

The LMR Spectra of Free Radicals

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Abstract of a thesis submitted for the degree of
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Laser Magnetic Resonance (LMR) is a very sensitive, accurate and high resolution spectroscopic technique. Transitions of paramagnetic species are brought into coincidence with a fixed frequency laser using Zeeman tuning. Three different LMR spectrometers are described, two of which use the CO laser as a radiation source and the other used optically pumped far-infrared lasers. These LMR spectrometers have been used to study four radicals, germanium hydride (GeH), tellurium deuteride (TeD), iron hydride (FeH) and iron deuteride (FeD).

Transitions in the fundamental and first hot bands of the GeH radical have been detected by CO LMR. The transitions occur within both $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{\frac{3}{2}}$ manifolds. These data have been fitted with previously published data for GeH and GeD to determine the parameters of a single model effective Hamiltonian which describes all naturally occurring isotopomers. Details of the Hamiltonian are given.

The same Hamiltonian was used to model transitions in the fundamental and first two hot bands of the TeD radical that were also recorded using CO LMR. Resonances from the seven most abundant isotopomers, including the two with $I = \frac{1}{2}$, have been identified.

Seven transitions in the fundamental band of FeH have been observed using Faraday CO LMR. Due to the complicated electronic structure for FeH it is not possible to model these data using a single model effective Hamiltonian. It has been possible to fit the parameters of a second order Zeeman expression to these FeH data and so determine accurate zero-field transition wavenumbers for six of these transitions.

Pure rotational transitions in the ground state of FeD have been observed using FIR LMR. As for FeH the parameters of second order Zeeman expressions can be fitted to these transitions and zero field wavenumbers determined.

Dedication

To Diana, David, Helena and Andrew.

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Chapter 1

Introduction

Infrared (IR) Spectroscopy (in the wavenumber range 300 to 4000 cm^{-1}) has been used for over 100 years [1]. Ro-vibrational transitions of all molecules fall within the IR region. It is estimated that the IR spectra of more than 10000 molecules have been studied to date. Chemists often use commercial low resolution (0.01 cm^{-1} or 300 MHz) IR spectrometers for analytical purposes. Using modern high resolution techniques to measure these transition frequencies provides valuable information about the molecule's vibrational structure. Vibrational parameters and force constants in a given electronic state may be determined. Recent technological developments (from about 1960) have opened up the field of high resolution (0.005 cm^{-1}) IR spectroscopy and the IR spectroscopy of transient molecules. These developments are:

1. The development of semiconductor detectors in the 1950's which provided the fast, sensitive detectors required for spectroscopy.
2. Fourier Transform spectroscopy; modern instruments such as that used by Burkholder *et al.* [2] have a resolution of 0.004 cm^{-1} .
3. Development of fast microcomputers which can handle rapid data acquisition and perform some data processing.
4. Lasers have revolutionised spectroscopy. Laser radiation is :
 - highly collimated,
 - monochromatic (typical linewidth of a few MHz),
 - of high spectral brightness (making sub-Doppler saturation spectroscopy possible) and
 - coherent (both spatially and temporally).

The first IR laser was the CO₂ laser (1964) and since then several other systems have been developed [3]. Because of these developments there is a great deal to be learnt from IR spectroscopy of many molecules. The study of van der Waals molecules, for example, gives information on intermolecular forces.

Laser Magnetic Resonance (LMR) is a very sensitive technique for recording transitions in paramagnetic species in the gas phase. Although the restriction of LMR to paramagnetic species is a limitation of the technique, it has the advantage of making LMR spectra very selective and free from swamping by absorptions from common species such as H₂O and CO₂ which have strong absorptions in the IR region. In Chapter 2 the principle of LMR is explained and details of the three spectrometers used to record the data presented in this thesis are given. Both the molecules studied in Chapters 4 and 5, GeH and TeD, have ²Π ground states, with coupling schemes that are a good approximation to Hund's case (a). A non-rigorous derivation of some of the matrix elements of a ²Π Hamiltonian using $\mathbf{N}^2$ as the rotational operator is given in Chapter 3. Fitting parameters of the Hamiltonian to experimental data is also discussed.

The remainder of this thesis is devoted to the study of the FeH radical. The spectroscopy of the transition metal hydrides is challenging from both an experimental and theoretical point of view. There are many low lying states of transition metal hydrides that are close enough in energy to perturb each other greatly. This makes the relative positions of the electronic states very difficult to calculate using existing *ab initio* techniques. If the positions of the levels could be determined experimentally, the data could be used as a guide in developing *ab initio* techniques. Reliable spectroscopic data is of great value to astronomers. The spectra of astronomical objects are rich in information both about the source and the intervening matter (red-shift, chemical composition ...) [4]. FeH has already been observed in stellar atmospheres [5] (by optical spectrometers). If accurate rest wavelengths are measured in the IR for FeH transitions, some of the unassigned absorption lines in the spectra of IR astronomical sources may be assigned to FeH in the interstellar medium. The results of an infrared LMR study of FeH in its ⁴Δ state are presented in Chapter 6. As a result of this study it was possible to determine the transition frequency of the Q($\frac{7}{2}$) transition to an accuracy of 3 MHz. A FIR LMR study of FeD has been carried out, the results of which are presented in Chapter 7. These results are compared with a similar study of FeH by Beaton [6]. Further work on FeH and FeD is discussed in Chapter 8.

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Chapter 2

Three Laser Magnetic Resonance (LMR) Spectrometers

2.1 Introduction

Three LMR spectrometers will be discussed in this chapter,

1. The intracavity CO LMR spectrometer of Dr.J.M.Brown at the University of Oxford. Details of recent improvements to the spectrometer are given. This spectrometer was used to record the TeD data presented in Chapter 5 and [2], and part of the GeH data presented in Chapter 4 and [1].
2. The Faraday CO LMR spectrometer of Professor W.Urban at the University of Bonn. This spectrometer was used to record the FeH data presented in chapter 6.
3. The FIR LMR spectrometer of Dr.K.M.Evenson at the National Institute of Standards and Technology (NIST) in Boulder, Colorado which was used to record the FeD data presented in chapter 7.

2.1.1 The principle of LMR

When an external magnetic field $\mathcal{B}$, is applied to a free radical ¹, the energy levels of that radical are split into Zeeman components which are shifted from the zero field energy E_0 according to,

$$E = E_0 + g_J \mu_B \mathcal{B} M_J \quad (2.1)$$

¹Here a free radical is any molecule possessing an unpaired electron spin

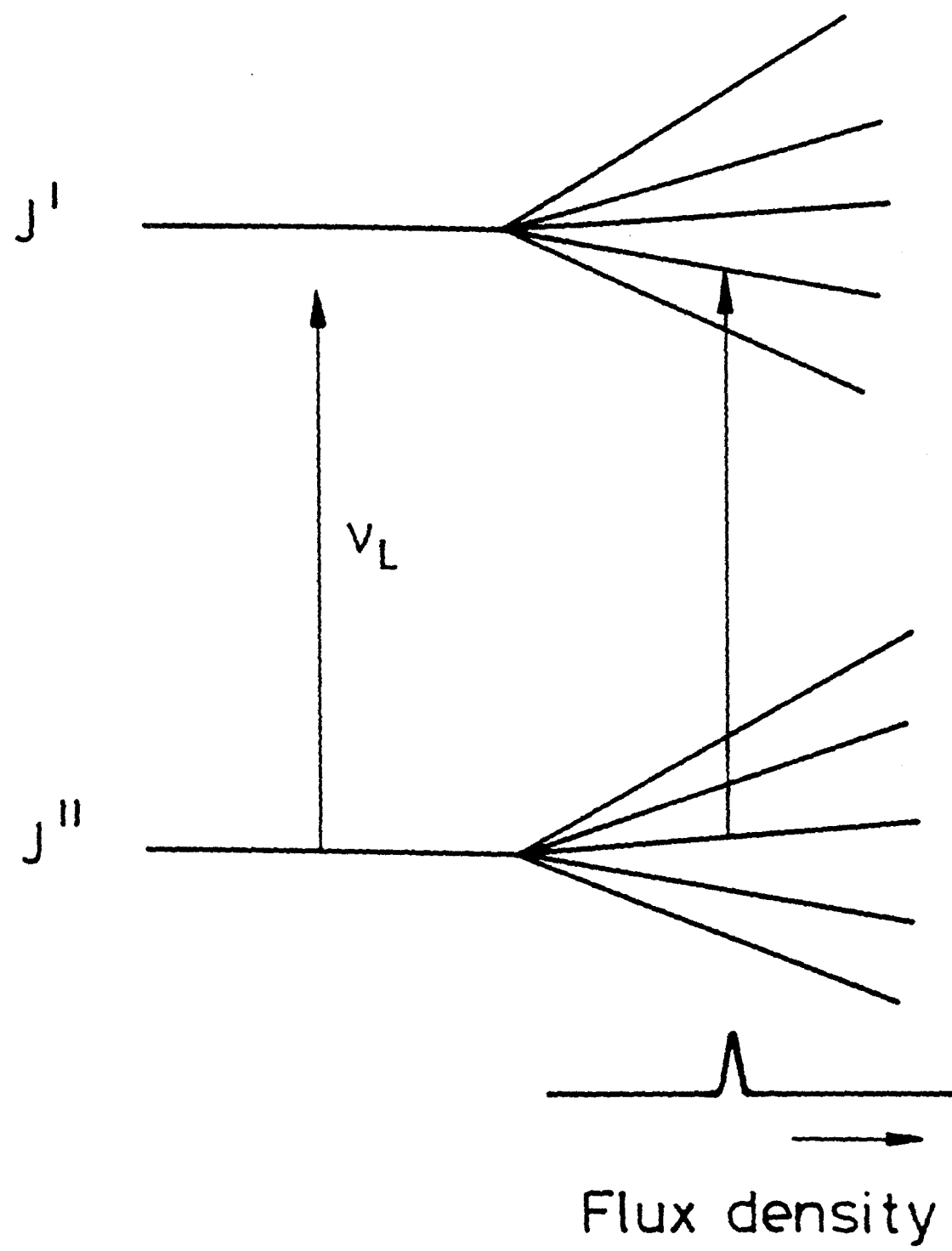


Figure 2.1: A Resonance

where g_J is the gyromagnetic ratio of the level J , and M_J is the projection of the rotational quantum number along the external field direction. When the difference in energy between two Zeeman components is equal to a fixed laser wavenumber, the power of the laser is attenuated, and this is recorded as a signal (see figure 2.1). The resonance condition can be written as,

$$\nu_L = \nu_0 + g'_J \mu_B \mathcal{B} M'_J - g''_J \mu_B \mathcal{B} M''_J \quad (2.2)$$

where ν_L is the laser wavenumber, ν_0 is the zero field transition wavenumber, and ' and '' denote the upper and lower states respectively.

The M_J selection rule depends on the orientation of the electric vector $\mathcal{E}$ of the laser beam with respect to the magnetic field if;

- $\mathcal{E} \parallel \mathcal{B}$ (π polarization) then $\Delta M_J = 0$ then equation 2.2 becomes,

$$\nu_L = \nu_0 + \Delta g_J \mu_B \mathcal{B} M''_J, \quad (2.3)$$

where $\Delta g_J = g'_J - g''_J$.

- $\mathcal{E} \perp \mathcal{B}$ (σ polarization) then $\Delta M_J = \pm 1$ then equation 2.2 becomes,

$$\nu_L = \nu_0 + \Delta g_J \mu_B \mathcal{B} M''_J \pm g'_J \mu_B \mathcal{B}. \quad (2.4)$$

2.1.2 Phase sensitive detection

In order to filter out $(1/f)$ noise from the laser phase sensitive detection is used on all three spectrometers described in this chapter.

If the amplitude of the Zeeman modulation applied is small compared with the linewidth of the absorption curve, the amplitude of the detector output is approximately proportional to the tangent of the absorption curve, see figure 2.2. The amplified detector output is then monitored by a lock-in amplifier at the modulation frequency ($1f$ detection), or at twice the modulation frequency ($2f$ detection). The lock-in amplifier then produces a d.c. output, which is proportional to the cosine of the phase difference between the amplified detector output and the modulation signal, for small modulation amplitudes. $1f$ detection gives the first derivative of the lineshape, and $2f$ gives the second derivative. Use of low modulation amplitudes allows resolution of narrow LMR signals, such as lamb dips, but will result in lower sensitivity. $1f$ detection is a more sensitive technique, but the noise level is higher, since it requires a lower modulation amplitude to obtain the optimum signal.

The choice of $1f$ or $2f$ detection will depend on:

1. The stability of the laser line, since as the laser noise falls off with $1/f$, $2f$ detection can give a better signal to noise ratio, for strong signals on noisy lines.
2. The intensity of the LMR signal, for weak signals on stable laser lines, $1f$ detection will give a better signal to noise ratio.

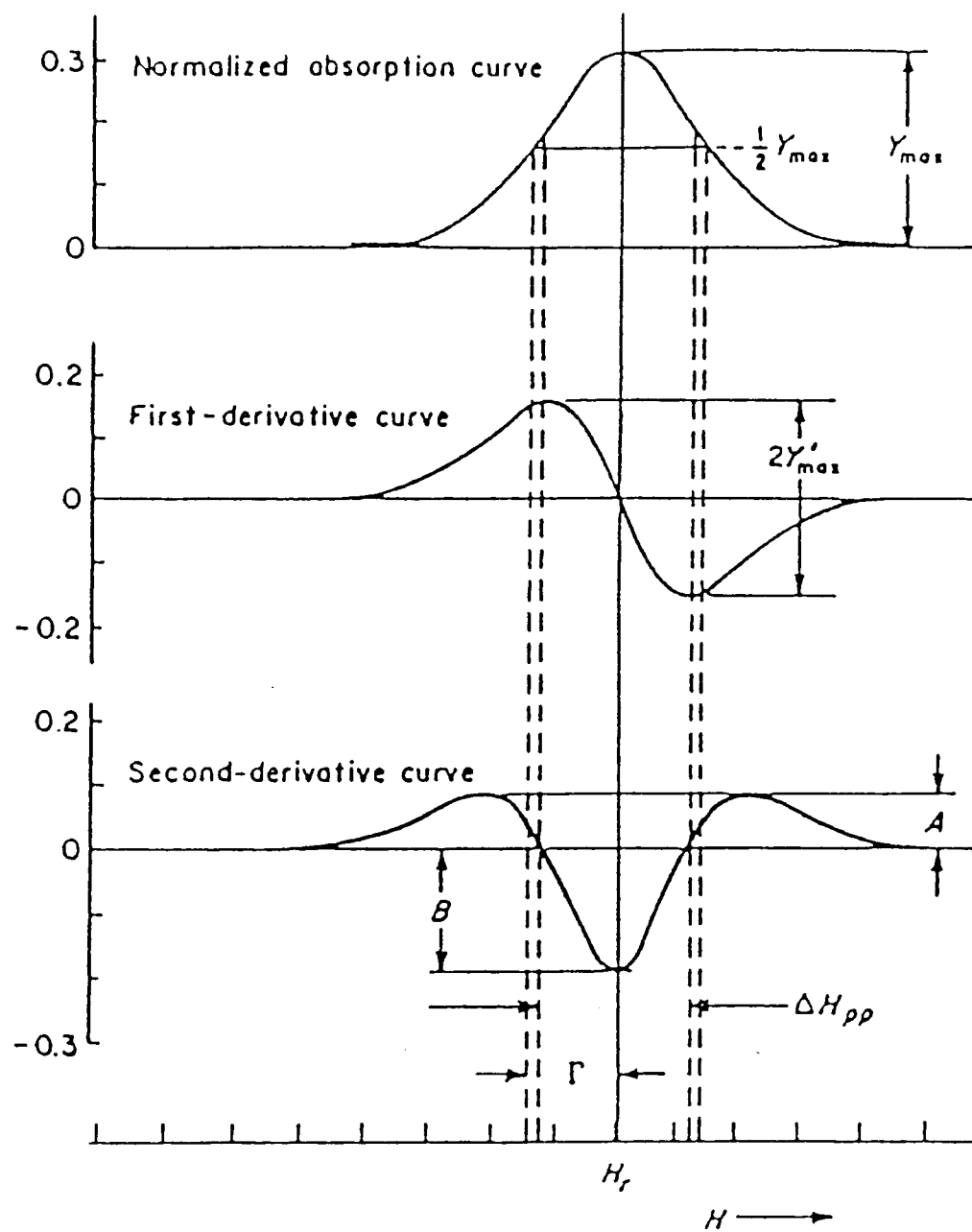


Figure 2.2: Phase sensitive detection

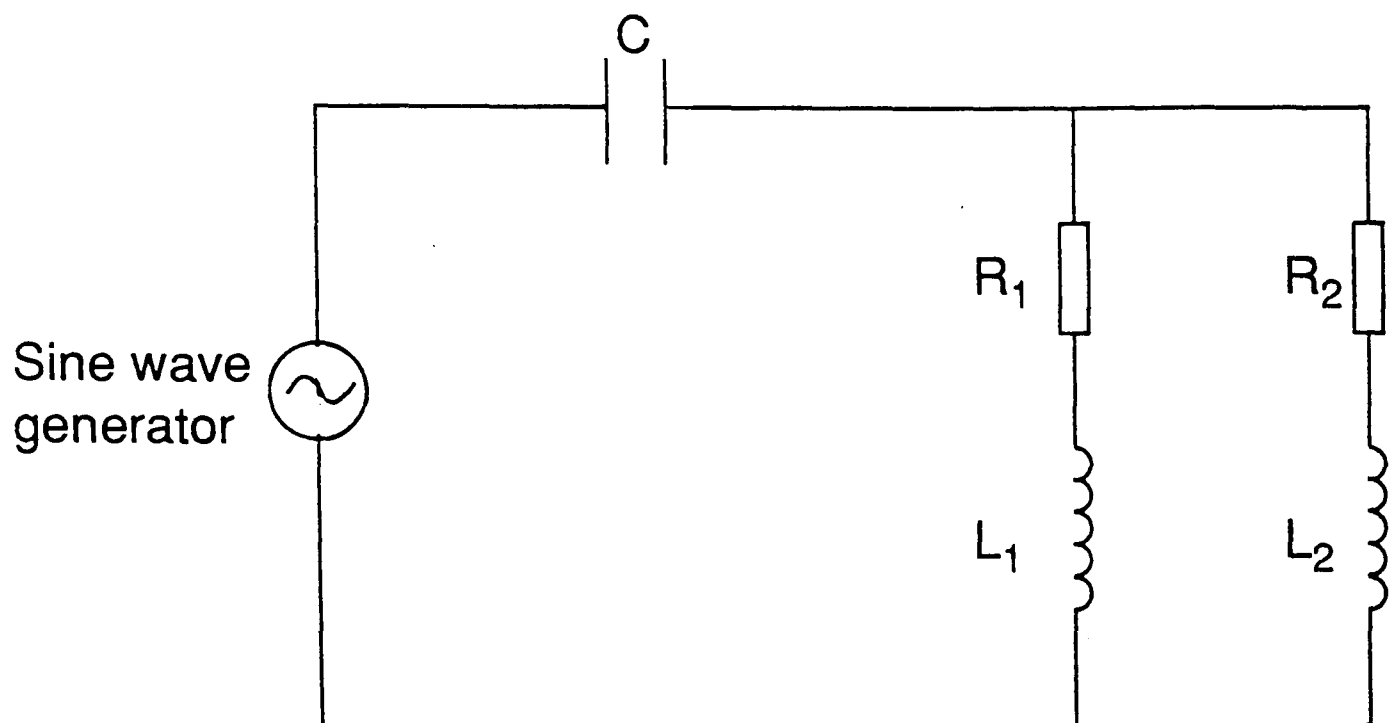


Figure 2.3: *LCR* circuit used for magnetic field modulation

2.1.3 Resonance in *LCR* circuits

For a resonant circuit [3], such as the one shown in figure 2.3, the quality factor Q is given by

$$Q = 2\pi \times \frac{\text{Energy stored}}{\text{Energy loss in one period}}. \quad (2.5)$$

For free standing coils,

$$Q = 2\pi \times \frac{\frac{1}{2}LI_0^2}{\frac{1}{2}RI_0^2t} \quad (2.6)$$

$$= \omega L/R \quad (2.7)$$

A typical current resonance curve is given as figure 2.4. In the case of a modulation circuit the inductance L and the resistance R are due to the coils attached to the polepieces of the magnet. Since the field at the centre of the coils is proportional to the number of turns on each former, for a circular coil,

$$B_z = \frac{n\mu_0 I a^2}{2(a^2 + z^2)^{\frac{3}{2}}}, \quad (2.8)$$

where n is the number of turns on the coil, I is the current, a is the radius of the coil and z is the perpendicular distance from the plane of the coil. Each turn adds to the resistance of the coil, and hence reduces the Q of the circuit. The coils are wired in parallel to reduce this effect.

The Q of the circuit is further reduced because the coils are attached to the pole pieces of a magnet. The energy loss in one period is greatly increased by:

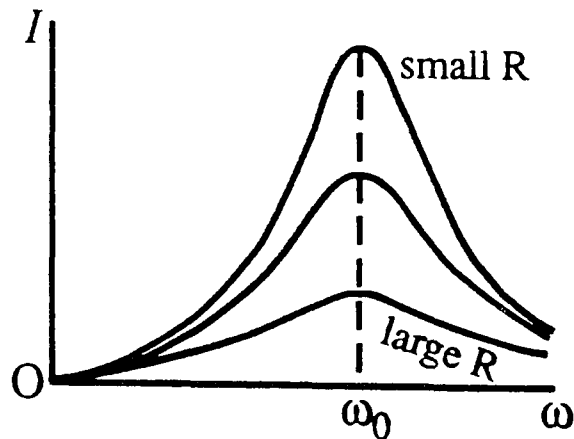


Figure 2.4: Resonance curve for LCR circuit

- hysteresis losses ($\propto f$)
- eddy current losses ($\propto f^2$),

hence the Q of the circuit is greatly reduced by increasing the modulation frequency. The noise of a CO laser [6], due to mechanical vibration, plasma inhomogeneities and power supply fluctuations decreases to a minimum of 2 kHz at higher wavenumbers. The modulation frequency should be selected to give a large enough modulation amplitude to make the spectrometers sufficiently sensitive to record weak broad signals, while avoiding the low kHz region.

In Oxford, because of the geometry of the magnet gap and reaction cell, it has been found to be advantageous to use oval coils. These are wound on copper formers which have been hollowed out to allow cooling water to flow through them. The copper formers are then mounted on circular perpex plates, which are bolted onto the pole pieces of the magnet in such a way that there is no short circuit between the former and the magnet, see fig 2.5. Due to the losses mentioned above it is difficult to calculate the amplitude of the modulation field. The field can, however, be measured *in situ* by suspending a search coil at the centre of the magnet gap. The field measured by the coil is given by,

$$B = \frac{V}{2\pi f A n}, \quad (2.9)$$

where V is the peak to peak voltage, measured on an oscilloscope, A is the area of the search coil and n is the number of turns. For the Oxford search coil,

$$B = 1.979 \times 10^5 \times \frac{V}{f} \text{ Gauss.} \quad (2.10)$$

where V is in volts, and f in Hz. It has been found that the maximum modulation amplitude of 30 G peak to peak is achieved with coils with inductances

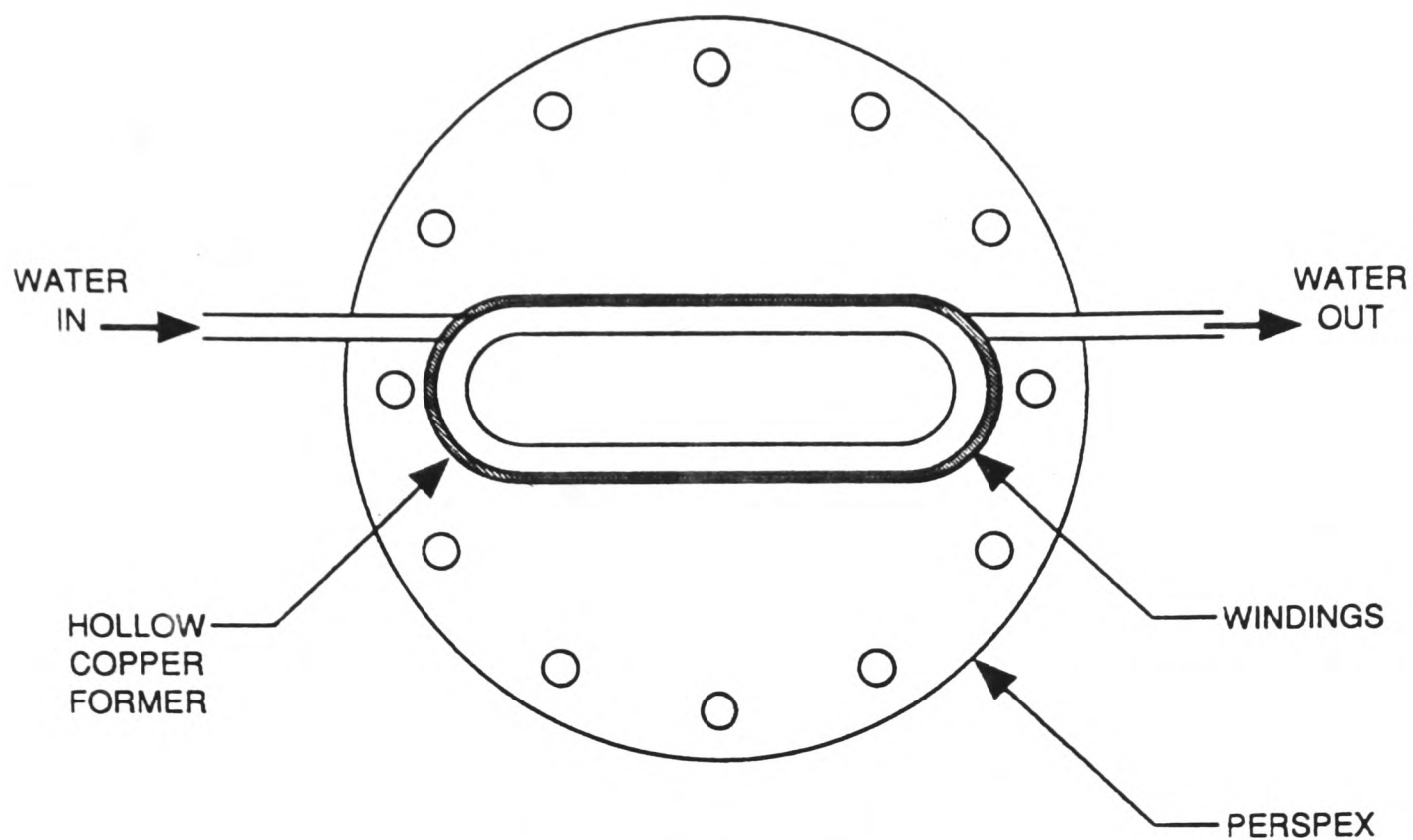


Figure 2.5: Modulation coils

of 4.48 mH and 4.58 mH and resistances of 7.3 Ω and 7.7 Ω with a capacitor of 239 nF, all measured at 1 kHz. This gives a resonant frequency of 3.5 kHz. Since 3.5 kHz is rather close to the laser noise of 2 kHz, $2f$ detection is mostly used.

2.2 The Oxford CO LMR Spectrometer

The Oxford intracavity absorption CO LMR spectrometer was designed and built by Robinson [4] and since that time several improvements have been made which are detailed below. A side view of the spectrometer is shown in figure 2.6.

2.2.1 The CO Laser

The radiation source for this spectrometer is a liquid nitrogen cooled CO laser described by Urban [5]. The CO laser gives line tunable radiation from 1250 to 2120 cm^{-1} (4.8 to 8.3 μm) when operating on CO transitions involving $\Delta v = 1$, and from 2460 to 3500 cm^{-1} (2.8 to 4.0 μm) when operating on CO transitions involving $\Delta v = 2$. The CO molecule has a deep potential well containing more than 50 bound vibrational states, figure 2.7. The principal mechanisms for exciting CO are:

1. Inelastic collisions between electrons and CO molecules producing CO^- . The CO^- then autoionizes leaving vibrationally excited CO. This process only populates vibrational levels up to $v = 8$.

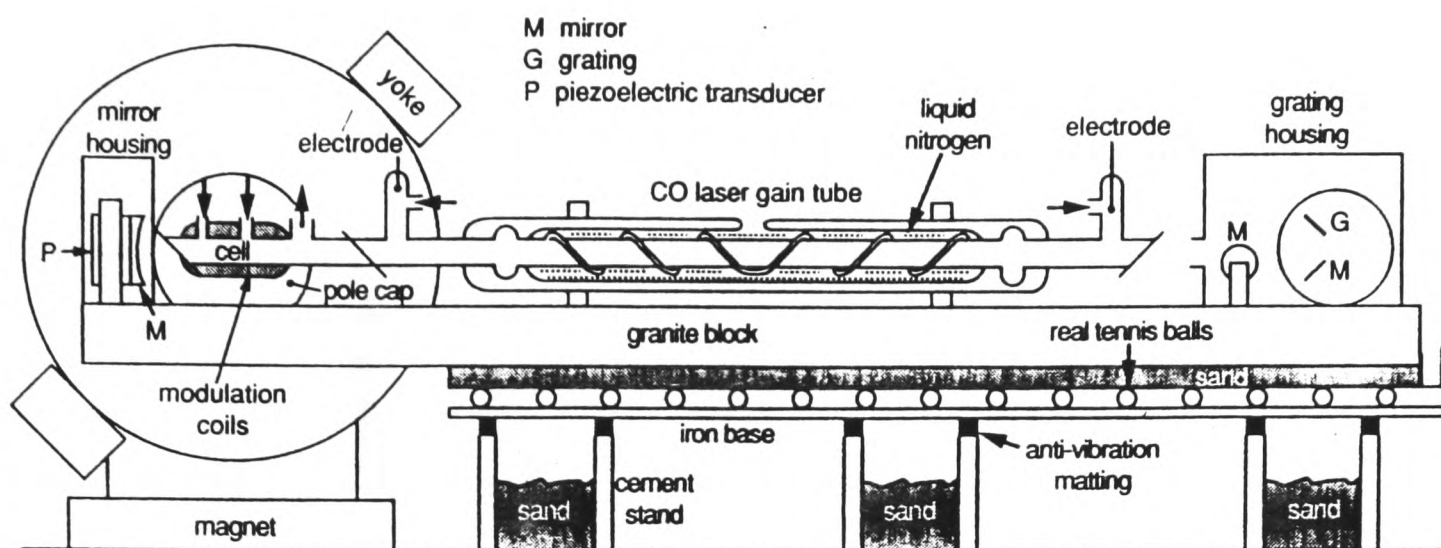


Figure 2.6: A side view of the carbon monoxide LMR spectrometer used in this work. The laser is mounted on a granite beam which projects through the electromagnet's gap and which is isolated from building vibrations. The laser cavity is formed by a gold-coated mirror at the magnet end and a highly reflecting diffraction grating at the other. The laser plasma is cooled close to liquid nitrogen temperatures to increase its gain. The sample cell is located within the laser cavity.

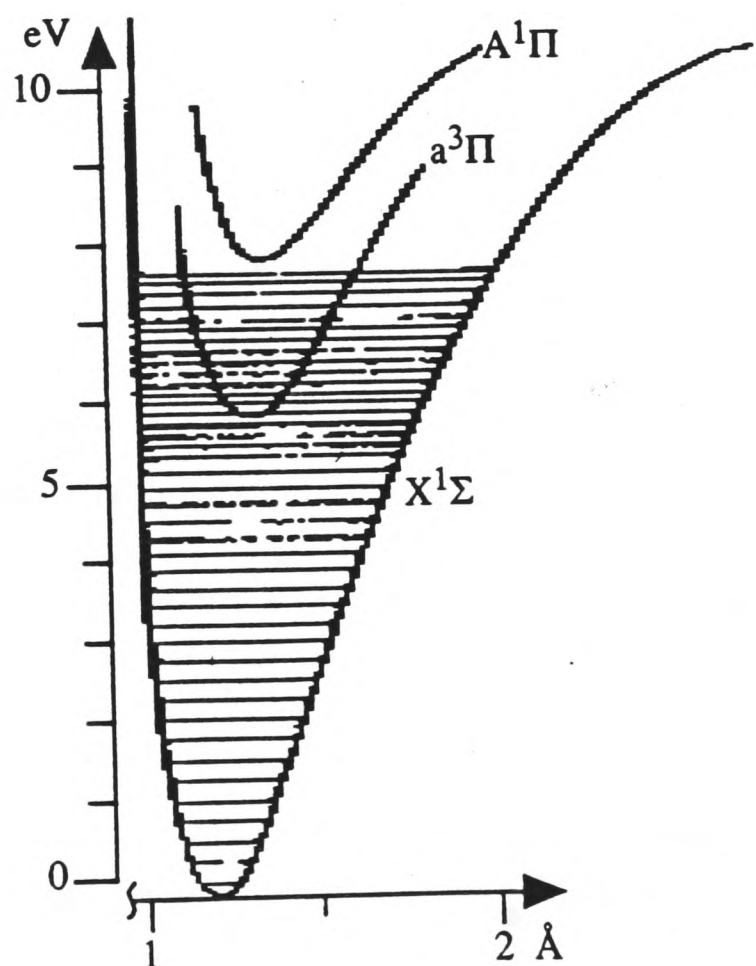


Figure 2.7: The potential curve of the CO molecule

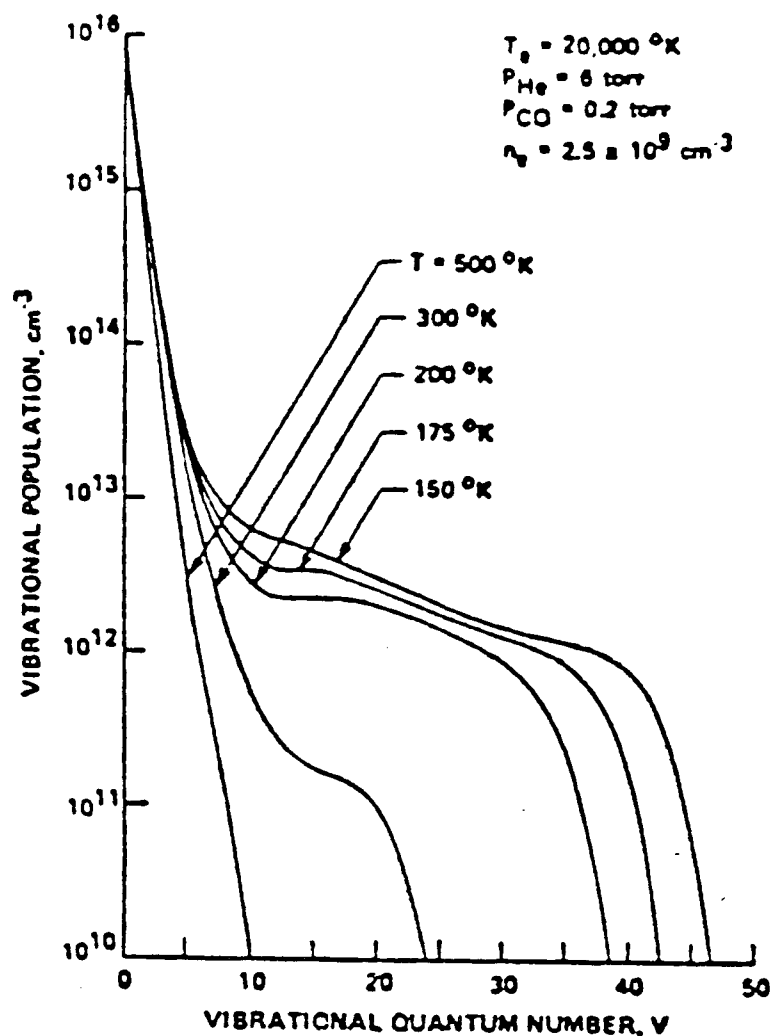
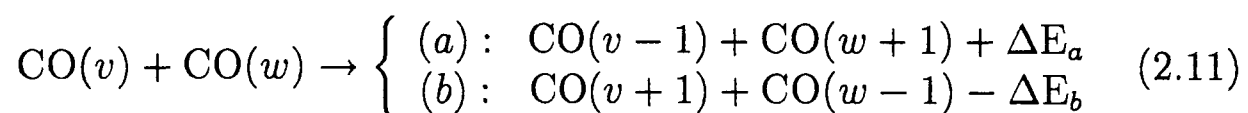


Figure 2.8: The vibrational population distribution in a liquid nitrogen cooled CO plasma.

2. Treanor (or $v - v$) pumping. If two CO molecules collide one in vibrational state v the other in state w with $w > v$, a vibrational quantum can be transferred from one to the other,



The energy differences ΔE_a and ΔE_b are due to the anharmonicity of the potential curve, figure 2.7. Path (a) is exothermic, while path (b) is endothermic, so ΔE_a goes into a translational degree of freedom, and ΔE_b has to be taken from the thermal reservoir. Once the difference $w - v$ becomes large enough, the anharmonicity defect ΔE_b becomes larger than the available thermal energy, so that path (a) will prevail.

3. Treanor pumping with nitrogen. Nitrogen has a similar vibrational structure to CO and so can also be involved in Treanor pumping.

These processes lead to the vibrational distribution shown in figure 2.8 which corresponds to a vibrational temperature of 40000 K. The gain tube is immersed in liquid nitrogen, giving the gain medium a rotational temperature

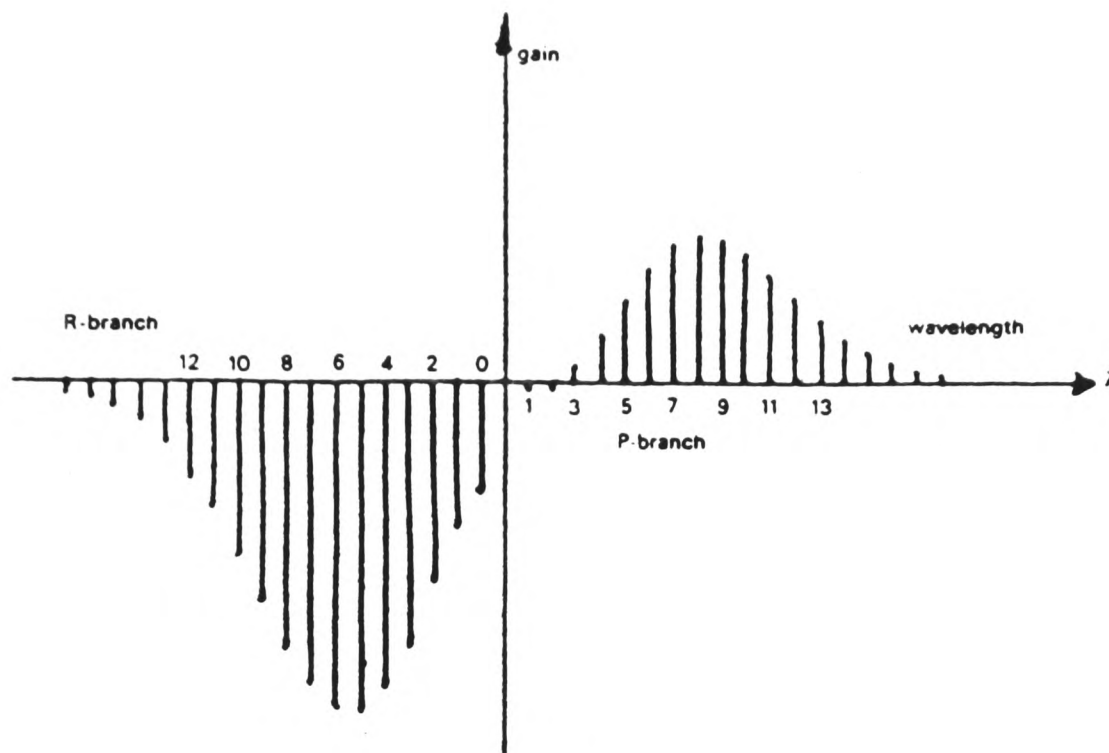


Figure 2.9: Gain distribution for a CO plasma with $N_{v+1}/N_v = 0.92$ at $T=120$ K

of, $T_{\text{rot}} \sim 120$ K. The discrepancy in vibrational and rotational temperatures leads to a “partial inversion” of adjacent vibrational states. This partial inversion leads to gain on some P-branch transitions, see figure 2.9. The rotational temperature affects the J value at which the maximum gain will occur. The vibrational distribution tends to control the lowest J value for which gain is present. These temperatures are controlled by the composition of the laser plasma, and by the discharge current through the plasma.

The major component of the gas of the lasing medium is helium, which supports the discharge and conducts heat to the walls of the discharge tube. Nitrogen is also present in the plasma, it has vibrational frequencies slightly higher than CO, and so can transfer energy into the lasing medium by collision. A high nitrogen content favours population of low v states of CO. Oxygen is an essential part of the plasma. Oxygen reduces the electron temperature shifting it to the region that favours vibrational CO excitation. In order to populate high v states, a high CO content is needed in the discharge, and this causes dissociation of CO;



which will spoil the discharge. Oxygen will drive the equilibrium back towards CO. Too much oxygen in the plasma will act as a VT (vibrational energy to translational energy) relaxer for CO, and may also lead to the build up of ozone in the tube.

The most effective way to control the rotational temperature is by adjusting the current through the discharge. Low current increases the gain of low J

lines, while high current increases the gain of high J lines.

The laser is tuned by rotating the diffraction grating in its Littrow mount shown in figure 2.10. The zeroth order reflection is coupled out to a detector mounted on a X-Y translator attached to the side of the grating box via the mirror system shown.

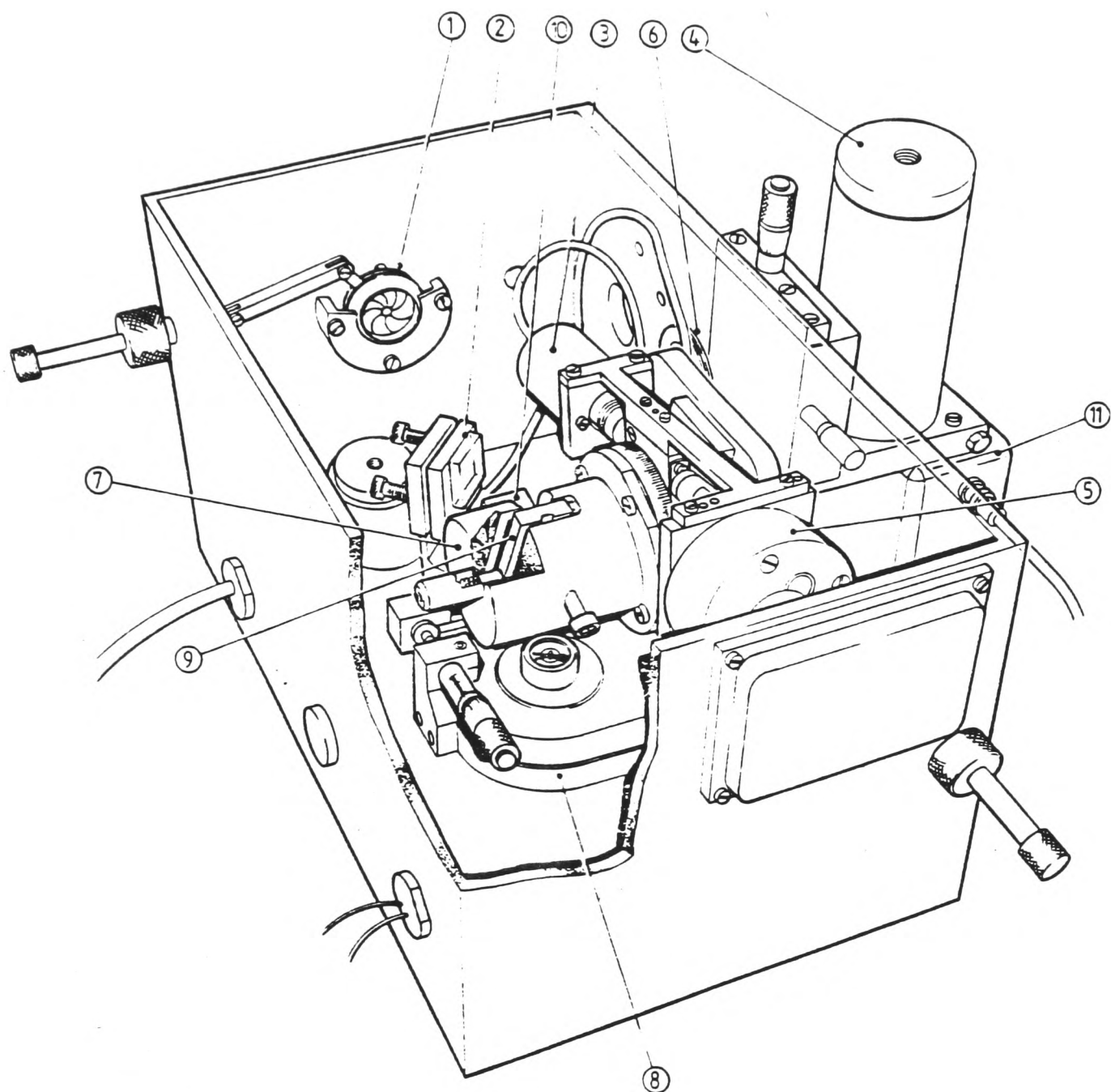
Details of the control system for the Oxford CO laser are shown in figure 2.11.

The laser is kept locked to the top of its gain profile by monitoring the detector output with a model 80.215 Lansing lock-in stabiliser. The Lansing unit forms a negative feed-back loop adjusting the laser end mirror using a piezo-electric transducer, see figures 2.11 and 2.12. Zeeman tuning of the radicals produced in the absorption cell is provided by a 15" Varian electromagnet, (with a range of 0 to 1.6 T), controlled by a Brücker B-H15 field controller. In order to filter out low frequency ($1/f$) noise from the laser, phase sensitive detection is used, see figure 2.12. This is achieved by superimposing an a.c. field on the steadily increasing (or decreasing) magnetic field, using a pair of coils wound on water cooled formers bolted to the pole pieces of the Varian magnet. The modulation field has an amplitude of 30 Gauss (peak to peak) at a frequency of 3.5 kHz. The amplified detector output is then monitored at the modulation frequency ($1f$ detection) or twice the modulation frequency ($2f$ detection) by an EG & G 5209 lock-in amplifier. The output of the lock-in is sent to a chart recorder and to the micro-computer which is simultaneously monitoring the B-H15, see figure 2.12.

2.3 The CO Faraday LMR Spectrometer at Bonn

The Faraday LMR at Bonn shown in figure 2.13 was used to record the FeH transitions reported Chapter 6 and by Zimmermann *et al.* [8] to record some of the GeD data used in Chapter 4. The radiation source is a CO laser, identical to the one used in Oxford, see section 2.2. The laser radiation is coupled out as the zeroth order reflection from the grating. The beam is then be passed down the axis of a solenoidal cryomagnet. The reaction cell inside the bore of the cryomagnet is surrounded by a solenoidal modulation coil, which is cooled by gas boiling off liquid nitrogen. The laser beam passes through a polariser before entering the bore of the magnet and an analyser after the magnet, but before the detector. These are used to produce a Faraday signal.

An Acusto Optic Modulator (AOM), can be introduced into the laser beam, and when turned on, it shifts the laser frequency by 90.8 MHz. This can be used to determine not only the sign of the tuning rate of a particular



1 Inter Cavity Iris	7 Littrow Mount
2 Adjustable Mirror	8 Turntable with Micrometer Adjustment
3 Angle Encoder	9 Diffraction Grating
4 Detector on X-Y Mount	10 90° Gold Mirror
5 Motor to Drive Littrow Mount	11 Detector Amplifier
6 Detector Iris	

Figure 2.10: A detailed view of the grating box which forms one end of the carbon monoxide laser. The laser beam enters the box through the adjustable iris at the top of the diagram. The grating angle can be varied to select the laser line to be used.

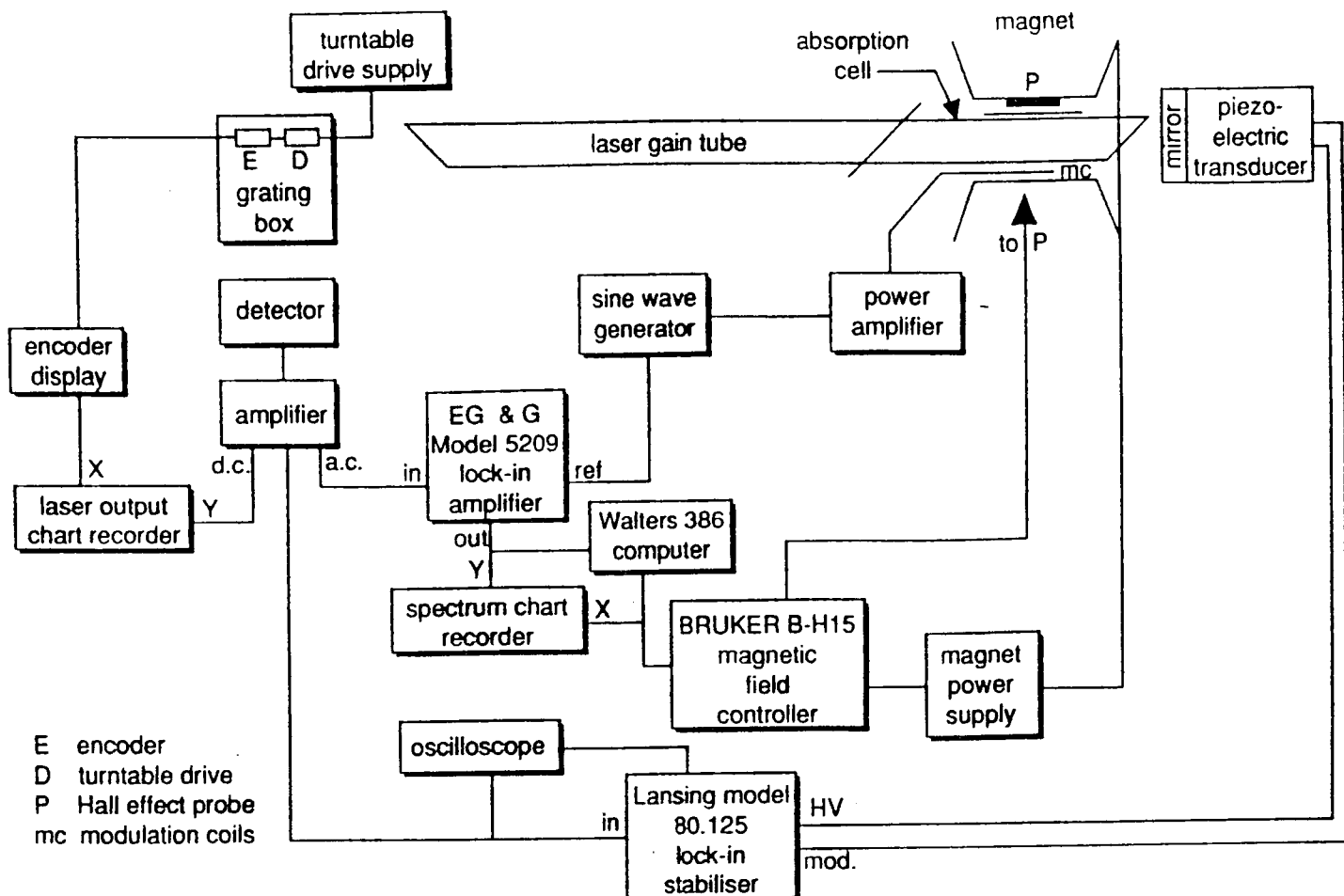


Figure 2.11: Block diagram showing the control system of the carbon monoxide LMR spectrometer.

transition, but an order of magnitude estimate of its magnitude as well.

2.3.1 The Faraday Effect

The Faraday configuration is shown in figure 2.14.

Linearly polarized light can be split into two circular components,

$$\mathcal{E} = \frac{1}{2} E_0 \exp[i(\omega t - kz)] \left[\begin{pmatrix} 1 \\ i \end{pmatrix} + \begin{pmatrix} 1 \\ -i \end{pmatrix} \right]. \quad (2.13)$$

When an LMR transition is induced, one of the components will be attenuated, depending on whether $\Delta M_J = \pm 1$, causing a rotation of the plane of polarization, and hence a change of intensity at the detector. Hinz *et al.* [9] define the complex propagation coefficients,

$$k_{\pm} = k_0(n_{\pm} - i\kappa_{\pm}). \quad (2.14)$$

As a resonance is scanned through, $n_{\pm}$, the refractive index, shows the behaviour of the dispersion curve and $\kappa_{\pm}$, the extinction coefficient show the absorption line shape. Hinz then shows that the intensity behind the analyser, for a small rotation of the analyser from the crossed position through an angle ϕ is,

$$I \simeq I_0[\phi^2 - \phi^2 k_0 l(\kappa_+ + \kappa_-) + \phi k_0 l(n_+ + n_-)], \quad (2.15)$$

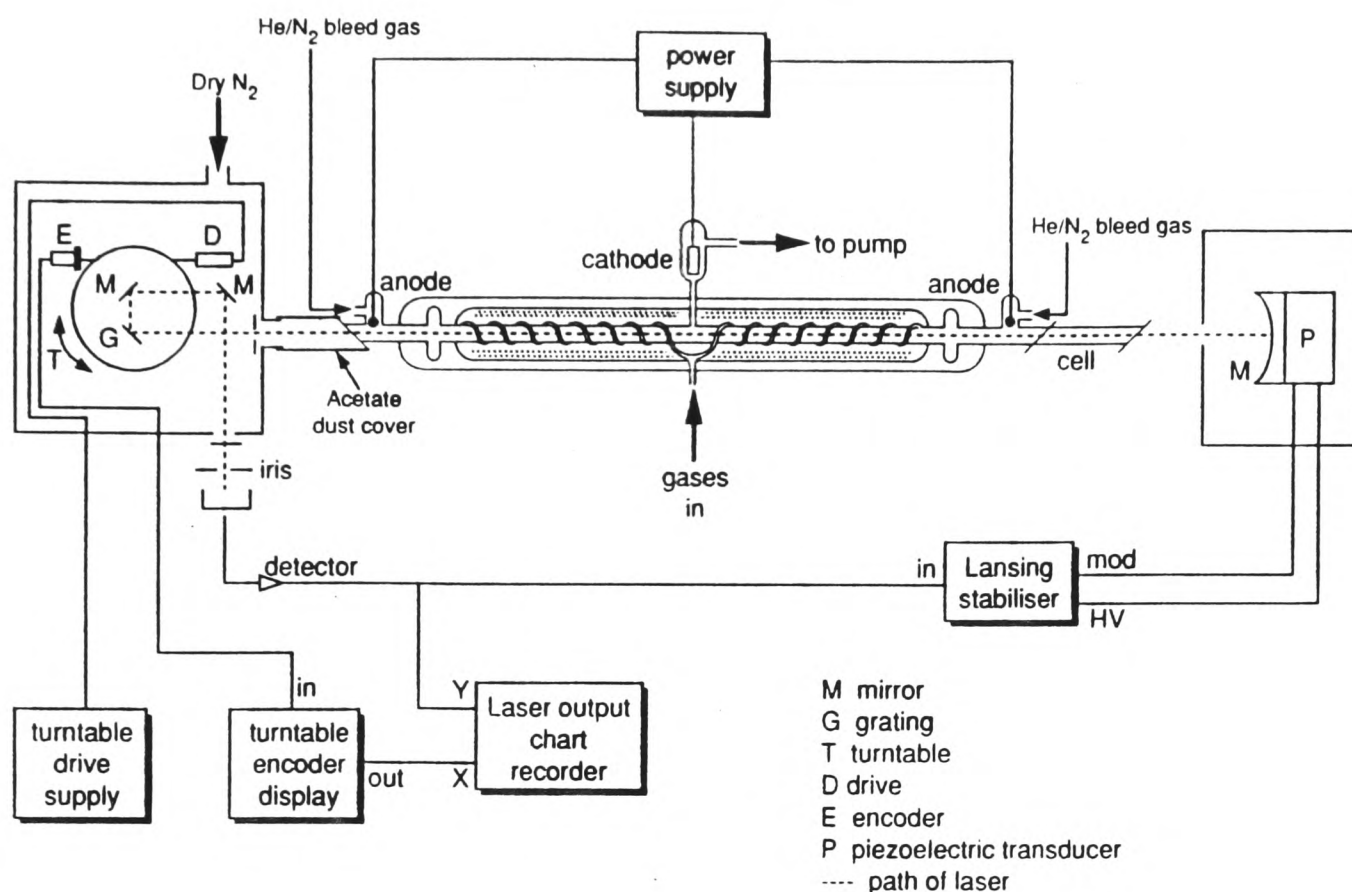


Figure 2.12: A schematic layout of the main components of the carbon monoxide laser used in the LMR spectrometer. The helium/nitrogen purge at either end of the laser tube is designed to reduce the amount of unexcited carbon monoxide in the laser cavity. It is crucial for the operation of the laser on the (2,1) and (1,0) bands.

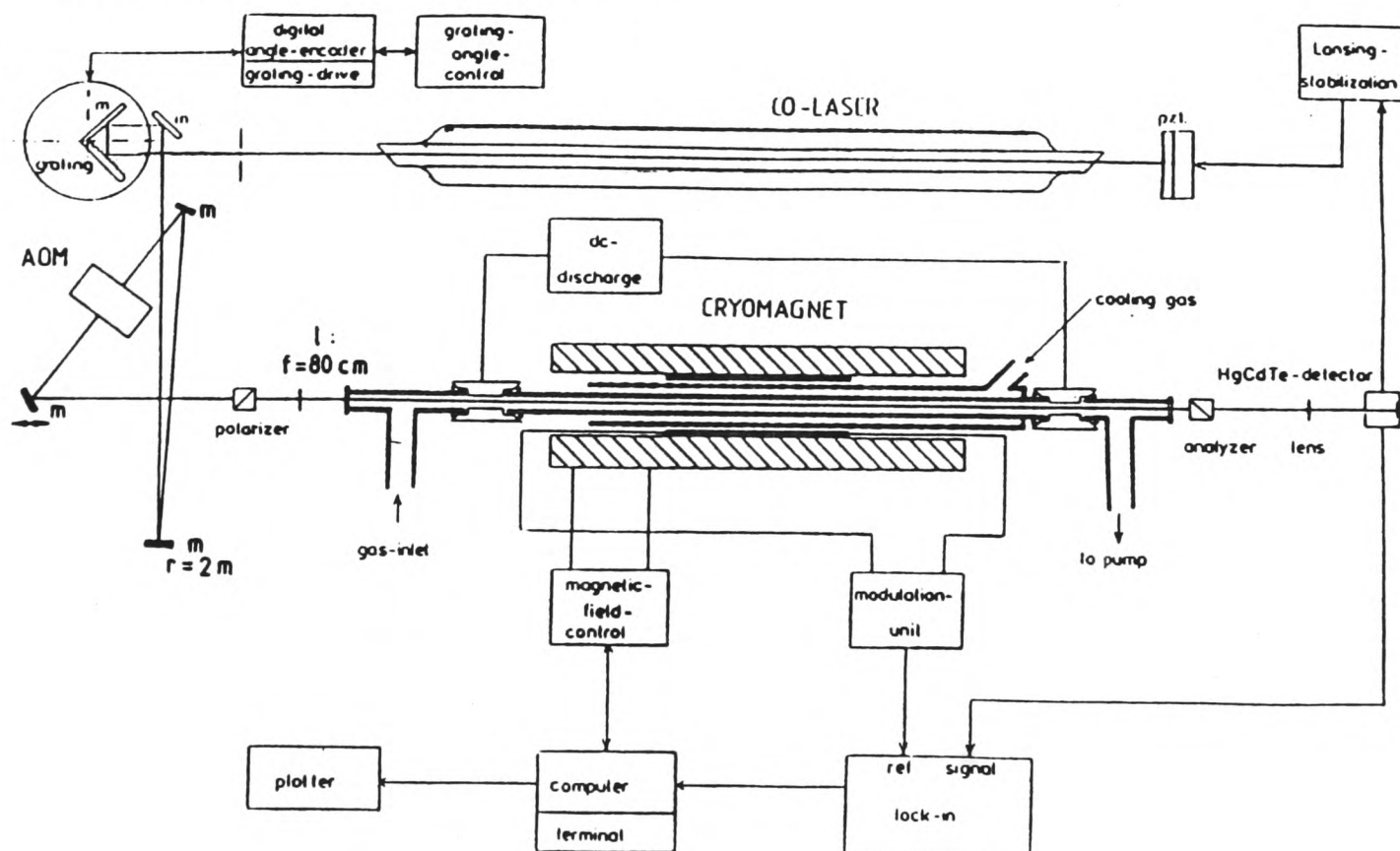


Figure 2.13: The CO Faraday LMR Spectrometer at Bonn

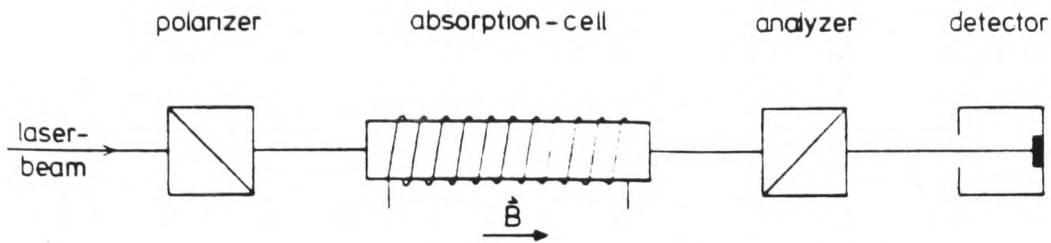


Figure 2.14: The Faraday Configuration

where l is the length active part of the absorption cell. The first term is the intensity through the analyser and so determines the laser noise at the detector. The second term is the absorption, which like the first term is reduced by ϕ^2 and is therefore negligible. The third term contains information about the Faraday rotation. At Bonn the analyser is rotated away from the cross position so that,

$$\frac{\delta\nu}{\delta B} \times \Delta M_J < 0 \Rightarrow \text{signal up} \quad (2.16)$$

$$\frac{\delta\nu}{\delta B} \times \Delta M_J > 0 \Rightarrow \text{signal down.} \quad (2.17)$$

This information, together with the tuning rates measured using the AOM can be used for assigning signals.

2.4 The NIST FIR LMR Spectrometer

Figure 2.15 is a schematic view of the spectrometer, designed by Dr. K. M. Evenson used to record the FeD spectra reported in this thesis. The FIR laser is pumped by a CO₂ laser, which operates from P or R(4) to P or R(40), and has a maximum power output of 35 W. The FIR cavity is defined by gold coated mirrors, which are 0.91 m apart and each have a focal length of 0.445 m. One of the mirrors is fixed, with the other mounted on a micrometer screw, which can be moved to optimise the length of the cavity for the required laser wavelength. Adjusting the length of the cavity, and hence shifting the laser frequency, can give the direction of the tuning rate of a signal, and this can help greatly with assigning the signal to a particular transition.

Two-thirds of the cavity volume are filled with the lasing gas. This is contained in a gold-lined Pyrex (pump) tube and pumped transversely by the CO₂ laser. Although the details of states involved in FIR laser action depend on the particular molecule, the mechanism which produces the population inversion is the same for all lines [7]. A particular vibrational absorption of the molecule,

$$(v'', J'') \rightarrow (v', J') \quad (2.18)$$

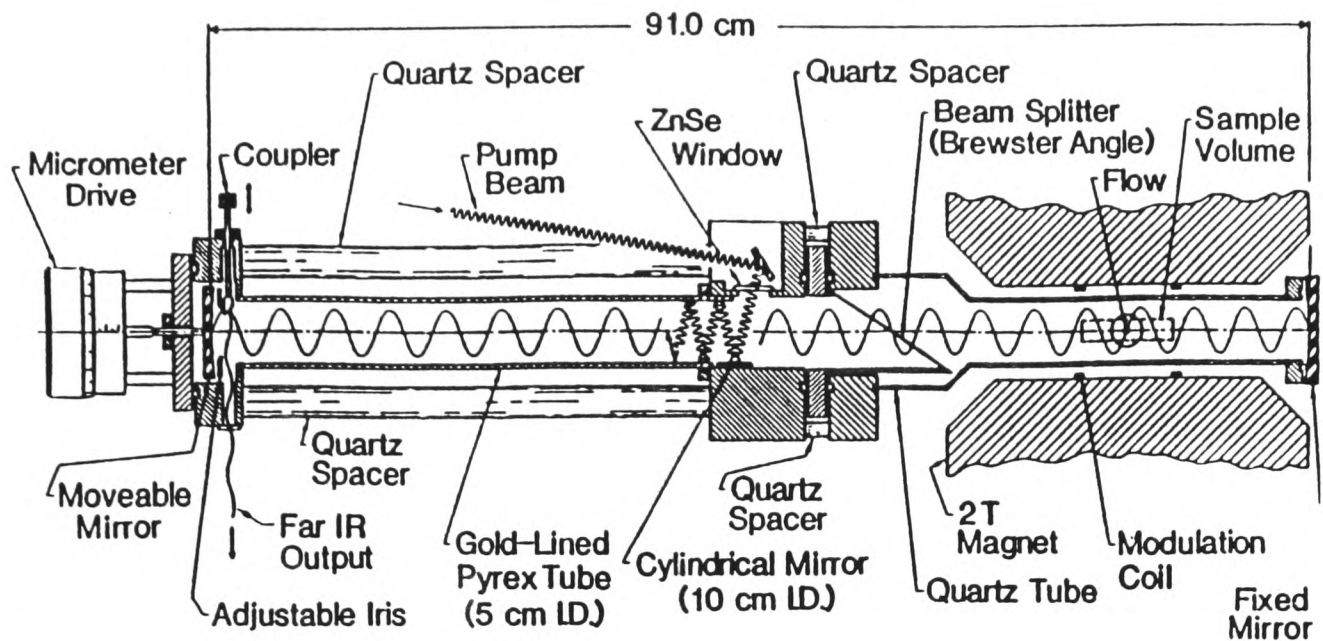


Figure 2.15: The NIST FIR LMR Spectrometer

is resonant with the radiation from the CO_2 pump laser. The population of the level (v', J') becomes much greater than that of $(v', J' - 1)$, which is only thermally populated. The molecule can then lase on the,

$$(v', J') \rightarrow (v', J' - 1) \quad (2.19)$$

transition. The molecule is then collisionally de-excited back to the (v'', J'') state.

A small fraction of the FIR laser power is coupled out by a 45° mirror (coupler) to a detector. There are two liquid helium cooled bolometers used at NIST, for $\lambda_L < 160\mu\text{m}$ the Ge detector is more sensitive; and for $\lambda_L > 160\mu\text{m}$ the InSb detector is more sensitive. This spectrometer has operated over 200 lines [10] between 0.3 and 4.7 THz (~ 1000 to $64\mu\text{m}$). Phase sensitive detection, see section 2.1.2 is used to record LMR signals.

The remainder of the cavity volume is separated from the lasing gas by a rotatable brewster window (beam splitter), made of polypropylene $\sim 5\mu\text{m}$. The beam splitter can be rotated to select π or σ transitions. The sample volume lies between the pole pieces of a 15" Walker electromagnet, which has a maximum field of 2 Tesla. Taped to the pole pieces of the magnet are a pair of Helmholtz coils which provide an a.c. modulation field driven at 14 kHz. Due to the narrower line width of rotational transitions (1 MHz) compared with ro-vibrational transitions (100 MHz), much smaller modulation fields are required. The modulation coils are therefore wound on small perspex formers with the only cooling being provided by still air. The d.c. magnetic field is measured by a rotating coil placed as near the sample volume as possible. The rotating coil is periodically calibrated against a proton NMR gaussmeter. Typically line centres can be measured to 0.5-1 G.

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Chapter 3

The Effective Hamiltonian

3.1 Introduction

A molecule is a collection of moving, charged, massive particles; electrons and nuclei. The full Hamiltonian (or energy matrix) of a molecule would by definition have to include terms due to all the electric and magnetic forces between these particles. It would be impractical to try to find analytical solutions of the full Hamiltonian even for the simplest molecules. To overcome this problem some approximations are made.

The Born-Oppenheimer approximation [1] allows Schrödinger's equation section 3.1.2 to be solved for the electrons moving in a stationary nuclear potential. Since the electrons are significantly lighter than the nuclei in a molecule, when the nuclei move the electrons instantaneously adjust to the new nuclear position. The breakdown of the Born-Oppenheimer approximation is discussed in section 3.10.3. The Van Vleck transformation [2] may be used to separate of the rotational energy of the molecule from its vibronic (vibrational+electronic) energy to give an operator which represents the energy levels of a single vibrational state

$$\mathcal{H} = \mathcal{H}_{ev} + \mathcal{H}_{rot}. \quad (3.1)$$

As a first approximation the rotational levels of a single electronic state are treated as having no coupling to other electronic states. This separation is only an approximation but where it breaks down, for example in Λ -doubling, the corrections to the Hamiltonian are usually small second order contributions, see section 3.6.

When constructing the effective Hamiltonian two important departures from classical electrodynamics must be taken into account;

1. The mass and size of molecules are so small that it is necessary to use quantum operators.

2. The particles in the molecule, especially the light electrons, are moving with velocities which are a significant fraction of the speed of light. Relativistic effects such as electron spin angular momentum are therefore important.

The effective Hamiltonian ($\mathcal{H}_{eff}$) is constructed by partitioning the contributions to the energy of the molecule and then summing them

$$\mathcal{H}_{eff} = \mathcal{H}_{rot} + \mathcal{H}_{so} + \mathcal{H}_{cd} + \mathcal{H}_{ld} + \mathcal{H}_{hfs} + \mathcal{H}_{sr} + \mathcal{H}_z + \mathcal{G}_v \quad (3.2)$$

where $\mathcal{H}_{rot}$ is the rotational energy term

$\mathcal{H}_{so}$ is the spin-orbit coupling term

$\mathcal{H}_{cd}$ is the centrifugal distortion term

$\mathcal{H}_{ld}$ is the lambda doubling term

$\mathcal{H}_{hfs}$ is the nuclear hyperfine interaction term

$\mathcal{H}_{sr}$ is the spin-rotation coupling term

$\mathcal{H}_z$ is the Zeeman interaction term

$\mathcal{G}_v$ is the vibrational energy term

All the terms in equation 3.2 are physically derivable, so that its parameters determined from experimental data are only prejudiced by the statistics of the data. This form of the effective Hamiltonian is sufficiently complete that when its parameters are fitted to the experimental data for GeH and TeH in this thesis, they can be used to calculate transition wavenumbers to within experimental accuracy. This is not true for the FeH data presented, which is treated in a different manner. This is because there are many close low-lying states of FeH which perturb each other. All the data for GeH and TeH involve $^2\Pi$ states, and both molecules are good approximations to Hund's case (a) [11], so that in the remainder of this chapter the terms in equation 3.2 will be derived for a molecule in a $^2\Pi$ state using a Hund's case (a) basis set. There are terms due to effects such as spin-spin coupling ($\mathcal{H}_{ss}$) which need to be included in a more general effective Hamiltonian, but as they are zero for $^2\Pi$ states, these have been omitted from equation 3.2.

3.1.1 Hund's coupling cases

Hund considered five limiting cases ((a) to (e)) for the coupling of angular momenta within a diatomic molecule. Most real molecules in lower electronic states show coupling that approximates to case (a) or (b). All the molecules studied in this thesis including FeH conform to case (a) coupling.

In Hund's case (a) the electronic orbital angular momentum $\mathbf{L}$ is coupled by the strong electrostatic axial internuclear field to the molecular axis. The spin-orbit ($L-S$) coupling is sufficiently strong to constrain the total electron

spin $\mathbf{S}$ to interact strongly with the axial field of the molecule. Thus the projections of $\mathbf{L}$ and $\mathbf{S}$ on the internuclear axis, Λ and Σ , are well defined quantities, “good quantum numbers”. We can define Ω

$$\Omega = \Lambda + \Sigma \quad (3.3)$$

Since Λ and Σ are good quantum numbers, Ω is also a good quantum number. The rotational angular momentum of the molecule $\mathbf{R}$ is perpendicular to the internuclear axis and hence to Ω , the component of $\mathbf{J}$ along the internuclear axis. The total angular momentum (excluding nuclear spin) is,

$$\mathbf{J} = \mathbf{L} + \mathbf{S} + \mathbf{R} \quad (3.4)$$

3.1.2 Schrödinger’s equation

In order to understand molecular spectra it is helpful to calculate the relative energies of the levels involved in the transitions which give rise to the observed spectrum. The energy of a state of a molecule is given by Schrödinger’s equation [12]

$$\mathcal{H}\Psi = E\Psi \quad (3.5)$$

For most practical applications the eigenvalues (E) of the effective Hamiltonian matrix are found by numerical diagonalization on fast electronic computers.

3.1.3 The Hamiltonian Matrix

For a molecule in a $^2\Pi$ state there are two possible values of Ω , “spin components”, $\frac{3}{2}$ and $\frac{1}{2}$. These arise from the two possible orientations of $\mathbf{L}$ and $\mathbf{S}$ with respect to the internuclear axis. Using a $|J \Omega\rangle$ basis set the Hamiltonian has the form:

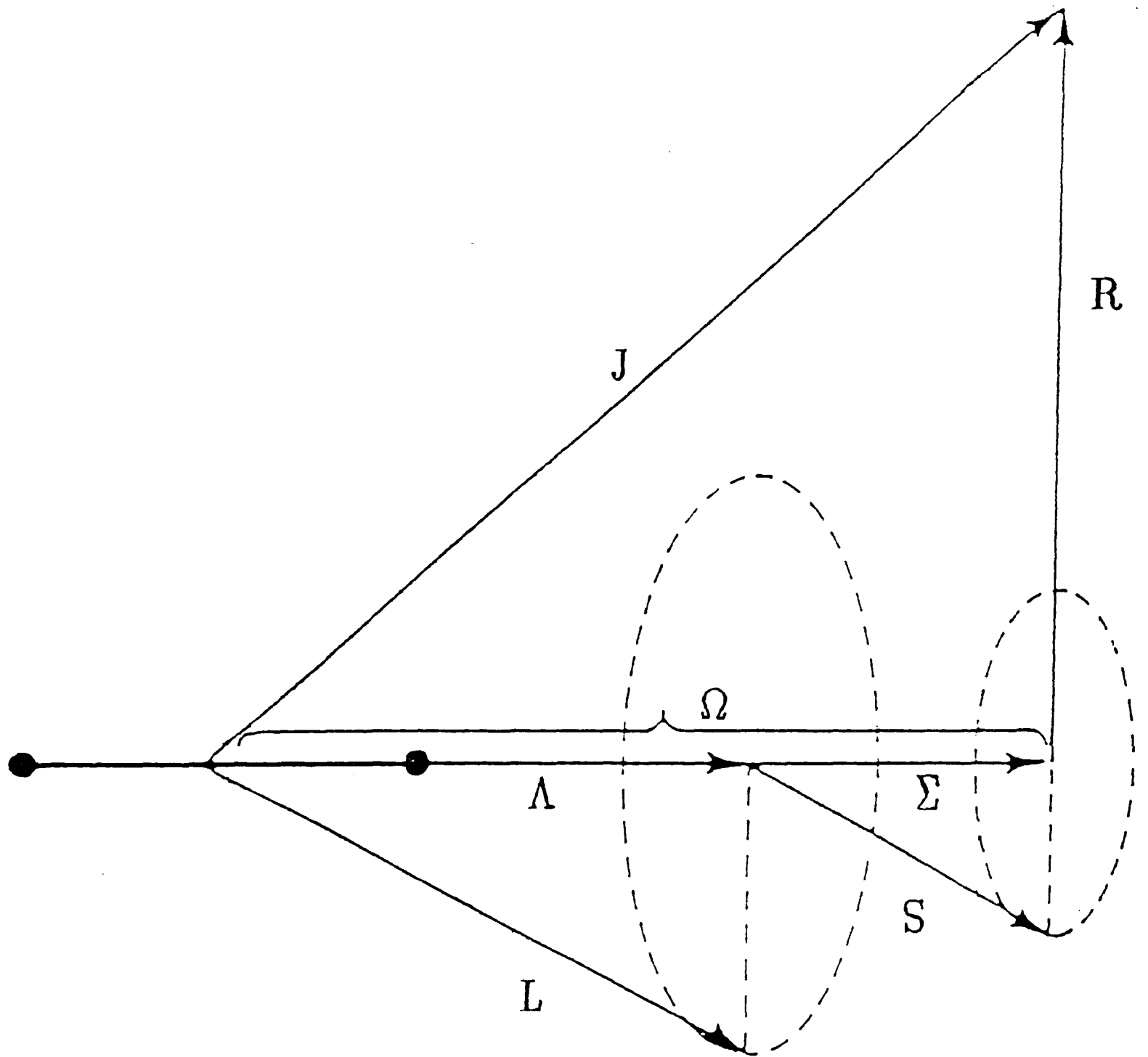
$$\mathcal{H} = \begin{pmatrix} \langle J \frac{3}{2} | \mathcal{H} | J \frac{3}{2} \rangle & \langle J \frac{3}{2} | \mathcal{H} | J \frac{1}{2} \rangle \\ \langle J \frac{1}{2} | \mathcal{H} | J \frac{3}{2} \rangle & \langle J \frac{1}{2} | \mathcal{H} | J \frac{1}{2} \rangle \end{pmatrix} \quad (3.6)$$

The Hamiltonian is an hermitian operator [10] and therefore the Hamiltonian matrix is symmetric.

3.2 The rotational Hamiltonian

Classically, the rotational kinetic energy of a rigid body is

$$E_{rot} = \frac{P^2}{2I} \quad (3.7)$$



where I is the moment of inertia and P is the angular momentum of the body. In order to convert this expression to a quantum system the angular momentum P must be replaced by an angular momentum operator,

$$\mathbf{P} \rightarrow \hbar \mathbf{R} \quad (3.8)$$

in 3.7.

The form of angular momentum operator has been a matter for debate [3]. $\mathbf{R}$ defined as

$$\mathbf{R} = \mathbf{J} - \mathbf{L} - \mathbf{S} \quad (3.9)$$

where $\mathbf{R}$, $\mathbf{J}$, $\mathbf{L}$, $\mathbf{S}$ are defined in section 3.1.1 is the correct form. However $\mathbf{L}$ does not have well defined matrix elements, so when calculating the matrix representation, either the elements involving $\mathbf{L}$ can be ignored or the $\mathbf{N}^2$ Hamiltonian introduced, where

$$\mathbf{N} = \mathbf{J} - \mathbf{S}. \quad (3.10)$$

For the rest of this chapter the $\mathbf{N}^2$ formalism will be used. Substituting $\mathbf{N}^2$ in 3.7 we write

$$\mathcal{H}_{rot} = B\mathbf{N}^2 \quad (3.11)$$

This expression has been rigorously derived by Howard and Moss [4]. B is the “rotational constant”,

$$B = \frac{\hbar}{4\pi c I} \quad (3.12)$$

in wavenumbers.

3.2.1 The vibrational dependence of the rotational constant

Since for vibrationally excited states of a diatomic molecule, the average inter-nuclear distance, r increases with the vibrational quantum number v and since

$$I = \mu r^2 \quad (3.13)$$

where μ is the reduced mass, the “rotational constant” has a vibrational dependence,

$$B_v = B_e + \alpha_B(v + \frac{1}{2}) + \beta_B(v + \frac{1}{2})^2 + \dots \quad (3.14)$$

B_v is the rotational constant in the vibrational state v , B_e is the equilibrium value for the rotational constant, calculated from substituting the equilibrium nuclear separation r_e in 3.13 and then 3.12. α_B and β_B are the first and second vibrational corrections to the rotational constant respectively.

In general the vibrational dependence of each parameter P_v is defined by the expression

$$P_v = P_e + \alpha_P(v + \frac{1}{2}) + \beta_P(v + \frac{1}{2})^2 + \dots \quad (3.15)$$

I believe this to be a logical extension of the formulae given in Herzberg's book [5].¹

3.2.2 The rotational Hamiltonian matrix

For a molecule approximating to Hund's case (a), section 3.1.1 N is not a good quantum number. However J and S are good quantum numbers so 3.11 can be rewritten as

$$\mathcal{H}_{rot} = B(\mathbf{J} - \mathbf{S})^2. \quad (3.18)$$

The components of $\mathbf{J}$ and $\mathbf{S}$ commute so that 3.18 expands to

$$\mathcal{H}_{rot} = B[J^2 + S^2 - 2(J_x S_x + J_y S_y + J_z S_z)]. \quad (3.19)$$

It is convenient to define the "ladder operators" [10].

$$J_{\pm} = J_x \pm iJ_y \quad (3.20)$$

$$S_{\pm} = S_x \pm iS_y \quad (3.21)$$

Equation 3.19 can then be written as

$$\mathcal{H}_{rot} = B[(J^2 + S^2 - 2J_z S_z) - (J_+ S_- + J_- S_+)] \quad (3.22)$$

In equation 3.22 the first set of terms are diagonal in Ω , whereas the terms involving the ladder operators are off diagonal in Ω ; for brevity these terms will be called $\mathcal{H}'$ and $\mathcal{H}''$ respectively. We now calculate the rotational elements of 3.6. For the diagonal elements,

$$\langle S \Sigma J \Omega | \mathcal{H}' | S \Sigma J \Omega \rangle = B[J(J+1) + S(S+1) - 2\Sigma\Omega] \quad (3.23)$$

¹Herzberg gives

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 + \dots \quad (3.16)$$

and

$$D_v = D_e + \beta_e(v + \frac{1}{2}) + \dots \quad (3.17)$$

on pages 106 and 107 of his book. In order to develop a general formula for a power series expansion in $(v + \frac{1}{2})$ with the minimum of confusion, it is preferable to use α , β , γ , etc. as the linear, quadratic, cubic, etc. coefficients. In our scheme therefore, Herzberg's γ_e is replaced by β_B and his β_e becomes α_D . Although there is good reason to define α_e , the vibrational correction to the rotational constant, with a negative sign as shown above (with this definition, the parameter always has a positive value for a diatomic molecule), there are no similar reasons for the other parameters. It seems less confusing therefore to define the parameter α_P with a positive sign in the power series expansion. Consequently, Herzberg's α_e becomes $-\alpha_B$, ie α_B is expected to be a negative quantity.

therefore

$$\langle J \frac{3}{2} | \mathcal{H}' | J \frac{3}{2} \rangle = B[J(J+1) - \frac{3}{4}] \quad (3.24)$$

and

$$\langle J \frac{1}{2} | \mathcal{H}' | J \frac{1}{2} \rangle = B[J(J+1) + \frac{5}{4}]. \quad (3.25)$$

To calculate the rotational off diagonal matrix elements of 3.6, the matrix elements of the ladder operators are required, from Mizushima [14],

$$\langle J \Omega \mp 1 | J_{\pm} | J \Omega \rangle = [(J \pm \Omega)(J \mp \Omega + 1)]^{\frac{1}{2}} \quad (3.26)$$

and

$$\langle S \Sigma \pm 1 | S_{\pm} | S \Sigma \rangle = [(S \mp \Sigma)(S \pm \Sigma + 1)]^{\frac{1}{2}} \quad (3.27)$$

therefore

$$\langle S \Sigma \pm 1 J \Omega \pm 1 | \mathcal{H}' | S \Sigma J \Omega \rangle = [(J \pm \Omega)(S \mp \Sigma)(J \mp \Omega + 1)(S \pm \Sigma + 1)]^{\frac{1}{2}} \quad (3.28)$$

giving

$$\langle \frac{1}{2} \frac{1}{2} J \frac{3}{2} | \mathcal{H}'' | \frac{1}{2} -\frac{1}{2} J \frac{1}{2} \rangle = -B[(J + \frac{3}{2})(J - \frac{1}{2})]^{\frac{1}{2}}. \quad (3.29)$$

If we define

$$z = (J + \frac{3}{2})(J - \frac{1}{2}) \quad (3.30)$$

then $\mathcal{H}_{rot}$ can be written as,

$$\mathcal{H}_{rot} = \begin{pmatrix} Bz & -Bz^{\frac{1}{2}} \\ -Bz^{\frac{1}{2}} & B(z+2) \end{pmatrix}. \quad (3.31)$$

3.3 Centrifugal Distortion

In section 3.2.1 the effect on the rotational constant of a change in inter-nuclear distance r due to vibrational excitation was discussed. The rotation of the molecule will also increase r due to centrifugal effects. The classical centrifugal force is defined as [5]

$$F_c = \frac{P^2}{\mu r^3} \quad (3.32)$$

Centrifugal effects will tend to decrease the effective rotational constant B_{eff} so we rewrite 3.11

$$\mathcal{H}_{rot} = B_{eff} \mathbf{N}^2 \quad (3.33)$$

then

$$\mathcal{H}_{rot} = (B - D\mathbf{N}^2)\mathbf{N}^2 \quad (3.34)$$

Due to anharmonic effects, for highly excited rotational levels higher order corrections become significant.

$$\mathcal{H}_{rot} = [B - D\mathbf{N}^2 + H(\mathbf{N}^2)^2 + L(\mathbf{N}^2)^3 + \dots]\mathbf{N}^2 \quad (3.35)$$

All the constants in equation 3.35 have the same vibrational dependence as B . For LMR transitions as the rotational quantum number J increases, the tuning rate decreases. Therefore equation 3.35 can be truncated to equation 3.34 for our purposes. An advantage of the $\mathbf{N}^2$ over the $\mathbf{R}^2$ formalism is that the effect of $\mathbf{N}^4$ acting on a basis function is the same as $\mathbf{N}^2$ acting twice on the function. However the effect of $\mathbf{R}^4$ acting on a basis function is not the same as $\mathbf{R}^2$ acting twice on the function, when projected onto a given electronic state. We can write,

$$\mathcal{H}_D = -D(\mathbf{N}^2)^2 \quad (3.36)$$

so that from equation 3.11

$$\mathcal{H}_D = -\frac{D}{B^2}[\mathcal{H}_{rot}]^2 \quad (3.37)$$

$$\mathcal{H}_D = -D \begin{pmatrix} z & -z^{\frac{1}{2}} \\ -z^{\frac{1}{2}} & z+2 \end{pmatrix} \begin{pmatrix} z & -z^{\frac{1}{2}} \\ -z^{\frac{1}{2}} & z+2 \end{pmatrix}. \quad (3.38)$$

giving

$$\mathcal{H}_D = -D(z+1) \begin{pmatrix} z & -2z^{\frac{1}{2}} \\ -2z^{\frac{1}{2}} & z+4 \end{pmatrix} \quad (3.39)$$

3.4 The Spin-Orbit Interaction

The orbital angular momentum of an electron is coupled to its spin via the interaction of the magnetic field produced by its orbital motion in the electric field of the nuclei and the electron's magnetic moment due to its spin.

$$\mathcal{H}_{so} = A\mathbf{L}\cdot\mathbf{S} \quad (3.40)$$

A is the “spin-orbit coupling constant”. This interaction depends on $\mathbf{S}$ and therefore Σ . From equation 3.3 ($\Omega = \Lambda + \Sigma$) we see that the interaction will change with Ω . In terms of Operators [15],

$$\langle \Lambda \ S \ \Sigma \ J \ \Omega | A\mathbf{L}\cdot\mathbf{S} | \Lambda \ S \ \Sigma' \ J \ \Omega' \rangle = A\Lambda\Sigma\delta_{\Sigma\Sigma'}, \quad (3.41)$$

So for matrix elements diagonal in Λ the spin orbit energy is diagonal in Ω . For a molecule in a ${}^2\Pi$ state the spin-orbit Hamiltonian matrix is,

$$\mathcal{H}_{so} = \begin{pmatrix} \frac{1}{2}A & 0 \\ 0 & -\frac{1}{2}A \end{pmatrix}. \quad (3.42)$$

3.4.1 Centrifugal Distortion to the Spin-Orbit Term

The centrifugal correction (A_D) to the Spin-Orbit coupling constant A is a measure of how A changes with inter-nuclear distance r . As r increases, the orbital electrons experience a different electric field. Since only terms diagonal in Λ are of interest, we can define,

$$\mathcal{H}_{A_D} = A_D L_z S_z \mathbf{N}^2 \quad (3.43)$$

$$\mathcal{H}_{A_D} = \frac{A_D}{AB} [\mathcal{H}_{so}] [\mathcal{H}_{rot}] \quad (3.44)$$

giving

$$\mathcal{H}_{A_D} = \frac{A_D}{2} \begin{pmatrix} z & -z^{\frac{1}{2}} \\ z^{\frac{1}{2}} & -(z+2) \end{pmatrix}. \quad (3.45)$$

This is not a symmetric matrix and so cannot represent an hermitian operator with real (observable) eigenvalues. This problem can be overcome by taking the hermitian average of $\mathbf{L} \cdot \mathbf{S}$, thus writing equation 3.43 as,

$$\mathcal{H}_{A_D} = \frac{1}{2} A_D (L_z S_z \mathbf{N}^2 + \mathbf{N}^2 L_z S_z) \quad (3.46)$$

so that 3.45 becomes

$$\mathcal{H}_{A_D} = \frac{A_D}{2} \begin{pmatrix} z & 0 \\ 0 & -(z+2) \end{pmatrix}. \quad (3.47)$$

3.5 The Spin-Rotation Interaction

The end over end rotation of the molecule produces a magnetic field. This is coupled to the electron's spin, mentioned in section 3.4. The Spin-Rotation interaction, is written as,

$$\mathcal{H}_{sr} = \gamma \mathbf{N} \cdot \mathbf{S}. \quad (3.48)$$

To calculate the matrix elements substitute $\mathbf{N} = \mathbf{J} - \mathbf{S}$ into 3.48, and recalling the derivation in 3.2

$$\mathbf{N} \cdot \mathbf{S} = J_z S_z - S(S+1) + \frac{1}{2}(J_- S_+ + J_+ S_-) \quad (3.49)$$

so that

$$[\mathbf{N} \cdot \mathbf{S}] = \begin{pmatrix} 0 & \frac{1}{2} z^{\frac{1}{2}} \\ \frac{1}{2} z^{\frac{1}{2}} & -1 \end{pmatrix}. \quad (3.50)$$

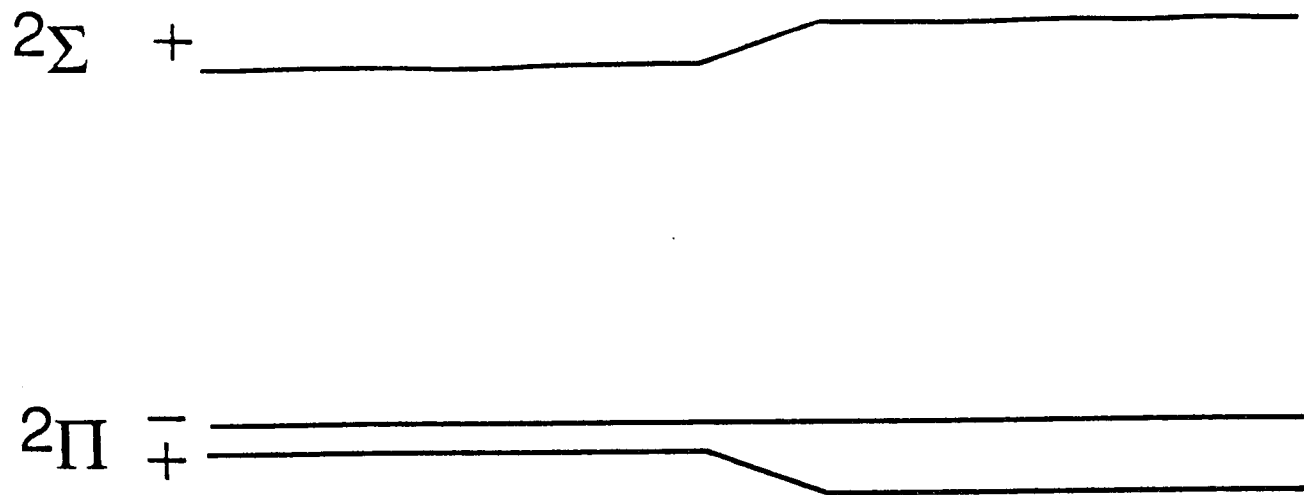


Figure 3.2: Λ -doubling

3.5.1 Centrifugal Distortion to the Spin-Rotation Term

As discussed in sections 3.3 and 3.4.1 it is necessary to introduce the first order centrifugal distortion correction to $\mathcal{H}_{sr}$

$$\mathcal{H}_{sr} = (\gamma + \gamma_D \mathbf{N}^2) \mathbf{N} \cdot \mathbf{S} \quad (3.51)$$

we can write the matrix elements of the term in parentheses as

$$\langle J \Omega | \gamma + \gamma_D \mathbf{N}^2 | J' \Omega' \rangle = (\gamma \delta_{\Omega\Omega'} + \gamma_D \langle J \Omega | \mathbf{N}^2 | J' \Omega' \rangle) \delta_{JJ'} \quad (3.52)$$

giving

$$[\gamma + \gamma_D \mathbf{N}^2] = \begin{pmatrix} \gamma + \gamma_D z & -\gamma_D z^{\frac{1}{2}} \\ -\gamma_D z^{\frac{1}{2}} & \gamma + \gamma_D(z+2) \end{pmatrix} \quad (3.53)$$

So that the Spin-Rotation matrix, including centrifugal distortion is,

$$\mathcal{H}_{sr} = \begin{pmatrix} \gamma + \gamma_D z & -\gamma_D z^{\frac{1}{2}} \\ -\gamma_D z^{\frac{1}{2}} & \gamma + \gamma_D(z+2) \end{pmatrix} \cdot \begin{pmatrix} 0 & \frac{1}{2} z^{\frac{1}{2}} \\ \frac{1}{2} z^{\frac{1}{2}} & -1 \end{pmatrix} \quad (3.54)$$

$$\mathcal{H}_{sr} = \begin{pmatrix} -\frac{1}{2} \gamma_D z & \frac{1}{2} z^{\frac{1}{2}} (\gamma + \gamma_D(z+2)) \\ \frac{1}{2} z^{\frac{1}{2}} (\gamma + \gamma_D(z+2)) & -\gamma - \frac{1}{2} \gamma_D(3z+4) \end{pmatrix}. \quad (3.55)$$

Both γ and γ_D have the vibrational dependence discussed in section 3.2.1.

3.6 Lambda Doubling

Λ -doubling arises from the parity dependence of the interaction between a $^2\Pi$ state and a Σ state [10]. The end over end rotation of the molecule causes $\mathbf{L}$ to be decoupled from the inter-nuclear axis. This interaction between the

rotational and electronic motions is a breakdown of the Born-Oppenheimer approximation [1]. If we write the rotational Hamiltonian ($\mathcal{H}_{rot}$) in terms of $\mathbf{R}^2$ instead of $\mathbf{N}^2$ we get

$$\mathcal{H}_{rot} = B\mathbf{R}^2 \quad (3.56)$$

$$\mathcal{H}_{rot} = B[\mathbf{J} - \mathbf{L} - \mathbf{S}]^2 \quad (3.57)$$

$$\mathcal{H}_{rot} = B[\mathbf{J}^2 + \mathbf{S}^2 + \mathbf{L}^2 + 2(\mathbf{L} \cdot \mathbf{S} - \mathbf{J} \cdot \mathbf{L} - \mathbf{J} \cdot \mathbf{S})] \quad (3.58)$$

$$\mathcal{H}_{rot} = B((\mathbf{J}^2 + \mathbf{S}^2 - 2J_z S_z) - (J_+ S_- + J_- S_+) + \mathbf{L}^2 - 2J_z L_z + 2\mathbf{L} \cdot \mathbf{S} - (J_+ L_- + J_- L_+)) \quad (3.59)$$

recalling section 3.4

$$\mathcal{H}_{so} = A\mathbf{L} \cdot \mathbf{S} = A(L_z S_z + \frac{1}{2}(L_+ S_- + L_- S_+)) \quad (3.60)$$

If we add equations 3.56 and 3.60 then we get two sets of terms,

$$\mathcal{H}' = B[(\mathbf{J}^2 + \mathbf{S}^2 - 2J_z S_z) - (J_+ S_- + J_- S_+) + \mathbf{L}^2 - 2J_z L_z] + AL_z S_z \quad (3.61)$$

and

$$\mathcal{H}'' = -B(J_+ L_- + J_- L_+) + \frac{1}{2}(A + 2B)(L_+ S_- + L_- S_+) \quad (3.62)$$

$\mathcal{H}'$ is similar to the Hamiltonian derived in sections 3.2 and 3.4 it is diagonal in Λ . The terms in $\mathcal{H}''$ are all off diagonal in Λ and so couple states differing in Λ by ± 1 .

The precession of $\mathbf{L}$ about the inter-nuclear axis can be in either a clockwise or anti-clockwise direction. For terms diagonal in Λ these states are degenerate but now it is necessary to calculate off diagonal matrix elements involving $L_{\pm}$ and a new basis set involving parity, $|\pm; J \Omega\rangle$, basis set is required. Using this new basis set,

$$\mathcal{H}_{ld} = \begin{pmatrix} 0 & \pm \frac{1}{2}q(z(z+1))^{\frac{1}{2}} \\ \pm \frac{1}{2}q(z(z+1))^{\frac{1}{2}} & \mp \frac{1}{2}(p+2q)(z+1)^{\frac{1}{2}} \end{pmatrix} \quad (3.63)$$

The upper and lower sign choices refer to e and f levels respectively. The convention of labeling the parity levels as e or f is given by Brown *et al.* [3]. For integral values of J , e levels have parity $(-1)^J$ and f levels $(-1)^{J+1}$. For half integral values of J (as for $^2\Pi$ states), e levels have parity $(-1)^{J-\frac{1}{2}}$ and f levels $(-1)^{J+\frac{1}{2}}$.

p and q are defined by Mulliken and Christy [17] and expressions for evaluating them for $^2\Pi$ states are given by Brown and Merer [18]

$$p = 4 \sum_{\Sigma v'} (-1)^k \frac{\langle ^2\Pi v | \mathcal{H}_{so} | ^2\Sigma v' \rangle \langle ^2\Sigma v' | BL_+ | ^2\Pi v \rangle}{E_{\Pi v} - E_{\Sigma v'}} \quad (3.64)$$

$$q = 2 \sum_{\Sigma v'} (-1)^k \frac{|\langle ^2\Sigma v' | BL_+ | ^2\Pi v \rangle|^2}{E_{\Pi v} - E_{\Sigma v'}} \quad (3.65)$$

3.6.1 Centrifugal Distortion Correction to the Λ -Doubling Term

The Λ -doubling centrifugal distortion matrix $\mathcal{H}_{ldcd}$ is obtained by substituting p_D and q_D for p and q in equation 3.63 to give a new matrix $\mathcal{H}'_{ld}$. As discussed in section 3.4.1 in order to obtain a hermitian operator it is necessary to take the hermitian average giving,

$$\mathcal{H}_{ldcd} = \frac{1}{2}(\mathcal{H}'_{ld} \cdot \mathbf{N}^2 + \mathbf{N}^2 \cdot \mathcal{H}'_{ld}) \quad (3.66)$$

this gives,

$$\mathcal{H}_{ldcd} = \begin{pmatrix} \mp \frac{1}{2} q_D z [z+1]^{\frac{1}{2}} & \pm \frac{1}{2} [z(z+1)]^{\frac{1}{2}} (q_D(z+1) + \frac{1}{2}(p_D + 2q_D)) \\ \text{sym} & \mp \frac{1}{2} (q_D z + (p_D + 2q_D)(z+2)) [z+1]^{\frac{1}{2}} \end{pmatrix} \quad (3.67)$$

We now have the zero field terms of equation 3.2.

$$\mathcal{H}_0 = \mathcal{H}_{rot} + \mathcal{H}_{cd} + \mathcal{H}_{so} + \mathcal{H}_{sr} + \mathcal{H}_{ld}. \quad (3.68)$$

We can tabulate (for clarity) the matrix elements of $\mathcal{H}_0$ diagonal in J

	$ \pm; J \frac{3}{2}\rangle$	$ \pm; J \frac{1}{2}\rangle$
$ \pm; J \frac{3}{2}\rangle$	$\frac{1}{2}(A + A_D z) - \frac{1}{2}\gamma_D z$ $+ Bz - Dz(z+1)$ $\mp q_D z(J + \frac{1}{2})$	$-\{B - \frac{1}{2}\gamma - \frac{1}{2}\gamma_D(z+2) - 2D(z+1)$ $\mp \frac{1}{2}q(J + \frac{1}{2}) \mp \frac{1}{4}(p_D + 2q_D(J + \frac{1}{2}))$ $\mp \frac{1}{2}q_D(J + \frac{1}{2})^3\} z^{\frac{1}{2}}$
$ \pm; J \frac{1}{2}\rangle$	<i>sym</i>	$-\frac{1}{2}\{A + A_D(z+2)\} - \gamma - \gamma_D \frac{1}{2}(3z+4)$ $+ B(z+2) - D(z^2 + 5z + 4)$ $\mp \frac{1}{2}(p + 2q)(J + \frac{1}{2})$ $\mp \frac{1}{2}(p_D + 2q_D)(J + \frac{1}{2})(z+2) \mp \frac{1}{2}q_D(J + \frac{1}{2})z$

3.7 Zeeman Interactions

When an external magnetic field $\mathcal{B}$ is applied to a molecule four principal interactions occur:

1. The interaction between the dipole moment caused by the electron orbital motion and the external field.
2. The interaction between the dipole moment caused by the electron spin and the external field.

3. The interaction between the dipole moment due to the end over end rotation of the nuclei and the external field.
4. The interaction between the dipole moment from the nuclear spin and the external field.

If nuclear spin is ignored we can write,

$$\mathcal{H}_z = \mu_B \mu_{\mathbf{J}} \cdot \mathbf{B} = \mu_B \langle \mu_J \rangle_z \mathcal{B}_z \quad (3.69)$$

$$\langle \mu_J \rangle_z = \langle \mu_L \rangle_z + \langle \mu_S \rangle_z - \langle \mu_r \rangle_z \quad (3.70)$$

μ_L is the component of $\mathbf{L}$ along $\mathbf{J}$,

$$\langle \mu_L \rangle = g_L \Lambda \cos(\mathbf{\Lambda}, \mathbf{J}) = g_L \Lambda \frac{\Omega}{(J(J+1))^{\frac{1}{2}}} \quad (3.71)$$

likewise

$$\langle \mu_S \rangle = g_S \Sigma \cos(\mathbf{\Sigma}, \mathbf{J}) = g_S \Sigma \frac{\Omega}{(J(J+1))^{\frac{1}{2}}} \quad (3.72)$$

and

$$\langle \mu_r \rangle = g_r^N |\mathbf{R}| \cos(\mathbf{\Lambda}, \mathbf{J}) = g_r^N \frac{R(R+1)}{(J(J+1))^{\frac{1}{2}}} \Omega \quad (3.73)$$

since $\mathbf{J}^2 = \mathbf{\Omega}^2 + \mathbf{R}^2$ so that $R(R+1) = J(J+1) - \Omega^2$.

$$\langle \mu_J \rangle = \frac{(g_L \Lambda + g_S \Sigma) - g_r^N (J(J+1) - \Omega^2)}{(J(J+1))^{\frac{1}{2}}} \Omega \quad (3.74)$$

Define M_J as the projection of J along the axis (z) defined by the magnetic field, so that

$$\langle \mu_J \rangle_z = \langle \mu_J \rangle \cos(\mathbf{J}, \hat{\mathbf{z}}) = \langle \mu_J \rangle \frac{M_J}{(J(J+1))^{\frac{1}{2}}} \quad (3.75)$$

therefore

$$\langle \mu_J \rangle_z = M_J \frac{(g_L \Lambda + g_S \Sigma) - g_r^N (J(J+1) - \Omega^2)}{J(J+1)} \Omega \quad (3.76)$$

and so,

$$\langle \mathcal{H}_z \rangle = \mathcal{B} \mu_B M_J \frac{(g_L \Lambda + g_S \Sigma) - g_r^N (J(J+1) - \Omega^2)}{J(J+1)} \Omega. \quad (3.77)$$

If we define

$$g_J = \frac{(g_L \Lambda + g_S \Sigma) - g_r^N (J(J+1) - \Omega^2)}{J(J+1)} \Omega \quad (3.78)$$

then

$$\langle \mathcal{H}_z \rangle = \mu_B g_J \mathcal{B} M_J. \quad (3.79)$$

A more general expression for the Zeeman Hamiltonian is,

$$\mathcal{H}_z = \mu_B g_L " \mathcal{B} \cdot \mathbf{L} " + \mu_B g_S " \mathcal{B} \cdot \mathbf{S} " - \mu_B g_r^N " \mathcal{B} \cdot \mathbf{R} " - \mu_N \sum_{\alpha} g_{I_{\alpha}} " \mathcal{B} \cdot \mathbf{I}_{\alpha} " \quad (3.80)$$

where

- μ_B is the Bohr magneton.
- μ_N is the nuclear magneton.
- g_L is the relativistically corrected orbital g -factor.
- g_S is the electron spin g -factor its value of 2.0023 comes from the solution of Dirac's equation corrected for the effects of quantum electrodynamics.
- g_r^N is the nuclear rotational g -factor there is also a small second order electron contribution g_r^e .
- $g_{I_{\alpha}}$ is the nuclear spin g -factor for the α^{th} nucleus, the summation is over all nuclei with non-zero spin.

The quotation marks around the inner products show that the angular momentum operators are defined in the molecule fixed frame but the magnetic field is space fixed. As mentioned in section 3.1.1 the nuclear spin is only weakly coupled to the molecule's angular momentum so even for small external magnetic fields it will decouple from the molecule and precess about the external field.

The Zeeman Hamiltonian matrix [16] is infinite because it contains non-zero elements off diagonal in J . Using a $|\pm; J \Omega M_J M_I\rangle$ basis set, where M_I is defined as the projection of the nuclear spin onto the axis defined by the magnetic field, the elements diagonal in J of $\mathcal{H}_z$ are,

$$\begin{pmatrix} \mu_B \mathcal{B} M_J \{3(g_L + \frac{1}{2}g_S)\} & \mu_B \mathcal{B} M_J (g_S + g_l + g_r) \\ -g_r(2(J + \frac{1}{2})^2 - 5)\}/[2J(J + 1)] & \pm g_r^e(J + \frac{1}{2})\}z^{\frac{1}{2}}/[2J(J + 1)] \\ -g_N \mu_N \mathcal{B} M_I & \\ & \mu_B \mathcal{B} M_J \{(g_L - \frac{1}{2}g_S - g_r(2z + 1)) \\ sym & (\pm g_l' - g_r^e)(J + \frac{1}{2})\}/[2J(J + 1)] \\ & -g_N \mu_N \mathcal{B} M_I \end{pmatrix} \quad (3.81)$$

- z is defined in equation 3.30 ($z = (J + \frac{1}{2})^2 - 1$)

- g_l is the anisotropic correction to g_L .
- g_l' and g_r^e are additional g -factors arising from Λ -doubling.

$\mathcal{H}_z$ is infinite since it has non-zero elements off diagonal in J . These elements are included, up to the prescribed limit, in the computer program. It has been found that a basis set of $\Delta J = \pm 2$ is sufficient to reproduce IR LMR data to within experimental accuracy for diatomic hydrides.

3.8 The Magnetic Hyperfine Interaction

As with electrons, nuclei with non-zero spin have magnetic moments. The nuclear magneton [6] defined as,

$$\mu_N = \frac{e\hbar}{2m_p} \quad (3.82)$$

where e is the electron charge, $\hbar$ is Planck's constant over 2π and m_p is the mass of the proton. μ_N is a factor of m_p/m_e (about 1800) smaller than μ_B so that,

1. the effects of nuclear spin are much smaller than those of electron spin, hence the terms hyperfine structure and fine structure.
2. the nuclear spins decouple from the molecular framework at low external magnetic field strengths, and quantize with respect to the external field (see 3.7).

The second point leads to the need for two treatments of hyperfine structure,

1. I-coupled; this is the most appropriate treatment for zero-field spectroscopic data such as that recorded by diode laser or Tunable-Far Infrared (TuFIR) spectroscopy.
2. I-decoupled; is the most appropriate treatment for LMR data. Since none of the diode laser data used in the fit of the GeH and GeD show hyperfine splittings this is the only case that need concern us.

The Magnetic Nuclear Hyperfine Hamiltonian [20] can be written as:

$$\mathcal{H}_{hfs} = aI_zl_z + b\mathbf{I}\cdot\mathbf{S} + \frac{1}{3}c(3I_zS_z - \mathbf{I}\cdot\mathbf{S}) - \frac{1}{2}d(S_+I_+ + S_-I_-) \quad (3.83)$$

- The first term represents the interaction of the nuclear spin magnetic moment with the magnetic field produced by the orbital motion of the electron,

$$a = 2g_I\mu_B\mu_N \left\langle \frac{1}{r^3} \right\rangle \quad (3.84)$$

- The second term is the Fermi contact interaction. It is due to the interaction of the magnetic moments of the nuclear and electron spin at the nucleus.

$$b_F = \frac{3}{2}g_S\mu_B g_N\mu_N \left\langle \frac{2\delta(r)}{3r^2} \right\rangle \quad (3.85)$$

- the last two terms arise from the interactions of the magnetic moments of the nuclear and electron spin. They are analogous to the classical dipole-dipole interaction.

$$c = \frac{3}{2}g_S\mu_B g_N\mu_N \left\langle \frac{3\cos^2\theta - 1}{r^3} \right\rangle \quad (3.86)$$

$$d = \frac{3}{2}g_S\mu_B g_N\mu_N \left\langle \frac{\sin^2\theta}{r^3} \right\rangle \quad (3.87)$$

In the above equations θ is the angle between the internuclear axis and the position vector $\mathbf{r}$ of the electron with its origin at the nucleus. The matrix elements diagonal in J are,

$$\mathcal{H}_{hf} = \begin{pmatrix} (\frac{3}{2}a + \frac{3}{4}b + \frac{3}{4}c)\mathcal{F}(M_J, M_I, J) & \frac{1}{2}(b_F - \frac{1}{3}c)\mathcal{F}(M_J, M_I, J)z^{\frac{1}{2}} \\ sym & (\frac{1}{2}a - \frac{1}{4}b - \frac{1}{4}c \mp \frac{1}{2}d(J + \frac{1}{2}))\mathcal{F}(M_J, M_I, J) \end{pmatrix} \quad (3.88)$$

Where

$$\mathcal{F}(M_J, M_I, J) = \begin{cases} \frac{M_J M_I}{J(J+1)} & \text{for } \Delta M_J = 0 \\ \frac{1}{2} \frac{\{(J \mp M_J)(J \pm M_J + 1)(I \pm M_I)(I \mp M_I + 1)\}^{\frac{1}{2}}}{J(J+1)} & \text{for } \Delta M_J = \mp 1. \end{cases} \quad (3.89)$$

Non-zero elements off diagonal in J are not shown here but are included in the computer program. When working with case(a) molecules it is sometimes convenient to define [15],

$$h_{\frac{3}{2}} = a + \frac{1}{2}(b + c) \quad (3.90)$$

$$h_{\frac{1}{2}} = a - \frac{1}{2}(b + c) \quad (3.91)$$

$$b_F = b - \frac{c}{3} \quad (3.92)$$

So that the matrix elements diagonal in J become,

$$\mathcal{H}_{hf} = \begin{pmatrix} \frac{3}{2}h_{\frac{3}{2}}\mathcal{F}(M_J, M_I, J) & (\frac{1}{2}b_F - \frac{1}{3}c)\mathcal{F}(M_J, M_I, J)z^{\frac{1}{2}} \\ sym & (\frac{1}{2}h_{\frac{1}{2}} \mp \frac{1}{2}d(J + \frac{1}{2}))\mathcal{F}(M_J, M_I, J) \end{pmatrix}. \quad (3.93)$$

3.9 The Vibrational Energy Term

The vibrational energy term $\mathcal{G}_v$ is separated from the other terms of $\mathcal{H}_{eff}$ by the Van Vleck transformation. Because $\mathcal{G}_v$ is much larger than any of the other contributions in this chapter, they can be thought of as perturbations to the vibrational energy. Since none of the transitions in this thesis involve a change of electronic state, using our basis set we can write,

$$\mathcal{H}_{ev} = \begin{pmatrix} \mathcal{G}_v & 0 \\ 0 & \mathcal{G}_v \end{pmatrix} \quad (3.94)$$

The form of $\mathcal{G}_v$ is [5],

$$\mathcal{G}_v = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \omega_e z_e(v + \frac{1}{2})^4 + \dots \quad (3.95)$$

where ω_e is the vibrational frequency, $\omega_e x_e$, $\omega_e y_e$ and $\omega_e z_e$ are the first, second and third anharmonicity constants. When fitting parameters of a Hamiltonian to experimental data it is often desirable to determine the directly observable band origin for $v = 1 - 0$ transitions, ν_0 .

$$\nu_0 = \omega_e - 2\omega_e x_e + \frac{13}{4}\omega_e y_e + 5\omega_e z_e. \quad (3.96)$$

3.10 Isotopic Scaling of Molecular Parameters

Chemical elements have isotopes of different masses [6], so when fitting molecular parameters to experimental data obtained from natural samples it is necessary to scale the parameters by appropriate factors to give parameters for a single isotopomer.

The reduced mass μ for a diatomic molecule is,

$$\mu = \frac{m_a m_b}{m_a + m_b} \quad (3.97)$$

where m_a and m_b are the masses of the two nuclei. In order to scale the parameters it is convenient to define ,

$$\rho_i = \frac{\mu^*}{\mu^i} \quad (3.98)$$

where μ^* is the reduced mass of the “reference” (normally the most abundant) isotopomer and μ^i is the reduced mass for the isotopomer for which the parameter is being scaled.

3.10.1 The vibrational isotopic dependence of molecular parameters

For a classical harmonic oscillator,

$$\omega = \left(\frac{k}{\mu} \right)^{\frac{1}{2}} \quad (3.99)$$

where ω is the vibrational frequency and k the force constant. So ω_e has a $(1/\mu)^{\frac{1}{2}}$ dependence. A general rule for the isotopic dependence of a parameter P , with a vibrational dependence $(v + \frac{1}{2})^k$, is that P^* (the parameter for the reference isotopomer) should be multiplied by $\rho_i^{\frac{k}{2}}$, so that

$$P^i(v + \frac{1}{2})^k \equiv \rho_i^{\frac{k}{2}} P^*(v + \frac{1}{2})^k \quad (3.100)$$

3.10.2 The rotational isotopic dependence of molecular parameters

Combining equations 3.12 and 3.13 we get,

$$B = \frac{\hbar}{4\pi c \mu r^2} \quad (3.101)$$

So B has a $(1/\mu)$ dependence. A general rule for the isotopic dependence of a parameter P^* , with a rotational dependence $(N^2)^l$ is that P should be multiplied by ρ_i^l so that

$$P^i(N^2)^l \equiv \rho_i^l P^*(N^2)^l. \quad (3.102)$$

These rules can be combined to give,

$$P_e^i(v + \frac{1}{2})^k(N^2)^l \equiv \rho_i^{(\frac{k}{2}+l)} P_e^*(v + \frac{1}{2})^k(N^2)^l, \quad (3.103)$$

where P_e^i is the scaled parameter for isotopomer i , N^2 is the rotational operator of the effective Hamiltonian, ρ_i is the ratio of the reduced mass of the reference isotopomer (μ^*) (normally the most abundant) to the reduced mass of isotopomer i , ($\rho_i = \frac{\mu^*}{\mu_i}$), P_e^* is the equilibrium value for the reference isotopomer. Using this relationship, equation 3.14 can, for example, be written

$$B_v^i = \rho_i B_e^* + \rho_i^{\frac{3}{2}} \alpha_B^* (v + \frac{1}{2}) + \rho_i^2 \beta_B^* (v + \frac{1}{2})^2 + \dots \quad (3.104)$$

3.10.3 The breakdown of the Born-Oppenheimer approximation

Equation 3.97 is only an approximation for a diatomic molecule because the electrons as well as the nuclei contribute to the reduced mass of the molecule. Since for a motion of the nuclei the electrons do not instantaneously adjust the new nuclear position that is the Born-Oppenheimer approximation breaks down. For different isotopomers the ratio of the electron to nuclear mass will be different therefore, the isotopic scaling described above needs to be revised [7]. Equation 3.103 is written

$$P_e^i(v + \frac{1}{2})^k(\mathbf{N}^2)^l \equiv \rho_i^{(\frac{k}{2}+l)} P_e^*(v + \frac{1}{2})^k(\mathbf{N}^2)^l \mathcal{F}(\Delta_{kl}), \quad (3.105)$$

where $\mathcal{F}(\Delta_{kl})$ is a function of Watson's dimensionless Δ_{kl} parameters [7] used to compensate for the small effects of the break down of the Born-Oppenheimer approximation [1],

$$\mathcal{F}(\Delta_{kl}) = \frac{1 + \frac{m_e}{m_a^*} \Delta_{kl}(a) + \frac{m_e}{m_b^*} \Delta_{kl}(b)}{1 + \frac{m_e}{m_a^*} \Delta_{kl}(a) + \frac{m_e}{m_b^*} \Delta_{kl}(b)} \quad (3.106)$$

where m_e is the electron mass, and m_a and m_b are the atomic masses of atoms a and b .

For example,

$$B_e^i = \rho_i B_e^* \frac{1 + \frac{m_e}{m_a^*} \Delta_{01}^a + \frac{m_e}{m_b^*} \Delta_{01}^b}{1 + \frac{m_e}{m_a^*} \Delta_{01}^a + \frac{m_e}{m_b^*} \Delta_{01}^b} \quad (3.107)$$

In order to model the GeH and TeD data in this thesis it has been necessary to program Δ corrections to ω_e and B_e . For all other parameters $\mathcal{F}(\Delta_{kl})$ was set equal to unity.

3.11 Computer Programs

The terms in equation 3.2 have been coded in FORTRAN. The program (called HUNDA) can be used to calculate the wavenumbers and resonant fields of transitions, using trial parameters, to help with the assignment of experimental data. The eigenvalues of $\mathcal{H}_{eff}$ are calculated using the Givens-Householder reduction [8] on most computers this is available as a library routine. Having assigned the data to transitions, the parameters of $\mathcal{H}_{eff}$ can then be refined using the least-squares fitting algorithm described in [9]. To compute the derivatives required for the least-squares fit the Hellmann-Feynman theorem [10] is used,

$$\frac{dE}{dP} = \left\langle \psi_i \left| \frac{\partial \mathcal{H}}{\partial P} \right| \psi_i \right\rangle \quad (3.108)$$

where P is a typical parameter and ψ_i is the i^{th} eigen function. The inversion of the “derivative matrix” is achieved using a library routine that uses LU decomposition [8].

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Chapter 4

The infrared spectrum of the GeH radical

4.1 Introduction

GeH is important because of its close relation to the CH radical. It is of interest to determine its structural parameters and compare them with the earlier group IV hydrides, CH [1] and SiH [2]. GeH was first identified by Kleman and Werhagen [3, 4] through the observation of the $a^4\Sigma^- - X^2\Pi$ and $A^2\Delta - X^2\Pi$ band systems in the visible and near-ultraviolet regions of the spectrum. Shortly afterwards Barrow *et al.* [5] reported another band system in the ultraviolet, which is probably the $B^2\Sigma^- - X^2\Pi$ transition, although this has not yet been analysed in detail. Klynning and Lindgren [6] recorded the $A^2\Delta - X^2\Pi$ system at higher resolution and determined the major molecular parameters for the two states. The same data were re-analysed by Veseth [7] in terms of a Hund's case (c) Hamiltonian.

More recent studies of GeH in its $X^2\Pi$ state have been made:

- (i) Brown *et al.* [8] have reported pure rotational transitions using the fore-runner of the FIR LMR described in Chapter 2, section 4. and fine-structure transitions recorded using CO₂ LMR (at 10 μ m wavelengths).
- (ii) Towle and Brown [14] observed rotation-vibration transitions in the fundamental and first hot band, using the carbon monoxide LMR spectrometer described in chapter 2, section 2.
- (iii) Zimmermann *et al.* [15] observed rotation-vibration transitions in the fundamental and first hot band of GeD, using the Faraday LMR spectrometer described in Chapter 2, section 3.
- (iv) Akiyama *et al.* [19] have observed 94 lines in the infrared spectrum of GeH using diode laser spectroscopy but have not published their

measurements, so these cannot be included in the fit of GeH and GeD transitions presented here.

- (v) Petri *et al.* [17] observed rotation-vibration transitions in the fundamental band of GeH using diode laser spectroscopy.
- (vi) Huhn *et al.* [18] observed rotation-vibration transitions in the fundamental and first hot bands of GeD, using diode laser spectroscopy.

All group IV hydrides have regular ($A > 0$) $^2\Pi$ ground states. The rotational levels of the $^2\Pi_{\frac{1}{2}}$ spin component depend only very weakly on an applied magnetic field.

For a molecule with a coupling scheme that is a good approximation to Hund's case (a),

$$g_J^{(1)} = \frac{(g_L\Lambda + g_S\Sigma)\Omega}{J(J+1)} \quad (4.1)$$

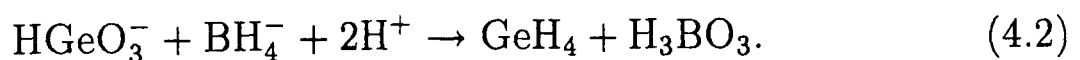
so that for $^2\Pi_{\frac{1}{2}}$ levels $g_J \approx 0$. Consequently transitions between $^2\Pi_{\frac{1}{2}}$ levels require a very close coincidence with a laser line if they are to be observed by LMR. They are also difficult to detect because they are undermodulated in an LMR experiment. Since the upper ($^2\Pi_{\frac{3}{2}}$) spin component is approximately 900 cm^{-1} above the lower ($^2\Pi_{\frac{1}{2}}$) spin component, it is sparsely populated by comparison. Hence all the transitions recorded by diode laser spectroscopy, in the list above, involve the $^2\Pi_{\frac{1}{2}}$ levels. All the LMR data in the above list involve the $^2\Pi_{\frac{3}{2}}$ levels, with the exception of the data of Brown *et al.* [8] and the $R(\frac{1}{2})$ transition in the fundamental vibration-rotation band of the ^{72}GeH which has recently been measured using CO LMR at Oxford, described in Chapter 2.

4.2 Experimental Details

This section describes the GeH experiments performed at Oxford.

4.2.1 The production of GeH

The precursor used for the production of GeH was germane, GeH_4 . Germane was produced following the method described in detail by Jolly [11]. Germanium dioxide was reduced by potassium borohydride in acid conditions,



This reaction was performed in the home-made vacuum line apparatus shown in 4.1. 3g germanium oxide, 6g potassium hydroxide and 4.5g potassium

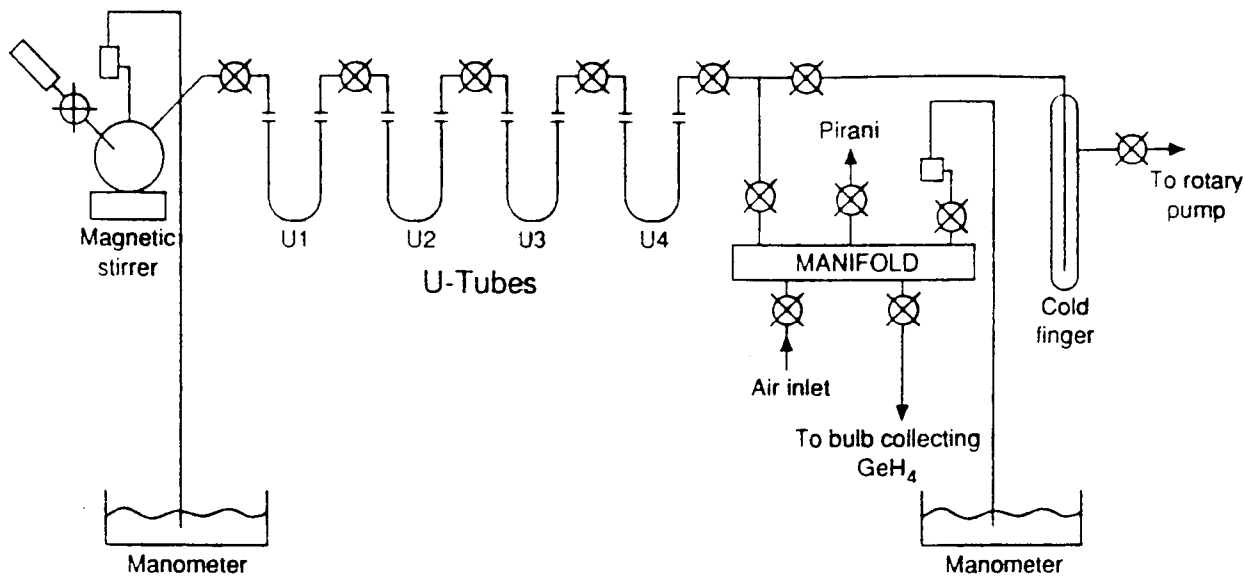
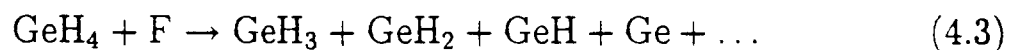


Figure 4.1: Vacuum line apparatus used in the preparation of germane

borohydride were dissolved in 75 cm³ of distilled water and added dropwise to 400 cm³ of glacial acetic acid. The products of the reaction were trapped at liquid nitrogen temperature in the U-tubes. The reaction produced higher order germanes, see [12]. These can be removed by fractional distillation prior to collection in the bulb. It was found that using germane that had been purified made no observable difference to the signal to noise ratio of the GeH signals, and so this step was not carried out for the majority of the preparations.

To produce GeH, germane was reacted with fluorine atoms,



Atomic fluorine was produced by running a microwave discharge through a 5% mixture of F₂ in helium. GeH signals could also be detected from the reaction of F₂ with germane but under optimum conditions they were about a third as strong as those produced by the reaction of atomic fluorine. The optimum GeH signals were obtained when the violet chemiluminescence from the reaction was maximised by eye. Evidence for the reaction scheme given in equation 4.3 comes from the formation of grey elemental germanium powder in the reaction cell. In addition, multiple line resonances of the type shown in figure 4.2.1 appear for two laser lines which must be due to a polyatomic molecule, possibly GeH₂. This molecule in its triplet state is expected to have a vibrational frequency similar to that of GeH [13]. The production of Ge powder makes it necessary to purge the volume of the cell between the Brewster windows and the reaction region in order to keep the windows clean. The windows were made of sheets of CaF₂, 1.5 mm thick. A number of different designs of reaction cell were tried to optimise the production of GeH. The best signal to noise ratio was achieved using the cell shown in

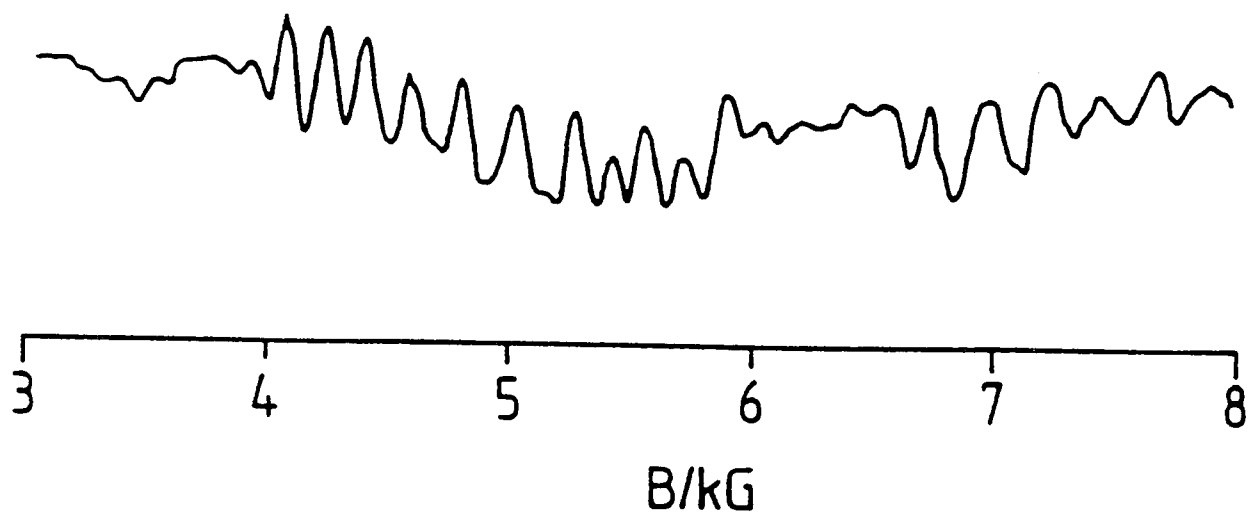


Figure 4.2: Unassigned signal on the $P(11)_{13-12}$ CO laser line

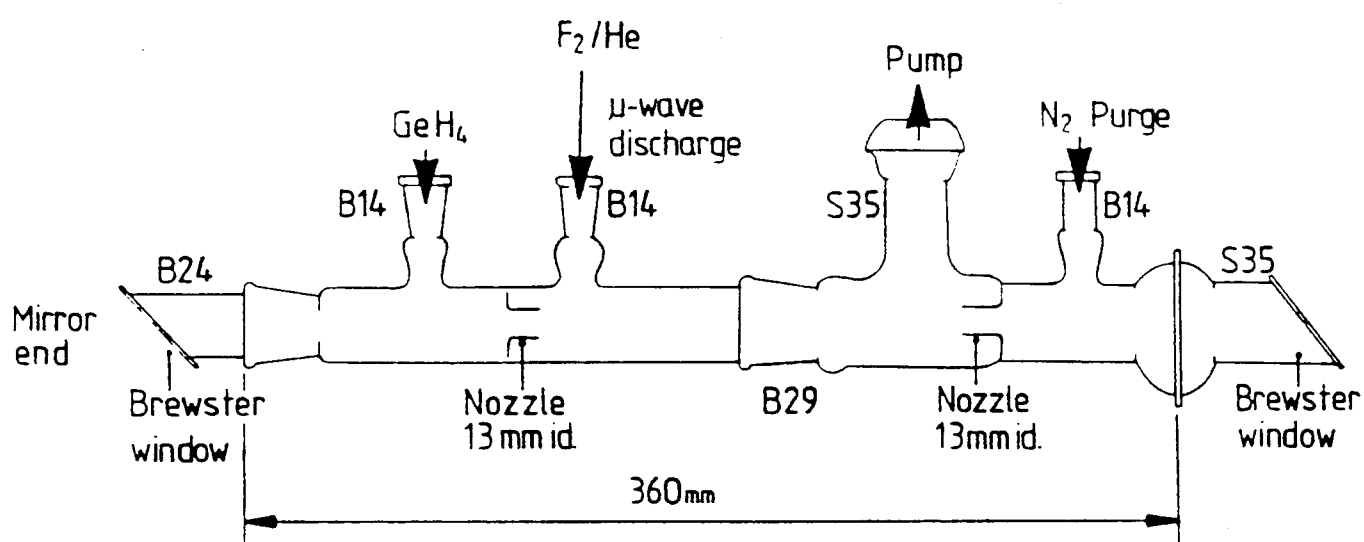


Figure 4.3: A diagram of the flow cell in which GeH radicals were formed by the reaction of fluorine atoms with germane, GeH_4 . With this arrangement, the free radicals are formed on the axis of the cell, in the path of the infrared laser beam. The purging systems are designed to minimize deposition on the Brewster windows.

figure 4.3. The germane was introduced into the cell at the mirror-end inlet, so that it passed through the nozzle before mixing with the fluorine atoms produced by the microwave discharge. With this arrangement the reaction flame was centred on the optical axis of the laser.

4.3 Results and analysis

The initial searches for signals with the Oxford CO LMR were guided by predictions made using term values calculated by Klynning and Lindgren from their analysis of the optical spectrum [6]. Once signals had been observed, the detailed assignments were made from consideration of the Zee-

Table 4.1: Zerofield wavenumbers for transitions of ^{72}GeH from [6] and the nearest CO laser wavenumber.

Transition	Zerofield wavenumber /cm $^{-1}$ for ^{72}GeH	CO laser line	CO laser wavenumber /cm $^{-1}$
$Q(\frac{3}{2})$	1835.16	$P(6)_{12-11}$	1834.60986
$Q(\frac{5}{2})$	1834.30	$P(6)_{12-11}$	1834.60986
$Q(\frac{9}{2})$	1831.09	$P(7)_{12-11}$	1830.94304
$P(\frac{5}{2})$	1801.74	$P(8)_{13-12}$	1801.85693
$R(\frac{3}{2})$	1867.72	$P(11)_{10-9}$	1866.74171

man patterns and the relative abundances of the different isotopomers. Germanium has five naturally occurring isotopes whose abundances are ^{70}Ge (20.5%), ^{72}Ge (27.4%), ^{73}Ge (7.8%), ^{74}Ge (36.5%), ^{76}Ge (7.8%). At Oxford signals were observed for the four isotopes with $I = 0$ (for ^{73}Ge $I = \frac{9}{2}$). Many of the lines were observed as Lamb dips, allowing resolution of closely spaced Zeeman patterns and improving the accuracy of the magnetic field measurement. Figure 4.4 shows the $Q(\frac{3}{2})$ transition of the (2,1) band recorded as the second derivative of the Doppler profile. To saturate transitions so that Lamb dips can be recorded;

1. The pressure in the reaction cell can be reduced to decrease pressure broadening, however this will usually have the effect of reducing the signal to noise by moving away from the optimum reaction conditions for production of the radical.
2. The modulation amplitude can be reduced to decrease modulation broadening.

Figure 4.5 shows the same two signals as figure 4.4 but with 2 Lamb dips (due to Λ doubling) burnt into the absorption profile. The $Q(\frac{3}{2})$ transition of the (1,0) band is shown in figure 4.6. As the transition is recorded at high field the three M_J components are separated by second order Zeeman effects. The smallest separation between two Lamb dips is 7 Gauss, which represents a resolution of about 10 MHz. When the wavenumbers of the transitions recorded by Petri *et al.* [17] using diode laser spectroscopy were compared with the wavenumbers of CO laser lines it was noted that there was a very close coincidence (0.01 cm^{-1}) between the $R(\frac{1}{2})$ transition due to the ^{72}GeH and the $P(15)_{10-9}$ laser line. Figure 4.7 shows two very broad peaks. The high field resonance ($M_J = \frac{3}{2} \leftarrow \frac{1}{2}$) is predicted to be three times stronger than the lower field resonance ($M_J = \frac{1}{2} \leftarrow -\frac{1}{2}$), so that the observed intensity gives credence to the assignment.

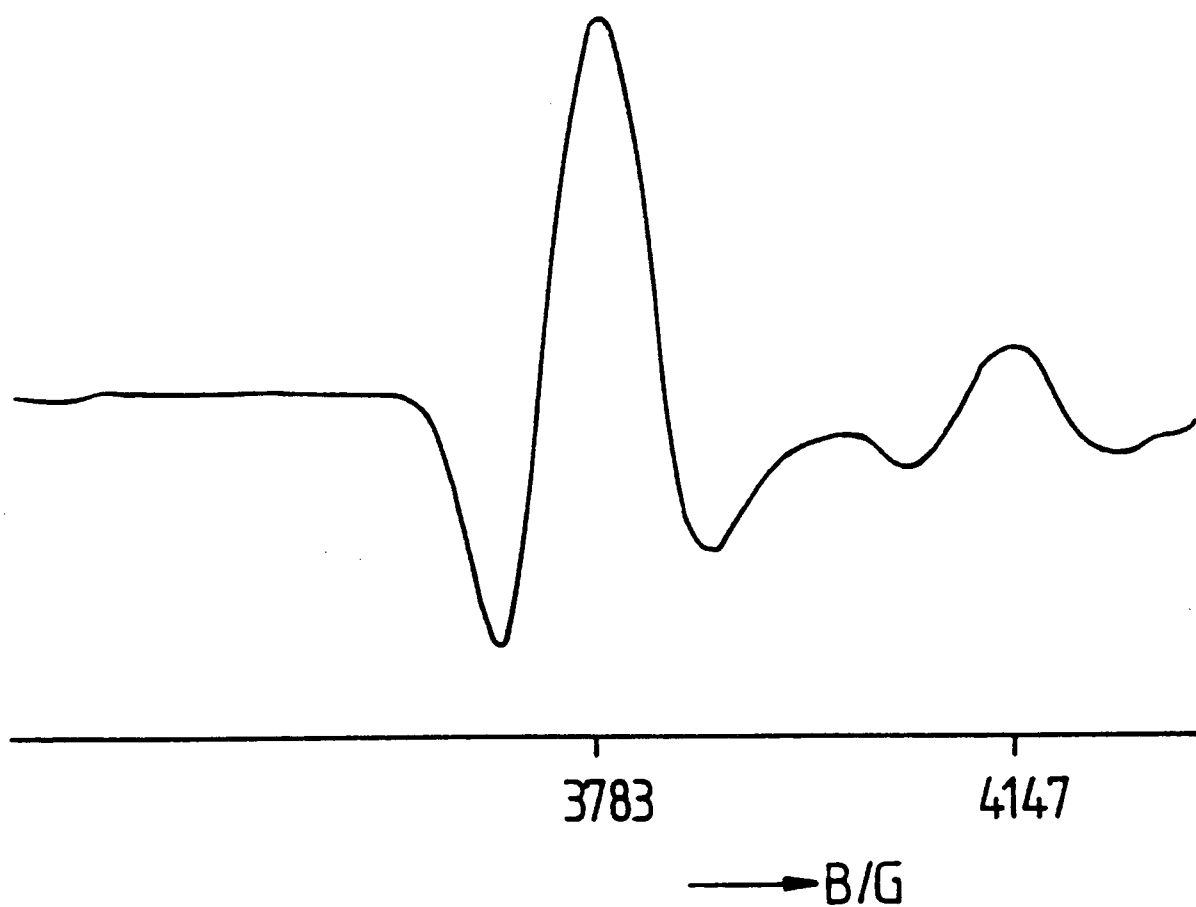


Figure 4.4: The $Q(\frac{3}{2})$ transition of the (2,1) band recorded on the $P(10)_{14-13}$ laser line. The signals shown are due to the ^{74}GeH and ^{76}GeH isotopomers at low and high field respectively. Because the signals are detected at twice the magnetic field modulation frequency $2f$, the line shape is similar to the second derivative of the absorption profile.

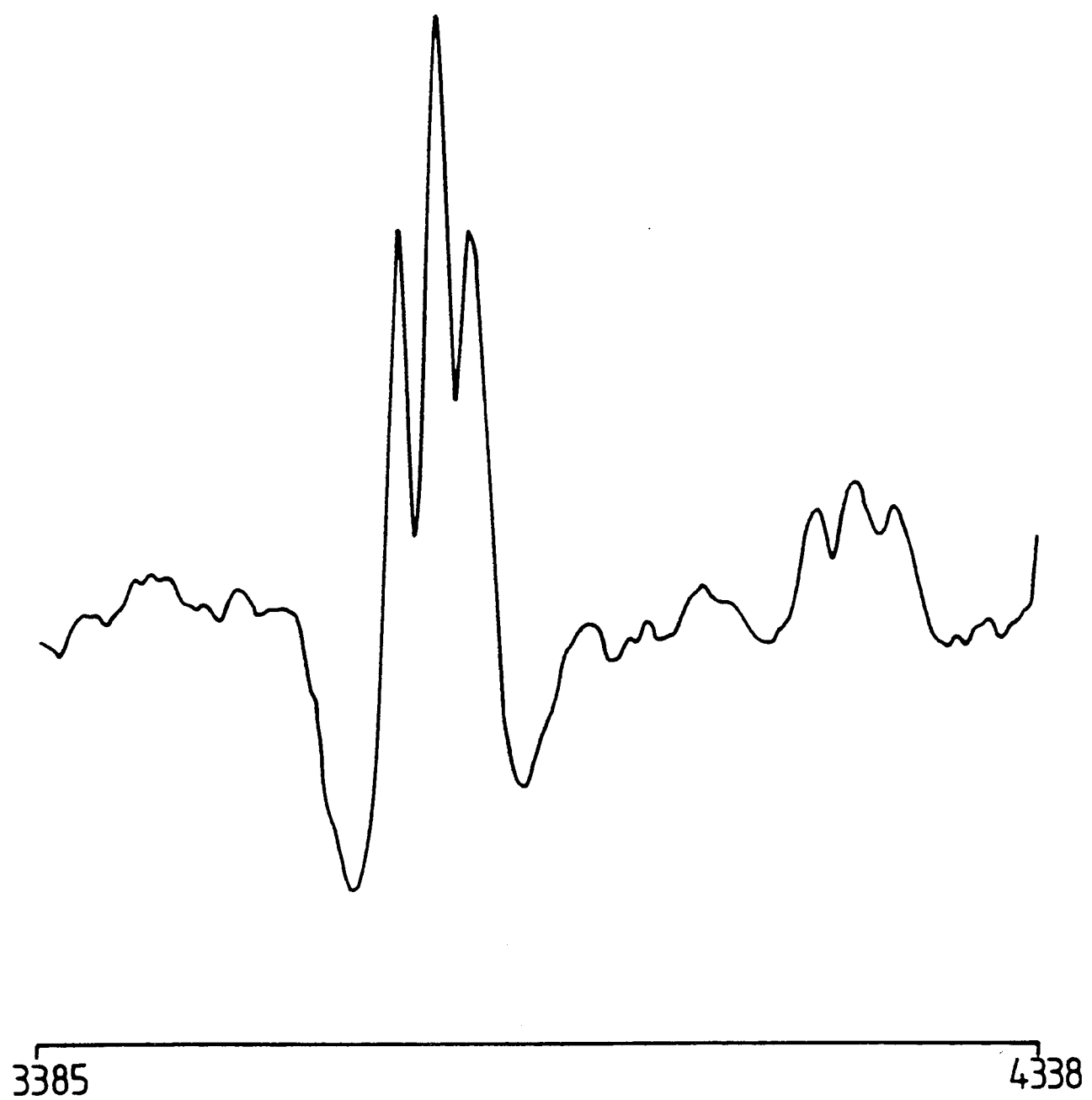


Figure 4.5: The $Q(\frac{3}{2})$ transition of the (2,1) band recorded on the $P(10)_{14-13}$ laser line. The signals shown are recorded as with 2 Lamb dips due to Λ doubling.

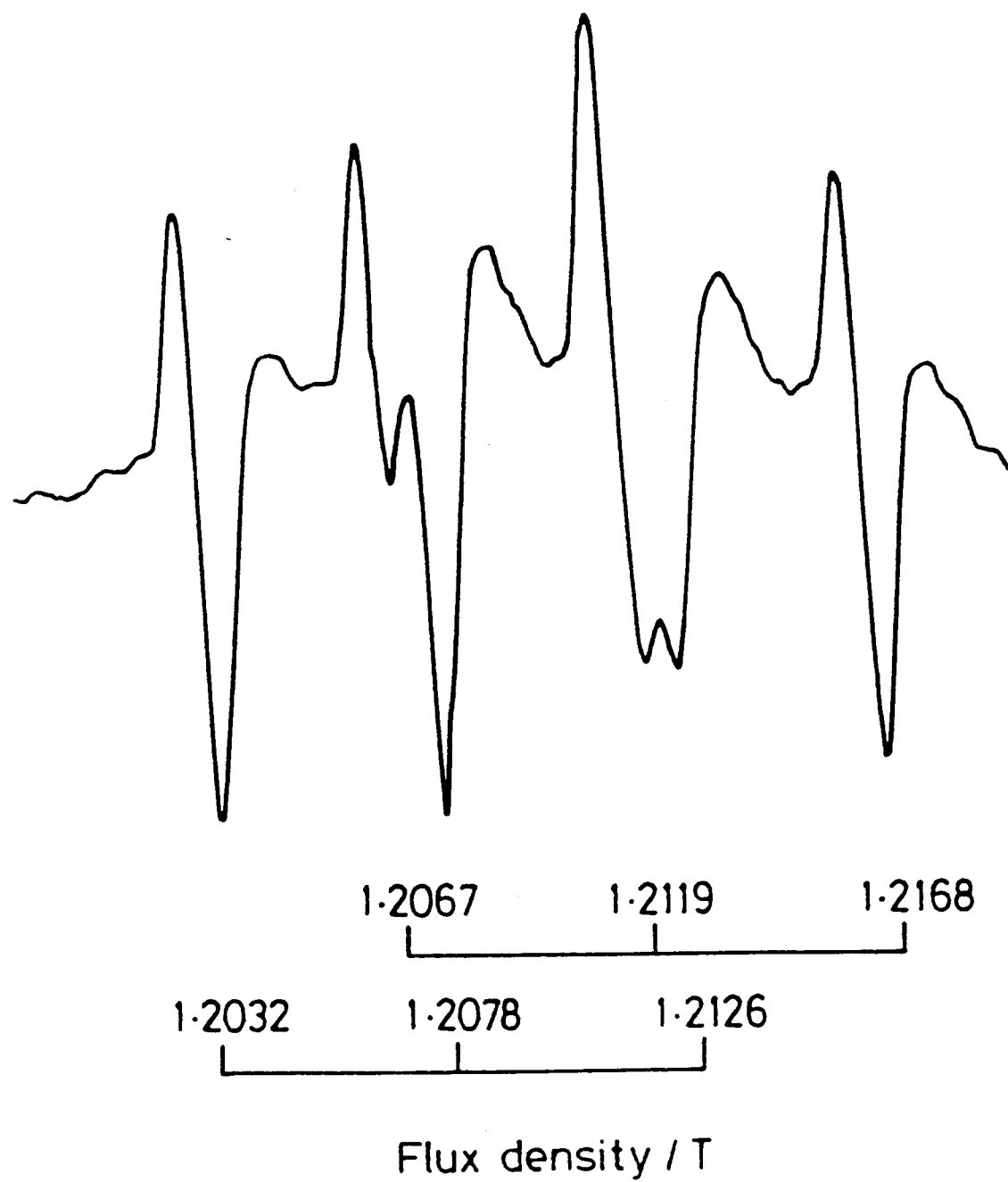


Figure 4.6: The $Q(\frac{3}{2})$ transition of the (1,0) band of ^{74}GeH recorded on the $P(6)_{12-11}$ laser line. The signals are recorded as lamb dips permitting the resolution of two sets of three M_J components, separated by Λ doubling.

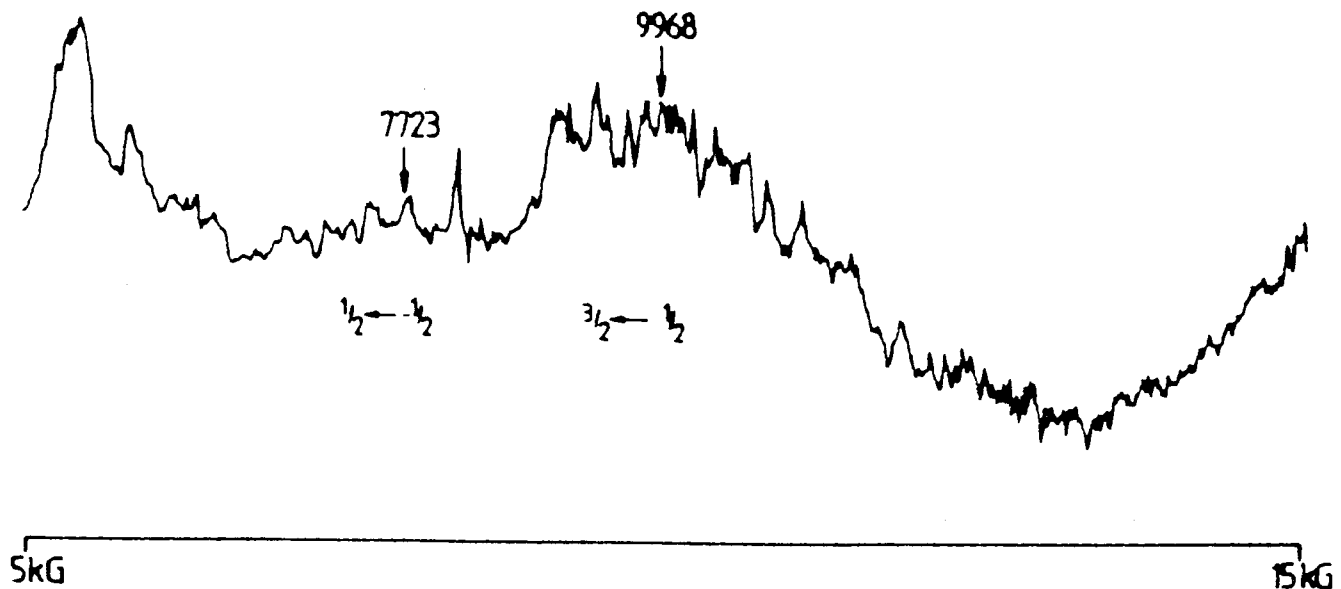


Figure 4.7: The $R(\frac{1}{2})$ transition of the (1,0) band of ^{72}GeH recorded on the $P(15)_{10-9}$ laser line.

The CO LMR data recorded at Oxford, together with the data published in [8], [15], [17], [18] were included in a fit of the parameters of the effective Hamiltonian described in Chapter 3.

All the parameters in table 4.2 have been determined simultaneously, apart from some of the small parameters which had to be constrained to theoretically estimated values. The relationships for these values are,

$$H_0 \simeq H_e = \frac{2}{3}D_e[12(B_e/\omega_e)^2 + \alpha_B/\omega_e], \quad (4.4)$$

$$p_D = -2p_e D_e/B_e, \quad (4.5)$$

$$q_D = -4q_e D_e/B_e, \quad (4.6)$$

$$g_l = -\gamma_e/2B_e \quad (4.7)$$

and

$$g_r^{e'} = -q_e/B_e. \quad (4.8)$$

These relationships are given in references [23], [24], [25] and [26] respectively. Since no new transitions which show hyperfine structure due to the ^{73}Ge nucleus have been observed since the work of Brown *et al.* [8], these data have been omitted from the fit. Furthermore, since the proton hyperfine splitting was not resolved for the $^2\Pi_{3/2}$ component, the parameters h_3 and b were constrained to zero. The value of g_s was constrained to 2.002, this being an estimate derived from the free spin value with a small relativistic correction.

The fit was performed using a computer program HUNDA in which the effective Hamiltonian was represented in a Hund's case (a) basis set. The

matrix representation was truncated at $\Delta J = \pm 2$ without loss in accuracy. The data points were weighted as the square of the experimental uncertainty. These uncertainties were taken to be as follows:

- (a) CO LMR measurements for GeH on Lamb dips: 0.0010 cm^{-1} or 30 MHz.
- (b) CO LMR Doppler limited measurements for GeH: 0.0010 cm^{-1} or 30 MHz.
- (c) Tunable diode laser measurements for GeH: 0.0030 cm^{-1} or 90 MHz.
- (d) CO LMR measurements for GeD: 0.0020 cm^{-1} or 60 MHz.
- (e) Tunable diode laser measurements for GeD: 0.0030 cm^{-1} or 90 MHz.
- (f) CO₂ LMR measurements for GeH: 0.00083 cm^{-1} or 25 MHz.
- (g) Far infrared LMR measurements for GeH on Lamb dips: 0.00003 cm^{-1} or 1 MHz.
- (h) Far infrared LMR measurements for GeH: 0.00010 cm^{-1} or 3 MHz.

The results of the fit are given in Table 1 Appendix A and Table 4.2. The standard deviation of the fit of 362 data points relative to the experimental uncertainties was 0.9239 which can be considered as eminently satisfactory.

4.4 Discussion

All the available infrared and far infrared data on the various isotopomers of GeH have been fitted with a single effective Hamiltonian. In particular, the deuterated forms have been included and this is one of the first fits in which data for both XH and XD have been fitted together. The internal consistency of the fit confirms that the assignments given in Appendix A are correct. This study also highlights the complementary nature of carbon monoxide LMR and diode laser spectroscopy. The former provides information on GeH in states with large magnetic moments but which are sparingly populated; the latter studies the molecule in the lower lying states in which it has very small magnetic moments.

The parameter values obtained in the fit are given in Table 4.2. The primary quantities determined are the vibrational and rotational parameters. Extrapolation back to the equilibrium values yields values for the harmonic wavenumber and the rotational constant:

$$\omega_e = 1900.3820(80) \text{ cm}^{-1} \text{ and } B_e = 6.7300522(17) \text{ cm}^{-1}.$$

Using the formula for a classical harmonic oscillator,

$$\omega_e = \left(\frac{k}{\mu} \right)^{\frac{1}{2}}, \quad (4.9)$$

this corresponds to a force constant $k_e = 211.651 \text{ N.m}^{-1}$. The equilibrium bond lengths can be estimated from,

$$r_e = \left(\frac{\hbar}{4\pi c \mu B} \right)^{\frac{1}{2}}, \quad (4.10)$$

giving an equilibrium bond length $r_e = 0.158724 \text{ nm}$. These values are consistent with those obtained from the optical spectrum ($\omega_e = 1908 \pm 35 \text{ cm}^{-1}$ and $B_e = 6.727 \pm 0.006 \text{ cm}^{-1}$) by Klynning and Lindgren [6] but are much more accurate. Table 4.3 gives a comparison of the transition wavenumbers calculated from Klynning and Lindgren's term values, with those determined from the parameters given in table 4.2.

By subjecting all the different isotopomers to a single fit, we have been able to learn more about the structural properties of the GeH radical:

Firstly, we have been able to determine the small effects of non-adiabatic mixing on the isotopic scaling on ω_e and B_e , the former for the H atom and the latter for the Ge and H atoms. These effects have been included using the formulation of Watson [10] and as expected, the dimensionless parameters Δ_{kl} are negative and have values close to unity. In particular, it is these effects on the rotational constant which account for the difficulty experienced by Brown *et al.* [8] in fitting the far infrared LMR data for the full range of germanium isotopes. As can be seen in Appendix A Table 1 (g) and (f), all the available far infrared data can now be fitted to within experimental error;

Secondly, we have been able to separate the effects of the two parameters A_D and γ on the molecular energy levels using the procedure described by Brown and Watson [28]. This separation has been achieved before for several different molecules by determining, for example, $\tilde{\gamma}_{eff}$ for XH and XD. This is, however, the first time that the same objective has been achieved by fitting all the data simultaneously. It is interesting to compare the value determined for γ_0 in Table 4.2 ($-0.109 \pm 0.015 \text{ cm}^{-1}$) with the value for $\tilde{\gamma}_0$ from the fit of the far infrared LMR data (-0.4895 cm^{-1} , [8]). This implies that the effective parameter arises predominantly from the A_D term, the centrifugal distortion of the spin-orbit coupling. This is the opposite of the behaviour shown by the CH radical [29], possibly because the spin-orbit coupling effects are so much larger for GeH. It should be mentioned that the separation of A_D and γ depends strongly on the relative weighting of the different parts of the data set. In the present study, the information on GeH comes mainly from the

far infrared LMR spectrum and so is much more accurate than that for GeD which comes from infrared laser measurements. For this reason alone, it is desirable to record the far infrared spectrum of GeD.

Table 4.2 gives a set of molecular parameters for ^{74}GeH which characterize the energy levels of the $X^2\Pi$ state to within experimental error, for all naturally occurring isotopomers. It is interesting to compare the values for the main parameters with those determined for the other Group IV hydrides (CH, SiH and SnH) in their ground $^2\Pi$ states. These are given in Table 4.4.

The trends in values down the group are broadly as expected [34]. The vibrational harmonic wavenumber gets smaller and the equilibrium bond length becomes longer. It is interesting to note that ω_e varies very nearly inversely as r_e for these molecules, a weaker dependence than predicted by the Morse-Clark formula [35, 36]:

$$r_e^3 \omega_e \sqrt{n} = C. \quad (4.11)$$

(Here n is the number of electrons outside the closed atomic shells, and C is constant.) The anharmonic correction to the vibrational wavenumber is 2.24 % for CH and drops to 1.75 % for the other 3 molecules in Table 3. The spin-orbit coupling constant A depends mainly on the distribution of the open shell electrons round the heavier atom, X. For group IV hydrides, the empirical relationship

$$A \propto Z_X^n \quad (4.12)$$

where $n=2.070$ describes the behaviour of the spin-orbit coupling constant very well. Using this expression, the spin-orbit splitting in the ground state of PbH is predicted to be 6039 cm^{-1} . Again, it may be helpful for future work to note that the vibrational dependence of the spin-orbit coupling constant increases linearly with A for heavier members of the group, so that for PbH $\alpha_A \approx -25 \text{ cm}^{-1}$.

Table 4.2: Values of constants for ^{74}GeH in $X^2\Pi$ state.

Parameter	Value ^a	Correlation κ_i^b
ν_0	1833.8351(11)	81.811
$\Delta_{10}(\text{Ge})$	-1.64 ^c	
$\Delta_{10}(\text{H})$	-0.8778(18)	7.756
$\omega_e x_e$	33.5024(28)	333.999
$\omega_e y_e$	0.14091(59)	276.049
B_0	6.631162(65)	7374.027
$\Delta_{01}(\text{Ge})$	-2.60(57)	1.347
$\Delta_{01}(\text{H})$	-2.586(54)	2.232
α_B	-0.19851(25)	242.874
β_B	0.00146(13)	250.539
$10^3 D_0$	0.33692(49)	574.453
$10^4 \alpha_D$	-0.506(23)	9.583
$10^7 H_0$	0.146 ^c	
A_0	892.628(15)	5248.106
α_A	3.6342(20)	67.652
A_D	0.00602(24)	24724.255
γ_0	-0.107(15)	27409.149
α_γ	-0.0340(24)	30.975
$10^3 \gamma_D$	-0.245(69)	5424.063
$(p + 2q)$	0.500162(43)	2.396
$\alpha_{(p+2q)}$	-0.01899(24)	1.140
$10^4 p_D + 2q_D$	-0.521400 ^c	
q	0.006638(20)	1.482
$10^5 q_D$	-0.13900 ^c	
$h_{\frac{1}{2}}$	0.00123(10)	1.129
$h_{\frac{3}{2}}$	0.0 ^c	
$10^3 d$	0.519(91)	1.136
g_S	2.0020 ^c	
g_L	1.00114(13)	2.815
g_r	-0.001296(19)	1.952
g_l^e	0.038 ^c	
$10^3 g_r^{e'}$	-0.985 ^c	
$(g_l' - g_r^{e'})$	0.03824(15)	1.481
g_N	5.58569 ^c	

^a Value quoted in cm^{-1} , with the numbers in parentheses corresponding to one standard deviation of the least squares fit.

^b Correlation parameter $\kappa_i = (\chi^{-1})_{ii}$ where χ is the matrix of correlation coefficients, see Watson *et al.* [36].

^c Parameter constrained to this value in the fit (see text).

Table 4.3: Comparison of zerofield transition wavenumbers for transitions of low J in the spectrum ^{72}GeH

Transition	Zerofield wavenumber ^a from [6]	Zerofield wavenumber from this study	
		+	–
$Q(\frac{3}{2})$	1835.16	1835.3775	1835.3790
$Q(\frac{5}{2})$	1834.30	1834.3766	1834.3706
$Q(\frac{9}{2})$	1831.09	1831.1915	1831.1617
$P(\frac{5}{2})$	1801.74	1801.9780	1801.9757
$R(\frac{3}{2})$	1867.72	1867.7761	1867.7739

^a All wavenumbers in cm^{-1} scaled for the ^{72}GeH isotopomer.

^b parity of the $v = 0$ level.

Table 4.4: Parameters of Group IV hydrides in $X^2\Pi$ state.

Parameter ^a	¹² CH	²⁸ SiH	⁷⁴ GeH ^h	¹²⁰ SnH ⁱ
ν_0	2732.97729 ^b	1971.0413 ^f	1833.8351	1660.1464
ω_e	2860.4118 ^b	2042.73696 ^f	1900.3820	1718.4231
$\omega_e x_e$	64.1082 ^b	36.0493 ^f	33.5024	29.31182
$\omega_e y_e$	0.2406 ^b	0.1240 ^f	0.14091	0.12071
B_0	14.192103 ^b	7.39143124 ^g	6.631162	5.315738
α_B	-0.53416 ^b	-0.21772 ^f	-0.19851	-0.148238
$10^3 D_0$	1.4530 ^b	0.401161 ^g	0.33692	0.20887
$10^8 H_0$	10.8 ^b	1.48 ^g	1.46	
A_0	28.1467 ^c	142.89571 ^f	892.628	2181.9960
α_A	0.2362 ^d	0.5779 ^f	3.6342	10.2924
A_D	0.0005894 ^e		0.00602	
γ_0	-0.02573 ^e	-0.047997 ^f	-0.107	-3.0788 ^j
k_e	448.198	239.166	211.561	173.884
r_e	0.1120	0.1520	0.158724	0.176905

^a Parameters in cm^{-1} , except for r_e which is given in nm and k_e which is given in Nm^{-1} .

^b value from Bernath [1].

^c value from Brazier and Brown [30].

^d value from Lubic and Amano [31].

^e value from Brown and Evenson [29].

^f value from Seebass *et al.* [2].

^g value from Brown, Curl, and Evenson [32].

^h value from present study.

ⁱ value from Zimmermann *et al.* [33].

^j this is an effective value with A_D constrained to zero.

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Chapter 5

The infrared spectrum of the TeD radical by laser magnetic resonance

5.1 Introduction

TeD is a heavy element relative of the OH radical. It is of interest to determine its structural parameters and compare them with those of the earlier group VI hydrides, OH, SH, and SeH all of which have been studied in the infrared region of the spectrum [1, 5]. TeH was first identified from its e.p.r. spectrum by Radford [6]; we have combined his observations with ours in the present work using isotopic scaling. Donovan *et al.* [7] have recorded 13 bands of TeH in the vacuum ultra-violet region using flash photolysis. Friedhoff *et al.* [8] have recorded the photo-electron spectrum of TeH^- , and determined an accurate value for the electron affinity. Recently Fink *et al.* [9] have observed near-infrared emission bands of TeH and TeD using a Fourier transform interferometer. The transitions involved are: (i) the fine structure transitions between the two spin components of the $X^2\Pi$ state and (ii) $v = 2 \rightarrow 0$ for TeH.

5.2 Experimental details

All the observations were made with an intracavity CO laser magnetic resonance spectrometer, which has been described Chapter 2. Figure 5.1 shows the CO laser spectrum in the region of the band origin of TeD. To use the CO laser in this long wavelength region a 150 line/mm grating was used along with CO plasma conditions that favour the population of high v states, i.e. low partial pressures of nitrogen and oxygen in the lasing plasma, as discussed

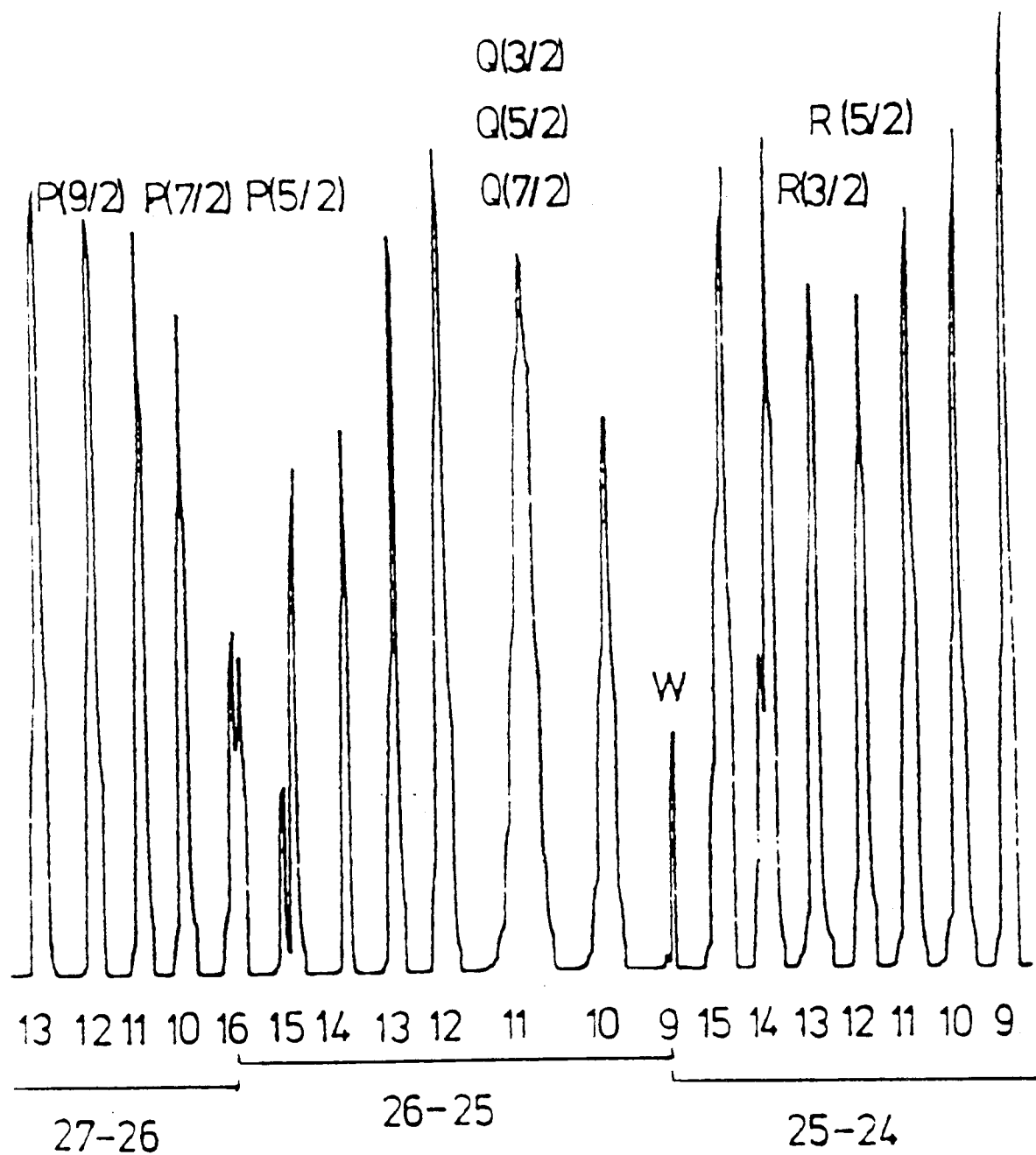


Figure 5.1: The CO Laser spectrum from 1450 to 1600 cm^{-1} with the transitions observed in TeD marked above the laser line on which they were observed.

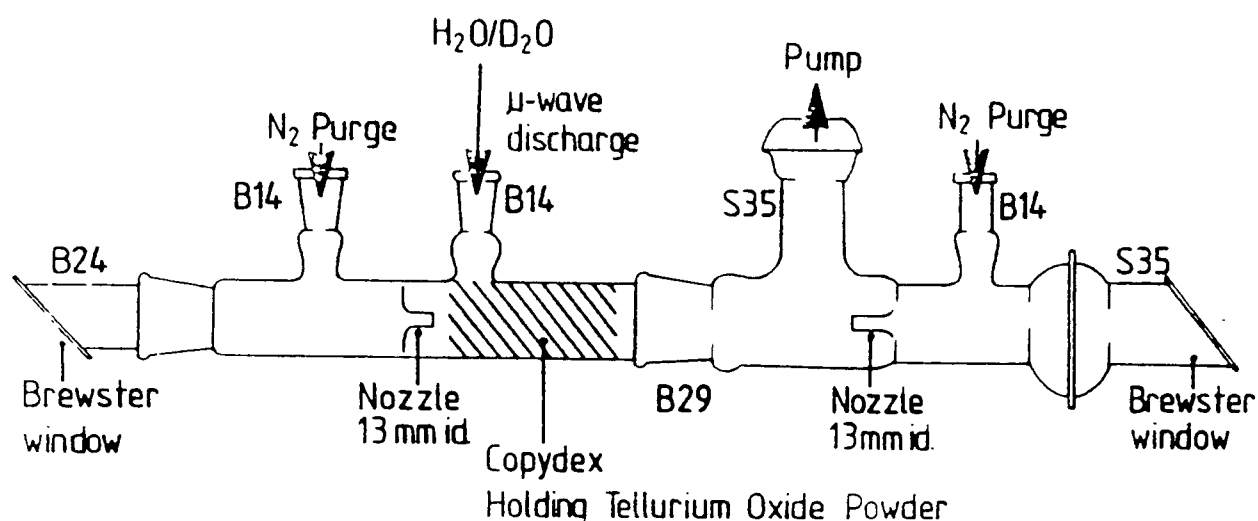


Figure 5.2: A diagram of the reaction cell used to produce TeD

in Chapter 2.

The TeD radicals were produced by the reaction of D atoms, generated in a microwave discharge through D₂O, with the amorphous brown allotrope of Te, in the intracavity reaction cell shown in figure 5.2. The brown Te was produced by flowing hydrazine over TeO₂ for half an hour with the pressure of the hydrazine set to approximately 2 Torr. The maximum signals were obtained with a D₂O pressure of approximately 0.4 mTorr for the fundamental band; significantly lower pressures, 0.1 mTorr, were required to optimise the hot bands.

5.3 Results and analysis

The initial searches for signals were guided by predictions made from the work of Fink *et al.* [9] who determined the vibrational interval of the first overtone band of TeH. Periodic trends were used to estimate the first anharmonicity constant ($\omega_e x_e$), see figure 5.3. These two constants were then scaled for TeD using the appropriate isotopic scaling factors, discussed in Chapter 3. Once signals had been observed, the detailed assignments were made from a consideration of the Zeeman patterns and from the relative abundances of the different isotopomers. Tellurium has eight naturally occurring isotopes [11]; signals have been observed for all but the least abundant ¹²⁰Te (0.1%). Five isotopes have $I = 0$, their natural abundances are; ¹³⁰Te (33.8%), ¹²⁸Te

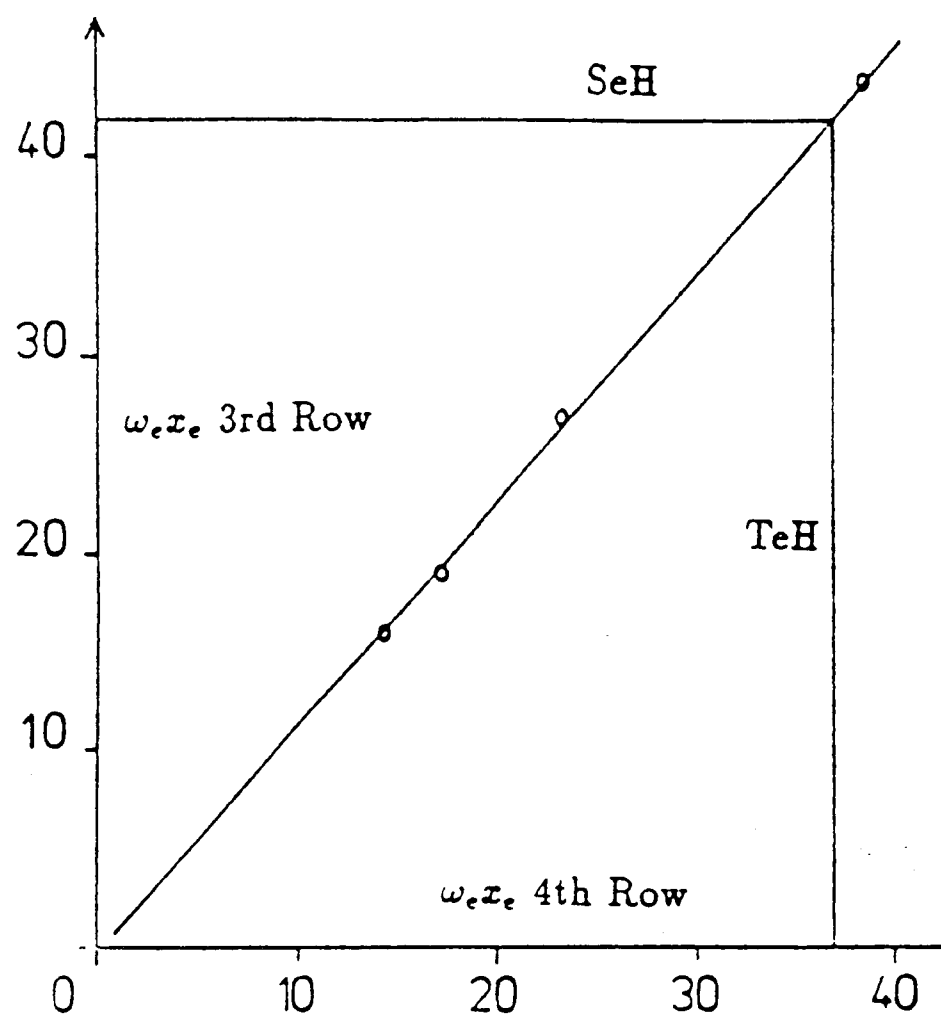


Figure 5.3: Plot of $\omega_e x_e$ values, from [10], for 4th row elements vs. $\omega_e x_e$ values 3th row elements.

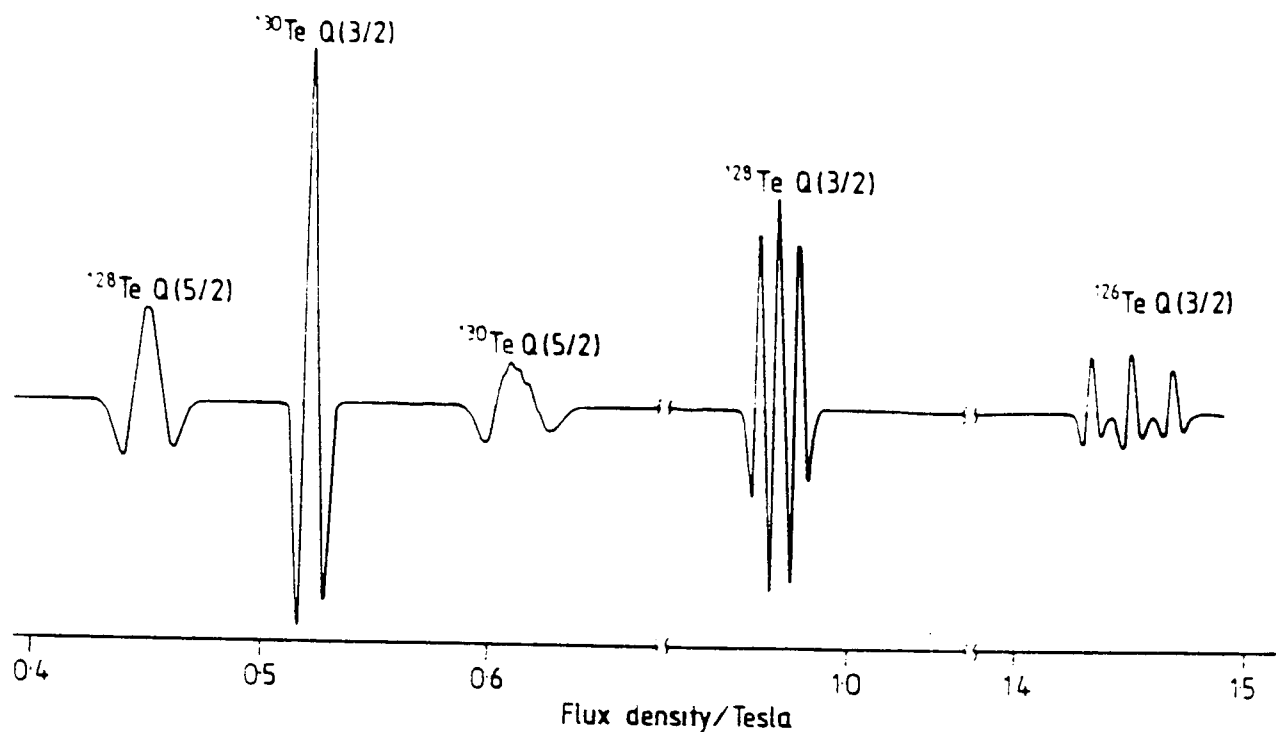


Figure 5.4: Part of the Q-branch region of the fundamental vibration-rotation band of the TeD radical in its $^2\Pi_{3/2}$ spin component.

(31.7%), ^{126}Te (18.9%), ^{124}Te (4.8%) and ^{122}Te (2.6%). Two isotopes have $I = \frac{1}{2}$, ^{125}Te (7.1%) and ^{123}Te (0.9%).

All group VI hydrides have $^2\Pi$ ground states. The observations reported here are all associated with the $^2\Pi_{3/2}$ spin component. This is due to the poor tunability of the $^2\Pi_{1/2}$ spin component, discussed in Chapter 4. Also, the levels of the $^2\Pi_{1/2}$ spin component lie about 3800 cm^{-1} above those of the $^2\Pi_{3/2}$ spin component and are therefore sparsely populated at room temperature.

Resonances were observed for eight transitions in the fundamental band ($v = 1 - 0$), two in the first hot band ($v = 2 - 1$), and two in the second hot band ($v = 3 - 2$). The details of the observations, together with their assignments, are given in Appendix B. Many of the lines were observed as Lamb dips, allowing resolution of closely spaced Zeeman patterns and improving the accuracy of measurement. Figure 5.4 shows the $Q(\frac{3}{2})$ and $Q(\frac{5}{2})$ transitions in the fundamental band for the various isotopomers near 1469.6 cm^{-1} . At high magnetic fields the lines are separated into three and five M_J components respectively by second order Zeeman effects. Figure 5.5 is a first order Zeeman diagram, for the transitions shown in figure 5.4. For a molecule with a coupling scheme that is a good approximation to Hund's case (a),

$$g_J^{(1)} = \frac{(g_l\Lambda + g_s\Sigma)\Omega}{J(J+1)}. \quad (5.1)$$

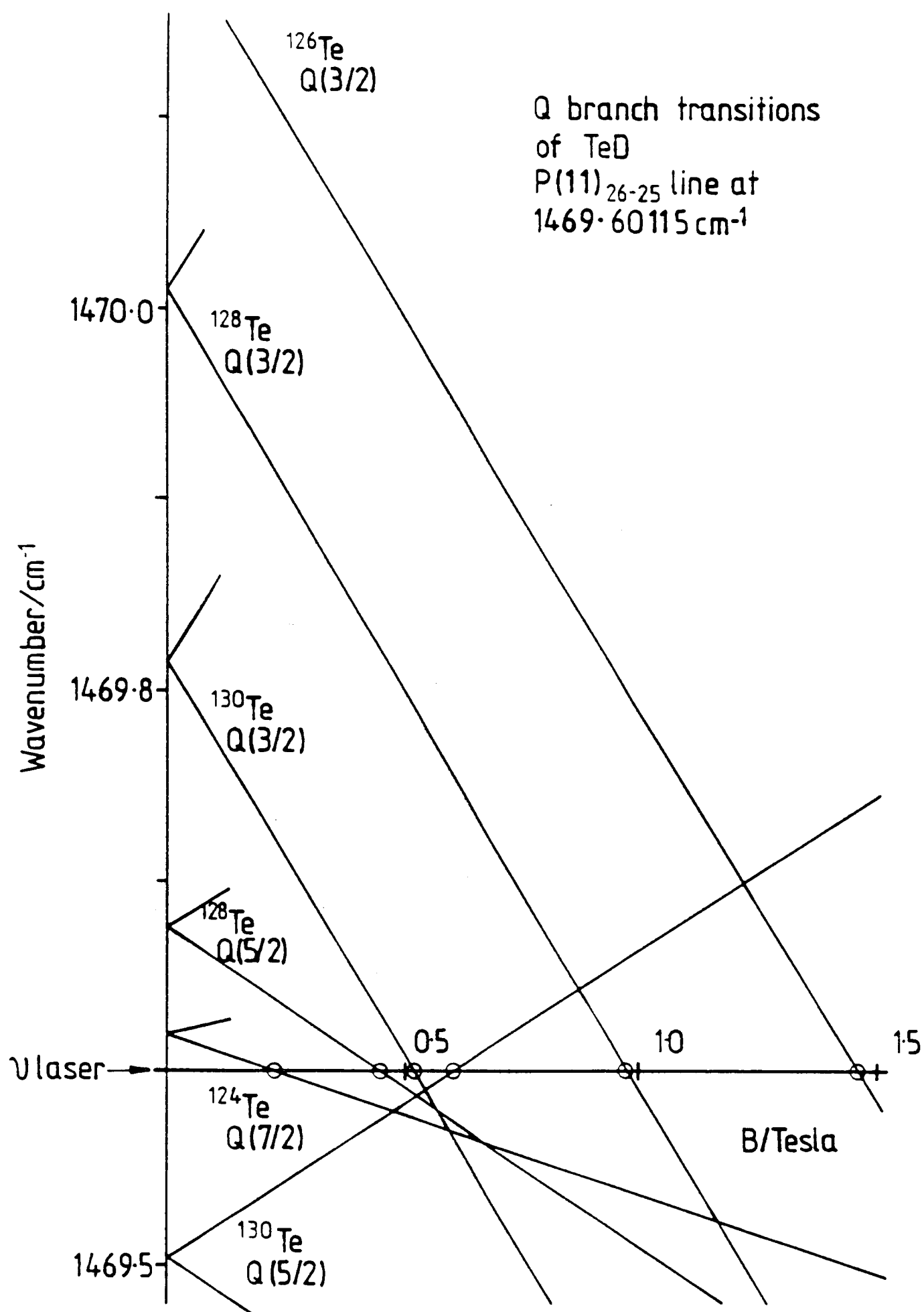


Figure 5.5: First order Zeeman diagram for the Q branch of TeD observed on P(11)₂₆₋₂₅

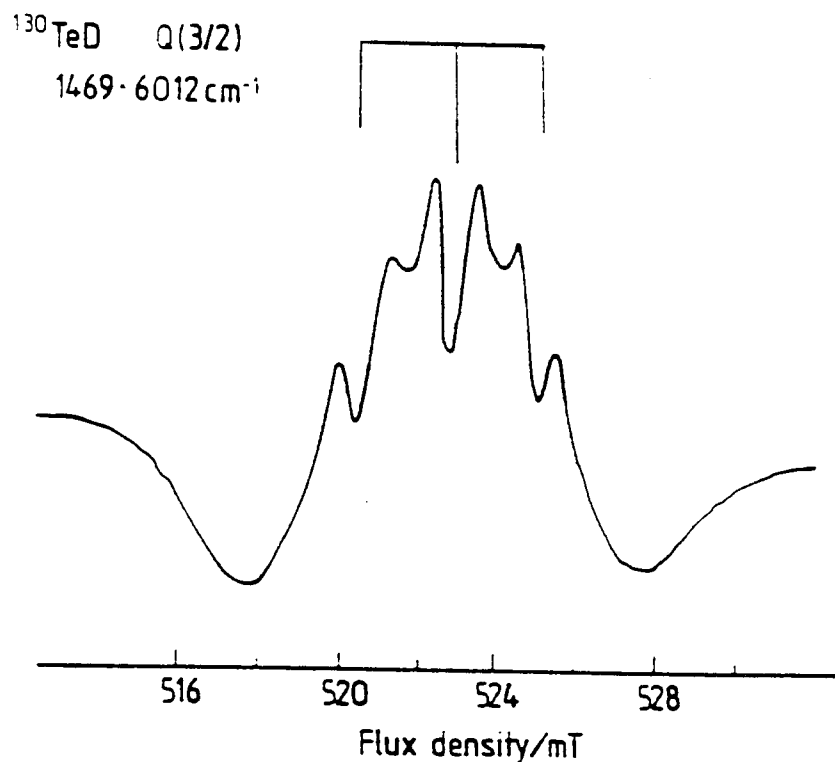


Figure 5.6: The M_J -structure of the $Q(\frac{3}{2})$ signal for the ^{130}TeD isotopomer, recorded as saturation (Lamb) dips. The signals are not resolved with Doppler-limited resolution, see 5.4

These first order g_J factors are used in the resonance condition for a $Q(J)$ LMR transition in σ polarization,

$$\nu_L = \nu_0 \pm g_J \mu_B B, \quad (5.2)$$

to calculate figure 5.5. The first order calculations predict the field positions of the observed resonances reasonably well. When a similar diagram is calculated for a transition in FeD , see chapter 8, second order effects have to be considered in order to reproduce the observed resonance pattern. Figure 5.6 shows an example of Lamb dips associated with the $Q(\frac{3}{2})$ transition of the ^{130}TeD isotopomer on the same laser line. In addition to the signals attributable to TeD , we have also observed some many -line absorption features, see figure 5.7. The appearance of these signals suggests that they are associated with a polyatomic species, possibly TeD_3 .

All the data given in Appendix B were subjected to a single fit to determine the parameters of an effective Hamiltonian described in Chapter 3, for

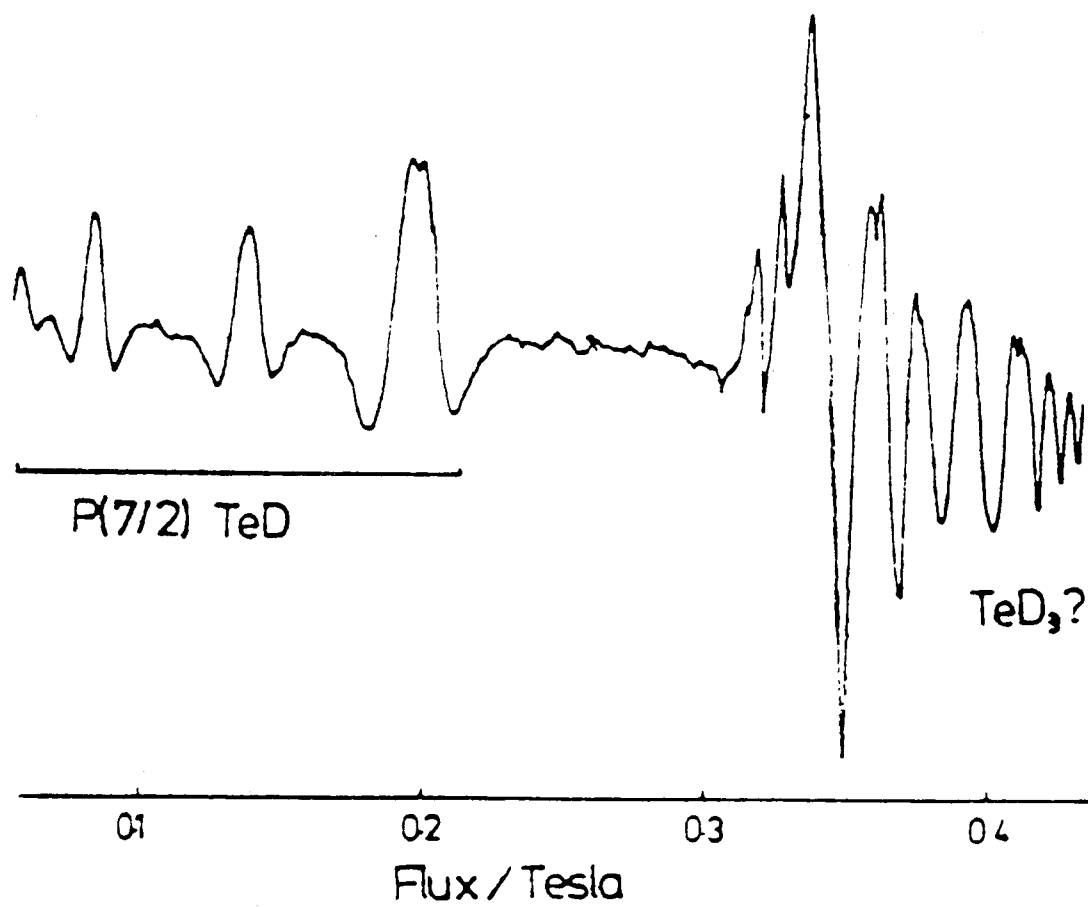


Figure 5.7: Resonances on the $P(10)_{27-26}$ laser line. At low field are resonances due to the $P(\frac{7}{2})$ transition in TeD, with a many-line feature at high field

Table 5.1: Values of constants for ^{130}TeD in the $X^2\Pi$ state.

Parameter	Value ^a	Correlation κ_i ^b
ν_0	1469.973324(41)	5.720
$\omega_e x_e$	18.64599(55)	49.154
$\omega_e y_e$	-0.04343(11)	49.110
$\Delta_{10}(\text{Te})$	-0.45(23)	2.754
B_0	3.070831(36)	59.674
α_B	-0.0588354(59)	8.571
D_0	0.0000529(14)	52.565
$10^8 H_0$	0.59	
A_0	-3814.34384	
A_D	-0.008015	
$p + 2q$	1.025885	
$p_D + 2q_D$	-0.00005413	
q	-0.00091	
$h_{\frac{3}{2}}$	-0.0436(12)	1.000
g_S	2.002	
g_L	1.00130(18)	135.103
g_r	-0.000298(92)	134.785

^a Value quoted in cm^{-1} where appropriate, with the values in parentheses corresponding to one standard deviation. All other parameters used in the fit were constrained to values taken from a refit of the data given in [9].

^b Correlation $\kappa_i = (\chi^{-1})_{ii}$ where χ is the matrix of correlation coefficients.

the dominant isotopomer, ^{130}TeD . In the fit the data were weighted according to the inverse square of the experimental line-widths, 0.5 MHz for the e.p.r. data, 10 MHz for saturated LMR signals (Lamb dips), and 100 MHz for Doppler limited LMR signals. In order to incorporate the different isotopic forms, the appropriate isotopic scaling factors were used. For the primary quantity in the observations, the harmonic vibrational frequency ω_e , it was also necessary to include the non-adiabatic correction to the isotopic scaling described in Chapter 3, Section 10.3. The results of the fit are given in Appendix B, which lists the residuals, and in Table 5.1, which gives the parameters determined in the process.

5.4 Discussion

Ten parameters for ^{130}TeD are well determined in the fit: ν_0 (the band origin for the fundamental band), $\omega_e x_e$, $\omega_e y_e$, $\Delta_{10}(\text{Te})$, B_0 , α_e , D_0 , g_L , g_r and $h_{\frac{3}{2}}$.

The g_I of the two tellurium isotopes with $I = \frac{1}{2}$ are -0.88828 for ^{125}Te and -0.73679 for ^{123}Te [11]. In order to fit a single parameter, $(h_{\frac{3}{2}})$ to the data for both isotopes the splitting in the transitions due to the ^{125}TeD isotopomer were scaled down in the ratio of the g_I values. The data given in Appendix B are the observed values for the transitions due to the ^{125}TeD isotopomer. The value of $h_{\frac{3}{2}}$ given in Table 5.1 is for ^{123}TeD .

The e.p.r. data [6] were included in the fit to determine g_L show lambda doubling. The lambda doubling parameters used in the fit were calculated from a refit of the $\mathbf{N}^2$ Hamiltonian [13] to the Fourier transform data of Fink *et al.* [9]. From the parameters in table 5.1, and equations given in Chapter 3, for ^{130}TeD , $\omega_e = 1507.40646(23) \text{ cm}^{-1}$ and $B_e = 3.100249(12) \text{ cm}^{-1}$. Using the equations given in Chapter 4, these correspond to values of $k_e = 265.5283 \text{ Nm}^{-1}$ and $r_e = 0.16558 \text{ nm}$. Table 5.2 compares these constants for the group VI deuterides. As for the Group IV hydrides, discussed in Chapter 4,

$$\omega_e \propto \frac{1}{r_e} \quad (5.3)$$

Table 5.2: Parameters of Group VI Deuterides in the $X^2\Pi$ state.

Parameter	^{16}OD	^{32}SD	^{80}SeD	$^{130}\text{TeD}^a$
ω_e^b	2720.24 ^c	1885.5 ^c	1719.7509 ^d	1507.40646
k_e^e	779.8990	396.8696	324.3366	265.5283
B_e^b	10.0209 ^c	4.900 ^c	4.003105 ^d	3.100249
r_e^f	0.09697	0.13406	0.14810	0.16558

^a value from this study

^b Parameters in cm^{-1} .

^c value from [10]

^d value from Fackerell [14]

^e value in Nm^{-1} .

^f value in nm.

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Chapter 6

The Infrared LMR spectrum of the FeH radical

6.1 Introduction

It is estimated that iron has a cosmic abundance of 0.003 % [1] . Since hydrogen is the most abundant element in the universe (92.5 %) it is to be expected that iron hydride will be found in the atmospheres of stars and the interstellar medium (ISM). FeH has been detected in the atmospheres of “cool” stars of spectral types M, S and K [2]. At present none of the numerous unassigned spectral lines due to molecules in the ISM have been assigned to transitions in FeH, but it is hoped that by calculating accurate zero field transition wavenumbers this study will help with these assignments.

6.1.1 The electronic structure of FeH

For an iron atom there are two low energy electronic configurations, $3d^6 4s^2$ and $3d^7 4s^1$. The molecular orbitals for FeH can be constructed as linear combinations of the hydrogen 1s orbital and iron orbitals. For the $3d^7 4s^1$ configuration of iron, the 4s orbital interacts with the hydrogen 1s orbital to give a pair of σ orbitals. This gives rise to the $3d^7 \sigma^2$ configuration. More than thirty molecular electronic states arise from this configuration, which are either doublets or quartets.

For iron in the $3d^6 4s^2$ configuration a 4s electron can be promoted to a 4p orbital and the sp hybrid σ orbital interacts with the hydrogen 1s orbital to give a $3d^6 \sigma^2 \sigma^*$ configuration. The $3d^6 \sigma^2 \sigma^*$ configuration gives rise to numerous doublet, quartet and sextet states. Mixing of these low lying electronic states leads to very complicated electronic spectra because this mixing allows intensity stealing by formally forbidden transitions. The spectra are further complicated by the large spin and orbital angular momenta in many of these

states. For example a $^4\Delta$ has four spin components and all the rotational levels are split by Λ type doubling.

6.1.2 Previous work

FeH was probably first observed in the laboratory in the mid 1950's [3] when a red band at 9896 Å was attributed to FeH. In 1974 Carroll and McCormack [4] reported two bands in the blue and the green region of the visible spectrum which were also assigned to FeH. Some of the lines they reported account for a few of the unassigned lines in the solar spectrum. In 1973 Klynning and Lindgren [5] recorded a band at 9890 Å. In 1976 Carroll *et al.* published spectra of FeH and FeD [6, 7], which showed five systems between 2300 Å and 8900 Å. In all of their studies FeH was formed in a King furnace by passing H_2 over iron heated to 2900 K.

In 1979 a study of FeH and FeD in an argon matrix, at a temperature of 4K was published [8]. This work determined vibrational constants which differ from those determined by optical work (and also those of the present study). In 1983 a partial analysis of two of the near infra-red bands of FeD was published. These term values were used to predict the frequencies of the rotational transitions in FeD presented in chapter 7. Also in 1983, Stevens *et al.* [9] published the laser photon electron spectrum of FeH^- and FeD^- . A careful analysis of these results showed that the electronic ground state is $^4\Delta$ with a $^6\Delta$ state (probably) only 1945 cm^{-1} above it. In 1987 Philips *et al.* [10] published a detailed rotational analysis of the near infra red bands and this is the starting point for the present study. Beaton *et al.* [11] have carried out a FIR LMR study of FeH using the spectrometer described in Chapter 2, and their ground state g_J factors are used in the calculations presented here.

6.2 Experimental

All except one of the FeH resonances presented in table 6.1 were recorded using the Faraday LMR described in chapter 2. Only the $Q(\frac{7}{2})\ ^4\Delta_{\frac{7}{2}} - ^4\Delta_{\frac{7}{2}}$ was recorded using the intracavity LMR spectrometer at Oxford this was used to avoid absorption of the $P(6)_{15-14}$ laser line by atmospheric water. The CO laser spectrum in the 1760 cm^{-1} region is shown in figure 6.1. FeH was produced by the reaction of iron penta-carbonyl, $Fe(CO)_5$ with hydrogen atoms. At Bonn the reaction took place in a d.c. electrical discharge through the same chemicals. It was found that the optimum signals were observed when the discharge current was 5 mA, the partial pressure of helium was 8 Torr and the partial pressure of hydrogen was 0.5 Torr. Iron carbonyl was carefully added to the discharge through a micrometering valve until

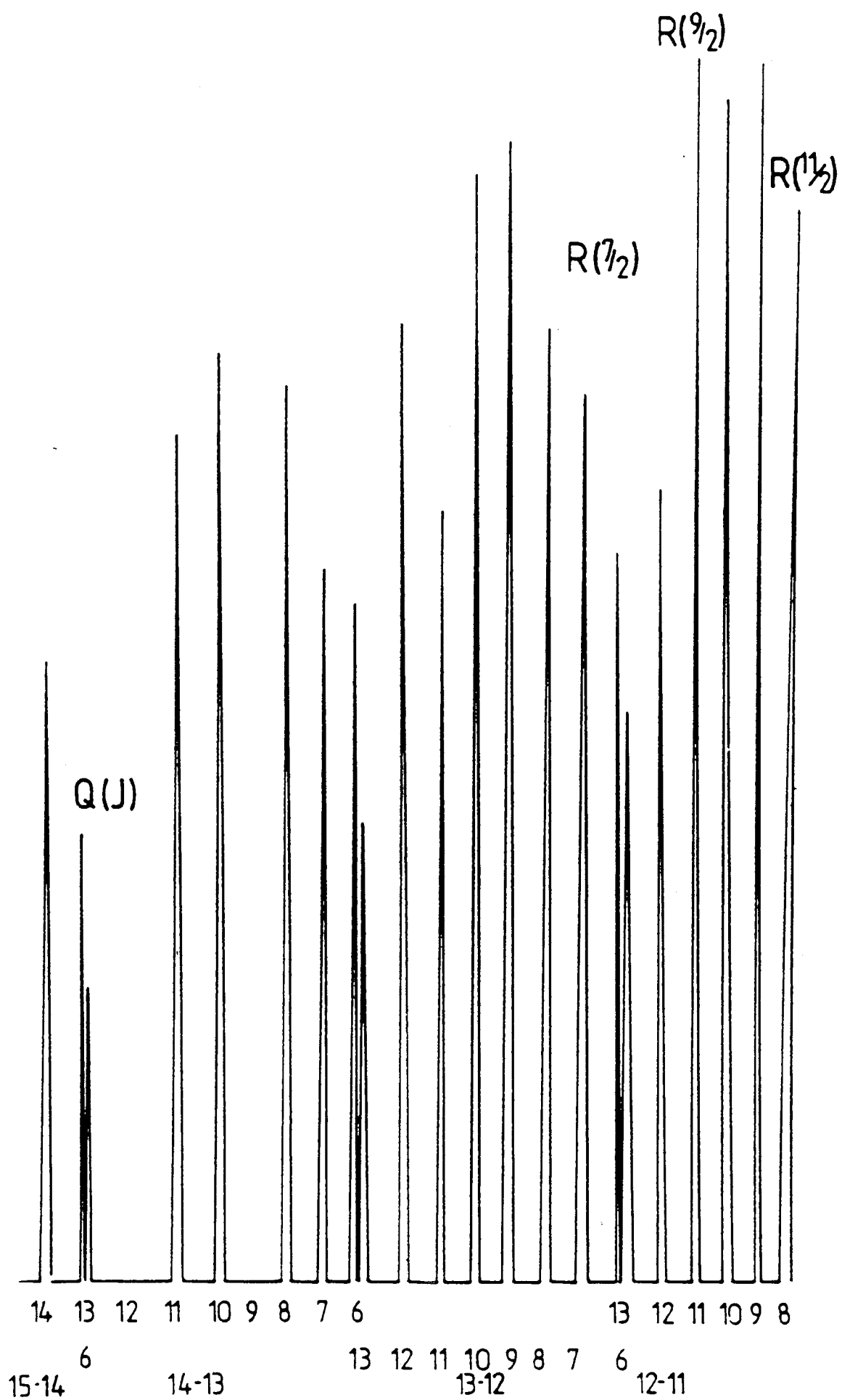


Figure 6.1: The CO laser spectrum around 1760 cm^{-1} , with transitions of FeH marked above the laser lines on which they were observed

Table 6.1: Transitions wavenumbers of the (1,0) band of FeH compared with the wavenumbers of CO laser lines.

Transition	Zerofield wavenumber ^a /cm ⁻¹ for FeH	CO laser line	CO laser wavenumber /cm ⁻¹
$P(\frac{9}{2}) \frac{7}{2} - \frac{7}{2}$	1711.62	$P(12)_{16-15}$	1711.620332
$Q(\frac{9}{2}) \frac{5}{2} - \frac{5}{2}$	1757.82 ^b	$P(13)_{14-13}$	1757.896825
$Q(\frac{9}{2}) \frac{5}{2} - \frac{5}{2}$	1758.52	$P(6)_{15-14}$	1758.492296
$Q(\frac{7}{2}) \frac{7}{2} - \frac{7}{2}$	1758.70	$P(6)_{15-14}$	1758.492296
$Q(\frac{7}{2}) \frac{7}{2} - \frac{7}{2}$	1758.70	$P(13)_{14-13}$	1757.896825
$Q(\frac{9}{2}) \frac{7}{2} - \frac{7}{2}$	1758.20	$P(13)_{14-13}$	1757.896825
$Q(\frac{11}{2}) \frac{7}{2} - \frac{7}{2}$	1757.50	$P(13)_{14-13}$	1757.896825
$R(\frac{7}{2}) \frac{7}{2} - \frac{7}{2}$	1805.28	$P(7)_{13-12}$	1805.522673
$R(\frac{9}{2}) \frac{7}{2} - \frac{7}{2}$	1815.74	$P(11)_{12-11}$	1815.937938
$R(\frac{11}{2}) \frac{7}{2} - \frac{7}{2}$	1867.72	$P(8)_{12-11}$	1827.242290

^aValues from [2] with Λ doubling averaged.

^bextrapolated, see text.

the voltage across the discharge increased by about 0.5 kV. Following this procedure it was possible to run for about 30 minutes before the iron deposits on the walls of the discharge tube caused a short circuit, necessitating the dismantling of the apparatus for cleaning.

For the signal recorded at Oxford and the FIR signals a microwave discharge run through 0.1 Torr hydrogen in about 2 Torr of helium was used to produce H atoms which reacted with the iron carbonyl vapour. The reaction can be summarized by equation 6.1



6.3 Results and Analysis

Signals which required the presence of iron carbonyl in the discharge, and were therefore assumed to be due to FeH, were observed on the laser lines listed in table 6.1. Six other laser lines ($P(16)_{14-13}$, $P(12)_{11-10}$, $P(12)_{12-11}$, $P(12)_{17-16}$, $P(14)_{12-11}$ and $P(13)_{16-15}$), in this region of the laser spectrum were searched using the Faraday LMR and no signals observed. The signals in table 6.1 were assigned to transitions using the proximity of the zero field wavenumber from the term values of Phillips and Davies to the wavenumber of the laser line. A computer program (FEHCALINT) was developed in order

to assign the M_J structure of the transitions. FEHCALINT calculated the first order g_J factors for the levels involved in the transition using the equation 6.2,

$$g_J^{(1)} = \frac{(g_L\Lambda + g_S\Sigma)\Omega}{J(J+1)}, \quad (6.2)$$

or read in g_J factors if they were known from elsewhere. The program then calculates approximate resonances for each of the M_J components for both π and σ polarization using equation 6.3

$$\nu_L = \nu_0 + g'_J\mu_B\mathcal{B}M'_J - g''_J\mu_B\mathcal{B}M''_J. \quad (6.3)$$

To help with the assignment of the Zeeman pattern the relative intensities can be calculated,

$$I \propto (3j)^2 \quad (6.4)$$

where $3j$ stands for

$$\begin{pmatrix} J \pm 1 & 1 & J \\ -(M \pm 1) & \pm 1 & M \end{pmatrix}. \quad (6.5)$$

$3j$ symbols are tabulated by Zare [14]. However in order to arrange them in the most convenient form for calculating the intensities of P and R LMR transitions, measured in σ polarization, the standard transpositions rules were used.

Using these predictions in conjunction with the tuning rate information from the side band measurement and the ΔM_J information from the direction of the Faraday rotation, discussed in chapter 2, it was possible to make unambiguous assignments of almost all resonances.

An attempt was made to fit the parameters of a Hamiltonian, for a $^4\Delta$ state, of the type described in Chapter 3 to the term values of Phillips and Davis for FeH. This was done for each spin component separately and in each case the standard deviation of the fit was worse than 2 cm^{-1} . This failure of the model is due to large perturbations caused by the presence of the low lying electronic states mentioned in section 6.1. It was not possible therefore to fit the LMR spectra with a single effective Hamiltonian. In order to extract g_J factors and zero field transition wavenumbers from the LMR data, the energy of a level, at a flux density $\mathcal{B}$, was described by the formula which treats the Zeeman effect to second order:

$$E = E_0 + g_J\mu_B\mathcal{B}M_J + C_1(\mu_B\mathcal{B})^2 + C_2(\mu_B\mathcal{B}M_J)^2. \quad (6.6)$$

Equation 6.3 can be rewritten as,

$$\nu_L = \nu_0 + \mu_B\Delta g_J\mathcal{B}M_J + (C'_1 - C''_1)(\mu_B\mathcal{B})^2 + C'_2(\mu_B\mathcal{B}M'_J)^2 - C''_2(\mu_B\mathcal{B}M''_J)^2. \quad (6.7)$$

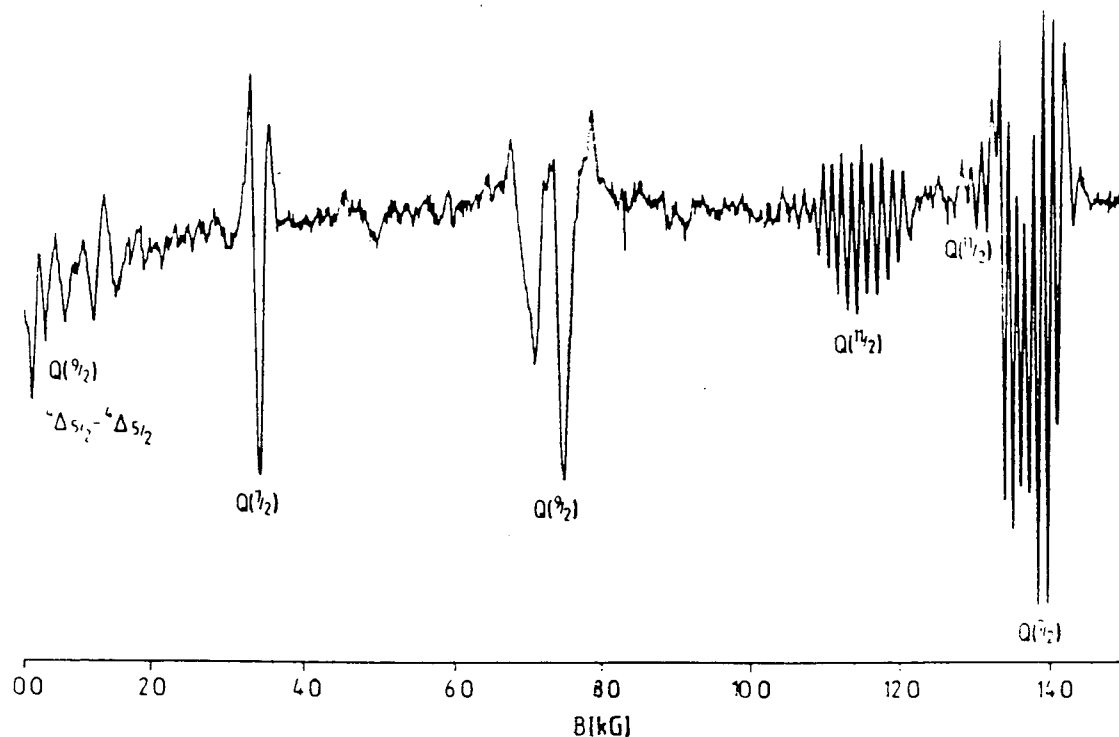


Figure 6.2: Some Q lines in the (1,0) band of FeH $^4\Delta$ state, observed on the $P(13)_{14-13}$ and the $P(6)_{15-14}$ CO laser lines.

6.3.1 Results of the fits

Fit of the $Q(\frac{7}{2})$ transition

Since the $Q(\frac{7}{2})$ transition has been observed on two laser lines, it is possible to fit all the parameters for the upper $v = 1$ state, constraining the lower state parameters to the values determined by Beaton [13] from the FIR data.

The $Q(\frac{7}{2})$ signal is shown in figure 6.2 was observed on the $P(13)_{14-13}$ and the $P(6)_{15-14}$ CO laser lines simultaneously. It was not possible to get the lines to lase individually at Bonn (this was due to a problem with a new angle encoder which had just been fitted), but the signal was measured at 3479.0 G on the $P(6)_{15-14}$ line at Oxford. On the $P(13)_{14-13}$ line, the $Q(\frac{7}{2})$ transition is resolved into its 7 M_J components, centred on 13700 G, by second order Zeemann effects. The 7 strong signals due to the $Q(\frac{7}{2})$ transition are superimposed by 11 weaker signals due to one Λ doublet of the $Q(\frac{11}{2})$ spectrum. When the $Q(\frac{7}{2})$ signals were recorded using a side band of the AOM the tuning rate of these transitions was measured to be negative and since the resonances point downwards, $\Delta M_J = -1$. It is not possible to determine whether the lowest field transition has $M_J'' = \frac{7}{2}$ (fit a) or $M_J'' = -\frac{5}{2}$ (fit b). Two fits were run, the results of which are given in table 6.2. The

Table 6.2: Parameters determined for the $v = 1, J = \frac{7}{2}$ level of FeH in its $^4\Delta_{\frac{7}{2}}$ state, from fits to the two possible assignments of the $Q(\frac{7}{2})$ transition

Parameter	fit a	fit b
ν_0^a	1758.694585(92)	1758.695979(94)
$g_{\frac{7}{2}}$	1.241192(79)	1.262717(77)
$g_{\frac{7}{2}}^b$	1.248042	1.248100
C_1^c	-0.00512(41)	0.00823(41)
C_2^c	0.003126(60)	0.003230(62)

^a parameter in cm^{-1}

^b value for $v = 0$ state constrained to that determined in [13]

^c parameter in cm.

assignments of the transitions are given in table 6.3.

Although the $P(\frac{9}{2})$ transition was observed on the $P(12)_{16-15}$ laser line the signal was at so low a field that it could not be measured accurately and consequently it was not split into its Zeeman components, see figure 6.3. This was unfortunate as a fit of the $P(\frac{9}{2})$ with the $Q(\frac{7}{2})$, which has a common upper state would have determined the order of the M_J stack in the Q transition. The results of the fits do however favour fit a over fit b. For the $v = 0$ level g_J has an average value of 1.248071 which is closer to the g_J value for the $v = 1$ state determined from assignment a. This favors fit a, since to first order the g_J values in the 2 levels are expected to be equal. Also the overall standard deviation of fit a ($8.586 \times 10^{-5} \text{ cm}^{-1}$) is slightly better than for fit b ($8.672 \times 10^{-5} \text{ cm}^{-1}$).

Fit of the $Q(\frac{9}{2})$ with $R(\frac{7}{2})$ transitions

The resonances due to the $R(\frac{7}{2})$ transition are shown in figure 6.4. When measured using the side band of the AOM it is found that this spectrum tunes positively. The fourth pair of resonances point upwards showing they are due to a transition involving $\Delta M_J = -1$ as discussed in Chapter 2. This leaves no uncertainty in the assignment. Using first order tuning rates the splitting due to Λ doubling of the four pairs of resonances observed is approximately 200 MHz. From the FIR study it is known that the Λ doubling in the $v = 0, J = \frac{7}{2}$ level is 72.6 MHz. For any given vibrational level the energy order of the parity doublets will alternate, see figure 6.5, so for a P or R transition,

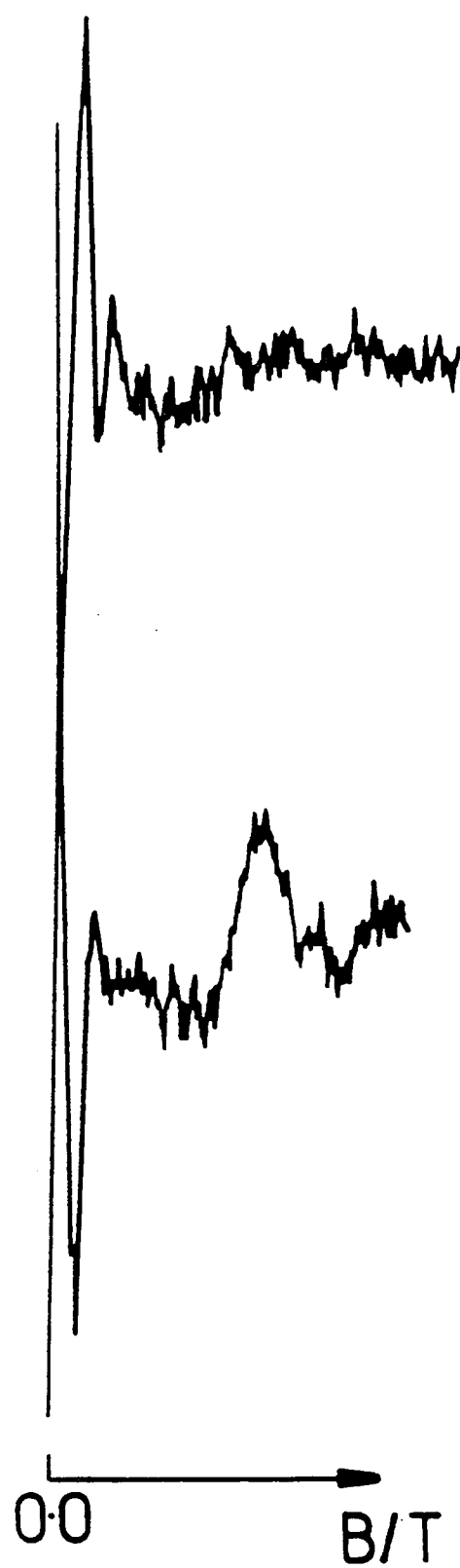


Figure 6.3: The $P(\frac{9}{2})$ transition in the spectrum of FeH observed on the $P(12)_{16-15}$ CO laser line. The phase of the signal was inverted on the two scans shown by rotating the analyser through the crossed position.

Table 6.3: The $Q(\frac{7}{2})$ transition of FeH observed on the $P(13)_{14-13}$ and $P(6)_{15-14}$ laser lines

M'_J	M''_J	ν_L / cm^{-1}	Obs. B/T	$o - c^a$	$(\delta\nu/\delta B)^b$
$\frac{5}{2}$	$\frac{7}{2}$	1757.896825	1.3363	-0.2	-1.808
$\frac{3}{2}$	$\frac{5}{2}$	1757.896825	1.3469	0.4	-1.790
$\frac{1}{2}$	$\frac{3}{2}$	1757.896825	1.3577	-0.8	-1.771
$-\frac{1}{2}$	$\frac{1}{2}$	1757.896825	1.3694	0.4	-1.751
$-\frac{3}{2}$	$-\frac{1}{2}$	1757.896825	1.3818	2.4	-1.730
$-\frac{5}{2}$	$-\frac{3}{2}$	1757.896825	1.3934	-3.5	-1.708
$-\frac{7}{2}$	$-\frac{5}{2}$	1757.896825	1.4075	1.3	-1.685
$-\frac{1}{2}$	$\frac{1}{2}$	1758.492296	0.3479	0.0	-1.744

^a in $\text{cm}^{-1} \times 10^4$. The standard deviation of the fit was $8.58 \times 10^{-5} \text{ cm}^{-1}$.
^b in MHz G^{-1} .

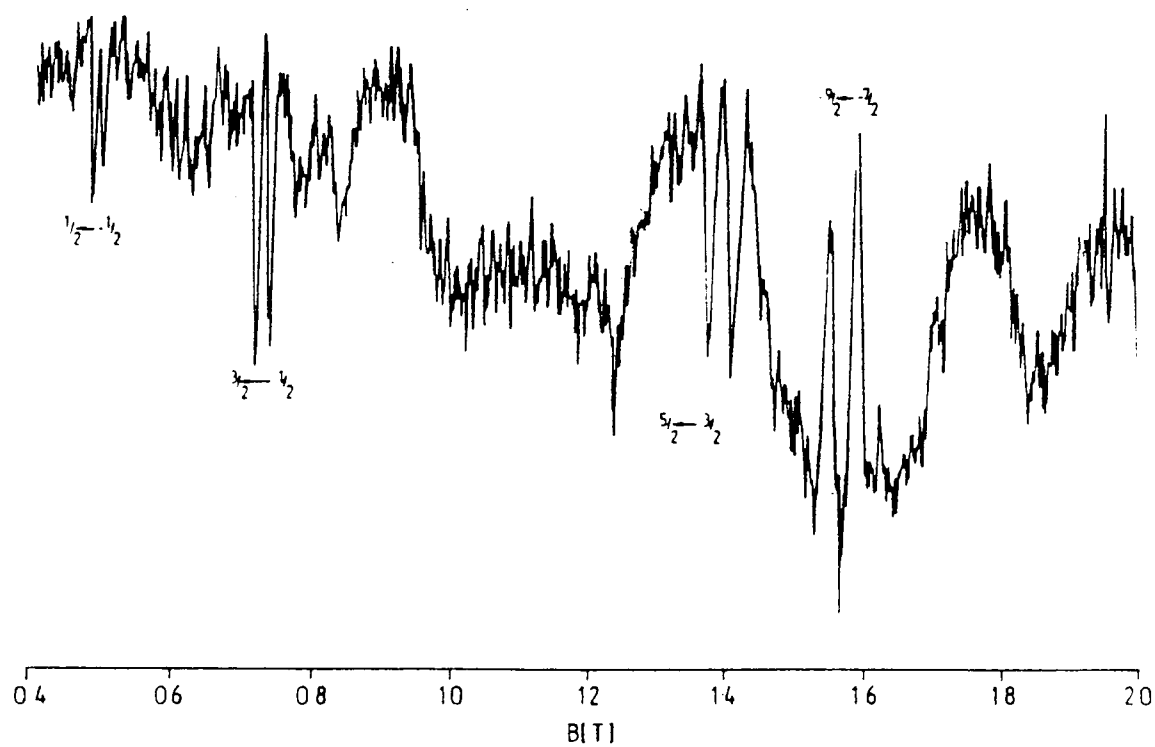


Figure 6.4: Resonances due to the $R(\frac{7}{2})$ transition in the $(1,0)$ band of FeH observed on the $P(7)_{13-12}$ CO laser line.

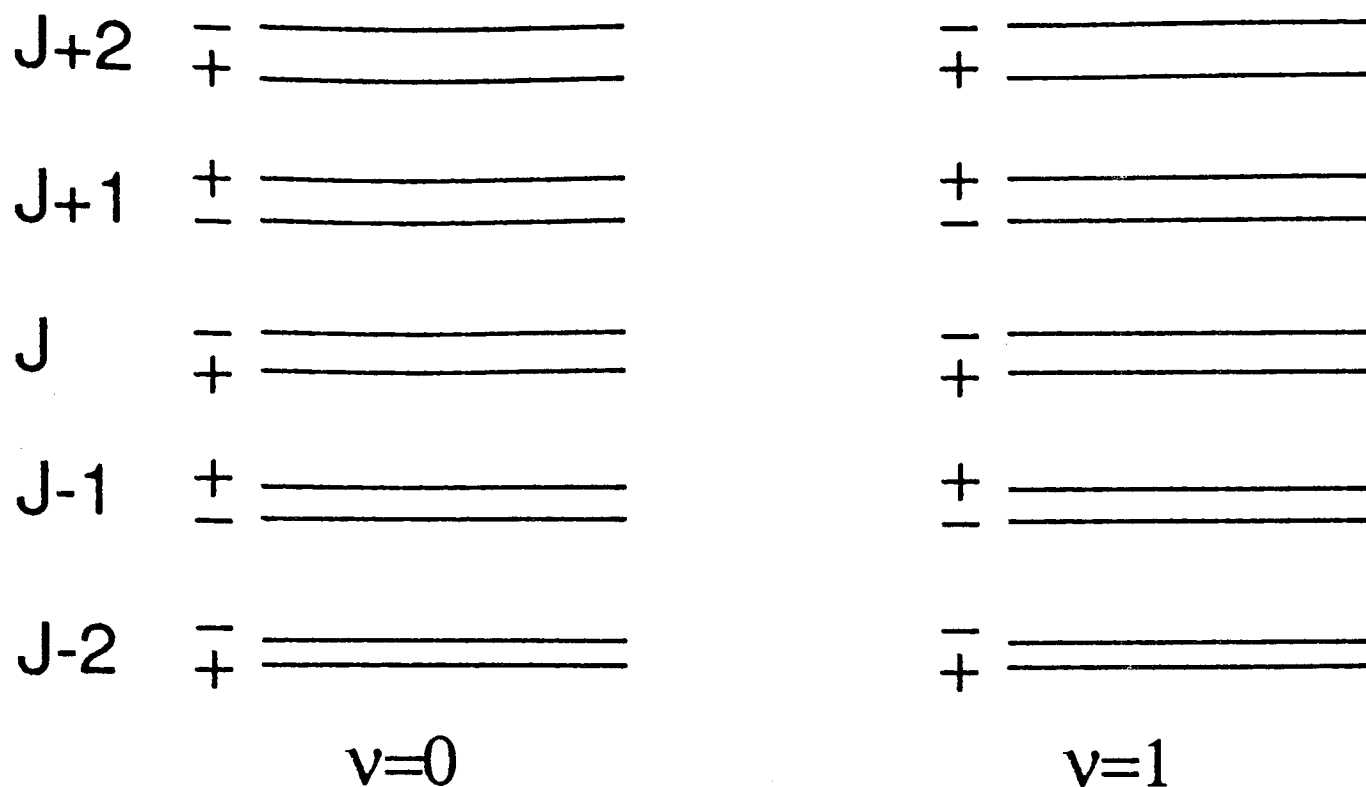


Figure 6.5: Alternation of parity levels with J .

the observed splitting is equal to the difference of the Λ doublings.

$$\Delta\nu_{obs} = \Delta\nu'_{\Lambda} - \Delta\nu''_{\Lambda}, \quad (6.8)$$

while for a Q transition,

$$\Delta\nu_{obs} = \Delta\nu'_{\Lambda} + \Delta\nu''_{\Lambda}. \quad (6.9)$$

Using these two equations the observed splitting for the $Q(\frac{9}{2})$ is 611 MHz which, using a first order estimate of the tuning rate, corresponds to a separation of 485 G. In figure 6.2 there are 2 broad resonances at approximately 7000 and 7500 G. These resonances tune in opposite directions each time the spectrum was recorded there was a marked difference between the intensities of the two lines. These observations lead to the conclusion that these resonances are both due to the $Q(\frac{9}{2})$ transition in resonance with the two laser lines and with the Λ doublets on one line being superimposed on the Λ doublets on the other line. Support is given for these assignments when they are fitted with the corresponding Λ doublet of the $R(\frac{7}{2})$ spectrum. We are concerned with a common upper state of a Q and an R transition as shown in figure 6.6; only one transition to one parity level is shown for clarity. We use parameters determined from FIR transitions to determine the separation of the two $v = 0$ states $\Delta\nu_{\Lambda}(\frac{9}{2})$. When transition is to the a state¹ of the $v = 1$ level, the zero field separation is given by:

$$E_0 = \nu_a + \Delta\nu_{\Lambda}(\frac{9}{2}). \quad (6.10)$$

¹The parity of the levels has not been determined so the recommendation by Brown *et al.* [12] is followed in which the lower energy level of a Λ doubled pair is labelled a and the upper level b.

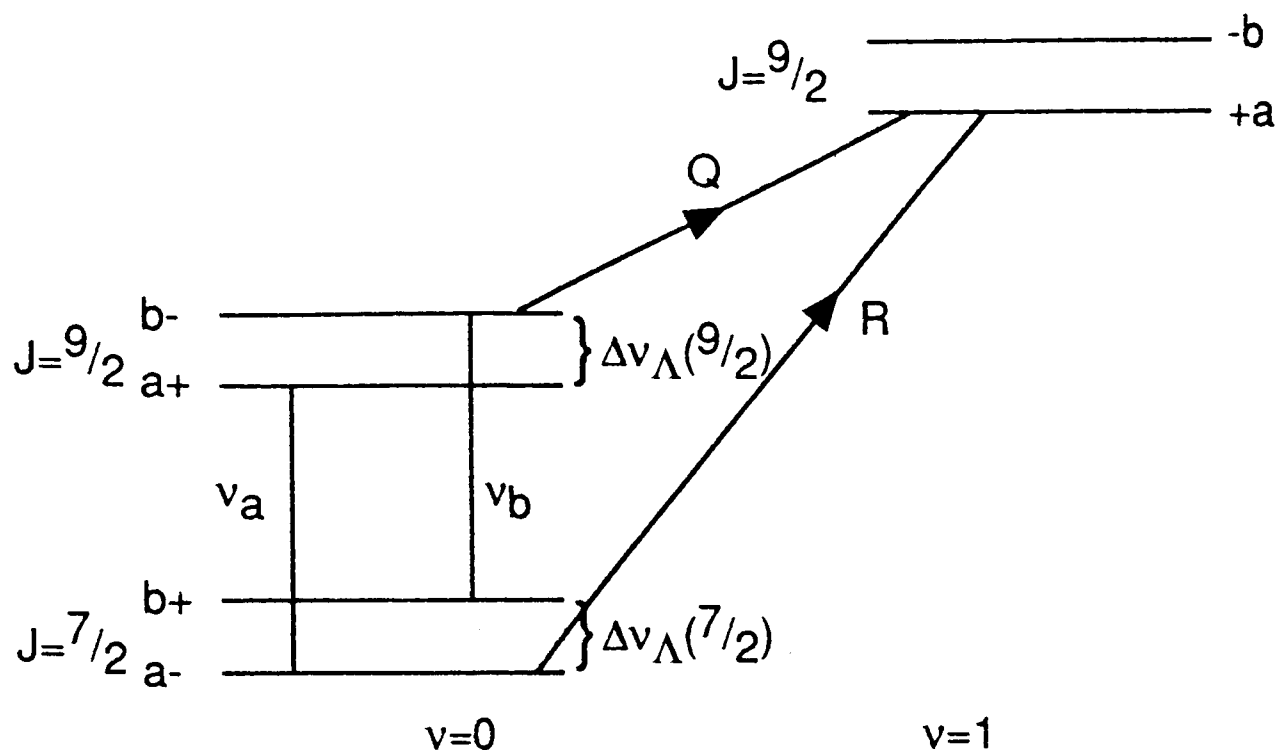


Figure 6.6: Energy levels involved in $R(\frac{7}{2})$ and $Q(\frac{9}{2})$ with arbitrary choice of parity.

The g_J and C_2 parameters are uniquely determined for each level however C_1 can only be determined as a difference between 2 levels involved in a transition, so it is taken to be the average of the two values determined from the FIR study. When the transition is to the b state of the $v = 1$ level

$$E_0 = \nu_b - \Delta\nu_\Lambda(\frac{9}{2}). \quad (6.11)$$

The parameters in table 6.4 are those determined for the $J = \frac{9}{2}$, $v = 1$ state.

Fit of the $Q(\frac{11}{2})$ transition with the $R(\frac{9}{2})$ transition

Resonances due to the $R(\frac{9}{2})$ transition are shown in figure 6.7. Assignment of this spectrum was made by checking that the product of the magnetic field separation of the M_J components and the first order tuning rate were approximately equal. It was found that on average the observed splitting is 624 MHz. From this the estimated splitting of the $Q(\frac{11}{2})$ is 2163 MHz which corresponds to a field separation of 2163 G if the first order tuning rate is 1.0 MHz/G. This separation is seen in figure 6.2, the higher field component of the $Q(\frac{11}{2})$ being superimposed on the $Q(\frac{7}{2})$. The parameters for the levels common to the two transitions were fitted in the same way as for the $Q(\frac{9}{2})$ and $R(\frac{7}{2})$. It was found that the lowest standard deviation ($0.541 \times 10^{-3} \text{ cm}^{-1}$) for the lowest level of the Λ doublet was achieved with $M_J'' = -\frac{11}{2}$ ($\Delta M_J = +1$) as the assignment for the lowest field resonance.

Table 6.4: Parameters determined for the $v = 1, J = \frac{9}{2}$ level of FeH in its $^4\Delta_{\frac{7}{2}}$ state.

Parameter	State a	State b
ν_0^a	1758.1883(48)	1758.2044(36)
$g_{\frac{9}{2}}$	0.8956(22)	0.8950(17)
$g_{\frac{9}{2}}^b$	0.902841	0.902740
$g_{\frac{7}{2}}^b$	1.248042	1.248100
$C_1(\frac{9}{2}^1 - \frac{7}{2}^0)^c$	0.036(17)	0.020(14)
$C_1(\frac{9}{2}^0 - \frac{7}{2}^0)^c$	0.02915	
$C_2(\frac{9}{2}^0)^d$	0.000290	0.000293
$C_2(\frac{7}{2}^0)^d$	0.002959	0.002910

^a parameter in cm^{-1}

^b value for $v = 0$ state, constrained to that determined in [13]

^c parameter in cm, with the Ω and v values given for the upper and lower states

^d value for $v = 0$ state, constrained to the average of the values determined in [13].

Table 6.5: The $Q(\frac{9}{2})$ transition of FeH observed on the $P(13)_{14-13}$ and $P(6)_{15-14}$ laser lines and the (a) component of the $R(\frac{7}{2})$ transition observed on the $P(7)_{13-12}$ laser line

M'_J	M''_J	ν_L/cm^{-1}	Obs. B/T	$o - c^a$	$(\delta\nu/\delta B)^b$
$-\frac{1}{2}$	$\frac{1}{2}$	1758.492296	0.7478	-7.65	1.257
$\frac{1}{2}$	$-\frac{1}{2}$	1757.896825	0.7011	5.04	-1.259
$\frac{1}{2}$	$-\frac{1}{2}$	1805.552673	0.4963	0.72	1.517
$\frac{3}{2}$	$\frac{1}{2}$	1805.552673	0.7323	1.42	1.033
$\frac{5}{2}$	$\frac{3}{2}$	1805.552673	1.4028	0.59	0.555
$-\frac{9}{2}$	$-\frac{7}{2}$	1805.552673	1.5894	-0.12	0.470

^a in $\text{cm}^{-1} \times 10^3$. The standard deviation of the fit was $5.38 \times 10^{-3} \text{ cm}^{-1}$.

^b in MHz G^{-1} .

Table 6.6: The $Q(\frac{9}{2})$ transition of FeH observed on the $P(13)_{14-13}$ and $P(6)_{15-14}$ laser lines and the (b) component of the $R(\frac{7}{2})$ transition the $P(7)_{13-12}$ laser line

M'_J	M''_J	ν_L / cm^{-1}	Obs. B/T	$o - c^a$	$(\delta\nu/\delta B)^b$
$\frac{1}{2}$	$-\frac{1}{2}$	1758.492296	0.7011	-5.40	1.249
$-\frac{1}{2}$	$\frac{1}{2}$	1757.896825	0.7478	7.35	-1.267
$\frac{1}{2}$	$-\frac{1}{2}$	1805.552673	0.4800	-0.71	1.511
$\frac{3}{2}$	$\frac{1}{2}$	1805.552673	0.7131	-1.00	1.024
$\frac{5}{2}$	$\frac{3}{2}$	1805.552673	1.3706	0.41	0.558
$-\frac{9}{2}$	$-\frac{7}{2}$	1805.552673	1.5486	-0.64	0.456

^a in $\text{cm}^{-1} \times 10^3$. The standard deviation of the fit was $5.38 \times 10^{-3} \text{ cm}^{-1}$.

^b in MHz G^{-1} .

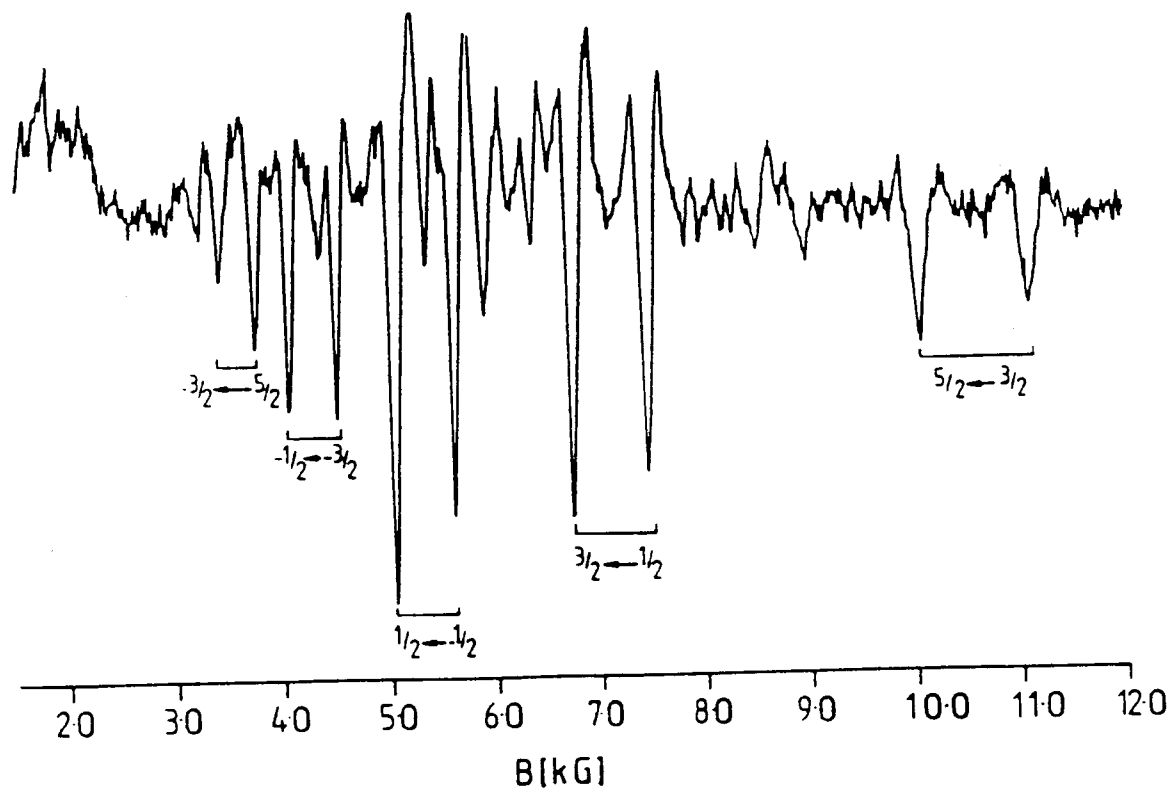


Figure 6.7: Resonances due to the $R(\frac{9}{2})$ transition in the (1,0) band of FeH observed on the $P(11)_{12-11}$ CO laser line.

Table 6.7: Parameters determined for the $v = 1, J = \frac{11}{2}$ level of FeH in its $^4\Delta_{\frac{7}{2}}$ state

Parameter	State a	State b
ν_0^a	1757.52079(34)	1757.507(24)
$g_{\frac{11}{2}}^b$	0.70240(10)	0.715(24)
$g_{\frac{11}{2}}^b$	0.711093	0.710588
$g_{\frac{9}{2}}^b$	0.902842	0.902740
$C_1(\frac{11}{2}^1 - \frac{9}{2}^0)^c$	0.0197(16)	-0.111(18)
$C_1(\frac{11}{2}^0 - \frac{9}{2}^0)^d$	0.00786075	
$C_2(\frac{11}{2}^1)^c$	0.000069(64)	0.0025(14)
$C_2(\frac{9}{2}^0)^e$	0.00002896	0.00002932
$C_2(\frac{11}{2}^0)^e$	-0.00000162	-0.00000165

^a parameter in cm^{-1}

^b value for $v = 0$ state, constrained to that determined in [13]

^c parameter in cm.

^d value for $v = 0$ state, constrained to the average of the values determined in [13].

^e value for $v = 0$ state, constrained to the value determined in [13].

Because of the superposition of the $Q(\frac{7}{2})$ and $Q(\frac{11}{2})$ only the first four low field resonances of the $Q(\frac{11}{2})$ can be measured, and the line shapes are probably distorted, leading to a loss of accuracy in the field measurements. A fit of these resonances with the $R(\frac{9}{2})$ resonances had a standard deviation of $0.552 \times 10^{-2} \text{ cm}^{-1}$. The upper state parameters determined in both fits are given in table 6.7.

The $Q(\frac{9}{2})$ transition of the $^4\Delta_{\frac{5}{2}} - ^4\Delta_{\frac{5}{2}}$ spin system

The previous paragraphs have accounted for all the resonances in figure 6.2 except for the 3 or 4 weak lines near to zero field. Phillips *et al.* give a term value for the only higher Λ doubling component of the $J = \frac{9}{2}$ level in the $^4\Delta_{\frac{5}{2}}$ $v = 1$ state. This term value gives a transition wavenumber of 1758.52 cm^{-1} for $Q(\frac{9}{2})$. Using first order g_J factors this transition comes into resonance with the $P(6)_{15-14}$ line at 940 G.

The term value for the lower Λ doubling component was estimated by fitting

Table 6.8: The $Q(\frac{11}{2})$ transition of FeH observed on the $P(13)_{14-13}$ laser line and the (a) component of the $R(\frac{9}{2})$ transition the $P(11)_{12-11}$ laser line

M'_J	M''_J	ν_L / cm^{-1}	Obs. B/T	$o - c^a$	$\delta\nu/\delta B^b$
$-\frac{9}{2}$	$-\frac{11}{2}$	1757.896825	1.2883	-0.55	0.850
$-\frac{7}{2}$	$-\frac{9}{2}$	1757.896825	1.3003	0.62	0.822
$-\frac{5}{2}$	$-\frac{7}{2}$	1757.896825	1.3136	-0.22	0.800
$-\frac{3}{2}$	$-\frac{5}{2}$	1757.896825	1.3153	0.23	0.790
$-\frac{3}{2}$	$-\frac{5}{2}$	1815.937938	0.3806	-3.74	1.604
$-\frac{1}{2}$	$-\frac{3}{2}$	1815.937938	0.4246	10.09	1.333
$\frac{1}{2}$	$-\frac{1}{2}$	1815.937938	0.5710	-4.54	1.050
$\frac{3}{2}$	$\frac{1}{2}$	1815.937938	0.7583	-3.53	0.765
$\frac{5}{2}$	$\frac{3}{2}$	1815.937938	1.1264	1.65	0.465

^a in $\text{cm}^{-1} \times 10^3$. The standard deviation of the fit was $5.52 \times 10^{-3} \text{ cm}^{-1}$.

^b in MHz G^{-1} .

the constants of the general equation,

$$G(J) = C + BJ(J+1) - D[J(J+1)]^2 \pm [Q + Q_D J(J+1)](J+\Omega)(J+\Omega-1) \cdots (J-\Omega+1), \quad (6.12)$$

which for $\Omega = \frac{5}{2}$ gives

$$G(J) = C + BJ(J+1) - D[J(J+1)]^2 \pm [Q + Q_D J(J+1)](J+\frac{5}{2})(J+\frac{3}{2})(J+\frac{1}{2})(J-\frac{1}{2})(J-\frac{3}{2}), \quad (6.13)$$

to the optical term values for the $^4\Delta_{\frac{5}{2}}$ component up to $J = \frac{19}{2}$. In equation 6.13 C , is the energy of the level, apart from rotational energy and Λ doubling, B is the rotational constant, D is the centrifugal distortion constant and Q and Q_D are the Λ doubling parameter and centrifugal distortion correction respectively, which are added, or subtracted to the energy. This procedure gives a term value which predicts a transition wavenumber of 1757.82 cm^{-1} . This transition will come into resonance with the $P(13)_{14-13}$ line at about 2500 G.

The $R(\frac{11}{2})$ transition observed on the $P(8)_{12-11}$ laser line

Three pairs of resonances were observed at high field on the $P(8)_{12-11}$ laser line. These are assigned to the $R(\frac{11}{2})$ transition, the M_J structure being assigned by ensuring the product of the tuning rate and the separation of the lines is approximately constant. For this transition, the observed Λ doubling

Table 6.9: The $Q(\frac{11}{2})$ transition of FeH observed on the $P(13)_{14-13}$ laser line and the (a) component of the $R(\frac{9}{2})$ transition the observed on $P(11)_{12-11}$ laser line

M'_J	M''_J	ν_L / cm^{-1}	Obs. B/T	$o - c^a$	$\delta\nu/\delta B^b$
$-\frac{9}{2}$	$-\frac{11}{2}$	1757.896825	1.0651	2.7	1.067
$-\frac{7}{2}$	$-\frac{9}{2}$	1757.896825	1.0795	-4.2	1.054
$-\frac{5}{2}$	$-\frac{7}{2}$	1757.896825	1.0909	0.1	1.042
$-\frac{3}{2}$	$-\frac{5}{2}$	1757.896825	1.1041	-1.3	1.030
$-\frac{1}{2}$	$-\frac{3}{2}$	1757.896825	1.1164	1.0	1.018
$\frac{1}{2}$	$-\frac{1}{2}$	1757.896825	1.1292	2.2	1.006
$\frac{3}{2}$	$\frac{1}{2}$	1757.896825	1.1423	2.8	0.995
$\frac{5}{2}$	$\frac{3}{2}$	1757.896825	1.1554	4.0	0.984
$\frac{7}{2}$	$\frac{5}{2}$	1757.896825	1.1694	2.7	0.973
$\frac{9}{2}$	$\frac{7}{2}$	1757.896825	1.1837	0.9	0.962
$\frac{11}{2}$	$\frac{9}{2}$	1757.896825	1.1980	-0.3	0.952
$-\frac{3}{2}$	$-\frac{5}{2}$	1815.937938	0.3468	-4.7	1.692
$-\frac{1}{2}$	$-\frac{3}{2}$	1815.937938	0.4136	4.5	1.414
$\frac{1}{2}$	$-\frac{1}{2}$	1815.937938	0.5156	4.9	1.136
$\frac{3}{2}$	$\frac{1}{2}$	1815.937938	0.6859	-0.5	0.861
$\frac{5}{2}$	$\frac{3}{2}$	1815.937938	1.0226	-14.8	0.588

^a in $\text{cm}^{-1} \times 10^4$. The standard deviation of the fit was $5.41 \times 10^{-4} \text{ cm}^{-1}$.

^b in MHz G^{-1} .

Table 6.10: The (a) component of the $R(\frac{11}{2})$ transition observed on the $P(8)_{12-11}$ laser line.

M'_J	M''_J	ν_L / cm^{-1}	Obs. B/T	$o - c^a$	$\delta\nu/\delta B^b$
$-\frac{11}{2}$	$-\frac{9}{2}$	1827.24229	2.2184	-0.25	1.819
$-\frac{9}{2}$	$-\frac{7}{2}$	1827.24229	2.5310	-0.01	1.307
$-\frac{7}{2}$	$-\frac{5}{2}$	1827.24229	2.9390	0.31	0.795

^a in cm^{-1} . The standard deviation of the fit was 0.28 cm^{-1} .

^b in MHz G^{-1} .

Table 6.11: The (b) component of the $R(\frac{11}{2})$ transition observed on the $P(8)_{12-11}$ laser line

M'_J	M''_J	ν_L / cm^{-1}	Obs. B/T	$o - c^a$	$\delta\nu/\delta B^b$
$-\frac{11}{2}$	$-\frac{9}{2}$	1827.24229	2.1219	-0.24	1.739
$-\frac{9}{2}$	$-\frac{7}{2}$	1827.24229	2.4214	-0.01	1.241
$-\frac{7}{2}$	$-\frac{5}{2}$	1827.24229	2.8177	0.29	0.744

^a in cm^{-1} . The standard deviation of the fit was 0.27 cm^{-1} .

^b in MHz G^{-1} .

is 1350 MHz. When $g_{\frac{11}{2}}$ is fitted to the 3 lines, values of 0.345(31) and 0.355(30) are determined for the a and b states respectively.

6.4 Discussion

The transition wave numbers determined from the fits in the previous section are in good agreement with those calculated from the term values of Phillips *et al.* [2] but are determined with greater accuracy. The values are compared in table 6.12. Table 6.13 gives a comparison of first order g_J factors with the values determined for the $v = 0$ and $v = 1$ levels.

The g_J factors determined from the experimental data are all larger than the first order values. This is due to significant second order contributions. Note that with the exception of the $g_{\frac{11}{2}}$ of the $v = 1$ b level, which is calculated from superimposed lines, the g_J factors in the $v = 1$ level are smaller than those for the $v = 0$ level. This suggests that the mixing with other electronic states is less in the $v = 1$ state.

Table 6.12: Comparison of the transition wavenumbers in the (1,0) band of FeH determined in this study with those determined by Phillips *et al.* [2]

Transition	ν_0^a		ν_0^b	
	a	b	a	b
$Q(\frac{7}{2}) \frac{7}{2} - \frac{7}{2}$	1758.70		1758.694585(92)	
$Q(\frac{9}{2}) \frac{7}{2} - \frac{7}{2}$	1758.19	1758.21	1758.1883(48)	1758.2044(14)
$Q(\frac{11}{2}) \frac{7}{2} - \frac{7}{2}$	1757.49	1757.50	1757.52079(14)	1757.507(24)
$R(\frac{7}{2}) \frac{7}{2} - \frac{7}{2}$	1805.27	1805.28	1805.2743(48)	1805.2822(14)
$R(\frac{9}{2}) \frac{7}{2} - \frac{7}{2}$	1815.75	1815.73	1815.74811(14)	1815.729(24)

^aValues from [2]. in cm^{-1}

^bValues from present study in cm^{-1}

Table 6.13: Comparison of g_J factors for the $v = 0$ and $v = 1$ levels of FeH in its $^4\Delta_{\frac{7}{2}}$ state.

Theory		Experimental			
J	$g_J^{(1)}$	$v = 0$		$v = 1$	
		a	b	a	b
$\frac{7}{2}$	1.1111	1.248071		1.241192	
$\frac{9}{2}$	0.7071	0.902841	0.902740	0.8956	0.8950
$\frac{11}{2}$	0.4895	0.711093	0.710588	0.70240	0.715

Table 6.14: Splittings (in MHz) due to Λ doubling in the $v = 0$ and $v = 1$ levels of FeH in its ${}^4\Delta_{7/2}$ state.

J	$v = 0$	$v = 1$
$\frac{7}{2}$	72.6	
$\frac{9}{2}$	338.0	273.0
$\frac{11}{2}$	1187.4	962.0
$\frac{13}{2}$	3480.9	2537.0

Additional evidence for this smaller mixing in the $v = 1$ state comes from the splitting of the rotational levels due to Λ doubling which is also smaller in the $v = 1$ level (see table 6.14).

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Chapter 7

The Far Infrared LMR spectrum of the FeD radical

7.1 Introduction

Due to the complexity of the FeH spectrum discussed in Chapter 6, a complementary study of FeD has been started. It was hoped that as the vibrational spacing in FeD is smaller than in FeH and therefore more distant in energy than from the nearest electronic state, the mixing of electronic states would be less. When parameters of a $^4\Delta$ Hamiltonian were fitted to term values of FeD calculated from the observations of Balfour *et al.* [1] and communicated by Lindgren [2], the overall standard deviation of the fit was 0.6 cm^{-1} . Although this is a better quality of fit than was achieved for FeH (2 cm^{-1}), clearly it would not be possible to model the experimental data for FeD to the experimental uncertainty in the far infrared (1 MHz) with an effective Hamiltonian, so the approach to fitting parameters to this data was identical to that used for FeH, i.e. the spectrum was modelled in terms of zero field frequencies and a quadratic Zeeman effect.

7.2 Experimental

All the data presented here were recorded on the FIR LMR spectrometer described in Chapter 2 section 4. The FeD molecules were produced by reacting iron carbonyl vapour with deuterium atoms produced by running a microwave discharge through a mixture of helium and deuterium. It was found that the optimum signal to noise ratio was obtained using 2 mb of helium and 0.1 mb deuterium, then opening the micrometering valve in the iron carbonyl line until a green flash was observed. These were the same conditions that Beaton [4] found produced optimum signal to noise for FeH.

Table 7.1: Far-infrared transitions observed for ^{56}FeD in the $X^4\Delta$ state

Transition	Zerofield		laser	laser	CO ₂ laser
	Frequency ^a		Frequency ^b	gas	line
	(a)	(b)			
$R(\frac{7}{2}) \frac{7}{2} - \frac{7}{2}$	808.3604		812.1954	CH ₃ OH	9P16
$R(\frac{5}{2}) \frac{5}{2} - \frac{5}{2}$	712.7716	713.0564	719.7511	CH ₃ OH	9P14
$R(\frac{3}{2}) \frac{3}{2} - \frac{3}{2}$	536.9967	541.2814	540.7851	CH ₂ CF ₂	10P14
$R(\frac{3}{2}) \frac{3}{2} - \frac{3}{2}$	536.9967	541.2814	538.3473	CD ₃ I	10P36
$R(\frac{5}{2}) \frac{3}{2} - \frac{3}{2}$	749.78	749.48	764.6426	CH ₃ OH	9P36
$R(\frac{3}{2}) \frac{1}{2} - \frac{1}{2}$	551.6781	569.6057	584.3382	HCOOH	9P28

^aValues in GHz from, or extrapolated from [2].

^bValues in GHz from [3]

7.3 Results and Analysis

The signals in table 7.1 were assigned to transitions using the proximity of the zero field frequency to the frequency of the laser line. The computer program (FEHCALINT) was then used to calculate the first order g_J factors for the levels involved in the transition. Changing the FIR LMR spectrometer between π and σ polarization only requires rotation of the beam splitter, see Chapter 2. Most of the spectra were recorded in both polarizations, the π ($\Delta M_J = 0$) spectra were assigned first, then the g_J values fitted to the assignments were used to predict the positions of the resonances in σ ($\Delta M_J = \pm 1$) polarization. π spectra are more easily assigned than σ spectra since the resonance condition for π transitions is,

$$\nu_L = \nu_0 + \Delta g_J \mu_B \mathcal{B} M_J'', \quad (7.1)$$

while for σ ,

$$\nu_L = \nu_0 + g_J' \mu_B \mathcal{B} M_J' - g_J'' \mu_B \mathcal{B} M_J''. \quad (7.2)$$

Using these predictions in conjunction with the tuning rate information from pulling experiments discussed in Chapter 2, it was possible to make unambiguous assignments of most resonances.

7.3.1 Results of the fits

Fit of the $R(\frac{7}{2}) \ ^4\Delta_{7/2} - \ ^4\Delta_{7/2}$ transition

The $R(\frac{7}{2})$ spectrum is shown in π polarization in figure 7.1. Resonances due to isotopomers containing the three most abundant isotopes of iron, ^{54}Fe (5.8%),

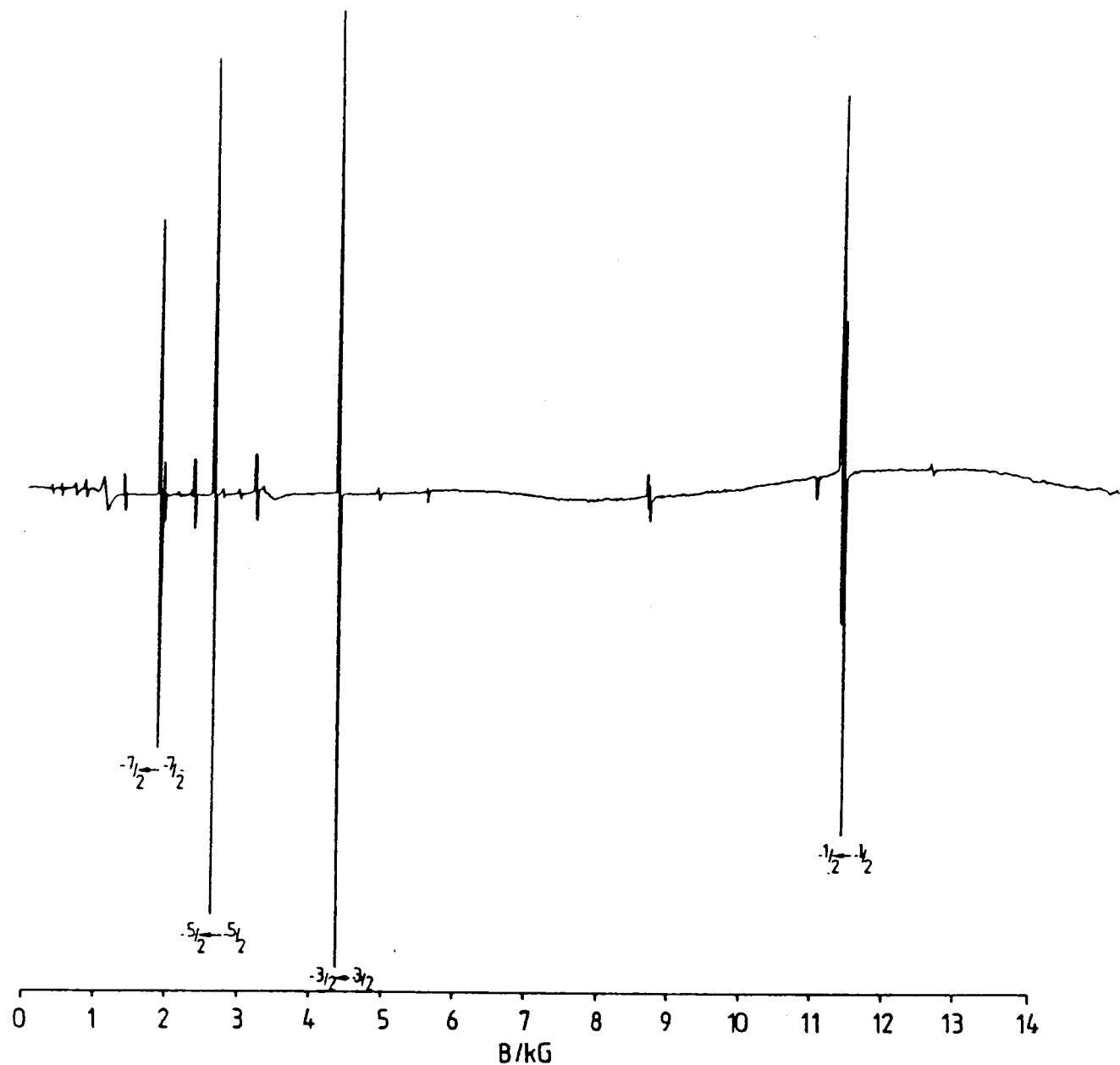


Figure 7.1: The $R(\frac{7}{2})$ transition in π polarization.

^{56}Fe (91.72%), and ^{57}Fe (2.2%), are observed.

As isotopic scaling of the parameters of the equation fitted to the data is not possible only resonances due to ^{56}FeD are modelled here. The strong signal at high field shows Λ doubling. The field separation of the two resonances is 20 G. Using the tuning rate for the transition ($M_J'' = -\frac{1}{2}$) calculated in the final fit (0.353 MHz/G) this corresponds to a separation of 7 MHz. The Λ doubling is not resolved on the lower field lines because of over modulation of the narrower, weaker resonances.

From equation 7.1 it can be seen that the magnetic field positions of the resonances, for π transitions, are in the ratio of M_J values involved in the resonances. In other words the ratios of the fields of the resonances for an $R(\frac{7}{2})$ transition will be 7:5:3:1 (or 1:1.40:2.33:7). The ratio of the observed fields is 1:1.39:2.29:5.99.

Table 7.2: Parameters determined for the $v = 0, J = \frac{9}{2}$ level

Parameter	Value
ν_0^a	808.6870(11) ^b
$g_{\frac{9}{2}}$	0.871988(57)
g_7^c	1.248071
C_1^d	0.002030(11)
C_2^d	-0.0000825(22)

^a Zero field frequency for the $R(\frac{7}{2})$ transition, in GHz

^b The values in parentheses correspond to one standard deviation of the least-squares fit, in units of the last quoted decimal place.

^c Average of values for FeH, from [4].

^d parameter in (GHz)⁻¹

Because of this large departure from the linear Zeeman effect at high field, the g_J factor for the upper state was fitted to the three low field lines, which was then used to predict and assign low field sigma lines. This procedure was repeated, fitting to second order parameters when possible until all the lines attributable to ⁵⁶FeD were assigned, see table 7.3. The ratio of the intensities of the resonances of the σ spectrum show which M_J'' gives the lowest field resonance. If $M_J'' = -\frac{7}{2}$ then the intensity ratio should be 1:3:6:10:15:21 for the $\Delta M_J = +1$ resonances with the first $\Delta M_J = -1$ resonance being 36 times stronger than the first $\Delta M_J = +1$ resonance. The observed ratio of intensities for the first three resonances of the σ spectrum is 1:2:3. This shows that the first observed resonance is due to $M_J'' = -\frac{5}{2}$, the $M_J'' = -\frac{7}{2}$ resonance being too weak to observe. The strong resonance due to first $\Delta M_J = -1$ transition comes between $M_J'' = \frac{1}{2}$ and $M_J'' = \frac{3}{2}$ of the $\Delta M_J = +1$ transitions.

Fit of the $R(\frac{5}{2}) \ ^4\Delta_{\frac{5}{2}} - \ ^4\Delta_{\frac{5}{2}}$ transition on the 416.5 μm laser line.

For this transition the resonances were assigned by following the same procedure as for the $R(\frac{7}{2}) \ ^4\Delta_{\frac{7}{2}} - \ ^4\Delta_{\frac{7}{2}}$ transition. Initial predictions were made by extrapolation of Lindgren's term values using the program tv5h described in Chapter 6. Figure 7.2 shows clearly resolved Λ doubling; transitions between the pairs of Λ doublets are fitted separately, see table 7.4. It is assumed that the selection rules for an R transition are $a \leftrightarrow a$ and $b \leftrightarrow b$ as for FeH. The ratios of the intensities of the resonances is as for the $R(\frac{7}{2}) \ ^4\Delta_{\frac{7}{2}} - \ ^4\Delta_{\frac{7}{2}}$ transition, showing that the lowest field resonance is not observed above the noise level.

Table 7.3: The $R(\frac{7}{2})$ transition of FeD observed on the 369.11 μm laser line

M'_J	M''_J	ν_L /GHz	Obs. B/T	$o - c^a$	$(\delta\nu/\delta B)^b$
$-\frac{7}{2}$	$-\frac{7}{2}$	812.1954	0.190300	-4.79	1.850
$-\frac{5}{2}$	$-\frac{5}{2}$	812.1954	0.265025	-0.04	1.332
$-\frac{3}{2}$	$-\frac{3}{2}$	812.1954	0.435550	0.89	0.821
$-\frac{1}{2}$	$-\frac{1}{2}$	812.1954	1.139000	0.00	0.353
$-\frac{3}{2}$	$-\frac{5}{2}$	812.1954	0.137900	3.80	2.546
$-\frac{1}{2}$	$-\frac{3}{2}$	812.1954	0.173950	0.02	2.023
$\frac{1}{2}$	$-\frac{1}{2}$	812.1954	0.235025	-0.32	1.502
$\frac{3}{2}$	$\frac{1}{2}$	812.1954	0.361525	0.37	0.983
$-\frac{9}{2}$	$-\frac{7}{2}$	812.1954	0.560550	0.48	0.629
$\frac{5}{2}$	$\frac{3}{2}$	812.1954	0.773150	-0.41	0.477

^a in MHz. The standard deviation of the fit was 2.54 MHz.

^b in MHz G^{-1} .

Table 7.4: Parameters determined from the $v = 0$, $R(\frac{5}{2})$ ${}^4\Delta_{\frac{5}{2}} - {}^4\Delta_{\frac{5}{2}}$ spectrum

Parameter	State a	State b
ν_0^a	714.46793(97) ^b	714.66914(51)
$g_{\frac{7}{2}}$	0.658241(58)	0.657272(31)
$g_{\frac{5}{2}}^c$	0.344706	0.31587
$C_1(\frac{7}{2} - \frac{5}{2})^d$	0.0020934(57)	0.0020800(32)
$C_2(\frac{7}{2})^d$	-0.0001238(22)	-0.0001236(12)

^a Zero field frequency for the $R(\frac{5}{2})$ transition, in GHz

^b The values in parentheses correspond to one standard deviation of the least-squares fit, in units of the last quoted decimal place.

^c Values for FeH from [4].

^d parameter in $(\text{GHz})^{-1}$.

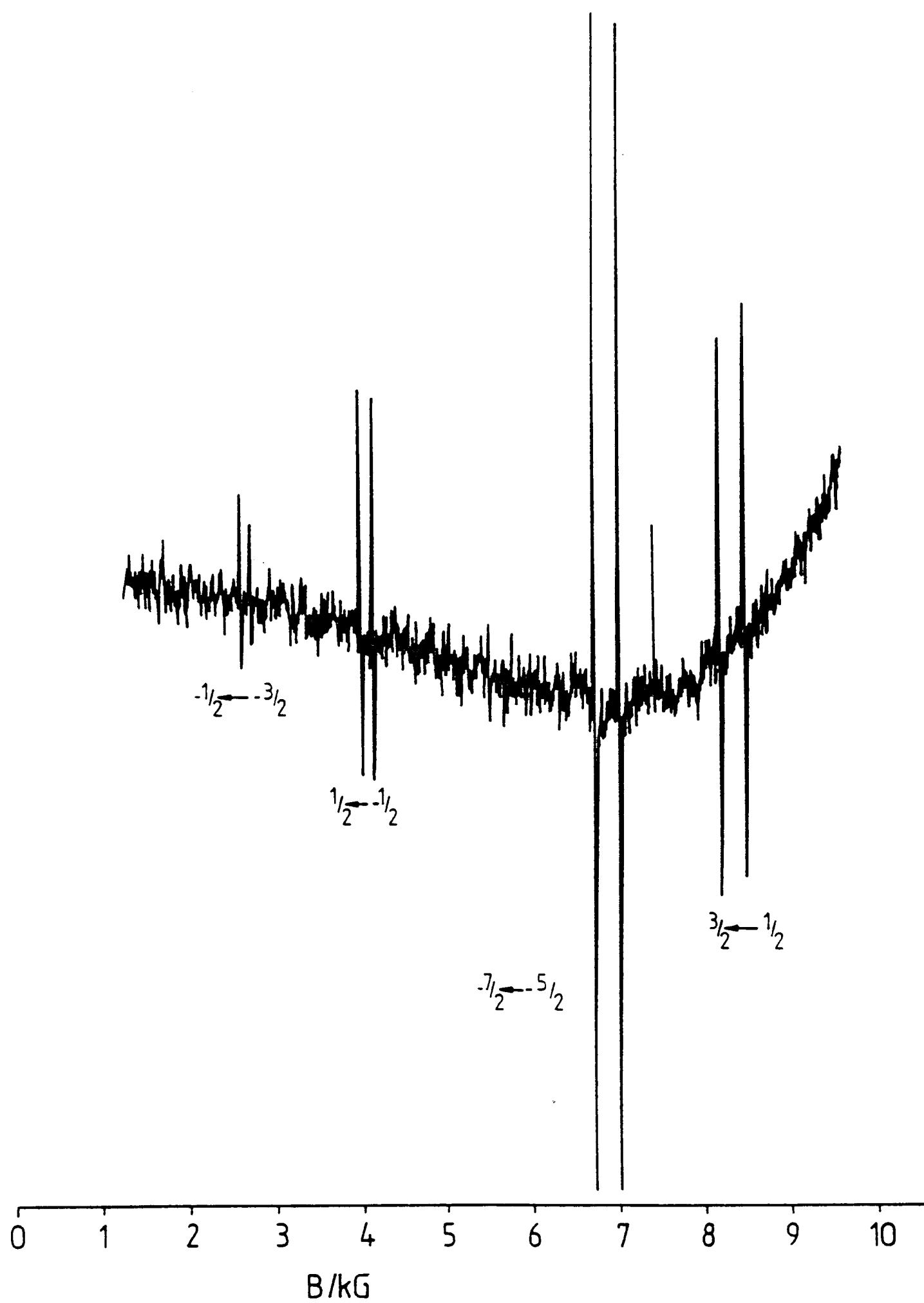


Figure 7.2: $R(\frac{5}{2}) \ ^4\Delta_{\frac{5}{2}} - \ ^4\Delta_{\frac{5}{2}}$ transition on the $416.5 \ \mu\text{m}$ laser line recorded in σ polarization.

Table 7.5: The (a) component of the $R(\frac{5}{2})$ transition of FeD observed on the 416.5 μm laser line

M'_J	M''_J	ν_L /GHz	Obs. B/T	$o - c^a$	$(\delta\nu/\delta B)^b$
$-\frac{5}{2}$	$-\frac{5}{2}$	719.7511	0.316725	1.09	1.676
$-\frac{3}{2}$	$-\frac{3}{2}$	719.7511	0.521150	-2.57	1.033
$-\frac{1}{2}$	$-\frac{1}{2}$	719.7511	1.364900	0.31	0.442
$-\frac{1}{2}$	$-\frac{3}{2}$	719.7511	0.273975	0.72	1.979
$\frac{1}{2}$	$-\frac{1}{2}$	719.7511	0.415950	0.59	1.287
$-\frac{7}{2}$	$-\frac{5}{2}$	719.7511	0.707950	0.21	0.754
$\frac{1}{2}$	$\frac{1}{2}$	719.7511	0.852600	-0.35	0.650

^a in MHz. The standard deviation of the fit was 1.72 MHz.

^b in MHz G^{-1} .

Table 7.6: The (b) component of the $R(\frac{5}{2})$ transition of FeD observed on the 416.5 μm laser line

M'_J	M''_J	ν_L /GHz	Obs. B/T	$o - c^a$	$(\delta\nu/\delta B)^b$
$-\frac{5}{2}$	$-\frac{5}{2}$	719.7511	0.304725	1.18	1.675
$-\frac{3}{2}$	$-\frac{3}{2}$	719.7511	0.501550	-0.86	1.031
$-\frac{1}{2}$	$-\frac{1}{2}$	719.7511	1.320300	0.06	0.438
$-\frac{1}{2}$	$-\frac{3}{2}$	719.7511	0.263825	0.06	1.937
$\frac{1}{2}$	$-\frac{1}{2}$	719.7511	0.400850	-0.53	1.284
$-\frac{7}{2}$	$-\frac{5}{2}$	719.7511	0.680200	-0.08	0.754
$\frac{1}{2}$	$\frac{1}{2}$	719.7511	0.823500	0.17	0.646

^a in MHz. The standard deviation of the fit was 0.90 MHz.

^b in MHz G^{-1} .

Table 7.7: Parameters determined from the $v = 0$, $R(\frac{3}{2})$, $\Omega = \frac{3}{2}$ spectrum

Parameter	State a	State b
ν_0^a	537.1846(52) ^b	541.28177(88)
$g_{\frac{5}{2}}$	0.5175(20)	0.49480(20)
$g_{\frac{3}{2}}$	0.8296(24)	0.87251(37)
$C_1(\frac{5}{2} - \frac{3}{2})^c$	0.001084(25)	0.0009642(56)
$C_2(\frac{5}{2})^c$	0.005193(62)	-0.0013633(15)

^a Zero field frequency for the $R(\frac{3}{2})$ transition, in GHz

^b The values in parentheses correspond to one standard deviation of the least-squares fit, in units of the last quoted decimal place.

^c parameter in $(\text{GHz})^{-1}$.

Fit of the $R(\frac{3}{2}) \ ^4\Delta_{\frac{3}{2}} - ^4\Delta_{\frac{3}{2}}$ transition on the 554 μm and 556.9 μm laser lines.

In order to predict the zero field frequency for the $R(\frac{3}{2}) \ ^4\Delta_{\frac{3}{2}} - ^4\Delta_{\frac{3}{2}}$ transition, Lindgren's term values have to be extrapolated as described in Chapter 6. Figure 7.3 is a Zeeman diagram showing π transitions tuning in resonance with the two laser lines between the two Λ doublets. The Zeeman effect is also seen to illustrate the strong departure from first order. Only the π spectrum was recorded on both laser lines. g_J factors for both the upper and lower states were fitted to the π resonances. Each resonance is observed on two laser lines at a different value of B on each line, using these 4 independent, measurable quantities it is possible to determine 3 parameters, ν_0 , g'_J , and g''_J . ν_0 , g'_J , and g''_J , which were used to calculate and assign the σ spectrum on the 556.9 μm line; the results of the final fits are given in table 7.7, with the assignments in tables 7.8 and 7.9.

Fit of the $R(\frac{5}{2}) \ ^4\Delta_{\frac{3}{2}} - ^4\Delta_{\frac{3}{2}}$ transition on the 392 μm laser line.

Only two resonances were observed for the $R(\frac{5}{2}) \ ^4\Delta_{\frac{3}{2}} - ^4\Delta_{\frac{3}{2}}$ transition, one in π and one in σ polarization. When $g_{\frac{7}{2}}$ was fitted to the most probable assignments, for the transitions a value of 0.170(24) was determined, using $g_{\frac{5}{2}} = 1.13155$ from FeH, and ν_0 from the extrapolation of Lindgren's term values. This seems reasonable as $g_{\frac{7}{2}}^{(1)} = 0.095$. The quality of the fit is poor (2.5 GHz) as second order parameters cannot be determined from such a small data set, and the resonances are at high fields.

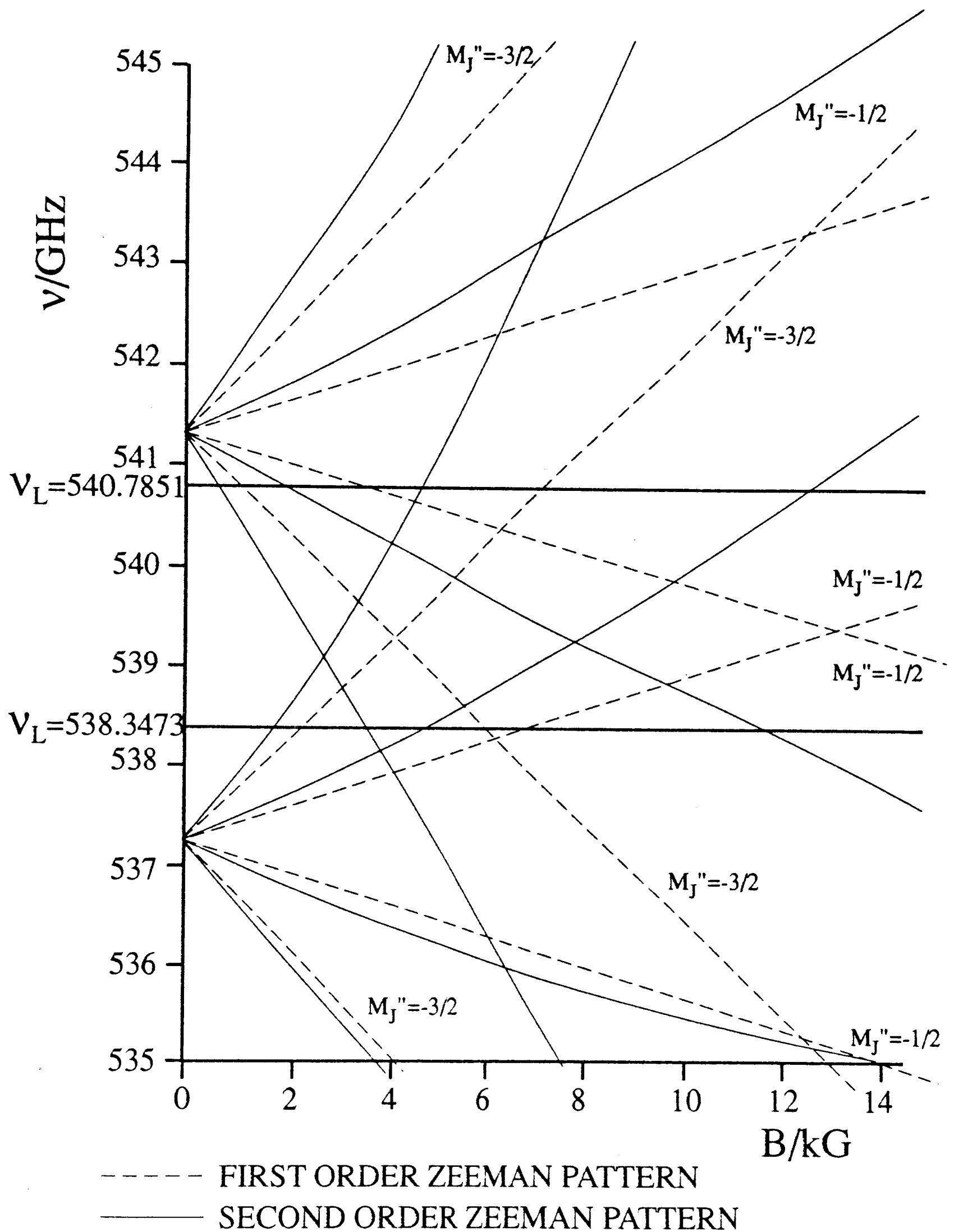


Figure 7.3: $R(\frac{3}{2}) \ ^4\Delta_{\frac{3}{2}} - \ ^4\Delta_{\frac{3}{2}}$ transition on the 554 μm and 556.9 μm laser lines in π polarization.

Table 7.8: The (a) component of the $R(\frac{3}{2})$ transition of FeD observed on the 554 μm and 556.9 μm laser lines.

M'_J	M''_J	ν_L /GHz	Obs. B/T	$o - c^a$	$(\delta\nu/\delta B)^b$
$-\frac{3}{2}$	$-\frac{3}{2}$	540.7851	0.466500	-0.54	0.889
$-\frac{1}{2}$	$-\frac{1}{2}$	540.7851	1.291700	0.55	0.339
$-\frac{3}{2}$	$-\frac{3}{2}$	538.3473	0.1663	3.84	0.739
$\frac{1}{2}$	$-\frac{1}{2}$	538.3473	0.484000	-3.91	0.264
$\frac{3}{2}$	$\frac{1}{2}$	538.3473	0.208325	0.03	0.610
$-\frac{5}{2}$	$-\frac{3}{2}$	538.3473	0.476450	0.01	0.577

^a in MHz. The standard deviation of the fit was 5.54 MHz.

^b in MHz G^{-1} .

Table 7.9: The (b) component of the $R(\frac{3}{2})$ transition of FeD observed on the 554 μm and 556.9 μm laser lines.

M'_J	M''_J	ν_L /GHz	Obs. B/T	$o - c^a$	$(\delta\nu/\delta B)^b$
$-\frac{3}{2}$	$-\frac{3}{2}$	540.7851	0.062450	0.15	-0.798
$-\frac{1}{2}$	$-\frac{1}{2}$	540.7851	0.189500	-0.15	-0.260
$-\frac{3}{2}$	$-\frac{3}{2}$	538.3473	0.363075	-0.86	-0.823
$\frac{1}{2}$	$-\frac{1}{2}$	538.3473	1.173550	0.06	-0.236
$\frac{3}{2}$	$\frac{1}{2}$	538.3473	0.307975	1.13	-0.949
$-\frac{3}{2}$	$-\frac{1}{2}$	538.3473	0.645000	-0.41	-0.481
$\frac{5}{2}$	$\frac{3}{2}$	538.3473	1.108750	0.08	-0.429

^a in MHz. The standard deviation of the fit was 1.05 MHz.

^b in MHz G^{-1} .

Table 7.10: The (b) component of the $R(\frac{5}{2}) \ ^4\Delta_{\frac{3}{2}} - ^4\Delta_{\frac{3}{2}}$ transition of FeD observed on the 392 μm laser line.

M'_J	M''_J	ν_L /GHz	Obs. B/T	$o - c^a$	$(\delta\nu/\delta B)^b$
$-\frac{5}{2}$	$-\frac{5}{2}$	764.6426	1.375000	2.17	1.597
$-\frac{7}{2}$	$-\frac{5}{2}$	764.6426	1.451000	-1.16	1.513

^a in GHz. The standard deviation of the fit was 2.46 GHz.

^b in MHz G^{-1} .

Table 7.11: Comparison of zero field frequencies of FeD Transitions

Transition	frequency ^a		frequency ^b	
	a	b	a	b
$R(\frac{7}{2}) \frac{7}{2} - \frac{7}{2}$	808.3604		808.6870(11)	
$R(\frac{5}{2}) \frac{5}{2} - \frac{5}{2}$	712.7716	713.0564	714.46793(97)	714.66914(51)
$R(\frac{3}{2}) \frac{3}{2} - \frac{3}{2}$	536.9967	541.2814	537.1846(52)	541.28177(88)

^aValues from or for $J < \frac{7}{2}$ extrapolated from [2] in GHz.

^bValues from present study in GHz.

The $R(\frac{3}{2}) \ ^4\Delta_{\frac{1}{2}} - \ ^4\Delta_{\frac{1}{2}}$ transition on the 513 μm laser line.

One resonance at 16885 G has been observed in π polarization on the 513 μm laser line. From an extrapolation of Lindgren's term values this resonance is most likely to be due to the $R(\frac{3}{2}) \ ^4\Delta_{\frac{1}{2}} - \ ^4\Delta_{\frac{1}{2}}$ transition. No FeH transition has been observed involving the $\ ^4\Delta_{\frac{1}{2}}$ spin component so first order g_J factors have to be used to estimate tuning rates of transitions. For the $\ ^4\Delta_{\frac{1}{2}}$ spin component, $g_{\frac{3}{2}}^{(1)} = -0.13$ and $g_{\frac{5}{2}}^{(1)} = -0.06$. In π polarization the tuning rates are 0.147 MHz/G for $M_J'' = \frac{3}{2}$ and 0.049 MHz/G for $M_J'' = \frac{1}{2}$. The resonance has a width of 60 G, which is equivalent to 8.8 MHz for $M_J'' = \frac{3}{2}$ and 2.9 MHz for $M_J'' = \frac{1}{2}$. The Doppler width for the resonance at 300 K is 1 MHz. It is most likely that the signal is due to $M_J'' = \frac{1}{2}$, the $M_J'' = \frac{3}{2}$ resonance not being observed above the noise level at lower field.

7.4 Discussion

The transition frequencies determined from the fits in the previous section are in reasonable agreement with those calculated from the term values of Lindgren [2]. They are compared in table 7.11. The Λ doubling observed for these transitions is compared with that observed on the same FeH transitions by Beaton [4], see table 7.12.

It can be seen from the matrix elements of the rotational and Λ -doubling Hamiltonian for the level J of a molecule in a $\ ^4\Delta$ state, given by Brown *et al.* [5], that the mass dependence of the splitting due to Λ -doubling for the $\Omega = \frac{7}{2}$ spin component,

$$\Delta\nu_{\Lambda} \propto \mu^{-7}, \quad (7.3)$$

Table 7.12: Observed splittings (in MHz) in the pure rotational transitions of FeH and FeD (for the $v = 0$ level) due to Λ doubling.

Transition	Ω	FeH	FeD
$R(\frac{7}{2})$	$\frac{7}{2}$	265.26	7.0
$R(\frac{5}{2})$	$\frac{5}{2}$	3253.57	201.21
$R(\frac{3}{2})$	$\frac{3}{2}$	25792.73	4097.17

for the $\Omega = \frac{5}{2}$ spin component,

$$\Delta\nu_{\Lambda} \propto \mu^{-5} \quad (7.4)$$

and for the $\Omega = \frac{3}{2}$ spin component,

$$\Delta\nu_{\Lambda} \propto \mu^{-3}. \quad (7.5)$$

where μ is the reduced mass. Table 7.12 shows that the experimental splittings are approximately in these ratios.

The mixing of the spin components for FeD is much less than in FeH due to the smaller rotational constant. Additional evidence for this smaller mixing of adjacent spin components comes from comparison of the value for $g_{\frac{9}{2}}$ (for $v = 0$ and $\Omega = \frac{7}{2}$ level) value for FeD and FeH. For FeH $g_{\frac{9}{2}} = 0.902791$ (averaged over the 2 Λ doublets) and for FeD $g_{\frac{9}{2}} = 0.871988$. The FeD value is closer to the first order value $g_{\frac{9}{2}}^{(1)} = 0.7071$ showing that it contains a smaller, but not insignificant second order contribution.

7.4.1 Further work.

It is highly desirable to measure the transitions reported here on other laser lines so that g_J factors can be calculated for both the upper and lower states along with second order parameters. It may also be possible to measure additional higher J transitions and some fine structure transitions. Further experiments on FeD are discussed in Chapter 8.

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Chapter 8

Conclusions and Further Work

This study has been carried out on three closely related LMR spectrometers. During the course of the experimental work described in this thesis a considerable effort has been made to improve the reliability and sensitivity of the Oxford CO LMR spectrometer, using ideas from the other two instruments as well as novel solutions to some of the unique problems of the Oxford instrument. These efforts have been rewarded not only in a significant reduction in down time of the spectrometer but an increase in the range, accuracy and sensitivity of the instrument. The modulation coil design described in detail in Chapter 2 has prevented the coils from over heating which used to cause the electrical insulation of the windings to break down. The short circuits between the turns of the coils caused the resistance and inductance of the coils to change resulting in a drift phase angle of the lock-in amplifier and a reduction in modulation amplitude, hence an overall drop in sensitivity of the spectrometer. Also bolting the coils to the pole pieces of the magnet has reduced the noise level by:

- reducing the amplitude of the sound produced by the motion of the coils, hence the acoustic coupling to the laser gain tube.
- ensuring that the variation of the modulation amplitude in the region of the sample is a good approximation to a sine wave.

The improvements to the grating mount have had three main benefits;

1. The time required to change and align the grating has been reduced from several days to a few hours. It is now possible to change between π and σ polarization in 1 day; this operation used to take more than a week.
2. It is now possible to align the grating more precisely, the main benefit of which is an increase in laser power allowing more transitions to be recorded as Lamb dips. It should be possible to measure signals

recorded as Lamb dips to an accuracy of 1 MHz (one tenth of the line width). However at present the accuracy is limited to 30 MHz by the uncertainty in the measurement of the magnetic field. This uncertainty in the field measurement should be greatly improved by monitoring the BH-15 field controller directly with a microcomputer and rebuilding the magnetic field power supply.

3. The greater precision in grating alignment together with improvements to the vacuum gas control system of the laser has made it possible to obtain gain on transitions of CO which under our condition of operation are close to the gain threshold. It is now possible to get laser action on P(17) transitions of CO for most vibrational bands and with particular attention to the gases in the CO plasma two lines (1,0) band have shown gain [2].

The most complete study reported here is that of GeH in Chapter 4. The 362 data points used in the fit involved transitions for all the possible isotopomers of GeH and GeD. Because of the range and quality of the data used in the fit it has been possible to separate A_D and γ directly, this is the first time this has been possible in such a fit. It has also been possible to determine non-adiabatic corrections to the harmonic frequency (ω_e) and rotational constant (B_e).

The experiments performed on TeD detailed in Chapter 5 have provided new information on the TeH radical. The TeH experiments have been undertaken subsequently by Gillett and Islam [2], coworkers on the Oxford CO LMR. A fit of the TeD and TeH data sets similar to that presented for GeH and GeD is currently in preparation.

The study of the (1,0) band of FeH in its $^4\Delta$ state is the first in the IR region to be reported. It is an exhaustive examination of all the CO laser line that are close to the transition wavenumbers predicted from [1]. A "sealed off" CO laser, which would enable the use of isotopic variants of CO in the lasing medium, may allow other transitions to be observed, it would also allow transitions already observed to be measured at an altered laser wavenumber and hence the zero-field wavenumber for the transition could be accurately determined. This would be very useful in the case of the $P(\frac{9}{2})$ transition which is close to zero field coincidence with the $P(12)_{16-15}$ $^{12}\text{C}^{16}\text{O}$ laser line. A similar study could be carried out on FeD in the technically difficult 1245 cm^{-1} (35-34 band of the CO laser) spectral region.

Carter [3, 4] has reported the observation of green and blue band systems for FeH in experiments employing laser induced fluorescence. These data have been used to determine vibrational intervals in the lower electronic states. In what appears to be the low lying $^6\Delta$ state, the intervals are between 1555 and 1632 cm^{-1} . These transitions could be searched for using CO LMR.

The data detailed in Chapters 4 to 7 provide clear evidence of the power of

LMR spectroscopy. LMR is a sensitive, discriminating and accurate technique. Using the Oxford LMR it is possible to measure the centres of Lamb dips to 1 MHz, compare favourably with 90 MHz accuracy of tunable diode laser spectroscopy [5].

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Appendix A. Wavenumbers of the infrared transitions of GeH and its isotopomers included in the least-squares fit.

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
<i>(a) Transitions of GeH with Lamb dips observed by CO LMR spectroscopy.</i>								
⁷⁶ GeH	<i>transitions</i>							
1	$Q(\frac{3}{2})$	+ ← -		$\frac{1}{2}$	$-\frac{1}{2}$	1769.19147	0.4120	-16.2
1	$Q(\frac{3}{2})$	- ← +		$\frac{1}{2}$	$-\frac{1}{2}$	1769.19147	0.4161	-17.0
0	$P(\frac{5}{2})$	- ← +		$\frac{3}{2}$	$\frac{1}{2}$	1801.85693	1.0651	9.5
0	$P(\frac{5}{2})$	+ ← -		$\frac{3}{2}$	$\frac{1}{2}$	1801.85693	1.0681	18.9
0	$Q(\frac{3}{2})$	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	1834.60986	0.3616	-9.6
0	$Q(\frac{3}{2})$	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	1834.60986	0.3661	-8.0
0	$R(\frac{3}{2})$	+ ← -		$\frac{1}{2}$	$\frac{3}{2}$	1866.74171	0.8539	-26.1
0	$R(\frac{3}{2})$	- ← +		$\frac{1}{2}$	$\frac{3}{2}$	1866.74171	0.8576	-30.4
⁷⁴ GeH	<i>transitions</i>							
1	$Q(\frac{3}{2})$	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	1769.19147	0.3744	0.7
1	$Q(\frac{3}{2})$	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	1769.19147	0.3781	0.0
0	$P(\frac{5}{2})$	- ← +		$\frac{3}{2}$	$\frac{1}{2}$	1801.85693	0.4244	17.4
0	$P(\frac{5}{2})$	+ ← -		$\frac{3}{2}$	$\frac{1}{2}$	1801.85693	0.4290	19.1
0	$P(\frac{5}{2})$	- ← +		$\frac{3}{2}$	$\frac{5}{2}$	1801.85693	1.2123	13.6
0	$P(\frac{5}{2})$	+ ← -		$\frac{3}{2}$	$\frac{5}{2}$	1801.85693	1.2259	13.4
0	$Q(\frac{3}{2})$	- ← +		$\frac{1}{2}$	$\frac{3}{2}$	1834.60986	1.2032	-17.4
0	$Q(\frac{3}{2})$	+ ← -		$\frac{1}{2}$	$\frac{3}{2}$	1834.60986	1.2067	-18.6
0	$Q(\frac{3}{2})$	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	1834.60986	1.2078	-17.5
0	$Q(\frac{3}{2})$	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	1834.60986	1.2119	-17.3
0	$Q(\frac{3}{2})$	- ← +		$-\frac{3}{2}$	$-\frac{1}{2}$	1834.60986	1.2126	-17.3
0	$Q(\frac{3}{2})$	+ ← -		$-\frac{3}{2}$	$-\frac{1}{2}$	1834.60986	1.2168	-17.7
⁷² GeH	<i>transitions</i>							
1	$Q(\frac{3}{2})$	- ← +		$\frac{1}{2}$	$\frac{3}{2}$	1769.19147	1.2000	8.1
1	$Q(\frac{3}{2})$	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	1769.19147	1.2046	7.4
1	$Q(\frac{3}{2})$	+ ← -		$\frac{1}{2}$	$\frac{3}{2}$	1769.19147	1.2046	11.7
1	$Q(\frac{3}{2})$	- ← +		$-\frac{3}{2}$	$-\frac{1}{2}$	1769.19147	1.2093	6.6
1	$Q(\frac{3}{2})$	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	1769.19147	1.2093	10.5
1	$Q(\frac{3}{2})$	+ ← -		$-\frac{3}{2}$	$-\frac{1}{2}$	1769.19147	1.2133	6.3
0	$P(\frac{5}{2})$	+ ← -		$-\frac{3}{2}$	$-\frac{1}{2}$	1801.85693	0.2381	15.2
0	$P(\frac{5}{2})$	- ← +		$-\frac{3}{2}$	$-\frac{1}{2}$	1801.85693	0.2405	3.4
0	$P(\frac{5}{2})$	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	1801.85693	0.4262	2.5
0	$P(\frac{5}{2})$	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	1801.85693	0.4335	-1.3
0	$P(\frac{5}{2})$	+ ← -		$-\frac{3}{2}$	$-\frac{5}{2}$	1801.85693	0.6663	2.8
0	$P(\frac{5}{2})$	- ← +		$-\frac{3}{2}$	$-\frac{5}{2}$	1801.85693	0.6805	2.9

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
<i>Transitions of GeH with Lamb dips observed by CO LMR spectroscopy (cont.).</i>								
⁷⁰ GeH	<i>transitions</i>							
0	P($\frac{5}{2}$)	+ ← −		− $\frac{3}{2}$	− $\frac{1}{2}$	1801.85693	0.9340	0.4
0	P($\frac{5}{2}$)	− ← +		− $\frac{3}{2}$	− $\frac{1}{2}$	1801.85693	0.9390	1.4
0	Q($\frac{5}{2}$)	+ ← −		− $\frac{5}{2}$	− $\frac{3}{2}$	1834.60986	0.8463	-2.6
0	Q($\frac{5}{2}$)	+ ← −		− $\frac{3}{2}$	− $\frac{1}{2}$	1834.60986	0.8504	-4.0
0	Q($\frac{5}{2}$)	+ ← −		− $\frac{1}{2}$	$\frac{1}{2}$	1834.60986	0.8559	-3.3
0	Q($\frac{5}{2}$)	+ ← −		$\frac{1}{2}$	$\frac{3}{2}$	1834.60986	0.8611	-3.2
0	Q($\frac{5}{2}$)	+ ← −		$\frac{3}{2}$	$\frac{5}{2}$	1834.60986	0.8664	-3.0
0	Q($\frac{5}{2}$)	− ← +		− $\frac{5}{2}$	− $\frac{3}{2}$	1834.60986	0.8889	2.6
0	Q($\frac{5}{2}$)	− ← +		− $\frac{3}{2}$	− $\frac{1}{2}$	1834.60986	0.8939	2.9
0	Q($\frac{5}{2}$)	− ← +		− $\frac{1}{2}$	$\frac{1}{2}$	1834.60986	0.8989	3.1
0	Q($\frac{5}{2}$)	− ← +		$\frac{1}{2}$	$\frac{3}{2}$	1834.60986	0.9042	3.6
0	Q($\frac{5}{2}$)	− ← +		$\frac{3}{2}$	$\frac{5}{2}$	1834.60986	0.9098	4.4

(b) *Transitions of GeH observed by CO LMR spectroscopy.*

⁷⁴ GeH	<i>transitions</i>							
0	P($\frac{5}{2}$)	− ← +		$\frac{1}{2}$	− $\frac{1}{2}$	1801.85693	0.7830	13.3
0	P($\frac{5}{2}$)	+ ← −		$\frac{1}{2}$	− $\frac{1}{2}$	1801.85693	0.7928	12.0
0	Q($\frac{9}{2}$)	− ← +		$\frac{1}{2}$	− $\frac{1}{2}$	1830.94304	0.5403 ^c	-189.9
0	Q($\frac{9}{2}$)	+ ← −		$\frac{1}{2}$	− $\frac{1}{2}$	1830.94304	1.1074 ^c	-177.2
⁷² GeH	<i>transitions</i>							
0	Q($\frac{5}{2}$)	− ← +		$\frac{1}{2}$	− $\frac{1}{2}$	1834.60986	1.3507	13.2
0	Q($\frac{5}{2}$)	+ ← −		$\frac{1}{2}$	− $\frac{1}{2}$	1834.60986	1.3970	1.5
0	R($\frac{1}{2}$)	− ← +		$\frac{1}{2}$	− $\frac{1}{2}$	1850.92272	0.7689	-12.1
0	R($\frac{1}{2}$)	− ← +		$\frac{3}{2}$	$\frac{1}{2}$	1850.92272	1.0875	-33.8

(c) *Transitions of GeH observed by diode laser spectroscopy*

⁷⁶ GeH	<i>transitions</i>							
0	R($\frac{3}{2}$)	+ ← −				1862.44530		11.1
0	R($\frac{3}{2}$)	− ← +				1862.88390		-0.8
0	R($\frac{5}{2}$)	+ ← −				1874.65340		60.7
⁷⁴ GeH	<i>transitions</i>							
0	R($\frac{1}{2}$)	+ ← −				1851.03370		-61.7
0	R($\frac{3}{2}$)	+ ← −				1862.76870		18.2
0	R($\frac{3}{2}$)	− ← +				1863.20720		3.8
0	R($\frac{5}{2}$)	− ← +				1874.56490		87.6
0	R($\frac{5}{2}$)	+ ← −				1874.97940		53.8
0	R($\frac{9}{2}$)	+ ← −				1897.29380		-19.6

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
<i>(c) Transitions of GeH observed by diode laser spectroscopy (cont.).</i>								
⁷³ GeH	<i>transitions</i>							
0	R($\frac{3}{2}$)	+ ← −				1862.93790		34.7
0	R($\frac{3}{2}$)	− ← +				1863.37470		2.6
0	R($\frac{5}{2}$)	− ← +				1874.73430		86.0
0	R($\frac{5}{2}$)	+ ← −				1875.14880		51.5
0	R($\frac{9}{2}$)	+ ← −				1897.46700		-20.6
⁷² GeH	<i>transitions</i>							
0	R($\frac{1}{2}$)	− ← +				1850.91000		-49.3
0	R($\frac{3}{2}$)	+ ← −				1863.10910		18.4
0	R($\frac{3}{2}$)	− ← +				1863.54860		12.5
0	R($\frac{5}{2}$)	− ← +				1874.90860		80.1
0	R($\frac{5}{2}$)	+ ← −				1875.32400		53.8
0	R($\frac{9}{2}$)	− ← +				1897.27820		15.8
0	R($\frac{9}{2}$)	+ ← −				1897.64760		-2.1
⁷⁰ GeH	<i>transitions</i>							
0	R($\frac{3}{2}$)	+ ← −				1863.46940		26.1
0	R($\frac{5}{2}$)	− ← +				1875.27270		82.6
0	R($\frac{5}{2}$)	+ ← −				1875.68950		68.9
0	R($\frac{9}{2}$)	− ← +				1897.64760		-7.8
0	R($\frac{9}{2}$)	+ ← −				1898.01890		-7.8
<i>(d) Transitions of GeD observed by CO LMR spectroscopy</i>								
⁷⁴ GeD	<i>transitions</i>							
1	Q($\frac{3}{2}$)			− $\frac{1}{2}$	$\frac{1}{2}$	1287.13789	0.5979	20.7
1	Q($\frac{5}{2}$)			$\frac{1}{2}$	− $\frac{1}{2}$	1287.13789	0.8404	8.8
0	P($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{1}{2}$	1304.96908	2.2879	-2.4
1	R($\frac{5}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1309.67938	0.4000	-5.8
1	R($\frac{5}{2}$)			− $\frac{1}{2}$	$\frac{1}{2}$	1309.67938	0.6332	-5.8
1	R($\frac{5}{2}$)			$\frac{7}{2}$	$\frac{5}{2}$	1309.67938	0.8414	-7.0
0	Q($\frac{9}{2}$)	− ← +		$\frac{1}{2}$	− $\frac{1}{2}$	1319.39147	0.1825	-7.9
0	Q($\frac{9}{2}$)	+ ← −		$\frac{1}{2}$	− $\frac{1}{2}$	1319.39147	0.2559	-8.1
0	R($\frac{3}{2}$)			− $\frac{1}{2}$	− $\frac{3}{2}$	1337.91532	0.8876	17.2
0	R($\frac{3}{2}$)			$\frac{1}{2}$	− $\frac{1}{2}$	1337.91532	1.5441	16.9
0	R($\frac{3}{2}$)			− $\frac{5}{2}$	− $\frac{3}{2}$	1337.91532	2.5602	18.0

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
<i>(d) Transitions of GeD observed by CO LMR spectroscopy (cont.).</i>								
⁷⁴ GeD	<i>transitions</i>							
0	R($\frac{5}{2}$)			$-\frac{3}{2}$	$-\frac{5}{2}$	1343.81888	0.2018	10.6
0	R($\frac{5}{2}$)			$-\frac{1}{2}$	$-\frac{3}{2}$	1343.81888	0.2738	16.0
0	R($\frac{5}{2}$)			$\frac{1}{2}$	$-\frac{1}{2}$	1343.81888	0.4344	16.5
0	R($\frac{5}{2}$)			$-\frac{7}{2}$	$-\frac{5}{2}$	1343.81888	0.5722	13.4
0	R($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{1}{2}$	1343.81888	1.0598	15.1
0	R($\frac{9}{2}$)			$\frac{5}{2}$	$\frac{7}{2}$	1355.78519	0.9288	-28.1
0	R($\frac{9}{2}$)			$\frac{3}{2}$	$\frac{5}{2}$	1355.78519	1.1310	-26.2
0	R($\frac{9}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1355.78519	1.4360	-28.8
0	R($\frac{9}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1355.78519	1.9713	-29.9
0	R($\frac{9}{2}$)	$- \leftarrow +$		$\frac{11}{2}$	$\frac{9}{2}$	1355.78822	2.0790	-24.1
0	R($\frac{9}{2}$)	$+ \leftarrow -$		$\frac{11}{2}$	$\frac{9}{2}$	1355.78822	2.1008	-28.0
⁷² GeD	<i>transitions</i>							
1	Q($\frac{3}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1287.13789	1.7856	25.2
1	Q($\frac{3}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1287.13789	1.8107	28.8
1	Q($\frac{3}{2}$)			$-\frac{3}{2}$	$-\frac{1}{2}$	1287.13789	1.8354	30.0
0	P($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{1}{2}$	1304.96908	1.2705	3.6
0	P($\frac{5}{2}$)			$\frac{1}{2}$	$-\frac{1}{2}$	1304.96908	2.4701	6.1
1	R($\frac{7}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1316.18711	0.3121	-42.1
1	R($\frac{7}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1316.18711	0.4541	-43.3
1	R($\frac{7}{2}$)			$\frac{9}{2}$	$\frac{7}{2}$	1316.18711	0.5363	-42.2
0	R($\frac{3}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1337.91532	0.1194	19.6
0	R($\frac{3}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1337.91532	0.2177	20.5
0	R($\frac{3}{2}$)			$\frac{5}{2}$	$\frac{3}{2}$	1337.91532	0.3489	18.7
0	R($\frac{7}{2}$)			$\frac{5}{2}$	$\frac{7}{2}$	1350.29467	0.5840	9.1
0	R($\frac{7}{2}$)			$\frac{3}{2}$	$\frac{5}{2}$	1350.29467	0.7228	8.6
0	R($\frac{7}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1350.29467	0.9470	6.9
0	R($\frac{7}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1350.29467	1.3750	6.1
0	R($\frac{7}{2}$)			$\frac{9}{2}$	$\frac{7}{2}$	1350.29467	1.6492	10.7
⁷⁰ GeD	<i>transitions</i>							
0	P($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{1}{2}$	1304.96908	0.2279	14.5
0	P($\frac{5}{2}$)			$\frac{1}{2}$	$-\frac{1}{2}$	1304.96908	0.4177	13.5
0	P($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{5}{2}$	1304.96908	0.6671	15.8
0	R($\frac{3}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1337.91532	1.2140	26.7
0	R($\frac{3}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1337.91532	2.3482	26.6

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
<i>(e) Transitions of GeD observed by diode laser spectroscopy.</i>								
⁷⁶ GeD	<i>transitions</i>							
0	P($\frac{11}{2}$)	+ ← -				1279.45560		-7.7
0	P($\frac{7}{2}$)	+ ← -				1293.97308		-35.8
⁷⁴ GeD	<i>transitions</i>							
0	P($\frac{11}{2}$)	- ← +				1279.59470		2.3
0	P($\frac{11}{2}$)	+ ← -				1279.87791		2.6
0	P($\frac{7}{2}$)	- ← +				1294.13419		-30.0
0	P($\frac{7}{2}$)	+ ← -				1294.40482		-35.2
0	P($\frac{5}{2}$)	+ ← -				1301.20594		-55.1
0	P($\frac{5}{2}$)	- ← +				1301.47032		-59.7
1	R($\frac{5}{2}$)	- ← +				1306.75296		31.7
1	R($\frac{7}{2}$)	+ ← -				1312.70248		-11.2
0	R($\frac{3}{2}$)	+ ← -				1334.51700		40.8
0	R($\frac{3}{2}$)	- ← +				1334.74778		43.0
⁷³ GeD	<i>transitions</i>							
0	P($\frac{11}{2}$)	- ← +				1279.81410		10.4
0	P($\frac{11}{2}$)	+ ← -				1280.09740		10.4
0	P($\frac{7}{2}$)	- ← +				1294.35870		-25.0
⁷² GeD	<i>transitions</i>							
0	P($\frac{11}{2}$)	- ← +				1280.04020		16.8
0	P($\frac{11}{2}$)	+ ← -				1280.32425		23.3
0	P($\frac{7}{2}$)	- ← +				1294.58939		-28.4
0	P($\frac{7}{2}$)	+ ← -				1294.86108		-25.1
1	R($\frac{3}{2}$)	- ← +				1301.34059		51.4
0	P($\frac{5}{2}$)	+ ← -				1301.66640		-53.8
0	P($\frac{5}{2}$)	- ← +				1301.93110		-57.2
0	R($\frac{3}{2}$)	+ ← -				1335.00052		31.0
0	R($\frac{3}{2}$)	- ← +				1335.23059		24.4
⁷⁰ GeD	<i>transitions</i>							
0	P($\frac{11}{2}$)	- ← +				1280.50841		9.6
0	P($\frac{11}{2}$)	+ ← -				1280.79182		7.3
0	P($\frac{7}{2}$)	- ← +				1295.07047		-23.1
0	P($\frac{7}{2}$)	+ ← -				1295.34224		-21.2
0	P($\frac{5}{2}$)	+ ← -				1302.15215		-57.6
0	P($\frac{5}{2}$)	- ← +				1302.41691		-62.6
0	Q($\frac{3}{2}$)	+ ← -				1319.62850		-21.5
0	R($\frac{3}{2}$)	+ ← -				1335.51371		46.1

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
<i>(f) Transitions of GeH observed by CO₂ LMR spectroscopy.</i>								
⁷⁴ GeH	<i>transitions</i>							
0	Q($\frac{3}{2}$)	+ ← −		$\frac{3}{2}$	$\frac{3}{2}$	880.37051	0.5223	-5.8
0	Q($\frac{3}{2}$)	− ← −		$\frac{3}{2}$	$\frac{3}{2}$	880.37051	0.5233	-3.7
0	Q($\frac{3}{2}$)	+ ← −		$\frac{3}{2}$	$\frac{1}{2}$	880.37051	0.5113	-3.8
0	Q($\frac{3}{2}$)	− ← −		$\frac{3}{2}$	$\frac{1}{2}$	880.37051	0.5133	-7.5
0	R($\frac{1}{2}$)	− ← −		− $\frac{3}{2}$	− $\frac{1}{2}$	898.64882	0.7486	12.4
0	R($\frac{3}{2}$)	− ← −		$\frac{5}{2}$	$\frac{3}{2}$	913.64451	0.3997	-2.7
0	R($\frac{3}{2}$)	− ← −		$\frac{3}{2}$	$\frac{1}{2}$	913.64451	0.6531	-5.1
⁷² GeH	<i>transitions</i>							
0	Q($\frac{3}{2}$)	− ← −		$\frac{3}{2}$	$\frac{3}{2}$	880.37051	0.5297	4.1
0	Q($\frac{3}{2}$)	+ ← −		$\frac{3}{2}$	$\frac{3}{2}$	880.37051	0.5310	-10.2
0	R($\frac{1}{2}$)	− ← −		− $\frac{3}{2}$	− $\frac{1}{2}$	898.64882	0.7535	12.1
⁷⁰ GeH	<i>transitions</i>							
0	Q($\frac{3}{2}$)	− ← −		$\frac{3}{2}$	$\frac{3}{2}$	880.37051	0.5377	5.8
0	Q($\frac{3}{2}$)	+ ← −		$\frac{3}{2}$	$\frac{3}{2}$	880.37051	0.5392	-9.7
0	R($\frac{1}{2}$)	− ← −		− $\frac{3}{2}$	− $\frac{1}{2}$	898.64882	0.7591	14.2
<i>(g) Transitions of GeH with Lamb dips observed by FIR LMR spectroscopy.</i>								
⁷⁴ GeH	<i>transitions</i>							
0	R($\frac{7}{2}$)	+ ← −		$\frac{1}{2}$	$\frac{1}{2}$	60.01283	1.4774	0.3
0	R($\frac{7}{2}$)	− ← +		$\frac{1}{2}$	$\frac{1}{2}$	60.01283	1.9320	0.4
0	R($\frac{7}{2}$)	+ ← −		$\frac{7}{2}$	$\frac{5}{2}$	60.01283	0.7822	0.0
0	R($\frac{7}{2}$)	− ← +		$\frac{7}{2}$	$\frac{5}{2}$	60.01283	1.0218	-0.2
⁷² GeH	<i>transitions</i>							
0	R($\frac{7}{2}$)	− ← +		$\frac{3}{2}$	$\frac{3}{2}$	60.01283	1.1135	0.3
0	R($\frac{7}{2}$)	+ ← −		− $\frac{3}{2}$	− $\frac{1}{2}$	60.01283	1.3565	-0.3
0	R($\frac{7}{2}$)	− ← +		$\frac{7}{2}$	$\frac{5}{2}$	60.01283	1.7427	0.0
⁷⁰ GeH	<i>transitions</i>							
0	R($\frac{7}{2}$)	+ ← −		$\frac{3}{2}$	$\frac{3}{2}$	60.01283	1.4449	0.2

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
<i>(h) Transitions of GeH observed by FIR LMR spectroscopy.</i>								
⁷⁶ GeH	<i>transitions</i>							
0	R($\frac{3}{2}$)	- ← +			$\frac{3}{2}$	33.11320	0.8795	-0.6
0	R($\frac{3}{2}$)	+ ← -			$\frac{5}{2}$	33.11320	1.6806	-0.2
0	R($\frac{3}{2}$)	- ← +			$\frac{5}{2}$	33.11320	1.6936	-0.4
0	R($\frac{5}{2}$)	- ← +			$\frac{3}{2}$	46.43119	1.1106	0.0
0	R($\frac{5}{2}$)	+ ← -			$\frac{5}{2}$	46.43119	1.1285	0.1
0	R($\frac{5}{2}$)	- ← +			$\frac{5}{2}$	46.60286	0.6520	0.5
0	R($\frac{5}{2}$)	+ ← -			$\frac{5}{2}$	46.60286	0.6776	0.4
0	R($\frac{5}{2}$)	- ← +			$\frac{3}{2}$	46.60286	1.0877	0.7
0	R($\frac{5}{2}$)	+ ← -			$\frac{3}{2}$	46.60286	1.1305	0.7
0	R($\frac{5}{2}$)	- ← +			$\frac{1}{2}$	46.60286	0.6115	-0.1
0	R($\frac{5}{2}$)	+ ← -			$\frac{1}{2}$	46.60286	0.6358	-0.2
0	R($\frac{5}{2}$)	- ← +		-	$\frac{1}{2}$	46.60286	0.9791	0.0
0	R($\frac{5}{2}$)	+ ← -		-	$\frac{1}{2}$	46.60286	1.0183	0.0
0	R($\frac{5}{2}$)	- ← +			$\frac{7}{2}$	46.60286	1.2168	0.3
0	R($\frac{5}{2}$)	+ ← -			$\frac{7}{2}$	46.60286	1.2635	0.2
0	R($\frac{7}{2}$)	+ ← -			$\frac{7}{2}$	60.01283	0.0262	0.0
0	R($\frac{7}{2}$)	+ ← -			$\frac{5}{2}$	60.01283	0.0367	0.0
0	R($\frac{7}{2}$)	+ ← -			$\frac{3}{2}$	60.01283	0.0618	0.3
0	R($\frac{7}{2}$)	- ← +			$\frac{7}{2}$	60.01283	0.0928	0.1
0	R($\frac{7}{2}$)	- ← +			$\frac{5}{2}$	60.01283	0.1305	0.4
0	R($\frac{7}{2}$)	+ ← -			$\frac{1}{2}$	60.01283	0.1869	0.6
0	R($\frac{7}{2}$)	- ← +			$\frac{3}{2}$	60.01283	0.2167	0.1
0	R($\frac{7}{2}$)	- ← +			$\frac{1}{2}$	60.01283	0.6480	0.2
0	R($\frac{7}{2}$)	+ ← -			$\frac{3}{2}$	60.01283	0.0225	-0.2
0	R($\frac{7}{2}$)	+ ← -			$\frac{1}{2}$	60.01283	0.0300	-0.1
0	R($\frac{7}{2}$)	+ ← -		-	$\frac{1}{2}$	60.01283	0.0449	0.0
0	R($\frac{7}{2}$)	+ ← -			$\frac{9}{2}$	60.01283	0.0469	-0.1
0	R($\frac{7}{2}$)	- ← +			$\frac{3}{2}$	60.01283	0.0802	-0.2
0	R($\frac{7}{2}$)	+ ← -		-	$\frac{3}{2}$	60.01283	0.0875	0.0
0	R($\frac{7}{2}$)	+ ← -			$\frac{7}{2}$	60.01283	0.0963	0.0
0	R($\frac{7}{2}$)	- ← +			$\frac{1}{2}$	60.01283	0.1068	0.1
0	R($\frac{7}{2}$)	- ← +			$\frac{9}{2}$	60.01283	0.1656	-0.3
0	R($\frac{7}{2}$)	- ← +		-	$\frac{3}{2}$	60.01283	0.3095	-0.4
0	R($\frac{7}{2}$)	- ← +			$\frac{7}{2}$	60.01283	0.3389	-0.2

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
<i>Transitions of GeH observed by FIR LMR spectroscopy (cont.).</i>								
⁷⁴ GeH	<i>transitions</i>							
0	R($\frac{3}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{3}{2}$	33.11320	0.9096	-0.7
0	R($\frac{3}{2}$)	- ← +		$\frac{3}{2}$	$\frac{3}{2}$	33.11320	0.9167	-0.8
0	R($\frac{3}{2}$)	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	33.11320	1.1342	0.2
0	R($\frac{3}{2}$)	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	33.11320	1.1435	0.1
0	R($\frac{3}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{3}{2}$	33.11320	1.7529	0.2
0	R($\frac{3}{2}$)	- ← +		$\frac{5}{2}$	$\frac{3}{2}$	33.11320	1.7660	0.2
0	R($\frac{5}{2}$)	- ← +		$\frac{3}{2}$	$\frac{5}{2}$	46.43119	1.1750	-0.2
0	R($\frac{5}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{5}{2}$	46.43119	1.1928	-0.5
0	R($\frac{5}{2}$)	- ← +		$\frac{5}{2}$	$\frac{5}{2}$	46.60286	0.7456	0.3
0	R($\frac{5}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{5}{2}$	46.60286	0.7713	0.3
0	R($\frac{5}{2}$)	- ← +		$\frac{3}{2}$	$\frac{3}{2}$	46.60286	1.2440	0.7
0	R($\frac{5}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{3}{2}$	46.60286	1.2867	0.5
0	R($\frac{5}{2}$)	- ← +		$\frac{3}{2}$	$\frac{5}{2}$	46.60286	0.5082	-0.4
0	R($\frac{5}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{5}{2}$	46.60286	0.5260	-0.2
0	R($\frac{5}{2}$)	- ← +		$\frac{1}{2}$	$\frac{3}{2}$	46.60286	0.6992	0.0
0	R($\frac{5}{2}$)	+ ← -		$\frac{1}{2}$	$\frac{3}{2}$	46.60286	0.7238	0.4
0	R($\frac{5}{2}$)	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	46.60286	1.1194	0.3
0	R($\frac{5}{2}$)	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	46.60286	1.1585	0.0
0	R($\frac{5}{2}$)	- ← +		$\frac{7}{2}$	$\frac{5}{2}$	46.60286	1.3920	0.2
0	R($\frac{5}{2}$)	+ ← -		$\frac{7}{2}$	$\frac{5}{2}$	46.60286	1.4390	0.4
0	R($\frac{7}{2}$)	+ ← -		$\frac{7}{2}$	$\frac{7}{2}$	60.01283	0.2133	0.0
0	R($\frac{7}{2}$)	- ← +		$\frac{7}{2}$	$\frac{7}{2}$	60.01283	0.2798	-0.3
0	R($\frac{7}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{5}{2}$	60.01283	0.2985	0.0
0	R($\frac{7}{2}$)	- ← +		$\frac{5}{2}$	$\frac{5}{2}$	60.01283	0.3917	-0.2
0	R($\frac{7}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{3}{2}$	60.01283	0.4972	0.0
0	R($\frac{7}{2}$)	- ← +		$\frac{3}{2}$	$\frac{3}{2}$	60.01283	0.6532	0.3
0	R($\frac{7}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{7}{2}$	60.01283	0.1480 ^c	0.2
0	R($\frac{7}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{5}{2}$	60.01283	0.1848 ^c	0.6
0	R($\frac{7}{2}$)	- ← +		$\frac{3}{2}$	$\frac{5}{2}$	60.01283	0.2419	-0.4
0	R($\frac{7}{2}$)	+ ← -		$\frac{1}{2}$	$\frac{3}{2}$	60.01283	0.2445	-0.2
0	R($\frac{7}{2}$)	- ← +		$\frac{1}{2}$	$\frac{3}{2}$	60.01283	0.3212	-0.4
0	R($\frac{7}{2}$)	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	60.01283	0.3635	-0.2
0	R($\frac{7}{2}$)	+ ← -		$\frac{9}{2}$	$\frac{7}{2}$	60.01283	0.3823	-0.1
0	R($\frac{7}{2}$)	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	60.01283	0.4780	-0.2
0	R($\frac{7}{2}$)	- ← +		$\frac{9}{2}$	$\frac{7}{2}$	60.01283	0.5010	-0.2
0	R($\frac{7}{2}$)	+ ← -		$-\frac{3}{2}$	$-\frac{1}{2}$	60.01283	0.7075	-0.2
0	R($\frac{7}{2}$)	- ← +		$-\frac{3}{2}$	$-\frac{1}{2}$	60.01283	0.9306	-0.3

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
<i>(h) Transitions of GeH observed by FIR LMR spectroscopy (cont.).</i>								
⁷² GeH	<i>transitions</i>							
0	R($\frac{3}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{3}{2}$	33.11320	0.9491	-0.2
0	R($\frac{3}{2}$)	- ← +		$\frac{3}{2}$	$\frac{3}{2}$	33.11320	0.9562	-0.4
0	R($\frac{3}{2}$)	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	33.11320	1.1838	-0.1
0	R($\frac{3}{2}$)	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	33.11320	1.1932	0.0
0	R($\frac{3}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{3}{2}$	33.11320	1.8291	0.4
0	R($\frac{3}{2}$)	- ← +		$\frac{5}{2}$	$\frac{3}{2}$	33.11320	1.8422	0.5
0	R($\frac{5}{2}$)	- ← +		$\frac{3}{2}$	$\frac{5}{2}$	46.43119	1.2432	0.0
0	R($\frac{5}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{5}{2}$	46.43119	1.2611	-0.1
0	R($\frac{5}{2}$)	- ← +		$\frac{5}{2}$	$\frac{5}{2}$	46.60286	0.8446	0.3
0	R($\frac{5}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{5}{2}$	46.60286	0.8703	0.2
0	R($\frac{5}{2}$)	- ← +		$\frac{3}{2}$	$\frac{3}{2}$	46.60286	1.4091	0.5
0	R($\frac{5}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{3}{2}$	46.60286	1.4520	0.5
0	R($\frac{5}{2}$)	- ← +		$\frac{3}{2}$	$\frac{5}{2}$	46.60286	0.5756	-0.3
0	R($\frac{5}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{5}{2}$	46.60286	0.5932	-0.6
0	R($\frac{5}{2}$)	- ← +		$\frac{1}{2}$	$\frac{3}{2}$	46.60286	0.7915	-0.4
0	R($\frac{5}{2}$)	+ ← -		$\frac{1}{2}$	$\frac{3}{2}$	46.60286	0.8160	-0.4
0	R($\frac{5}{2}$)	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	46.60286	1.2669	-0.2
0	R($\frac{5}{2}$)	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	46.60286	1.3063	-0.2
0	R($\frac{5}{2}$)	- ← +		$\frac{7}{2}$	$\frac{5}{2}$	46.60286	1.5776	0.3
0	R($\frac{5}{2}$)	+ ← -		$\frac{7}{2}$	$\frac{5}{2}$	46.60286	1.6244	0.5
0	R($\frac{7}{2}$)	+ ← -		$\frac{7}{2}$	$\frac{7}{2}$	60.01283	0.4111	-0.2
0	R($\frac{7}{2}$)	- ← +		$\frac{7}{2}$	$\frac{7}{2}$	60.01283	0.4778	-0.5
0	R($\frac{7}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{5}{2}$	60.01283	0.5752	-0.3
0	R($\frac{7}{2}$)	- ← +		$\frac{5}{2}$	$\frac{5}{2}$	60.01283	0.6695	0.3
0	R($\frac{7}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{3}{2}$	60.01283	0.9571	-0.2
0	R($\frac{7}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{7}{2}$	60.01283	0.2850 ^c	0.1
0	R($\frac{7}{2}$)	- ← +		$\frac{5}{2}$	$\frac{7}{2}$	60.01283	0.3312 ^c	-0.5
0	R($\frac{7}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{5}{2}$	60.01283	0.3549 ^c	-0.4
0	R($\frac{7}{2}$)	- ← +		$\frac{3}{2}$	$\frac{5}{2}$	60.01283	0.4127	-0.8
0	R($\frac{7}{2}$)	+ ← -		$\frac{1}{2}$	$\frac{3}{2}$	60.01283	0.4710	-0.3
0	R($\frac{7}{2}$)	- ← +		$\frac{1}{2}$	$\frac{3}{2}$	60.01283	0.5482	-0.3
0	R($\frac{7}{2}$)	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	60.01283	0.7004	0.2
0	R($\frac{7}{2}$)	+ ← -		$\frac{9}{2}$	$\frac{7}{2}$	60.01283	0.7377	-0.1
0	R($\frac{7}{2}$)	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	60.01283	0.8141	-0.6
0	R($\frac{7}{2}$)	- ← +		$\frac{9}{2}$	$\frac{7}{2}$	60.01283	0.8562	-0.2
0	R($\frac{7}{2}$)	+ ← -		$\frac{7}{2}$	$\frac{5}{2}$	60.01283	1.5055	0.0
0	R($\frac{7}{2}$)	- ← +		$-\frac{3}{2}$	$-\frac{1}{2}$	60.01283	1.5796	-0.4

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
⁷⁰ GeH	<i>transitions</i>							
0	R($\frac{3}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{3}{2}$	33.11320	0.9905	-0.8
0	R($\frac{3}{2}$)	- ← +		$\frac{3}{2}$	$\frac{3}{2}$	33.11320	0.9977	-0.7
0	R($\frac{3}{2}$)	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	33.11320	1.2364	-0.2
0	R($\frac{3}{2}$)	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	33.11320	1.2458	-0.2
0	R($\frac{3}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{3}{2}$	33.11320	1.9091	-0.2
0	R($\frac{3}{2}$)	- ← +		$\frac{5}{2}$	$\frac{3}{2}$	33.11320	1.9228	0.8
0	R($\frac{5}{2}$)	- ← +		$\frac{3}{2}$	$\frac{5}{2}$	46.43119	1.3152	-0.1
0	R($\frac{5}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{5}{2}$	46.43119	1.3333	0.2
0	R($\frac{5}{2}$)	- ← +		$\frac{5}{2}$	$\frac{5}{2}$	46.60286	0.9494	0.0
0	R($\frac{5}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{5}{2}$	46.60286	0.9750	0.0
0	R($\frac{5}{2}$)	- ← +		$\frac{3}{2}$	$\frac{3}{2}$	46.60286	1.5837	0.2
0	R($\frac{5}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{3}{2}$	46.60286	1.6269	0.4
0	R($\frac{5}{2}$)	- ← +		$\frac{3}{2}$	$\frac{5}{2}$	46.60286	0.6468	-0.4
0	R($\frac{5}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{5}{2}$	46.60286	0.6645	-0.6
0	R($\frac{5}{2}$)	- ← +		$\frac{1}{2}$	$\frac{3}{2}$	46.60286	0.8892	-0.7
0	R($\frac{5}{2}$)	+ ← -		$\frac{1}{2}$	$\frac{3}{2}$	46.60286	0.9140	-0.2
0	R($\frac{5}{2}$)	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	46.60286	1.4234	0.2
0	R($\frac{5}{2}$)	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	46.60286	1.4629	0.0
0	R($\frac{5}{2}$)	- ← +		$-\frac{7}{2}$	$\frac{5}{2}$	46.60286	1.7743	0.6
0	R($\frac{5}{2}$)	+ ← -		$-\frac{7}{2}$	$\frac{5}{2}$	46.60286	1.8211	0.8
0	R($\frac{7}{2}$)	+ ← -		$\frac{7}{2}$	$\frac{7}{2}$	60.01283	0.6209	-0.3
0	R($\frac{7}{2}$)	- ← +		$\frac{7}{2}$	$\frac{7}{2}$	60.01283	0.6885	0.2
0	R($\frac{7}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{5}{2}$	60.01283	0.8698	0.6
0	R($\frac{7}{2}$)	- ← +		$\frac{5}{2}$	$\frac{5}{2}$	60.01283	0.9622	-0.5
0	R($\frac{7}{2}$)	- ← +		$\frac{3}{2}$	$\frac{3}{2}$	60.01283	1.6005	0.3
0	R($\frac{7}{2}$)	+ ← -		$\frac{5}{2}$	$\frac{7}{2}$	60.01283	0.4298 ^c	-0.5
0	R($\frac{7}{2}$)	+ ← -		$\frac{3}{2}$	$\frac{5}{2}$	60.01283	0.5357 ^c	-0.4
0	R($\frac{7}{2}$)	- ← +		$\frac{3}{2}$	$\frac{5}{2}$	60.01283	0.5942	-0.2
0	R($\frac{7}{2}$)	+ ← -		$\frac{1}{2}$	$\frac{3}{2}$	60.01283	0.7103	-0.6
0	R($\frac{7}{2}$)	- ← +		$\frac{1}{2}$	$\frac{3}{2}$	60.01283	0.7881	-0.3
0	R($\frac{7}{2}$)	+ ← -		$-\frac{1}{2}$	$\frac{1}{2}$	60.01283	1.0544	-0.4
0	R($\frac{7}{2}$)	+ ← -		$\frac{9}{2}$	$\frac{7}{2}$	60.01283	1.1146	-0.3
0	R($\frac{7}{2}$)	- ← +		$-\frac{1}{2}$	$\frac{1}{2}$	60.01283	1.1694	-0.6
0	R($\frac{7}{2}$)	- ← +		$\frac{9}{2}$	$\frac{7}{2}$	60.01283	1.2330	-0.3

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
<i>(i) Transitions of GeH with hyperfine structure observed by FIR LMR spectroscopy.</i>								
⁷⁶ GeH	<i>transitions</i>							
0	R($\frac{1}{2}$)	+ ← -	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	19.97694	1.3575	0.4
0	R($\frac{1}{2}$)	+ ← -	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	19.97694	1.4325	0.3
0	R($\frac{1}{2}$)	+ ← -	$-\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	19.97694	1.1242	-0.4
0	R($\frac{1}{2}$)	+ ← -	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	19.97694	1.1467	-0.4
0	R($\frac{3}{2}$)	- ← +	$-\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	33.11320	1.7775	-1.8
0	R($\frac{3}{2}$)	- ← +	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	33.11320	1.7775	-1.4
⁷⁴ GeH	<i>transitions</i>							
0	R($\frac{1}{2}$)	- ← +	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	19.49308	1.4719	-1.0
0	R($\frac{1}{2}$)	- ← +	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	19.49308	1.4932	-1.0
0	R($\frac{1}{2}$)	- ← +	$-\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	19.49308	1.6494	-0.2
0	R($\frac{1}{2}$)	- ← +	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	19.49308	1.6699	-0.4
0	R($\frac{1}{2}$)	+ ← -	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	19.97694	0.2863	0.2
0	R($\frac{1}{2}$)	+ ← -	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	19.97694	0.3936	0.2
0	R($\frac{1}{2}$)	+ ← -	$-\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	19.97694	0.2430	0.1
0	R($\frac{1}{2}$)	+ ← -	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	19.97694	0.2908	0.0
0	R($\frac{1}{2}$)	+ ← -	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	19.97694	0.3670	0.3
0	R($\frac{1}{2}$)	+ ← -	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	19.97694	0.5470	0.6
0	R($\frac{3}{2}$)	- ← +	$-\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	33.11320	0.6571	-0.3
0	R($\frac{3}{2}$)	- ← +	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	33.11320	0.7081	-0.3
0	R($\frac{3}{2}$)	- ← +	$\frac{1}{2}^d$	$\frac{5}{2}$	$\frac{1}{2}$	33.11320	0.2505	-0.7
0	R($\frac{3}{2}$)	- ← +	$-\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	33.11320	0.3328	-0.5
0	R($\frac{3}{2}$)	- ← +	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	33.11320	0.3328	-0.6
0	R($\frac{3}{2}$)	- ← +	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	33.11320	0.4684	-0.7
0	R($\frac{3}{2}$)	- ← +	$-\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	33.11320	0.4972	-0.6
0	R($\frac{3}{2}$)	- ← +	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	33.11320	0.8600 ^c	-0.9
0	R($\frac{3}{2}$)	- ← +	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	33.11320	0.9475	-0.8

v''	Trans.	Par.	M_I^a	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^b
⁷² GeH	<i>transitions</i>							
0	R($\frac{1}{2}$)	- ← +	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	19.49308	0.8613	-0.2
0	R($\frac{1}{2}$)	- ← +	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	19.49308	0.8830	-0.2
0	R($\frac{1}{2}$)	- ← +	$-\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	19.49308	0.9630	0.2
0	R($\frac{1}{2}$)	- ← +	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	19.49308	0.9825	0.0
0	R($\frac{1}{2}$)	+ ← -	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	19.97694	0.7400	0.1
0	R($\frac{1}{2}$)	+ ← -	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	19.97694	1.0901	-0.5
0	R($\frac{1}{2}$)	+ ← -	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	19.97694	0.6056	0.6
0	R($\frac{1}{2}$)	+ ← -	$\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	19.97694	0.6096	0.5
0	R($\frac{1}{2}$)	+ ← -	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	19.97694	0.7930	0.3
0	R($\frac{1}{2}$)	+ ← -	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	19.97694	0.9577	-0.3
0	R($\frac{3}{2}$)	- ← +	$\frac{1}{2}$	$-\frac{5}{2}$	$-\frac{3}{2}$	33.11320	1.1840	-0.2
0	R($\frac{3}{2}$)	- ← +	$-\frac{1}{2}$	$-\frac{5}{2}$	$-\frac{3}{2}$	33.11320	1.1908	1.0
0	R($\frac{3}{2}$)	- ← +	$\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	33.11320	1.7244	0.6
0	R($\frac{3}{2}$)	- ← +	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	33.11320	1.7340	0.5
⁷⁰ GeH	<i>transitions</i>							
0	R($\frac{1}{2}$)	- ← +	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	19.49308	0.2135	0.5
0	R($\frac{1}{2}$)	- ← +	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	19.49308	0.2380	0.3
0	R($\frac{1}{2}$)	- ← +	$-\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	19.49308	0.2415	0.7
0	R($\frac{1}{2}$)	- ← +	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	19.49308	0.2605	0.5
0	R($\frac{1}{2}$)	+ ← -	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	19.97694	1.9380	0.0
0	R($\frac{1}{2}$)	+ ← -	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	19.97694	1.5407	1.0
0	R($\frac{1}{2}$)	+ ← -	$\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	19.97694	1.5538	1.1

^a $\Delta M_I = 0$.

^b (o-c)/10⁻⁴cm⁻¹.

^c resonance given zero weight in the fit.

^d for this resonance $\Delta M_I = -1$.

Appendix B. Observed resonances in the IR LMR spectrum of various TeD isotopomers and in the e.p.r. spectrum of ^{130}TeH .

v''	Trans.	Par.	M_I^b	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^c
^{130}TeH	<i>e.p.r.</i>	<i>transitions</i>						
0	$Q(\frac{3}{2})$	$+\leftarrow-$		$\frac{1}{2}$	$-\frac{1}{2}$	0.30741^d	0.8191	0.1
0	$Q(\frac{3}{2})$	$-\leftarrow+$		$\frac{1}{2}$	$-\frac{1}{2}$	0.30741^d	0.8196	-0.1
^{122}TeD	<i>transitions</i>							
0	$P(\frac{9}{2})$			$-\frac{7}{2}$	$-\frac{5}{2}$	1442.15056	0.4051	-4.3
0	$P(\frac{9}{2})$			$-\frac{5}{2}$	$-\frac{3}{2}$	1442.15056	0.5054	2.4
0	$P(\frac{9}{2})$			$-\frac{3}{2}$	$-\frac{1}{2}$	1442.15056	0.6580	-1.1
0	$P(\frac{7}{2})$			$-\frac{5}{2}$	$-\frac{3}{2}$	1448.73914	0.0667	-1.4
0	$P(\frac{7}{2})$			$-\frac{3}{2}$	$-\frac{1}{2}$	1448.73914	0.0921	1.0
0	$P(\frac{7}{2})$			$-\frac{1}{2}$	$\frac{1}{2}$	1448.73914	0.1437	0.1
0	$P(\frac{7}{2})$			$-\frac{5}{2}$	$-\frac{7}{2}$	1448.73914	0.2041^a	0.0
0	$P(\frac{5}{2})$			$\frac{3}{2}$	$\frac{5}{2}$	1455.19384	0.0849	-1.2
0	$P(\frac{5}{2})$			$\frac{1}{2}$	$-\frac{1}{2}$	1455.19384	0.0505	-1.1
0	$R(\frac{3}{2})$			$\frac{1}{2}$	$-\frac{1}{2}$	1485.82716	0.9830	2.6
0	$R(\frac{3}{2})$			$-\frac{1}{2}$	$-\frac{3}{2}$	1485.82716	0.5636	-3.5
^{123}TeD	<i>transitions</i>							
0	$P(\frac{9}{2})$		$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	1442.15056	0.1821^e	-20.1
0	$P(\frac{9}{2})$		$-\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	1442.15056	0.1370	-3.3
0	$P(\frac{9}{2})$		$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	1442.15056	0.2182	-3.3
0	$P(\frac{9}{2})$		$-\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	1442.15056	0.1713^e	8.1
0	$P(\frac{9}{2})$		$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	1442.15056	0.3085	-3.5
0	$P(\frac{9}{2})$		$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	1442.15056	0.2652	-1.6
0	$P(\frac{9}{2})$		$\frac{1}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	1442.15056	0.3609^e	23.0
0	$P(\frac{9}{2})$		$-\frac{1}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	1442.15056	0.3518	0.2
^{124}TeD	<i>transitions</i>							
0	$P(\frac{9}{2})$			$\frac{7}{2}$	$\frac{5}{2}$	1442.15056	0.6580	-7.0
0	$P(\frac{9}{2})$			$\frac{5}{2}$	$\frac{3}{2}$	1442.15056	0.8059	-2.0
0	$P(\frac{9}{2})$			$\frac{3}{2}$	$\frac{1}{2}$	1442.15056	1.0446	0.4
0	$P(\frac{5}{2})$			$\frac{3}{2}$	$\frac{5}{2}$	1455.19384	1.2607	-0.8
0	$P(\frac{7}{2})$			$\frac{5}{2}$	$\frac{3}{2}$	1448.73914	0.6186	3.2
0	$P(\frac{7}{2})$			$\frac{3}{2}$	$\frac{1}{2}$	1448.73914	0.8426	-0.9
0	$P(\frac{5}{2})$			$\frac{3}{2}$	$\frac{1}{2}$	1455.19384	0.4127	-1.9
0	$P(\frac{5}{2})$			$\frac{1}{2}$	$-\frac{1}{2}$	1455.19384	0.7584	-0.3
0	$Q(\frac{7}{2})$			$-\frac{1}{2}$	$\frac{1}{2}$	1469.60115	0.2197	1.0
0	$R(\frac{3}{2})$			$-\frac{1}{2}$	$-\frac{3}{2}$	1485.82716	0.9507	11.5

v''	Trans.	Par.	M_I^b	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^c
¹²⁵ TeD	<i>transitions</i>							
0	P($\frac{5}{2}$)		$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	1455.19384	0.6268	3.0
0	P($\frac{5}{2}$)		$-\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	1455.19384	0.5746	1.3
0	P($\frac{5}{2}$)		$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	1455.19384	1.1474	-1.3
0	P($\frac{5}{2}$)		$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	1455.19384	1.0914	-0.2
0	R($\frac{3}{2}$)		$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	1485.82716	1.1702	3.2
0	R($\frac{3}{2}$)		$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	1485.82716	1.1120	3.5
¹²⁶ TeD	<i>transitions</i>							
0	P($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{1}{2}$	1455.19384	0.7894	-1.5
0	P($\frac{5}{2}$)			$\frac{1}{2}$	$-\frac{1}{2}$	1455.19384	1.4885	-8.3
0	Q($\frac{3}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1469.60115	1.4366	12.6
0	Q($\frac{3}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1469.60115	1.4539	12.3
0	Q($\frac{3}{2}$)			$-\frac{3}{2}$	$-\frac{1}{2}$	1469.60115	1.4716	13.1
1	Q($\frac{3}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1432.01925	1.1231	7.9
1	Q($\frac{3}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1432.01925	1.1341	8.8
1	Q($\frac{3}{2}$)			$-\frac{3}{2}$	$-\frac{1}{2}$	1432.01925	1.1447	7.8
¹²⁸ TeD	<i>transitions</i>							
0	P($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{1}{2}$	1455.19384	1.1588	-1.0
0	Q($\frac{5}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1469.60115	0.4544	0.4
0	Q($\frac{3}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1469.60115	0.9716 ^a	-0.1
0	Q($\frac{3}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1469.60115	0.9794 ^a	-0.4
0	Q($\frac{3}{2}$)			$-\frac{3}{2}$	$-\frac{1}{2}$	1469.60115	0.9874 ^a	-0.4
0	R($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{5}{2}$	1490.43223	1.0554	-1.7
0	R($\frac{5}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1490.43223	1.4355	6.4
1	Q($\frac{3}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1432.01925	0.6871	4.9
1	Q($\frac{5}{2}$)			$\frac{1}{2}$	$-\frac{1}{2}$	1432.01925	0.2301	-1.5
2	Q($\frac{3}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1394.14191	0.4855	2.6
¹³⁰ TeD	<i>transitions</i>							
0	P($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{1}{2}$	1455.19384	1.5267	-25.2
0	Q($\frac{3}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1469.60115	0.5206 ^a	-0.7
0	Q($\frac{3}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1469.60115	0.5230 ^a	0.0
0	Q($\frac{3}{2}$)			$-\frac{3}{2}$	$-\frac{1}{2}$	1469.60115	0.5253 ^a	0.0
0	Q($\frac{5}{2}$)			$-\frac{3}{2}$	$-\frac{5}{2}$	1469.60115	0.5993 ^a	0.8
0	Q($\frac{5}{2}$)			$-\frac{1}{2}$	$-\frac{3}{2}$	1469.60115	0.6028 ^a	0.6
0	Q($\frac{5}{2}$)			$\frac{1}{2}$	$-\frac{1}{2}$	1469.60115	0.6065 ^a	0.6
0	Q($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{1}{2}$	1469.60115	0.6108 ^a	0.3
0	Q($\frac{5}{2}$)			$\frac{5}{2}$	$\frac{3}{2}$	1469.60115	0.6154 ^a	0.0

v''	Trans.	Par.	M_I^b	M_J'	M_J''	ν_L/cm^{-1}	Obs. B/T	o-c ^c
¹³⁰ TeD	<i>transitions</i>							
0	R($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{5}{2}$	1490.43223	0.3824	1.1
0	R($\frac{5}{2}$)			$\frac{1}{2}$	$\frac{3}{2}$	1490.43223	0.5198 ^a	0.3
0	R($\frac{5}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1490.43223	0.8118 ^a	-0.7
0	R($\frac{5}{2}$)			$\frac{7}{2}$	$\frac{5}{2}$	1490.43223	1.1729 ^a	-0.4
1	Q($\frac{5}{2}$)			$-\frac{3}{2}$	$-\frac{5}{2}$	1432.01925	1.2087	-5.6
1	Q($\frac{5}{2}$)			$-\frac{1}{2}$	$-\frac{3}{2}$	1432.01925	1.2219	-6.2
1	Q($\frac{5}{2}$)			$\frac{1}{2}$	$-\frac{1}{2}$	1432.01925	1.2368	-6.1
1	Q($\frac{5}{2}$)			$\frac{3}{2}$	$\frac{1}{2}$	1432.01925	1.2557	-8.3
1	Q($\frac{5}{2}$)			$\frac{5}{2}$	$\frac{3}{2}$	1432.01925	1.2739	-4.3
1	Q($\frac{3}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1432.01925	0.2542	2.7
2	Q($\frac{3}{2}$)			$-\frac{1}{2}$	$\frac{1}{2}$	1394.14191	0.0762	-2.6

^a Measurement made on Lamb dip.

^b $\Delta M_I = 0$

^c (o-c)/10⁻⁴cm⁻¹

^d e.p.r. at a frequency of 9216.0 MHz [6].

^e resonance given zero weight in the fit.

