0 (i.e.  $n = 2 \leftarrow 1$  and  $1 \leftarrow 1$  respectively); the  $n = 1 \leftarrow 1$  is expected to be the strongest band, but the  $n = 2 \leftarrow 1$  by no means forbidden in a strict sense<sup>†</sup>. Similarly for the  $R(1)$  correlating transitions of  $T$  symmetry, there is the possibility of five upper  $T$  state destinations. Transitions to the  $n' = 1$   $T$  state will be strongest, followed by the  $n' = 2$   $T$  state, with the transitions to  $n' = 3$  the weakest since

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<sup>†</sup> In the case of the isolated silane monomer, the pure  $T_d$  symmetry forbids the  $\Delta n = 1$   $T_1 \leftarrow T_1$  transition.

for these  $\Delta n = +2$ . As well as energy levels, ro-vibrational SiH<sub>4</sub> transitions were predicted<sup>†</sup> with intensities calculated explicitly according to § 4.10.

With the vibrational anisotropic term  $V_2^v$  set to zero, the best agreement based on the above criteria was obtained by setting  $V_3 = 25.5 \text{ cm}^{-1}$  and  $V_4 = -3.5 \text{ cm}^{-1}$ . Although these values reproduced the splittings  $\alpha$  and  $\beta$  well, to within 0.5 %, the values of the band origins were  $\approx 0.35 \text{ cm}^{-1}$  too low for the  $P(1)$  pair and  $\approx 0.25 \text{ cm}^{-1}$  too high for the  $R(0)$  pair. Changing the values of  $V_3$  and  $V_4$  to preserve the splittings but improve the band origin agreement for one pair resulted in worse agreement for the other. However, as the simulation was to provide only a general guide to the identities of the states involved in the unassigned transitions, this did not prove to be a problem. A proper least squares fit involving all the band origins and including the  $V_2^v$  term required first the assignment of these bands and the fitting of their transitions to an appropriate model.

### 4.11.1 Calculation of Coriolis terms

Strongly Coriolis interacting, nearby states will demonstrate the pseudo-Case 1 coupling observed for the  $R(0)$  and  $P(1)$  bands, whereas more distant, weakly interacting states should demonstrate behaviour more in line with the Ar-SiH<sub>4</sub> observations, i.e. energy level spacings given approximately by  $2B$ ,  $4B$ ,  $6B$  etc., with the Coriolis term introducing only a small second order correction to the rotational constant. This latter case would explain the band centred at  $2202.5 \text{ cm}^{-1}$  reported in § 4.5.4 which appeared to involve an unperturbed  $j=2$ ,  $v_3=1$  state, despite the expectation of strong Coriolis interaction with neighbouring  $K$  states of  $T$  symmetry.

However, the number of  $T$  states in the  $j'=1$  and  $j'=2$  levels (two and five respectively) may potentially result in very complex coupling if states differing in  $K$  by  $\pm 1$  deriving from several different  $n$  states are close in energy. For example, the  $K=0$  state deriving from  $n=1$ ,  $j=1$  may Coriolis interact with both the  $|1^+\rangle$  state from  $n=1$ ,  $j=1$  and the  $|1^+\rangle$  state from  $n=2$ ,  $j=1$ , and similarly for the  $K=0$  state from  $n=2$ ,  $j=1$ . The situation in the  $j'=2$  level with its five  $T$  states each with  $|0\rangle$ ,  $|1^+\rangle$ ,  $|2^+\rangle$  and  $|1^-\rangle$ ,  $|2^-\rangle$  states clearly has the possibility of being far worse!

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<sup>†</sup> These correspond to the band origins for each separate  $\Delta K = 0, \pm 1$  transition of the Ne-SiH<sub>4</sub> complex transitions.

As well as predicting the rotational energy levels of Ne-SiH<sub>4</sub> in the ground and first excited vibrational states, the Coriolis coupling terms were therefore calculated explicitly in order to provide a guide to the degree of interaction between states of the same symmetry. Using these values as a guide, the interaction Hamiltonian for the  $j' = 1$  and  $j' = 2$  levels can be correctly set up in order to fit the observed transitions.

The Coriolis matrix elements are given in equation (4.9) and reproduced below:

$$\langle JjkK | \mathbf{H}_{\text{cor}} | JjkK \pm 1 \rangle = -B[J(J+1) - K(K \pm 1)]^{1/2} \times [j(j+1) - K(K \pm 1)]^{1/2} \quad (4.60)$$

This expression is only off diagonal in  $K$ . The expression for the second order correction to the energy of some state  $|i\rangle$  which interacts with a state  $|f\rangle$  is given by

$$\Delta E = \sum_f \frac{\langle i | \mathbf{H}_{\text{cor}} | f \rangle \langle f | \mathbf{H}_{\text{cor}} | i \rangle}{E_i - E_f}, \quad i \neq f \quad (4.61)$$

The states  $|i\rangle$  and  $|f\rangle$  are linear combinations of the symmetric top basis functions used to construct the Hamiltonian:

$$\begin{aligned} |i\rangle &= \sum_p c_p |Jj_p k_p K\rangle \\ |f\rangle &= \sum_q c_q |Jj_q k_q K\rangle \end{aligned} \quad (4.62)$$

where  $c_p$  and  $c_q$  are the eigenvector elements of the two states. The contribution to the rotational energy is then given by

$$\begin{aligned} \Delta E &= \sum_f \frac{\left\{ \sum_{pq} c_p c_q \langle Jj_p k_p K | \mathbf{H}_{\text{cor}} | Jj_q k_q K \pm 1 \rangle \right\}^2}{E_i - E_f} \\ &= B^2 [J(J+1) - K(K \pm 1)] \sum_f \frac{1}{E_i - E_f} \\ &\quad \times \left\{ \sum_{pq} c_p c_q [j_p(j_p+1) - K(K \pm 1)]^{1/2} \delta_{j_p j_q} \delta_{k_p k_q} \right\}^2 \end{aligned} \quad (4.63)$$

and the contribution to the rotational constant is given by removing the  $[J(J+1) - K(K \pm 1)]$  term from this expression<sup>†</sup>. The Coriolis matrix element connecting the states is given by

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<sup>†</sup> Strictly speaking the  $-K(K \pm 1)$  part has been included in the splitting parameter  $\alpha$ , and the first order rotational energy is given by expressions which are functions of only  $J(J+1)$ . However, the discrepancy is very small when compared with the value of the rotational constant itself.

$$\chi = \left\{ \sum_{pq} c_p c_q [j_p(j_p+1) - K(K\pm 1)]^{1/2} \delta_{j_p j_q} \delta_{k_p k_q} \right\}^2 \quad (4.64)$$

In order to gauge the degree of Coriolis interaction, the value of  $\chi$  was evaluated for each pair of interacting levels in the ground and first excited vibrational state (with  $V_3 = 25.5 \text{ cm}^{-1}$  and  $V_4 = -3.5 \text{ cm}^{-1}$  as before). The exact solution to the Coriolis interaction for a pair of interacting levels is given in equation (4.15) and may be rewritten

$$E = BJ(J+1) \pm \left\{ \frac{\Delta E^2}{4} + \xi J(J+1) \right\}^{1/2} \quad (4.65)$$

where  $E$  is the energy relative to the vibrational band origin,  $\xi = 2B^2 j^*(j^*+1)$  and  $\Delta E = E_i - E_f$  and is equivalent to  $\alpha$ , the separation of the perturbing levels. The square root can be expanded as a Taylor series thus:

$$\begin{aligned} \left\{ \frac{\Delta E^2}{4} + \xi J(J+1) \right\}^{1/2} &= \frac{\Delta E}{2} \left\{ 1 + \left[ \frac{4\xi J(J+1)}{\Delta E^2} \right] \right\}^{1/2} \\ &\approx \frac{\Delta E}{2} \left\{ 1 + \frac{2\xi J(J+1)}{\Delta E^2} - \frac{2\xi^2 J^2(J+1)^2}{\Delta E^4} \right\} \\ &= \frac{\Delta E}{2} + \frac{\xi J(J+1)}{\Delta E} - \frac{\xi^2 J^2(J+1)^2}{\Delta E^3} \end{aligned} \quad (4.66)$$

Depending upon the magnitude of the interaction, and the energy separation of the interacting states, the Coriolis interaction will introduce a modification to the rotational and centrifugal distortion constants. The correction to the rotational constant is given by the coefficient of  $J(J+1)$  (i.e.  $\xi/\Delta E$ ) and the correction to the centrifugal distortion constant by the coefficient of  $J^2(J+1)^2$  (i.e.  $\xi^2/\Delta E^3$ ). The  $R(0)$  and  $P(1)$  bands have both been fitted to a single centrifugal distortion constant, although the rotational constants have been floated separately for the ground and first excited vibrational levels, and for  $K=0$  and  $K=1$  states. This suggests that a valid criterion for judging whether an interaction can be modelled using second order perturbation theory by ‘correcting’ the rotational constant by the factor  $\xi/\Delta E$ , is to examine the value of the correction term for the centrifugal distortion constant. If the contribution to the energy resulting from the  $D_J$ -like term is greater than the experimental accuracy the Coriolis interaction is significant; a correction to  $B$  will not be sufficient and either  $D$  must be floated separately for each interacting state, or explicit evaluation of the Coriolis term is required. Line positions can generally be fitted to

$\approx 0.0004 \text{ cm}^{-1}$ , which if taken to be ‘better than  $0.001 \text{ cm}^{-1}$ ’ gives the following condition for ‘significant’ Coriolis interaction, i.e. that which cannot be modelled by second order perturbation theory:

$$\frac{\xi^2 J^2 (J+1)^2}{\Delta E^3} < 0.001 \text{ cm}^{-1} \quad (4.67)$$

Substituting equation (4.64) into this expression by approximating  $\xi = 2B^2\chi$  (for  $|0\rangle$ ,  $|1^+\rangle$  interaction) gives

$$\frac{4\chi^2 B^4 J^2 (J+1)^2}{\Delta E^3} < 0.001 \text{ cm}^{-1} \quad (4.68)$$

The two bands analysed gave a value of  $j^* \approx 0.5$ , indicating that for  $j=1$   $\chi$  is typically  $\sim 1.0$ . For  $B = 0.08 \text{ cm}^{-1}$  and  $J_{\text{max}} \approx 6$  equation (4.68) gives the approximate condition

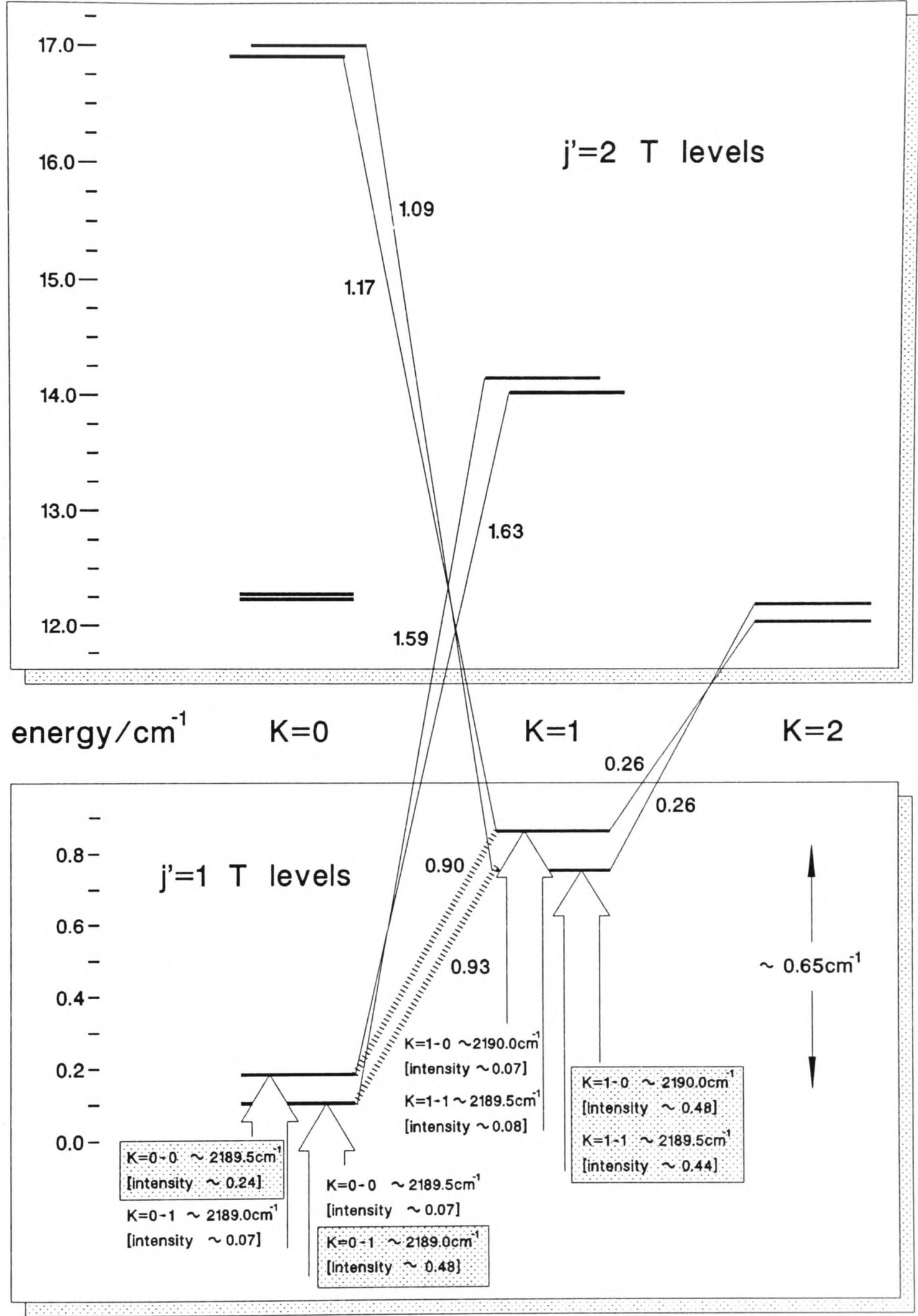
$$\Delta E > 6.7 \chi^{2/3} \text{ cm}^{-1} \quad (4.69)$$

Thus for  $\chi = 1.0$  the two interacting states must be separated by more than  $6.7 \text{ cm}^{-1}$  in order to model the Coriolis interaction by second order perturbation theory. If the states are closer than this, there is a significant contribution to the centrifugal distortion type term in the expansion and either the interaction must be dealt with explicitly in the Hamiltonian, or  $D$  allowed to float separately for each interacting state.

### 4.11.2 $j = 1 \leftarrow 1$ $T \leftarrow T$ transitions

Figure 4.11 shows the predicted energies of the first excited vibrational state  $j' = 1$   $T$  state energy levels and the calculated Coriolis interactions affecting these states, many of which arise from interactions with levels belonging to  $j' = 2$ . Coriolis interactions which were calculated to be significant using the above criteria are indicated by means of thick dotted lines linking the interacting states, whilst those interactions which are weak enough to be treated by a correction to the rotational constant are joined by means of thin unbroken lines. The number next to the line gives the value of  $\chi$ .

There are several surprising features. The first point to note is that the only significant interaction is between the  $|0\rangle$  and  $|1^+\rangle$  states arising from each  $n$  state, and that these interactions are both exclusive and distinct. The  $|0\rangle$  state belonging to  $n = 1$



**Figure 4.11** Calculated energies and Coriolis matrix elements for  $j' = 1$  T states ( $V_2^v = 0.0 \text{ cm}^{-1}$ ,  $V_3 = 25.5 \text{ cm}^{-1}$ ,  $V_4 = -3.5 \text{ cm}^{-1}$ ).

only interacts with the  $|1^+\rangle$  state from  $n=1$  and not with that from  $n=2$ . The system clearly possesses some ‘hidden’ symmetry which distinguishes the  $T$  states belonging to  $n=1$  from those belonging to  $n=2$  (although the value of  $n$  should be seen more as a useful label than as a bona fide good quantum number). This is something of a relief and suggests that the energy levels for the  $j'=1$  state can be modelled in exactly the same way as before, i.e. a two level problem. Each pair of interacting levels will have their own sets of splitting and mixing parameters which must be kept separate.

The interactions with other levels from  $j'=2$  are all well below the criterion established in equations (4.60) and (4.61). The largest coefficient  $\chi$  was calculated to be  $\approx 1.6$  for interaction between opposite pairs of levels from  $j'=2, K=1$  at  $\approx 14\text{ cm}^{-1}$  and  $j'=2, K=0$  at  $0.1\text{ cm}^{-1}$  and  $0.2\text{ cm}^{-1}$ . Equation (4.69) indicates that a spacing greater than  $\sim 9\text{ cm}^{-1}$  results in a second order correction to the rotational constant only and no further contributions; the spacing of  $\sim 14\text{ cm}^{-1}$  is well within this ‘second order’ criterion and thus requires no explicit treatment in the Hamiltonian. It is interesting to note that the ‘hidden symmetry’ is still apparent in these weaker interactions; each lower  $T$  state belonging to a pair of levels in  $j'=2$  interacts with the upper level of the pair in  $j'=1$ , and vice versa. The pair of levels belonging to  $j'=2, K=0$  at  $12.25\text{ cm}^{-1}$  is unaffected by any of the  $j'=1$  levels<sup>†</sup>, intimating the possibility of three distinct symmetry ‘sub-states’.

The origin of this symmetry effect is obscure, and may be the result of residual  $T_d$  symmetry in what is otherwise a system characterised by the  $T$  permutation group, i.e. just the pure rotations of  $T_d$ . This would have the effect of introducing distinguishability in the form of the  $T_1$  and  $T_2$  labelling and permit Coriolis interaction only between like symmetry states. Such a partial removal of full  $T_d$  symmetry could be due to the form of the intermolecular potential used.

The calculated intensities and approximate (to the nearest half wavenumber) band origins for transitions out of the ground vibrational  $j''=1$   $K=0$  and  $K=1$  levels are also shown in **figure 4.11**, with the strongest transitions highlighted by means of a shaded box. Of these transitions, those originating from  $K=1$  in  $j''=1$  will have the disadvantage of unfavourable Boltzmann population which reduces the calculated intensity by a factor of 0.145 (assuming a jet temperature of 0.5 K). This effect was particularly noticeable in the

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<sup>†</sup> ‘Unaffected’ implies  $\chi < 0.001\text{ cm}^{-1}$ .



very weak  $K = 0 \leftarrow 1$  transitions of the  $j = 0 \leftarrow 1$  band (§ 4.5.2). The strongest transitions would be expected for the  $j' = 1$  levels which are predominantly ' $n = 1$ ' in character, although significant mixing by the potential of different  $n$  states is expected, and this is the origin of the weaker transitions to the other pair of levels.

The two  $T$  states are predicted to be separated by only about  $0.2 \text{ cm}^{-1}$  in  $K = 0$  and  $K = 1$ , and the calculated splitting is  $\approx 0.65 \text{ cm}^{-1}$ . The predictions correspond well to the cluster of lines between  $2189.5 \text{ cm}^{-1}$  and  $2191.5 \text{ cm}^{-1}$ , and the method of combination differences was used to identify the  $^R P_0$  and  $^R R_0$  branches (the spacing between  $R(J)$  and  $P(J+2)$  must be identical to that in the  $j = 0 \leftarrow 1$  band already assigned in § 4.5.2). The  $R$  and  $Q$  branches of this  $K = 1 \leftarrow 0$  band are significantly more intense than the  $P$  branch, indicating that for  $K = 0 \leftarrow 0$  a strong  $P$  branch is expected. The  $^R P_0$  transitions converge to a band head at  $J = 5$ .

The analogous  $^{22}\text{Ne-SiH}_4$   $K = 1 \leftarrow 0$  band was identified as a series of much weaker lines almost coincident with its stronger  $^{20}\text{Ne-SiH}_4$  counterpart, demonstrating the same intensity enhancement effect described in § 4.5.2. As expected, a smaller rotational constant for the  $^{22}\text{Ne}$  isotopomer was indicated by higher  $J$  lines 'lagging behind' the  $^{20}\text{Ne-SiH}_4$  transitions.

The other, weaker,  $K = 1 \leftarrow 0$  band was located approximately  $0.4 \text{ cm}^{-1}$  lower in wavenumber, contrary to the prediction which placed it  $\sim 0.1 \text{ cm}^{-1}$  higher. Unlike the strong band, this showed no intensity borrowing by the  $^R R_0$  band at the expense of the  $^R P_0$ , which did not form a band head but rather has spacings which initially contract and then expand, indicative of stronger Coriolis interaction in both the ground vibrational  $j = 1$ ,  $|0\rangle$  states than the  $v_3 = 1$ ,  $j = 1$   $|1^+\rangle$  states.

The assignments are shown in **figure 4.12**. However, the corresponding  $K = 0 \leftarrow 0$  bands proved far from trivial to identify. Predictions based upon the calculated splitting of  $\sim 0.65 \text{ cm}^{-1}$  and a rotational constant of  $0.08 \text{ cm}^{-1}$ , with the other terms fitted using the  $K = 1 \leftarrow 0$  lines, placed the  $^Q P_0$  band associated with the higher frequency, stronger  $K = 1 \leftarrow 0$  band between the dense monomer  $Q$  branch region and the cluster of lines above  $2189.5 \text{ cm}^{-1}$ . The other  $K = 0 \leftarrow 0$  transitions, corresponding to the lower frequency, weaker  $K = 1 \leftarrow 0$  band, were predicted to be centred on the edge of the  $\text{SiH}_4$   $Q$  branch region.

A tentative  $P$  branch was assigned as the  $K = 0 \leftarrow 0$  companion to the most intense  $K = 1 \leftarrow 0$  band, and this is shown in **figure 4.12**. Unfortunately, there are no  $R$  branch





transitions to confirm the identification of these  ${}^2P_0$  lines. Several other possible assignments were considered; indeed, the density of lines in this region yielded several possible fits which were equally good, but ultimately rejected on the basis of either rotational constants or intensity.

The data were fitted to two separate models. The problem of the ambiguous  $K=0 \leftarrow 0$  bands was eliminated by initially fitting the  $K=1 \leftarrow 0$  bands to only a rotational constant and centrifugal distortion constant. In order to model the anticipated strong Coriolis interaction, both rotational and centrifugal distortion constants were fitted separately to the symmetric  $|1^+\rangle$  and anti-symmetric  $|1^-\rangle$   $K$  states of each  $j'=1$   $T$  state. This produced a tolerably good fit with parameters listed in **table 4.9** (fit 1). This in itself is surprising since the strength of the calculated Coriolis interaction would be expected to invalidate the perturbation theory approach adopted in § 4.11.1; the expansion in equation (4.66) is valid provided

$$\frac{8B^2\chi J(J+1)}{\Delta E^2} \leq 1 \quad (4.70)$$

For levels which are closely spaced ( $< 1 \text{ cm}^{-1}$ ), with a value of  $\chi$  close to unity, this expression is no longer true even at moderate values of  $J$ . Even if this term does not become prohibitively large, then a significant contribution from the third order term

$$E^{(3)} = + \frac{16B^6\chi^3 J^3(J+1)^3}{\Delta E^5} \quad (4.71)$$

would be expected. If the  $K=0$  and  $K=1$  states are separated by  $\sim 0.4 \text{ cm}^{-1}$  (i.e. if the  ${}^2P_0$  branch is correctly assigned), and  $\chi = 0.90$ , then equation (4.69) is no longer satisfied when  $J=2$  and the perturbation theory approach should fail. The fact that it apparently succeeds indicates limitations in the theory.

A second fit, including the tentative  ${}^2P_0$  lines, was therefore undertaken, this time modelling the interaction explicitly by diagonalising the Coriolis matrix (fit 2). Surprisingly, the quality of the fit actually deteriorated slightly, with  $\sigma_{\text{fit}}$  rising from a value of  $0.00108 \text{ cm}^{-1}$  for fit 1 to  $0.00115 \text{ cm}^{-1}$ . These parameters are listed in **table 4.10**.

Both fit 1 and fit 2 included the whole data set from the  $j=0 \leftarrow 1$   $T \leftarrow T$  transitions, and the related constants were allowed to float freely. Both **table 4.9** and **4.10** list only the upper state  $j=1$  constants; for the final fitted values of the ground state  $j=1$  and first excited vibrational state  $j=0$  constants, the reader is referred to the final 'global fit' of all

**Table 4.9** Upper state fitted parameters for  $j = 1 \leftarrow 1$   $T \leftarrow T$  transitions of Ne-SiH<sub>4</sub> using perturbation theory model.

| <i>fit 1</i>          | <i>value</i> <sup>¶</sup> /cm <sup>-1</sup> |                   |
|-----------------------|---------------------------------------------|-------------------|
| <i>parameter</i>      | <i>band 1</i>                               | <i>band 2</i>     |
| $v_{K=1\leftarrow 0}$ | 2 190.221 66 (25)                           | 2 189.841 57 (32) |
| $v_{K=1\leftarrow 1}$ | 2 189.550 33 (61)                           | 2 189.170 24 (67) |
| $B'_{K=1+}$           | 0.088 036 (46)                              | 0.088 124 (69)    |
| $D'_{K=1+}$           | 0.000 020 9 (15)                            | 0.000 165 6 (30)  |
| $B'_{K=1-}$           | 0.085 110 (55)                              | 0.087 62 (16)     |
| $D'_{K=1-}$           | -0.000 013 3 (20)                           | 0.000 037 (12)    |
| $\sigma_{\text{fit}}$ | 0.001 083                                   |                   |

<sup>¶</sup> Figures in parentheses represent one standard deviation uncertainty.

**Table 4.10** Upper state fitted parameters for  $j = 1 \leftarrow 1$   $T \leftarrow T$  transitions of Ne-SiH<sub>4</sub> using Coriolis model (band 1 only).

| <i>fit 2</i>                     | <i>value</i> <sup>¶</sup> /cm <sup>-1</sup> |
|----------------------------------|---------------------------------------------|
| <i>parameter</i>                 | <i>band 1</i>                               |
| $v_{K=1\leftarrow 0}$            | 2 190.220 66 (68)                           |
| $v_{K=1\leftarrow 1}$            | 2 189.549 14 (102)                          |
| $v_{K=0\leftarrow 0}$            | 2 189.803 91 (31)                           |
| $v_{K=0\leftarrow 1}$            | 2 189.132 39 (65)                           |
| $B'_{K=0}$                       | 0.071 618 (61)                              |
| $B'_{K=1}$                       | 0.085 294 (54)                              |
| $\gamma$                         | 0.416 75 (37)                               |
| $\sqrt{2}B'\{j^*(j^*+1)\}^{1/2}$ | 0.038 18 (15)                               |
| $D'_+$                           | -0.000 017 4 (14)                           |
| $D'_-$                           | -0.000 008 2 (20)                           |
| $\sigma_{\text{fit}}$            | 0.001 149                                   |

<sup>¶</sup> Figures in parentheses represent one standard deviation uncertainty.

the  $T$  state transitions, including the  $j = 2 \leftarrow 1$  transitions, in § 4.11.3 and § 4.11.4.

The two fits taken together provide important insights into the nature of the difficulty, if not the solution. The first important observation is the similarity in the effective rotational constants fitted to the  $|1^+\rangle$  (and to a lesser extent the  $|1^-\rangle$ ) states. They are calculated to engage in very similar Coriolis interactions with neighbouring states (see **figure 4.11**) which are themselves ‘equivalent’ pairs of levels distinguished by the subtle symmetry properties alluded to in the previous section. Therefore the second order effect on the rotational constants should be very similar. The  $|1^+\rangle$  levels are strongly interacting with the  $|0\rangle$  levels which lie slightly lower in energy, with the result that the rotational constants of the two  $|1^+\rangle$  levels are elevated, and those of the two  $|0\rangle$  levels depressed.

From fit 1 of the  $j = 1 \leftarrow 0$   $A \leftarrow A$  bands in § 4.5.1, the  $v_3 = 1$ ,  $j = 1$  levels, both  $K = 0$  and  $K = 1$ , were fitted to the same rotational constant of  $0.0808 \text{ cm}^{-1}$ . If this is taken to be a good indication of the value to be expected in the  $T$  states of this level, clearly there is substantial second and higher order perturbation to increase  $B$  by as much as 10 %. However, the two  $K = 1 \leftarrow 0$   $Q$  branches are significant in providing  $B$  values for the  $|1^-\rangle$  levels, which should show very little change from the ‘real’ value. The only possible interaction partners for the  $|1^-\rangle$  levels are higher energy  $|2^-\rangle$  states, such as the two levels belonging to  $j = 2$ ,  $K = 2$  lying at  $\sim 12 \text{ cm}^{-1}$  (see **figure 4.11**). Therefore the rotational constants fitted (using a perturbation theory approach) to the  $|1^-\rangle$  levels should be effective values depressed from the correct  $B$  value by Coriolis interaction with these higher lying states. In fact, the  $B$  values fitted are  $0.0851 \text{ cm}^{-1}$  (for the strongest  $K = 1 \leftarrow 0$  band) and  $0.0876 \text{ cm}^{-1}$  (for the weaker  $K = 1 \leftarrow 0$  band), pointing to apparently much larger rotational constants than anticipated.

Comparison with fit 2 of the  $j = 1 \leftarrow 0$   $A \leftarrow A$  bands suggests one answer to this problem. The  $B$  values for  $K = 0$  and  $K = 1$  were allowed to float independently in this fit, and although the result is called into question by the high correlation between these and the Coriolis term (see § 4.5.1), gave  $B_{K=0} = 0.07817 \text{ cm}^{-1}$  and  $B_{K=1} = 0.08269 \text{ cm}^{-1}$ . It is thus possible that the  $K = 1$  state has a higher rotational constant than the  $K = 0$ , and for the  $j = 1$   $T$  state may indeed be as high as this analysis indicates. For a  $K = 1 - K = 2$  interaction,  $\xi = B^2\chi$  (see equations (4.64) and (4.66)), giving the second order correction to  $B$  arising from the interaction to be approximately  $-1.5 \times 10^{-4} \text{ cm}^{-1}$ . This yields ‘true’  $B$  values of

approximately  $0.0853 \text{ cm}^{-1}$  and  $0.0878 \text{ cm}^{-1}$  for the stronger and weaker band respectively. Centre of mass separations corresponding to these constants are  $4.01 \text{ \AA}$  and  $3.95 \text{ \AA}$ .

It is not clear why the two  $|1^- \rangle$  states should have such different rotational constants. Moreover, the centrifugal distortion constant for band 1 (the stronger band) is negative, whilst that for band 2 is positive. A negative value for  $D$  is consistent with the  $|1^- \rangle$  level interacting strongly with a  $|2^- \rangle$  state higher in energy; the coefficient of  $J^2(J+1)^2$  in the expansion is then positive since the negative sign in equation (4.65) multiplies the bracket expanded in equation (4.66). If this term becomes larger in magnitude than the true centrifugal distortion constant then the effective  $D$  will become negative. However, the calculated contribution to  $D$  is only  $\sim -2 \times 10^{-9} \text{ cm}^{-1}$  which cannot account for the  $-1.3 \times 10^{-5} \text{ cm}^{-1}$  ascribed to  $D$  for band 1 in fit 1, or indeed the  $-8.2 \times 10^{-6} \text{ cm}^{-1}$  in fit 2.

Fit 2 is perhaps more revealing as to the nature of the problem. The  $B$  values fitted to the  $|1^+ \rangle$  states in fit 1 indicated very strong Coriolis interaction for each with a lower level (the  $|0 \rangle$  state of the pair), yet not so strong that the transitions could not be fitted to a perturbation theory model. The tentative assignments for the  $K=0 \leftarrow 0$   $P$  branch were included in fit 2 in an effort to diagonalise the Coriolis matrix and model the interaction explicitly. The rotational constants for the  $|1^+ \rangle$  and  $|1^- \rangle$  states were tied as  $B_{K=1}$ , which was floated separately to  $B_{K=0}$ . The results are shown in **table 4.10**.

Apart from the slight decrease in the quality of the fit, the most noticeable features are the small value of  $B_{K=0}$  ( $0.0716 \text{ cm}^{-1}$ ), the large value of  $B_{K=1}$  (close to the fit 1 value for  $|1^- \rangle$  in band 1) and above all the very small value of the Coriolis parameter,  $\sqrt{2B'}\{j^*(j^*+1)\}^{1/2}$  ( $0.0382 \text{ cm}^{-1}$ ). The values of the rotational constants (particularly  $B_{K=0}$ ) still appear to be suffering second order perturbation, despite the Coriolis interaction having been modelled explicitly. There appears to be strong Coriolis interaction, but as a consequence of the model used this results in modification of the  $B$  values rather than increasing the Coriolis term  $\sqrt{2B'}\{j^*(j^*+1)\}^{1/2}$ . The simulation indicates that the  $|0 \rangle$ ,  $|1^+ \rangle$  pair are the only significantly interacting levels based on the criterion of equation (4.69), yet it appears that the interaction cannot be modelled in the same way as for the ground state  $j=1$   $T$  levels, or the upper state  $j=1$   $A$  levels. The fit is adequate, but not good, and the physical meaning of the constants obtained questionable.

There are potentially three factors which could affect the Coriolis term. The first factor is the effect of the vibrational anisotropy on the upper state Coriolis interactions. The initial calculations were performed with  $V_2^v$  set to zero and indicated no ‘cross Coriolis interaction’, i.e. between opposite pairs of levels such that each  $|0\rangle$  state interacts with *both*  $|1^+\rangle$  states. Therefore,  $V_2^v$  was set to  $1.0\text{ cm}^{-1}$  and the Coriolis matrix elements recalculated. Although this did introduce some ‘cross interaction’, it was several orders of magnitude smaller than the main Coriolis term and therefore could not be responsible for the observed behaviour of the levels.

The second factor is the possibility of centrifugal distortion within the term itself such that

$$\langle 0 | \mathbf{H}_{\text{cor}} | 1^+ \rangle = -\sqrt{2} [B - DJ(J+1)] [J(J+1)j(j+1)]^{1/2} \quad (4.72)$$

However, this will lead to a smaller than anticipated Coriolis interaction and is therefore of the wrong sign to explain these results.

The third possibility is to consider the radial dependence of the parameter  $j^*$ , the effective  $j$  quantum number. At large values of  $R$ , the centre of mass separation,  $j^* = j$  as the anisotropy of the potential tends to zero, which for the  $j = 1$  states under consideration means that as  $R \rightarrow \infty$ ,  $j^* \rightarrow 1$ . The previous fits of the  $R(0)$  (§ 4.5.1) and  $P(1)$  bands (§ 4.5.3) have given values for  $j^*$  in ‘ $j = 1$ ’ of  $\sim 0.5$ , whereas fit 2 in **table 4.10** gives  $j^* \approx 0.27$ . To try to incorporate this into the fit, the off diagonal term was expressed as a power series in  $J(J+1)$  as follows:

$$\langle 0 | \mathbf{H}_{\text{cor}} | 1^+ \rangle = -\left\{ \xi^{1/2} [J(J+1)]^{1/2} + \lambda [J(J+1)]^{3/2} \right\} \quad (4.73)$$

where  $\xi = 2B^2 j^*(j^* + 1)$  as before and  $\lambda$  is an empirical parameter modelling the centrifugal distortion of  $j^*$ . Equation (4.65) then becomes

$$E = BJ(J+1) \pm \left\{ \frac{\Delta E^2}{4} + \xi J(J+1) + 2\xi^{1/2}\lambda J^2(J+1)^2 + \lambda^2 J^3(J+1)^3 \right\}^{1/2} \quad (4.74)$$

The bracket can be expanded in the same way as before to give

$$E \approx BJ(J+1) \pm \left\{ \frac{\Delta E}{2} + \frac{\xi J(J+1)}{\Delta E} + \frac{2\xi^{1/2}\lambda J^2(J+1)^2}{\Delta E} + \frac{\lambda^2 J^3(J+1)^3}{\Delta E} - \frac{\xi^2 J^2(J+1)^2}{\Delta E^3} - \dots \right\} \quad (4.75)$$

Another correction to the centrifugal distortion is then introduced; if the  $2\xi^{1/2}\lambda/\Delta E$  term becomes larger than the  $\xi^2/\Delta E^4$  term, the overall effect is to reduce  $D$  and if it is much larger,  $D$  may become negative. This criterion can be used to estimate a value for  $\lambda$ , giving

$$\lambda \geq \frac{\xi^{3/2}}{2\alpha^2} \quad (4.76)$$

For  $\xi^{1/2} \approx 0.04 \text{ cm}^{-1}$  and  $\Delta E \approx 0.4 \text{ cm}^{-1}$ ,  $\lambda \approx 1.7 \times 10^{-4} \text{ cm}^{-1}$ . It would be unfeasible to attempt to fit  $\lambda$  because of correlation problems, therefore fit 2 was repeated for varying trial values of  $\lambda$ . Unfortunately, whilst this resulted in a slight rise in the value of  $B_{K=0}$ , the value of  $\xi (\sqrt{2}B' \{j^*(j^*+1)\}^{1/2})$  fell as  $\lambda$  was increased.

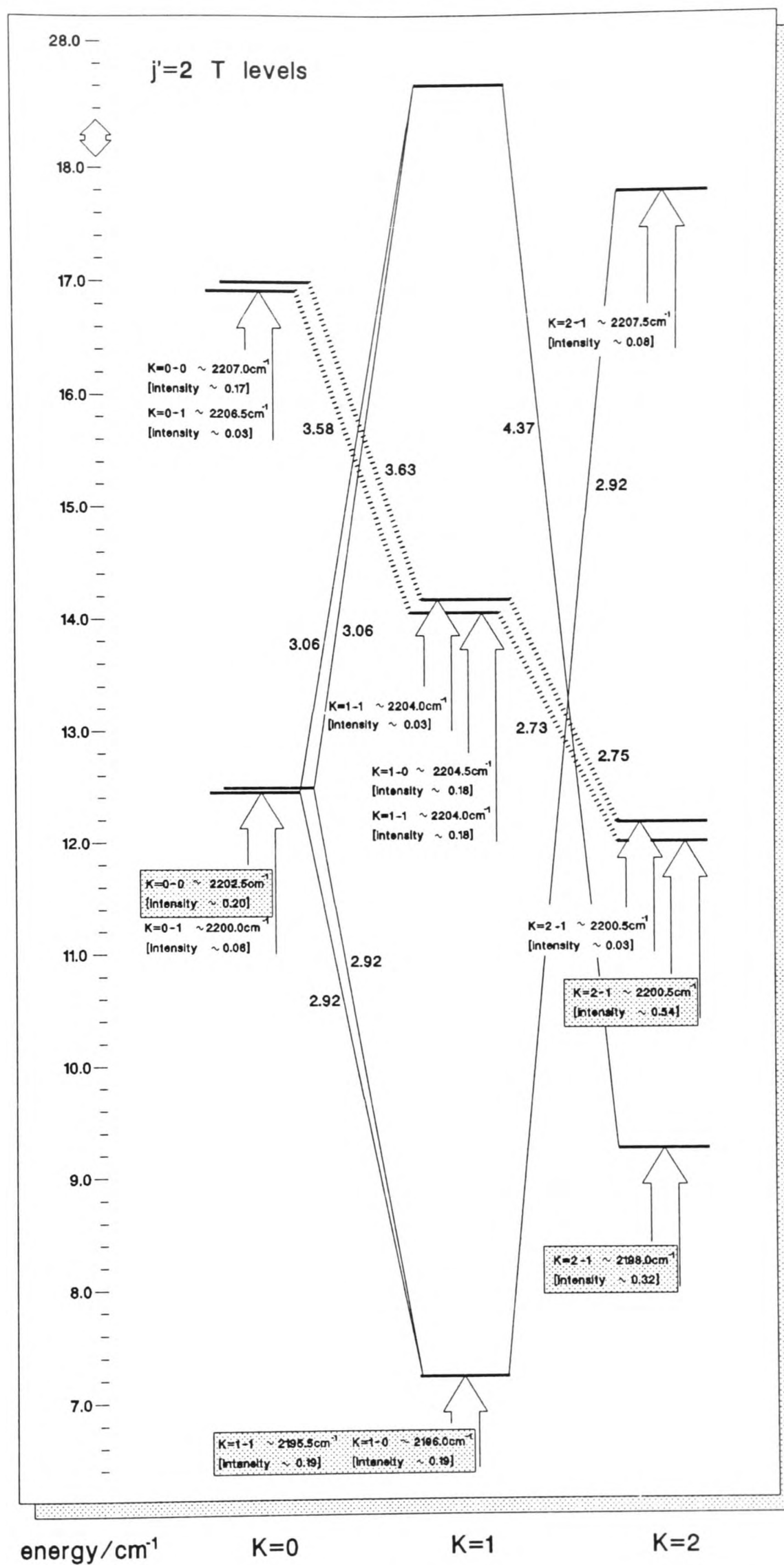
To summarise, the  $j = 1 \leftarrow 1$   $T \leftarrow T$  transitions have all been assigned, with the exception of the band 2  $K = 0 \leftarrow 0$  lines which may be obscured by the monomer  $Q$  branch region. However, the nature of the two  $\nu_3 = 1$ ,  $j = 1$   $T$  states has been only partially determined. There is undoubtedly strong Coriolis interaction between the  $|0\rangle$  and  $|1^+\rangle$  pairs of levels, but the theory applied to the  $A$  states in the same silane ro-vibrational level was unsuccessful in elucidating the precise nature of this interaction. It is likely that higher order interactions, which are at present undetermined, are responsible for the deviation from the expected behaviour.

### 4.11.3 $j = 2 \leftarrow 1$ $T \leftarrow T$ transitions

The Ne-SiH<sub>4</sub> transitions correlating with the silane  $R(1)$  transition are the most profoundly affected by the intermolecular potential. Whilst the  $R(0)$ ,  $P(1)$  and  $Q(1)$  complex bands are relatively localised in the vicinity of the appropriate monomer transition, the  $R(1)$  Ne-SiH<sub>4</sub> transitions lie between  $5 \text{ cm}^{-1}$  below and  $3 \text{ cm}^{-1}$  above the silane  $R(1)$  line at  $2200.342 \text{ cm}^{-1}$ .

**Figure 4.13** shows the calculated energy levels for the  $\nu_3 = 1$ ,  $j = 2$   $T$  states together with the Coriolis interactions. As before, the strongest transitions (within the range of the experimental spectrum) are highlighted by a shaded box. There are two sets of strongly interacting  $K = 0$ , 1 and 2 levels, and the ordering of these levels is the reverse of that assumed in § 4.5.4;  $E_{K=0} > E_{K=1} > E_{K=2}$ . **Table 4.7** (§ 4.6.2) shows the correlation between the  $T$  states and the value of  $n$ ; there are three  $T$  states belonging to  $n = 3$ , and one each





**Figure 4.13** Calculated energies and Coriolis matrix elements for  $j' = 2$   $T$  states ( $V_2^v = 0.0 \text{ cm}^{-1}$ ,  $V_3 = 25.5 \text{ cm}^{-1}$ ,  $V_4 = -3.5 \text{ cm}^{-1}$ ).



belonging to  $n = 2$  and  $n = 1$ . The originating  $T$  state in the ground vibrational level belongs to  $n = j = 1$ , and thus the strongest transitions would be expected to the upper  $T$  state with the most  $n = 1$  character.

The assignments for the lines to higher frequency of the silane  $R(1)$  transitions are shown in **figure 4.14**. To avoid ambiguities which may arise, new notation has been introduced to distinguish between the symmetric and antisymmetric states in  $K = 1$  and  $K = 2$ . The subscript  $e$  or  $f$  in front of the  $\Delta J$  designation gives the symmetry of the *originating* level; thus  ${}^eR_1$  indicates  $|2^+\rangle \leftarrow |1^+\rangle$  with  $\Delta J = +1$ , whilst  ${}^fR_1$  indicates  $|2^-\rangle \leftarrow |1^-\rangle$  with  $\Delta J = +1$ . Note that  ${}^fQ_1$  indicates  $|2^+\rangle \leftarrow |1^-\rangle$  since  $\Delta J = 0$  and the parity must change.

The transitions around  $2202.5\text{ cm}^{-1}$  have already been alluded to in § 4.5.4 as terminating at a virtually unperturbed level. This level was readily identified as the lower level of the pair of  $K = 0$  levels lying at  $\sim 12.5\text{ cm}^{-1}$ . The calculated Coriolis matrix elements for the two  $K = 1$  states with which it interacts are almost the same, although the greater energy separation for the highest lying  $K = 1$  state at  $\sim 27.6\text{ cm}^{-1}$  will result in an overall elevation of the rotational constant by  $\sim 0.005\text{ cm}^{-1\dagger}$ . This level was therefore fitted to a  $B$  and  $D$  value as described in the previous sections.

A strong  $R$  branch starting at  $2201.0\text{ cm}^{-1}$  which splits into two distinct series was assigned to the  $K = 2 \leftarrow 1$  band, the two sets of lines corresponding to the  $|2^+\rangle \leftarrow |1^+\rangle$  and  $|2^-\rangle \leftarrow |1^-\rangle$  transitions. The  $Q$  branch for the  $|2^+\rangle \leftarrow |1^-\rangle$  transitions was also identified. The  $K = 2$  level demonstrates strong Coriolis interaction with the  $K = 1$  level as shown in **figure 4.13**, sufficient at high  $J$  to produce significant third order correction to the energy (equation (4.71)). However, since no transitions to the  $K = 1$  or  $K = 0$  levels were observed, a fit to a Hamiltonian of the type given in § 4.5.4 was not possible, and the transitions were fitted to separate  $B$  values and a common  $D$ . The fact that  $D$  was not required to float separately for the  $|2^+\rangle$  and  $|2^-\rangle$  levels is perhaps surprising, indicating that the Coriolis interaction is largely dealt with by the first order correction to the rotational energy.

As can be seen from **figure 4.14**, there are still many unassigned lines between  $2200.5\text{ cm}^{-1}$  and  $2202.5\text{ cm}^{-1}$ , most notably the strong lines marked with a ‘ $\nabla$ ’ which

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<sup>†</sup> Approximate Coriolis corrections are given in this section since the potential has yet to be fitted to the experimental band origins.

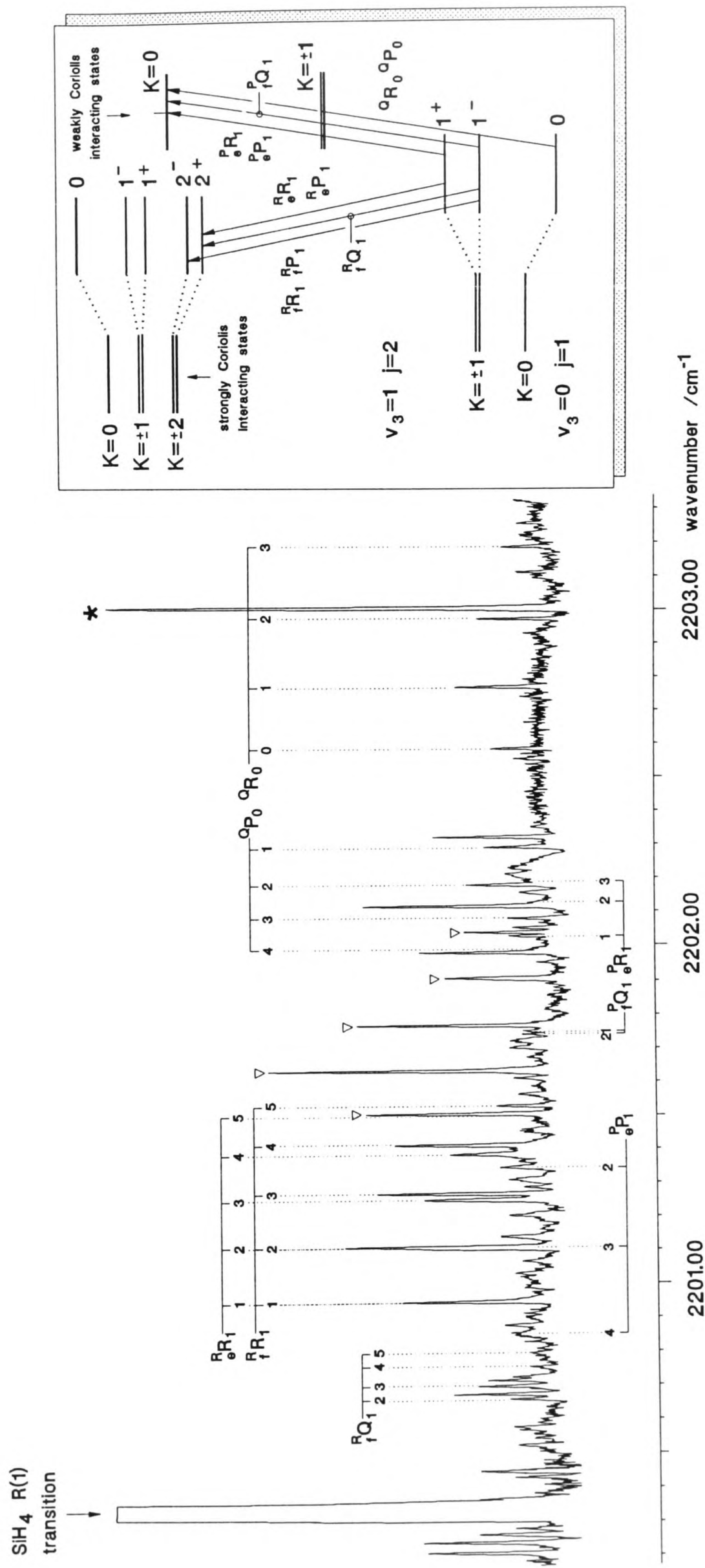


Figure 4.14 Ne-SiH<sub>4</sub> transitions above 2200.0 cm<sup>-1</sup> correlating to SiH<sub>4</sub> R(1).

appear to form a series. However, they do not correspond to any of the predicted band centres and are probably due to (SiH<sub>4</sub>)<sub>2</sub> or silane monomer transitions.

The remaining band due to  $j = 2 \leftarrow 1$   $T \leftarrow T$  lies much lower in frequency and is centred at 2195.5 cm<sup>-1</sup>; it corresponds to the lowest lying  $T$  state in  $v_3 = 1$ ,  $j = 2$  which has  $K = 1$ . The similarity between the  $K = 1 \leftarrow 0$  band and the strong  $K = 1 \leftarrow 0$   $Q(1)$  analogue is marked. Both display a very intense  $^R R_0$  branch but weak  $^P P_0$  branch, with strong  $^R Q_0$  transitions. The assignments are shown in **figure 4.15**.

The lines were fitted as described above with the entire data set for all the  $T \leftarrow T$  transitions. In view of the poor quality of the  $Q(1)$  bands, these transitions were down-weighted in the fit by one tenth, corresponding to a standard deviation for these measurements approximately three times the normal experimental error of 0.0004 cm<sup>-1</sup>. The fitted parameters for the  $v_3 = 1$ ,  $j = 2$   $T$  state levels are given in **table 4.11**.

There are a number of surprising aspects to the constants. The  $B$  value for the  $|0\rangle$  state lying at  $\sim 12.5$  cm<sup>-1</sup> in **figure 4.13** is 0.0785 cm<sup>-1</sup>, of which  $\sim 0.005$  cm<sup>-1</sup> is due to the net Coriolis interaction with the  $|1^+\rangle$  states lying at  $\sim 7.3$  cm<sup>-1</sup> and  $\sim 27.6$  cm<sup>-1</sup>, giving a true rotational constant of  $\sim 0.074$  cm<sup>-1</sup>. This corresponds to a centre of mass separation of  $\sim 4.32$  Å. The  $K = 0$   $B$  value of fit 2 for the  $j = 1 \leftarrow 0$   $A \leftarrow A$  transitions was found to be 0.0782 cm<sup>-1</sup>, which with approximate correction for the Coriolis depression from interaction with higher  $K = 1$  states ( $+0.002$  cm<sup>-1</sup>) gives a true value of  $\sim 0.08$  cm<sup>-1</sup>, with  $R \approx 4.13$  Å. A larger centre of mass separation in  $j = 2$  compared with  $j = 1$  is consistent with the higher energy of the former state, although the change in  $R$  of  $+4\%$  is large.

The results of fit 2 in § 4.5.1 referred to above, and the analysis of the  $Q(1)$  bands in the previous section, both intimated the possibility of considerable change in the centre of mass separation  $R$  with the  $K$  quantum number, with  $R$  decreasing as  $K$  increased. This theorem is further reinforced by the rotational constants calculated for the  $K = 2$  states which according to **figure 4.13** should be depressed by the strong Coriolis interaction with the  $K = 1$  state only 4 cm<sup>-1</sup> higher in energy. The  $B$  values of 0.0888 cm<sup>-1</sup> and 0.0825 cm<sup>-1</sup> for the  $|1^+\rangle$  and  $|1^-\rangle$  states respectively are thus lower than the true values, and these scale to approximately 0.098 cm<sup>-1</sup> and 0.091 cm<sup>-1</sup> when the Coriolis interaction is accounted for. However, since the symmetric state  $|1^+\rangle$  interacts strongly with both the  $|0\rangle$  and  $|2^+\rangle$  states, an accurate correction requires diagonalisation of a  $3 \times 3$  matrix. These  $B$  values give an average value of  $R$  for  $K = 2$  of  $\sim 3.81$  Å, an apparent decrease of

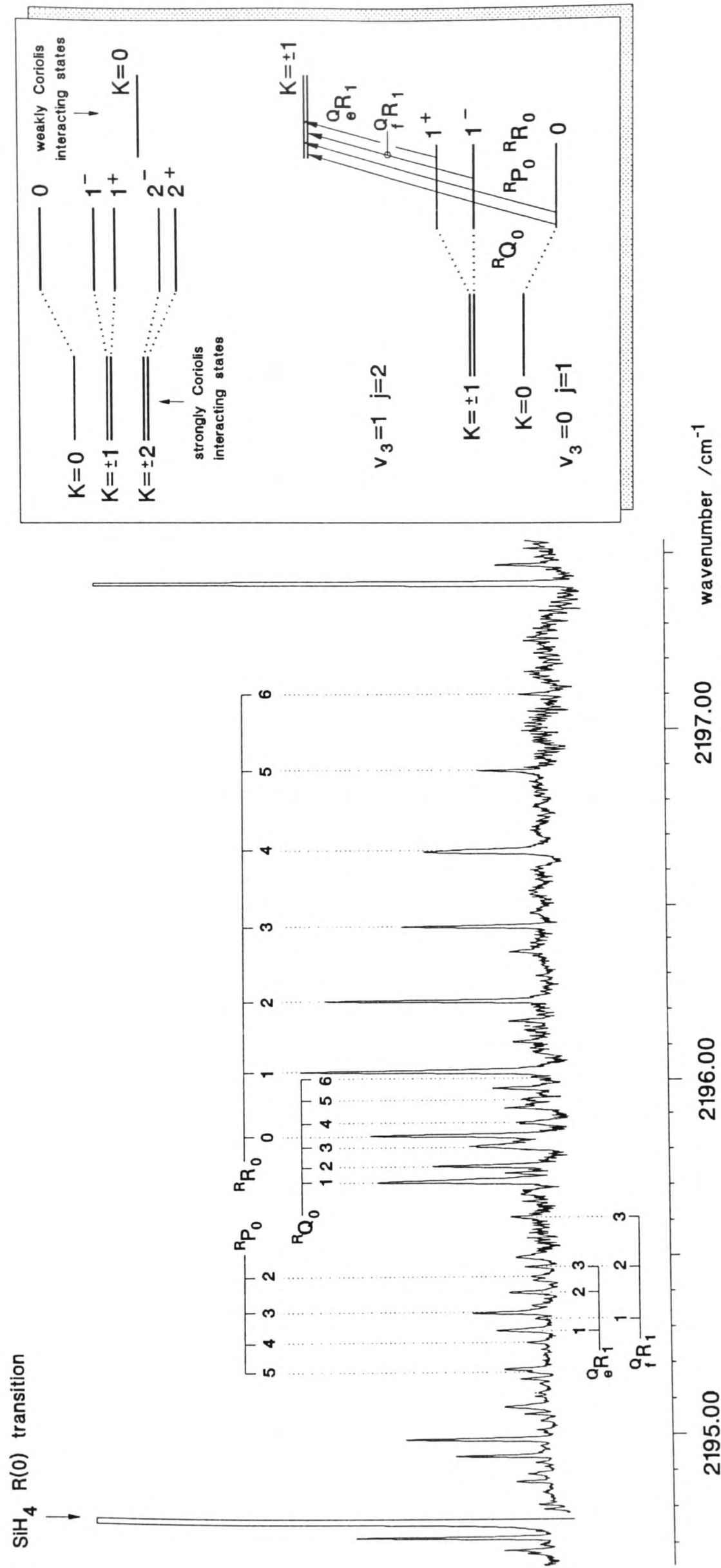


Figure 4.15 Ne-SiH<sub>4</sub> transitions below 2200.0 cm<sup>-1</sup> correlating to SiH<sub>4</sub> R(1).

**Table 4.11** Upper state fitted parameters for  $j = 2 \leftarrow 1$   $T \leftarrow T$  transitions of Ne-SiH<sub>4</sub> using perturbation theory model.

| parameter                    | value <sup>¶</sup> /cm <sup>-1</sup> |
|------------------------------|--------------------------------------|
| $\nu_{K=0 \leftarrow 0}$     | 2 202.423 43 (27)                    |
| $B'_{K=0}$                   | 0.078 517 (74)                       |
| $D'_{K=0}$                   | 0.000 010 (4)                        |
| $\nu_{K=2 \leftarrow 1}$     | 2 201.288 26 (62)                    |
| $B'_{K=2+}$                  | 0.088 833 (56)                       |
| $B'_{K=2-}$                  | 0.082 512 (53)                       |
| $D'_{K=2}$                   | 0.000 084 (1)                        |
| $\nu_{K=1 \leftarrow 0}$     | 2 195.686 67 (22)                    |
| $\nu_{K=1 \leftarrow 1}$     | 2 195.014 60 (46)                    |
| $B'_{K=1+}$                  | 0.078 873 (29)                       |
| $B'_{K=1-}$                  | 0.078 659 (27)                       |
| $D'_{K=1}$                   | 0.000 020 1 (5)                      |
| $\sigma_{\text{global fit}}$ | 0.001 032                            |

<sup>¶</sup> Figures in parentheses represent one standard deviation uncertainty.

over 10 % relative to the  $K = 0$  value.

For the remaining state to which transitions from  $j'' = 1$  were observed,  $K = 1$  (at  $\sim 7.3$  cm<sup>-1</sup> in **figure 4.13**), the fitted value of  $B$  is 0.0789 cm<sup>-1</sup> for  $|1^+\rangle$  and 0.0787 cm<sup>-1</sup> for  $|1^-\rangle$ . The  $|1^+\rangle$  state is depressed by Coriolis interaction with both  $K = 0$  states at  $\sim 12.5$  cm<sup>-1</sup> and the  $K = 2$  state lying at  $\sim 17.8$  cm<sup>-1</sup>, decreasing  $B$  by  $\sim 0.011$  cm<sup>-1</sup>. The true rotational constant for the  $|1^+\rangle$  state is therefore closer to 0.090 cm<sup>-1</sup>. The  $|1^-\rangle$  state can interact only with the  $|2^-\rangle$  state arising from  $K = 2$ , and its correction factor is therefore smaller ( $+0.002$  cm<sup>-1</sup>), giving a true  $B$  of approximately 0.0803 cm<sup>-1</sup>.

The discrepancies between rotational constants for the symmetric and the antisymmetric states in both  $K = 1$  and  $K = 2$  are due in part to the approximate nature of the potential used thus far, and the consideration of only the strongest Coriolis interactions, but also to the breakdown of the second order perturbation theory approximation being used to fit the data. The much higher anisotropic potential of Ar-SiH<sub>4</sub> enabled this

approach to be used very successfully, but considerably larger Coriolis matrix elements in Ne-SiH<sub>4</sub> push the approximation to its limits, and in some cases beyond. The corrected values for the rotational constants presented in this section are therefore only semi-quantitative, and the only firm conclusion which can be drawn from the experimental data is that the rotational constant of Ne-SiH<sub>4</sub> almost certainly increases as  $K$  increases. The sheer number of interacting states in  $j=2$  and higher levels means that any one ro-vibrational level is heavily modified by its surrounding levels, and its nature is not therefore conducive to standard procedures for determining the structure of the complex in that level. Indeed, with such highly non-rigid species, the usefulness of conventional structural information may be called into question, and spectroscopy enters the domain of molecular dynamics.

#### 4.11.4 Global fit parameters for other levels

As explained in the previous section, **table 4.11** gives the values of the parameters for the  $\nu_3 = 1, j = 2$  levels obtained by fitting all the transitions arising from the ground state  $j = 1$  level. Clearly the larger data set will result in modification to the parameters and residuals already fitted for the  $\nu_3 = 1, j = 0$  and  $\nu_3 = 0, j = 1$  levels, and these values are given in **table 4.12**; the residuals for the entire global fit are given in appendix II. However, although a larger data set will generally result in better determined values for the fitted constants, the approximate expressions used to fit the transitions to the upper vibrational state  $j = 1$  and  $j = 2$  levels potentially introduce artificial corrections to these constants. In fact, the change is very small when compared with the values listed in **table 4.4**. The  $K = 1$  rotational constant for  $\nu_3 = 0, j = 1$  changes by only 0.3 %, which corresponds to value of  $R$  approximately 5 % larger at 4.118 Å; the other  $B$  values change by smaller amounts than this, indicating slightly smaller values of  $R$  in  $\nu_3 = 0, j = 1, K = 0$  (4.138 Å) and  $\nu_3 = 1, j = 0, K = 0$  (4.146 Å).

The small differences in these and the other parameters in no way undermines the interpretation of the data already presented in § 4.5.3, and there is therefore nothing further to add.

**Table 4.12** Globally fitted parameters for  $j=0 \leftarrow 1$   $T \leftarrow T$  transitions of Ne-SiH<sub>4</sub>.

| <i>Parameter</i>                  | <i>value</i> <sup>¶</sup> /cm <sup>-1</sup> |
|-----------------------------------|---------------------------------------------|
| $\nu_{K=0 \leftarrow 0}$          | 2 184.992 74 (21)                           |
| $\nu_{K=0 \leftarrow 1}$          | 2 184.320 68 (55)                           |
| $B'$                              | 0.079 671 (37)                              |
| $B''_{K=1}$                       | 0.080 771 (27)                              |
| $B''_{K=0}$                       | 0.079 985 (36)                              |
| $\beta$                           | 0.672 05 (24)                               |
| $\sqrt{2}B''\{j^*(j^*+1)\}^{1/2}$ | 0.099 87 (5)                                |
| $D'_j$                            | 0.000 020 (1)                               |
| $D''_j$                           | 0.000 017 7 (7)                             |
| $\sigma_{\text{global fit}}$      | 0.001 012                                   |

<sup>¶</sup> Figures in parentheses represent one standard deviation uncertainty.

### 4.12 Fitting of the intermolecular potential

Altogether fifteen band origins were determined from the experimental spectrum, including the two tentative assignments from the  $Q(1)$  associated bands. Since all of the  $T$  state transitions originate from a common rotational level in the ground vibrational state ( $j'' = 1$ ), and therefore a common  $K = 0, K = \pm 1$  splitting, there is a certain degree of correlation between the band origins of  $T$  symmetry transitions.

The potential was fitted to the observed band origins using an iterative least squares method [62]. Four parameters were fitted to the experimental data: the vibrational band origin  $\nu_0$ ,  $V_2^v$  (the vibrational anisotropy for  $\nu_3 = 1$ ),  $V_3$  and  $V_4$  (these terms comprising the rotational anisotropy common to both ground and first excited vibrational state). The initial values of these parameters were set at the SiH<sub>4</sub>  $\nu_3$  band origin (2189.19 cm<sup>-1</sup>), 0.0, 25.5 cm<sup>-1</sup> and -3.5 cm<sup>-1</sup> respectively; these last three values were those used to simulate the energy levels prior to the assignment of the  $Q(1)$  and  $R(1)$  bands in § 4.11. The  $V_3$  and  $V_4$  values were constrained to be the same in  $\nu_3 = 0$  and  $\nu_3 = 1$ ;  $V_2^v$ , of course, only operates



in the first excited vibrational level. Having calculated the band origins and residuals, the eigenvectors of the energy levels were used to calculate the derivatives of the residuals with respect to the constants being fitted using the Hellmann-Feynman theorem [63]. The derivatives were used to calculate new values of the constants, assuming a linear relationship between the residuals and the parameters, and the whole process repeated until a minimum sum of the squares was reached. A maximum  $j=9$  in the basis functions converged the energy levels to within the experimental error of  $0.0004\text{ cm}^{-1}$ .

In view of the uncertainty in the assignments of the  $Q(1)$  bands terminating in  $K=0$  in  $v_3=1$ , a total of 3 fits were made. The parameters obtained, together with the results of the Ar-SiH<sub>4</sub> fit from Ref. 25, are given in **table 4.13**, and the corresponding residuals for the Ne-SiH<sub>4</sub> fits are listed in **table 4.14**. In addition, **figure 4.16** illustrates the energy levels calculated using the parameters from fit 1 together with the Ar-SiH<sub>4</sub> energy levels from Ref. 25 for comparison purposes. Although illustrated on the same wavenumber scale, the energies of each set of levels is relative to the free rotor limit *in the complex in question*, i.e. the (isotropic) potential ' $V_0$ ' remaining if  $V_2^v$ ,  $V_3$  and  $V_4$  are 'switched off'. Hence the Ar-SiH<sub>4</sub> energy levels are shown relative to an origin specific to the Ar-SiH<sub>4</sub> complex, and similarly for the Ne-SiH<sub>4</sub> levels. This isotropic part of the potential cannot be determined from the experimental data, and manifests as a shift in the vibrational band origin  $\Delta v = v_{\text{SiH}_4} - v_0$ . The purpose of representing them on the same scale is to illustrate the difference in the relative separations of the internal rotor states of SiH<sub>4</sub>.

Fit 1 incorporates all the observed band origins including the  $Q(1)$  transitions to  $K=0$ . However, the identification of the  $v_3=1$ ,  $j=1$ ,  $K=1$  levels for the two sets of transitions terminating in  $K=1$  is not that predicted on intensity grounds. The experimental spectrum (see **figure 4.12**) shows an intensity ratio of  $\sim 3:1$  for the two sets of  $K=1 \leftarrow 0$  lines, with the higher  $K=1$  state participating in the transitions of greater intensity. However, the calculation predicts the intensity ratio to be the other way round, with the stronger transitions to the 'lower' (predicted)  $K=1$  state. Thus in fit 3 the assignments have been reversed in order to harmonise with the theoretical predictions. This has the effect of increasing the standard deviation of the fit from  $0.297\text{ cm}^{-1}$  to  $0.343\text{ cm}^{-1}$ . However, the fit 3 residuals for the transitions to these two  $K=1$  states (being of opposite sign) demonstrate that the levels remain 'the wrong way round'. The  $A$  symmetry  $v_3=1$ ,  $j=1$  level splitting and energy is reproduced slightly better in fit 3,



**Table 4.13** Effective constants determined for the intermolecular potential of Ne-SiH<sub>4</sub><sup>¶</sup>.

| <i>Parameter</i>           | <i>fit 1</i>  | <i>fit 2</i>  | <i>fit 3</i>  | <i>Ar-SiH<sub>4</sub></i> |
|----------------------------|---------------|---------------|---------------|---------------------------|
| $\nu_0 / \text{cm}^{-1}$   | 2 189.38 (43) | 2 189.43 (47) | 2 189.44 (49) | 2 189.025 1 (23)          |
| $V_2^\nu / \text{cm}^{-1}$ | − 1.23 (74)   | − 0.94 (81)   | − 0.44 (90)   | 0.586 (67)                |
| $V_3 / \text{cm}^{-1}$     | 27.4 (13)     | 28.0 (15)     | 27.8 (15)     | 87.4 (27)                 |
| $V_4 / \text{cm}^{-1}$     | − 3.19 (33)   | − 3.31 (36)   | − 3.40 (36)   | − 6.91 (76)               |
| $\sigma / \text{cm}^{-1}$  | 0.297         | 0.317         | 0.343         | 0.023                     |

<sup>¶</sup> Figures in parentheses represent one standard deviation uncertainty.**Table 4.14** Residuals of the fitted band origins in the Ne-SiH<sub>4</sub> spectrum.

| <i>Transition</i> |                      | <i>Band origin</i><br>$/ \text{cm}^{-1}$ | <i>(obs − calc) / cm<sup>−1</sup></i> |              |              |
|-------------------|----------------------|------------------------------------------|---------------------------------------|--------------|--------------|
|                   |                      |                                          | <i>fit 1</i>                          | <i>fit 2</i> | <i>fit 3</i> |
| <i>R</i> (0)      | $K = 0 \leftarrow 0$ | 2 193.640 54                             | − 0.302                               | − 0.223      | − 0.110      |
|                   | $K = 1 \leftarrow 0$ | 2 194.297 92                             | 0.219                                 | 0.139        | 0.026        |
| <i>P</i> (1)      | $K = 0 \leftarrow 0$ | 2 184.992 75                             | − 0.075                               | − 0.147      | − 0.124      |
|                   | $K = 0 \leftarrow 1$ | 2 184.320 68                             | − 0.083                               | 0.049        | − 0.046      |
| <i>Q</i> (1)      | $K = 1 \leftarrow 0$ | 2 190.221 66                             | − 0.003                               | − 0.030      | 0.102        |
|                   | $K = 1 \leftarrow 1$ | 2 189.550 33                             | − 0.010                               | 0.166        | 0.181        |
|                   | $K = 0 \leftarrow 0$ | 2 189.803 91                             | 0.345                                 | ---          | 0.348        |
|                   | $K = 0 \leftarrow 1$ | 2 189.132 39                             | 0.337                                 | ---          | 0.427        |
|                   | $K = 1 \leftarrow 0$ | 2 189.841 57                             | − 0.202                               | − 0.272      | − 0.362      |
|                   | $K = 1 \leftarrow 1$ | 2 189.170 24                             | − 0.209                               | − 0.075      | − 0.282      |
| <i>R</i> (1)      | $K = 1 \leftarrow 0$ | 2 195.686 67                             | − 0.241                               | − 0.263      | − 0.363      |
|                   | $K = 1 \leftarrow 1$ | 2 195.014 60                             | − 0.249                               | − 0.068      | − 0.284      |
|                   | $K = 0 \leftarrow 0$ | 2 202.423 43                             | − 0.071                               | − 0.148      | − 0.131      |
|                   | $K = 0 \leftarrow 1$ | 2 201.751 36                             | − 0.078                               | 0.048        | − 0.053      |
|                   | $K = 2 \leftarrow 1$ | 2 201.288 26                             | 0.610                                 | 0.786        | 0.686        |

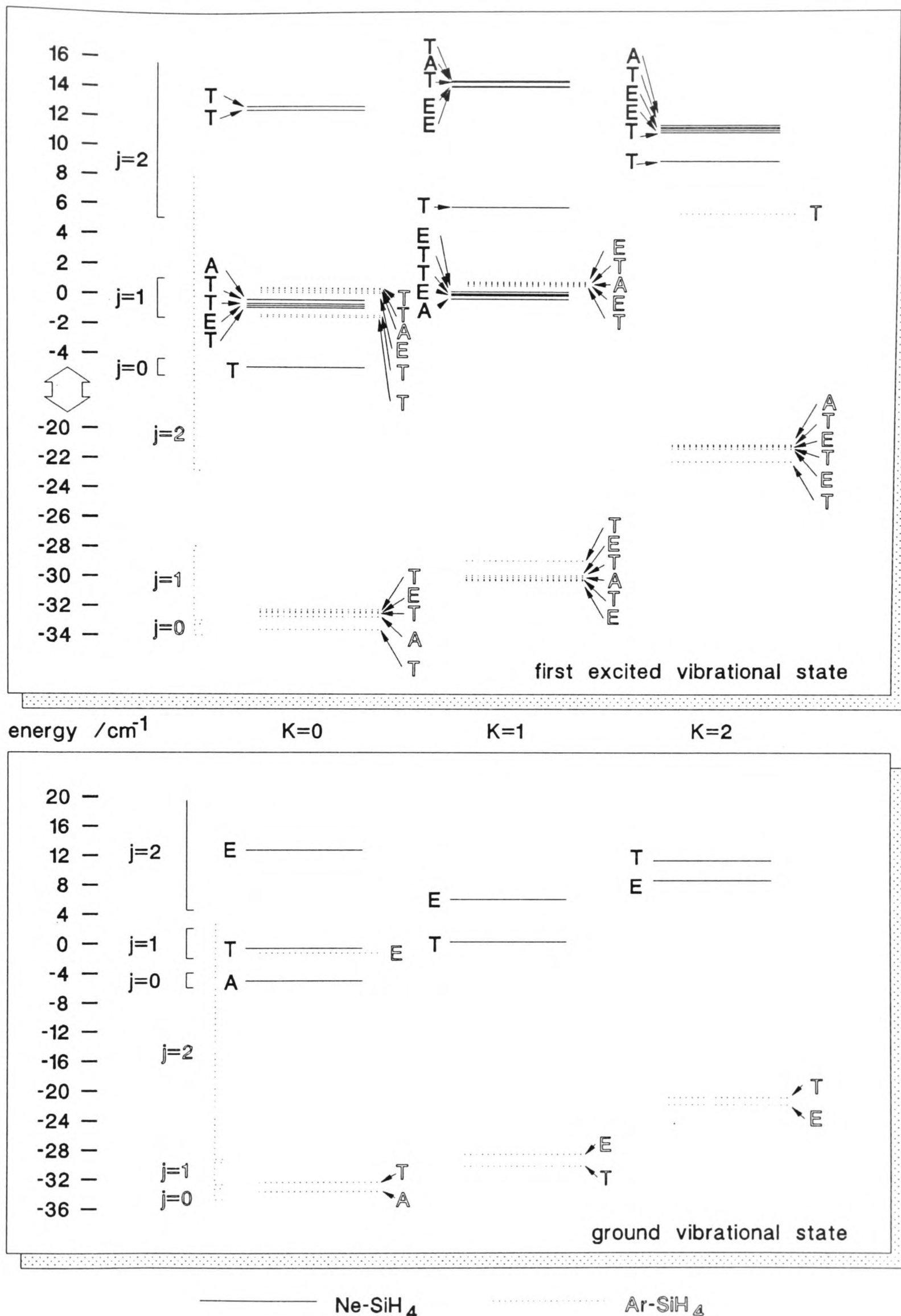


Figure 4.16 Ne-SiH<sub>4</sub> and Ar-SiH<sub>4</sub> ro-vibrational energy levels.

although the  $\nu_3=0, j=1$   $T$  symmetry level deteriorates slightly compared to fit 1. Fit 2 is simply fit 1 with the  $Q(1) K=0 \leftarrow 0$  and  $K=0 \leftarrow 1$  origins removed; rather than improve the quality of the fit, however, the standard deviation increases slightly from  $0.297 \text{ cm}^{-1}$  to  $0.317 \text{ cm}^{-1}$ .

The significant feature of all three fits is that the variation in each parameter between fits is less than one standard deviation in every case. In addition, the poorly fitted  $K=2$  level was found not to benefit at all by a negative starting value for  $V_4$ ; the fit simply restored the parameter to a positive value. (The  $T_4$  term is diagonal in  $K=0$  for  $j \geq 2$ , and therefore  $V_4$  has a correspondingly greater effect on the energy levels than the  $V_3$  term.) The good agreement between the parameter values for the three fits indicates that the Ne-SiH<sub>4</sub> potential is relatively insensitive to the  $Q(1)$  assignments. The sign of  $V_3$  cannot be determined from the experimental spectrum, since its only diagonal effect (in  $K \geq 1$ ) is to interchange (experimentally indistinguishable) states of the same symmetry. A positive value for  $V_3$  indicates energy minima on the faces of the SiH<sub>4</sub> tetrahedron, with the maxima above the corners (the hydrogen atoms), and as with Ar-SiH<sub>4</sub> this seems a reasonable assumption. Its value ( $\sim 28 \text{ cm}^{-1}$ ) is approximately one third of that determined for Ar-SiH<sub>4</sub> ( $\sim 87 \text{ cm}^{-1}$ ), demonstrating the much lower anisotropy of the neon complex.

The  $V_4$  term, however, can be determined with its sign, and its value of  $\sim -3.3 \text{ cm}^{-1}$  is indicative of energy minima at the mid-points of the six edges of the SiH<sub>4</sub> tetrahedron. The  $T_4$  maxima are therefore the eight corners of the cube defining the tetrahedron, four of which are occupied sites (corresponding to the  $T_3$  maxima) and four of which are above the faces of the tetrahedron (corresponding to the  $T_3$  minima). This latter tension between the  $T_3$  and  $T_4$  terms results in high correlation between the values of  $V_3$  and  $V_4$ , with a higher value of  $V_3$  required to obtain the same depth in the potential minimum as for a zero (or positive) value of  $V_4$ .

The  $V_2^\nu$  vibrational anisotropic term is poorly determined, indicating little effect on the ro-vibrational energy levels of the complexed SiH<sub>4</sub>. Its value was found to be small ( $\sim 0.6 \text{ cm}^{-1}$ ) for Ar-SiH<sub>4</sub>, and in a less anisotropic complex such as Ne-SiH<sub>4</sub> the triply degenerate  $\nu_3$  vibration would be expected to be even less perturbed. The value of the band origin  $\nu_0$  ( $\sim 2189.4 \text{ cm}^{-1}$ ) is within  $\sim 0.2 \text{ cm}^{-1}$  of the SiH<sub>4</sub>  $\nu_3$  band origin ( $2189.1865 \text{ cm}^{-1}$ ), although its value is considerably less well determined than for Ar-SiH<sub>4</sub>. Any small difference in the value of  $V_3$  in the ground and first excited vibrational states

is strongly correlated with  $\Delta\nu$ , the difference in the band origins between the free SiH<sub>4</sub> and the complexed molecule.

The overall quality of the fit appears at first sight to be poor, with a standard deviation of  $\sim 0.3 \text{ cm}^{-1}$ . This is an order of magnitude worse than the  $0.023 \text{ cm}^{-1}$  standard deviation of the Ar-SiH<sub>4</sub> fit. However, in view of the fixed  $R$  approximation made, which will be increasingly invalid as the anisotropy becomes lower, such a result is perhaps not so bad. The wide variation in the values of the rotational constants for the various  $K$  states (§ 4.5.1 **table 4.1**, § 4.11.2-4, **tables 4.9, 4.10, 4.11** and **4.12**) may indicate significantly different values of  $R$  depending upon the values of  $j$  and  $K$ . The large residual of  $\sim 0.61 \text{ cm}^{-1}$  (fit 1) for the  $R(1) K=2 \leftarrow 1$  appears to add weight to this interpretation.

As well as the radial dependence of the anisotropic part of the potential, the isotropic potential will also show an  $R$  dependence. Whereas the anisotropic terms both split energy levels of differing  $K$  and shift the energies of these levels, the isotropic part of the potential will only contribute to an overall shift in the levels. At different intermolecular separations, the ‘hardness’ of the rotating SiH<sub>4</sub> isotropic wall experienced by the neon atom will change. The difficulty of fitting with no  $R$  dependence is the inability of the program to distinguish between fitting the absolute energies of the levels (since it is assumed that the isotropic part contributes a constant shift) and fitting the splittings of the various  $K$  states. One option would be to allow slightly different isotropic contributions in different rotational states.

The possibility of incorporating the code by Hughes [59] into a general purpose package [64] for performing calculations of bound state energies in weakly bound molecular systems is currently being reviewed. It should then be possible to solve the radial part of the problem, determining the parameters  $V_2^v$ ,  $V_3$  and  $V_4$  as a function of the intermolecular separation  $R$ .

It is appropriate to make a final comment concerning the difference in the symmetry types of the transitions observed for Ar-SiH<sub>4</sub> and Ne-SiH<sub>4</sub>. The Ar-SiH<sub>4</sub> spectrum contained 3 bands originating from the  $j''=2, K=1$  state of  $E$  symmetry, whereas no  $E \leftarrow E$  transitions were observed in Ne-SiH<sub>4</sub>. The fraction of complex molecules with nuclear spin functions of  $E$  symmetry is identical for both Ar-SiH<sub>4</sub> and Ne-SiH<sub>4</sub>, being equal to  $1/8$  (§ 4.10.1). The Ne-SiH<sub>4</sub>  $j''=2$   $E$  states lie much closer together in energy (at  $5.97 \text{ cm}^{-1}$ ,  $8.64 \text{ cm}^{-1}$  and  $12.70 \text{ cm}^{-1}$  for  $K=1, 2$  and  $0$  respectively) than the corresponding

Ar-SiH<sub>4</sub> *E* states (at  $-28.8\text{ cm}^{-1}$ ,  $-22.0\text{ cm}^{-1}$  and  $-1.28\text{ cm}^{-1}$  for  $K = 1, 2$  and  $0$  respectively) (see **figure 4.16**). A Boltzmann distribution at the low rotational temperatures in the jet predicts little difference in the proportion of *E* spin populations of each complex occupying the lowest  $K = 1$  state (100 % for Ar-SiH<sub>4</sub> versus 98 % for Ne-SiH<sub>4</sub>), but such an analysis assumes rotational relaxation to be independent of the size of quantum separating the two levels. In the case of Ar-SiH<sub>4</sub>, the larger energy spacing between  $K = 1$  and  $K = 2$  results in better cooling in the earlier, high density region of the expansion when higher energy collisional relaxation can occur. The lower energy collisions required to cool  $K = 2$  states to  $K = 1$  in Ne-SiH<sub>4</sub> occur later in the expansion when the density is lower, and the cooling is thus less effective. There will therefore be a larger population difference between the lowest  $K = 1$  *E* states for Ar-SiH<sub>4</sub> and Ne-SiH<sub>4</sub> than predicted by Boltzmann statistics, with a higher fraction of the *E* spin complexes occupying  $K = 1$  in Ar-SiH<sub>4</sub> and consequent higher transition intensities.

In addition the overall population of Ne-SiH<sub>4</sub> in the jet is smaller compared to Ar-SiH<sub>4</sub>; fewer Ne-SiH<sub>4</sub> complexes are formed than Ar-SiH<sub>4</sub> because of neon's lower polarisability. There are a number of lines in the region of the predicted  $P(2) K = 0 \leftarrow 1$   $E \leftarrow E$  band origin ( $2182.71\text{ cm}^{-1}$ ) which appear to form a series (see **figure 4.4a**), but these resisted all attempts at fitting, and may well be due to (SiH<sub>4</sub>)<sub>2</sub> or possibly weak monomer transitions.

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# Chapter 5

## Other work

### 5.1 Spectroscopy of air sensitive compounds

A recent paper reporting the vibrational spectra of zinc, cadmium and mercury dimethyl species recorded using FTIR has specifically highlighted the need for high resolution studies of jet-cooled samples [1], where rotational cooling would greatly simplify very complex structure. To this end, work has been carried out on a number of unstable/ air-sensitive compounds, including  $\text{GaH}(\text{BH}_4)_2$ ,  $\text{Al}(\text{BH}_4)_3$ ,  $\text{LiAlH}_4$ , and  $\text{Zn}(\text{CH}_3)_2$ .

A teflon side mixing nozzle was constructed to minimise metal catalysed decomposition reactions. The nozzle operates by admitting gas (when the poppet is open) via a teflon tube located perpendicular to the direction of poppet movement. The poppet is an enlarged teflon version of the standard fitting, enabling effective sealing of the nozzle when in its ‘closed’ rest position. The major advantage of this system is that the gas mixture is never in contact with the metal housing of the nozzle body, preventing metal catalysed decomposition. However, the only signals observed so far in the jet have been those of dimethylzinc. **Figure 5.1** illustrates the complexity of the  $\text{CH}_3$  asymmetric stretching mode, where there is expected to be strong Coriolis interaction between the  $\nu_8$  and  $\nu_{12}$  modes [2]. The FTIR spectrum shows two prominent series of  $Q$  branch bunches; the strongest single  $Q$  branch lies at  $\sim 2965\text{ cm}^{-1}$  and is thought to be equivalent to  $^RQ_0$  in  $\nu_8$ . A portion of the jet spectrum is also shown, demonstrating the significant improvement in resolution.

Unfortunately, further work was prevented by the very small amount of (synthesised) sample available and dimethylzinc proved impossible to obtain commercially. However, the favourable preliminary results indicate that the rapid-scanning spectrometer can be used successfully to obtain jet-cooled spectra of unstable inorganic compounds.

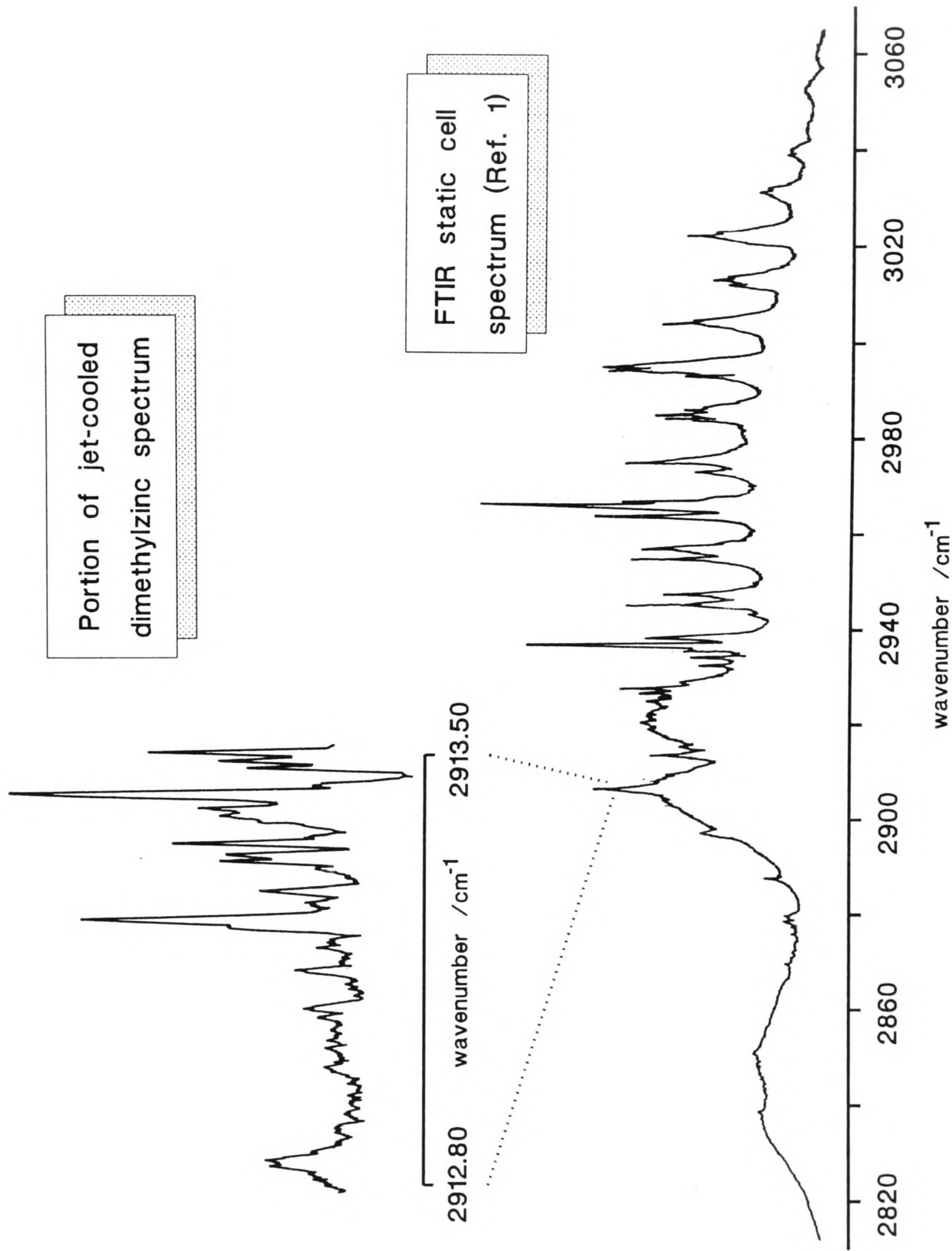


Figure 5.1 Infrared spectrum of  $\text{Zn}(\text{CH}_3)_2$  in the region of the  $\nu_3$  asymmetric methyl stretching vibration.

## 5.2 Electric discharge nozzle

The use of electric discharge nozzles as a means of producing rotationally cold radical species is well established [3, 4], providing a cheap and convenient alternative to laser photolysis. A significant amount of time has been spent attempting to produce such species by means of a specially engineered discharge nozzle. The design is illustrated in **figure 5.2**. The high voltage electrode is housed within an insulator sheath, with the outer casing of the nozzle assembly at zero volts, the intention being to shield the expansion from the effects of high electric fields and so minimise perturbations in the jet. This is particularly important should any ionic species be generated by the nozzle.

This work has been hampered by the difficulty of attaining the optimum operating conditions, for which the discharge is stable over the whole duration of the gas pulse (2-3 ms). This type of experiment, relying as it does on real time data acquisition rather than a gated detection and averaging scheme, demands sustained sparking whilst acquisition is occurring. The nozzle is pulsed to maintain low chamber pressure at high nozzle throughputs, and therefore the discharge must also be easy to initiate.

The ND radical has been studied in the submillimetre-wave region [5], and the far infrared by LMR [6] in its excited  $a^1\Delta$  state. However, no  $v=1 \leftarrow 0$  infrared transitions have been observed and the vibrational origin remains unknown. Mixtures of ND<sub>3</sub> (1-3 %) in Ar and Ne were discharged under optimum conditions of 400-420 V nozzle electrode potential difference and  $\sim 0.1$  atm absolute nozzle backing pressure. The very low backing pressures were required to sustain the discharge over the duration of the gas pulse. The presence of the discharge was confirmed by observing high frequency optical noise on the InSb detector. During scans this was removed by the use a germanium disc, although this also had the effect of attenuating the laser power by a factor of 10 ( $\sim 0.03 \mu\text{W}$  compared to  $\sim 0.3 \mu\text{W}$ ).

ND has a  $^3\Sigma$  ground state with Hund's case (b) coupling scheme [7]. The spin  $S$  is thus not coupled to the internuclear axis. The molecular rotation produces a small magnetic moment in the direction of  $N$ , the end over end rotational angular momentum, resulting in magnetic coupling between  $N$  and  $S$  to give  $J$ , the overall angular momentum. Thus the quantum number  $J$  can take values

$$J = N+S, N+S-1, \dots, |N-S| \quad (5.1)$$

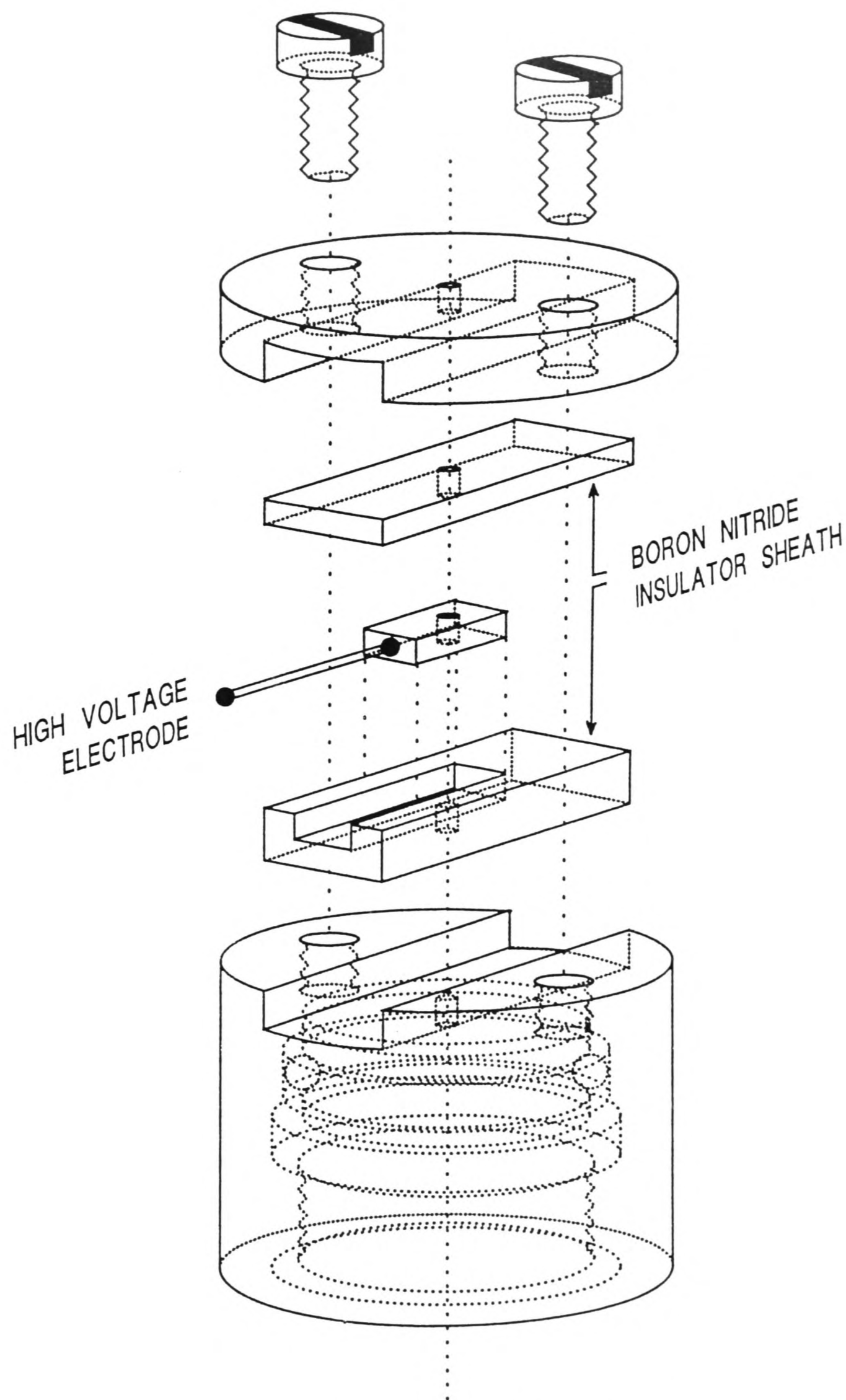


Figure 5.2 Shielded electric discharge nozzle<sup>¶</sup>.

<sup>¶</sup> Constructed by Mr L. Hill of the PTCL mechanical workshop.

In this case  $S=1$  and therefore every  $N$  level (with the exception of  $N=0$ ) is split into three  $J$  components,  $N+1$ ,  $N$  and  $N-1$ . The spin-rotation Hamiltonian [7] can be written

$$\begin{aligned} H &= B(\hat{J}-\hat{S})^2 + \frac{2}{3}\lambda(3\hat{S}_z^2 - \hat{S}^2) + \gamma\hat{S}\cdot(\hat{J}-\hat{S}) \\ &= B\hat{N}^2 + \frac{2}{3}\lambda(3\hat{S}_z^2 - \hat{S}^2) + \gamma\hat{S}\cdot\hat{N} \end{aligned} \quad (2.2)$$

where  $\lambda$  is half the separation between the  $J=N$  state and the  $J=N\pm 1$  states and  $\gamma$  is the spin-rotation coupling constant; for ND  $\lambda=0.9184\text{ cm}^{-1}$  and  $\gamma=-0.0294\text{ cm}^{-1}$ [6]. The rotational energy levels can be calculated from the Schlapp expressions [8]

$$\begin{aligned} F_N(N) &= B_v N(N+1) \\ F_{N-1}(N) &= B_v N(N+1) - (2N-1)B_v - \lambda + \left[\lambda^2 - 2B_v\lambda + B_v^2(2N-1)^2\right]^{1/2} - \gamma N + \frac{1}{2}\gamma \\ F_{N+1}(N) &= B_v N(N+1) + (2N+3)B_v - \lambda - \left[\lambda^2 - 2B_v\lambda + B_v^2(2N+3)^2\right]^{1/2} + \gamma(N+1) + \frac{1}{2}\gamma \end{aligned} \quad (2.3)$$

Unfortunately the lack of an experimentally observed vibrational band origin limits the usefulness of predicted transition frequencies. However, the known vibrational parameters of NH [9] were scaled and used together with the above expressions to calculate transition frequencies for ND. In addition transitions were calculated by the ‘Hund  $b$ ’ computer program.

The strongest lines are those for which  $\Delta N = \Delta J$ . The P(1) ( $N'J' \leftarrow N''J''$  0 1  $\leftarrow$  1 2) transition was predicted to lie at  $\sim 2297.21\text{ cm}^{-1}$  and searches were made between 2293 and  $2309\text{ cm}^{-1}$ , a search window limited by the performance of diode laser modes available, but no transitions were detected. This may in part have been due to the very low laser power, but in general TDLs are not the laser source of choice for the study of diatomics. The large rotational constants (for ND  $B_0=8.7815\text{ cm}^{-1}$ ) result in widely spaced lines ( $\sim 17\text{ cm}^{-1}$ ), and with diode laser modes extending only  $\sim 1\text{ cm}^{-1}$  very accurate predictions are necessary to combat the extreme search problem. FTIR is more suited to this type of study.

However, confirmation that the discharge does indeed produce vibrationally excited species was provided by the observation of a CO hot band transition, shown in **figure 5.3**. The vibrational temperature obtained in the discharge expansion was estimated from the intensity of the  $v=1 \leftarrow 0$  line to be  $1600 \pm 300\text{ K}$ .

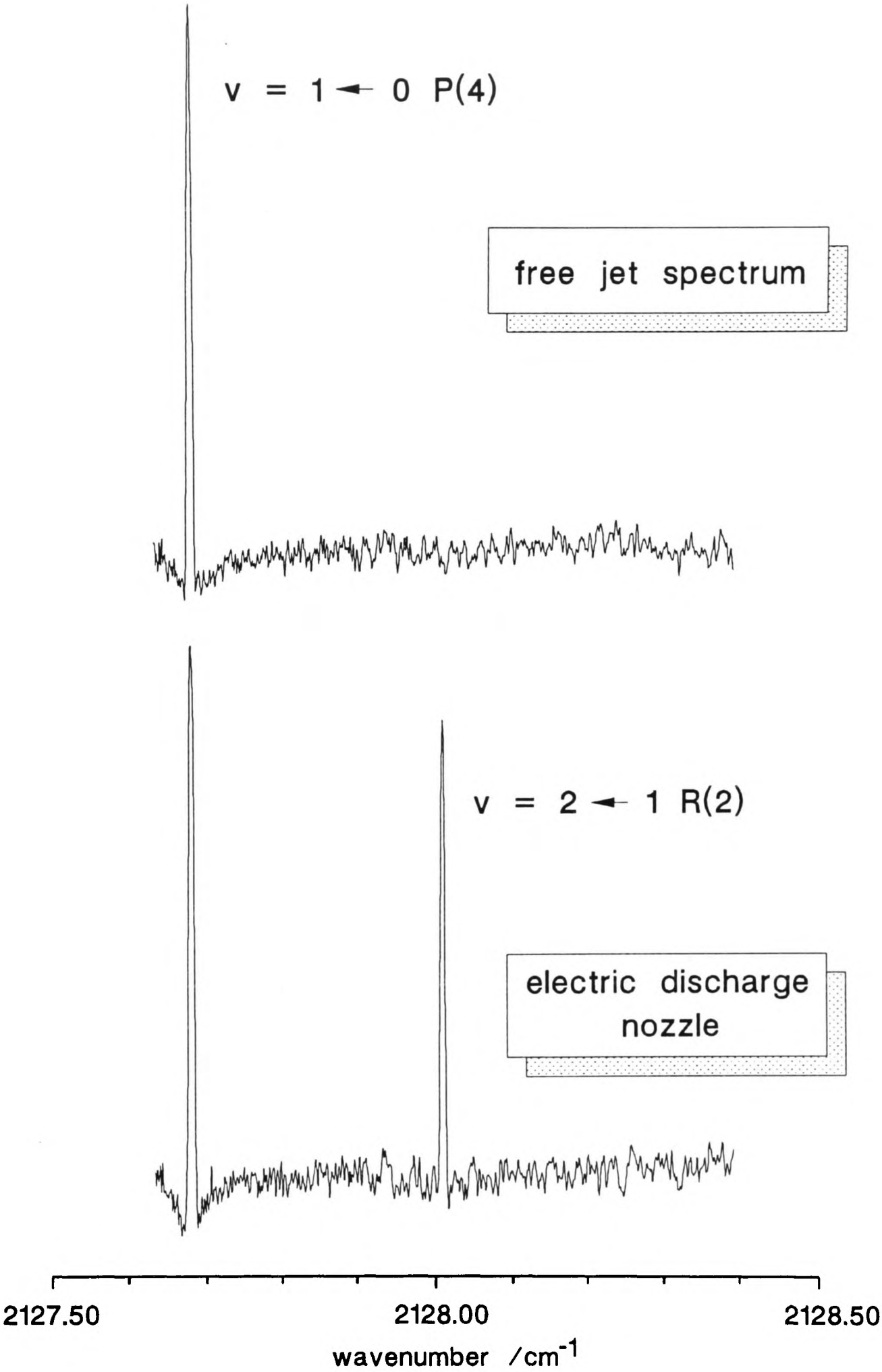


Figure 5.3 Increase in  $T_{\text{vib}}$  due to electric discharge (5 % CO in Ne).



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# Appendix I

## I.i <sup>12</sup>CO-OCS transitions

Transition frequencies and residuals for the ro-vibrational and pure rotational transitions of <sup>12</sup>CO-OCS (most abundant isotopomer). Ro-vibrational transitions are in units of cm<sup>-1</sup>, and pure rotational transitions in units of MHz. Appropriate weights are given; a weight of 1.00 indicates a standard deviation in the precision of the line position measurement of 0.0004 cm<sup>-1</sup> (for the ro-vibrational transitions). Microwave transitions are weighted at 1 × 10<sup>9</sup> corresponding to a precision in the line position measurement of ~0.4 kHz.

### I.i.i <sup>12</sup>CO-OCS pure rotational transitions

| <i>J'</i> | <i>K<sub>a</sub>'</i> | <i>K<sub>c</sub>'</i> | <i>J''</i> | <i>K<sub>a</sub>''</i> | <i>K<sub>c</sub>''</i> | <i>observed</i><br>/ MHz | <i>calculated</i><br>/ MHz | <i>residual</i><br>/ MHz | <i>wt</i><br>/ 10 <sup>9</sup> |
|-----------|-----------------------|-----------------------|------------|------------------------|------------------------|--------------------------|----------------------------|--------------------------|--------------------------------|
| 4         | 0                     | 4                     | 3          | 0                      | 3                      | 10 514.075 8             | 10 514.076 0               | −0.000 18                | 0.25                           |
| 5         | 0                     | 5                     | 4          | 0                      | 4                      | 13 071.566 6             | 13 071.566 2               | 0.000 39                 | 0.15                           |
| 4         | 1                     | 4                     | 3          | 1                      | 3                      | 10 055.863 3             | 10 055.863 1               | 0.000 16                 | 0.25                           |
| 5         | 1                     | 5                     | 4          | 1                      | 4                      | 12 552.123 2             | 12 552.123 2               | −0.000 01                | 0.25                           |
| 1         | 1                     | 1                     | 0          | 0                      | 0                      | 8 071.178 9              | 8 071.179 2                | −0.000 32                | 0.25                           |
| 2         | 1                     | 2                     | 1          | 0                      | 1                      | 10 456.021 6             | 10 456.021 5               | 0.000 10                 | 1.00                           |
| 3         | 1                     | 3                     | 2          | 0                      | 2                      | 12 710.385 9             | 12 710.385 9               | 0.000 01                 | 1.00                           |
| 4         | 1                     | 4                     | 3          | 0                      | 3                      | 14 846.684 6             | 14 846.685 0               | −0.000 43                | 0.25                           |
| 5         | 1                     | 5                     | 4          | 0                      | 4                      | 16 884.732 4             | 16 884.732 3               | 0.000 15                 | 0.25                           |
| 6         | 1                     | 6                     | 5          | 0                      | 5                      | 18 850.891 7             | 18 850.891 7               | −0.000 04                | 0.40                           |
| 3         | 1                     | 2                     | 3          | 0                      | 3                      | 6 392.607 4              | 6 392.607 4                | 0.000 04                 | 1.00                           |
| 5         | 1                     | 4                     | 5          | 0                      | 5                      | 7 808.177 8              | 7 808.177 8                | −0.000 03                | 0.40                           |
| 5         | 0                     | 5                     | 4          | 1                      | 4                      | 8 738.957 1              | 8 738.957 2                | −0.000 07                | 0.40                           |
| 2         | 2                     | 0                     | 2          | 1                      | 1                      | 16 250.821 9             | 16 250.821 8               | 0.000 08                 | 1.00                           |
| 2         | 2                     | 1                     | 2          | 1                      | 2                      | 17 042.525 8             | 17 042.525 9               | −0.000 06                | 1.00                           |
| 3         | 2                     | 1                     | 3          | 1                      | 2                      | 15 891.075 3             | 15 891.075 4               | −0.000 07                | 0.25                           |
| 3         | 2                     | 2                     | 3          | 1                      | 3                      | 17 445.127 0             | 17 445.127 0               | −0.000 01                | 0.40                           |
| 4         | 2                     | 2                     | 4          | 1                      | 3                      | 15 460.168 2             | 15 460.168 3               | −0.000 07                | 0.40                           |

| <i>J'</i> | <i>K<sub>a</sub>'</i> | <i>K<sub>c</sub>'</i> | <i>J''</i> | <i>K<sub>a</sub>''</i> | <i>K<sub>c</sub>''</i> | <i>observed</i><br>/ MHz | <i>calculated</i><br>/ MHz | <i>residual</i><br>/ MHz | <i>wt</i><br>/ 10 <sup>9</sup> |
|-----------|-----------------------|-----------------------|------------|------------------------|------------------------|--------------------------|----------------------------|--------------------------|--------------------------------|
| 4         | 2                     | 3                     | 4          | 1                      | 4                      | 17 984.937 6             | 17 984.937 6               | 0.000 01                 | 1.00                           |
| 5         | 2                     | 3                     | 5          | 1                      | 4                      | 14 998.669 5             | 14 998.669 4               | 0.000 08                 | 0.25                           |
| 6         | 2                     | 4                     | 6          | 1                      | 5                      | 14 554.362 5             | 14 554.362 5               | −0.000 01                | 0.40                           |
| 2         | 2                     | 0                     | 3          | 1                      | 3                      | 9 501.633 1              | 9 501.633 1                | 0.000 01                 | 1.00                           |

I.i.ii <sup>12</sup>CO-OCS ro-vibrational transitions

| <i>J'</i> | <i>K<sub>a</sub>'</i> | <i>K<sub>c</sub>'</i> | <i>J''</i> | <i>K<sub>a</sub>''</i> | <i>K<sub>c</sub>''</i> | <i>observed</i><br>/ cm <sup>−1</sup> | <i>calculated</i><br>/ cm <sup>−1</sup> | <i>residual</i><br>/ cm <sup>−1</sup> | <i>wt</i> |
|-----------|-----------------------|-----------------------|------------|------------------------|------------------------|---------------------------------------|-----------------------------------------|---------------------------------------|-----------|
| 1         | 1                     | 0                     | 1          | 0                      | 1                      | 2 062.747 53                          | 2 062.748 64                            | −0.001 11                             | 0.30      |
| 2         | 1                     | 1                     | 2          | 0                      | 2                      | 2 062.756 87                          | 2 062.756 67                            | 0.000 20                              | 1.00      |
| 3         | 1                     | 2                     | 3          | 0                      | 3                      | 2 062.769 05                          | 2 062.769 29                            | −0.000 24                             | 1.00      |
| 4         | 1                     | 3                     | 4          | 0                      | 4                      | 2 062.787 24                          | 2 062.787 18                            | 0.000 06                              | 1.00      |
| 5         | 1                     | 4                     | 5          | 0                      | 5                      | 2 062.810 88                          | 2 061.811 16                            | −0.000 28                             | 0.80      |
| 6         | 1                     | 5                     | 6          | 0                      | 6                      | 2 062.842 20                          | 2 062.842 13                            | 0.000 07                              | 0.40      |
| 7         | 1                     | 6                     | 7          | 0                      | 7                      | 2 062.880 74                          | 2 062.880 90                            | −0.000 16                             | 0.30      |
| 8         | 1                     | 7                     | 8          | 0                      | 8                      | 2 062.927 59                          | 2 062.928 02                            | −0.000 43                             | 0.50      |
| 2         | 0                     | 2                     | 1          | 1                      | 1                      | 2 062.550 81                          | 2 062.551 35                            | −0.000 54                             | 1.00      |
| 3         | 0                     | 3                     | 2          | 1                      | 2                      | 2 062.645 32                          | 2 062.646 10                            | −0.000 78                             | 1.00      |
| 5         | 0                     | 5                     | 4          | 1                      | 4                      | 2 062.842 20                          | 2 062.841 63                            | 0.000 57                              | 0.40      |
| 6         | 0                     | 6                     | 5          | 1                      | 5                      | 2 062.940 41                          | 2 062.940 40                            | 0.000 01                              | 1.00      |
| 8         | 0                     | 8                     | 7          | 1                      | 7                      | 2 063.134 89                          | 2 063.134 62                            | 0.000 27                              | 0.50      |
| 9         | 0                     | 9                     | 8          | 1                      | 8                      | 2 063.227 30                          | 2 063.228 33                            | −0.001 03                             | 1.00      |
| 10        | 0                     | 10                    | 9          | 1                      | 9                      | 2 063.319 52                          | 2 063.319 07                            | 0.000 45                              | 0.50      |
| 1         | 0                     | 1                     | 1          | 1                      | 0                      | 2 062.366 13                          | 2 062.366 73                            | −0.000 60                             | 0.80      |
| 2         | 0                     | 2                     | 2          | 1                      | 1                      | 2 062.356 13                          | 2 061.356 58                            | −0.000 45                             | 0.80      |
| 3         | 0                     | 3                     | 3          | 1                      | 2                      | 2 062.340 43                          | 2 062.340 81                            | −0.000 38                             | 1.00      |
| 4         | 0                     | 4                     | 4          | 1                      | 3                      | 2 062.318 36                          | 2 062.318 77                            | −0.000 41                             | 1.00      |
| 9         | 0                     | 9                     | 9          | 1                      | 8                      | 2 062.088 97                          | 2 062.087 73                            | 0.001 24                              | 0.50      |

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | <i>observed</i><br>/ $\text{cm}^{-1}$ | <i>calculated</i><br>/ $\text{cm}^{-1}$ | <i>residual</i><br>/ $\text{cm}^{-1}$ | <i>wt</i> |
|------|--------|--------|-------|---------|---------|---------------------------------------|-----------------------------------------|---------------------------------------|-----------|
| 1    | 1      | 1      | 0     | 0       | 0       | 2 062.829 09                          | 2 062.828 44                            | 0.000 65                              | 1.00      |
| 2    | 1      | 2      | 1     | 0       | 1       | 2 062.906 95                          | 2 062.907 25                            | −0.000 30                             | 1.00      |
| 3    | 1      | 3      | 2     | 0       | 2       | 2 062.981 75                          | 2 062.981 34                            | 0.000 41                              | 1.00      |
| 4    | 1      | 4      | 3     | 0       | 3       | 2 063.051 43                          | 2 063.051 11                            | 0.000 32                              | 1.00      |
| 5    | 1      | 5      | 4     | 0       | 4       | 2 063.116 95                          | 2 063.117 22                            | −0.000 27                             | 1.00      |
| 6    | 1      | 6      | 5     | 0       | 5       | 2 063.181 24                          | 2 063.180 54                            | 0.000 70                              | 0.80      |
| 7    | 1      | 7      | 6     | 0       | 6       | 2 063.241 46                          | 2 063.242 08                            | −0.000 62                             | 1.00      |
| 9    | 1      | 9      | 8     | 0       | 8       | 2 063.364 23                          | 2 063.363 90                            | 0.000 33                              | 0.20      |
| 10   | 1      | 10     | 9     | 0       | 9       | 2 063.425 62                          | 2 063.425 81                            | −0.000 19                             | 0.50      |
| 0    | 0      | 0      | 1     | 1       | 1       | 2 062.288 91                          | 2 062.287 62                            | 0.001 29                              | 0.30      |
| 2    | 0      | 2      | 3     | 1       | 3       | 2 062.131 79                          | 2 062.131 45                            | 0.000 34                              | 1.00      |
| 3    | 0      | 3      | 4     | 1       | 4       | 2 062.059 26                          | 2 062.058 81                            | 0.000 45                              | 0.50      |
| 4    | 0      | 4      | 5     | 1       | 5       | 2 061.989 05                          | 2 061.989 05                            | 0.000 00                              | 0.50      |
| 5    | 0      | 5      | 6     | 1       | 6       | 2 061.921 33                          | 2 061.921 33                            | 0.000 00                              | 1.00      |
| 6    | 0      | 6      | 7     | 1       | 7       | 2 061.855 37                          | 2 061.854 67                            | 0.000 70                              | 0.20      |
| 2    | 1      | 1      | 2     | 2       | 0       | 2 062.016 40                          | 2 062.015 75                            | 0.000 65                              | 1.00      |
| 3    | 1      | 3      | 3     | 2       | 2       | 2 061.975 60                          | 2 061.975 46                            | 0.000 14                              | 1.00      |
| 3    | 1      | 2      | 3     | 2       | 1       | 2 062.027 31                          | 2 062.025 98                            | 0.001 33                              | 0.50      |
| 4    | 1      | 4      | 4     | 2       | 3       | 2 061.956 48                          | 2 061.955 97                            | 0.000 51                              | 0.30      |
| 4    | 1      | 3      | 4     | 2       | 2       | 2 062.038 35                          | 2 062.037 99                            | 0.000 36                              | 1.00      |
| 5    | 1      | 5      | 5     | 2       | 4       | 2 061.930 04                          | 2 061.931 45                            | −0.001 41                             | 0.50      |
| 5    | 1      | 4      | 5     | 2       | 3       | 2 062.051 33                          | 2 062.050 41                            | 0.000 92                              | 1.00      |
| 6    | 1      | 6      | 6     | 2       | 5       | 2 061.903 02                          | 2 061.901 84                            | 0.001 18                              | 0.40      |
| 1    | 1      | 1      | 2     | 0       | 2       | 2 062.565 41                          | 2 062.563 29                            | 0.002 12                              | 0.50      |
| 2    | 1      | 2      | 3     | 0       | 3       | 2 062.466 53                          | 2 062.466 42                            | 0.000 11                              | 1.00      |
| 4    | 1      | 4      | 5     | 0       | 5       | 2 062.263 12                          | 2 062.264 38                            | −0.001 26                             | 0.50      |
| 6    | 1      | 6      | 7     | 0       | 7       | 2 062.059 26                          | 2 062.058 31                            | 0.000 95                              | 0.50      |
| 7    | 1      | 7      | 8     | 0       | 8       | 2 061.956 48                          | 2 061.956 40                            | 0.000 08                              | 0.20      |
| 8    | 1      | 8      | 9     | 0       | 9       | 2 061.855 37                          | 2 061.856 27                            | −0.000 90                             | 1.00      |
| 3    | 3      | 1      | 3     | 2       | 2       | 2 063.501 29                          | 2 063.502 66                            | −0.001 37                             | 0.10      |
| 3    | 3      | 0      | 3     | 2       | 1       | 2 063.501 29                          | 2 063.501 07                            | 0.000 22                              | 0.10      |
| 4    | 3      | 2      | 4     | 2       | 3       | 2 063.501 29                          | 2 063.501 33                            | −0.000 04                             | 0.15      |



| <i>J'</i> | <i>K'<sub>a</sub></i> | <i>K'<sub>c</sub></i> | <i>J''</i> | <i>K''<sub>a</sub></i> | <i>K''<sub>c</sub></i> | <i>observed</i><br>/ cm <sup>-1</sup> | <i>calculated</i><br>/ cm <sup>-1</sup> | <i>residual</i><br>/ cm <sup>-1</sup> | <i>wt</i> |
|-----------|-----------------------|-----------------------|------------|------------------------|------------------------|---------------------------------------|-----------------------------------------|---------------------------------------|-----------|
| 5         | 3                     | 3                     | 5          | 2                      | 4                      | 2 063.501 29                          | 2 063.500 25                            | 0.001 04                              | 0.15      |
| 6         | 3                     | 4                     | 6          | 2                      | 5                      | 2 063.501 29                          | 2 063.499 76                            | 0.001 53                              | 0.10      |
| 6         | 3                     | 3                     | 6          | 2                      | 4                      | 2 063.478 08                          | 2 063.478 60                            | -0.000 52                             | 0.50      |
| 7         | 3                     | 5                     | 7          | 2                      | 6                      | 2 063.501 29                          | 2 063.500 26                            | 0.001 03                              | 0.05      |
| 7         | 3                     | 4                     | 7          | 2                      | 5                      | 2 063.462 26                          | 2 063.463 33                            | -0.001 07                             | 0.20      |
| 2         | 2                     | 0                     | 1          | 1                      | 1                      | 2 063.303 13                          | 2 063.303 20                            | -0.000 07                             | 1.00      |
| 2         | 2                     | 1                     | 1          | 1                      | 0                      | 2 063.293 55                          | 2 063.293 99                            | -0.000 44                             | 1.00      |
| 3         | 2                     | 2                     | 2          | 1                      | 1                      | 2 063.371 77                          | 2 063.371 99                            | -0.000 22                             | 1.00      |
| 4         | 2                     | 2                     | 3          | 1                      | 3                      | 2 063.501 29                          | 2 063.50283                             | -0.001 54                             | 0.35      |
| 4         | 2                     | 3                     | 3          | 1                      | 2                      | 2 063.444 52                          | 2 063.444 95                            | -0.000 43                             | 1.00      |
| 5         | 2                     | 3                     | 4          | 1                      | 4                      | 2 063.612 55                          | 2 063.612 18                            | 0.000 37                              | 1.00      |
| 5         | 2                     | 4                     | 4          | 1                      | 3                      | 2 063.512 29                          | 2 063.512 90                            | -0.000 61                             | 0.50      |
| 6         | 2                     | 5                     | 5          | 1                      | 4                      | 2 063.576 53                          | 2 063.575 93                            | 0.000 60                              | 1.00      |
| 7         | 2                     | 6                     | 6          | 1                      | 5                      | 2 063.635 20                          | 2 063.634 18                            | 0.001 02                              | 0.50      |
| 6         | 2                     | 4                     | 5          | 1                      | 5                      | 2 063.730 36                          | 2 063.729 53                            | 0.000 83                              | 0.20      |
| 2         | 2                     | 1                     | 2          | 1                      | 2                      | 2 063.134 89                          | 2 063.134 86                            | 0.000 03                              | 0.20      |
| 2         | 2                     | 0                     | 2          | 1                      | 1                      | 2 063.107 22                          | 2 063.108 43                            | -0.001 21                             | 0.50      |
| 3         | 2                     | 2                     | 3          | 1                      | 3                      | 2 063.146 98                          | 2 063.146 86                            | 0.000 12                              | 1.00      |
| 3         | 2                     | 1                     | 3          | 1                      | 2                      | 2 063.095 47                          | 2 063.094 92                            | 0.000 55                              | 1.00      |
| 4         | 2                     | 3                     | 4          | 1                      | 4                      | 2 063.163 09                          | 1 063.162 95                            | 0.000 14                              | 1.00      |
| 4         | 2                     | 2                     | 4          | 1                      | 3                      | 2 063.078 00                          | 2 063.078 44                            | -0.000 44                             | 1.00      |
| 5         | 2                     | 3                     | 5          | 1                      | 4                      | 2 063.059 20                          | 2 063.060 23                            | -0.001 03                             | 0.50      |
| 1         | 1                     | 1                     | 2          | 2                      | 0                      | 2 061.822 66                          | 2 061.822 37                            | 0.000 29                              | 1.00      |
| 2         | 1                     | 1                     | 3          | 2                      | 2                      | 2 061.750 68                          | 2 061.750 79                            | -0.000 11                             | 0.50      |
| 2         | 1                     | 2                     | 3          | 2                      | 1                      | 2 061.722 05                          | 2 061.723 12                            | -0.001 07                             | 1.00      |
| 3         | 1                     | 2                     | 4          | 2                      | 3                      | 2 061.673 82                          | 2 061.674 14                            | -0.000 32                             | 1.00      |
| 3         | 1                     | 3                     | 4          | 2                      | 2                      | 2 061.617 79                          | 2 061.617 27                            | 0.000 52                              | 0.50      |
| 4         | 1                     | 3                     | 5          | 2                      | 4                      | 2 061.600 94                          | 2 061.601 40                            | -0.000 46                             | 0.30      |
| 4         | 1                     | 4                     | 5          | 2                      | 3                      | 2 061.503 46                          | 2 061.503 63                            | -0.000 17                             | 0.30      |
| 5         | 1                     | 4                     | 6          | 2                      | 5                      | 2 061.532 47                          | 2 061.532 46                            | 0.000 01                              | 0.20      |
| 3         | 3                     | 0                     | 2          | 2                      | 1                      | 2 063.769 55                          | 2 063.767 95                            | 0.001 60                              | 0.50      |
| 3         | 3                     | 1                     | 2          | 2                      | 0                      | 2 063.769 55                          | 2 063.767 62                            | 0.001 93                              | 0.50      |

| <i>J'</i> | <i>K<sub>a</sub>'</i> | <i>K<sub>c</sub>'</i> | <i>J''</i> | <i>K<sub>a</sub>''</i> | <i>K<sub>c</sub>''</i> | <i>observed</i><br>/ cm <sup>-1</sup> | <i>calculated</i><br>/ cm <sup>-1</sup> | <i>residual</i><br>/ cm <sup>-1</sup> | <i>wt</i> |
|-----------|-----------------------|-----------------------|------------|------------------------|------------------------|---------------------------------------|-----------------------------------------|---------------------------------------|-----------|
| 4         | 3                     | 1                     | 3          | 2                      | 2                      | 2 063.854 31                          | 2 063.854 81                            | −0.000 50                             | 0.50      |
| 4         | 3                     | 2                     | 3          | 2                      | 1                      | 2 063.854 31                          | 2 063.853 17                            | 0.001 14                              | 0.50      |
| 5         | 3                     | 2                     | 4          | 2                      | 3                      | 2 063.939 34                          | 2 063.941 76                            | −0.002 42                             | 0.20      |
| 5         | 3                     | 3                     | 4          | 2                      | 4                      | 2 063.939 34                          | 2 063.936 83                            | 0.002 51                              | 0.20      |
| 6         | 3                     | 3                     | 5          | 2                      | 4                      | 2 064.029 57                          | 2 064.029 24                            | 0.000 33                              | 0.80      |
| 6         | 3                     | 4                     | 5          | 2                      | 3                      | 2 064.017 79                          | 2 064.017 71                            | 0.000 08                              | 1.00      |
| 7         | 3                     | 4                     | 6          | 2                      | 5                      | 2 064.118 36                          | 2 064.117 77                            | 0.000 59                              | 1.00      |
| 7         | 3                     | 5                     | 6          | 2                      | 4                      | 2 064.094 24                          | 2 064.094 77                            | −0.000 53                             | 1.00      |
| 4         | 4                     | 0                     | 3          | 3                      | 1                      | 2 064.239 00                          | 2 064.239 95                            | −0.000 95                             | 0.50      |
| 4         | 4                     | 1                     | 3          | 3                      | 0                      | 2 064.239 00                          | 2 064.239 95                            | −0.000 95                             | 0.50      |
| 5         | 4                     | 1                     | 4          | 3                      | 2                      | 2 064.325 21                          | 2 064.325 52                            | −0.000 31                             | 0.30      |
| 5         | 4                     | 2                     | 4          | 3                      | 1                      | 2 064.325 31                          | 2 064.325 47                            | −0.000 16                             | 0.30      |
| 7         | 4                     | 3                     | 6          | 3                      | 4                      | 2 064.494 07                          | 2 064.494 41                            | −0.000 34                             | 0.20      |
| 7         | 4                     | 4                     | 6          | 3                      | 3                      | 2 064.494 07                          | 2 064.493 81                            | 0.000 26                              | 0.20      |

I.ii <sup>13</sup>CO-OCS pure rotational transitions

| <i>J'</i> | <i>K<sub>a</sub>'</i> | <i>K<sub>c</sub>'</i> | <i>J''</i> | <i>K<sub>a</sub>''</i> | <i>K<sub>c</sub>''</i> | <i>observed</i><br>/ MHz | <i>calculated</i><br>/ MHz | <i>residual</i><br>/ MHz | <i>wt</i><br>/ 10 <sup>9</sup> |
|-----------|-----------------------|-----------------------|------------|------------------------|------------------------|--------------------------|----------------------------|--------------------------|--------------------------------|
| 7         | 2                     | 5                     | 7          | 1                      | 6                      | 14 246.298 2             | 14 246.298 3               | −0.000 11                | 0.40                           |
| 6         | 2                     | 4                     | 6          | 1                      | 5                      | 14 626.012 6             | 14 626.012 4               | 0.000 17                 | 0.40                           |
| 5         | 2                     | 3                     | 5          | 1                      | 4                      | 15 068.175 6             | 15 068.175 6               | −0.000 02                | 1.00                           |
| 4         | 2                     | 2                     | 4          | 1                      | 3                      | 15 523.381 3             | 15 523.381 4               | −0.000 10                | 1.00                           |
| 3         | 2                     | 1                     | 3          | 1                      | 2                      | 15 946.100 6             | 15 946.100 6               | −0.000 05                | 1.00                           |
| 6         | 2                     | 4                     | 5          | 2                      | 3                      | 15 956.715 7             | 15 956.715 1               | 0.000 60                 | 0.15                           |
| 2         | 2                     | 0                     | 2          | 1                      | 1                      | 16 297.804 4             | 16 297.804 4               | −0.000 01                | 1.00                           |
| 5         | 1                     | 5                     | 4          | 0                      | 4                      | 16 770.743 9             | 16 770.744 0               | −0.000 07                | 1.00                           |
| 2         | 2                     | 1                     | 2          | 1                      | 2                      | 17 069.560 8             | 17 069.560 8               | −0.000 02                | 1.00                           |
| 7         | 1                     | 7                     | 6          | 1                      | 6                      | 17 298.443 4             | 17 298.443 6               | −0.000 22                | 0.15                           |

| <i>J'</i> | <i>K'<sub>a</sub></i> | <i>K'<sub>c</sub></i> | <i>J''</i> | <i>K''<sub>a</sub></i> | <i>K''<sub>c</sub></i> | <i>observed</i><br>/ MHz | <i>calculated</i><br>/ MHz | <i>residual</i><br>/ MHz | <i>wt</i><br>/ 10 <sup>9</sup> |
|-----------|-----------------------|-----------------------|------------|------------------------|------------------------|--------------------------|----------------------------|--------------------------|--------------------------------|
| 3         | 2                     | 2                     | 3          | 1                      | 3                      | 17 461.795 0             | 17 461.794 9               | 0.000 08                 | 0.10                           |
| 8         | 0                     | 8                     | 7          | 1                      | 7                      | 17 462.258 0             | 17 462.258 0               | 0.000 01                 | 0.40                           |
| 3         | 1                     | 2                     | 3          | 0                      | 3                      | 6 382.403 4              | 6 382.403 4                | 0.000 05                 | 1.00                           |
| 4         | 1                     | 3                     | 4          | 0                      | 4                      | 6 972.275 8              | 6 972.275 7                | 0.000 05                 | 0.25                           |
| 3         | 1                     | 3                     | 2          | 1                      | 2                      | 7 456.945 5              | 7 456.944 9                | 0.000 60                 | 0.15                           |
| 5         | 1                     | 4                     | 5          | 0                      | 5                      | 7 756.339 9              | 7 756.339 6                | 0.000 28                 | 0.40                           |
| 3         | 0                     | 3                     | 2          | 0                      | 2                      | 7 817.488 7              | 7 817.488 6                | 0.000 09                 | 0.25                           |
| 1         | 1                     | 1                     | 0          | 0                      | 0                      | 8 052.219 2              | 8 052.219 4                | −0.000 18                | 1.00                           |
| 2         | 2                     | 1                     | 3          | 1                      | 2                      | 8 051.686 1              | 8 051.685 7                | 0.000 41                 | 0.40                           |
| 3         | 1                     | 2                     | 2          | 1                      | 1                      | 8 237.052 8              | 8 237.052 7                | 0.000 09                 | 0.25                           |
| 5         | 0                     | 5                     | 4          | 1                      | 4                      | 8 534.977 1              | 8 534.977 2                | −0.000 06                | 1.00                           |
| 6         | 1                     | 5                     | 6          | 0                      | 6                      | 8 760.410 0              | 8 760.410 3                | −0.000 30                | 0.40                           |
| 4         | 1                     | 4                     | 3          | 1                      | 3                      | 9 931.740 5              | 9 931.740 6                | −0.000 11                | 0.40                           |
| 4         | 0                     | 4                     | 3          | 0                      | 3                      | 10 380.297 8             | 10 380.297 9               | −0.000 06                | 0.40                           |
| 2         | 1                     | 2                     | 1          | 0                      | 1                      | 10 409.214 1             | 10 409.213 9               | 0.000 19                 | 0.40                           |
| 4         | 2                     | 3                     | 3          | 2                      | 2                      | 10 457.579 7             | 10 457.579 5               | 0.000 22                 | 0.15                           |
| 4         | 2                     | 2                     | 3          | 2                      | 1                      | 10 547.451 5             | 10 547.451 0               | 0.000 49                 | 0.15                           |
| 5         | 1                     | 5                     | 4          | 1                      | 4                      | 12 397.828 2             | 12 397.828 1               | 0.000 11                 | 0.25                           |
| 3         | 1                     | 3                     | 2          | 0                      | 2                      | 12 638.961 8             | 12 638.961 7               | 0.000 07                 | 1.00                           |
| 5         | 0                     | 5                     | 4          | 0                      | 4                      | 12 907.893 0             | 12 907.893 0               | −0.000 05                | 0.15                           |
| 5         | 2                     | 4                     | 4          | 2                      | 3                      | 13 059.155 9             | 13 059.155 9               | 0.000 00                 | 0.25                           |

I.iii <sup>12</sup>CO-OC<sup>34</sup>S pure rotational transitions

| <i>J'</i> | <i>K'<sub>a</sub></i> | <i>K'<sub>c</sub></i> | <i>J''</i> | <i>K''<sub>a</sub></i> | <i>K''<sub>c</sub></i> | <i>observed</i><br>/ MHz | <i>calculated</i><br>/ MHz | <i>residual</i><br>/ MHz | <i>wt</i><br>/ 10 <sup>9</sup> |
|-----------|-----------------------|-----------------------|------------|------------------------|------------------------|--------------------------|----------------------------|--------------------------|--------------------------------|
| 1         | 1                     | 1                     | 0          | 0                      | 0                      | 7 921.732 6              | 7 921.732 5                | 0.000 10                 | 0.40                           |
| 2         | 1                     | 2                     | 1          | 0                      | 1                      | 10 267.951 3             | 10 267.951 4               | −0.000 15                | 0.40                           |



| <i>J'</i> | <i>K<sub>a</sub>'</i> | <i>K<sub>c</sub>'</i> | <i>J''</i> | <i>K<sub>a</sub>''</i> | <i>K<sub>c</sub>''</i> | <i>observed</i><br>/ MHz | <i>calculated</i><br>/ MHz | <i>residual</i><br>/ MHz | <i>wt</i><br>/ 10 <sup>9</sup> |
|-----------|-----------------------|-----------------------|------------|------------------------|------------------------|--------------------------|----------------------------|--------------------------|--------------------------------|
| 3         | 1                     | 3                     | 2          | 0                      | 2                      | 12 485.528 4             | 12 485.528 4               | 0.000 02                 | 0.25                           |
| 4         | 1                     | 4                     | 3          | 0                      | 3                      | 14 586.782 9             | 14 586.782 9               | 0.000 00                 | 1.00                           |
| 5         | 1                     | 5                     | 4          | 0                      | 4                      | 16 591.376 7             | 16 591.376 7               | −0.000 03                | 1.00                           |
| 2         | 2                     | 1                     | 2          | 1                      | 2                      | 16 710.233 5             | 16 710.233 5               | 0.000 01                 | 0.25                           |
| 2         | 2                     | 0                     | 2          | 1                      | 1                      | 15 929.349 5             | 15 929.349 4               | 0.000 10                 | 0.25                           |
| 4         | 1                     | 3                     | 4          | 0                      | 4                      | 6 872.437 4              | 6 872.437 5                | −0.000 09                | 0.25                           |
| 3         | 1                     | 2                     | 3          | 0                      | 3                      | 6 272.776 1              | 6 272.776 1                | −0.000 04                | 0.25                           |
| 3         | 1                     | 3                     | 2          | 1                      | 2                      | 7 429.016 5              | 7 429.017 2                | −0.000 68                | 0.04                           |
| 5         | 1                     | 4                     | 5          | 0                      | 5                      | 7 670.684 2              | 7 670.684 0                | 0.000 16                 | 0.25                           |
| 3         | 0                     | 3                     | 2          | 0                      | 2                      | 7 792.747 5              | 7 792.747 6                | −0.000 09                | 0.10                           |
| 3         | 2                     | 2                     | 2          | 2                      | 1                      | 7 827.237 2              | 7 826.627 5                | 0.609 72                 | 10 <sup>−6</sup>               |
| 2         | 2                     | 1                     | 3          | 1                      | 2                      | 7 700.576 7              | 7 701.221 0                | −0.644 26                | 10 <sup>−7</sup>               |
| 3         | 1                     | 2                     | 2          | 1                      | 1                      | 8 218.630 0              | 8 218.630 1                | −0.000 13                | 0.10                           |
| 6         | 1                     | 5                     | 6          | 0                      | 6                      | 8 694.051 4              | 8 694.051 5                | −0.000 05                | 0.25                           |
| 5         | 0                     | 5                     | 4          | 1                      | 4                      | 8 619.665 7              | 8 619.665 7                | −0.000 05                | 1.00                           |
| 4         | 1                     | 4                     | 3          | 1                      | 3                      | 9 894.002 4              | 9 894.002 1                | 0.000 29                 | 0.10                           |
| 4         | 0                     | 4                     | 3          | 0                      | 3                      | 10 345.308 1             | 10 345.307 8               | 0.000 27                 | 0.25                           |
| 5         | 0                     | 5                     | 4          | 0                      | 4                      | 12 861.141 7             | 12 861.140 8               | 0.000 89                 | 0.04                           |
| 5         | 2                     | 3                     | 5          | 1                      | 4                      | 14 698.281 3             | 14 698.281 2               | 0.000 11                 | 0.25                           |
| 6         | 2                     | 4                     | 6          | 1                      | 5                      | 14 263.015 2             | 14 263.015 2               | −0.000 01                | 1.00                           |
| 3         | 2                     | 1                     | 3          | 1                      | 2                      | 15 575.233 2             | 15 575.233 4               | −0.000 22                | 0.20                           |

# Appendix II

## II.i Ne-SiH<sub>4</sub> $j = 1 \leftarrow 0$ $A \leftarrow A$ transitions

Transition wavenumbers and residuals for the  $j = 1 \leftarrow 0$   $A \leftarrow A$  bands (including the <sup>22</sup>Ne-SiH<sub>4</sub> lines). All values are in units of cm<sup>-1</sup>, and appropriate weights are given; a weight of 1.00 indicates a standard deviation in the precision of the line position measurement of 0.0004 cm<sup>-1</sup>.

### II.i.i <sup>20</sup>Ne-SiH<sub>4</sub> fit 1 (§ 4.5.1, table 4.1, figure 4.5)

|          | <i>P(J)</i>                      |                 |           | <i>R(J)</i>     |                 |           |
|----------|----------------------------------|-----------------|-----------|-----------------|-----------------|-----------|
|          | <i>observed</i>                  | <i>residual</i> | <i>wt</i> | <i>observed</i> | <i>residual</i> | <i>wt</i> |
| <i>J</i> | <i>K =  0⟩ ←  0⟩</i>             |                 |           |                 |                 |           |
| <b>0</b> |                                  |                 |           | 2 193.770 97    | −0.000 52       | 1.00      |
| <b>1</b> | 2 193.480 56                     | −0.000 33       | 1.00      | 2 193.877 99    | −0.000 10       | 1.00      |
| <b>2</b> | 2 193.290 75                     | 0.000 15        | 1.00      | 2 193.969 06    | 0.000 13        | 1.00      |
| <b>3</b> | 2 193.077 16                     | −0.000 45       | 0.33      | 2 194.049 98    | 0.000 31        | 1.00      |
| <b>4</b> | 2 192.853 10                     | 0.002 72        | 0.10      | 2 194.124 35    | 0.000 63        | 1.00      |
| <b>5</b> |                                  |                 |           | 2 194.193 50    | 0.000 52        | 1.00      |
| <b>6</b> |                                  |                 |           | 2 194.258 14    | −0.000 34       | 1.00      |
| <i>J</i> | <i>K =  1<sup>+</sup>⟩ ←  0⟩</i> |                 |           |                 |                 |           |
| <b>0</b> |                                  |                 |           | 2 194.489 30    | −0.000 35       | 1.00      |
| <b>1</b> |                                  |                 |           | 2 194.705 54    | −0.000 90       | 1.00      |
| <b>2</b> | 2 194.009 84                     | 0.001 09        | 1.00      | 2 194.937 89    | −0.001 50       | 1.00      |
| <b>3</b> | 2 193.906 22                     | 0.000 25        | 1.00      | 2 195.181 75    | −0.000 46       | 1.00      |
| <b>4</b> | 2 193.821 41                     | 0.000 57        | 1.00      | 2 195.432 79    | 0.001 90        | 1.00      |
| <b>5</b> | 2 193.747 48                     | −0.000 24       | 0.45      |                 |                 |           |
| <b>6</b> | 2 193.682 69                     | −0.000 50       | 1.00      |                 |                 |           |
| <b>7</b> | 2 193.625 16                     | −0.000 20       | 0.25      |                 |                 |           |
| <b>8</b> | 2 193.572 78                     | −0.000 42       | 0.10      |                 |                 |           |



II.i.ii <sup>20</sup>Ne-SiH<sub>4</sub> fit 2 (§ 4.5.1, table 4.1, figure 4.5)

|          | <i>P(J)</i>                      |                 |           | <i>R(J)</i>     |                 |           |
|----------|----------------------------------|-----------------|-----------|-----------------|-----------------|-----------|
|          | <i>observed</i>                  | <i>residual</i> | <i>wt</i> | <i>observed</i> | <i>residual</i> | <i>wt</i> |
| <i>J</i> | <i>K =  0⟩ ←  0⟩</i>             |                 |           |                 |                 |           |
| 0        |                                  |                 |           | 2 193.770 97    | 0.000 20        | 1.00      |
| 1        | 2 193.480 56                     | −0.000 01       | 1.00      | 2 193.877 99    | 0.000 32        | 1.00      |
| 2        | 2 193.290 75                     | −0.000 29       | 1.00      | 2 193.969 06    | 0.000 19        | 1.00      |
| 3        | 2 193.077 16                     | −0.001 56       | 0.33      | 2 194.049 98    | 0.000 08        | 1.00      |
| 4        | 2 192.853 10                     | 0.001 52        | 0.10      | 2 194.124 35    | 0.000 22        | 1.00      |
| 5        |                                  |                 |           | 2 194.193 50    | 0.000 09        | 1.00      |
| 6        |                                  |                 |           | 2 194.258 14    | −0.000 62       | 1.00      |
| <i>J</i> | <i>K =  1<sup>+</sup>⟩ ←  0⟩</i> |                 |           |                 |                 |           |
| 0        |                                  |                 |           | 2 194.489 30    | −0.000 04       | 1.00      |
| 1        |                                  |                 |           | 2 194.705 54    | 0.000 08        | 1.00      |
| 2        | 2 194.009 84                     | 0.000 23        | 1.00      | 2 194.937 89    | −0.000 39       | 1.00      |
| 3        | 2 193.906 22                     | −0.000 28       | 1.00      | 2 195.181 75    | −0.000 15       | 1.00      |
| 4        | 2 193.821 41                     | 0.000 42        | 1.00      | 2 195.432 79    | 0.000 16        | 1.00      |
| 5        | 2 193.747 48                     | −0.000 05       | 0.45      |                 |                 |           |
| 6        | 2 193.682 69                     | −0.000 09       | 1.00      |                 |                 |           |
| 7        | 2 193.625 16                     | 0.000 29        | 0.25      |                 |                 |           |
| 8        | 2 193.572 78                     | 0.000 00        | 0.10      |                 |                 |           |

II.i.iii <sup>22</sup>Ne-SiH<sub>4</sub> (§ 4.5.2, table 4.2, figure 4.7)

|          | <i>P(J)</i>                        |                 |           | <i>R(J)</i>     |                 |           |
|----------|------------------------------------|-----------------|-----------|-----------------|-----------------|-----------|
|          | <i>observed</i>                    | <i>residual</i> | <i>wt</i> | <i>observed</i> | <i>residual</i> | <i>wt</i> |
| <i>J</i> | <i>K</i> =  0⟩ ←  0⟩               |                 |           |                 |                 |           |
| 0        |                                    |                 |           | 2 193.740 36    | −0.001 18       | 0.25      |
| 1        | 2 193.464 20                       | 0.000 06        | 1.00      | 2 193.845 95    | 0.000 07        | 1.00      |
| 2        |                                    |                 |           | 2 193.936 52    | 0.000 37        | 1.00      |
| 3        | 2 193.091 55                       | 0.000 02        | 1.00      | 2 194.017 11    | −0.000 08       | 1.00      |
| 4        |                                    |                 |           | 2 194.091 48    | −0.000 08       | 1.00      |
| 5        |                                    |                 |           | 2 194.160 10    | −0.000 22       | 1.00      |
| 6        |                                    |                 |           | 2 194.223 81    | 0.000 17        | 1.00      |
| <i>J</i> | <i>K</i> =  1 <sup>+</sup> ⟩ ←  0⟩ |                 |           |                 |                 |           |
| 0        |                                    |                 |           | 2 194.471 44    | −0.000 37       | 1.00      |
| 1        |                                    |                 |           | 2 194.687 58    | 0.000 63        | 1.00      |
| 2        |                                    |                 |           | 2 194.920 04    | −0.000 27       | 1.00      |

II.ii **Ne-SiH<sub>4</sub> T ← T transitions**

Transition wavenumbers and residuals for the *T* ← *T* bands. The first section gives the initial fit to just the *j*=0 ← 1 *T* ← *T* transitions. Sections (ii) and (iii) contain the fits to the two *j*=1 ← 1 *T* ← *T* bands, and section (iv) gives the wavenumbers and residuals for the overall global fit. All values are in units of cm<sup>−1</sup>, and appropriate weights are given; a weight of 1.00 indicates a standard deviation in the precision of the line position measurement of 0.0004 cm<sup>−1</sup>.

II.ii.i *j* = 0 ← 1 *T* ← *T* transitions (§ 4.5.3, table 4.3, figure 4.8)

|          | <i>P</i> ( <i>J</i> )              |                 |           | <i>R</i> ( <i>J</i> ) |                 |           | <i>Q</i> ( <i>J</i> )              |                 |           |
|----------|------------------------------------|-----------------|-----------|-----------------------|-----------------|-----------|------------------------------------|-----------------|-----------|
|          | <i>observed</i>                    | <i>residual</i> | <i>wt</i> | <i>observed</i>       | <i>residual</i> | <i>wt</i> | <i>observed</i>                    | <i>residual</i> | <i>wt</i> |
| <i>J</i> | <i>K</i> =  0⟩ ←  0⟩               |                 |           |                       |                 |           | (no <i>Q</i> branch)               |                 |           |
| 0        |                                    |                 |           | 2 185.152 10          | −0.000 05       | 1.00      |                                    |                 |           |
| 1        | 2 184.860 97                       | −0.000 28       | 1.00      | 2 185.339 67          | −0.000 10       | 1.00      |                                    |                 |           |
| 2        | 2 184.752 42                       | 0.000 18        | 1.00      | 2 185.548 96          | 0.000 15        | 0.25      |                                    |                 |           |
| 3        | 2 184.658 30                       | 0.000 15        | 1.00      | 2 185.771 83          | 0.000 50        | 0.05      |                                    |                 |           |
| 4        | 2 184.573 70                       | 0.000 17        | 1.00      |                       |                 |           |                                    |                 |           |
| 5        | 2 184.495 11                       | 0.000 10        | 0.45      |                       |                 |           |                                    |                 |           |
| 6        | 2 184.420 52                       | −0.000 15       | 0.45      |                       |                 |           |                                    |                 |           |
| 7        | 2 184.495 11                       | −0.000 39       | 0.25      |                       |                 |           |                                    |                 |           |
| <i>J</i> | <i>K</i> =  0⟩ ←  1 <sup>+</sup> ⟩ |                 |           |                       |                 |           | <i>K</i> =  0⟩ ←  1 <sup>−</sup> ⟩ |                 |           |
| 1        | 2 184.130 61                       | 0.001 06        | 0.45      | 2 184.608 46          | 0.000 39        | 1.00      | 2 184.317 47                       | −0.000 68       | 1.00      |
| 2        | 2 184.913 62                       | −0.000 21       | 0.45      | 2 184.710 18          | −0.000 22       | 0.33      |                                    |                 |           |
| 3        |                                    |                 |           | 2 184.794 73          | 0.000 26        | 0.10      | 2 184.307 92                       | 0.001 59        | 0.10      |
| 4        |                                    |                 |           |                       |                 |           | 2 184.297 05                       | 0.000 16        | 1.00      |
| 5        |                                    |                 |           |                       |                 |           | 2 184.284 09                       | −0.001 02       | 1.00      |
| 6        |                                    |                 |           |                       |                 |           | 2 184.271 63                       | 0.000 63        | 1.00      |



II.ii.ii  $j = 1 \leftarrow 1$   $T \leftarrow T$  transitions, fit 1 (§ 4.11.2, table 4.9, figure 4.12)

| band 1 |                                            |           |      |              |           |      |                                            |           |      |
|--------|--------------------------------------------|-----------|------|--------------|-----------|------|--------------------------------------------|-----------|------|
|        | $P(J)$                                     |           |      | $R(J)$       |           |      | $Q(J)$                                     |           |      |
|        | observed                                   | residual  | wt   | observed     | residual  | wt   | observed                                   | residual  | wt   |
| $J$    | $K =  1^+ \rangle \leftarrow  0 \rangle$   |           |      |              |           |      | $K =  1^- \rangle \leftarrow  0 \rangle$   |           |      |
| 0      |                                            |           |      | 2 190.397 80 | 0.000 15  | 1.00 |                                            |           |      |
| 1      |                                            |           |      | 2 190.617 31 | −0.000 49 | 1.00 | 2 190.260 41                               | −0.000 20 | 1.00 |
| 2      | 2 189.998 15                               | 0.000 42  | 1.00 | 2 190.875 08 | −0.000 08 | 1.00 | 2 190.332 27                               | −0.000 61 | 1.00 |
| 3      | 2 189.935 69                               | −0.000 70 | 1.00 | 2 191.161 80 | 0.000 50  | 1.00 | 2 190.431 52                               | −0.000 64 | 1.00 |
| 4      | 2 189.899 91                               | −0.000 69 | 1.00 | 2 191.469 30 | −0.000 17 | 1.00 | 2 190.555 33                               | 0.000 64  | 1.00 |
| 5      | 2 189.888 37                               | 0.001 80  | 0.10 |              |           |      | 2 190.699 22                               | −0.000 23 | 1.00 |
| $J$    | $K =  1^+ \rangle \leftarrow  1^+ \rangle$ |           |      |              |           |      | $K =  1^- \rangle \leftarrow  1^+ \rangle$ |           |      |
| 1      |                                            |           |      | 2 189.888 37 | 0.001 42  | 1.00 |                                            |           |      |
| 2      | 2 189.160 39                               | −0.000 02 | 1.00 | 2 190.037 69 | −0.000 16 | 1.00 |                                            |           |      |
| $J$    | $K =  1^- \rangle \leftarrow  1^- \rangle$ |           |      |              |           |      | $K =  1^+ \rangle \leftarrow  1^- \rangle$ |           |      |
| 2      | 2 189.236 14                               | 0.000 88  | 0.25 | 2 190.089 98 | 0.001 76  | 0.25 |                                            |           |      |

| band 2 |                                          |           |      |              |           |      |                                          |           |      |
|--------|------------------------------------------|-----------|------|--------------|-----------|------|------------------------------------------|-----------|------|
|        | $P(J)$                                   |           |      | $R(J)$       |           |      | $Q(J)$                                   |           |      |
|        | observed                                 | residual  | wt   | observed     | residual  | wt   | observed                                 | residual  | wt   |
| $J$    | $K =  1^+ \rangle \leftarrow  0 \rangle$ |           |      |              |           |      | $K =  1^- \rangle \leftarrow  0 \rangle$ |           |      |
| 0      |                                          |           |      | 2 190.016 01 | −0.001 14 | 1.00 |                                          |           |      |
| 1      |                                          |           |      | 2 190.234 22 | 0.001 19  | 1.00 | 2 189.888 69                             | 0.003 36  | 1.00 |
| 2      | 2 189.615 76                             | −0.001 47 | 1.00 | 2 190.473 40 | −0.001 89 | 1.00 | 2 189.964 12                             | −0.001 87 | 1.00 |
| 3      | 2 189.551 75                             | −0.000 13 | 1.00 |              |           |      | 2 190.075 17                             | 0.000 37  | 1.00 |
| 4      | 2 189.501 38                             | 0.000 65  | 0.25 |              |           |      |                                          |           |      |
| 5      | 2 189.452 00                             | 0.001 64  | 1.00 |              |           |      |                                          |           |      |
| 6      | 2 189.383 61                             | −0.000 50 | 1.00 |              |           |      |                                          |           |      |

II.ii.iii  $j = 1 \leftarrow 1$   $T \leftarrow T$  transitions, fit 2 (§ 4.11.2, table 4.10, figure 4.12)

| band 1   |                                            |                 |           |                 |                 |           |                                            |                 |           |
|----------|--------------------------------------------|-----------------|-----------|-----------------|-----------------|-----------|--------------------------------------------|-----------------|-----------|
|          | <i>P(J)</i>                                |                 |           | <i>R(J)</i>     |                 |           | <i>Q(J)</i>                                |                 |           |
|          | <i>observed</i>                            | <i>residual</i> | <i>wt</i> | <i>observed</i> | <i>residual</i> | <i>wt</i> | <i>observed</i>                            | <i>residual</i> | <i>wt</i> |
| <i>J</i> | $K =  1^+ \rangle \leftarrow  0 \rangle$   |                 |           |                 |                 |           | $K =  1^- \rangle \leftarrow  0 \rangle$   |                 |           |
| 0        |                                            |                 |           | 2 190.397 80    | 0.000 05        | 1.00      |                                            |                 |           |
| 1        |                                            |                 |           | 2 190.617 31    | −0.001 20       | 1.00      | 2 190.260 41                               | 0.000 54        | 1.00      |
| 2        | 2 189.998 15                               | 0.000 53        | 1.00      | 2 190.875 08    | −0.000 03       | 1.00      | 2 190.332 27                               | −0.000 32       | 1.00      |
| 3        | 2 189.935 69                               | −0.001 18       | 1.00      | 2 191.161 80    | 0.001 62        | 1.00      | 2 190.431 52                               | −0.000 80       | 1.00      |
| 4        | 2 189.899 91                               | −0.000 53       | 1.00      | 2 191.469 30    | −0.000 67       | 1.00      | 2 190.555 33                               | 0.000 31        | 1.00      |
| 5        | 2 189.888 37                               | 0.002 75        | 0.10      |                 |                 |           | 2 190.699 22                               | −0.000 06       | 1.00      |
| <i>J</i> | $K =  1^+ \rangle \leftarrow  1^+ \rangle$ |                 |           |                 |                 |           | $K =  1^- \rangle \leftarrow  1^+ \rangle$ |                 |           |
| 1        |                                            |                 |           | 2 189.888 37    | 0.000 80        | 1.00      |                                            |                 |           |
| 2        | 2 189.160 39                               | 0.000 01        | 1.00      | 2 190.037 69    | −0.000 18       | 1.00      |                                            |                 |           |
| <i>J</i> | $K =  1^- \rangle \leftarrow  1^- \rangle$ |                 |           |                 |                 |           | $K =  1^+ \rangle \leftarrow  1^- \rangle$ |                 |           |
| 2        | 2 189.236 14                               | 0.001 74        | 0.25      | 2 190.089 98    | 0.001 49        | 0.25      |                                            |                 |           |
| <i>J</i> | $K =  0 \rangle \leftarrow  0 \rangle$     |                 |           |                 |                 |           | (no <i>Q</i> branch)                       |                 |           |
| 1        | 2 189.673 59                               | 0.001 09        | 1.00      |                 |                 |           |                                            |                 |           |
| 2        | 2 189.539 20                               | −0.001 44       | 1.00      |                 |                 |           |                                            |                 |           |
| 3        | 2 189.404 19                               | −0.000 14       | 1.00      |                 |                 |           |                                            |                 |           |
| <i>J</i> | $K =  0 \rangle \leftarrow  1^+ \rangle$   |                 |           |                 |                 |           | $K =  0 \rangle \leftarrow  1^- \rangle$   |                 |           |
| 1        |                                            |                 |           | 2 189.357 10    | 0.002 08        | 0.10      |                                            |                 |           |
| 2        |                                            |                 |           | 2 189.404 35    | 0.004 43        | 0.10      |                                            |                 |           |
| 3        |                                            |                 |           | 2 189.415 12    | −0.000 14       | 1.00      |                                            |                 |           |

| band 2   |                                          |                 |           |                 |                 |           |                                          |                 |           |
|----------|------------------------------------------|-----------------|-----------|-----------------|-----------------|-----------|------------------------------------------|-----------------|-----------|
|          | <i>P(J)</i>                              |                 |           | <i>R(J)</i>     |                 |           | <i>Q(J)</i>                              |                 |           |
|          | <i>observed</i>                          | <i>residual</i> | <i>wt</i> | <i>observed</i> | <i>residual</i> | <i>wt</i> | <i>observed</i>                          | <i>residual</i> | <i>wt</i> |
| <i>J</i> | $K =  1^+ \rangle \leftarrow  0 \rangle$ |                 |           |                 |                 |           | $K =  1^- \rangle \leftarrow  0 \rangle$ |                 |           |
| 0        |                                          |                 |           | 2 190.016 01    | − 0.001 59      | 1.00      |                                          |                 |           |
| 1        |                                          |                 |           | 2 190.234 22    | 0.000 97        | 1.00      | 2 189.888 69                             | 0.003 63        | 1.00      |
| 2        | 2 189.615 76                             | − 0.001 71      | 1.00      | 2 190.473 40    | − 0.001 81      | 1.00      | 2 189.964 12                             | − 0.000 96      | 1.00      |
| 3        | 2 189.551 75                             | 0.000 14        | 1.00      |                 |                 |           | 2 190.075 17                             | − 0.000 12      | 1.00      |
| 4        | 2 189.501 38                             | 0.000 85        | 0.25      |                 |                 |           |                                          |                 |           |
| 5        | 2 189.452 00                             | 0.001 85        | 1.00      |                 |                 |           |                                          |                 |           |
| 6        | 2 189.383 61                             | − 0.000 60      | 1.00      |                 |                 |           |                                          |                 |           |



II.ii.iv Global fit for all *T←T* transitions (§ 4.11.3, tables 4.11/12, figures 4.14/15)

| <i>j</i> = 0 ← 1 |                                    |                 |           |                       |                 |           |                                    |                 |           |
|------------------|------------------------------------|-----------------|-----------|-----------------------|-----------------|-----------|------------------------------------|-----------------|-----------|
|                  | <i>P</i> ( <i>J</i> )              |                 |           | <i>R</i> ( <i>J</i> ) |                 |           | <i>Q</i> ( <i>J</i> )              |                 |           |
|                  | <i>observed</i>                    | <i>residual</i> | <i>wt</i> | <i>observed</i>       | <i>residual</i> | <i>wt</i> | <i>observed</i>                    | <i>residual</i> | <i>wt</i> |
| <i>J</i>         | <i>K</i> =  0⟩ ←  0⟩               |                 |           |                       |                 |           | (no <i>Q</i> branch)               |                 |           |
| 0                |                                    |                 |           | 2 185.152 10          | 0.000 10        | 1.00      |                                    |                 |           |
| 1                | 2 184.860 97                       | − 0.000 28      | 1.00      | 2 185.339 67          | 0.001 11        | 1.00      |                                    |                 |           |
| 2                | 2 184.752 42                       | 0.000 53        | 1.00      | 2 185.548 96          | 0.003 16        | 0.25      |                                    |                 |           |
| 3                | 2 184.658 30                       | 0.000 68        | 1.00      | 2 185.771 83          | 0.006 11        | 0.05      |                                    |                 |           |
| 4                | 2 184.573 70                       | 0.000 61        | 1.00      |                       |                 |           |                                    |                 |           |
| 5                | 2 184.495 11                       | 0.000 16        | 0.45      |                       |                 |           |                                    |                 |           |
| 6                | 2 184.420 52                       | − 0.000 68      | 0.45      |                       |                 |           |                                    |                 |           |
| 7                | 2 184.495 11                       | − 0.001 56      | 0.25      |                       |                 |           |                                    |                 |           |
| <i>J</i>         | <i>K</i> =  0⟩ ←  1 <sup>+</sup> ⟩ |                 |           |                       |                 |           | <i>K</i> =  0⟩ ←  1 <sup>−</sup> ⟩ |                 |           |
| 1                | 2 184.130 61                       | − 0.000 19      | 0.45      | 2 184.608 46          | 0.000 35        | 1.00      | 2 184.317 47                       | − 0.001 01      | 1.00      |
| 2                | 2 184.913 62                       | − 0.003 18      | 0.45      | 2 184.710 18          | − 0.000 53      | 0.33      |                                    |                 |           |
| 3                |                                    |                 |           | 2 184.794 73          | 0.000 17        | 0.10      | 2 184.307 92                       | 0.000 77        | 0.10      |
| 4                |                                    |                 |           |                       |                 |           | 2 184.297 05                       | − 0.000 71      | 1.00      |
| 5                |                                    |                 |           |                       |                 |           | 2 184.284 09                       | − 0.001 51      | 1.00      |
| 6                |                                    |                 |           |                       |                 |           | 2 184.271 63                       | 0.001 24        | 1.00      |

| <i>j</i> = 1 ← 1, band 1 |                                                  |                 |           |                       |                 |           |                                                  |                 |           |
|--------------------------|--------------------------------------------------|-----------------|-----------|-----------------------|-----------------|-----------|--------------------------------------------------|-----------------|-----------|
| <i>J</i>                 | <i>P</i> ( <i>J</i> )                            |                 |           | <i>R</i> ( <i>J</i> ) |                 |           | <i>Q</i> ( <i>J</i> )                            |                 |           |
|                          | <i>observed</i>                                  | <i>residual</i> | <i>wt</i> | <i>observed</i>       | <i>residual</i> | <i>wt</i> | <i>observed</i>                                  | <i>residual</i> | <i>wt</i> |
| <i>J</i>                 | <i>K</i> =  1 <sup>+</sup> ⟩ ←  0⟩               |                 |           |                       |                 |           | <i>K</i> =  1 <sup>−</sup> ⟩ ←  0⟩               |                 |           |
| 0                        |                                                  |                 |           | 2 190.397 80          | 0.000 62        | 0.10      |                                                  |                 |           |
| 1                        |                                                  |                 |           | 2 190.617 31          | −0.000 37       | 0.10      | 2 190.260 41                                     | 0.000 90        | 0.10      |
| 2                        | 2 189.998 15                                     | 0.001 07        | 0.10      | 2 190.875 08          | 0.000 94        | 0.10      | 2 190.332 27                                     | −0.000 22       | 0.10      |
| 3                        | 2 189.935 69                                     | −0.001 05       | 0.10      | 2 191.161 80          | 0.002 35        | 0.10      | 2 190.431 52                                     | −0.001 04       | 0.10      |
| 4                        | 2 189.899 91                                     | −0.001 51       | 0.10      | 2 191.469 30          | −0.000 71       | 0.10      | 2 190.555 33                                     | −0.000 03       | 0.10      |
| 5                        | 2 189.888 37                                     | −0.000 30       | 0.01      |                       |                 |           | 2 190.699 22                                     | 0.000 25        | 0.10      |
| <i>J</i>                 | <i>K</i> =  1 <sup>+</sup> ⟩ ←  1 <sup>+</sup> ⟩ |                 |           |                       |                 |           | <i>K</i> =  1 <sup>−</sup> ⟩ ←  1 <sup>+</sup> ⟩ |                 |           |
| 1                        |                                                  |                 |           | 2 189.888 37          | 0.001 14        | 0.10      |                                                  |                 |           |
| 2                        | 2 189.160 39                                     | −0.001 59       | 0.10      | 2 190.037 69          | −0.001 35       | 0.10      |                                                  |                 |           |
| <i>J</i>                 | <i>K</i> =  1 <sup>−</sup> ⟩ ←  1 <sup>−</sup> ⟩ |                 |           |                       |                 |           | <i>K</i> =  1 <sup>+</sup> ⟩ ←  1 <sup>−</sup> ⟩ |                 |           |
| 2                        | 2 189.236 14                                     | 0.001 18        | 0.03      | 2 190.089 98          | 0.001 03        | 0.03      |                                                  |                 |           |
| <i>J</i>                 | <i>K</i> =  0⟩ ←  0⟩                             |                 |           |                       |                 |           | (no <i>Q</i> branch)                             |                 |           |
| 1                        | 2 189.673 59                                     | 0.000 89        | 0.10      |                       |                 |           |                                                  |                 |           |
| 2                        | 2 189.539 20                                     | −0.001 42       | 0.10      |                       |                 |           |                                                  |                 |           |
| 3                        | 2 189.404 19                                     | 0.000 08        | 0.10      |                       |                 |           |                                                  |                 |           |
| <i>J</i>                 | <i>K</i> =  0⟩ ←  1 <sup>+</sup> ⟩               |                 |           |                       |                 |           | <i>K</i> =  0⟩ ←  1 <sup>−</sup> ⟩               |                 |           |
| 1                        |                                                  |                 |           | 2 189.357 10          | 0.002 49        | 0.10      |                                                  |                 |           |
| 2                        |                                                  |                 |           | 2 189.404 35          | 0.004 53        | 0.10      |                                                  |                 |           |
| 3                        |                                                  |                 |           | 2 189.415 12          | −0.000 22       | 1.00      |                                                  |                 |           |



| <i>j</i> = 1 ← 1, band 2 |                                    |                 |           |                       |                 |           |                                    |                 |           |
|--------------------------|------------------------------------|-----------------|-----------|-----------------------|-----------------|-----------|------------------------------------|-----------------|-----------|
| <i>J</i>                 | <i>P</i> ( <i>J</i> )              |                 |           | <i>R</i> ( <i>J</i> ) |                 |           | <i>Q</i> ( <i>J</i> )              |                 |           |
|                          | <i>observed</i>                    | <i>residual</i> | <i>wt</i> | <i>observed</i>       | <i>residual</i> | <i>wt</i> | <i>observed</i>                    | <i>residual</i> | <i>wt</i> |
| <i>J</i>                 | <i>K</i> =  1 <sup>+</sup> ⟩ ←  0⟩ |                 |           |                       |                 |           | <i>K</i> =  1 <sup>-</sup> ⟩ ←  0⟩ |                 |           |
| 0                        |                                    |                 |           | 2 190.016 01          | − 0.001 72      | 0.10      |                                    |                 |           |
| 1                        |                                    |                 |           | 2 190.234 22          | 0.001 21        | 0.10      | 2 189.888 69                       | 0.003 67        | 0.10      |
| 2                        | 2 189.615 76                       | − 0.001 86      | 0.10      | 2 190.473 40          | − 0.000 66      | 0.10      | 2 189.964 12                       | − 0.000 80      | 0.10      |
| 3                        | 2 189.551 75                       | − 0.000 32      | 0.10      |                       |                 |           | 2 190.075 17                       | − 0.000 21      | 0.10      |
| 4                        | 2 189.501 38                       | 0.000 04        | 0.03      |                       |                 |           |                                    |                 |           |
| 5                        | 2 189.452 00                       | 0.001 06        | 0.10      |                       |                 |           |                                    |                 |           |
| 6                        | 2 189.383 61                       | − 0.000 39      | 0.10      |                       |                 |           |                                    |                 |           |

| <i>j</i> = 2 ← 1 |                                                  |                 |           |                       |                 |           |                                                  |                 |           |
|------------------|--------------------------------------------------|-----------------|-----------|-----------------------|-----------------|-----------|--------------------------------------------------|-----------------|-----------|
| <i>J</i>         | <i>P</i> ( <i>J</i> )                            |                 |           | <i>R</i> ( <i>J</i> ) |                 |           | <i>Q</i> ( <i>J</i> )                            |                 |           |
|                  | <i>observed</i>                                  | <i>residual</i> | <i>wt</i> | <i>observed</i>       | <i>residual</i> | <i>wt</i> | <i>observed</i>                                  | <i>residual</i> | <i>wt</i> |
| <i>J</i>         | <i>K</i> =  1 <sup>+</sup> ⟩ ←  0⟩               |                 |           |                       |                 |           | <i>K</i> =  1 <sup>-</sup> ⟩ ←  0⟩               |                 |           |
| 0                |                                                  |                 |           | 2 195.843 74          | − 0.000 60      | 1.00      |                                                  |                 |           |
| 1                |                                                  |                 |           | 2 196.026 72          | − 0.000 98      | 1.00      | 2 195.713 26                                     | 0.000 83        | 1.00      |
| 2                | 2 195.443 76                                     | − 0.000 60      | 1.00      | 2 196.228 65          | − 0.001 49      | 1.00      | 2 195.757 72                                     | − 0.000 07      | 1.00      |
| 3                |                                                  |                 |           | 2 196.442 19          | − 0.001 46      | 1.00      | 2 195.814 92                                     | − 0.000 33      | 1.00      |
| 4                | 2 195.256 49                                     | − 0.000 94      | 1.00      | 2 196.660 18          | − 0.001 74      | 0.40      | 2 195.878 78                                     | − 0.000 20      | 1.00      |
| 5                | 2 195.174 93                                     | 0.002 06        | 1.00      | 2 196.880 13          | − 0.000 49      | 1.00      | 2 195.946 06                                     | 0.000 94        | 1.00      |
| 6                |                                                  |                 |           | 2 197.097 38          | 0.000 61        | 1.00      | 2 196.010 29                                     | − 0.000 89      | 1.00      |
| <i>J</i>         | <i>K</i> =  1 <sup>+</sup> ⟩ ←  1 <sup>+</sup> ⟩ |                 |           |                       |                 |           | <i>K</i> =  1 <sup>-</sup> ⟩ ←  1 <sup>+</sup> ⟩ |                 |           |
| 2                | 2 194.608 71                                     | − 0.000 43      | 0.40      | 2 195.398 14          | 0.003 09        | 1.00      |                                                  |                 |           |
| 3                |                                                  |                 |           | 2 195.472 25          | − 0.000 24      | 1.00      |                                                  |                 |           |
| <i>J</i>         | <i>K</i> =  1 <sup>-</sup> ⟩ ←  1 <sup>-</sup> ⟩ |                 |           |                       |                 |           | <i>K</i> =  1 <sup>+</sup> ⟩ ←  1 <sup>-</sup> ⟩ |                 |           |
| 1                | 2 195.325 02                                     | 0.00 64         | 1.00      |                       |                 |           |                                                  |                 |           |
| 2                | 2 195.472 25                                     | 0.000 61        | 1.00      |                       |                 |           |                                                  |                 |           |
| 3                | 2 195.613 28                                     | 0.000 24        | 1.00      |                       |                 |           |                                                  |                 |           |

| <i>j</i> = 2 ← 1 |                                                  |                 |           |                       |                 |           |                                                  |                 |           |
|------------------|--------------------------------------------------|-----------------|-----------|-----------------------|-----------------|-----------|--------------------------------------------------|-----------------|-----------|
|                  | <i>P</i> ( <i>J</i> )                            |                 |           | <i>R</i> ( <i>J</i> ) |                 |           | <i>Q</i> ( <i>J</i> )                            |                 |           |
|                  | <i>observed</i>                                  | <i>residual</i> | <i>wt</i> | <i>observed</i>       | <i>residual</i> | <i>wt</i> | <i>observed</i>                                  | <i>residual</i> | <i>wt</i> |
| <i>J</i>         | <i>K</i> =  0⟩ ←  0⟩                             |                 |           |                       |                 |           | (no <i>Q</i> branch)                             |                 |           |
| 0                |                                                  |                 |           | 2 202.579 90          | − 0.000 52      | 1.00      |                                                  |                 |           |
| 1                | 2 202.292 54                                     | 0.000 60        | 1.00      | 2 202.762 75          | 0.000 05        | 1.00      |                                                  |                 |           |
| 2                | 2 202.180 12                                     | − 0.000 19      | 1.00      | 2 202.964 45          | 0.000 31        | 1.00      |                                                  |                 |           |
| 3                | 2 202.082 44                                     | 0.000 69        | 1.00      | 2 203.177 40          | − 0.000 10      | 1.00      |                                                  |                 |           |
| <i>J</i>         | <i>K</i> =  0⟩ ←  1 <sup>+</sup> ⟩               |                 |           |                       |                 |           | <i>K</i> =  0⟩ ←  1 <sup>−</sup> ⟩               |                 |           |
| 1                | 2 201.561 22                                     | − 0.000 27      | 0.50      | 2 202.029 43          | − 0.002 82      | 0.50      | 2 201.748 77                                     | 0.001 87        | 0.50      |
| 2                | 2 201.342 85                                     | − 0.002 37      | 0.33      |                       |                 |           | 2 201.739 25                                     | 0.001 11        | 0.50      |
| <i>J</i>         | <i>K</i> =  2 <sup>+</sup> ⟩ ←  1 <sup>+</sup> ⟩ |                 |           |                       |                 |           | <i>K</i> =  2 <sup>+</sup> ⟩ ←  1 <sup>−</sup> ⟩ |                 |           |
| 2                |                                                  |                 |           |                       |                 |           | 2 200.663 73                                     | 0.001 52        | 1.00      |
| 3                |                                                  |                 |           | 2 201.247 36          | − 0.000 51      | 1.00      | 2 200.701 81                                     | − 0.001 64      | 1.00      |
| 4                |                                                  |                 |           | 2 201.380 48          | 0.002 69        | 1.00      |                                                  |                 |           |
| 5                |                                                  |                 |           | 2 201.490 55          | − 0.001 50      | 1.00      | 2 200.799 02                                     | 0.000 30        | 0.33      |
| <i>J</i>         | <i>K</i> =  2 <sup>−</sup> ⟩ ←  1 <sup>−</sup> ⟩ |                 |           |                       |                 |           | <i>K</i> =  2 <sup>−</sup> ⟩ ←  1 <sup>+</sup> ⟩ |                 |           |
| 1                |                                                  |                 |           | 2 200.947 27          | 0.000 46        | 0.20      |                                                  |                 |           |
| 2                |                                                  |                 |           | 2 201.108 56          | − 0.001 77      | 0.33      |                                                  |                 |           |
| 3                |                                                  |                 |           | 2 201.265 93          | − 0.000 37      | 1.00      |                                                  |                 |           |
| 4                |                                                  |                 |           | 2 201.407 51          | − 0.000 46      | 1.00      |                                                  |                 |           |
| 5                |                                                  |                 |           | 2 201.527 66          | 0.000 66        | 1.00      |                                                  |                 |           |

# Appendix III

## Transition dipole moment matrix elements

The transition dipole moment matrix element between two eigenstates of a system  $|m\rangle$  and  $|n\rangle$  characterised by quantum numbers  $v, J, M, K$ , where  $v$  is the vibrational state,  $J$  is the quantum number associated with the rotational angular momentum  $\mathbf{J}$ ,  $M\hbar$  is the space fixed projection of  $\mathbf{J}$ , and  $K\hbar$  is the body fixed projection of  $\mathbf{J}$ , may be written

$$\mu_{nm} = \langle v' J' M' K' | T_0^1(\mu) | v'' J'' M'' K'' \rangle \quad (\text{III.1})$$

where  $T_0^1(\mu)$  is a spherical tensor operator equal to the component of the dipole moment in the direction of the space fixed  $Z$  axis,  $\mu_Z$ . This can be rewritten in the body fixed axis system using the rotation operator  $D_{0q}^{1*}$ :

$$\mu_{nm} = \langle v' J' M' K' | \sum_q D_{0q}^{1*} T_q^1(\mu) | v'' J'' M'' K'' \rangle \quad (\text{III.2})$$

where  $q=0$  (parallel transitions),  $\pm 1$  (perpendicular transitions). This can be reduced using 3- $j$  symbols thus:

$$\begin{aligned} \mu_{nm} = & (-1)^{M'-K'} [(2J'+1)(2J''+1)]^{1/2} \begin{pmatrix} J' & 1 & J'' \\ -M' & 0 & M'' \end{pmatrix} \begin{pmatrix} J' & 1 & J'' \\ K' & q & K'' \end{pmatrix} \\ & \times \langle v' | T_q^1(\mu) | v'' \rangle \end{aligned} \quad (\text{III.3})$$

The Coriolis interaction between eigenstates of the same symmetry separated by  $\Delta K = \pm 1$  results in a mixing of the interacting states to give some linear combination of eigenstates thus:

$$\begin{aligned} |f\rangle &= \sum_{K'} a_{K'} |J' M' K'\rangle \\ |i\rangle &= \sum_{K''} b_{K''} |J'' M'' K''\rangle \end{aligned} \quad (\text{III.4})$$

The square of the transition dipole matrix element (equation (III.3)) is then given by:

$$\begin{aligned}
|\mu_{nm}|^2 = (2J' + 1)(2J'' + 1) \times & \left[ \sum_M \begin{pmatrix} J' & 1 & J'' \\ -M & 0 & M \end{pmatrix}^2 \right] \\
& \times \left[ \sum_q \sum_{K'' K'} a_{K'} b_{K''} (-1)^{J' - K'} \begin{pmatrix} J' & 1 & J'' \\ K' & q & K'' \end{pmatrix} \times \langle v' | T_q^1(\mu) | v'' \rangle \right]^2
\end{aligned} \quad (\text{III.5})$$

The phase factor  $(-1)^{M' - K'}$  has been rewritten as  $(-1)^{J' - M'}(-1)^{J' - K'}$ ; the  $(-1)^{J' - M'}$  term appears in the first sum as a squared quantity and is thus always equal to 1. This first summation can be shown to be equal to 1/3 for  $P$ ,  $Q$  and  $R$  transitions:

$$\sum_{M=-J}^J \begin{pmatrix} J & 1 & J \\ -M & 0 & M \end{pmatrix}^2 = \sum_{M=-J}^J \frac{M^2}{J(J+1)(2J+1)} = \frac{1}{3} \quad (\text{III.6})$$

$$\begin{aligned}
\sum_{M=-J}^J \begin{pmatrix} J+1 & 1 & J \\ -M & 0 & M \end{pmatrix}^2 &= \sum_{M=-J}^J \frac{[(J+1)^2 - M^2]}{(J+1)(2J+1)(2J+3)} \\
&= \frac{J+1}{(2J+3)} - \frac{J}{3(2J+3)} = \frac{1}{3}
\end{aligned} \quad (\text{III.7})$$

Equation (III.5) can then be rewritten:

$$\begin{aligned}
|\mu_{nm}|^2 = \frac{1}{3} (2J' + 1)(2J'' + 1) \\
\times \left[ \sum_q \sum_{K'' K'} a_{K'} b_{K''} (-1)^{J' - K'} \begin{pmatrix} J' & 1 & J'' \\ K' & q & K'' \end{pmatrix} \times \langle v' | T_q^1(\mu) | v'' \rangle \right]^2
\end{aligned} \quad (\text{III.8})$$

The intensity effects apparent in **figure 4.5** are a consequence of the constructive and destructive interference which occurs in the remaining squared term in equation (III.8).