

FTIR Studies of Chemical Processes



Julian Few

Trinity College

University of Oxford

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Abstract

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This thesis presents the study of a selection of gas phase chemical processes using time-resolved Fourier transform infrared (FTIR) emission spectroscopy. Such processes include molecular energy transfer, chemical reaction and photodissociation. The major focus of this thesis was the investigation of collisional energy transfer from the electronically excited states of NO and OH, with particular attention paid to the fate of the electronic energy.

NO A $^2\Sigma^+(\nu = 0)$ is prepared by laser excitation, pumping the overlapped Q₁ and P₂₁ band heads of the NO A-X (0,0) transition at 226.257 nm. The quenching of this state by O₂ and CO₂ was studied. Experiments were performed to investigate what channels contribute to the quenching process, the branching ratio of these different channels and the partitioning of energy among the various products. Quenching by O₂ was found to proceed mostly through non-reactive channels. High vibrational excitation of NO X $^2\Pi$ was observed, with population detected in $\nu = 22$, representing 79 % of the available energy. The O₂ product was found to be formed in more than one electronic state: the ground state, X $^3\Sigma_g^-$, and a high-lying electronically excited state, such as the A $^3\Sigma_u^+$, A' $^3\Delta_u$ or c $^1\Sigma_u^-$ states. A reactive channel producing vibrationally excited NO₂ was observed, but was found to be a minor process with an upper limit of 18 % for the branching ratio. In contrast the quenching of NO A $^2\Sigma^+(\nu = 0)$ by CO₂ was found to proceed predominately by reaction, with a branching ratio of 76 %. While emission from NO₂ was observed, it was weak, and therefore it was concluded that the main reaction products were CO, O(3P) and NO X $^2\Pi(\nu = 0)$. The nascent strong CO₂ ν_3 emission band from the non-reactive channel exhibited a large red-shift from

its fundamental position. This indicates that the CO_2 vibrational distribution is significantly hotter than statistical. Investigations were then performed studying the quenching of $\text{NO } A^2\Sigma^+(\nu = 1)$ by NO and CO_2 , with both systems exhibiting similar characteristics to the quenching of the ground vibrational level of $\text{NO } A^2\Sigma^+$. From comparison of the emission intensity of the CO fundamental and $\text{CO}_2 \nu_3$ mode following quenching of the $\nu = 0$ and 1 levels of the $\text{NO } A^2\Sigma^+$ state, it was concluded that the branching ratio for reactive quenching was larger in the latter case.

Secondly, experiments were performed to measure the rate constants for the quenching of $\text{NO } A^2\Sigma^+(\nu = 0)$ by the noble gases. The noble gases are inefficient quenchers of electronically excited NO and therefore careful experimental design was required to minimise the influence of impurities on the results. All the rate constants were found to be of the order of $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The value for Xe was 50 times smaller than reported previously in the literature. In light of this new measurement, a re-analysis of experiments, performed previously in the group, on the electronic quenching of $\text{NO } A^2\Sigma^+(\nu = 0)$ by Xe was performed. A very hot vibrational distribution of $\text{NO } X^2\Pi$ was obtained.

Next, the collisional quenching of $\text{OH } A^2\Sigma^+(\nu = 0)$ by H_2 was investigated. OH radicals were generated *in situ* by the photolysis of HNO_3 at 193 nm, which were excited to the $A^2\Sigma^+(\nu = 0)$ state on the overlapped $Q_1(1)$ and $P_{21}(1)$ rotational lines at 307.935 nm. Reactive quenching was found to be the major pathway, in agreement with the literature. Copious emission from vibrationally excited water was observed. Comparison of this emission with theoretical calculations revealed a hotter distribution than predicted. It was concluded that the energy channelled into the vibrational modes of H_2O is in excess of 60 % of the available energy. Experiments performed with D_2 allowed the non-reactive channel to be studied; a cold vibrational distribution of the $\text{OH } X^2\Pi$ was observed.

Finally the reaction between CN radicals and cyclohexane was studied. CN was generated by the photolysis of ICN at 266 nm. Prompt emission from HCN in the C-H stretching region was observed meaning the new bond was formed in a vibrationally excited state. Analysis of the emission revealed HCN was populated up to $\nu_3 = 2$. Excellent agreement with the results of a theoretical study of the system was found.

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Chapter 1

Introduction

1.1 Gas phase chemical processes

Chemical processes that occur in the gas phase have significant relevance in many fields, for example, in industrial and environmental settings. The species studied in this thesis are intimately involved with many key processes occurring in atmospheric and combustion environments. The study of gas phase chemical processes also provides insight into the fundamental nature of chemical interactions since, free from neighbouring atom effects that exist in the condensed phases, such processes are able to be probed in high detail; slower collision rates between molecules mean that the nascent, collision-free products from energy transfer and reactive processes can be probed and the rates of these process can be determined with greater accuracy. Measurements of rate constants, branching ratios for various channels and the state-specific distribution of energy and angular momentum among products allow the mechanism of the process to be discerned.

The technique employed for the investigations in this thesis is time-resolved

Fourier transform infrared (FTIR) emission spectroscopy. The principles of this technique, along with its advantages and disadvantages will be discussed in Sections 1.4 and 2.4.

1.2 Collisional energy transfer

The collisional transfer of energy between species is a vast topic, intimately connected to the fundamental nature of chemical interactions and with particular application to environments where molecules are formed in excited states, such as flames, atmospheric reactions and solar photodissociation. Non-reactive collisions between gas phase molecules proceed with a great variety of efficiencies. In the simplest example, a collision between two noble gas atoms in their ground electronic states, energy can only normally be transferred between the translational modes of the two atoms, which means that kinetic energy is conserved and therefore all collisions are elastic – ignoring very high energy collisions which can lead to electronic energy transfer. When a collision involving molecules is considered, there are now rotational and vibrational modes which can donate or accept energy. The energy transfer processes available are termed R-R, R-T, V-V, V-R and V-T where V, R and T stand for vibration, rotation and translation respectively. Therefore kinetic energy is not necessarily conserved in collisions between molecules. These inelastic collisions, allowing energy to be exchanged between the different degrees of freedom of the molecules, are responsible for bringing gas samples into thermal equilibrium. With the advent of laser techniques, individual quantum states of molecules can be generated and probed, enabling energy transfer processes to be studied with quantum state resolution.

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The typical rates of the various energy transfer processes show a large range in efficiencies. These differences can be explained by consideration of the relative timescales of the collisions and the molecular motions involved. For any general system, an adiabaticity parameter, ξ , may be defined thus [1]:

$$\xi = \frac{\tau_{\text{perturbation}}}{\tau_{\text{response}}} \quad (1.1)$$

With regards to collisional energy transfer between vibration, rotation and translation, $\tau_{\text{perturbation}}$ is the collision time, and τ_{response} is the time period of the respective molecular motions. The two limits of this function are termed the adiabatic limit, for $\xi \gg 1$ and the sudden limit, where $\xi \ll 1$. Energy transfer is efficient in the sudden limit and very inefficient in the adiabatic limit. In other words, for energy transfer to occur, the collision time must be comparable to that of the molecular motions involved. The collision time is defined as a/v_{rel} where a is the ‘range’ of the intermolecular forces and v_{rel} is the relative velocity of the colliding molecules. The time constant for vibrational motion of molecules is much smaller than for rotation, hence the R-T energy transfer will have a smaller ξ and is therefore a more efficient process. As the temperature is raised, v_{rel} is increased and the collision time is reduced, which will increase the rate of V-T transfer, while reducing the rate of R-T transfer. Additionally, since $\tau_{\text{vibration}}$ is related to the stiffness of the bond, a less stiff bond will have lower frequency and therefore a longer time of vibration. Thus collisional V-T energy transfer occurs faster for lower energy vibrations.

An alternative way to consider the efficiencies of V,R-T transfer processes is to see how much energy is channelled into translational degrees of freedom. It

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is widely observed that efficient energy transfer processes proceed with minimal energy released as translational energy. This explains the efficiency of resonant energy transfer such as that shown in reaction (1.2).



The spacing of rotational energy levels are generally two to three orders of magnitude smaller than vibrational levels, so a R-T energy transfer releases less energy into translation and so is faster. An extension of this is that the energy spacing between rotational levels within a molecule increase for higher J , and thus rotational relaxation of higher rotational states, for example, by noble gases will be less efficient. This is opposite to the trend for V-T transfer; the anharmonicity of electronic potential surfaces means the spacing of adjacent vibrational states decreases for increasing ν and so the efficiency of V-T energy transfer increases for the higher vibrational levels. The fast nature of R-T energy transfer is utilised extensively within this thesis; large pressures of Ar will be employed to achieve fast R-T relaxation of product species to ensure all molecules are rotationally thermalised, which will simplify the analysis of the emission features. The relative rates of V-T and R-T energy transfer means that the rate of vibrational relaxation of product species is essentially unaffected by the high pressure of Ar. Another manifestation of efficient R-T transfer evident in experiments described in this thesis is rotational hole filling. In the electronic quenching experiments described in Chapters 3, 4 and 5, the intensity of the NO A-X LIF signal and the IR emission from quenching products was increased upon the addition of 50 Torr of Ar. This is because the narrow bandwidth of the laser radiation allows excita-

tion from a single quantum state of the NO molecule. Rapid R-T energy transfer causes re-population of the depleted state within the duration of the laser pulse, allowing a greater transfer of population to the electronically excited state. The first investigations performed in this group on the electronic quenching of NO $A^2\Sigma^+$ [2] involved a series of experiments on the rotational hole filling effect. A greater increase in the LIF signal was observed following the pumping of a low rotational state of NO $X^2\Pi(\nu = 0)$ compared to higher rotational states, as expected considering that R-T is more efficient for lower J as discussed above.

For collisions that involve the change of rotational state of either collisional partner, conservation of total angular momentum, $\mathbf{J}$, in addition to conservation of energy, must be satisfied. In the simplest case the angular momentum associated with two colliding closed-shell molecules is the sum of the rotational angular momentum, $\mathbf{j}$, and the orbital angular momentum, $\mathbf{l}$, which depends on the relative motion of the molecular partners. If either of the molecules have open-shell electronic configurations, then electron spin, $\mathbf{S}$, and electronic orbital angular momentum, $\mathbf{L}$, will contribute to the total angular momentum. To understand the efficiency of a particular energy transfer process, conservation of energy and angular momentum must both be considered. It is often the case that ΔJ has a greater effect governing the probability of an energy transfer process than the amount of energy released as translational energy does. For example, the propensity for transfer of rotational energy is strongly dependent on the shape of the potential energy surface, and on the relative orientation of the collision partners. A crossed molecular beam (CMB) study on the collisions of OH $X^2\Pi$ with Ar by van Beek *et al.* found that a collision on the H-end of the molecule produced greater rotational excitation in the OH product compared to a collision on the

O-end [3]. A wide variety of techniques, including resonance enhanced multi-photon ionisation (REMPI) velocity map imaging (VMI) [4], CMB [5], Zeeman quantum beat spectroscopy (ZQBS) [6] and polarisation spectroscopy (PS) [7], are able to investigate collisional energy transfer processes with quantum state resolution. Studies of specific properties of collisions, including collisional depolarisation rates and the scattering angle dependence of orientation and alignment of rotational angular momentum in products have been performed [8–10], and allow insight into the forces acting on the molecules during the collision event.

V-V energy transfer is also found to follow the same general principle that a process is more efficient when the energy released as translational energy is minimised. Callear in 1965 found an empirical linear relationship between the probability of V-V transfer occurring and ΔE , the difference in energy between the donor and acceptor vibrational states [11]. Assuming only single quantum transitions, they observed that the greater the mis-match of spacing of vibrational energy levels in the two molecules, the lower the probability of the transition. A previous study performed in the group on the state specific relaxation of vibrationally excited NO X $^2\Pi(\nu)$ by O₂ observed some interesting effects [2]. The V-V relaxation process can be generalised as shown in process (1.3).



The vibrational quenching by O₂ was observed to peak for levels $\nu = 12$ – 13 in NO. This is readily explained by the near resonant energy matching of the NO ($\nu = 13(12) \rightarrow \nu = 12(11)$) and the O₂ ($\nu = 1 \leftarrow \nu = 0$) transitions. The anharmonicity of the NO ground electronic state means that for higher and lower

vibrational levels the energy match becomes poorer, so more energy is taken up by the translational modes and so the rate of V-V transfer becomes slower. This effect can be observed in the data presented in Chapter 3 on the electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by O₂. The vibrational relaxation of NO X $^2\Pi(\nu)$ by NO X $^2\Pi(\nu = 0)$ was studied in the same work [2] and it was found that for $\nu = 1-9$, the vibrational relaxation rates decrease, due to the increasing mis-match between the energy of the NO ($\nu \rightarrow \nu - 1$) and the NO ($\nu = 1 \leftarrow \nu = 0$) transitions. For higher ν the rate constants were found to increase. This was ascribed to the increasing importance of V-T energy transfer, which will be more efficient for the higher vibrational levels as the anharmonicity of the energy surface results in closer spacing of adjacent vibrational states and the energy mis-match with NO X $^2\Pi(1 \leftarrow 0)$ becomes too great for efficient V-V transfer. Multi-quantum V-V transitions were considered, and such processes will be more probable for higher vibrational levels than lower ones, as NO ($\nu \rightarrow \nu - 2$) and the NO ($\nu = 1 \leftarrow \nu = 0$) transitions become closer in resonance. While the work presented in this thesis does not investigate these energy transfer processes, the effect of V-V and V-T transfer are evident, as the experiment is able to measure the time dependent vibrational distributions of post quenching species. A significant aim of the present work is to determine nascent vibrational distributions. The detection rise time of the experiment, $\sim 2-3 \mu\text{s}$, means observed spectra can not necessarily be considered nascent, and therefore kinetic simulations consisting of single quantum cascade processes are fitted to the vibrational distribution to allow nascent distributions to be extracted. Thus the experiment is able to acquire data on the kinetics of a processes as well as dynamics.

1.2.1 Collisional electronic quenching

The energy transfer process of prime interest in this thesis, as yet unmentioned, is the transfer of electronic energy. Non-radiative removal of an electronically excited state upon collision with another molecule is often termed quenching. This process is the least well understood of all the inelastic collisional processes, as more than one potential energy surface is involved. Electronic energy can be deposited into the various internal modes of the both collision partners (translation, rotation, vibration) as well as into electronic energy. The latter process can be very efficient if there are near-resonant electronic levels available. Reactive processes, as will be seen later, can play a very important part in quenching collisions. Interest in such processes is long standing and many species that have been studied, for example NO, OH, CH, NH, PH, SiF, SO₂, CN and N₂⁺.

The CN A-X system is the most comprehensively studied system, with extensive experimental and theoretical considerations. There exist spectroscopic perturbations of specific rotational levels of the A ²Π state in the isolated CN radical resulting from near resonant energy matching between specific rovibrational levels of the electronically excited state and the ground state ($\nu_X \approx \nu_A + 4$). Historically, one of the first mechanisms proposed for electronic energy transfer is through such perturbations. For CN-rare gas systems, collision induced transfer from unperturbed levels is a relatively efficient process which partially masks the effect of the gateway levels [12]. It is found that the rotational distribution in the CN X ²Σ⁺ state following collisional energy transfer exhibit an alternation effect, and significantly, transitions generally proceeded with small changes to the rotational angular momentum, even if it is accompanied by quite large changes

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in energy [13]. This is an example of where conservation of angular momentum dominates the dynamics of a process rather than simple energy gap principles.

Collision induced transitions between different excited electronic states have been studied for CH and SiX ($X = \text{Cl}, \text{F}$) [14–16]. The behaviour observed following the electronic excitation of CH radicals in the presence of CO_2 [17] is different from that seen in the CN system; the collision induced transfer between the $\text{A } ^2\Delta$ and $\text{B } ^2\Sigma^-$ states proceeds with a wide range of observed ΔN , where N is the quantum number for the total angular momentum excluding spin, with the distribution peaking close in energy to the initially excited level, indicating that for this system, as with V-V and V-T transfer discussed earlier, minimising the energy released to translation is an important factor. Study of electronic transfer from the $\text{C } ^2\Delta$ state to the $\text{B } ^2\Sigma^+$ state of SiF found that the resultant vibrational distributions were similar to the respective Franck-Condon factors for the transitions, which suggest a ‘sudden’ interaction, where the quenching molecule has little effect on the potential energy surface of the SiF molecule.

There are clearly a variety of behaviours that are exhibited by different systems for the collisional transfer of energy between electronic states. An early model proposed for the rate constant of collision induced energy transfer between specific vibrational levels of two electronic states, $k_{A\nu, A'\nu'}$, is the empirical scaling law, shown in Equation 1.4 [18, 19].

$$k_{A\nu, A'\nu'} = k_{A, A'} q_{\nu, \nu'} \exp(-\Delta E/kT) \quad (1.4)$$

This model originates from the energy gap law observed for inelastic collisions within one electronic state as discussed earlier, and is modified by the overall

quenching rate constant for transfer between the states, $k_{A,A'}$, and the Franck-Condon overlap between the specific vibrational levels in the two electronic states, $q_{\nu,\nu'}$. ΔE is the energy gap between the initial and final state. However, such a model fails in the majority of cases [12] as there are too many system-specific variables that are not considered, such as the strength of interaction between the quencher and the electronically excited molecule, angular momentum constraints, or whether there are any gateway perturbations which will dominate the energy transfer process. And finally, an additional complication for such system is the possibility of reactive processes, which are energetically feasible due to the large amount of energy in the system.

1.2.2 Collisional quenching models of NO and OH

An important conclusion from the above discussion is that the observed behaviour of collisional energy transfer is highly dependent on the system in question, and any empirical observations will not necessarily translate into other systems. Therefore only the models that have been applied to the electronic quenching of NO $A^2\Sigma^+$ and OH $A^2\Sigma^+$ will be discussed in detail, as these are the systems that will be investigated in the thesis. These electronically excited states of NO and OH lie much higher in energy than, for example, CN, with $\nu_A = 0 \sim \nu_X = 30$ and $\nu_A = 0 \sim \nu_X = 12$ respectively, and gateway type transitions to near resonant vibrational states of the ground electronic surface, as observed for CN, have not been spectroscopically identified. Also there are no ‘nested’ electronically excited states of the same multiplicity near the $A^2\Sigma^+$ state of either molecule, so transfer similar to that observed for CH and SiX will not have a significant yield.

Historically two models have been proposed to explain the observed temperature dependence and collision partner dependence of the quenching cross sections of NO $A^2\Sigma^+$ and OH $A^2\Sigma^+$. These are the Collision Complex model and the Charge Transfer model, and they have been developed over time by numerous groups.

The Collision Complex model assumes a long range attractive potential between the electronically excited molecule, A^* , and the collisional partner, M , allowing the formation of a collision complex between the two molecules which will lead to quenching of the electronically excited species. Van der Waals complexes between NO $A^2\Sigma^+$ and noble gases have been observed experimentally [20–22]. Early development of this model focused on the attractive potential [23–25]. More recently, work by Parmenter and Seaver [26] and Lin *et al.* [27] investigated the dependence of the magnitude of the quenching cross sections on the depth of the potential well, ϵ_{A^*M} , between the electronically excited molecule, A^* , and the collision partner, M . With the assumption that the (unknown) value of ϵ_{A^*M} can be approximated by the geometric mean of the well depths of the excited collision partner dimers, an expression for the collision cross section, $\sigma_{Q,M}$, was derived, and is shown below in Equation 1.5.

$$\ln \sigma_{Q,M} = C + \epsilon_{A^*M}/kT = C + (\epsilon_{MM}\epsilon_{A^*A^*})^{1/2}/kT \quad (1.5)$$

This description shows that a stronger interaction between the electronically excited molecule and quencher will lead to a faster quenching process. Such models, while successful on a qualitative level, fail completely for a number of inefficient quenchers of NO $A^2\Sigma^+$, such as CO, N₂ and Ar, and have not been successful

at explaining the temperature dependence of the quenching cross sections [28]. Drake *et al.* [29] extended this model, employing a Parmenter-Seaver well depth correlation for strong quenchers, and suggesting a completely different mechanism to explain the observed small quenching cross sections for collision partners such as CO, N₂ and Ar. It was proposed that for these molecules, collision complexes did not form, but that quenching proceeded *via* transfer from NO A ²Σ⁺ to another excited electronic state, such as a ⁴Π, b ⁴Σ⁻ and B ²Π. This mechanism however, would predict a high rotational dependence of the quenching cross section, which is not observed.

The Charge Transfer model, which is often termed the ‘harpoon’ model, is based on the work Asscher and Haas [30]. In this model, the NO(OH) A ²Σ⁺ molecule acts as an electron donor, and as the quenching molecule approaches, it receives an electron from the NO(OH). This transfer occurs at a distance r_c which is the crossing point of the neutral van der Waals potential energy surface with the ionic-pair energy surface. Vertical transitions to the ground electronic state of the ion occur, and as the ions separate, they cross back onto the neutral energy surface. The model is relatively successful at calculating the magnitude and temperature dependence of the quenching cross sections of NO A ²Σ⁺, particularly for quenchers that have a positive electron affinity. Developments to this model have been made by Haas and Greenblatt [31]. However, in spite of such improvements the model still fails for quenchers with zero or negative electron affinities, for which the model predicts a zero quenching cross section.

Attempts have been made to combine the two models. Paul *et al.* [32] and Paul [33] describe models for the quenching of the NO A ²Σ⁺ and OH A ²Σ⁺ states respectively where the harpoon model is combined with the action of a

collision complex. While this combined model obtained better agreement with the observed temperature dependence of the quenching cross sections for numerous quenchers, it still cannot explain the behaviour of the weakest quenchers, such as the noble gases and N_2 . A further development to the model for the quenching of $\text{OH A } ^2\Sigma^+$ was made by Bailey *et al.* [34]. It was noted that at low temperatures the combined model proposed by Paul [33] failed to match the experimentally observed trend. The observed strong negative temperature dependence below around 400 K indicates that attractive forces dominate the quenching process. In the model proposed by Bailey *et al.* [34] the collision complex addition suggested by Paul [33] was discarded in favour of a simple attractive surface, based on a Lennard-Jones potential, which is modified appropriately to account for dipole moment effects.

The attempts at modelling the collisional quenching of electronically excited OH and NO as described above all fail to take into account system specific features, such as reactive processes, or efficient energy transfer due to near-resonant levels, which cannot be generalised. Recently, work by Lester, Bowman and co-workers [35–37] on the collisional quenching of $\text{OH A } ^2\Sigma^+$ have calculated the potential energy surfaces for a number of systems, finding conical intersections between the $\text{OH A} + M$ and $\text{OH X} + M$ surfaces. The conical intersections are found to be in high symmetry geometries, which explains the strong dependence of the quenching cross section on the rotational state of the $\text{OH A } ^2\Sigma^+$ molecule. The experimentally observed rotational distribution of $\text{OH X } ^2\Pi$ molecules, and the reactive branching ratio can be rationalised by the geometry of the conical intersections. This combination of experiment and theory allows significant advancement in the understanding of the quenching process and the flow of energy

1.3. Hydrogen atom abstraction reactions

into the degrees of freedom of the products. Another recent work on the collisions of electronically excited OH molecules has been performed by Brouard and co-workers [38]. This focused on non-quenching collisions between OH A $^2\Sigma^+(\nu = 0)$ and Kr. They report experimentally determined inelastic rotational scattering cross sections, using ZQBS, which are found to be in good agreement with calculations performed using a potential energy surface (PES). While this work does not answer the question of where the electronic energy goes following a quenching collision, it allows the PES of electronically excited molecules with collision partners to be developed and compared with experiment.

1.3 Hydrogen atom abstraction reactions

The reactive transfer of a H atom between two molecules provide some of the simplest reactive processes and thus have been studied extensively both experimentally and theoretically. In 1969 Polanyi demonstrated the effect the position of the energy barrier along the reaction coordinate has on the internal excitation of the products [39]. Polanyi formulated a series of eponymous rules, which describe the relationship between the location of the barrier for a process and the propensity for vibrational energy release. These are readily demonstrated by considering a simple potential energy surface for the reaction $A + BC \rightarrow AB + C$, which show that a reaction with an early barrier forms products with vibrational excitation, while a reaction with a late barrier proceeds with energy release into translation. An early barrier will mean the transition state that more closely resembles the reactants rather than the products. This means the new bond that is formed is initially stretched beyond its equilibrium position, and will therefore be

1.3. Hydrogen atom abstraction reactions

vibrationally excited as the products move away from the transition state on the PES. For such a PES, the angle between the R_{AB} and R_{BC} axes is called the skew angle. The extent of the skew of the two axes is dependent on the relative masses of the atoms involved. The angle β between the axes is defined in Equation 1.6.

$$\cos^2 \beta = \frac{m_A m_C}{m_{AB} m_{BC}} \quad (1.6)$$

Polanyi’s rules can only be applied when the skew angle is 90° . This is generally the case if the attacking atom, A , or departing atom, C , is light compared to the other atoms. Such systems are termed $\mathcal{L}\mathcal{H}\mathcal{H}'$. In systems with small skew angles, which include those where the transferring atom is light, $\mathcal{H}\mathcal{L}\mathcal{H}'$, non-Polanyi behaviour may be observed. For example in the reaction $\text{Cl} + \text{HI} \rightarrow \text{HCl} + \text{I}$, the skew angle is around 11° and despite a late barrier, around 70 % of the energy is channelled into the HCl vibrational mode. The dynamics of $\mathcal{H}\mathcal{L}\mathcal{H}'$ systems can be very complicated because in general, due to the heavy nature of both the attacking and departing atoms, the time of the collision will be much greater than the time for the exchange of the light atom [40]. This means the light atom can cross the potential barrier many times during the course of the collision, and simulations have shown that the $\mathcal{L}\mathcal{H}'$ molecule can undergo complete rotation during the course of the collision [41]. Such dynamics can clearly not be explained by simple statements referring to the position of the potential barrier.

The hydrogen abstraction reaction studied in Chapter 7 is that of CN with cyclohexane. While this not a three atom process, it can be thought of as one as a first approximation. Indeed CN is often termed a pseudo halogen as it is isoelectronic to Cl. This is an example of a $\mathcal{H}\mathcal{L}\mathcal{H}'$ system, with an associated

skew angle, β , of 13° . Therefore Polanyi’s rules cannot be expected to apply. The motivation for studying this system does not purely lie in the reaction dynamics. Recently there has been great interest in solution phase processes, and how they differ from or are similar to their gas phase counterparts [42–46]. Extensive work, both experimentally and theoretically, has been performed by Orr-Ewing and co-workers [44, 45] on the solution phase reaction between CN and cyclohexane. Vibrational excitation of nascent HCN products has been detected by ultrafast absorption spectroscopy, and mode specific vibrational distributions have been calculated from *quasi*-classical trajectories. While the CN + H-R gas phase reaction has been studied for many small alkanes [47–52], to our knowledge no gas phase determination of the nascent HCN vibrational distribution from the reaction of CN with cyclohexane has been reported.

1.4 Time-resolved FTIR

The experimental technique employed for the experiments described in this thesis was Fourier transform infrared (FTIR) emission spectroscopy. FTIR is a powerful and versatile analytical technique, which can boast two significant advantages over dispersive spectrometers. First, radiation of all frequencies are observed at the detector simultaneously allowing a rapid acquisition of data—the Fellgett advantage—and secondly, the optical throughput of an FTIR instrument is greater than that for a dispersive instrument with light confining slits—the Jacquinot advantage—allowing much greater signal-to-noise levels to be achieved.

The time resolution will depend on the mode of operation used. In conventional FTIR operation the limit of the time resolution is ~ 100 ms which is much

longer than the timescales of the processes studied in this thesis, which range from 1 μs to 1000 μs . This can be improved significantly by using step-scan mode, which was first introduced by Murphy and co-workers [53]. For experiments performed using this technique, the time resolution is limited only by the detection response time, which for the work performed in this thesis is around 2–3 μs . The details of this will be discussed in Chapter 2.

Time-resolved FTIR spectroscopy can be employed to study either absorption or emission, and it is the latter that is employed for the experiments in the thesis. This technique is ideally suited for studying complex systems where the available energy is distributed over many degrees of freedom of the product molecules, because of the great amount of information about the system that can be collected in a short period of time. The technique allows the temporal behaviour of populations of all emitting vibrational states of all product molecules to be observed simultaneously. Other experimental techniques such as laser induced fluorescence (LIF) and REMPI, whilst having superior sensitivity to FTIR, can only probe one state at a time. Clearly these techniques are not ideally suited for studying the electronic quenching of NO A $^2\Sigma^+$. Previous work on this system in the group [2, 54] observed high vibrational excitation in the NO X $^2\Pi$ product, which would require many experiments to obtain a distribution *via* LIF or REMPI; with FTIR they are observed simultaneously. As well as determining the extent of vibrational excitation of a given product, another benefit of detecting all emission simultaneously is that product identification and branching ratios can be readily determined. With systems as complex as electronic quenching, there may be multiple pathways in operation, producing a variety of species. The vibrational energies of molecules are well known in the literature,

and so frequency position and structure of emission features allow assignments to be made. Branching ratios of competing channels can be obtained from the observed emission intensity of different species, with consideration of the relative IR transition moments and the spectral response of the spectrometer. Both of these advantages of FTIR emission spectroscopy will be used extensively in this thesis. An example of the suitability of the technique for product identification and branching ratio determination is the photolysis of HNO_3 by 193 nm radiation, as described in Chapter 6. With such high energy radiation, a multitude of dissociation pathways are possible. All the emission features were successfully assigned, identifying two dominant photolysis pathways, in agreement with the literature. Interestingly, and unexpectedly, emission was observed from vibrationally excited HNO_3 implying that efficient vibrational energy transfer from photo-products to surrounding HNO_3 molecules was occurring. By quantifying the degree of vibrational excitation in product molecules the energy deposition into the different species can be determined. In Chapter 4 it was found that following the quenching of $\text{NO A } ^2\Sigma^+(\nu = 0)$ by CO_2 a far greater proportion of energy was channelled into the vibrational modes of CO_2 than $\text{NO X } ^2\Pi$, from which information of the dynamics of the quenching process can be obtained. The time-resolved nature of the experiment means that the temporal behaviour of all the emission features can be monitored, and so kinetic information about vibrational relaxation rates and energy transfer can be obtained.

However, there are disadvantages to the FTIR technique. Molecules without IR active modes, such as O_2 and H_2 cannot be detected, and so no information on how much energy is channelled into their vibrational modes can be collected. As mentioned earlier, for IR emission spectroscopy, the ground vibrational state of

molecules cannot be probed. Knowing the population in the ground vibrational state is required in order to obtain accurate branching ratios between channels, and so the ground state populations need to be estimated. The method employed in this thesis for the determination of the ground vibrational state population is Surprisal analysis. A Surprisal plot compares the measured vibrational distribution, $P(f_\nu)$ where f_ν is the fraction of the available energy appearing in vibrational level ν , with that expected from a statistical distribution of the energy, $P^0(f_\nu)$, the so called ‘Prior’ distribution [55]. A linear relationship of the form

$$\ln \left[\frac{P(f_\nu)}{P^0(f_\nu)} \right] = -\lambda_0 - \lambda_1 f_\nu \quad (1.7)$$

has been found for many reactive and photodissociative processes [56, 57]. λ_0 and λ_1 are known as Suprisal parameters which describe the linear relationship. The parameter of interest is λ_1 which contains information about the energy of a particular distribution; a negative value of λ_1 indicates a vibrational distribution which is hotter than statistical. By fitting the data in this manner, Surprisal parameters are obtained, from which the population in the ground vibrational state can be calculated, thus completing the vibrational distribution. The Prior distribution depends on the number of degrees of freedom of the reactants and products for a given system. Those suitable for the processes studied in this thesis are all presented in Appendix B. Finally FTIR is less sensitive than techniques such as LIF and REMPI by several orders of magnitude. The detection limit is around 10^{11} molecule cm^{-3} for emission spectroscopy, while laser-based techniques can detect as few as 10^6 molecule cm^{-3} .

1.5 Electronic spectroscopy of NO and OH

A substantial portion of the work presented in this thesis involves collisions of electronically excited NO and OH. Early studies produced the desired states either by broadband flash methods [58] or by taking advantage of spectral-lines of an available light source that conveniently fall within the absorption band, such as the Cadmium lines at 226.5 nm and 214.4 nm, as employed by McGee *et al.* [59]. These methods, however, either suffer from poor selectivity (of rotational or even vibrational excitation) or poor tunability. Use of tunable, narrow line-width laser radiation, such as that produced from a dye laser and employed in this thesis, enable state specific excitation at rotational level resolution. A brief outline of the electronic absorption spectroscopy of the the A-X transition in NO and OH is given below.

The electronically excited A state of both NO and OH are $^2\Sigma^+$ states. As Σ states have no orbital angular momentum, ($\Lambda = 0$), both of these electronic states are well described by Hund's coupling case (b), where the spin is coupled to the axis of rotation. For a doublet state this coupling results in two manifolds of rotational levels, F_1 and F_2 , where the quantum number for total angular momentum is given by $J = N + \frac{1}{2}$ and $J = N - \frac{1}{2}$ respectively, where N is the quantum number for the total angular momentum excluding spin.

The ground states of both OH and NO are both $^2\Pi$ states. For low rotational levels, these states are well described by Hund's case (a) (this description becomes less appropriate for high rotational levels, especially in OH). In this regime both the electronic orbital angular momentum and the electronic spin angular momentum are strongly coupled to the internuclear axis. The component of the total

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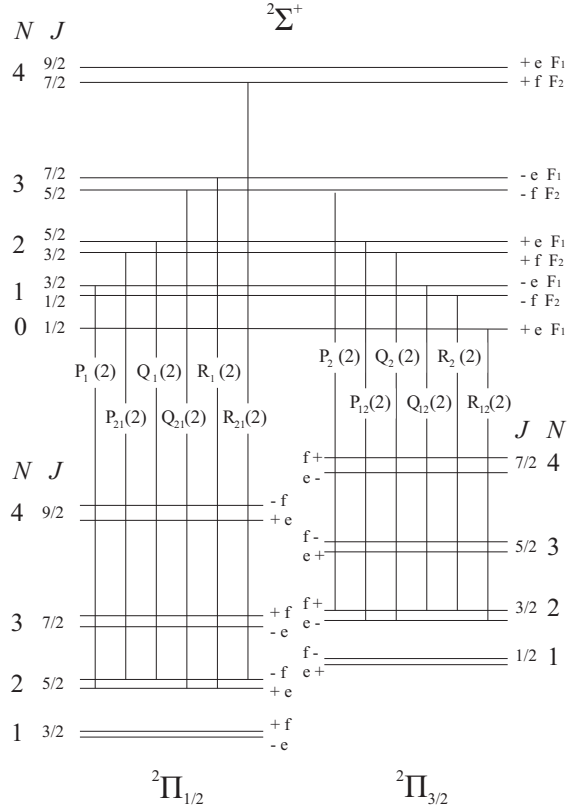


Figure 1.1: Schematic showing the 12 electronic $A^2\Sigma^+ \leftarrow X^2\Pi$ transitions from a single rotational level $N'' = 2$. The splitting between the e and f levels has been exaggerated. The case shown represents NO with the $2\Pi_{1/2}$ state being lower in energy.

angular momentum along the internuclear axis is given by $\Omega = \Lambda + \Sigma$, where $\Sigma = S, S - 1, \dots - S$. Spin-orbit coupling in OH and NO splits the 2Π state into two well separated spin-orbit states, $2\Pi_{1/2}$ and $2\Pi_{3/2}$. For NO the $2\Pi_{1/2}$ state is lower in energy, whereas for OH the spin-orbit coupling is inverted and the $2\Pi_{3/2}$ component is lower in energy. Finally each level is further split by coupling of the nuclear rotation and the electronic orbital angular momentum, known as Λ -doubling. The Λ -doublet components with identical N and J have different parities, either $+$ or $-$, which can also be labelled e or f if the parity equals

1.5. Electronic spectroscopy of NO and OH

$+(-1)^{J-1/2}$ or $-(-1)^{J-1/2}$ respectively.

The $A^2\Sigma^+ \leftarrow X^2\Pi$ transitions are subject to the following selection rules:

$$\Delta J = 0, \pm 1 \quad + \leftrightarrow - \quad + \leftrightarrow + \quad - \leftrightarrow - \quad (1.8)$$

In this thesis these electronic transitions are labelled using the nomenclature $\Delta J_{c'c''}(N'')$, although if $c' = c''$ then only one subscript is written. c' refers to the upper state manifold, F_1 or F_2 , and c'' indicates the spin-orbit state of the $X^2\Pi$ molecule: for NO, $c'' = 1$ represents the $^2\Pi_{1/2}$ and $c'' = 2$ indicates the $^2\Pi_{3/2}$ state. For OH this ground state labelling is reversed. In total there are 12 transitions originating from a given N'' state, and these are shown in Figure 1.1 along with the labelling as employed in this thesis.

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Chapter 2

Experimental methods

2.1 Overview

All the time-resolved emission spectra presented within this thesis were acquired with a commercial interferometer (Bruker IFS 66/S), which was operated in step-scan mode. The processes studied were all laser initiated, either by a photolysis process producing reactive species *in situ* or by forming electronically excited states of molecules by absorption. A variety of laser systems were employed to generate the desired wavelengths, and a description of these is presented in Section 2.2. The laser radiation was aligned into the reaction cell where it was multi-passed by UV mirrors within the cell. The subsequent IR emission from vibrationally excited products from the process under investigation—reaction, photolysis or energy transfer—was collected by IR mirrors mounted in the cell and aligned into the spectrometer. This is explained in more detail in Section 2.3. Operating the spectrometer in step-scan mode afforded the time-resolved spectra. The IR emission was detected by either an InSb or an HgCdTe detector, both

operating at 77 K. The output signal was amplified by both a pre-amplifier and a main amplifier, before being digitised with a transient recorder board. The data were then averaged for every mirror position, sorted and underwent Fourier transformation. A schematic plan of the experimental arrangement is shown in Figure 2.1, and essential aspects of this will be described in more detail in the following sections.

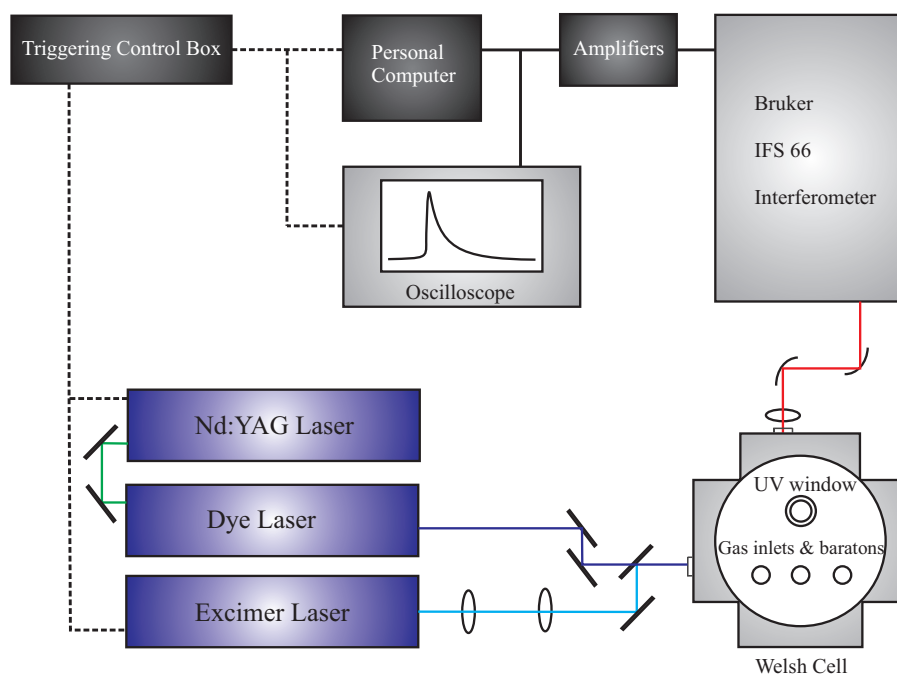


Figure 2.1: Schematic of the experimental arrangement used for data acquisition. The optical beam paths are represented by coloured lines. Black lines show the electronic signal path and the dashed lines show the connectivity of the triggering electronics.

2.2 Laser systems

A variety of laser systems were employed in the experiments described in this thesis. The pumping and photolysis laser wavelengths required were 193 nm, 215 nm, 226 nm, 266 nm and 308 nm. The details of how these wavelengths were achieved are described below.

2.2.1 Excimer laser

The generation of OH radicals for the experiments described in Chapter 6 involved the photolysis of HNO_3 and N_2O at 193 nm produced by an ArF excimer laser (Lambda-Physik). Excimer lasers operate on electronic transitions of a rare gas halide exciplex to generate short pulses of UV radiation. These exciplex molecules are bound in the excited electronic state, but unstable in the ground state, which has a mainly repulsive surface. Thus molecules relaxing from the excited state to the ground state will dissociate, maintaining a population inversion between the two electronic states. Laser radiation is initiated by passing a high voltage discharge (22 kV to 30 kV) through a gas sample containing the rare gas and halogen molecules of choice. This dissociates the halogen creating halide ions, X^- , and ionises the rare gas to form R^+ . In the presence of a buffer of Ne in a three body collision, an electronically excited exciplex is formed. The wavelength of the laser radiation depends on the identity of the halogen and rare gas. To generate 193 nm radiation, the excimer gas chamber is filled to a total pressure of 3.2 bar from a premixed cylinder containing Ar, F_2 (5 % in He) and Ne (Linde Group) in the ratio 6:4:90. The laser was operated at 10 Hz repetition rate and the pulse duration was 25 ns. The UV beam is divergent upon leaving the cavity,

and was collimated with a cross section of $\sim 1.0 \text{ cm}^2$ by use of two UV fused-silica planar-convex lenses (Edmund Optics Ltd, $f = 200 \text{ mm}$ and 150 mm). The laser radiation was aligned into the reaction cell by two UV mirrors (Laseroptik, reflectivity $(R) > 99.9\%$ at 193 nm and an angle of incidence $(\theta_i) = 45^\circ$). The laser beam path was continuously purged with dry N_2 gas to reduce attenuation due to absorption by O_2 . Typical laser pulse energies used were around 60 mJ , as measured at the entrance to the reaction cell.

2.2.2 Nd:YAG laser and dye laser

The majority of the laser radiation employed for the work in this thesis was generated by a Sirah Cobra-Stretch SFM 355 dye laser, pumped by a Continuum Powerlite Precision II 8010 Nd:YAG laser. This system allows sum frequency mixing (SFM) of the dye fundamental and Nd:YAG third harmonic at 355 nm , in addition to the more common frequency doubling of the dye fundamental, resulting in more efficient generation of deep UV wavelengths using more reliable red laser dyes. The principles of both laser systems are described below.

2.2.2.1 Nd:YAG laser

Nd:YAG lasers are solid state, optically pumped lasers capable of producing high energies of laser radiation at 1064 nm . The active gain medium is triply ionised neodymium set in a $\text{Y}_2\text{Al}_5\text{O}_{12}$ (YAG) host. Flash lamps optically excited Nd^{3+} from the ground state ($^4\text{I}_{9/2}$) to a collection of excited states which relax to the $^4\text{F}_{3/2}$ state, the lifetime of which is $\sim 230 \mu\text{s}$. A population inversion now exists between this level and the $^4\text{I}_{11/2}$ state and relaxation is accompanied by the emission of a photon of 1064 nm . Population in the lower state rapidly relaxes to

the ground state ($^4I_{9/2}$), thus maintaining the population inversion.

The Nd:YAG laser consists of two stages, the oscillator and the amplifier. The oscillator cavity is formed by a highly reflective rear mirror and a partially reflective output coupler. Within the cavity is an Nd:YAG rod pumped with a single, water-cooled Xe flash lamp, a beam expanding telescope and a Pockels cell. The laser output from the oscillator cavity is passed into the amplifier Nd:YAG rod, which itself is pumped by two Xe flash lamps. The fundamental Nd:YAG radiation at 1064 nm can be used to generate higher harmonics at 532 nm, 355 nm and 266 nm by using suitable non-linear crystals.

An injection seeder system (Continuum, SI-2000) was used in conjunction with the Nd:YAG laser, to achieve a single mode operation of the Nd:YAG cavity, resulting in laser radiation with a narrower line width, a requirement due to the SFM with 355 nm operation, where doing SFM with an unseeded YAG output would result in the laser line width for the deep UV output being too high. In unseeded operation, once sufficient gain is reached in the Nd:YAG oscillator rod, the Q-switch is opened. Only spontaneous emission of the right characteristics—resonant with a longitudinal mode the cavity and of a frequency within the gain bandwidth—will be amplified upon multiple passes through the Nd:YAG rod; spontaneous emission at other frequencies or in directions not aligned with the optical axis of the cavity will not be amplified. The isotropic nature of spontaneous emission means the initial intensity of on-axis light able to be amplified is very small, and thus many round trips of light are required to achieve sufficient amplification. By injecting a narrow line width seed laser (continuous wave Yb doped fiber laser, $\Delta\nu < 10$ kHz) with a power of > 10 mW, orders of magnitude more intense than any spontaneous noise emission from the Nd:YAG rod, into

the Nd:YAG cavity, the initial intensity of light on-axis with the cavity is much greater, thus allowing a faster build up of radiation intensity. The narrow line width of the seed laser means it excites a single mode of the cavity, and after amplification by the Nd:YAG gain media, the power in this single mode will be 1000 times greater than any other mode of the cavity. Thus the output radiation from the laser will have a much narrower line width when operating in seeded mode.

The specific Nd:YAG lasers employed for the work described in this thesis were a Continuum Powerlite Precision II 8010 with a seeder and a Continuum Powerlite 9020 laser employed solely for the generation of 266 nm radiation (see Section 2.2.3.3).

2.2.2.2 Dye laser

Dye lasers use optically pumped liquid gain media, in the form of organic dyes dissolved in a solvent, to generate laser radiation. Organic dyes typically have broadband absorption and fluorescence spectra, and therefore are highly tunable. For the experiments performed for this thesis the dye laser was pumped by the second harmonic output of an Nd:YAG laser at 532 nm. This excites the dye molecules up to the vibrational levels of the S_1 state. Collisions with the solvent molecules cause rapid vibrational relaxation of these levels within the S_1 state. Depopulation of this state can occur either *via* intersystem crossing to the T_1 state, or by spontaneous emission to the rovibrational levels of the S_0 state. Collisional broadening of these spectral transitions by the solvent molecules result in a broadband fluorescence continuum. High pumping intensities, as is provided by Nd:YAG laser radiation, forms a population inversion between the ground

vibrational level of the S_1 state and the vibrational levels of the S_0 state, and so laser radiation can be generated. The short lifetimes of the S_1 state mean that the laser emission will occur on the timescale of the pumping laser pulse. The laser wavelength was selected by the combination of a grating, which disperses the radiation, and a tuning mirror, which moves in an arc to select the desired wavelength and retro-reflect it through the cavity. The line width achievable by such a system is ~ 3.5 pm. By varying the choice of organic dye, solvent and concentration, radiation from 540 nm to 1000 nm was achieved using 532 nm as the pumping source. Shorter wavelength radiation was then generated either by frequency doubling the output, or by frequency mixing with the third harmonic output of the Nd:YAG at 355 nm. In such cases an arrangement of a compensator crystal and four Pellin-Broca prisms separated the doubled radiation from the fundamental, and prevented a drift in the alignment of the laser beam as the either the wavelength or the angle of the doubling/mixing crystal was changed. The dye laser used for all the work in this thesis was a SIRAH Cobra-Stretch SFM 355 (CSTR-G-24).

2.2.3 Generation of laser radiation between 215 nm and 308 nm

Laser radiation at 215 nm, 226 nm, 266 nm and 308 nm were all generated by either the Nd:YAG or the dye laser pumped by the Nd:YAG. Specific details of the optical setup in each case will be briefly described below.

2.2.3.1 215 nm radiation

Laser radiation of 215 nm was generated by frequency mixing the third harmonic of the Nd:YAG laser with 544 nm fundamental output from the dye laser. The Nd:YAG fundamental was frequency doubled with a temperature controlled type II angle-tuned potassium dideuterium phosphate (KD*P) crystal, generating 532 nm radiation with pulse energies of around 700 mJ. 260 mJ of this was separated off with a partially reflective mirror with a 1064 nm anti-reflection coating. The transmitted radiation (a mixture of 1064 nm and 532 nm) was frequency mixed with a second KD*P crystal to generate 355 nm radiation with typical pulse energies of ~ 210 mJ. The second harmonic radiation was employed to pump the dye laser. The dye solution for the oscillator dye cell consisted of Fluorescein 27 dissolved in methanol, with a concentration of 0.48 g L^{-1} . NaOH was added with a concentration of 0.2 g L^{-1} . The amplifier cell contained the same dye at a four times weaker concentration. The efficiency of the dye laser at this wavelength, 544 nm, is just under 20 % and produced 55 mJ of radiation per pulse. A Coherent WavemasterTM wavemeter was employed to monitor the fundamental wavelength of the dye laser, allowing the desired wavelength to be selected, to within an accuracy of ± 0.01 nm. This was subsequently mixed with the third harmonic output from the Nd:YAG using an angle-tuned temperature controlled beta barium borate (BBO) crystal to produce 215 nm radiation. An arrangement of four Pellin-Broca prisms separated the 215 nm radiation from the remaining 355 nm and 514 nm light, which was then aligned into the cell by two dichroic UV mirrors (CVI Melles Griot, 25 mm diameter, $R > 97.5\%$ at 215 nm, $\theta_i = 45^\circ$). Pulse energies of the radiation as measured at the cell were around 2 mJ.

2.2.3.2 226 nm radiation

Laser radiation at 226 nm was generated in a similar way to 215 nm as described in Section 2.2.3.1, with the dye laser configured generate 624 nm radiation. Pulse energies of 80 mJ were achieved by using DCM dye dissolved in ethanol with concentrations of 0.3 g L^{-1} and 0.1 g L^{-1} for the oscillator and amplifier dye cells respectively. This was then frequency mixed with 355 nm radiation to produce 6 mJ per pulse of 226 nm radiation. This was aligned into the cell by two dichroic mirrors (Laser Components UK, 25 mm diameter, $R > 95 \%$ at 226 nm, $\theta_i = 45^\circ$).

2.2.3.3 266 nm radiation

The Continuum Powerlite 9020 laser was employed for the generation of laser radiation at 266 nm. The fundamental output from the laser was frequency doubled twice by two phase matched KD*P crystals, producing 266 nm radiation with a pulse energy of 40 mJ. The tuning of the second crystal was controlled in real time by monitoring the intensity of a partial reflection with a photodiode. This was necessary due to instability resulting from self heating of the crystal by absorption of a small amount of the 266 nm output, which was not a problem at 532 nm. The laser was operated at 20 Hz repetition rate and the beam area was around 0.5 cm^2 . Two dichroic UV mirrors were employed to align the radiation into the cell (CVI, 25 mm diameter, $R > 99 \%$ at 266 nm, $\theta_i = 45^\circ$).

2.2.3.4 308 nm radiation

308 nm radiation was generated by frequency doubling of 616 nm radiation from the dye laser with a temperature controlled BBO crystal. The Nd:YAG optical

arrangement was altered from that employed for lasing at 215 nm and 226 nm (see Sections 2.2.3.1 and 2.2.3.2) as only 532 nm radiation was required, and so higher powers—400 mJ per pulse—of 532 nm radiation could be used to pump the dye laser. A mixture of dyes Rhodamine 610 and Rhodamine 640 in a ratio 4:1 were dissolved in ethanol. The total concentration of dye in solvent was 0.21 g L^{-1} in the oscillator dye cell and 0.031 g L^{-1} in the amplifier dye cell. Pulse energies of 100 mJ were achieved, which afforded 25 mJ per pulse of 308 nm radiation upon frequency doubling. This laser radiation was aligned into the cell with two UV dichroic mirrors (Laser Optik, 50 mm, $R > 99.6\%$ at 308 nm, $\theta_i = 45^\circ$). Laser radiation at this wavelength was employed for the OH $A^2\Sigma^+$ quenching experiments detailed in Chapter 6. OH was generated *in situ*, which required the 193 nm radiation from the excimer laser (see Section 2.2.1). The 193 nm and 308 nm laser beams were overlapped spatially prior to entering the reaction cell, as shown in Figure 2.1. The temporal delay between the lasers was controlled by an external pulse/delay generator (Stanford Research Systems Inc., DG 535), which was also used to control the timing of the data collection electronics.

2.3 Welsh cell

The reaction cell used for the IR emission experiments described on this thesis was based in the designs detailed by Woodbridge [1]. It contained both multi-pass laser optics and Welsh cell IR collection optics [2] which maximised the intensity of IR emission reaching the detector thus enabling a greater signal-to-noise ratio. A plan view of the interior of the cell is shown in Figure 2.2. The cell consists of a six way cross; all arms are 20 cm in diameter and 34 cm long

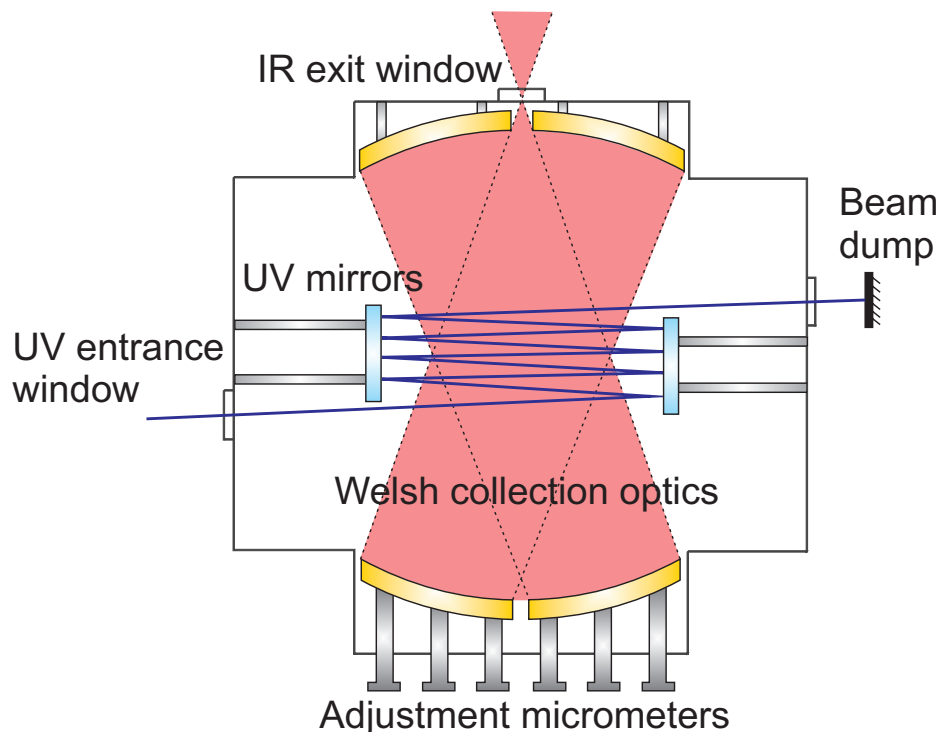


Figure 2.2: Plan view of the interior of the Welsh cell, illustrating both the multipass laser optics and the IR Welsh cell collection optics.

ended with 28.5 cm flanges. The top flange supports the gas inlets, capacitance manometers (Datametrics Barocell 600A 10 Torr Head, MKS Baratron 122-AA 1000 Torr Head), and a Spectrosil-B window (UQG, 40 mm diameter) for laser induced fluorescence (LIF) measurements. The cell was evacuated through the bottom flange. For the experiments described in Chapters 3, 4 and 5 a Turbo-molecular pump (Leybold Turbo Vac 51C) backed by a rotary pump (Edwards ED100) was used. A Penning gauge (Edwards CP25-K) was attached between the cell and the turbo pump. In this manner a baseline pressure of 1×10^{-4} mbar was achieved. For the experiments performed in Chapters 6 and 7 the turbo pump was isolated and bypassed, as corrosive gases employed in those experiments can

adversely affect the bearings leading to mechanical failure.

Laser radiation entered the cell through a UV window (Crystran, UV grade CaF_2 , 40 mm diameter, 3 mm thick) positioned on a side flange. Two high reflectivity 0° UV mirrors held in parallel 150 mm apart multi passed the laser radiation up to seven times. Different mirrors were employed depending on the wavelengths involved in the experiment. Table 2.1 lists the manufacturers and the reflectivity of those used.

Table 2.1: Details of UV mirrors employed for multipassing the laser radiation within the reaction cell. All mirrors were 50 mm in diameter.

Wavelength / nm	Reflectivity at 0° / %	Supplier
193	> 96	Laseroptik
215	> 97	CVI Melles Griot
226	> 97	CVI Melles Griot
266	> 97	CVI Melles Griot
308 and 193	> 96	Laseroptik

Welsh optics [2] were employed to maximise the collection of IR emission from species within the cell. These consisted of 4 semicircular mirrors, 100 mm in diameter with a 200 mm radius of curvature. These were positioned vertically, two at the front of the cell, either side of the IR exit window, and two at the rear. In this manner the mirrors were held around 200 mm apart. The front two mirrors were fixed in place, while the rear two were each attached to three micrometers (Caburn MDC-66004) allowing the IR collection system to be optimised. Only a small fraction of the IR emission from species within the cell will be directed towards the exit window (and therefore the detector). The mirrors allow collection of a greater proportion of the IR emission by imaging the emission originally directed away from the detector back onto the exit window, through a series of reflections off the front and rear mirrors. If aligned correctly the enhancement

2.4. Principles of time-resolved FTIR spectroscopy

of the IR signal is the sum of $(1 + R + R^2 + R^3 + \dots) \approx 1/(1-R)$, where R is the reflectivity of the mirrors. Therefore if $R = 0.95$, then a twenty-fold increase in the signal should be achievable. For the experiments in Chapters 3, 4 and 5 custom-made gold coated mirrors (Graseby Specac) were employed. These were substituted for silver coated mirrors with an MgF_2 coating (CVI Melles Griot) for the experiments described in Chapters 6 and 7 to protect them from the corrosive gases. The collected IR emission leaves the cell by an IR window (IR grade CaF_2 or BaF_2 , 35 mm diameter, 3 mm thickness, Crystran) situated in centre of the front flange between the two IR mirrors. A CaF_2 lens (UQG, 50 mm diameter, $f = 180$ mm) positioned 5 cm from the cell, focuses the IR beam, which is then aligned into the spectrometer by two gold coated mirrors: a parabolic mirror (Bruker, 42 mm diameter, $f = 153$ mm) and a plane mirror (Mirror Technique Ltd., 50 mm diameter, $R = 98\%$).

2.4 Principles of time-resolved FTIR spectroscopy

The optical arrangement of the spectrometer (Bruker IFS 66/S) employed for the collection of the IR emission spectra presented in this thesis is shown in Figure 2.3. For the emission experiments, a collimated beam of IR light enters the spectrometer *via* the side port. If absorption experiments are performed, such as those used for obtaining transmission curves of optical filters, the IR emission from one of the IR sources was used (mid-infrared or near-infrared), selected by adjustment of mirrors M_1 and M_2 . The IR beam is intercepted by a beam splitter positioned at 45° , splitting the beam into two equal intensity, perpendicular beams. These are back-reflected to the beam splitter by two mirrors

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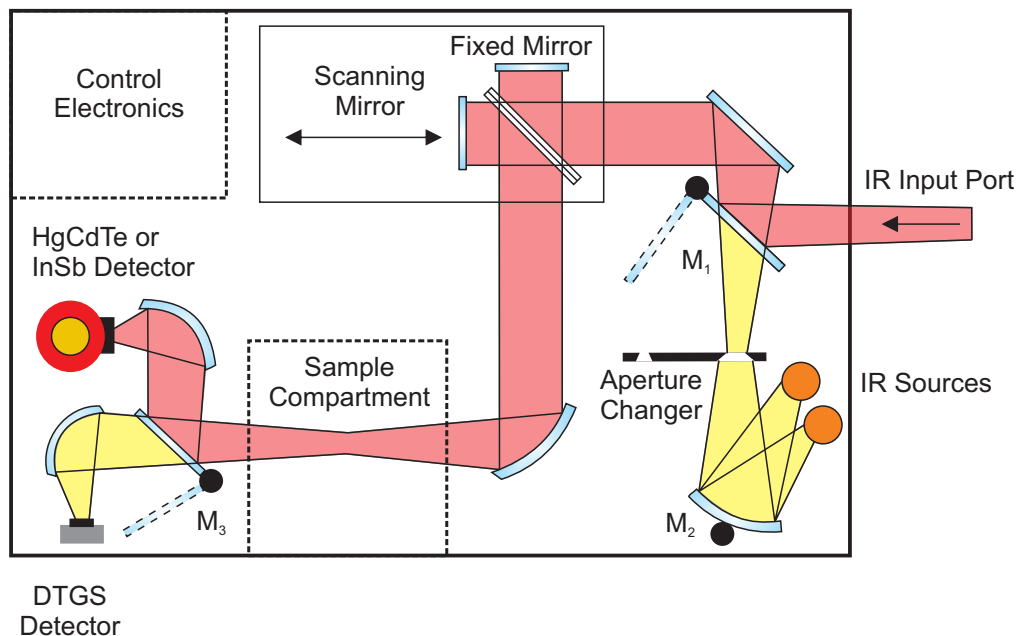


Figure 2.3: Layout of the Bruker IFS 66/S spectrometer.

positioned normal to the to the direction of the beams. One mirror is fixed but the other mirror is able to be translated along the optical axis. The two beams are recombined at the beam splitter, and interference will occur. If both mirrors are equidistant from the beam splitter then each beam will have travelled the same distance before recombining. Thus all frequencies within the beam will be in phase and will constructively interfere. If the movable mirror is displaced along the optical axis a distance δ from the equidistant position, then a path difference of 2δ (and therefore a phase difference) will exist between the two beams at point of recombination. The interference of each frequency component of the beam will depend on the relationship of the frequency of the radiation and the path difference. By scanning the movable mirror, an interferogram is generated, where the intensity of the recombined beam is measured as a function of mirror

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displacement, δ .

To achieve the high time resolution required for the investigating of the gas phase processes detailed in Chapters 3, 4, 5, 6 and 7, the spectrometer was operated in step-scan mode. In this regime, rather than recording an interferogram in real time as the mirror is scanned, a time trace of the emission is recorded while the mirror is held stationary at a given position. This is possible because of the well defined time frame of the experiment, which is the short duration laser pulse, whether that is to generate electronically excited molecules, or to initiate a reaction by a photolysis step. While the mirror is held stationary, the chemical process is initiated and the resulting IR emission recorded as function of time. This is repeated to allow averaging of the recorded IR signals (typically 40 to 60 laser shots) before the mirror is moved to a new position. For any given experiment, there are two parameters defining the stepping mirror behaviour, the choice of which depend on the characteristics of the IR emission beam and the desired spectral resolution. These are:

- Δ , the total distance travelled by the stepping mirror from position where $\delta = 0$
- δ_{step} , the distance travelled by the mirror between adjacent sampling points

An interferogram is a continuous function of mirror displacement δ . By operating the spectrometer in step scan mode, this continuous function is being discretely sampled, at a frequency of $1/\delta_{step}$. The Nyquist criterion states that in order to perform alias free sampling of a continuous waveform, the sampling frequency must be at least twice that of the highest frequency component of the waveform,

2.4. Principles of time-resolved FTIR spectroscopy

ν_{max} . In other words,

$$\frac{1}{\delta_{step}} > 2\nu_{max}. \quad (2.1)$$

The mirror movement is monitored by observing the interference pattern of an internal HeNe laser, with a wavelength of 633 nm. Being monochromatic, the interferogram exhibits sinusoidal behaviour about an average value as a function of δ . The difference in δ between the maxima will be half the wavelength of the HeNe laser. To be able to determine the position of the mirror exactly, it is only stepped in integer multiples of half the wavelength of the HeNe laser as the maxima and minima of the interference pattern are the best defined features. This means the mirror can be stepped by 316.5 nm, 633 nm and 949.5 nm and so on. These values of δ_{step} correspond to ν_{max} frequencies (also called Nyquist frequency) of 15 798 cm⁻¹, 7899 cm⁻¹ and 5266 cm⁻¹ respectively. If any emission is detected above the Nyquist frequency for a given experiment, then aliasing will occur. Radiation of frequency $(\nu_{max} + \omega)$ will be ‘folded-back’ into the recorded spectrum and appear at a frequency given by $(\nu_{max} - \omega)$. In the case that $\omega > \nu_{max}$, then folding will occur along each multiple of ν_{max} until it appears in the range of the recorded spectrum. Experimentally ν_{max} is kept to a minimum in order to reduce acquisition time, as explained below. Therefore an array of optical filters were employed to isolate the emission bands and prevent higher frequency radiation from reaching the detector.

Δ defines the spectral resolution of the resulting spectrum. In order to be able to resolve two frequencies R wavenumbers apart, the distance Δ covered by the scanning mirror (from $\delta = 0$) must be large enough that the interference patterns from these frequencies are distinct. For an unapodised interferogram,

2.4. Principles of time-resolved FTIR spectroscopy

the resolution is defined as $0.6/\Delta$. In this work apodisation functions were used to improve the spectral line shape following Fourier transformation (FT), which reduces the resolution a certain degree. For the apodisation used in this thesis, a mirror travel $\Delta = 1/R$ was required to achieve a resolution of $R \text{ cm}^{-1}$. The number of points N , for an experiment recording a double sided interferogram is given below in Equation 2.2.

$$N = 2\Delta/\delta_{step} = 4\nu_{max}/R \quad (2.2)$$

The number of points recorded for an interferogram can be reduced by specifying a lower spectral limit, ν_{min} [3]. In this case the ν_{max} term in Equation 2.2 is replaced by $(\nu_{max} - \nu_{min})$, and the spectrum is said to be under-sampled.

From the IR traces, recorded at each mirror position, time-resolved interferograms can be extracted. These are converted into the frequency domain by Fourier transformation. Before this is performed the interferograms are processed as follows:

1. The interferograms are multiplied by an apodisation function in order to suppress side-lobes in the spectrum. These appear as a result of the finite length of the interferogram, defined by the extremes of the mirror travel. The apodisation function employed in for this thesis was the Blackman-Harris three-term function.
2. The interferograms were then zero filled, whereby zeros are added symmetrically to each end of the interferogram. This increases the number of data points per wavenumber in the spectrum following Fourier transformation, which gives greater digital resolution (n.b. not the same as spectral reso-

2.4. Principles of time-resolved FTIR spectroscopy

lution) without the introduction of artifacts [4, 5]. A zerofilling factor of 4 was used meaning the interferogram length was increased four fold.

3. Finally the apodised, zerofilled interferogram underwent FT, and the resultant spectra were phase corrected. Whilst ideally the interferogram should be symmetric around the point of zero path difference, such a case is not normally realised, due to imperfections in the optical setup, IR collimation and error in defining mirror displacement, δ . This causes phase shifts which are not necessarily a constant function with frequency. Asymmetric inputs to the FT afford spectra with real and imaginary components. The Mertz method corrects for phase as shown in Equation 2.3

$$S(\nu) = \text{Re}[C(\nu) \exp(-i\theta(\nu))] \quad (2.3)$$

where $S(\nu)$ is the actual spectrum, $C(\nu)$ is the complex spectrum resulting from the FT of the asymmetric interferogram, and $\theta(\nu)$ is the phase angle of the complex spectrum as a function of wavenumber.

2.4.1 Acquisition of time-resolved FTIR emission spectra

The interferograms were collected by high sensitivity, liquid nitrogen cooled photovoltaic IR detectors. The two detectors used were a HgCdTe detector (IR Associates 12.5, spectral range 830 – 5500 cm^{-1} , detectivity $> 5 \times 10^{10} \text{ cm Hz}^{0.5} \text{ W}^{-1}$) and an InSb detector (Bruker D413/3F, spectral range 1850 – 10 000 cm^{-1} , detectivity $> 1.5 \times 10^{11} \text{ cm Hz}^{0.5} \text{ W}^{-1}$). The spectral response functions of both of these detectors were determined by comparison of the recorded emission spec-

2.4. Principles of time-resolved FTIR spectroscopy

trum of a blackbody source (Omega BB703) with the corresponding theoretical prediction at the operating temperature, 673 K, as determined using Equation 2.4 [6].

$$I(\nu, T) = \frac{2 \times 10^8 h c^2 \nu^3}{\exp(\frac{100 h \nu c}{kT}) - 1} \quad (2.4)$$

$I(\nu, T)$ is the energy emitted per wavenumber, ν , at a given temperature T . h and k are Planck's constant and the Boltzmann constant respectively, and c is the speed of light in m s^{-1} . A variety of optical filters were used to transmit only the desired emission, which allowed experiments to be performed with lower Nyquist frequencies, reducing acquisition time without risking any aliasing effects. The measured spectra were later corrected for the filter transmission curves which were obtained using the deuterated triglycine sulphate (DTGS) detector (Bruker ID301/8) and the internal mid-IR source. The InSb detector was employed for all experiments above 1850 cm^{-1} due to its superior sensitivity, while the MCT was employed for the experiments observing emission lower than 1850 cm^{-1} and for investigative survey spectra. Outputs from the detectors were pre-amplified before being passed through an AC amplifier (1 Hz – 1 MHz band pass, 10 – 60 dB gain). The amplified signals were then digitised by a transient digitiser board (Bruker PAD1232a, 10 MHz, 12 bit ADC). The digitiser card had two inputs which allowed for normalisation procedures (for example to the laser power) to be performed on a shot-by-shot basis.

A personal computer running OPUS 5.5 was used to control the data acquisition and analysis procedures described above. This allowed the spectral and temporal resolution to be specified, which had limits of 0.25 cm^{-1} and 250 ns respectively. In addition the spectral limits, apodisation function and phase cor-

reaction method could also be chosen. A Stanford delay generator (DG535) was employed to control the relative timing of the laser and the data acquisition procedure.

2.5 Reagents and gas handling

Table 2.2 details gases and reagents used for the experiments in this thesis. Certain gases required further purification prior to use. NO contained impurities

Table 2.2: Reagents with supplier and specification purity

Reagent	Supplier	Stated Purity / %
Ar	BOC	> 99.9995
cC ₆ H ₁₂	Fisher-Scientific	> 99
CO ₂	BOC	> 99.995
D ₂	CK GAS	99.6, (99.8 isotopic purity)
H ₂	BOC	> 99.995
He	BOC	> 99.995
HNO ₃	Fisher-Scientific	70 w/w
HNO ₃	Sigma-Aldrich	100 (fuming)
ICN	Fisher-Scientific	98
Kr	BOC	> 99.999
N ₂ O	BOC	> 99.995
NO	MG Gases	> 95.5
Ne	BOC	> 99.994
O ₂	BOC	> 99.5
Xe	BOC	> 99.999

such as NO₂ and N₂O. These were removed by using a liquid nitrogen/2-methyl butane slush bath (−160°C). The purity of the remaining NO was determined by an absorption spectrum. This method did not produce pure NO in sufficient amounts to allow flowing samples, and therefore all NO experiments (Chapters 3, 4 and 5) were performed on static samples.

For the experiments in Chapter 5 a water filter (All-Pure™) and an oxygen

filter (OxiClearTM) increase the purity of the noble gases employed in the experiments. The water filter was specified to reduce the concentration of water and carbon dioxide to < 1 ppb and the oxygen filter reduced the concentration of oxygen at the outlet to < 5 ppb.

The experiments described in Chapter 6 required OH molecules to be generated *in situ*. This was achieved by photolysis of HNO_3 at 193 nm. A calibrated mass flow controller (Tylan) allowed Ar to be passed through a bubbler containing $\sim 50 \text{ cm}^3$ of fuming HNO_3 . Adjustment of the Ar flow rate, a needle valve in-between the bubbler and the cell and the pumping efficiency allowed control of the partial pressure of HNO_3 in the cell. The flow of collisional partners into the cell was also controlled by calibrated mass flow controllers.

References

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Chapter 3

Electronic quenching of NO

A $^2\Sigma^+(\nu = 0)$ by O₂

3.1 Introduction

Nitric oxide is an important molecule in the chemistry of both atmospheric and combustion environments. Observations on its γ band ($A^2\Sigma^+ \leftarrow X^2\Pi$) have been widely used for spectroscopic diagnostics in a variety of photochemical, gas discharge and combustion systems. Laser induced fluorescence (LIF) has often been the technique of choice [1]. At atmospheric pressures and above, typical of a combustion environment, measurements are often performed under conditions where collisional quenching processes are fast enough to return molecules to the probed state during the excitation pulse, and thus the outcome of such quenching processes needs to be understood for accurate interpretation of the measurements. As well as this practical importance, the understanding of the dynamics of the quenching mechanisms is of fundamental interest.

Many studies have reported rate constants for the quenching of NO A $^2\Sigma^+$ by numerous colliders at a range of temperatures [2–15]. What is still largely unknown is the fate of the electronic energy – how it is partitioned into the degrees of freedom of the recoiling species, and whether or not reactive quenching takes place. In this chapter, the collisional quenching of NO A $^2\Sigma^+(\nu = 0)$ by molecular oxygen will be investigated, with particular attention paid to the amount of energy channelled in the vibrational modes of NO X $^2\Pi$ as a result of a non-reactive quenching event. The occurrence of any reactive and other energy transfer processes will be investigated as well. The vibrational excitation of the oxygen as a result of collisional quenching cannot be determined by infrared emission because it is infrared inactive.

3.2 Previous investigations

As mentioned Section 3.1, until recently the majority of the work on the electronic quenching of NO A $^2\Sigma^+$ focused the determination of rate constants for quenching by a variety of collision partners at a range of temperatures. Two such studies which have investigated the room temperature quenching of the NO A $^2\Sigma^+(\nu = 0)$ state are Greenblatt *et al.* [2] and Nee *et al.* [3]. The collision partners studied by Greenblatt *et al.* were NO, N₂O, H₂O, O₂, SF₆ and CO₂. All were found to be fast quenchers of the NO A $^2\Sigma^+(\nu = 0)$ state, with quenching rate constants that are of the order of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Nee *et al.* [3] extended this list of quenchers to include the noble gases He, Ar, Xe as well as N₂. There was good agreement between the measured quenching rate constants for the collision partners common to both studies. N₂ and the noble gases were found to be

3.2. Previous investigations

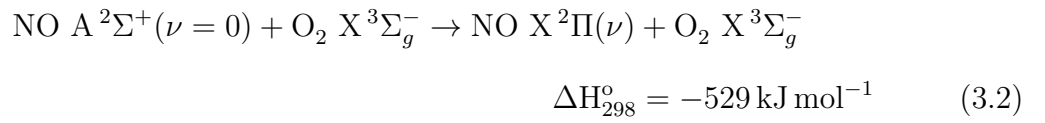
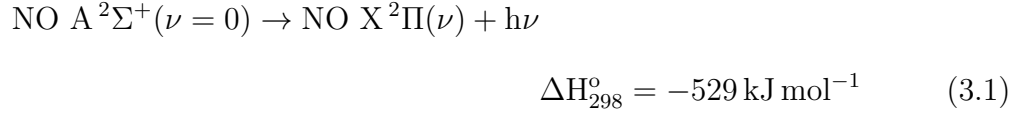
inefficient quenchers of NO $A^2\Sigma^+(\nu = 0-2)$ with reported quenching coefficients of the order of $\leq 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As discussed by Nee *et al.* [3], the large difference in the rate constants can be explained by considering the respective quenching mechanism. Molecules which have a positive electron affinity are able to proceed *via* the Charge Transfer mechanism [9], as described in Chapter 1. This includes most of the faster quenchers (NO, N_2O , H_2O , O_2 , SF_6), and while there was adequate agreement between measured and predicted quenching cross sections for the majority of these collision partners, there were discrepancies. In particular two molecules which exhibited significant disagreement between calculated and measured quenching cross sections were O_2 and CO_2 . The Charge Transfer model does not consider additional processes such as resonant energy transfer and reaction, both of which can have a significant effect on the rate of the quenching process, and so this suggests other processes could be involved when NO $A^2\Sigma^+(\nu = 0)$ is quenched by O_2 and CO_2 .

While the kinetics of the collisional quenching of electronically excited NO has received the most attention, there have been a few studies which investigated the outcome of such processes. As early as 1961, Basco *et al.* [16] detected population in NO $X^2\Pi(\nu = 1)$ following quenching of NO $A^2\Sigma^+$ by NO, CO, N_2O , H_2O and N_2 , demonstrating that collisional quenching can result in vibrationally excited products. A study some years later by Mauldin and Ravishankara [17] focused specifically on collisions of NO $A^2\Sigma^+(\nu = 0)$ with O_2 . They prepared electronically excited NO $A^2\Sigma^+$ molecules with 226.33 nm radiation, and employed 130 nm resonance fluorescence to detect any $O(^3P)$ atoms resulting from reactive collisions between NO $A^2\Sigma^+$ and O_2 .

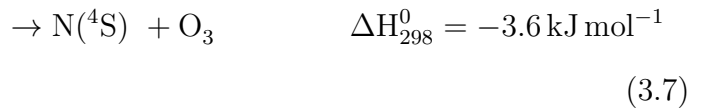
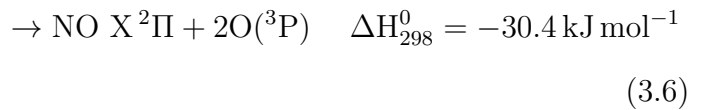
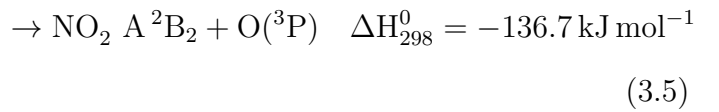
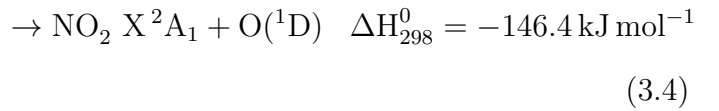
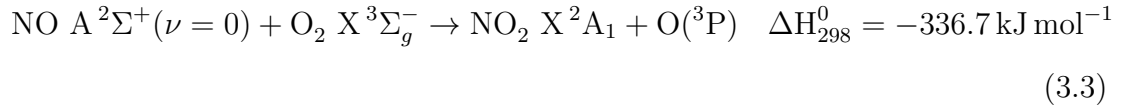
In addition to radiative relaxation and non-reactive quenching shown below

3.2. Previous investigations

in Equations 3.1 and 3.2, releasing 529 kJ mol^{-1} to be distributed among the products,



there are many other thermodynamically allowed channels from such a collision, shown in processes (3.3)–(3.8). The O_2^* product from process (3.8) represents any electronically excited state of O_2 .



Mauldin and Ravishankara observed production of $O(^3P)$ atoms following collision of $NO\ A^2\Sigma^+(\nu = 0)$ with O_2 , confirming that reactive processes were occurring. The overall rate constant for removal of the $A^2\Sigma^+(\nu = 0)$ state by O_2 was measured to be $1.59 \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, agreeing well with later determinations of the rate constant [2, 3]. They inferred from their data the relative importance of some of the processes shown above and concluded that reaction, producing $O(^3P)$ (channels (3.3), (3.5) and (3.6)), dominated the quenching process. More recently work by Settersten *et al.* [18] measured the fraction of population that is returned to $NO\ X^2\Pi(\nu = 0)$ upon collision of $NO\ A^2\Sigma^+(\nu = 0)$ with CO_2 , CO , H_2O and O_2 , reporting a branching ratio of 0.6 for CO_2 and ~ 0.3 for the remaining molecules. This contrasts with the theoretical predictions of both the Charge Transfer and Collision Complex models; Paul *et al.* [19] argued that the Charge Transfer model predicts strong vibrational excitation of $NO\ X^2\Pi$ following quenching, and Settersten *et al.* [18] concluded that the similarity of the branching ratios for $NO\ X^2\Pi(\nu = 0)$ following quenching of $NO\ A^2\Sigma^+(\nu = 0)$ for all quenchers studied (with the exception of CO_2) indicates the quenching process is sudden, and does not proceed *via* a long lived complex.

3.3 Preliminary experiments

All the experiments in this chapter were performed on static samples of 50 mTorr of NO , purified as described in Chapter 2, with various partial pressures of oxygen to achieve the desired quantum yield of quenching by O_2 . A high pressure of 50 Torr of Ar was used to ensure rotational thermalisation of the products, which also had the benefit of providing larger signals sizes due to rotational hole

3.3. Preliminary experiments

filling effects allowing more molecules to be excited up to the NO A $^2\Sigma^+(\nu = 0)$ state [20]. NO was pumped up to its first electronically excited state on the overlapped Q₁ and P₂₁ band heads of the NO A-X (0,0) transition with radiation at 226.257 nm. The electronically excited state would then be removed either by radiative relaxation or through collisions with other molecules present, by a combination of reactive and non-reactive processes.

This experimental procedure has been employed previously in the group and experiments confirming that the process described above is indeed occurring have been performed and detailed elsewhere [21, 22], but for the sake of completeness they will be (briefly) explained here also. The presence of NO A $^2\Sigma^+(\nu = 0)$ was confirmed by observing fluorescence from the NO A-X transition following the laser excitation of 5 mTorr of NO, as shown in Figure 3.1. The LIF was detected by a photomultiplier tube (PMT), operating at a supply voltage of -1 kV which is within its linear response region, positioned against a UV-grade CaF₂ window on the top face of the reaction cell. Optical filters were employed to block any laser scatter by isolating fluorescence from the off-resonant NO A-X (0,9), (0,10) and (0,11) transitions which lie within the region 350 nm to 400 nm. Zero time was defined as the maximum PMT output when a small amount of laser scatter was allowed to be detected. The lifetime of the LIF signal was found to be $(201.0 \pm 2.4) \times 10^{-9}$ s. This has excellent agreement with the predicted lifetime of 203×10^{-9} s as calculated from radiative lifetime of the NO A $^2\Sigma^+(\nu = 0)$ state, $(205 \pm 7) \times 10^{-9}$ s as measured by Luque *et al.* [7], and the contribution of self-quenching, which has a rate coefficient of 2.7×10^{-10} cm³ molecule⁻¹ s⁻¹ [2, 21].

Having confirmed the presence of NO A $^2\Sigma^+(\nu = 0)$ in the cell, it was nec-

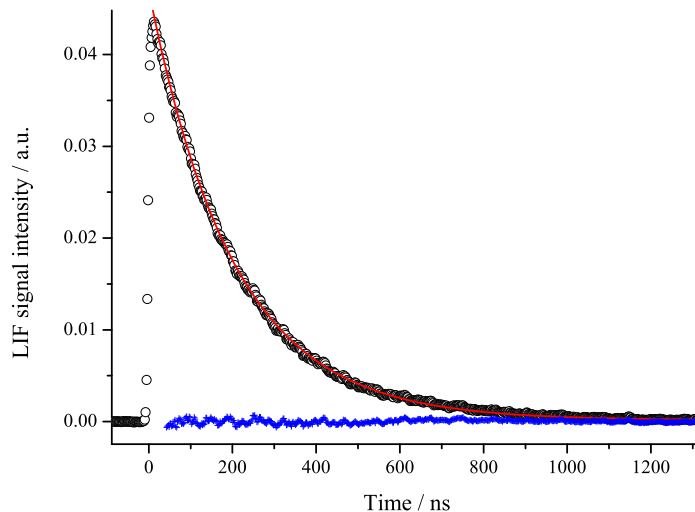


Figure 3.1: Laser induced fluorescence observed following excitation of 5 mTorr NO on the overlapped Q_1 and P_{21} band heads of the A-X(0,0) transition (o). The fitted single exponential decay function is shown, (red), which has a decay time of $(201.0 \pm 2.4) \times 10^{-9}$ s. Residuals to the fit from 40 ns are also shown (+). Optical filters were employed to transmit fluorescence in the range 345 nm to 400 nm.

essary to determine that the infrared emission observed following the excitation pulse was from products of quenching processes, rather than the result of undesired processes such as photolysis of impurities. This was done by collecting an excitation spectrum, where the integrated LIF and infrared emission intensities were recorded as the wavelength of the pumping laser was scanned across the NO $A^2\Sigma^+(\nu = 0) \leftarrow NO X^2\Pi(\nu = 0)$ transition. If the peaks and troughs of the two spectra correspond, it demonstrates that the infrared signal is dependent on the amount of NO $A^2\Sigma^+(\nu = 0)$ generated, and hence is a result of processes involving electronically excited NO. One possible impurity is NO_2 , which is photolysed by 226 nm light to produce vibrationally excited NO $X^2\Pi$ [24]. The UV absorption spectrum of NO_2 near 226 nm is broad and unstructured, so this pro-

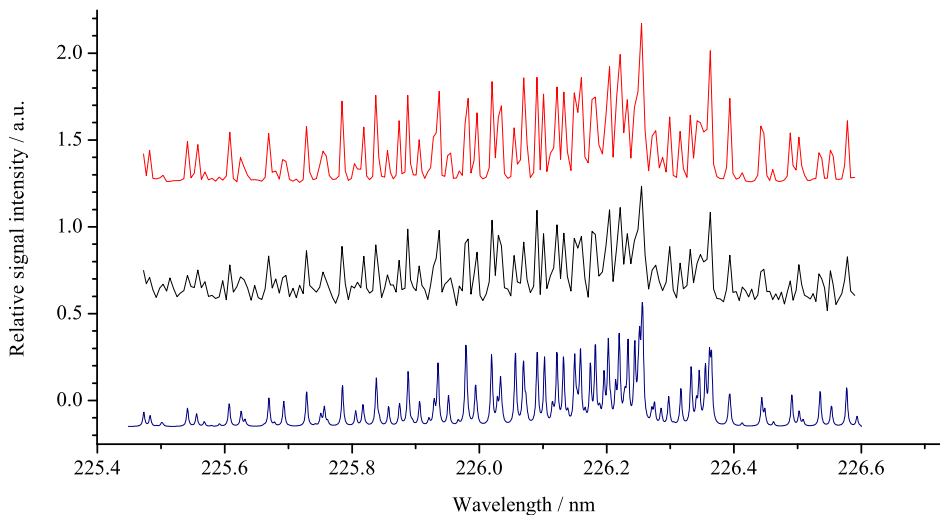


Figure 3.2: Variation of total intensity of LIF signal between 345 nm and 400 nm (red) and infrared emission, in the spectral region 2500 cm^{-1} to 4000 cm^{-1} (black) following the excitation 50 mTorr of NO in the presence of 1.1 Torr of O_2 and 50 Torr of Ar, as the pumping wavelength is scanned across the NO $\text{A } ^2\Sigma^+ (\nu = 0) \leftarrow \text{X } ^2\Pi (\nu = 0)$ transition. The step size was 0.004 nm, with 64 shots recorded per point. Also shown is the LIFBASE spectral simulation for the NO A-X (0,0) band at a resolution of 0.004 nm (blue) [23]. The traces are vertically offset for clarity.

cess would manifest itself as an offset of the baseline in the excitation spectrum. Such excitation spectra have been recorded previously for a sample of 50 mTorr of NO [22], however, it was felt to be prudent to repeat the experiment for a gas mixture typical of those used for the experiments described in this chapter: 50 mTorr of NO with 1.17 Torr of O_2 and 50 Torr of Ar. An excitation spectrum was acquired, simultaneously recording the intensity of NO A-X LIF and the NO $\text{X } ^2\Pi$ vibrational overtone emission as the wavelength of the excitation laser was scanned in steps of 0.004 nm across the NO A-X (0,0) absorption band. The harmonic mixing crystal in the dye laser was tuned across a preset curve in order to maintain a constant laser fluence during the scan. As can be seen in Fig-

ure 3.2, both the LIF and infrared emission signals show excellent agreement of the location of maxima with the predicted LIFBASE spectrum [23], which takes into account both Doppler and pressure broadening, as well as the bandwidth of the laser. The agreement between the relative intensities of the peaks across the range is less good; the NO A-X (0,0) transition was near saturation at the laser powers employed in the experiment, and as such the range of observed peak intensities across the scan is less than that found in the LIFBASE spectrum.

3.4 Results

The excitation spectrum shown in Figure 3.2 confirmed that NO A $^2\Sigma^+(\nu = 0)$ was being generated in the cell in sufficient quantities to allow observation of vibrationally excited products from quenching processes and that no unwanted processes were occurring. Experiments investigating the collisional quenching of electronically excited NO by O₂ were then performed. Two liquid nitrogen cooled detectors, a HgCdTe and an InSb, were used allowing observation of emission from 800 cm⁻¹ to 10 000 cm⁻¹.

Figure 3.3 shows a contour plot of the emission observed in the region of 1200 cm⁻¹ to 1900 cm⁻¹, obtained under conditions such that the quantum yield of quenching of NO A $^2\Sigma^+(\nu = 0)$ by O₂ is around 0.5. There are two distinct emission features that can be seen in Figure 3.3. The long lived intense emission around 1800 cm⁻¹ is the fundamental NO emission. The shorter lived emission at 1400 cm⁻¹ to 1600 cm⁻¹ was only observed when O₂ was present in the reaction cell. It has been assigned as emission from the $\Delta\nu_3 = -1$ band of vibrationally excited NO₂, formed by the reaction shown in Equation 3.3. This is direct evidence

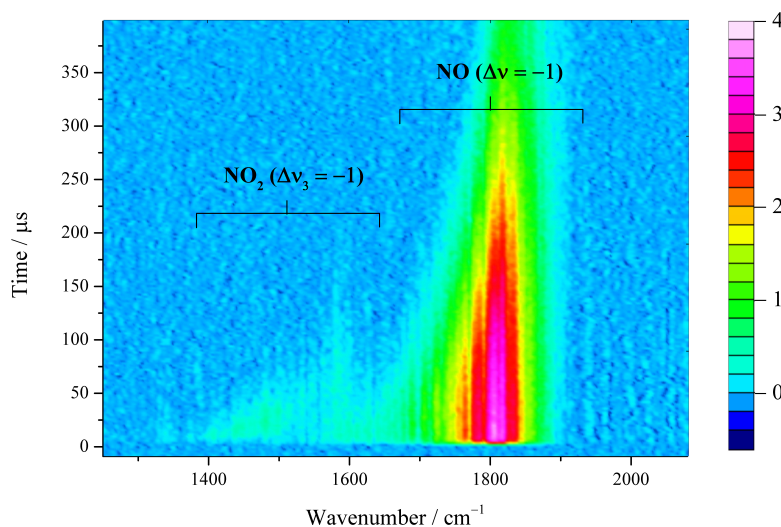


Figure 3.3: IR emission following the pumping of 50 mTorr of NO to its $A^2\Sigma^+(\nu=0)$ state in the presence of 1.17 Torr of O_2 . Emission was observed with a HgCdTe detector, and spectra were recorded at a resolution of 5 cm^{-1} . Red denotes high intensity and blue represents low intensity. The right-hand edge of the NO fundamental emission has been cut off due to the optical filter employed.

that a reactive process is occurring. The co-product is $O(^3P)$, so this observation is consistent with that of Mauldin and Ravishankara [17]. The highest intensity NO emission in Figure 3.3 comes from the region of the $\nu = 2 \rightarrow 1$ and $\nu = 1 \rightarrow 0$ vibrational transitions. The average of the Einstein emission coefficients for these two bands is 17 s^{-1} [25], which is ~ 10 times smaller than that for NO_2 [26]. As the observed NO emission is at least four times more intense than the NO_2 emission this suggests that the generation of vibrationally excited NO_2 is a minor channel.

The vibrational bands of the NO $X^2\Pi$ fundamental emission spectrum are closely overlapped, which means that to distinguish accurately the relative contribution of the different bands (and therefore to extract a vibrational distribution) requires high resolution spectra. This is very time consuming which is problem-

atic as static samples are used and so degradation of the gas sample can occur. It is far preferable to use the NO $X^2\Pi$ first overtone emission spectrum. Overlap of adjacent P and R branches for a 300 K thermalised rotational distribution results in structured emission spectrum, even at a modest resolution of 20 cm^{-1} [20], which means less acquisition time is required. An additional advantage over using the fundamental emission spectrum is derived from the Einstein A factors of the bands. While overtone transitions have smaller emission coefficients than fundamental transitions, they increase more rapidly for the higher vibrational levels. This means the overtone emission spectrum is very sensitive to population in high vibrational levels of NO $X^2\Pi$, which will allow accurate determination of the extent of vibrational excitation following quenching of the NO $A^2\Sigma^+(\nu = 0)$ state.

Experiments were then performed using the InSb detector to observe the NO overtone emission. Figure 3.4 shows the emission observed when NO $A^2\Sigma^+(\nu = 0)$ is quenched by O_2 with a quantum yield of 0.5. The well structured NO overtone emission between 2800 cm^{-1} and 3800 cm^{-1} can be seen, along with an unstructured emission overlaying it, in the region of 2500 cm^{-1} to 2800 cm^{-1} . This latter emission is the $\Delta\nu_1 = \Delta\nu_3 = -1$ combination band of NO_2 , which is expected given that it was shown in Figure 3.3 that reactive quenching is taking place to produce vibrationally excited NO_2 . The presence of this overlapping emission could be problematic with regard to analysis of the NO overtone band which extends down to 2500 cm^{-1} . However, this unwanted emission can be removed by the addition of a large pressure of Ar due to the different vibrational relaxation coefficients by Ar for the two molecules. The vibrational quenching of NO $X^2\Pi(\nu)$ has been studied previously by this research group [24] and vibra-

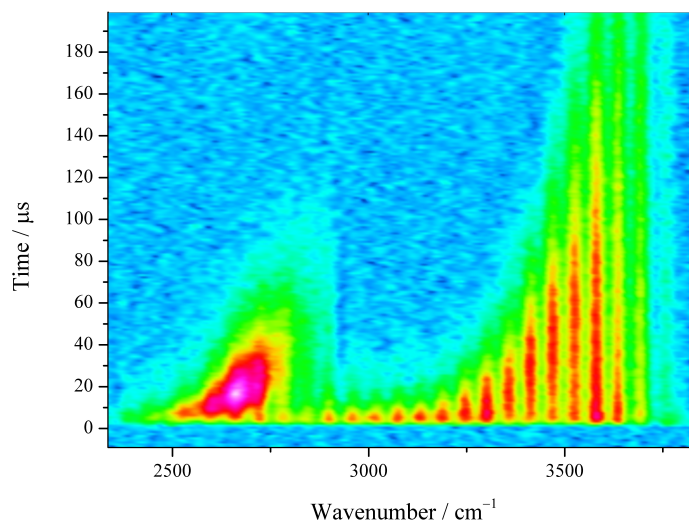


Figure 3.4: IR emission observed in the region of the NO vibrational overtone emission band following the pumping of 50 mTorr NO on the overlapped Q_1 and P_{21} band heads of the NO $A^2\Sigma^+(\nu = 0) \leftarrow X^2\Pi(\nu = 0)$ transition in the presence of 1.17 Torr of O_2 . Spectrum taken with the InSb detector at a resolution of 20 cm^{-1} . Red represents high intensity and blue represents low intensity.

tional relaxation rate constants of the order of $10^{-15} - 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ were reported for NO $X^2\Pi(\nu = 8-12)$, probably increasing for higher ν if the trend matches that found by relaxation with helium, measured in the same work. The vibrational relaxation of NO_2 has been investigated by a number of groups [27–30], although a fully quantum state resolved set of vibrational relaxation rate constants has not been reported. Golde *et al.* [27] measured relative rate constants of vibrational relaxation of the $\Delta\nu_1 = \Delta\nu_3 = -1$ emission band by a variety of quenchers, from which it was estimated that the rate constant for relaxation by Ar was $6 \times 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. More recent works by Toselli *et al.* [31] and Hartland *et al.* [29] measured the average amount of energy removed per collision as a function of the internal energy of the NO_2 molecule for a variety of different

collision partners. From these measurements it is difficult to extract any meaningful state-specific or even mode-specific relaxation rate constants. However, Toselli *et al.* [31] estimated from their results that the relaxation rate constant for the NO₂ (0,1,0) state by Ar was $(5.1 \pm 1.0) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A study by Sander and co-workers [28] measured an overall relaxation rate constant of vibrationally excited NO₂ by Ar to be $(5.1 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and it was concluded that relaxation *via* the ν_2 manifold was the dominant mechanism. This rate constant is faster than those estimated by Toselli *et al.* [31] and Golde *et al.* [27], although there was good agreement between the relative relaxation rate constants for a variety of quenchers between the work of Golde *et al.* and that of Sander and co-workers [28]. Although these results are not comprehensive, and differ by up to an order of magnitude, it is clear that Ar is more efficient at quenching the vibrational levels of NO₂ than it is for NO. Ar can thus be used to remove vibrationally excited NO₂ without significantly affecting the nascent NO X²Π(ν) distribution.

A pressure of 400 Torr of Ar was chosen, which will reduce the lifetime of vibrationally excited NO₂ to less than 2 μs as calculated, conservatively, using the value reported by Toselli *et al.* [31], being the slowest of those listed above. Confirmation of this can be obtained from Figure 3.5 (a), which shows a series of early time (4 μs) emission spectra observed with different pressures of Ar present. The effect of the Ar is immediately apparent; the intensity of the emission below 2900 cm^{-1} becomes much reduced as the pressure of Ar is increased from 0 Torr to 400 Torr. To observe the effect Ar has on the NO X²Π overtone emission, attention is drawn to the region above 3000 cm^{-1} where there are no underlying emission features. The most noticeable effect is observed as the pressure of argon

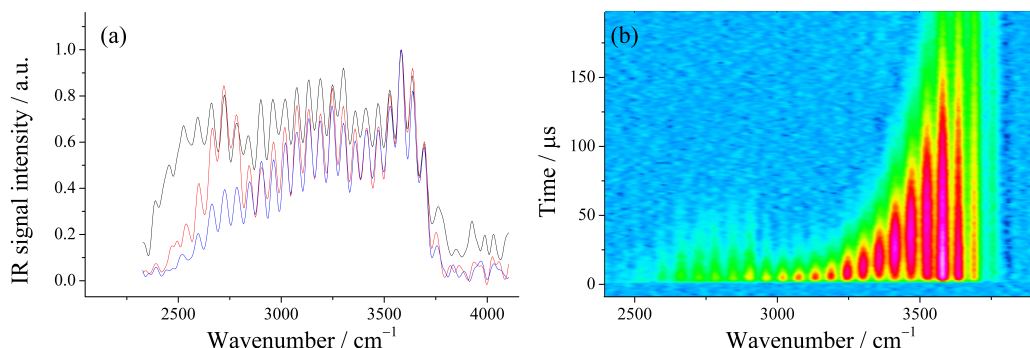


Figure 3.5: (a) IR emission observed at 4 μ s following the pumping of 50 mTorr NO on the overlapped Q₁ and P₂₁ band heads of the NO A $^2\Sigma^+(\nu = 0) \leftarrow$ X $^2\Pi(\nu = 0)$ transition in the presence of 1.17 Torr of O₂ and 0 Torr of Ar (black), 50 Torr of Ar (red) and 400 Torr of Ar (blue). Spectra are scaled according to their maximum values. (b) Contour plot of IR emission observed following the pumping of 50 mTorr NO on the overlapped Q₁ and P₂₁ band heads of the NO A $^2\Sigma^+(\nu = 0) \leftarrow$ X $^2\Pi(\nu = 0)$ transition in the presence of 1.17 Torr of O₂ and 400 Torr of Ar. Red represents high intensity and blue represents low intensity. All spectra were taken with the InSb detector at 20 cm⁻¹ resolution.

is raised from 0 Torr to 50 Torr which is due to the rotational thermalisation of the NO X $^2\Pi$ by Ar, rather than vibrational relaxation; there is very little difference between the spectra above 3000 cm⁻¹, observed in the presence of 50 Torr and 400 Torr of Ar, confirming that any effect on the vibrational relaxation of NO X $^2\Pi$ is minimal. Figure 3.5 (b) shows a contour plot of emission observed following the quenching of NO A $^2\Sigma^+(\nu = 0)$ in the presence of 400 Torr of Ar, where the NO₂ has been fully relaxed, which is apparent from comparison with the contour plot presented in Figure 3.4. The apparent bimodal appearance of the NO overtone spectra at later time is due to the efficient relaxation of the levels $\nu = 12$ –14 by O₂ rather than any underlying NO₂ emission in the region 2500–2900 cm⁻¹. Hancock *et al.* [32] found that rate constants for the vibrational relaxation of NO X $^2\Pi$ by O₂ peaked for $\nu = 13$ as the energy of the NO X $^2\Pi(13 \rightarrow 12)$ transition

most closely matched that of the O_2 ($1 \leftarrow 0$) transition, thus explaining the short observed lifetime of emission within the region 2900 cm^{-1} to 3300 cm^{-1} .

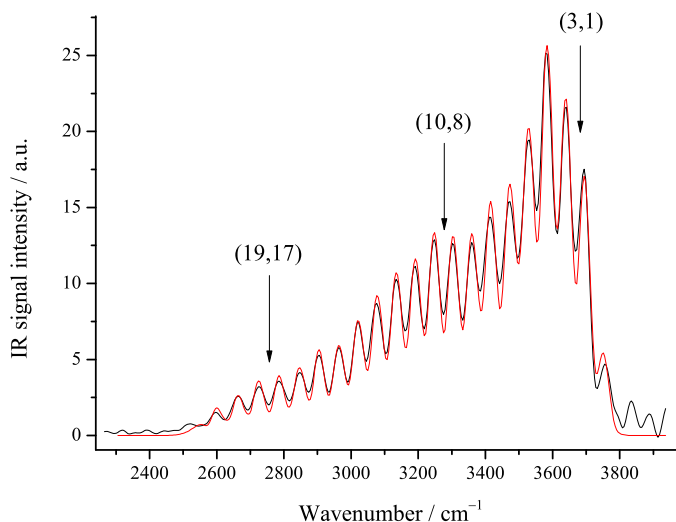


Figure 3.6: IR emission observed at $4\text{ }\mu\text{s}$ following the pumping of 50 mTorr NO on the overlapped Q_1 and P_{21} band heads of the $\text{NO } A^2\Sigma^+(\nu = 0) \leftarrow X^2\Pi(\nu = 0)$ transition in the presence of 1.17 Torr of O_2 and 400 Torr of Ar (black). Also shown is the fitted spectral simulation (red). Spectra were taken with the InSb detector at 20 cm^{-1} resolution. The spectrum has been corrected for filter and detector functions and selected band origins are shown.

Now that the infrared emission observed in Figure 3.5 (b) has been confirmed as the NO overtone emission band, without any other overlapping emission features, analysis can be performed to allow a nascent vibrational distribution to be obtained. First, the experimental data were corrected for optical filter transmission curves and detector response function. A spectral simulation of appropriate resolution was generated for each vibrational overtone transition, using the procedures outlined in Appendix A. The rotational temperature for all levels was set as 300 K. These simulations were then fitted, in a least squares manner, to the experimental spectrum by varying the relative weighting of each individual over-

tone simulation. An example of the fitted simulation can be seen in Figure 3.6. The relative weighting directly corresponds to the populations in each vibrational level. This was performed for time points 4 μs to 200 μs following the laser pulse, which yielded a vibrational population distribution $\text{NO } X^2\Pi(\nu = 2-22)$ for each microsecond. The temporal behaviour of the vibrational levels was then mod-

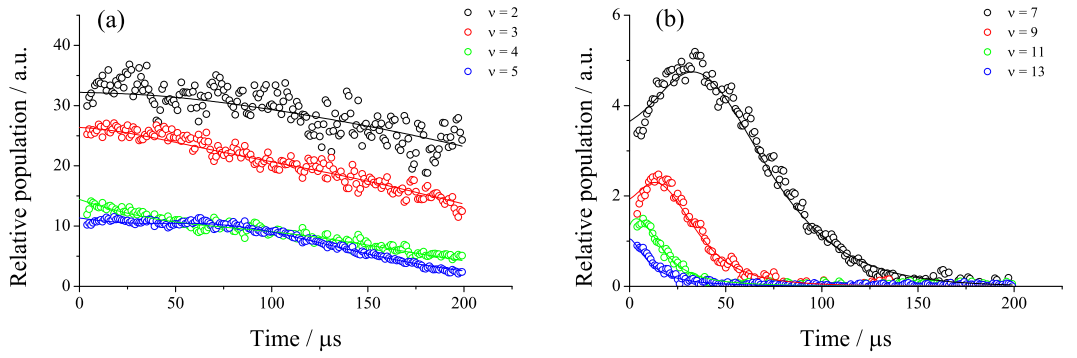
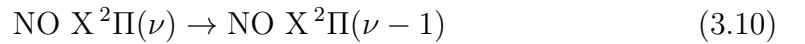
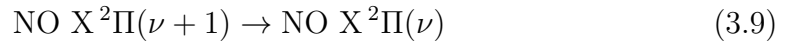


Figure 3.7: Temporal behaviour of selected vibrational levels of NO from 4 μs following the excitation of 50 mTorr to the $\text{NO } A^2\Sigma^+(\nu = 0)$ state in the presence of 1.17 Torr of O_2 and 400 Torr of Ar. Also shown are the fitted profiles for these vibrational levels as determined using the single quantum cascade model.

elled using a kinetic scheme where the only processes affecting the population of a given level are relaxation of the level above, and relaxation of the given level to the level below, as summarised by Equations 3.9 and 3.10.



Multi-quantum step and radiative decay processes were neglected on account of their low probabilities. By fitting this model to all the vibrational levels simultaneously, using the state-specific decay constants and initial populations as the

fitting parameters, the nascent vibrational distribution of NO X $^2\Pi(\nu = 2-22)$ was obtained. Figure 3.7 shows a selection of the fitted profiles for a number of vibrational states and the extrapolation to zero time. This procedure was performed for three different pressures of oxygen, corresponding to a quantum yield of quenching by O₂ to be $\Phi_{\text{O}_2} = 0, 0.2$ and 0.5 . The nascent vibrational distributions obtained from each set of conditions are shown Figure 3.8. From this figure

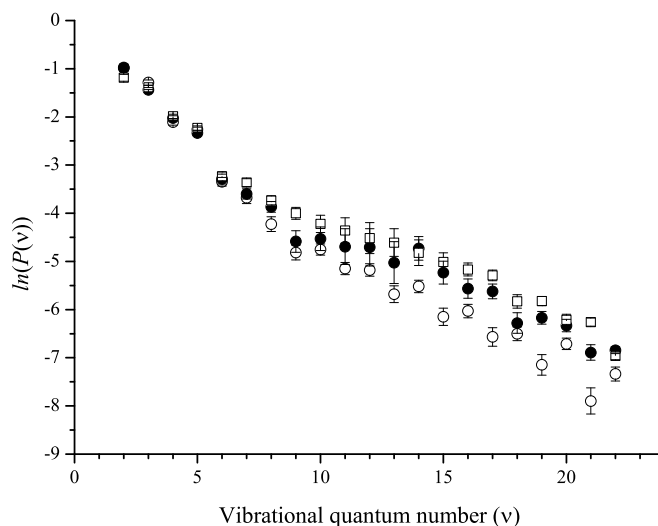
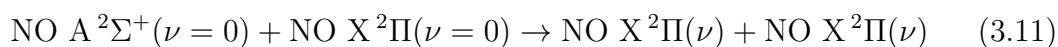


Figure 3.8: Log plot of nascent vibrational distribution of NO X $^2\Pi(\nu = 2-22)$ for three different pressures of O₂: 0 mTorr ($\circ$), 300 mTorr ($\bullet$) and 1170 mTorr ($\square$), for which the $\Phi_{\text{O}_2} = 0, 0.2$ and 0.5 respectively.

is it apparent that as the pressure of oxygen, and therefore Φ_{O_2} , is increased the relative population in the higher vibrational levels of nascent NO X $^2\Pi$ also increases, indicating that quenching of NO A $^2\Sigma^+(\nu = 0)$ by O₂ produces a hotter distribution than that resulting from conditions where fluorescence is dominant. Additionally, it can be seen that the nascent populations for the vibrational levels $\nu = 10-14$ have a greater associated uncertainty, which is due to the short lifetime

of these states as a result of the efficient vibrational relaxation by oxygen.

The nascent vibrational distributions presented in Figure 3.8 contain contributions from all channels that produce vibrationally excited NO X $^2\Pi$; as well as non-reactive quenching by O₂ (Equation 3.2), radiative decay and self-quenching (Equations 3.1 and 3.11) both occur in the reaction cell.



In addition to the channels listed above reactive quenching by oxygen also takes place. However, none of the reactive quenching pathways, described by processes (3.3), (3.5) and (3.7), will produce vibrationally excited NO X $^2\Pi$, and so do not need to be considered further with respect to the nascent NO X $^2\Pi(\nu)$ distribution.

The contributions of the various processes to the measured NO X $^2\Pi(\nu)$ distributions presented in Figure 3.8 are dependent on the respective quantum yields, as shown in Equation 3.12, where $P(\nu)_x$ is the vibrational distribution of NO X $^2\Pi$ produced solely by a given process x .

$$P(\nu)_{\text{measured}} = \Phi_{\text{O}_2}P(\nu)_{\text{O}_2} + \Phi_{\text{NO}}P(\nu)_{\text{NO}} + \Phi_fP(\nu)_f \quad (3.12)$$

$$P(\nu)_{\text{measured}} = \Phi_{\text{O}_2}P(\nu)_{\text{O}_2} + (1 - \Phi_{\text{O}_2})P(\nu)_{\text{NO}+f} \quad (3.13)$$

To reveal the vibrational distribution of NO X $^2\Pi$ resulting from the quenching of NO A $^2\Sigma^+(\nu = 0)$ by O₂, the contributions from the self-quenching and fluorescence processes need to be subtracted from the measured populations. The nascent vibrational distribution measured when $\Phi_{\text{O}_2} = 0.5$ was used for the subtraction process. Why a larger quantum yield of quenching by oxygen was not

used will be discussed below. As long as the partial pressure of NO was 50 mTorr the ratio of Φ_{NO} and Φ_f remains a constant 1:12, irrespective of the value of Φ_{O_2} . Therefore these two channels can be considered a single process and hence Equation 3.13 can be used for the subtraction. The combined distribution of NO $\text{X}^2\Pi(\nu)$ from self-quenching and fluorescence (in the ratio 1:12) can be simply determined by performing experiments where the partial pressures of NO, O_2 and Ar in the cell are 50 mTorr, 0 mTorr and 400 Torr respectively. The nascent distribution of NO $\text{X}^2\Pi(\nu)$ was obtained from this experiment, using the same procedure as described above and was found to be consistent with published NO $\text{X}^2\Pi$ vibrational distributions for self-quenching [20] and fluorescence [23]. Figure 3.9 (a) shows the NO overtone spectra simulated from the nascent vibrational distributions $P(\nu)_{\text{measured}}$ ($\Phi_{\text{O}_2} = 0.5$) and $P(\nu)_{\text{NO}+f}$. These spectra were then scaled according to the measured IR signal intensity following the quenching of NO $\text{A}^2\Sigma^+(\nu = 0)$ for the two cases. The IR signal used for this scaling was emission from overtone transitions originating in NO $\text{X}^2\Pi(\nu = 2-5)$ (3650 cm^{-1} to 3850 cm^{-1}), as these states have the greatest population. Optical filters were employed to block other emission frequencies. To ensure correct scaling, these measurements were taken directly after each other with the identical optical set-up. The IR signals were then normalised by the nascent NO A-X LIF intensity to account for any variation in the laser pulse intensity/wavelength, and hence the initial quantity of NO $\text{A}^2\Sigma^+(\nu = 0)$ molecules. After this normalisation, a marginal decrease in the IR emission intensity within the region 3650 cm^{-1} to 3850 cm^{-1} was observed upon addition of oxygen to the reaction cell; a 4% drop was measured as the partial pressure of oxygen was raised from 0 Torr to 1.17 Torr, ($\Phi_{\text{O}_2} = 0.5$), with the pressure of NO and Ar remaining the same at

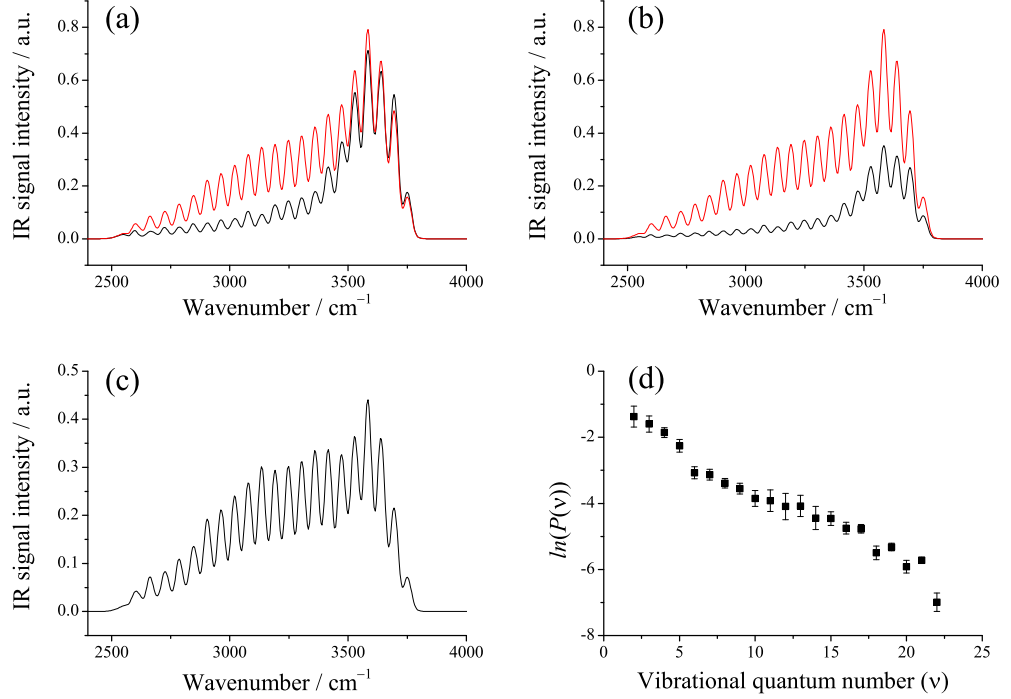


Figure 3.9: Plots showing the scaling and subtraction methodology as described in the main text. Nascent infrared spectra simulated from nascent vibrational distributions obtained from experiments where the quantum yield of quenching by oxygen is 0 (black) and 0.506 (red). The spectra shown have been scaled according to the measured infrared traces, (a), and additionally to the combined quantum yield of self-quenching and fluorescence for the respective experiments, (b). (c) shows the resultant nascent vibrational spectrum of NO from quenching by oxygen only, obtained by subtracting the two spectra shown in (b). (d) A log plot of the nascent vibrational distribution of NO $X^2\Pi$ resulting solely from the non-reactive collisional quenching of NO $A^2\Sigma^+(\nu = 0)$ by O_2 , normalised for levels $\nu = 2-5$.

50 mTorr and 400 Torr respectively. This allows the simulated spectra, shown in Figure 3.9 (a), to be put on a common intensity scale. The spectrum corresponding to self-quenching and fluorescence only is now multiplied by $(1 - \Phi_{O_2})$, which is how much it will contribute to the spectrum generated from the $P(\nu)_{measured}$ ($\Phi_{O_2} = 0.5$) distribution as indicated in Equation 3.13. These spectra scaled in this manner are shown in Figure 3.9 (b). Subtracting these two spectra results

in the spectrum that corresponds to $\Phi_{\text{O}_2} = 1$, from which the nascent vibrational distribution of $\text{NO X}^2\Pi$ can be extracted, as shown in Figure 3.9 (c) and (d) respectively. This whole procedure was repeated with different optical filters employed to allow scaling to different regions of the overtone emission spectrum, and consistent results were found for all cases. The $\Phi_{\text{O}_2} = 0.5$ quenching data was used for this procedure for a number of reasons. While using a higher partial pressure of O_2 will result in the IR emission (and the measured $\text{NO X}^2\Pi(\nu)$ distribution) being dominated by the process of interest, it will cause faster relaxation of the vibrational levels of $\text{NO X}^2\Pi$ particularly affecting levels around $\nu = 11$. More significantly the scaling procedure described above becomes unreliable for high quantum yields of quenching; the lifetime of the $\text{NO A}^2\Sigma^+(\nu = 0)$ state becomes short enough that the LIF signal is affected by the rise time of the PMT and therefore extrapolation to find the nascent LIF intensity, required for the scaling of the IR emission, is unreliable.

The population in $\text{NO X}^2\Pi(\nu = 0,1)$ now needs to be considered. Using the fundamental emission band to obtain information on the ratio of $\nu = 1$ and $\nu = 2$ was found to be unreliable due to the cold gas filter effect of NO in the reaction chamber. This is illustrated in Figure 3.10 which shows a late time emission spectrum of NO, alongside a simulated emission band for the $\text{NO X}^2\Pi(\nu = 1 \rightarrow 0)$ transition. At such a late time, $\sim 600\mu\text{s}$, the spectrum will be dominated by emission from thermalised $\text{NO X}^2\Pi(\nu = 1)$. Self-absorption will affect the relative intensities of the P, Q and R branches of the emission band. This is because, for a given rotational level in the ground state, the intensity of the Q branch transition is weaker [33], and so less self-absorption occurs. This means the detected Q branch emission intensity will increase relative to that of the P and

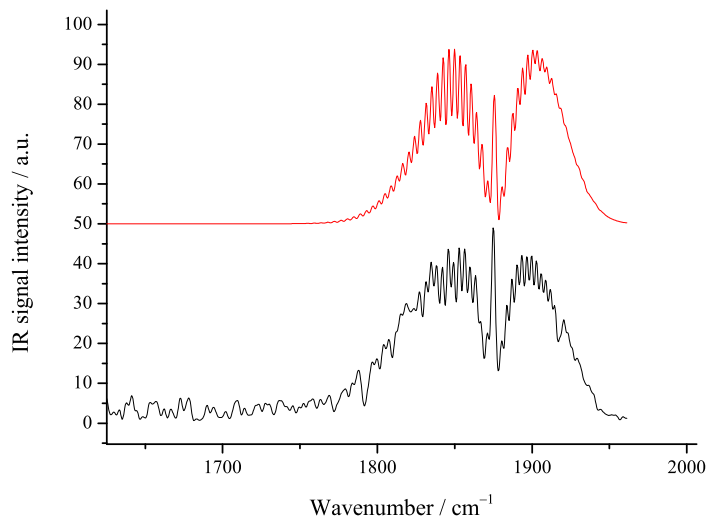


Figure 3.10: IR emission observed following pumping of 50 mTorr of NO to its $A^2\Sigma^+$ state with 226.257 nm radiation in the presence of 50 Torr Ar. The spectrum is sum of emission recorded between 590–600 μ s after the laser pulse (black). The spectrum recorded with HgCdTe detector at 2 cm^{-1} . Also shown, vertically offset for clarity, is the simulated NO $X^2\Pi(1 \rightarrow 0)$ emission spectrum (red).

R branches. Figure 3.10 clearly shows this to be the case. Given that self-absorption is occurring, it is not possible to use the fundamental emission to get accurate information on the relative population of NO $X^2\Pi(\nu = 1)$. Instead Surprisal analysis was used to estimate the populations of NO $X^2\Pi(\nu = 0,1)$ following the non-reactive quenching of NO $A^2\Sigma^+(\nu = 0)$ by O_2 , as has been done previously for similar systems [20–22]. The Prior distribution for this process, two diatomic molecules colliding and resulting in two diatomic molecules, can be calculated by methods outlined by Muckerman [34] (see Appendix B) and is shown in Equation 3.14, where f_ν represents the fraction of the available energy

in a given vibrational level, ν , and N is a normalization factor.

$$P^0(f_\nu) = N(1 - f_\nu)^{7/2} \quad (3.14)$$

Figure 3.11 (a) shows the Surprisal plot for this distribution with $\ln[P(f_\nu)/P^0(f_\nu)]$ against f_ν for $\nu = 2-22$. As described in Chapter 1, Surprisal plots often exhibit a linear relationship of the form shown in Equation 3.15.

$$\ln \left(\frac{P(f_\nu)}{P^0(f_\nu)} \right) = -\lambda_0 - \lambda_1(f_\nu) \quad (3.15)$$

It is evident in Figure 3.11 (a), however, that there is a non-linear trend at low ν . In particular, the population of the lower vibrational levels ($\nu = 2-5$) are greater than those expected by a linear fit to the higher vibrational levels alone. A possible cause for this behaviour at low ν is that the subtraction process has been performed incorrectly, and that there is still a contribution from fluorescence (process (3.1)), which preferentially populates the lower vibrational levels. However, as described above, the subtraction procedure was performed in a variety of manners and consistent distributions were obtained, and therefore another explanation is needed.

Often non-linear Surprisal plots indicate that multiple processes are occurring. In acquiring these populations, it has been assumed that the only channels in operation are radiative transfer (fluorescence), quenching by O_2 and self-quenching as shown in Equations 3.1, 3.2 and 3.11. There are other processes, so far neglected, which could contribute to the removal of $NO A^2\Sigma^+(\nu = 0)$ and still produce vibrationally excited $NO X^2\Pi$, in particular the production of electron-

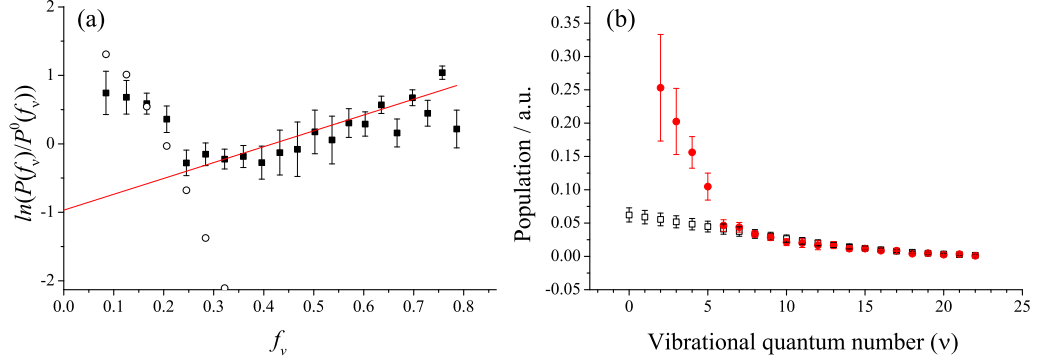
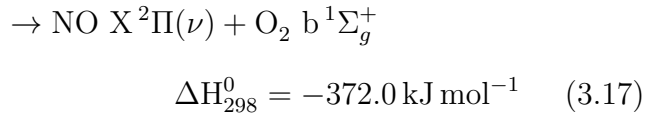
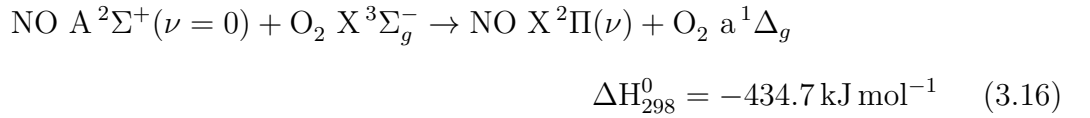
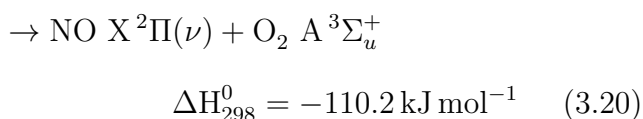
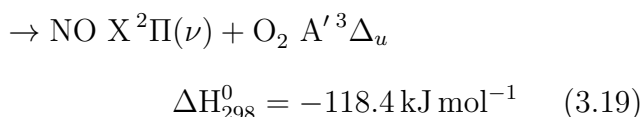
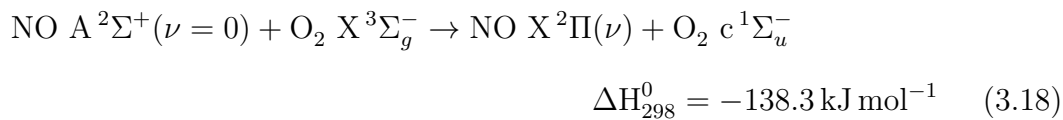


Figure 3.11: (a) A Surprisal plot of the nascent vibrational distribution of NO X $^2\Pi(\nu = 2\text{--}22)$ following pumping of 50 mTorr NO on the overlapped Q₁ and P₂₁ band heads of the NO A $^2\Sigma^+(\nu = 0) \leftarrow$ X $^2\Pi(\nu = 0)$ transition and subsequent quenching by O₂, (■). A linear fit to the data for $\nu > 6$ is plotted (red), yielding a Surprisal parameter λ_1 , defined as the negative of the gradient of such a plot, of -2.32 ± 0.29 . Also shown is the surprisal plot of the distribution expected in the absence of any quenching processes and governed purely by radiative transfer (○). (b) Plot of vibrational distribution for levels $\nu = 0\text{--}22$ as predicted by the linear fit to the data shown in (a), (□). Also shown is the raw measured nascent distribution (●).

ically excited O₂, shown in Equation 3.8. This process will generate NO X $^2\Pi$ with a lower degree of vibrational excitation as there will be less energy available. Oxygen has five electronically excited states that are accessible as a result of a collision of an NO A $^2\Sigma^+(\nu = 0)$ molecule with O₂, which are shown below in processes (3.16)–(3.20), along with the energy released in each case.





These electronic states of O_2 can be thought of as two distinct groups:

1. The $a^1\Delta_g$ and $b^1\Sigma_g^+$ states of O_2 are relatively low lying, and so formation of these states will allow the $\text{NO } X^2\Pi$ co-product to be formed in high vibrational states (up to a maximum of $\nu = 19\text{--}23$)
2. The $A^3\Sigma_u^+$, $A'^3\Delta_u$ and $c^1\Sigma_u^-$ states are comparatively high energy states. The energy remaining after formation of one of these states would be able to populate $\text{NO } X^2\Pi$ up to $\nu = 5\text{--}6$.

All these states correlate to the $2\text{O}(^3\text{P})$ dissociation products and if sufficient energy was transferred to the oxygen molecule to allow dissociation (process (3.6)), the remaining energy, which amounts to 2537.4 cm^{-1} would be able to populate up to $\nu = 1$ in $\text{NO } X^2\Pi$ co-product, and thus does not explain the observed trend shown in Figure 3.11. However, the experiments performed here provide no direct measurement of the $\text{NO } X^2\Sigma^+(\nu = 1)$ state, and so cannot discount that this process occurs. On the basis of the energy available for the internal excitation of the NO and O_2 product molecules for the different quenching processes listed in Equations (3.16)–(3.20), it can be reasoned that the formation of O_2 in one of

the high electronic states is more likely to be occurring. From the Surprisal plot shown in Figure 3.11 (a), it is only for the low vibrational levels of NO X²Π($\nu = 2-5$), that strong deviation from the linear trend of the higher levels is seen. This corresponds well to the range of vibrational levels in NO X²Π able to be populated in conjunction with O₂ in one of the high energy electronic states.

The contributions of the two processes (formation of ground state and electronically excited O₂) to the measured distribution can be distinguished by fitting a straight line to the Surprisal plot for $\nu > 6$, which cannot be populated in conjunction with formation of O₂ in either the c, A or A' states as shown in Figure 3.11 (a). The populations for $\nu \leq 6$ for this channel (formation of ground state NO and O₂) are estimated from the Surprisal parameters. This distribution is subtracted from the original nascent distribution, both shown in Figure 3.11 (b), the result being the NO X²Π distribution that is generated alongside electronically excited O₂. Surprisal analysis was then performed on this distribution; the Prior distribution is still described by Equation 3.14, and the energy available for the NO X²Π internal excitation was taken as 11 500 cm⁻¹, corresponding to formation of O₂ in the c¹Σ_u⁻ state. The Surprisal plot for this process is shown in Figure 3.12 (a), and the complete NO X²Π vibrational distributions from the two processes shown in Equations 3.2 and 3.8 are presented in Figure 3.12 (b). The sum of the NO X²Π vibrational distributions resulting from the two processes are in the ratio of 1:1.16, which indicates that O₂ X³Σ_g⁻ and O₂* will be produced in roughly equal quantities. Using the Surprisal parameters from the fit, the populations for $\nu = 0,1$ can be estimated, and these populations are presented in Table 3.1.

The distribution corresponding to the formation of NO and O₂ both in their

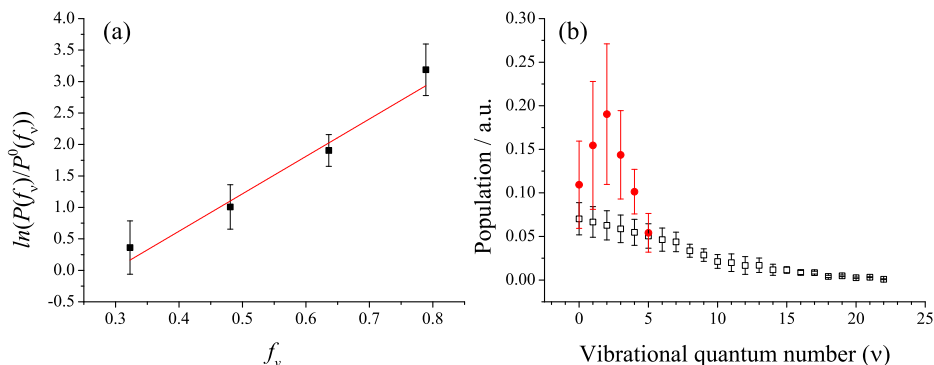


Figure 3.12: (a) Surprisal plot of nascent vibrational distribution ascribed to NO as a result of process (3.8) with $\text{O}_2 \text{ c}^1\Sigma_u^-$ formed as the co-product. (■). A best fit line is also plotted (red), which corresponds to a Surprisal parameter, λ_1 of -5.9 ± 0.8 , (red). (b) shows the distributions resulting from processes (3.2) (□) and (3.8) (●).

ground electronic states (process (3.2)), which although slightly hotter than statistical, is not inverted. In contrast the other distribution presented in Table 3.1 is inverted peaking at $\nu = 2$. The fraction of the reaction exothermicity which goes into the vibrational excitation of NO can be calculated from the Surprisal parameters, which were -2.32 and -5.9 for processes (3.2) and (3.18) respectively. These correspond to 24.6% and 38.9% of the available energy channelled into the NO vibrational mode (statistical is 18%).

In order to assess the presence of any unobserved process, such as reactive quenching (channel (3.3)), the variation of NO $X^2\Pi$ overtone emission intensity as a function of Φ_{O_2} is compared with the predicted variation, using the measured populations from O_2 quenching shown in Table 3.1. If the measured variation exhibit a bigger-decrease/smaller-increase than predicted, then this is evidence of a process which does not produce NO $X^2\Pi(\nu \geq 2)$. Such a process will be referred to as an unobservable process, and could for example be process (3.3) or (3.6). The result of this analysis shows that upon the addition of 1.17 Torr of O_2 the

3.4. Results

Table 3.1: Nascent normalised populations ($\nu = 0-22$) of NO X $^2\Pi$ resulting from the non-reactive quenching of NO A $^2\Sigma^+(\nu = 0)$ by O₂. Two distributions are shown each corresponding to a specific process, with the O₂ product being formed in a different electronic state in each case.

Vibrational level	Normalised population of NO X $^2\Pi(\nu = 0-22)$	
	NO X $^2\Pi + O_2$ X $^3\Sigma_g^-$ Process (3.2)	NO X $^2\Pi + O_2$ c $^1\Sigma_u^-$ Process (3.18)
0	0.197 $\pm$ 0.042	0.145 $\pm$ 0.067
1	0.177 $\pm$ 0.037	0.205 $\pm$ 0.097
2	0.159 $\pm$ 0.034	0.253 $\pm$ 0.107
3	0.127 $\pm$ 0.031	0.191 $\pm$ 0.067
4	0.098 $\pm$ 0.015	0.135 $\pm$ 0.034
5	0.066 $\pm$ 0.013	0.072 $\pm$ 0.030
6	0.029 $\pm$ 0.005	
7	0.027 $\pm$ 0.005	
8	0.021 $\pm$ 0.003	
9	0.018 $\pm$ 0.003	
10	0.013 $\pm$ 0.003	
11	0.012 $\pm$ 0.004	
12	0.010 $\pm$ 0.004	
13	0.011 $\pm$ 0.003	
14	0.007 $\pm$ 0.003	
15	0.007 $\pm$ 0.002	
16	0.005 $\pm$ 0.001	
17	0.005 $\pm$ 0.001	
18	0.003 $\pm$ 0.001	
19	0.003 $\pm$ 0.001	
20	0.002 $\pm$ 0.001	
21	0.002 $\pm$ 0.001	
22	0.001 $\pm$ 0.001	

measured decrease of IR intensity in the overtone region is slightly greater than the decrease predicted from the obtained distributions for the quenching processes (3.2) and (3.8). The calculated branching ratio for unobservable channels is $(18 \pm 7)\%$ when the two distributions presented in Table 3.1 are combined in the ratio of 1:1.16.

3.5 Discussion

The results presented in the previous section are now discussed in the light of previous investigations of the system. Mauldin and Ravishankara [17] studied the collisions between NO A $^2\Sigma^+(\nu = 0)$ and O₂, and by detecting O(³P) atoms demonstrated that reactive processes, such as channels (3.6), (3.3) and (3.5) occur. The co-products were not identified, so the relative importance of the processes that generate O(³P) atoms was not established. The direct observation of the NO₂ $\Delta\nu_3 = -1$ and $\Delta\nu_3 = \Delta\nu_1 = -1$ emission bands in this chapter, shown in Figure 3.3 and Figure 3.4 respectively, confirm the existence of the formation of NO₂ in the ground electronic state as a co-product to O(³P). The emission coefficients of these NO₂ bands are around 10 to 20 times larger than those for the NO fundamental and overtone transitions. Thus while the NO₂ emissions appear intense in the contour plots, they are not strong enough to indicate a significant branching ratio. Also the formation of electronically excited NO₂ (process (3.5)) is believed to be negligible as experiments performed to detect any NO₂ $1^2B_2 \rightarrow 1^2A_1$ fluorescence observed no such emission. It was calculated at the end of the previous section that the yield for all processes that do not produce NO X $^2\Pi(\nu \geq 2)$, which include all reactive channels, is 18 %. This value is consistent with the observed intensity of NO₂ emission, i.e. that reaction is not the dominant pathway. The lack of information of the amount of ground state NO₂ formed prevent any quantification of this channel. Mauldin and Ravishankara [17], while being unable to calculate the branching ratios for the reactive channels, concluded that formation of O(³P) was a major channel. However, this conclusion was based on estimates of the absolute O(³P) concentration

from their signal, which has a large associated uncertainty, and is not supported by the experiments presented in this chapter. Experiments designed specifically to probe for electronically excited O_2 products would need to be performed to confirm the existence of process (3.8) and to determine the contribution of the many available electronic states of O_2 .

Settersten *et al.* [18] investigated the fraction of NO $A^2\Sigma^+(\nu = 0)$ molecules that are channelled into NO $X^2\Pi(\nu = 0)$ state following a collision with various quenching molecules. A value of $(28 \pm 3) \%$ was reported for the quenching by O_2 . To calculate the equivalent figure from the two distributions shown, in Table 3.1, combined in the correct ratio of 1:1.16, the population in the NO $X^2\Pi(\nu = 0)$ state is multiplied by the branching ratio for the non-reactive quenching process, 0.82. These give the quantum yield for producing of NO $X^2\Pi(\nu = 0)$ as 0.14, which is lower than the value reported by Settersten *et al.*. This value is a lower limit, as the calculation assumes that the unobservable processes do not contribute to the NO $X^2\Pi(\nu = 0)$ yield. This assumption is true for the reactive processes that form NO_2 (channels (3.3) and (3.5)). However, the process which results in the dissociation of O_2 (channel (3.6)) can only produce NO $X^2\Pi(\nu = 0,1)$ as a co-product and therefore is classed as an unobservable process as defined earlier. Closer agreement between this work and that of Settersten *et al.* is found if this channel, the dissociation of O_2 , was dominant among the unobserved processes. In this case the branching ratio for NO $X^2\Pi(\nu = 0)$ will be increased by up to 18 %, giving an upper limit of 32 %. It is clear that experiments measuring the ratio of NO_2 and $O(^3P)$ products are required to determine the relative contributions of processes (3.6) and (3.3).

One of the disadvantages of FTIR for studying this system is that the vi-

brational mode of O_2 is not infrared active, and therefore no information on the extent of vibrational excitation in the O_2 product is obtained. Such information would allow a much greater insight into the mechanism for the quenching process. For example, if the O_2 exhibits a similar degree of vibrational excitation to the NO product, i.e. a hotter than statistical distribution, then a four membered ring type complex between the NO $A^2\Sigma^+$ and O_2 can be envisaged. The release of the electronic energy into internal energy would lead to vibrational excitation of the whole ring, and therefore both NO and O_2 will be formed in a vibrationally excited state upon the break up of the complex. However, if the O_2 was formed vibrationally cold, then it is more likely that a T-shaped arrangement of the NO and O_2 formed, which can be likened to the transition state for the photolysis of NO_3 . NO and O_2 bonds lie perpendicular in this arrangement, and the degree which vibrational excitation of the NO can transfer into the vibrational mode of the O_2 is limited.

3.6 Summary

This chapter has applied the technique of time-resolved FTIR emission spectroscopy to studying the electronic quenching NO $A^2\Sigma^+(\nu = 0)$ by O_2 . It has found that both reactive and non-reactive pathways were involved in the quenching process; emission from vibrationally excited NO_2 from the $\Delta\nu_3 = -1$ and $\Delta\nu_3 = \Delta\nu_1 = -1$ bands was observed, and hence a high pressure of Ar was employed to prevent interference of this latter emission with the NO overtone. Analysis of the NO overtone emission demonstrated that NO was formed with a significant degree of vibrational excitation. Population was observed in levels

as high as $\nu = 22$. The NO X $^2\Pi(\nu = 2-22)$ distribution formed purely as a result of quenching by O₂ was obtained by subtracting appropriately scaled distributions representing self-quenching by NO and from radiative transfer. This was found to be slightly hotter than statistical. Surprisal analysis showed an indication of non-linearity, raising the possibility of an additional process occurring, the formation of electronically excited O₂. NO X $^2\Pi(\nu = 0-22)$ vibrational distributions were found for both cases and are presented in Table 3.1. Results were discussed in light of previous studies, with both agreement and discrepancies found. The obtained distributions indicate unobservable processes are occurring with a small quantum yield of 0.18. All processes that produce O(³P) atoms are classed as unobservable processes and therefore this work disagrees with the qualitative conclusions of Mauldin and Ravishankara [17], that production of O(³P) is a major pathway. Work by Settersten *et al.* [18] calculated the branching ratio for population returning to the NO X $^2\Pi(\nu = 0)$ state, as a result of all processes contributing to quenching. While results presented in this chapter are not inconsistent with this value, it leads to the implication that the dissociation of O₂ (channel (3.6)) dominates over the formation of NO₂ (channel (3.3)). It is clear that further work, investigating the branching ratios of the various reactive and non-reactive pathways, is required before this system is fully understood.

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Chapter 4

Electronic quenching of NO

A $^2\Sigma^+(\nu = 0, 1)$ by CO₂

4.1 Introduction

The electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by CO₂ provides a more complicated system than that studied in Chapter 3. CO₂, being a triatomic molecule, has more vibrational modes that the electronic energy can be partitioned into. Unlike O₂, CO₂ has vibrational modes that are infrared active. A previous study of the quenching of NO A $^2\Sigma^+(\nu = 0)$ by CO₂ by Settersten *et al.* [1] suggests it to be very different from that of O₂, CO and H₂O, as it is twice as efficient at forming NO X $^2\Pi(\nu = 0)$ than all the other collision partners. Moreover, as will be discussed later, quenching by CO₂ provides an excellent system on which to observe the effect of vibrational excitation in the NO A $^2\Sigma^+$ molecule, as sufficient energy is available to allow certain processes to become observable, by producing vibrationally excited, rather than ground state products.

This system has been studied previously within the research group, using FTIR emission spectroscopy to observe the vibrationally excited products [2]. The nascent vibrational distribution of NO X $^2\Pi$ was obtained, however, a full understanding of the system was not reached, particularly with regard to the degree of excitation in the CO₂ molecule following electronic quenching, and the branching ratios of the reactive and non-reactive channels.

This chapter looks to extend this type of study to the collisional quenching of NO A $^2\Sigma^+(\nu = 0,1)$ by CO₂ and aims to determine how much of the electronic energy of the A $^2\Sigma^+$ state of NO appears as vibrational excitation in the ground state NO molecule, and whether or not the energy appears as internal excitation of the quenching molecule itself and if there is a contribution from reactive quenching.

4.2 Quenching of NO A $^2\Sigma^+(\nu = 0)$

CO₂ is a rapid electronic quencher of NO A $^2\Sigma^+(\nu = 0)$, with a rate constant of $\sim 4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [3–10], and it was measured in this work to be $(4.25 \pm 0.01) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (see Section 5.2). CO₂ is considerably slower at vibrational relaxation of NO X $^2\Pi(\nu)$; the vibrational quenching rate constants increase monotonically with increasing ν with the highest reported value, quenching of $\nu = 12$ state, being $1.76 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [11]. Early time observations should thus enable nascent populations in NO X $^2\Pi(\nu)$ produced by electronic quenching to be observed before substantial vibrational relaxation takes place. CO₂ has large Einstein A factors for the $\Delta\nu_3 = -1$ transitions near 2000 cm^{-1} , of the order of ten times that for the NO fundamental band,

and this will aid in the identification of emission features resulting from energy transfer to them. The quenching process may also give rise to other vibrationally excited products, produced for example by dissociation of the collision partner.

4.2.1 NO X $^2\Pi(\nu)$ nascent distribution

The NO X $^2\Pi(\nu)$ vibrational distribution has previously been determined using the same experimental arrangement as employed in this thesis [2]. While the main aim of this chapter is to extend the investigations on this system, a brief account of the experiments and analysis employed to obtain the NO X $^2\Pi$ vibrational distribution is included, as it is of significance when considering the system as a whole.

Vibrational excitation of NO X $^2\Pi(\nu)$ was observed by emission in both the fundamental and overtone regions when a mixture of NO and Ar was irradiated near 226 nm. On addition of CO₂ these bands decreased in intensity, and new features were observed, ascribed to emission from high vibrational levels of CO₂, most notably in the $\Delta\nu_3 = -1$ bands near 2000 cm⁻¹. First, the overtone region of emission from NO X $^2\Pi(\nu)$ between 2800 cm⁻¹ and 3800 cm⁻¹ was considered. Previous work has described the tests used to ensure that the observed IR emission is the result of collisional deexcitation of NO A $^2\Sigma^+(\nu = 0)$ and not from, for example, products of a two photon excitation step [12]. Figure 4.1 shows vibrational overtone spectra recorded 25 μ s after pumping 50 mTorr NO and 200 Torr Ar at 226.257 nm with and without CO₂, taken at a resolution of 20 cm⁻¹. For the NO/Ar mixture the vibrational levels are formed by fluorescence at low ν (with a quantum yield $\Phi_f = 0.92$) and self-quenching at high ν ($\Phi_{\text{NO}} = 0.08$). Quantum

4.2. Quenching of NO $A^2\Sigma^+(\nu = 0)$

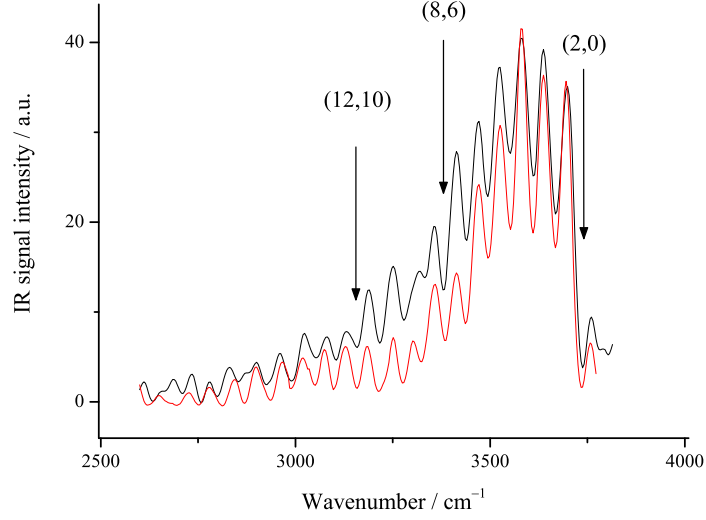
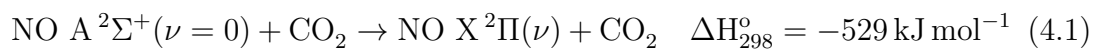


Figure 4.1: NO $X^2\Pi(\Delta\nu = -2)$ emission spectrum recorded at 25 μs following excitation of 50 mTorr of NO $X^2\Pi$ in the overlapped Q_1 and P_{21} band heads of the NO $A^2\Sigma^+(\nu = 0) \leftarrow X^2\Pi(\nu = 0)$ transition in the presence of 466 mTorr CO_2 ($\Phi_{\text{CO}_2} = 0.53$, black) and 200 Torr Ar at a resolution of 20 cm^{-1} . Shown also on this figure is the corresponding spectrum produced from fluorescence and self-quenching by NO, which has a Franck-Condon distribution for the low vibrational levels ($\Phi_{\text{NO}} = 0.08$, $\Phi_{\text{CO}_2} = 0$, red). Selected band origins are shown. In this figure the two spectra are arbitrarily scaled for clarity: the relative intensities are discussed in the text.

yields are calculated from fluorescence decay rates [13, 14] and self-quenching rate constants [3, 5, 7, 15]. A selection of band origins are marked on the figure. Also shown in Figure 4.1 is a spectrum when 0.466 Torr CO_2 (quenching quantum yield $\Phi_{\text{CO}_2} = 0.53$) is added, and it can be seen that the emission now stretches to higher vibrational levels. The quantum yield is calculated using measured rate constants for quenching of NO $A^2\Sigma^+(\nu = 0)$ by CO_2 which are generally in good agreement [3–10]. The emission in the NO overtone region was perturbed at early times by strong emission from two combination bands of vibrationally excited CO_2 ($\Delta\nu_3 = \Delta\nu_1 = -1$ and $\Delta\nu_3 = -1$, $\Delta\nu_2 = -2$), but the addition

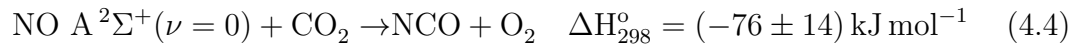
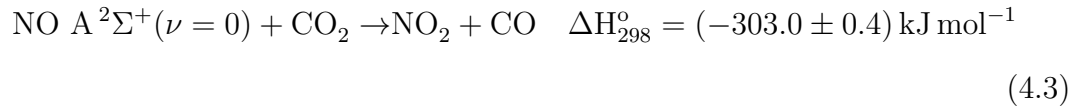
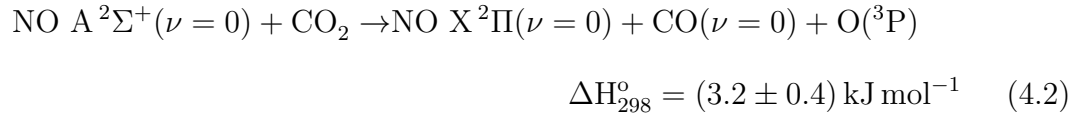
4.2. Quenching of NO A $^2\Sigma^+(\nu = 0)$

of Ar removed the emission within around 20 μs . Several NO overtone spectra were summed from 20 μs to 40 μs and fitted with a spectral simulation [12] with the results averaged. The rates of vibrational relaxation of NO X $^2\Pi(\nu)$ by CO₂ under these conditions are negligible [16]. The emission spectra presented in Figure 4.1 have contributions from both NO self-quenching and fluorescence as well as from quenching by CO₂. To separate these contributions the spectra (which were often taken on different days) need to be placed upon a common intensity scale, as was performed in Chapter 3. Optical filters were used to isolate specific wavelength bands, and the intensities passed by the filter were measured with and without CO₂ on a timescale of a few minutes. These infrared intensities were again scaled to the respective peak intensities of the simultaneously measured NO A-X UV fluorescence in order to allow for any variation of laser intensity, and also for any change in the rotational hole filling during the excitation pulse brought about by a change of gas composition [12]. Such scaling showed that the addition of CO₂ resulted in a marked decrease of the overtone intensity. For example, emission through a filter centred at 3720 cm^{-1} passing radiation in the NO X $^2\Pi(\nu = 2 \rightarrow 0)$ to NO X $^2\Pi(\nu = 5 \rightarrow 3)$ bands was reduced by some 40 % when the quantum yield of CO₂ quenching was increased from 0 to 0.53. Figure 4.1 shows that addition of CO₂ results in a relative increase in populations of vibrational levels of NO X $^2\Pi(\nu = 5-12)$, and the increase in Einstein A coefficients of these higher levels would imply that if quenching produced exclusively NO X $^2\Pi(\nu)$ in the observed emitting levels by process (4.1)



4.2. Quenching of NO A $^2\Sigma^+(\nu = 0)$

then the overall overtone emission intensity should increase instead of decrease. However, there are three other potential reactive processes which need to be considered, none of which form vibrationally excited NO X $^2\Pi$:



The occurrence of these three processes could result in a decrease in NO X $^2\Pi(\nu)$ emission intensity. These processes are discussed below, where they are termed unobserved channels, where unobserved here refers to processes which either do not form NO, or produce NO exclusively in levels which are not seen in the overtone spectra (i.e. $\nu \leq 1$). The second step in the extraction of populations from process (4.1) is to take the normalised set of spectra and to subtract from each spectrum with CO₂ the spectrum observed without CO₂ present, multiplied by the appropriate quantum yield of fluorescence and self-quenching (for example 0.47 in the data of Figure 4.1). The resulting spectrum, now the result of CO₂ quenching alone, is fitted to obtain vibrational distributions. However, population in the levels NO X $^2\Pi(\nu = 0, 1)$ is not known, and these are estimated as before [12] from a Surprisal analysis of the data as described in Chapter 1. For collisions of NO A $^2\Sigma^+(\nu = 0)$ with CO₂, the only exothermic channel producing vibrationally excited NO X $^2\Pi(\nu)$ is the energy transfer process (4.1) and for this

4.2. Quenching of NO A $^2\Sigma^+(\nu = 0)$

the Prior distribution is calculated by the methods outlined by Muckerman [17]

$$P^0(f_\nu) = N(1 - f_\nu)^{\frac{13}{2}} \quad (4.5)$$

where N is a normalisation factor. Figure 4.2 shows the appropriate Surprisal plot of $\ln[P(f_\nu)/P^0(f_\nu)]$ against f_ν for $\nu = 3$ –14. The low Einstein A coefficient for the NO X $^2\Pi(\nu = 2 \rightarrow 0)$ transition, in combination with the strong CO₂ combination band emission at early time, made the evaluation of the weak emission contribution from NO X $^2\Pi(\nu = 2)$ unreliable, and thus only data for $\nu = 3$ –14 are presented. The population in levels $\nu = 0$ –2 are estimated by an extrapolation. The subtraction procedure resulted in populations in levels $\nu > 14$, which

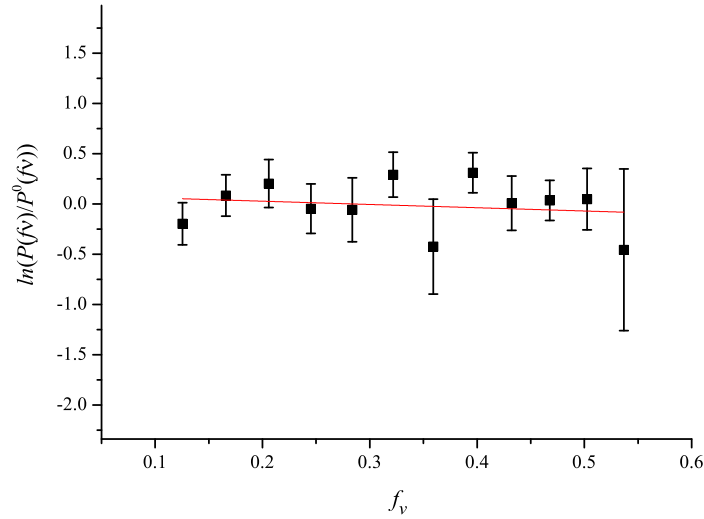


Figure 4.2: A Surprisal plot of the nascent vibrational distributions of NO X $^2\Pi(\nu = 3$ –14), measured by Gowrie [2], following pumping of 50 mTorr NO on the overlapped Q₁ and P₂₁ band heads of the A $^2\Sigma^+(\nu = 0) \leftarrow$ X $^2\Pi(\nu = 0)$ transition and quenching by CO₂ (■). A linear fit to the data is also plotted, (red), yielding a Surprisal parameter λ_1 , defined as the negative of the gradient of such a plot, of 0.33 ± 0.14 .

4.2. Quenching of NO A $^2\Sigma^+(\nu = 0)$

are thermodynamically possible for process (4.1), being zero within the noise of the experiment, and the reasons for this are discussed later. The Surprisal parameter λ_1 , defined as the negative of the gradient of such a plot, is found to be 0.33 ± 0.14 . This indicates that the distribution, although close to the Prior, shows that NO takes a marginally lower than statistical share of the available energy: 11.4 % instead of the statistical 11.8 %. The measured $\nu = 3$ –14 populations and the extrapolated populations for $\nu = 0, 1$ and 2 are given in Table 4.1, summed to unity.

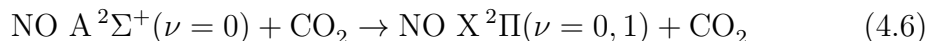
Table 4.1: Vibrational populations for NO X $^2\Pi(\nu = 0$ –14), measured by Gowrie [2], produced under conditions of exclusive quenching of NO A $^2\Sigma^+(\nu = 0)$ by CO₂ from a combination of the experimental data for populations of NO X $^2\Pi(\nu > 2)$ and Surprisal analysis for the populations of NO X $^2\Pi(\nu = 0$ –2). Relative populations are summed to unity with errors presented as $\pm 1\sigma$.

ν	NO X $^2\Pi(\nu)$ vibrational population
0	0.250 $\pm$ 0.024
1	0.186 $\pm$ 0.023
2	0.137 $\pm$ 0.025
3	0.100 $\pm$ 0.021
4	0.098 $\pm$ 0.020
5	0.080 $\pm$ 0.019
6	0.045 $\pm$ 0.011
7	0.031 $\pm$ 0.010
8	0.031 $\pm$ 0.007
9	0.011 $\pm$ 0.005
10	0.015 $\pm$ 0.003
11	0.007 $\pm$ 0.002
12	0.005 $\pm$ 0.001
13	0.003 $\pm$ 0.001
14	0.001 $\pm$ 0.001

Now the population distributions for the three processes occurring in data such as presented in Figure 4.1 are known, namely for CO₂ quenching (shown in Table 4.1), NO self-quenching [12] and fluorescence [13, 14]. For $\nu = 1 \rightarrow 0$ emission the fundamental band taken at high resolution again showed evidence of

4.2. Quenching of NO A $^2\Sigma^+(\nu = 0)$

self-absorption (the weak Q branch lines were proportionally stronger than the R and P branches, see Figure 3.10) and thus extracting the $\nu = 1$ population from an emission spectrum is unreliable. The populations in Table 4.1, together with the measured reduction in overtone intensity with increasing CO₂ concentrations, enables the deduction that process (4.1) forming the observed channels (ie $\nu \geq 2$) together with the extrapolated populations in $\nu = 0,1$ accounts for $(26 \pm 5) \%$ of the removal of NO A $^2\Sigma^+(\nu = 0)$ in collisions with CO₂. This implies that there are additional unobserved channels, accounting for 74% of the quenching collisions, such as a separate mechanism forming unobserved NO X $^2\Pi(\nu = 0, 1)$ by process (4.6), or the reactive processes (4.2), (4.3), (4.4):



It is noted also that Table 4.1 shows the fractional population of $\nu = 0$ produced by process (4.1) is 25% which, with a 26% quantum yield, would imply that process (4.1) alone yields a ground state population in NO X $^2\Pi(\nu = 0)$ of 6.5% resulting from quenching by CO₂, far smaller than the figure of 60% deduced by Settersten *et al.* [1] from their LIF measurements. The resolution of this difference is discussed below in Section 4.2.5.

4.2.2 Reactive quenching

It was determined in the previous section that the combined quantum yield of reactive channels (4.2), (4.3), (4.4) (producing CO, NO₂ and NCO) and process (4.6) was 0.74. Experiments were performed to observe emission from these reaction products. A high pressure of CO₂ was employed, 4.3 Torr, as this reduces

4.2. Quenching of NO $A^2\Sigma^+(\nu = 0)$

the intensity of the emission from NO allowing easier observation of potentially weak emission from reaction products. Figure 4.3 shows spectrum of emission observed when $\Phi_{\text{CO}_2} = 0.9$. The spectrum is recorded at 30 μs following the excitation laser pulse, and by this time the CO_2 emission has shifted to low vibrational levels near 2300 cm^{-1} . Here not only is the relatively long lived NO fundamental band observed, but also a feature near 2100 cm^{-1} . This is assigned to the CO ($\nu = 1 \rightarrow 0$) transition, confirmed by experiments in which a cold gas filter containing CO removed the emission entirely with very little effect on the CO_2 emission. The cold gas filter experiments also showed that the emission from CO ($\nu = 1$) was not prompt, in contrast to that from nascent NO and CO_2 , and had a relatively long lifetime.

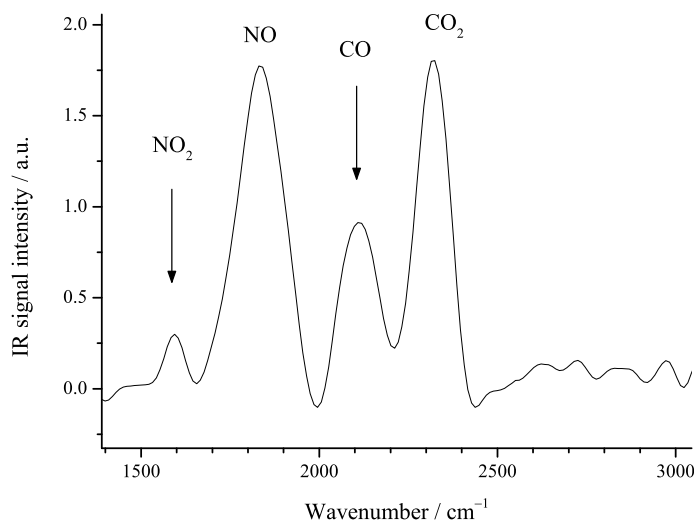


Figure 4.3: An emission spectrum recorded 30 μs after excitation of 50 mTorr NO $X^2\Pi$ to the $A^2\Sigma^+(\nu = 0)$ state with 226.257 nm radiation in the presence of 4.3 Torr CO_2 and 50 Torr Ar. Spectra was recorded with a HgCdTe detector at 50 cm^{-1} resolution. Emission features are labelled.

Process (4.2) producing CO has been suggested by Settersten *et al.* [1] as a

4.2. Quenching of NO A $^2\Sigma^+(\nu = 0)$

possible explanation for a surprisingly large cross section for quenching of NO A $^2\Sigma^+(\nu = 0)$ by CO₂. As can be seen for process (4.2) at 298 K the reaction is slightly endothermic ($\Delta H_{298}^{\circ} = 3.2 \text{ kJ mol}^{-1}$), but becomes slightly exothermic at low temperatures ($\Delta H_0^{\circ} = -3.0 \text{ kJ mol}^{-1}$). This implies that the reaction is thermodynamically feasible for lower than room temperature distributions of energy in the reactants. Such a pathway, however, would produce NO and CO in their vibrational ground states, and thus the observed CO ($\nu = 1$) therefore cannot be formed directly. The emission intensity of CO ($\nu = 1$) was found to increase but with the same temporal behaviour following a prolonged period (3 hours) of 226 nm irradiation. The evidence suggests that it is not a nascent emitting product, but is presumably formed by efficient near resonant energy transfer to CO ($\nu = 0$) from vibrationally excited NO X $^2\Pi(\nu)$ or CO₂. Process (4.2) therefore could account for this observation, but an alternate option would be reaction (4.3) to produce CO together with NO₂. As can be seen in Figures 4.4 and 4.3, there is weak emission near 1600 cm^{-1} which is attributed to vibrationally excited NO₂ in the $\Delta\nu_3 = -1$ band. As for the O₂ case discussed in Chapter 3, the intensity of the NO₂ emission is far lower than that from vibrationally excited NO in the fundamental region, despite the Einstein A coefficient for the (0,0,1) $\rightarrow$ (0,0,0) transition being approximately a factor of 10 greater than that for NO X $^2\Pi(\nu = 1 \rightarrow 0)$ [18]. If process (4.3) does occur, then it would need to produce a far lower quantum yield of vibrationally excited products than does process (4.1), both in NO₂ and CO. There is sufficient energy liberated in process (4.3) to populate CO up to $\nu = 10$, yet no emission from highly excited CO either in the fundamental or overtone regions was observed. Although observations cannot rule out process (4.3) as having a significant quantum yield, they support the pro-

4.2. Quenching of NO A $^2\Sigma^+(\nu = 0)$

cess partitioning little energy into vibration of the products. If processes (4.3) and (4.4) are neglected, then the observations can be explained thus. CO₂ quenches NO A $^2\Sigma^+(\nu = 0)$ in process (4.1) to produce NO X $^2\Pi(\nu)$ with a vibrational distribution close to statistical and with a quantum yield of $(26 \pm 5)\%$. The remaining 74 % of quenching collisions come from process (4.6) forming unobserved NO X $^2\Pi(\nu = 0,1)$ or reaction in process (4.2) which can only produce NO in $(\nu = 0)$, or a combination of the two. The CO₂ product comes from processes (4.1) and (4.6). The low quantum yield for process (4.1) also helps to explain why its vibrational distribution obtained by subtraction yields negligible population in levels above $\nu = 14$. The vibrational distribution for NO self-quenching [12] yields a Surprisal parameter of -2.16 ± 0.44 , compared with the CO₂ quenching value of 0.33. Although these values are both close to statistical, the hotter NO quenching distribution and the smaller number of degrees of freedom available to the products in comparison with process (4.1) means that quenching by NO will dominate the formation of high vibrational levels under the present conditions, and this effect is exacerbated by the reduced quantum yield of process (4.1).

4.2.3 CO₂ emission analysis

Attention is now turned to the vibrational excitation of the CO₂ quenching product, specifically to the $\Delta\nu_3 = -1$ emission band between 1800 cm⁻¹ and 2350 cm⁻¹. Figure 4.4 presents a contour plot of the infrared emission observed with the HgCdTe detector following irradiation of 50 mTorr NO at 226 nm in the presence of 46 mTorr CO₂ and 50 Torr Ar. The plot shows the frequency dependence of the emission in the region 1250 cm⁻¹ to 3500 cm⁻¹ with the intensity rep-

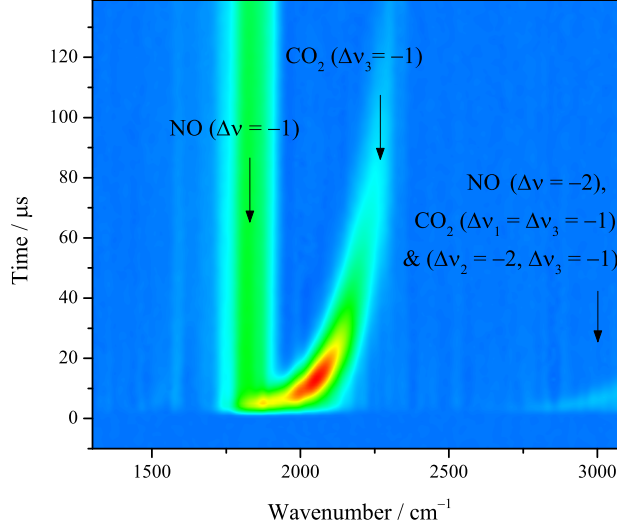


Figure 4.4: Contour plot of IR emission spectrum recorded at a resolution of 20 cm^{-1} following the initial excitation of 50 mTorr NO to the NO A $^2\Sigma^+(\nu = 0)$ state in the presence of 50 Torr Ar and 46 mTorr ($\Phi_{\text{CO}_2} = 0.1$). This was acquired with a HgCdTe detector. Band assignments are marked. Red represents high intensity and blue represents low intensity.

resented as contours of different colours. The conditions represent the case when collisional quenching by CO_2 has a quantum yield of $\Phi_{\text{CO}_2} = 0.1$. Three features are clearly seen. First, long lived emission between 1700 cm^{-1} and 1850 cm^{-1} is in the position expected for the fundamental bands of NO produced with a vibrational distribution as given in Table 4.1. Vibrational relaxation of NO X $^2\Pi(\nu)$ is slow on the time scale shown in Figure 4.4. Secondly, a stronger feature between 1800 cm^{-1} and 2300 cm^{-1} is seen to cascade rapidly to higher wavenumbers with time and is assigned to highly vibrationally excited CO_2 , formed directly by energy transfer from NO A $^2\Sigma^+(\nu = 0)$ by process (4.1), emitting in $\Delta\nu_3 = -1$ transitions, and rapidly quenched in collisions with CO_2 and Ar. The third set of emission bands above $\sim 3000\text{ cm}^{-1}$ is assigned to emission from the NO first

overtone and (at early times) from combination bands of CO_2 . No emission from

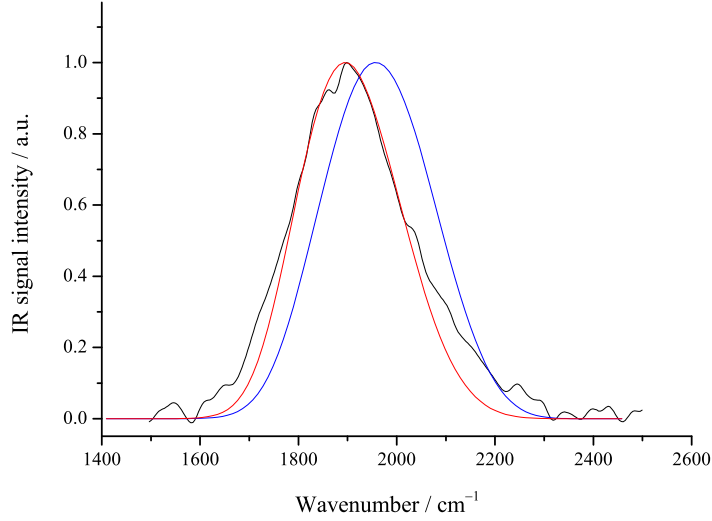


Figure 4.5: IR emission spectrum recorded $4\ \mu\text{s}$ after pumping 50 mTorr NO to its $A^2\Sigma^+(\nu = 0)$ state in the presence of 46 mTorr CO_2 (black curve, $\Phi_{\text{CO}_2} = 0.1$). Also shown is the simulated spectra predicted according to the best fit Surprisal parameter, $\lambda_1 = -4.5$ (red), as well as the simulated spectra from a statistical (Prior) distribution (blue). The spectra are normalised for clarity.

the CO_2 $(0,0,1) \rightarrow (0,0,0)$ transition is observed, even at late times because of self-absorption. Figure 4.5 shows the intensity distribution of the CO_2 band at early times ($4\ \mu\text{s}$) with the long lived NO fundamental emission subtracted. This was a facile procedure as the low pressure of CO_2 present meant the initial distribution and kinetic behaviour of the NO fundamental emission was barely affected. This latter claim was confirmed by the observation that there was no effect on the temporal behaviour of emission at various frequencies across the NO emission band upon the addition of 46 mTorr of CO_2 . Therefore emission spectra taken without CO_2 present can be appropriately scaled according to the NO emission intensity and subtracted from the spectra obtained with 46 mTorr of CO_2 . The

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spectrum presented in Figure 4.5 was taken in the absence of Ar, as relaxation of the high vibrational levels of CO₂ by 50 Torr of Ar was pronounced within the time scale of the experiments. The lack of structure and the wide spectral width of the band suggests that the CO₂ is formed over a range of vibrational states, CO₂ (ν_1, ν_2, ν_3), which are not resolved in the spectra, making accurate extraction of populations by a simple spectral simulation difficult due to the large number of adjustable parameters. First, the observed spectrum is compared to that for a Prior distribution for CO₂ in process (4.1), calculated, *via* the methods outlined previously [17] as

$$P^0(\nu_1, \nu_2, \nu_3) = N(f_\nu)^3(1 - f_\nu)^{\frac{7}{2}} \quad (4.7)$$

where again f_ν represents the fraction of the available energy in level (ν_1, ν_2, ν_3), and N is a normalization factor. After calculating the values of P^0 for each possible combination of levels (ν_1, ν_2, ν_3), each $\Delta\nu_3 = -1$ band from a given (ν_1, ν_2, ν_3) level was represented by two (P and R branches with separation of ca. 25 cm⁻¹) or three (P, Q, R branches) lines representing transitions between levels with or without $\ell = 0$. Positions of band origins were calculated according to Herzberg [19] and several were confirmed by comparison with those measured by Bailly *et al.* [20]. The intensity of each band was calculated using Equation 4.8

$$I(\nu_1, \nu_2, \nu_3) = P^0(\nu_1, \nu_2, \nu_3) \left[\frac{\bar{\nu}(\nu_1, \nu_2, \nu_3)}{\bar{\nu}(0, 0, 1)} \right]^4 \nu_3 A_{001} N_{PQR} \quad (4.8)$$

where A_{001} is the Einstein A coefficient for the ν_3 fundamental transition, $\bar{\nu}$ the frequency of the $\Delta\nu_3 = -1$ transition and N_{PQR} is a factor taking into account the relative intensities of P, Q and R branches. The quartic term allows for the dependence of the spontaneous emission coefficient on the transition frequency,

and the ν_3 quantum number dependence assumes harmonic oscillator behaviour. Fermi resonance between ν_1 and ν_2 was considered for levels with $\nu_1 < 10$. The resulting simulated spectrum was then corrected for instrumental spectral response and is compared with the experimental spectrum in Figure 4.5. It can be seen that the simulated spectrum for a Prior distribution peaks at higher wavenumbers than is observed experimentally, suggesting that the observed distribution is vibrationally hotter than statistical. In order to quantify the shift, a Surprisal parameter, λ_1 is introduced to the population function as shown in Equation 4.9.

$$P = P^0(\nu_1, \nu_2, \nu_3) \exp(-\lambda_1 f_\nu) = N(f_\nu)^3 (1 - f_\nu)^{\frac{7}{2}} \exp(-\lambda_1 f_\nu) \quad (4.9)$$

A negative Surprisal parameter λ_1 , representing a hotter than statistical distribution, shifts the peak of the calculated emission to lower wavenumbers as expected. Figure 4.5 shows the fit obtained with $\lambda_1 = -4.5$, which simulates the observed peak well, but predicts a narrower distribution. Vibrational mode specific Surprisal parameters have been used to model triatomic infrared emission where the simple analysis yielded distributions broader than observed [21], but was not attempted in this present case because of the difficulty of finding a unique combination of the three adjustable parameters with confidence. A Surprisal parameter of -4.5 implies the average vibrational energy in CO_2 produced by process (4.1) is 59 % of that available compared with 47 % expected statistically.

The possibility of the emission arising from CO_2 and N_2O produced by reac-

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tion of NCO, formed in process (4.4), with NO is dismissed.



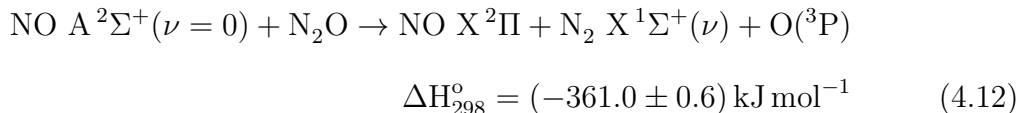
The infrared emission arising from reactions (4.10) and (4.11) peaks at 2100 cm^{-1} [21], considerably shifted from that shown in Figure 4.5. In addition, the present emission (both in the CO_2 fundamental and combination band regions) is always seen to be prompt, appearing with the rise time of the detector, of the order of 2–3 μs , whereas that from the reactive processes (4.10) and (4.11) would be expected to have a rise time an order of magnitude larger at 50 mTorr NO, calculated from the rate constant of $3.1 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ [21].

4.2.4 Comparison with quenching by N_2O

Comparison is now made between this system and that of quenching of NO A $^2\Sigma^+(\nu = 0)$ by N_2O , which has been studied previously in the group [2, 22]. Both systems are similar in that the quenchers are both triatomic, meaning that there is a large number of possible modes that the electronic energy can be channelled into as a result of a collision with an NO A $^2\Sigma^+(\nu = 0)$ molecule. Of particular interest in the study of the N_2O system is the kinetic behaviour of the N_2O $\Delta\nu = -1$ band. The nascent emission of this band was found to be weak, with the peak of the emission close to the fundamental band position at 2223 cm^{-1} , which then increased in intensity with time. This was explained by energy transfer from vibrationally excited N_2 , formed by the reactive quenching

4.2. Quenching of NO A $^2\Sigma^+(\nu = 0)$

process shown in Equation 4.12.



It was concluded that this pathway was the dominant quenching process. This contrasts with the equivalent emission band of CO_2 , which at early time is intense and dramatically red-shifted from its fundamental position. Clearly the two systems have very different efficiencies at channelling energy into the vibrational modes of the quenching molecule. It was attempted to accurately scale the nascent emissions from N_2O and CO_2 . To do this, an experiment was performed in which both CO_2 and N_2O were present. Partial pressures were chosen such that there was equal contribution from each molecule to the quenching of electronically excited NO molecule ($\Phi_{\text{N}_2\text{O}} = \Phi_{\text{CO}_2} = 0.05$). Due to the large shift of the CO_2 emission, the nascent N_2O emission was apparent as a shoulder on the high wavenumber side of the CO_2 emission. Experiments were then performed with CO_2 and N_2O quenching the NO A $^2\Sigma^+(\nu = 0)$ state separately with a quantum yield of 0.1. Early time (4 μs) spectra from these experiments were then scaled according to the emission observed from the mixed quenching experiment. The NO fundamental emission was subtracted from all the spectra, in the same manner as described earlier. The result of the above procedure is shown in Figure 4.6 where the nascent CO_2 and N_2O emission, correctly scaled, can be seen. The Einstein A coefficients for the $\Delta\nu_3 = -1$ transitions in the two triatomic molecules are similar to within a factor of 2: for the $(0,0,1) \rightarrow (0,0,0)$ transitions the values are 340 s^{-1} for CO_2 and 195 s^{-1} for N_2O [23]. The difference

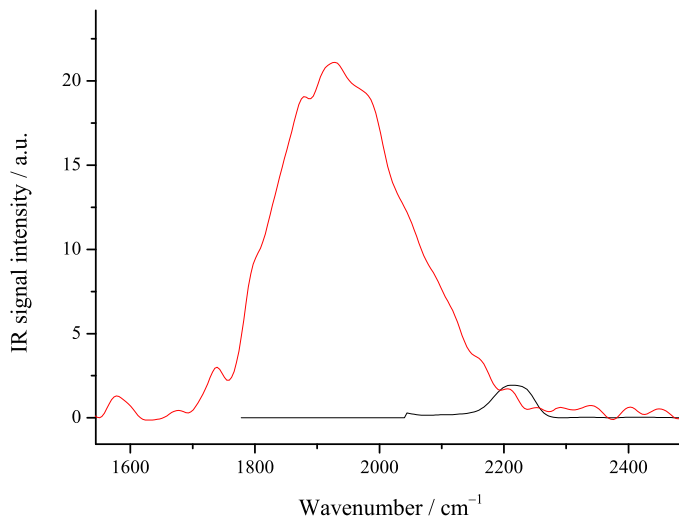


Figure 4.6: IR emission spectrum recorded at a resolution of 20 cm^{-1} following the pumping of 50 mTorr NO on the overlapped Q_1 and P_{21} band heads of the NO $A^2\Sigma^+(\nu = 0) \leftarrow X^2\Pi(\nu = 0)$ transition in the presence of 50 Torr Ar and either 46 mTorr CO_2 (red, $\Phi_{\text{CO}_2} = 0.1$) or 45 mTorr N_2O (black, $\Phi_{\text{N}_2\text{O}} = 0.1$). The spectra have been scaled according to an experiment where NO $A^2\Sigma^+(\nu = 0)$ was quenched by both N_2O and CO_2 with equal quantum yields. The NO $X^2\Pi(\Delta\nu = -1)$ signal has been subtracted.

in the intensities can be rationalised by considering the respective efficiencies for non-reactive quenching in the two systems; the non-reactive quenching by CO_2 (channel (4.1)) has a lower limit of 0.26, while the equivalent process for N_2O quenching was reported to be a minor channel, with the reactive process (4.12) dominating [22]. Therefore it appears clear that non-reactive quenching of NO $A^2\Sigma^+(\nu = 0)$ by N_2O is far less efficient at populating vibrationally excited levels in the acceptor molecule than is the equivalent quenching process by CO_2 (channel (4.1)). It is also noted that the N_2O vibrational distribution peaks far more closely to its fundamental band (2223 cm^{-1}) than does that for CO_2 (2349 cm^{-1}), showing that CO_2 vibrational excitation accounts for a much greater proportion

of the available energy than does N_2O .

4.2.5 Discussion

The results are first compared with those of previous investigations. Settersten *et al.* [1] found a population of NO X $^2\Pi(\nu = 0)$ produced by the quenching of NO A $^2\Sigma^+(\nu = 0)$ by CO_2 of some 60 %, considerably higher than the population produced by other quenching partners CO, O_2 and H_2O . Observations in this chapter suggest that an upper limit for the quantum yield for NO X $^2\Pi(\nu = 0)$ is the sum of the appropriate fraction of process (4.1), 6 %, and the sum of the other two major processes (4.6) and (4.2), 74 %, giving a total of 80 %. A lower value could arise from any NO X $^2\Pi(\nu = 1)$ formed in (4.6) and from contributions from (4.3) and (4.4). Therefore the results presented here concur with Settersten *et al.* [1] that the formation of vibrationally unexcited NO X $^2\Pi(\nu = 0)$ is the major process. Cohen and Hecklen [24] employed end product analysis to measure the production of CO following the excitation of NO A $^2\Sigma^+(\nu = 0, 1)$ in the presence of CO_2 , and concluded that CO was a major reaction product. More recently Codnia *et al.* [25] have measured end products NO_2 and CO formed in a 1:1 ratio following the quenching of NO A $^2\Sigma^+(\nu = 2)$ with CO_2 . Under their experimental conditions both processes (4.2) and (4.3) would yield these products as recombination of O atoms formed in process (4.2) with NO would occur. They concluded that 25 % of the quenching process takes place by reaction. Although these observations differ markedly, the present data are unable to provide a clear distinction because of the unknown branching ratio of the channels producing unobserved NO X $^2\Pi(\nu = 0, 1)$.

4.2. Quenching of NO A $^2\Sigma^+(\nu = 0)$

This supports the conclusions of Settersten *et al.* [1] that corrections will be required to saturated LIF signals from NO at pressures of CO₂ such that repopulation of the observed ground vibrational state is likely during the excitation pulse. For example, these results indicate that for a mixture of air with 5 % CO₂ at atmospheric pressure, some 25 % of the excited NO A $^2\Sigma^+(\nu = 0)$ will be returned to the probed NO X $^2\Pi(\nu = 0)$ state by collisions solely with CO₂ in a time of around 2 ns, shorter than most standard LIF pulses. Although quenching by O₂ returns a smaller fraction of the NO A $^2\Sigma^+(\nu = 0)$ molecules to NO X $^2\Pi(\nu = 0)$ than does CO₂ [1], under the same conditions the process would result in some 20 % repopulation of the ground state in this example. Measurements of the temperature dependence of the quenching rate constants with CO₂ [5, 7, 15] have been used to infer the quenching mechanism. Between 215 K and 520 K the values decrease with increasing temperature, and at higher temperatures achieved in shock tube studies (up to 2400 K), then show a modest increase. The decrease has been explained in terms of formation of a collision complex [5, 7, 15] and would be in agreement with the statistical distributions observed here in NO, but for both quenching molecules an extra mechanism needs to be invoked to explain the dominance of the reactive channels. The mild increase in quenching rate constant for CO₂ has been explained by a model [26] which allows both collision complex formation and, at higher energies, a charge transfer (harpoon) mechanism leading to the formation of NO⁺ and CO₂⁻. Both mechanisms are assumed to occur, their fractional importance depending upon the position of the centripetal barrier to complex formation relative to that of the electron transfer distance r_c (the crossing point of neutral and ionic states) [5]. If the harpooning mechanism is ‘sudden’, producing NO⁺ in $\nu = 0$, then electron transfer to give NO X $^2\Pi$ would

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

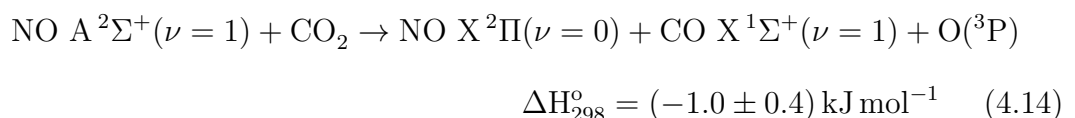
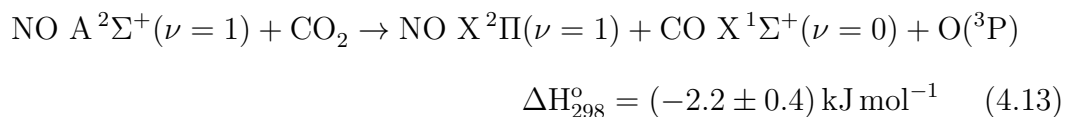
result in a vibrational distribution reflecting the NO X $^2\Pi$ —NO $^+$ Franck-Condon factors, which peak at low ν ($\nu = 1$ and 2) [1] and thus could contribute to any unobserved NO formed by process (4.6), but cannot be dominant in producing $\nu = 0$ because of the unfavourable Franck-Condon factors. It is noted, however, that the application of such models to collisional electronic quenching has been called into question [27]. Franck-Condon arguments applied to CO $_2$ —CO $_2^-$ would predict considerable vibrational excitation in all degrees of freedom because of the large geometry change expected between the neutral molecule and the anion [28]. If the ion-pair state crossed immediately to form CO $_2$ above the barrier to dissociation, process (4.2) would result forming CO and O(3P) products. This argument would predict that reaction would dominate at higher temperatures as suggested by Settersten *et al.* [7]. A second prediction would be that the distance r_c would be increased by vibrational excitation in NO A $^2\Sigma^+$ and would lead to a higher quantum yield of reaction. In addition it would be expected that a greater proportion of NO $_2$ formed by reaction between NO A $^2\Sigma^+(\nu = 1)$ with CO $_2$ would be vibrationally excited, as it seems reasonable that any excitation in the NO reactant would be retained during the reaction, to form NO $_2$ in a vibrationally excited state. These latter predictions will be addressed in the following section, which describe the investigation of the quenching of NO A $^2\Sigma^+(\nu = 1)$ by CO $_2$.

4.3 Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

The electronic quenching of NO A $^2\Sigma^+(\nu = 1)$ has received less attention in the literature than the quenching of NO A $^2\Sigma^+(\nu = 0)$, with comparatively few stud-

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

ies investigating the effect of vibrational excitation in NO A $^2\Sigma^+$ on the kinetics and dynamics of the quenching process [3, 6]. A study by Nee *et al.* [3] investigating the quenching of NO A $^2\Sigma^+(\nu = 0-3)$ by a variety of collision partners found that in general the quenching rate coefficients increased as a function of vibrational excitation in the NO A $^2\Sigma^+$ molecule. This is ascribed to the contribution of vibrational relaxation within the electronically excited state by the collision partner, which results in a faster quenching process. A potentially interesting feature of the NO A $^2\Sigma^+(\nu = 1) + \text{CO}_2$ system is that enough energy is liberated to allow the formation of CO and NO X $^2\Pi$ with one quanta of vibrational excitation between them, as shown in Equations 4.13 and 4.14, a process which is not energetically feasible when CO₂ quenches NO $^2\Sigma^+(\nu = 0)$ (process (4.2)).



4.3.1 Preliminary experiments

Prior to the experiments investigating the quenching of NO A $^2\Sigma^+(\nu = 1)$ by CO₂ being performed, various preliminary experiments were required. First, as was performed in Section 3.3 for the quenching of the NO A $^2\Sigma^+(\nu = 0)$ state, an excitation spectrum was acquired where the intensity of the LIF signal, from the NO A $^2\Sigma^+(\nu = 1)$ state, and IR emission following the excitation pulse, are measured as a function of pumping wavelength. This allows confirmation that

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

NO $A^2\Sigma^+(\nu = 1)$ is being generated, and that the resultant IR emission is from products of quenching pathways rather than from other undesired processes. A sample of 50 mTorr of NO was pumped in the range of 214.640 nm to 215.520 nm, which contains many rotational lines of the NO $A^2\Sigma^+(\nu = 1) \leftarrow X^2\Pi(\nu = 0)$ transition. IR emission between 2200 cm^{-1} and 4000 cm^{-1} , corresponding to the NO overtone emission, and LIF, in the range of 345 nm to 400 nm, which corresponds to the $A^2\Sigma^+(\nu = 1) \rightarrow X^2\Pi(\nu = 10-12)$ transitions, were recorded as the laser was scanned in steps of 0.77 pm. Figure 4.7 (a) shows how the inte-

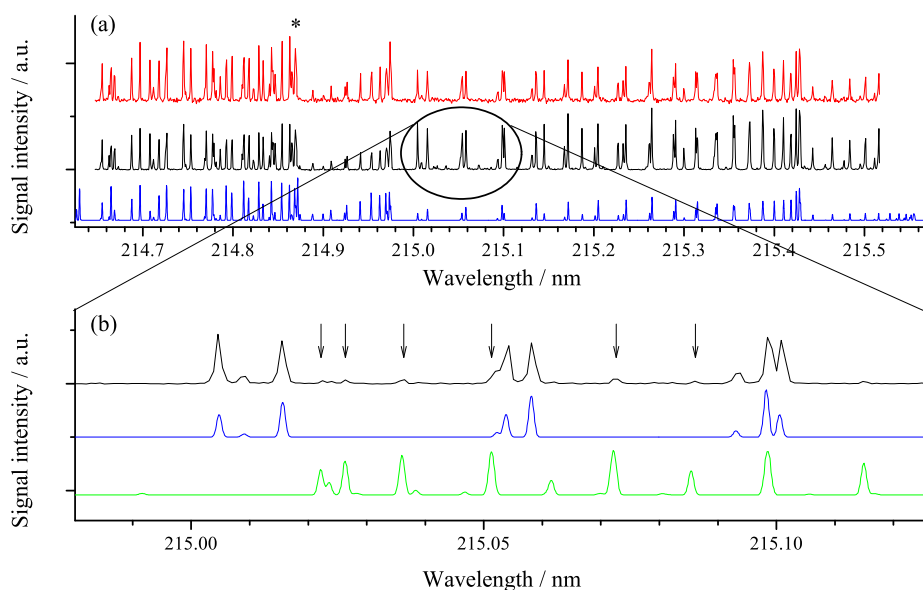


Figure 4.7: Excitation spectrum obtained following pumping of 50 mTorr of NO as the pumping laser is scanned across the region 214.640 nm to 215.520 nm. (a) Full range of scan, with IR emission from the region 2200 cm^{-1} to 4000 cm^{-1} (red) and LIF detected in the range of 345 nm to 400 nm (black). Also shown is the simulated NO $A^2\Sigma^+(\nu = 1) \leftarrow X^2\Pi(\nu = 0)$ absorption spectrum from the LIFBASE spectral simulation program [29] (blue). (b) shows a narrower range of the excitation spectrum with the LIF trace (black) and NO $A^2\Sigma^+(\nu = 1) \leftarrow X^2\Pi(\nu = 0)$ simulation (blue). In addition the NO $B^2\Pi(\nu = 1) \leftarrow X^2\Pi(\nu = 0)$, also from the LIFBASE simulation program [29] (green). The arrows above the excitation spectrum in (b) show the positions of the B-X absorptions.

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

grated IR and LIF intensities vary as a function of excitation wavelength, and it can be seen that both the IR and the LIF excitation spectra match the line positions of the NO A-X (1,0) absorption spectrum as predicted by the LIFBASE spectral simulation program [29] extremely well. Additionally, there is very good agreement between the relative intensities of the LIF and the IR excitation spectra, indicating that the IR emission is dependent only on the NO A $^2\Sigma^+(\nu = 1)$ being formed, and is not due to photolysis of an impurity. However, there are weak features, resolvable in the LIF data (which has a superior signal-to-noise ratio) that do not correspond to any NO A-X (1,0) transition lines. Figure 4.7 (b) shows a few of these features, indicated with ($\downarrow$) on an expanded x axis, where it is apparent that these features are a result of excitation to the NO B $^2\Pi(\nu = 1)$ state, which is almost isoenergetic with the NO A $^2\Sigma^+(\nu = 1)$ state. The temporal behaviour of the LIF signal following the excitation of one of these lines exhibits a lifetime of around 950 ns, longer than that of the NO A $^2\Sigma^+(\nu = 1)$ state. The radiative lifetime of the NO B $^2\Pi(\nu = 1)$ state is 1.72 μs [30]. The rate constant for quenching of NO B $^2\Pi(\nu = 1)$ by NO has not been measured, but if it is assumed that, as for the A $^2\Sigma^+$ state, the quenching coefficients of $\nu = 0$ and 1 are similar, then the predicted lifetime of NO B $^2\Pi(\nu = 1)$ under the present conditions (50 mTorr of NO) is 970 ns, taking the quenching rate constant of NO B $^2\Pi(\nu = 0)$ as $2.79 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [31]. The pumping wavelength used for the majority of the experiments within the rest of this chapter was 214.872 nm, which does not overlap with the NO B-X (1,0) transitions.

Next, a low resolution survey spectrum of IR emission following the excitation of a sample of 50 mTorr of NO to the A $^2\Sigma^+(\nu = 1)$ state was recorded and is

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

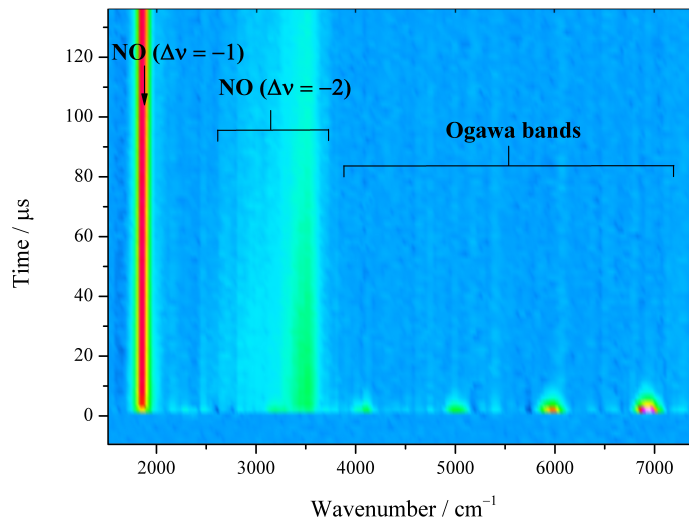


Figure 4.8: Spectrum of emission observed in the range 1800 cm^{-1} to 7500 cm^{-1} following the excitation of 50 mTorr of NO to the $A^2\Sigma^+(\nu = 1)$ state with radiation at 214.872 nm . Spectrum recorded with InSb detector and acquired at 40 cm^{-1} resolution. Red represents high intensity and blue represents low intensity.

shown in Figure 4.8, where a number of emission features are seen. The long-lived bands at $\sim 1900\text{ cm}^{-1}$ and 3500 cm^{-1} are the fundamental and first overtone vibrational emissions of NO $X^2\Pi$ respectively. At higher wavenumbers, $> 4000\text{ cm}^{-1}$, there are emission features that have not been observed following excitation of NO to the $A^2\Sigma^+(\nu = 0)$ state. There are four equally spaced bands at around 4000 cm^{-1} , 5000 cm^{-1} , 6000 cm^{-1} and 7000 cm^{-1} . All the features exhibit the same kinetics, strongly suggesting that the emissions all originate from the same state, with the spacing of the bands representing the energy separation of the lower states. The emission is likely to be electronic in nature as its frequency is too high to be ascribed to the strong fundamental vibrational transitions, and it is too intense to be emission from overtone or combination bands. To rule out the possibility of two photon processes being responsible, a power dependence exper-

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

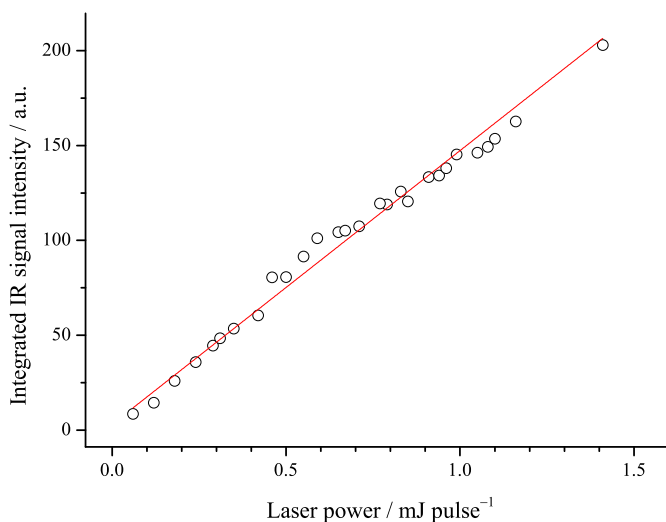


Figure 4.9: The dependence of IR emission intensity at 6000 cm^{-1} on laser pulse energy. Emission was detected following pumping of 50 mTorr of NO at 214.872 nm. A linear fit is also shown (red).

iment was performed, where the intensity of the IR emission from these bands was measured as a function of laser fluence. If the emission is the result of a (non-saturated) single photon process then a linear relationship will be observed. If two photon processes are even partly responsible, then the data will exhibit a non-linear trend. The result of this experiment is shown in Figure 4.9, and it is clear that there is a strong linear relationship, confirming these emission bands are a result of a one photon process. Absorption of a single photon of 215 nm provides the molecule with $46\,500\text{ cm}^{-1}$ of energy. There are five electronic states that can be accessed, the $X^2\Pi$, $A^2\Sigma^+$, $B^2\Pi$, $a^4\Pi$ and $b^4\Sigma^-$ as can be seen in the potential energy diagram presented by Copeland *et al.* [32], reproduced in Figure 4.10. The vibrational wavenumbers are given by the vibrational constants are 1904.1 cm^{-1} , 2374.4 cm^{-1} , 1037.5 cm^{-1} , 1016.2 cm^{-1} and 1262.4 cm^{-1} [33] [34]

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

[35] [36] respectively. Given the spacing of the observed emission bands (around

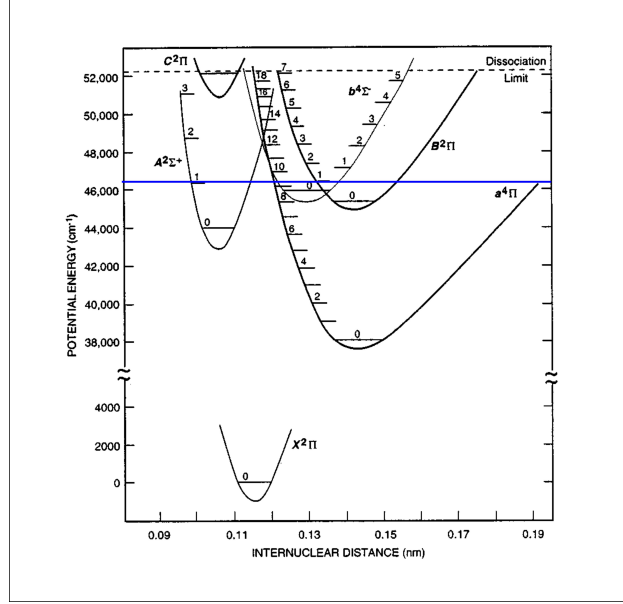


Figure 4.10: The potential energy curves for the different electronic states of NO below $55\,000\text{ cm}^{-1}$, as shown in reference [32]. The energy corresponding to absorption of one photon of 215 nm is also shown (blue).

1000 cm^{-1}), only the $B^2\Pi$ and the $a^4\Pi$ states have the correct vibrational spacing to be the lower states for the observed transitions, and with consideration of the respective potential energy curves shown in Figure 4.10 it is clear that the $B^2\Pi$ state is too high in energy to be the acceptor levels. This leads to the conclusion that the lower state of these transitions are the vibrational levels of the $a^4\Pi$ state. These transitions are intense, indicating that it is an allowed transition, so the upper state must also be a quartet state, the $b^4\Sigma^-$ state. Consideration of the relative energies of the vibrational levels of the two states allows identification of the observed transitions to be the Ogawa bands, $b^4\Sigma^-(\nu = 0) \rightarrow a^4\Pi(\nu)$. An early time ($2\text{ }\mu\text{s}$) spectrum is shown in Figure 4.11 (a), with the positions of the Ogawa transitions indicated, calculated from constants presented by Huber

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

et al. [36]. The $b^4\Sigma^-(\nu = 0) \rightarrow a^4\Pi(\nu = 0)$ band is not shown as the optical filter employed does not transmit at the relevant frequency. This assignment of these emission features allows a further peak to be identified, corresponding to emission from the NO $b-a(0,5)$ band at 3140 cm^{-1} . Further confirmation of the assignment was provided by a high resolution spectrum the $b^4\Sigma^-(\nu = 0) \rightarrow a^4\Pi(\nu = 2)$ at around 6000 cm^{-1} , and comparing it to a spectrum simulated in PGOPHER [37] using the rotational constants presented by Huber *et al.* [36]. A rotational temperature of 500 K was found to provide the best match to the experimental data and, as can be seen in Figure 4.11 (b), the agreement between the simulation and experimental data is convincing. The observation of

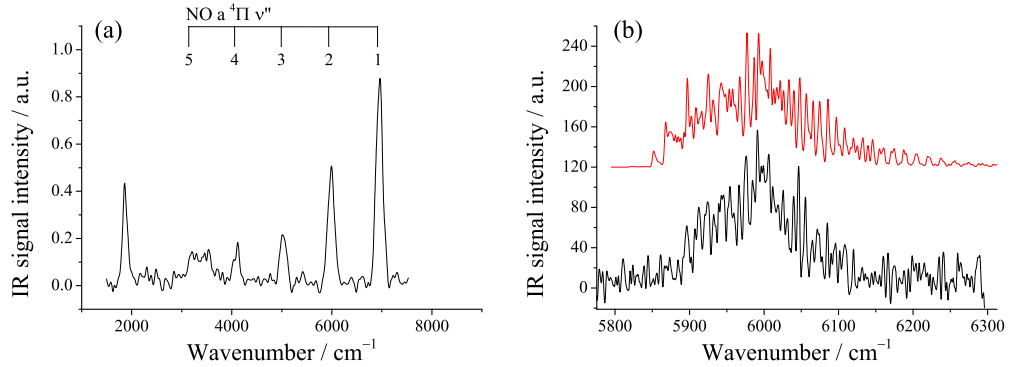


Figure 4.11: (a) Spectrum of emission at $2\text{ }\mu\text{s}$ following the excitation of 50 mTorr of NO at 214.872 nm , recorded at a resolution of 40 cm^{-1} . The positions of the Ogawa bands are marked. (b) Spectrum of the $b^4\Sigma^-(\nu = 0) \rightarrow a^4\Pi(\nu)$ emission band at $\sim 6000\text{ cm}^{-1}$, recorded $2\text{ }\mu\text{s}$ after the excitation pulse and at a resolution of 2 cm^{-1} (black). Also shown is a simulated spectrum, offset for clarity, with a rotational temperature of 500 K (red). An InSb detector was used to record the emission in both cases.

the Ogawa bands emitting promptly upon the absorption of a single photon of 215 nm indicates that NO is rapidly transferring from the $A^2\Sigma^+(\nu = 1)$ state to the $b^4\Sigma^-(\nu = 0)$ state. The rise time of the signal was reduced by the addition of Ar, indicating the transition is collisionally induced. The $A^2\Sigma^+(\nu = 1)$ state

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

is almost isoenergetic with the B $^2\Pi(\nu = 1)$ state, so there could be fast transfer to the B $^2\Pi$ state first before collisional transfer to the b $^4\Sigma^-(\nu = 0)$. A work by Heldt *et al.* [38] studied the transfer from the quartet states of NO, a $^4\Pi$ and b $^4\Sigma^-$ to the B $^2\Pi$ state, and found they it occurred *via* a few specific rotational states in a gateway-type process. Therefore it is not unlikely that the reverse process could happen. This would produce b $^4\Sigma^-(\nu = 0)$ state molecules in a few specific rotational states. The rotational temperature of the b $^4\Sigma^-(\nu = 0)$ state is estimated from the emission spectra in Figure 4.11 (b) to be around 500 K, thus while full rotational thermalisation has not occurred there is clearly a range of rotationally populated levels, indicating that some collisional redistribution has occurred. The effect of the initial rotational excitation in the A $^2\Sigma^+(\nu = 1)$ state was investigated by varying the excitation wavelength. The observed emission, at a resolution of 10 cm^{-1} , exhibited no observable change in the Ogawa emission features. Another possible mechanism is that vibrational relaxation within the A $^2\Sigma^+$ state could occur first, populating a distribution of rotational levels in the ground vibrational state, some of which could be gateway levels to either the B $^2\Pi$ or b $^4\Sigma^-$ states. The rotational distribution in the resultant NO A $^2\Sigma^+(\nu = 0)$ state following vibrational relaxation from the NO A $^2\Sigma^+(\nu = 1)$ state has not been measured, but it has for the equivalent process in OH [39]. Quite broad rotational distributions were observed, with up to one third of the vibration energy appearing in rotation. To fully rationalise the transfer mechanism, high resolution experiments probing for B $^2\Pi$ state molecules will need to be performed to assess their contribution. An estimate of the branching ratio for this process can be obtained by comparison of the intensities of the NO X $^2\Pi$ overtone emission and the two nearby Ogawa bands at 3140 cm^{-1} and 4050 cm^{-1} . The emission

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

coefficients for these two bands are 876 s^{-1} and 2600 s^{-1} respectively [40], several orders of magnitude greater than those for the NO X $^2\Pi$ overtone emission. The peak of the overtone emission as seen in Figure 4.11 (a) comes at $\sim 3550\text{ cm}^{-1}$, which corresponds to the NO X $^2\Pi(\nu = 5 \rightarrow 3)$ transition, which has an Einstein A coefficient of 7 s^{-1} [41]. Fluorescence is the dominant removal process of NO A $^2\Sigma^+(\nu = 1)$ under the current experimental conditions, which channels around 10 % into the NO X $^2\Pi(\nu = 5)$ state. After correcting for the InSb detection function and consideration of the relative intensities of these emissions and their respective emission coefficients, it is concluded that transfer of NO from the A $^2\Sigma^+(\nu = 1)$ state to the b $^4\Sigma^-(\nu = 0)$ state accounts for less than 0.5 % of NO A $^2\Sigma^+(\nu = 1)$ generated and as such, this processes is negligible and will not affect the following investigations into the quenching of NO A $^2\Sigma^+(\nu = 1)$ by CO_2 . The addition of 50 Torr of Ar removed these emission features by $1\text{ }\mu\text{s}$ so there were no issues with regard to overlapping spectral emission features.

4.3.2 IR emission from within the NO A $^2\Sigma^+$ state

The electronic quenching of NO A $^2\Sigma^+(\nu = 1)$ has not been previously studied using FTIR emission spectroscopy. However, the quenching of the equivalent state in OH has [2]. In that work strong IR emission from within the electronic excited state was observed. In light of these observations, experiments were performed to ascertain whether such emission could be observed in NO. Figure 4.12 (a) shows a contour plot of the NO X $^2\Pi$ vibrational overtone emission spectrum obtained following the quenching of NO A $^2\Sigma^+(\nu = 1)$ by 50 mTorr of NO in the presence of 50 Torr of Ar. In addition to the structured NO overtone emission, there is

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

a short-lived emission feature appearing at 2400 cm^{-1} . Figure 4.12 (b) shows a spectrum recorded $1\text{ }\mu\text{s}$ after the excitation pulse, which shows clearly a doublet, centred at 2350 cm^{-1} , which lies in the correct position to be the P and R branches of the NO $A^2\Sigma^+(\nu = 1) \rightarrow \text{NO } A^2\Sigma^+(\nu = 0)$ vibrational transition; the transition is not expected to have a Q branch as both states are Σ states. Further experiments were then performed to confirm the identify of the emission. The

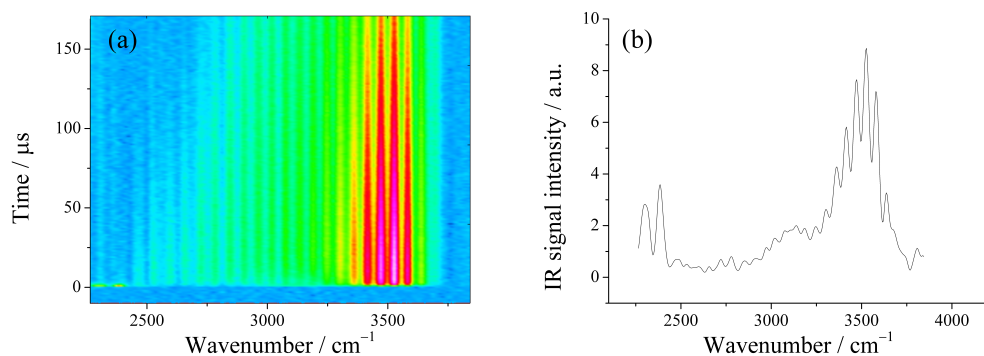


Figure 4.12: (a) Contour plot of emission observed following the pumping of 50 mTorr of NO to its $A^2\Sigma^+(\nu = 1)$ state in the presence of 50 Torr of Ar. Emission was detected with InSb detector, and spectra recorded at a resolution of 20 cm^{-1} . Red represents high intensity and blue represents low intensity. (b) Spectrum taken at $1\text{ }\mu\text{s}$ following the pumping laser. The spectrum has been corrected for optical filter and detector functions.

narrow line width of the excitation laser ($\sim 3.5\text{ pm}$), allowed NO to be excited on either a single, or a couple of overlapped lines, generating NO $A^2\Sigma^+(\nu = 1)$ in a few specific rotational states. In the experiment shown in Figure 4.12, 50 Torr of Ar was present, which will rotationally thermalise the distribution, allowing clear observation of strong P and R branches. If the emission is from vibrational transitions within the $A^2\Sigma^+$ state, in the absence of Ar, the emission spectrum should show a distinct dependence of the excitation wavelength, as different rotational levels in the NO $A^2\Sigma^+(\nu = 1)$ state are populated. Experiments were

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

performed at high resolution (1 cm^{-1}) exciting NO at four wavelengths, listed in Table 4.2 along with the quantum state assignments. For each experiment, only a few sharp emission features were observed, which were seen to shift as the pumping wavelength was varied. The spectra from these experiments, together with a simulated NO A $^2\Sigma^+(\nu = 1) \rightarrow$ NO A $^2\Sigma^+(\nu = 0)$ emission spectrum using vibrational and rotational constants from Danielak *et al.* [34] and the PGO-PHER simulation program [37] are shown in Figure 4.13. As can be seen the positions of the various emission features match well to vibration-rotational lines of the simulated spectrum. Table 4.2 lists the expected A $^2\Sigma^+$ state emission lines for each pumping wavelength. All the observed lines, indicated by (*) in Figure 4.13 are expected and appear at the correct frequency. There were two emission lines that were expected but not observed (marked in red in Table 4.2), but it is believed these lines are simply lost in the noise, given the relatively poor signal-to-noise ratio. It is fairly convincing that the emission observed in this region is NO A $^2\Sigma^+(\nu = 1 \rightarrow 0)$ vibrational emission. Under the experimental conditions the lifetime of the NO A $^2\Sigma^+(\nu = 1)$ state is 180 ns. The sampling rate of the experiment is 1 MHz, and the reason A $^2\Sigma^+$ state IR emission appears in the spectra shown in Figure 4.12, and lasts for a few microseconds is due to the rise (and fall) time of the detection system. In order to understand the intensity of the emission, relative to the overtone transitions in the X $^2\Pi$ state, it is first necessary to deconvolute the time response of the detection system. The response function was determined by measuring the temporal output of the InSb when a tiny fraction of Nd:YAG fundamental laser scatter was detected. The amplification settings were kept the same as those used for the acquisition of the spectra shown in Figure 4.12. The FWHM of the laser pulse is 17 ns, which is

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

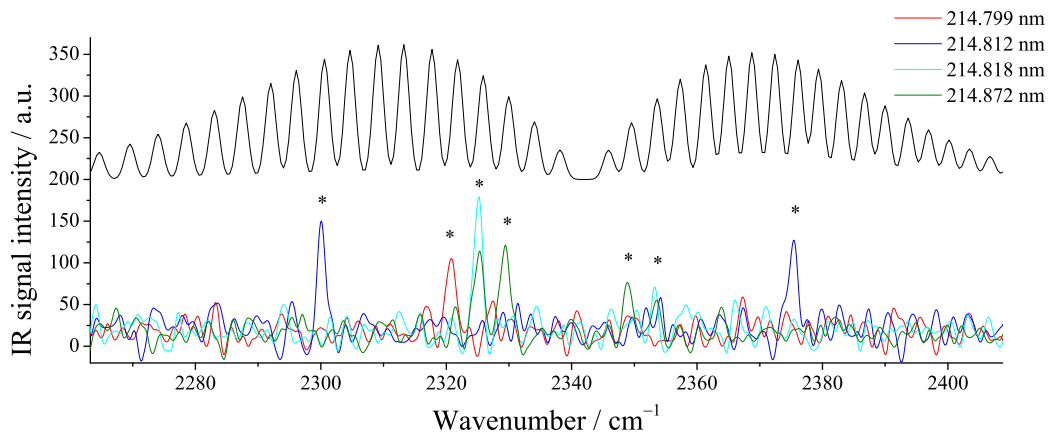


Figure 4.13: Emission spectra observed following the excitation of a sample of 50 mTorr of NO at 214.799 nm (red), 214.812 nm (blue), 214.818 nm (cyan) and 214.872 nm (green). Spectra obtained at a resolution of 1 cm^{-1} with an InSb detector. Also shown (black) is the NO $A^2\Sigma^+(\nu = 1 \rightarrow 0)$ simulated emission spectrum, offset for clarity, with a rotational temperature of 300 K. Features considered to be resolvable over the noise are indicated (*).

short enough, relative to the timescale of the detection system, not to require deconvolution. An exponential decay function, with a decay time of 180 ns was convoluted with the detection response function, and the output scaled to match the measured temporal profile of the $A^2\Sigma^+$ state emission. This revealed that the true nascent intensity of the $A^2\Sigma^+$ state emission was factor of 8.9 times larger than it appears in the 1 μs spectrum shown in Figure 4.12 (a). This is then compared to the overtone emission from within the ground electronic state of NO at 5 μs , to avoid the influence of the rise time of the detector. Fitting a spectral simulation to the overtone spectrum allows the relative contribution of each vibrational band to be determined. At the low pressure of NO employed it was assumed that the population distribution was given by the respective emission coefficients of the NO $A-X(1,\nu)$ transitions, allowing the measured populations to be scaled relative to the initial population excited to the NO $A^2\Sigma^+(\nu = 1)$

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

Table 4.2: Table showing the wavelength positions and identities of the transitions in the NO A-X (1,0) band employed for the experiments observing NO A $^2\Sigma^+$ vibrational fundamental emission. The nomenclature for the transitions are as defined in Section 1.5. Also listed are the upper states that are generated by excitation for each line and the expected NO A $^2\Sigma^+(\nu = 1 \rightarrow 0)$ emission lines. The expected emission lines marked in **red** were not observed.

λ / nm	Absorption Lines	Upper state populated			Expected emission lines
		J'	N'	F	
214.799	R ₁ (3)	4.5	4	1	P(5), R(3)
	Q ₂₁ (3)	3.5	4	2	
214.812	Q ₁ (9)	9.5	9	1	P(10), R(8)
	P ₂₁ (9)	8.5	9	2	
214.818	R ₁ (2)	3.5	3	1	P(4), R(2)
	Q ₂₁ (2)	2.5	3	2	
214.872	Q ₁ (2)	2.5	2	1	P(3), R(1)
	P ₂₁ (2)	1.5	2	2	
	Q ₁ (3)	3.5	3	1	P(4), R(2)
	P ₂₁ (3)	2.5	3	2	

state. As the intensity of emission is proportional to the emission coefficient and the population of the emitting state, an estimate for the Einstein A factor for the NO A $^2\Sigma^+(\nu = 1 \rightarrow 0)$ transition can be made simply by comparing the relative intensity of the different emission bands (after correction for detection response). The intensity of the emission from the $\nu = 5-7$ levels were chosen for the comparison, as they were the most intense, due to a favourable combination of their overtone emission coefficients and their initial population resulting from radiative transfer from the NO A $^2\Sigma^+(\nu = 1)$ state. In this manner a value of $\sim(2.4 \pm 0.5) \text{ s}^{-1}$ is obtained for the emission coefficient for the IR emission from within the A $^2\Sigma^+$ state of NO. This is a factor of 6 weaker than the Einstein A coefficient for the equivalent X $^2\Pi$ state transition. While this value has not been reported in the literature, a value can be obtained by considering the dipole moment function, $\frac{\partial \mu}{\partial r}$, which (in the harmonic oscillator approximation) is related

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

to the emission coefficient by the relationship shown in Equation 4.15.

$$A_{\nu',\nu''} \propto \bar{v}_{\nu',\nu''}^3 |R|^2 \propto \bar{v}_{\nu',\nu''}^3 \left(\frac{\partial \mu}{\partial r} \right)^2 \quad (4.15)$$

The dipole moment function for the X $^2\Pi$ state has been reported as 2.24 D Å⁻¹ and 2.0 D Å⁻¹ by Langhoff *et al.* [42] and Buldakov *et al.* [43] respectively. For the A $^2\Sigma^+$ state the dipole moment function has been calculated as 0.067 D Å⁻¹ and 0.089 D Å⁻¹ by Langhoff *et al.* [42] and Grey *et al.* [44]. Using values of 1876 cm⁻¹ and 2342 cm⁻¹ for the transition frequencies within the X $^2\Pi$ and A $^2\Sigma^+$ states respectively, the calculated emission coefficient for the A $^2\Sigma^+$ state of NO lies within the range 0.02 s⁻¹ to 0.045 s⁻¹, which is much smaller than that estimated from the spectra presented in Figure 4.12. This suggests that either the calculation of the dipole moment function for the A $^2\Sigma^+$ state are in error, or some effect is occurring in the reaction cell to increase the intensity of the emission. It is felt unlikely that lasing is occurring as this would cause much greater intensity in the P branch compared to the R branch, due to the respective line strengths of the branches. It is acknowledged that there is a high degree of uncertainty in the Einstein A factor calculated from the spectra shown in Figure 4.12. The A $^2\Sigma^+$ state emission is observed by a detection system that is at least two orders of magnitude too slow to be able to produce a signal that represents the temporal profile of the emission. However, using faster detectors is not feasible due to the low intensity of the emission, which requires a certain degree of amplification.

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

4.3.3 Self-quenching of NO A $^2\Sigma^+(\nu = 1)$

Attention is now turned to the quenching of NO A $^2\Sigma^+(\nu = 1)$ by NO. Previous work by Hancock and Saunders [12] studying the self-quenching of NO A $^2\Sigma^+(\nu = 0)$ found the resultant NO X $^2\Pi(\nu)$ vibrational distribution to be hotter than statistical. The system under current consideration has an additional process that could occur which is vibrational relaxation within the A state. The vibrational relaxation by NO has a rate coefficient of $(8.8 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as measured by Imajo *et al.* [45]. The relaxation by Ar has not been measured, but is expected to be considerably slower. At the pressures employed in the experiments described in this section—500 mTorr of NO and 50 Torr Ar—vibrational relaxation within the A state will only account for 5 % of the collisional removal of the NO A $^2\Sigma^+(\nu = 1)$ state (calculated assuming the vibrational relaxation by Ar is similar to that by N₂, measured by Imajo *et al.* [45] to be $(2.0 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The experiment shown in Figure 4.12 was performed with a low pressure of NO, where radiative removal (fluorescence) of the NO A $^2\Sigma^+(\nu = 1)$ state is the dominant process. In order to investigate the dynamics of self-quenching of the NO A $^2\Sigma^+(\nu = 1)$, a higher quantum yield of self-quenching, Φ_{NO} (and therefore a higher pressure of NO) is required. Figure 4.14 shows a contour plot of the observed emission following quenching of NO A $^2\Sigma^+(\nu = 1)$ by 500 mTorr of NO. The emission observed corresponds to a hot vibrational distribution, and comparison between this contour plot and of that shown in Figure 4.12 highlights the striking effect of self-quenching pathway on the resultant NO X $^2\Pi(\nu)$ vibrational distribution. Under these conditions $\Phi_{\text{NO}} = 0.43$ with radiative transfer accounting for the rest, as the quenching by

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

argon is negligible. These data were then analysed in the same way as before.

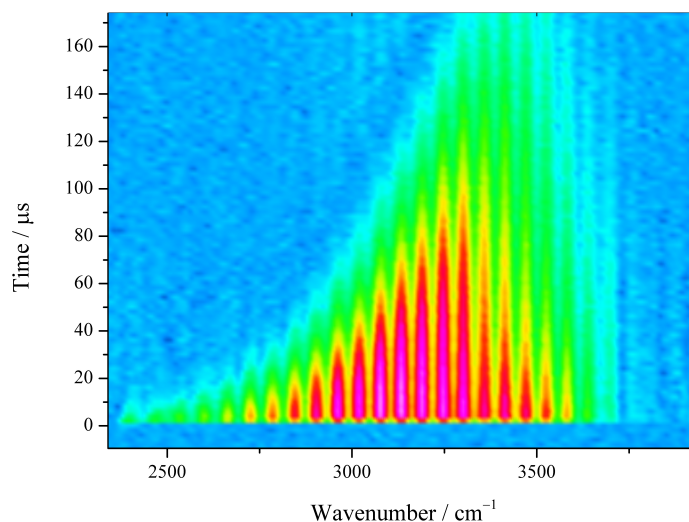


Figure 4.14: Contour plot of the vibrational overtone emission spectrum of NO $X^2\Pi$ observed following the pumping of 500 mTorr of NO on the overlapped Q_1 and P_{21} band heads of the NO $A^2\Sigma^+(\nu = 1) \leftarrow X^2\Pi(\nu = 0)$ transition at 214.872 nm in the presence of 50 Torr of Ar. Emission recorded at a resolution of 20 cm^{-1} with the InSb detector. Red represents high intensity and blue represents low intensity.

A spectral simulation, with a rotational temperature of 300 K was fitted to each time slice to afford a time dependent vibrational distribution. A kinetic model, which assumed multi-step and radiative processes were negligible, was then fitted to the temporal behaviour of the vibrational levels, allowing extrapolation to zero time so that a nascent vibrational distribution can be obtained. The vibrational distributions and their fits are shown in Figure 4.15. The distribution, as mentioned above, is hot with population observed in vibrational levels as high as $\nu = 24$. As before, Surprisal analysis was used to estimate the populations in NO $X^2\Pi(\nu = 0, 1)$. Since $\Phi_{\text{NO}} = 0.43$, the nascent distribution still contains a substantial contribution from fluorescence. NO self-quenching produces a hotter

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

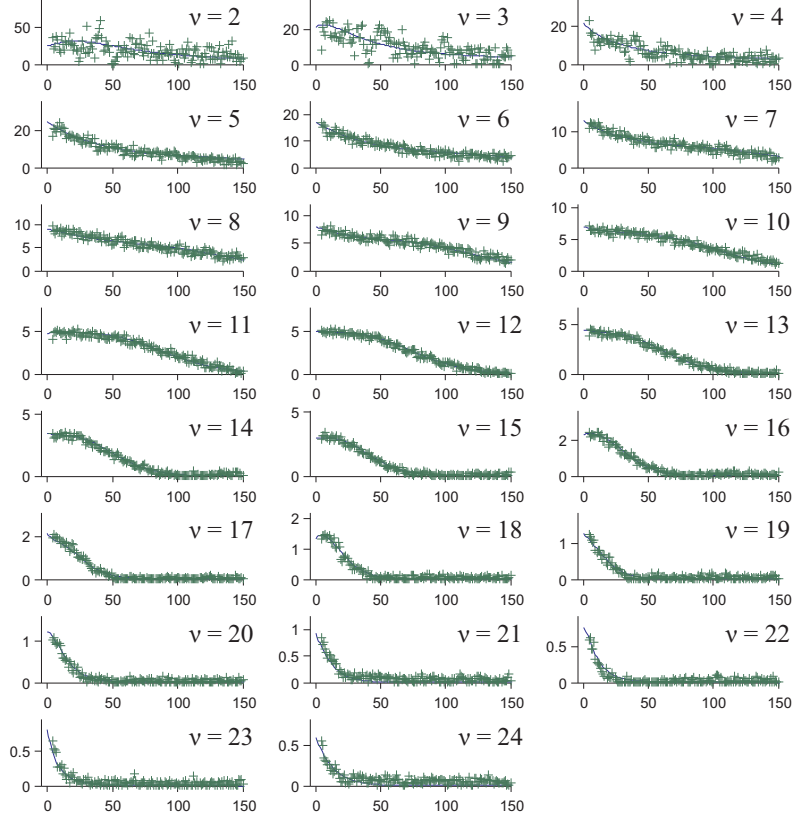


Figure 4.15: Plots of the time dependent vibrational distributions of NO $X^2\Pi(\nu)$, shown between $4\mu s$ and $150\mu s$ following the laser pulse, for of vibrational states $\nu = 2$ – 24 as labelled (+). Also shown are the distributions as obtained from the a global fitting of the kinetic model (blue). The x axis of all plots shows time in μs .

NO $X^2\Pi(\nu)$ distribution than fluorescence, which means Surprisal analysis can be performed using only the higher vibrational levels, which are populated only by self-quenching collisions. This process was used by Hancock and Saunders [12] when investigating the self-quenching of NO $A^2\Sigma^+(\nu = 0)$. For that work, vibrational levels $\nu > 7$ were used in the Surprisal analysis. Radiative transfer from the NO $A^2\Sigma^+(\nu = 1)$ state populates higher vibrational levels of NO $X^2\Pi$ than radiative transfer from the NO $A^2\Sigma^+(\nu = 0)$ state. From consideration of the

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

state-to-state emission coefficients for the NO A $^2\Sigma^+(\nu = 1) \rightarrow$ NO X $^2\Pi(\nu)$ transitions [29] it can be determined that less than 0.1 % of the molecules undergoing radiative decay will populate vibrational levels $\nu > 12$ in NO X $^2\Pi$. It is then reasonable to assume all the population in these levels results from the collisional quenching of NO A $^2\Sigma^+(\nu = 1)$ by NO, and so will be included in the Surprisal analysis procedure. The Prior distribution for this system (AB+CD $\rightarrow$ AB+CD) is calculated using methods outlined by Muckermann [17], and is shown in Equation 4.16.

$$P^0(f_\nu) = N(1 - f_\nu)^{\frac{7}{2}} \quad (4.16)$$

Figure 4.16 presents the Surprisal plot of $\ln[P(f_\nu)/P^0(f_\nu)]$ against f_ν for $\nu = 2$ –24. It is evident that there is a distinctly non-linear trend, which is explained by radiative transfer which will preferentially populate the lower vibrational levels of NO X $^2\Pi$. Focusing attention on the higher levels, the plot becomes approximately linear. A linear fit to these higher levels give values of 1.26 ± 0.20 and -3.3 ± 0.3 for the Surprisal parameters λ_0 and λ_1 respectively, as defined in Equation 1.7. From these Surprisal parameters populations for $\nu = 0$ –12 levels were estimated. This distribution was then subtracted from the measured one, which, if the analysis is robust, should match the distribution produced by radiative transfer, which is obtained from the emission coefficients of the NO A $^2\Sigma^+(\nu = 1) \rightarrow$ NO X $^2\Pi(\nu)$ transition. These two distributions are presented in Figure 4.17 (b), and exhibit good agreement with each other. Figure 4.17 (c) shows two distributions produced solely as a result of the quenching of NO A $^2\Sigma^+(\nu = 1)$ by NO, one predicted by the Surprisal parameters, and the other as calculated by subtracting the appropriately scaled vibrational distribution due to radiative transfer (as shown in red

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

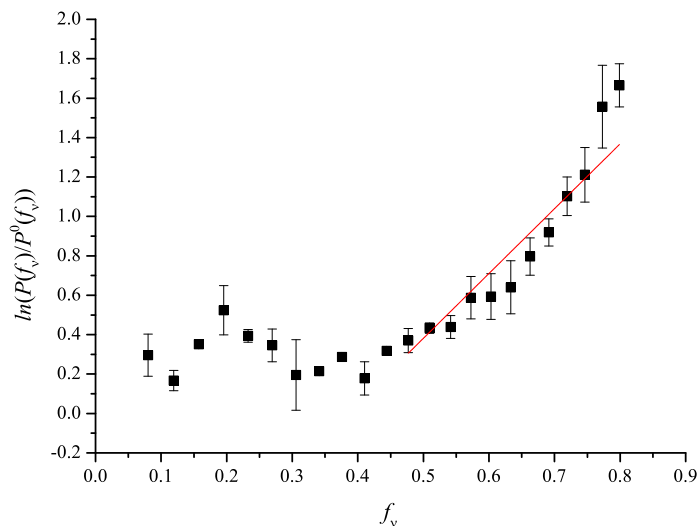


Figure 4.16: A Surprisal plot of the nascent vibrational distribution of NO X $^2\Pi(\nu = 2-24)$ following the pumping of 500 mTorr of NO at 214.872 nm to the NO A $^2\Sigma^+(\nu = 1)$ state (■). Distribution shown contains contributions from fluorescence and self-quenching. A linear fit to levels $\nu = 13-24$ is shown, (red), yielding a Surprisal parameter λ_1 of -3.29 ± 0.30 .

in Figure 4.17 (c)) from the measured vibrational distribution. This vibrational distribution is presented in Table 4.3, with the low vibrational levels ($\nu = 0-4$) estimated from the Surprisal parameters. Comparisons can now be drawn between this work and that of Hancock and Saunders performed previously in the group studying the self-quenching of NO A $^2\Sigma^+(\nu = 0)$ [12]. The Surprisal parameter, λ_1 , describing the NO X $^2\Pi$ vibrational distribution measured by Hancock *et al.* was -2.16 ± 0.44 . This represents 24 % of the available energy; the fraction of energy channelled into the vibrational mode of NO following self-quenching of NO A $^2\Sigma^+(\nu = 1)$ is 28 % (statistical is 18 %). Both are hotter than statistical, and by a similar amount. Any contribution from vibrational relaxation within the electronically excited state prior to quenching has been neglected due to its

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

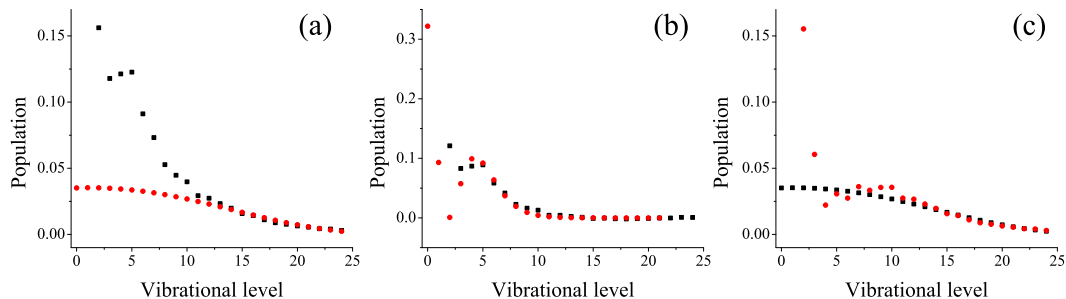


Figure 4.17: (a) plot showing the raw nascent vibrational distribution obtained from the experiment shown in Figure 4.14 (black) and the distribution described by the Surprisal parameters calculated from the Surprisal plot shown in Figure 4.16 (red). (b) Plot showing the NO $X^2\Pi(\nu)$ distribution resulting from radiative transfer from the NO $A^2\Sigma^+(\nu = 1)$ state, as calculated from the emission coefficients for the transition (red) [29]. Also shown (black) is the experimentally determined distribution for the same processes, as calculated by subtraction of the two spectra in (a). (c) Plot showing the distribution described by the Surprisal parameters calculated from the Surprisal plot shown in Figure 4.16 (black) and the experimentally determined distribution (red) resulting purely from the quenching of NO $A^2\Sigma^+(\nu = 1)$ by NO, as calculated by subtraction of the red data in (b) from the black data in (a).

low quantum yield, and given the similar distribution of NO $X^2\Pi$ formed in each case, it would not have a significant effect on the measured distribution.

4.3.4 Quenching by CO_2

4.3.4.1 NO $X^2\Pi(\nu)$ distribution

Attention is now turned to the electronic quenching of NO $A^2\Sigma^+(\nu = 1)$ by CO_2 . The previous section has shown the similarity between the quenching of NO $A^2\Sigma^+(\nu = 0 \text{ and } 1)$ by NO. However, with CO_2 as the quenching molecule, an additional quenching channel becomes thermodynamically accessible when NO is excited up to the $A^2\Sigma^+(\nu = 1)$ state, the formation of vibrationally excited CO, which is shown in process (4.14). Experiments were performed, with pressures such that the quantum yield of quenching of the NO $A^2\Sigma^+(\nu = 1)$ state by CO_2

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

Table 4.3: Vibrational populations for NO X $^2\Pi(\nu = 0-24)$ produced under conditions of exclusive quenching of NO A $^2\Sigma^+(\nu = 1)$ by NO from a combination of the experimental data for populations of NO X $^2\Pi(\nu > 5)$ and Surprisal analysis for the populations of NO X $^2\Pi(\nu = 0-4)$. Relative populations are summed to unity with errors presented as $\pm 1\sigma$.

ν	NO X $^2\Pi(\nu)$ vibrational population
0	0.075 $\pm$ 0.013
1	0.075 $\pm$ 0.013
2	0.073 $\pm$ 0.013
3	0.072 $\pm$ 0.013
4	0.069 $\pm$ 0.012
5	0.052 $\pm$ 0.012
6	0.046 $\pm$ 0.012
7	0.061 $\pm$ 0.008
8	0.056 $\pm$ 0.006
9	0.060 $\pm$ 0.005
10	0.060 $\pm$ 0.004
11	0.046 $\pm$ 0.004
12	0.045 $\pm$ 0.004
13	0.039 $\pm$ 0.004
14	0.033 $\pm$ 0.004
15	0.027 $\pm$ 0.004
16	0.024 $\pm$ 0.004
17	0.019 $\pm$ 0.004
18	0.015 $\pm$ 0.005
19	0.013 $\pm$ 0.004
20	0.011 $\pm$ 0.004
21	0.009 $\pm$ 0.003
22	0.007 $\pm$ 0.002
23	0.007 $\pm$ 0.001
24	0.005 $\pm$ 0.001

was 0.5. First, the NO distribution is considered. As before the NO X $^2\Pi$ overtone emission is used to determine the NO distributions. The CO₂ $\Delta\nu_3 = \Delta\nu_1 = -1$ and $\Delta\nu_3 = -1$, $\Delta\nu_2 = -2$ combination emission bands overlap significantly with the NO overtone emission. However, a high pressure of Ar (200 Torr) rapidly relaxes these bands, so that by around 20 μ s it has been fully relaxed, revealing the structured NO overtone emission. A contour plot of such an experiment is shown

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

in Figure 4.18. Analysis of the NO overtone emission was performed, fitting the spectral simulation to each spectrum following the excitation pulse. A kinetic model was then employed to fit the resultant time dependent vibrational populations, extrapolating to obtain a nascent distribution. This process naturally has a greater uncertainty than normal, since the earliest time slice used in the fit was 22 μs , as can be seen in Figure 4.19. The contribution from self-quenching

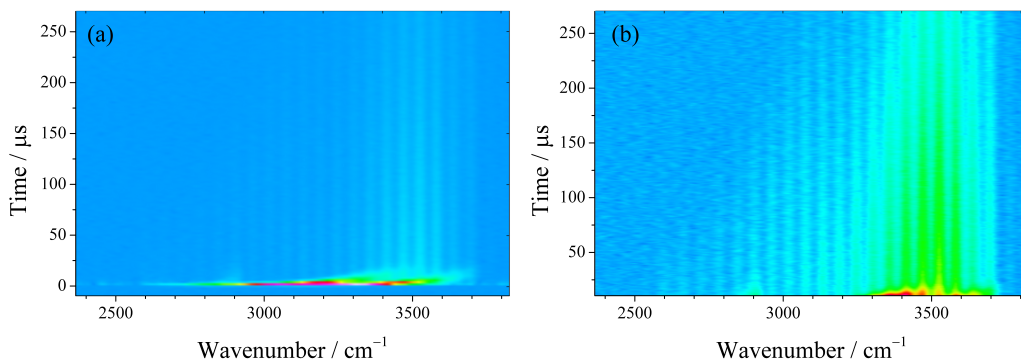


Figure 4.18: (a) Contour plot of the vibrational overtone emission spectrum of NO $X^2\Pi$ observed following the excitation of 50 mTorr of NO on the overlapped Q_1 and P_{21} band heads of the NO $A^2\Sigma^+(\nu = 1) \leftarrow X^2\Pi(\nu = 0)$ transition at 214.872 nm in the presence of 485 mTorr of CO_2 and 200 Torr of Ar. (b) Contour plot of the same data as present in (a) but shown only from 10 μs to allow the NO overtone emission to be seen more clearly. Emission recorded at a resolution of 20 cm^{-1} with the InSb detector. Red represents high intensity and blue represents low intensity.

and fluorescence processes needs to be subtracted from the nascent vibrational distribution, and this was achieved in a similar way to that described earlier and in Chapter 3. IR traces of emission in the region 3000 cm^{-1} to 4000 cm^{-1} , corresponding to overtone emission from levels $\nu = 2\text{--}15$, were taken for a series of different pressures of CO_2 . These traces were scaled according to the simultaneously measured NO A-X LIF emission, so as to correct for any variation in laser power or rotational hole filling effects occurring for the different traces. These are shown in Figure 4.20 (a), together with exponential fits to the late time data,

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

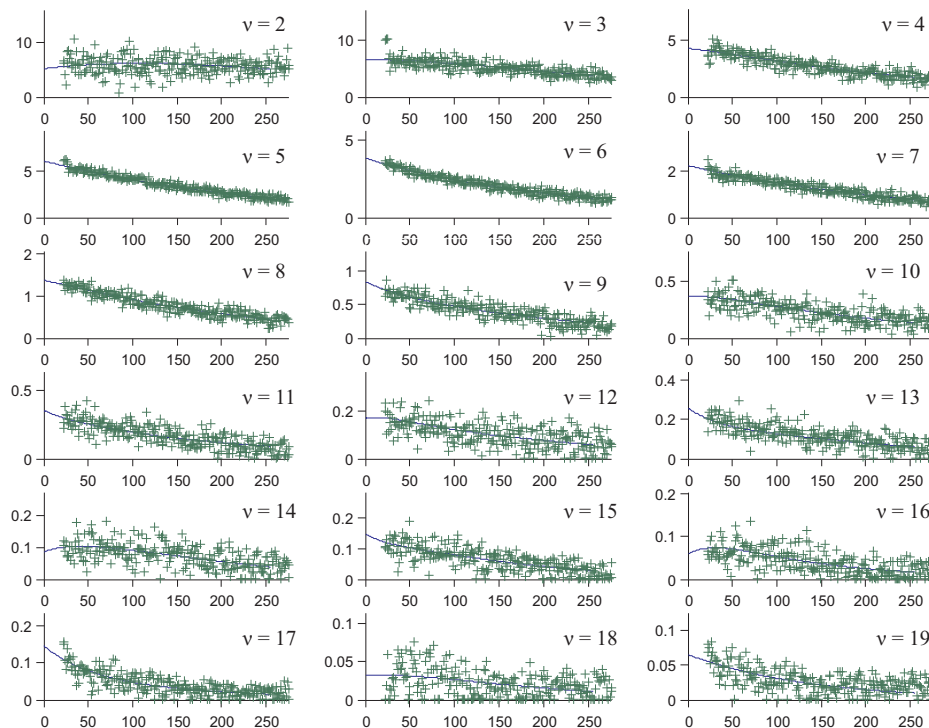


Figure 4.19: Plots of the time dependent vibrational distributions of NO $X^2\Pi(\nu)$, shown between 22 μs and 150 μs after the laser pulse, for vibrational states $\nu = 2$ –19 as labelled (+). Also shown are the distributions as obtained from the global fitting of the kinetic model (blue). The x axis of all plots shows time in μs .

to allow an estimate for the nascent NO $X^2\Pi$ overtone emission intensity within the specified wavelength region. It is immediately obvious that the late time IR signal intensity drops dramatically as CO_2 is added. The amount by which the intensity decreases is almost exactly the same as the decrease in the combined quantum yield of fluorescence and self-quenching as the pressure of CO_2 is increased. This alone suggests strongly that very little NO $X^2\Pi(\nu \geq 2)$ is formed as a result of the quenching NO $A^2\Sigma^+(\nu = 1)$ by CO_2 . Nevertheless the analysis procedure was continued. Nascent spectra were simulated using the raw nascent populations as determined by the kinetic fits shown in Figure 4.19, and using the

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

distribution resulting from NO self-quenching and fluorescence, calculated from the distribution shown in Table 4.3. These spectra were then scaled according to the emission intensities within the region of 3000 cm^{-1} to 4000 cm^{-1} as taken from the appropriate IR traces in Figure 4.20 (a) and are shown in Figure 4.20 (b). Subtraction of these two spectra will reveal the nascent NO X $^2\Pi$ overtone emission due solely to quenching of NO A $^2\Sigma^+(\nu = 1)$ by CO₂. However, it is evident that, within error, the two spectra are essentially the same. This then confirms the initial conclusion that very little energy is channelled into the higher vibrational levels ($\nu \geq 2$) of NO X $^2\Pi$ upon collision of CO₂ with NO A $^2\Sigma^+(\nu = 1)$. It

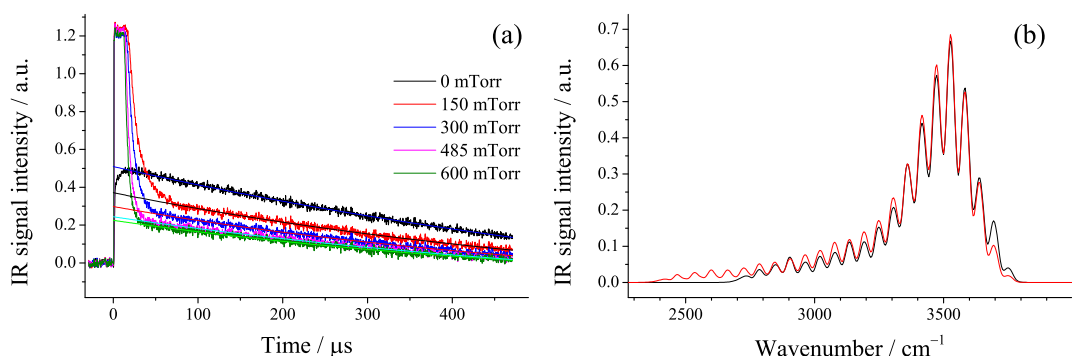


Figure 4.20: (a) Temporal behaviour of IR emission in the region of 3000 cm^{-1} to 4000 cm^{-1} observed following the excitation of 50 mTorr of NO on the overlapped Q₁ and P₂₁ band heads of the NO A $^2\Sigma^+(\nu = 1) \leftarrow$ X $^2\Pi(\nu = 0)$ transition at 214.872 nm in the presence of 200 Torr of Ar and various partial pressures of CO₂. Traces are scaled according to the $t = 0$ intensity of the simultaneously measured NO A-X LIF emission. Single exponential fits to the late time data ($t > 80\text{ }\mu\text{s}$) are shown. (b) NO X $^2\Pi(\nu)$ overtone emission spectrum simulated from the nascent vibrational distribution measured when NO A $^2\Sigma^+(\nu = 1)$ is quenched by CO₂ and NO with respective quantum yields 0.51 and 0.04 (with radiative transfer accounting for the rest) (black). Also shown is the NO X $^2\Pi(\nu)$ overtone emission spectrum simulated from the nascent vibrational distribution measured when NO A $^2\Sigma^+(\nu = 1)$ is quenched by NO with a quantum yield of 0.08 (red). The spectra have been scaled according the measured NO X $^2\Pi$ overtone emission intensities and for respective quantum yields, as described in the text.

is apparent that the fundamental emission needs to be considered in order to gain

4.3. Electronic quenching of NO $A^2\Sigma^+(\nu = 1)$

some information about the NO $X^2\Pi$ vibrational distribution under these conditions. IR traces were taken in the same manner as above, this time observing emission in the region 1850 cm^{-1} to 1925 cm^{-1} as a function of the partial pressure of CO_2 . These traces are shown in Figure 4.21 (a). The emission within this region originates from two sources; the early time ($< 20\text{ }\mu\text{s}$) intense feature is the $\text{CO}_2 \Delta\nu_3 = -1$ emission. This emission rapidly cascades to higher wavenumbers,

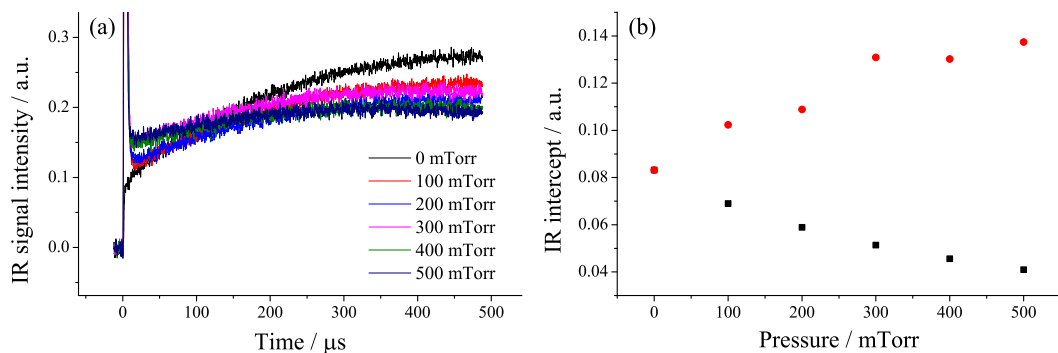


Figure 4.21: (a) Temporal behaviour of IR emission in the region of 1850 cm^{-1} to 1925 cm^{-1} observed following the excitation of 50 mTorr of NO on the overlapped Q_1 and P_{21} band heads of the NO $A^2\Sigma^+(\nu = 1) \leftarrow X^2\Pi(\nu = 0)$ transition at 214.872 nm in the presence of 200 Torr of Ar and various partial pressures of CO_2 . Traces are scaled according to the $t = 0$ intensity of the simultaneously measured NO A-X LIF emission. (b) Nascent IR emission intensity shown as a function of CO_2 pressure. IR emission is attributable to the NO $X^2\Pi$ fundamental emission in the region of 1850 cm^{-1} to 1925 cm^{-1} (●) obtained by extrapolation of the late time data shown in (a). Also shown is the combined quantum yield of self-quenching and fluorescence for each partial pressure of CO_2 (■). These have been scaled to match the IR intercept for 0 mTorr of CO_2 .

and out of the transmission range of the optical filter employed. The longer time emission is attributed to the NO fundamental emission. As the pressure of CO_2 is increased, two effects are observed: the initial intensity of the NO emission (ignoring the early time CO_2 emission) decreases, while the reverse effect is seen for the long time emission ($> 200\text{ }\mu\text{s}$). The frequency of radiation transmitted by the

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

filter employed corresponds to emission from the NO X $^2\Pi(\nu = 1-3)$ vibrational levels. This indicates that as the partial pressure of CO₂ is raised the nascent population of these three levels increase, which suggests that while quenching of NO A $^2\Sigma^+(\nu = 1)$ by CO₂ does not populate the higher vibrational levels of NO X $^2\Pi$, it is efficient at channeling population into the lower vibrational states. Self-absorption by NO present in the cell will reduce the intensity of the NO X $^2\Pi(\nu = 1 \rightarrow 0)$ emission, and so the observed increase in the early time signal as function of CO₂ pressure shown in Figure 4.21 (a) will be a lower limit. At later time the intensity of emission in this region increases due to vibrational relaxation of the higher vibrational levels of NO X $^2\Pi$, whose fundamental emission bands fall outside the range of the filter transmission. In the absence of CO₂ the lifetime of the emission from the NO X $^2\Pi(\nu = 1)$ state is long, because any collisional relaxation by ground state NO molecules will regenerate the NO X $^2\Pi(\nu = 1)$ state, so the only process removing population from this state is radiative decay, which has a lifetime of ~ 80 ms. As the partial pressure of CO₂ is increased the population channelled into the higher vibrational modes of NO X $^2\Pi$ will decrease, as determined above. This will mean that there is less NO X $^2\Pi(\nu > 3)$ able to relax down to the lower levels of NO and contribute to the late time intensity of the detected emission traces. In addition CO₂ will decrease the lifetime of the NO X $^2\Pi(\nu = 1)$ state. The relaxation rate constant of this state by CO₂ has been previously determined by the group to be $0.27 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [11], which although slow means that the lifetime of NO X $^2\Pi(\nu = 1)$ will be reduced by a factor of 5 upon the addition of 500 mTorr of CO₂. Both of these effects combine to explain the observed trend in late time signal in Figure 4.21 (a). Figure 4.21 (b) shows a plot of the intensity of the nascent NO emission (obtained by

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

fitting an exponential function to the late time signal and extrapolating to zero time) against pressure of CO₂ present in the cell. Also shown is the combined quantum yield of fluorescence and self-quenching. This clearly shows that the intensity of the emission of this region increases as CO₂ is added. Given that the equivalent traces in the overtone region indicated that minimal population was observed for levels $\nu \geq 2$, it can be concluded that increased population in NO X $^2\Pi(\nu = 1)$ is primarily responsible for the increase in the observed emission.

4.3.4.2 Emission from CO₂ and reaction products

The energy channelled into the CO₂ vibrational modes following quenching of NO A $^2\Sigma^+(\nu = 1)$ by CO₂ is now considered. In order to obtain an accurate indication of the extent of the nascent vibrational excitation of CO₂ a low pressure of CO₂ is required, in the absence of Ar, to limit the rate of vibrational relaxation. An experiment was performed observing emission when the NO A $^2\Sigma^+(\nu = 1)$ state was quenched by CO₂ with a quantum yield of 0.1, to allow comparison to the CO₂ emission observed following the quenching of the ground vibrational level in the electronically excited A $^2\Sigma^+$ state of NO. The two early time spectra (4 μ s after the laser pulse) are shown in Figure 4.22 . It is evident that the spectra shown in Figure 4.22 are very similar. This means that the amount of energy partitioned into the CO₂ vibrational modes is approximately the same in each system, and so the CO₂ takes a marginally smaller fraction of the available energy following the quenching of NO A $^2\Sigma^+(\nu = 1)$. This indicates that the energy associated with the vibrational excitation of the electronically excited NO is not distributed among the products with the same efficiencies as the rest of the available energy, but instead remains with the NO molecule.

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

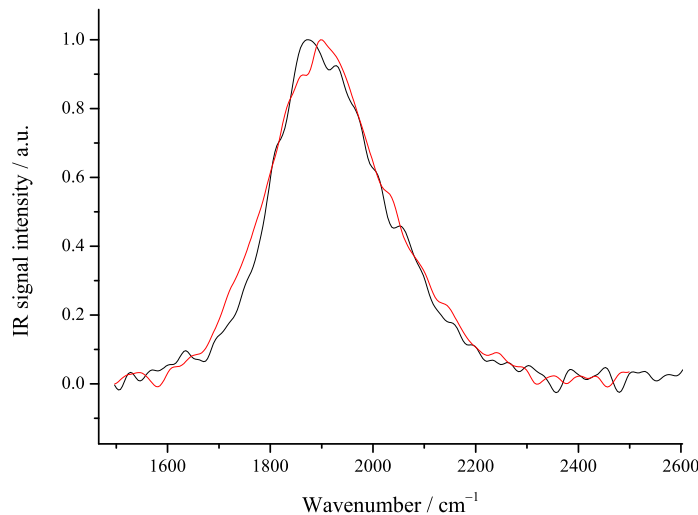


Figure 4.22: Emission observed in the region of 1500 cm^{-1} to 2500 cm^{-1} following the excitation of NO with radiation at 214.872 nm (black) and 226.257 nm (red). CO_2 was present in each case, with partial pressures of 46 mTorr and 54 mTorr so that Φ_{CO_2} is 0.1 for each experiment. Emission was detected with the HgCdTe detector and spectra recorded at a resolution of 20 cm^{-1} . Spectra have been normalised according to the maximum value for clarity.

In order to investigate the reactive channels, producing CO and NO_2 , experiments were performed under conditions such that the collisional quenching of the NO A $^2\Sigma^+(\nu = 1)$ state accounted for 90% of the removal processes. The subsequent emission, in the region 1200 cm^{-1} to 2500 cm^{-1} , is compared in Figure 4.23 to that observed following the quenching of NO A $^2\Sigma^+(\nu = 0)$ by CO_2 with an equivalent quantum yield of quenching. The quenching of NO A $^2\Sigma^+(\nu = 0)$ by CO_2 was found to produce excitation in the ν_3 mode of CO_2 , which represented 59% of the available energy. Without robust NO X $^2\Pi$ vibrational distributions produced by the quenching of NO A $^2\Sigma^+(\nu = 1)$ by CO_2 , absolute scaling between the two sets of experimental data is not possible. Instead the emission features are scaled according to the intensity of the CO_2 $\Delta\nu_3 = -1$ emission band. In

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

Figure 4.23 there are four emission features, observed in both sets of data. From left to right these are assigned as the NO₂ $\Delta\nu_3 = -1$ band at 1600 cm⁻¹, the NO X $^2\Pi$ fundamental band at 1900 cm⁻¹, the CO fundamental band near 2100 cm⁻¹ and the CO₂ $\Delta\nu_3 = -1$ band which relaxes to around 2300 cm⁻¹. The earliest time spectra shown is 11 μ s as this is the first time at which the CO emission feature is resolvable from the CO₂ emission. It is evident from Figure 4.23 that the relative intensities of these features are different for the two excitation wavelengths; the emission features observed following the excitation of NO X $^2\Pi$ with 215 nm radiation are all seen to have increased intensity relative to the CO₂ emission at ~ 2300 cm⁻¹. It was found in Section 4.2.1 that collisions between

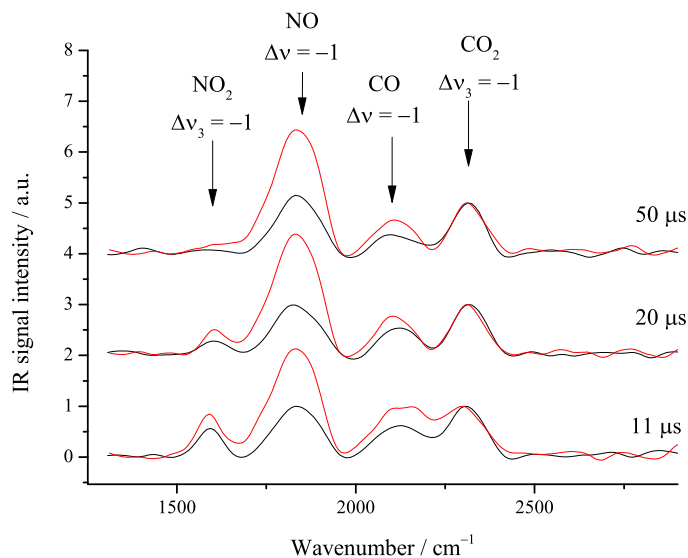


Figure 4.23: IR emission spectra observed following quenching of NO A $^2\Sigma^+(\nu = 0)$ (black) and NO A $^2\Sigma^+(\nu = 1)$ (red) by CO₂. Partial pressures in each case were selected so that $\Phi_{\text{CO}_2} = 0.9$. Spectra were obtained at a resolution of 40 cm⁻¹ by a liquid nitrogen cooled InSb detector.

NO A $^2\Sigma^+(\nu = 0)$ and CO₂ were dominated by a reactive process forming NO X $^2\Pi(\nu = 0)$, CO and O(3P), as shown in Equation 4.2. The formation of vibra-

4.3. Electronic quenching of NO A $^2\Sigma^+(\nu = 1)$

tionally excited CO₂ only occurred *via* the non-reactive processes (4.1) and (4.6). The lower limit for the branching ratio of these two channels was found to be 26 % and is therefore not the dominant process. It was predicted the branching ratio for reactive quenching would increase as a result of increasing the vibrational excitation in the electronically excited NO molecule, and therefore it is expected that reactive channels will dominate the quenching processes. First, it is noted that, while the NO₂ emission is seen to be more intense following quenching of NO A $^2\Sigma^+(\nu = 1)$, it is still weak compared to the NO fundamental emission, and consideration of the relative Einstein emission coefficients reveal that the formation of vibrationally excited NO₂ is a minor channel, as it was for the quenching of NO A $^2\Sigma^+(\nu = 0)$ by CO₂. Therefore the main quenching processes will be (4.13) or (4.14), which both proceed with the dissociation of CO₂. In order to distinguish between these two channels, the emission from NO and CO need to be compared. Both show a greater intensity relative to the CO₂ emission following excitation of NO at 215 nm compared to 226 nm. However, the relative increase is greater for the NO emission, which implies that process (4.13) dominates over process (4.14), with the vibrational excitation remaining with the NO molecule, as predicted at the end of Section 4.2.5. This is because the additional energy in the NO A $^2\Sigma^+(\nu = 1)$ + CO₂ system is localised in the NO vibrational mode, and therefore it is expected that this will be retained during the quenching processes and therefore all products which contain the NO functional group (*ie* NO X $^2\Pi$ and NO₂) should exhibit a greater degree of vibrational excitation.

Finally the CO and the CO₂ emissions are compared. In light of the conclusion that the reactive quenching pathway preferentially forms NO X $^2\Pi(\nu = 1)$ rather than CO($\nu = 1$), it can be assumed that the mechanism for generating the

observed vibrationally excited CO is the same for each system, vibrational energy transfer to the ground state CO molecule. Therefore the amount of $\text{CO}(\nu = 1)$ formed is proportional only to the quantum yield of the reactive quenching pathway. Similarly the intensity of the CO_2 emission will be proportional to the branching ratio for non-reactive quenching processes. This means that by comparing the relative intensities of the CO and CO_2 emissions following excitation of NO at 215 nm and 226 nm reveal that the branching ratio of reactive quenching is larger in the former case.

4.4 Conclusions

The observed $\text{NO X } ^2\Pi(\nu)$ distribution found following quenching of $\text{NO A } ^2\Sigma^+(\nu = 0)$ by CO_2 is close to statistical, a conclusion also reached for the products of self-quenching in a previous study [12]. Although this appears to favour a complex forming mechanism [5, 7, 8, 28] the results are consistent with the simple energy transfer as given by process (4.1) to be a minor channel. Comparison of this system to the quenching of $\text{NO A } ^2\Sigma^+(\nu = 0)$ by N_2O [2] found that the energy transferred to internal modes of the triatomics is markedly different in the two acceptor molecules, with far more energy appearing in CO_2 than in N_2O . A possible rationalisation is that reaction (4.12) dominates for collisions with N_2O with non-reactive quenching being a minor process, but for CO_2 , as there is a greater yield of unobserved processes, that either channels (4.1) or (4.6) could give vibrational excitation in CO_2 . If it were process (4.1), then the collision complex argument would need modification to account for the greater than statistical fraction of the available energy appearing as triatomic vibration. Although the

results presented in the chapter cannot distinguish between channels (4.6) and (4.2) as being responsible for the high fraction of unobserved NO, it is clear that the processes must compete with energy transfer (4.1). For example if a NO-CO₂ complex is formed, as it decomposes, trajectories could favour extension of the C-O bond, with process (4.2) taking place when little energy is available in NO and when dissociation becomes thermodynamically accessible. This bond extension (or other vibrational excitation in CO₂) appears to persist even when the NO has reached a statistical distribution, and presumably reflects the vibrationally specific exit channels: for example, a T-shaped NO-CO₂ complex could dissociate with NO having a statistical distribution, and the departing O-C-O moiety having an extended O-C bond which cannot transfer vibrational energy to the NO at right angles to it.

Investigation of the effect of vibrational excitation of the NO A ²Σ⁺ state on the quenching processes revealed a change in the relative branching ratio for the different channels. The intensity of the NO X ²Π vibrational overtone emission was observed to decrease in the same manner as (1-Φ_{CO₂}) as Φ_{CO₂} was increased from 0 to 0.5. This lead to the conclusion that effectively no energy was channelled into the NO X ²Π(ν ≥ 2) following the collision with of NO A ²Σ⁺(ν = 1) with a CO₂ molecule. In contrast the intensity of emission from NO X ²Π(ν = 1) was found to increase as the pressure of CO₂ was increased. This was explained by the increased branching ratio of reactive processes, specifically channel (4.13), where CO (ν = 0) and NO X ²Π(ν = 1) are formed. Comparison of the emission intensity from CO₂ with the emission from CO and NO₂ revealed that the CO and NO₂ emission increased following the quenching of NO A ²Σ⁺(ν = 1), which supports the conclusion that the branching ratio for reactive channels is larger

for this system. However, the observed red-shift of the CO₂ emission was similar to that following the quenching of NO A ²Σ⁺(ν = 0) by CO₂, suggesting that a similar mechanism for the non-quenching collisions occurs in both cases.

A nascent vibrational distribution of NO X ²Π following the self-quenching of NO A ²Σ⁺(ν = 1) was obtained, and found to be similar to the equivalent distribution following the self-quenching of NO A ²Σ⁺(ν = 0) [12], with the energy partitioned into the NO vibration mode representing 28 % and 24 % of the available energy respectively. The interesting observation of the Ogawa bands, while not relevant to the aims of this chapter, are an example of energy transfer between excited states which has not been previously studied. Finally the observation of vibrational emission from within the A ²Σ⁺ state of NO highlight an area for further research. This has been observed previously in the group for electronically excited OH, and in both cases the intensity of the observed emission was far greater than was expected from the Einstein A coefficients, calculated simply from dipole moment functions.

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Chapter 5

Electronic quenching of NO

A $^2\Sigma^+(\nu = 0)$ by the noble gases

5.1 Introduction

The electronic quenching of NO A $^2\Sigma^+$ by noble gases provides systems which are simpler in nature than those studied in the previous chapters; the noble gas atom does not possess rotational or vibrational modes, and has no low lying electronic energy levels and therefore there are fewer possible channels for the disposition of electronic energy of NO A $^2\Sigma^+$. Such systems also have the potential to be modelled theoretically as has successfully been achieved for the rotational energy transfer between excited state OH molecules and noble gas atoms [1–4]. The quenching mechanism of these systems has been explained by the Collision Complex model [5, 6], rather than the Charge Transfer model [7] given the large negative electron affinities of the noble gases. There is evidence of complexes forming between NO X $^2\Pi$ and noble gases [5, 8, 9], hence it is possible that

quenching proceeds *via* a complex between the noble gas and the electronically excited NO. Indeed, given that the $A^2\Sigma^+$ state of NO has a larger dipole moment than the ground state [10], this would induce stronger attraction forces between NO and the rare gas.

Previous studies of the quenching rate constants of NO $A^2\Sigma^+(\nu = 0)$ by the noble gases have found them to be small. Work by Nee *et al.* [11] measured the quenching rate constants of NO $A^2\Sigma^+(\nu = 0)$ by He, Ar and Xe, and found these to be of the order of $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively, all of which are several orders of magnitude slower than the quenching by O_2 and CO_2 as studied in Chapters 3 and 4. The quenching of NO $A^2\Sigma^+(\nu = 0)$ by Ar [12] and Xe [13], has been studied previously in this group. Studying such inefficient quenchers can be problematic, since high pressures are needed to obtain sufficient quantum yields of quenching. The reaction cell employed for the experiments is designed for the low pressure regime, and therefore the pressure of the gas mixture in the cell was restricted to 650 Torr, thus limiting the maximum quantum yield of quenching achievable. In addition to low quantum yields, using such high pressures of noble gas means the system is highly susceptible to interference from impurities. Common impurities would include water vapour and oxygen, both of which are extremely efficient quenchers of NO $A^2\Sigma^+$ [11, 14, 15], and so even a small percentage impurity could dominate the observed kinetics. Xenon was found by Nee *et al.* [11] to be the most efficient quencher out of the the noble gases included in the study, and this can be explained by the fact that the polarisability of the noble gases increases down the group, and therefore that the dipole-induced dipole force between the electronically excited NO and the noble gas will be strongest for Xe.

This chapter aims to measure the rate constants for the electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by the noble gases, using laser induced fluorescence (LIF), for comparison with those reported by Nee *et al.* [11].

5.2 Experimental set-up

In order to measure these quenching rate constants accurately, the vacuum cell employed for the IR emission experiments was not used. In this cell, the UV beam is multi-passed, to ensure an adequate signal-to-noise ratio for the IR emission experiments. LIF has a far greater sensitivity and so does not require multi-passing of the UV beam. In addition, such multi-passing of the UV beam could affect the kinetics of observed emission [16]. Consequently, a single pass cell was used, with LIF detected by a photomultiplier tube (PMT) located orthogonal to the laser beam. Given that these experiments are highly sensitive to small impurities entering the cell the whole system was meticulously checked for leaks using a Leybold Pheonix leak detector, and adjustments made until no external leak greater than 1×10^{-8} mbar s $^{-1}$ was found. The cell was then left open to a turbo pump for a week to try to remove as much gas adsorbed to the cell walls as possible. The minimum pressure achieved was 1×10^{-6} mbar. A measurement of the leak/desorption rate was performed, where the cell was isolated from the pump and left for a period of 24 hours, and the pressure increase corresponded to an average desorption rate of around 3.3×10^{-6} mbar s $^{-1}$. Given that collecting a single set of data takes around 20 minutes, this means there will be 3 mTorr of gas coming off the cell walls. All gases were connected to the cell *via* stainless steel tubes.

5.2. Experimental set-up

First it was necessary to ensure that the experiment was operating correctly. To do this the quenching rate constant of NO $A^2\Sigma^+(\nu = 0)$ by CO_2 was measured, as this rate constant is well determined in the literature [11, 14, 15, 17, 18]. For this experiment the laser was tuned to the overlapped Q_1 and P_{21} band heads of the NO $A-X(0,0)$ transition at 226.257 nm. Optical filters placed in front of the PMT were employed to transmit emission in the region of 345 nm to 400 nm, which corresponds to the emission bands NO $A^2\Sigma^+(\nu = 0) \rightarrow X^2\Pi(\nu = 9-11)$. A small amount of NO, ~ 5 mTorr, was allowed into the cell along with CO_2 ,

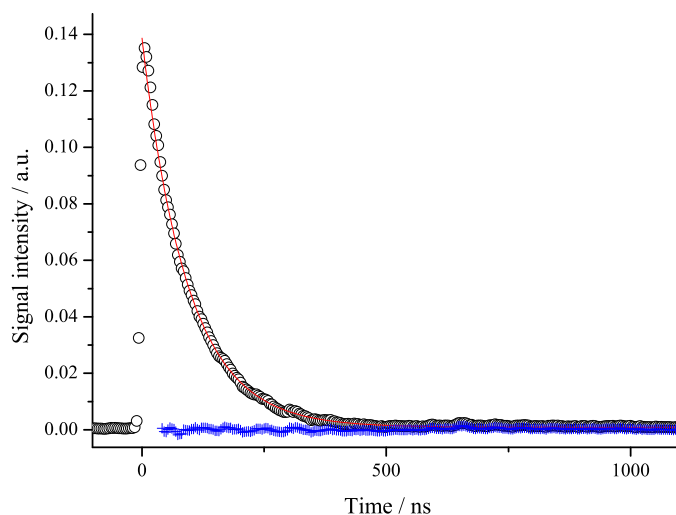


Figure 5.1: LIF intensity, in the range of 345 nm to 400 nm, as a function of time ($\circ$) recorded following excitation of ~ 5 mTorr of NO on the overlapped Q_1 and P_{21} band heads of the $A \leftarrow X$ transition in the presence of 396 mTorr CO_2 . Also shown is the single exponential fit to the data (red) and the residuals from 40 ns ($+$).

whose partial pressure varied from 0 Torr to 2 Torr. For each pressure of CO_2 a LIF trace was obtained, averaged for around 1000 laser shots. The temporal decay of these LIF signals were fitted with a single exponential function, as shown in Figure 5.1, to yield a decay rate for each given pressure of CO_2 . A quench-

5.2. Experimental set-up

ing rate constant was extracted by fitting a linear function to a plot of decay rate against pressure of CO_2 , an example of which is shown in Figure 5.2. The quenching rate constant was found to be $(4.25 \pm 0.11) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which agrees extremely well with previous measurements by Greenblatt *et al.* [17] and Paul and co-workers [18, 19]: $(4.30 \pm 0.26) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(4.29 \pm 0.10) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. While this figure is greater than a more recent measurement of the rate constant reported by Nee *et al.* [11] it is not significantly so. Additional confidence in the results is taken from the intercepts of the plots, such as that shown in Figure 5.2, which all lie in the range $5 \times 10^6 \text{ s}^{-1}$ to $5.3 \times 10^6 \text{ s}^{-1}$, agreeing well with the range of measurements of the radiative lifetime of the $\text{NO } A^2\Sigma^+(\nu = 0)$ state found in the literature [20–22]

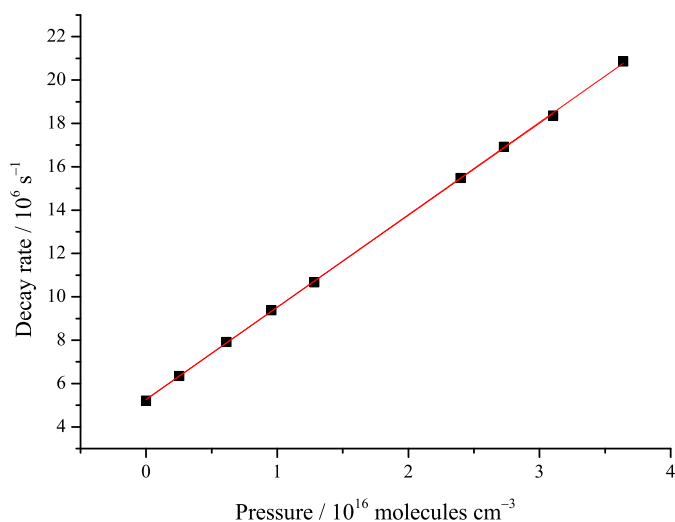


Figure 5.2: Decay rate of LIF signal plotted as a function pressure of CO_2 (■). A linear fit is also shown (red), with a gradient of $4.25 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and an intercept of $5.27 \times 10^6 \text{ s}^{-1}$.

5.2. Experimental set-up

Before experiments were performed to measure the quenching rate constants of NO A $^2\Sigma^+(\nu = 0)$ by the noble gases, an addition was made to the experimental arrangement. For CO₂, the largest pressure used was around 2 Torr, corresponding to a quantum yield of quenching of 0.8. For the noble gases, pressures were used up to 650 Torr, with higher pressures being prevented by limitations of the cell not being designed for greater than atmospheric pressures. As stated earlier, the combination of using high pressures of noble gas and low efficiency with which they quench the A $^2\Sigma^+$ state of NO means the results are highly susceptible to impurities within the gas sample. The gases used have stated purity specifications of N4.4 or above, meaning a maximum impurity of 0.006 %. If the impurity was a fast quencher of NO A $^2\Sigma^+(\nu = 0)$, with a quenching rate constant of $\sim 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, then this impurity would manifest itself as a contribution to the quenching rate constants of between $0.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is large enough to have a significant effect on the results. If impurities were entering the cell *via* a leak, then consideration of the composition of air and the respective quenching rate constants indicate that oxygen and water vapour are most likely to affect the observed kinetics. To limit the partial pressure of impurities within the gas samples, a water filter (All-Pure™) and an oxygen filter (OxiClear™) were incorporated into the noble gas line directly before the cell, to ensure the gas entering the cell was free of oxygen and water vapour. The specifications for the water filter reduced the concentration of water vapour and carbon dioxide to $< 1 \text{ ppb}$ and the oxygen filter reduced the concentration of oxygen at the outlet to $< 5 \text{ ppb}$. This will reduce their contributions to the quenching rate constants to less than $1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

5.3 Results

Experiments were performed to measure the quenching rate constants of NO $A^2\Sigma^+(\nu = 0)$ by the He, Ne, Ar, Kr and Xe. The experiment was repeated six times for each noble gas, and an example of the LIF traces for a single run are shown in Figure 5.3. Figure 5.3 (a) presents the raw LIF traces which clearly show that as Kr is added the intensity of the signal decreases. This is contrary to the effect observed in previously in the group [12], that upon addition of 50 Torr of Ar to a sample of 50 mTorr of NO, the LIF and IR signal both increase. This

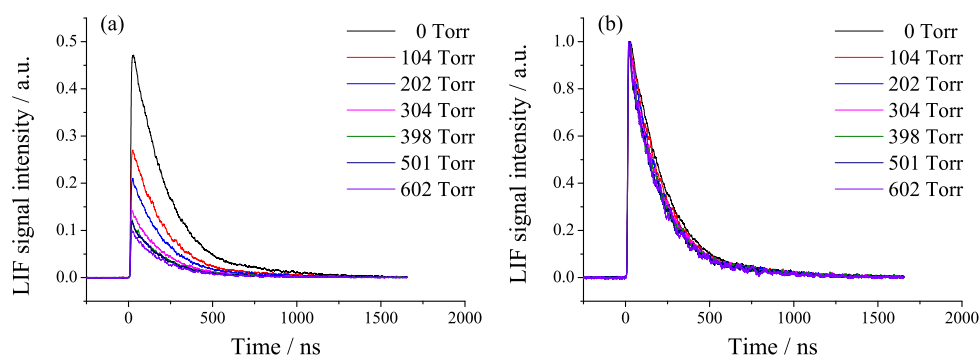


Figure 5.3: Temporal behaviour of LIF signal following excitation of ~ 5 mTorr NO to its $A^2\Sigma^+$ state as the pressure of Kr is increased from 0 Torr to 600 Torr during a single experiment. The traces are presented in two ways: (a) as they were detected by the PMT, and (b) scaled according to the maximum value.

effect is explained by rotational hole filling during the laser pulse [12]. The reason for the decrease of the LIF signal in the present case is that pressure broadening of the absorption line outweighs the rotational hole filling effects, which are much reduced compared to the experiments performed previously in the group [12], due to there being a much lower partial pressure of NO in the cell. The pressure broadening of rotational lines of the NO A-X (0,0) transition by Ar [23, 24] and He [24] have been reported as $0.5 \text{ cm}^{-1} \text{ atm}^{-1}$ and $0.38 \text{ cm}^{-1} \text{ atm}^{-1}$ respectively.

This means that adding 600 Torr of Ar will reduce the peak cross section of a single absorption line to 20 % of the value when collisional broadening is negligible compared to Doppler broadening. This agrees well with the observed variation of LIF intensity as the pressure of krypton is increased, as shown in Figure 5.3 (a). In Figure 5.3 (b) the same traces are presented, normalised by maximum value, to indicate how minimal the effect of 600 Torr of krypton is on the temporal behaviour of the LIF intensity. The LIF traces were fitted to single exponential functions as before, and the quenching rate constants extracted from linear fits to plots of quenching rate against pressure of quencher. An example of such a plot is shown in Figure 5.4 (a). Figure 5.4 (b) shows the same data compared

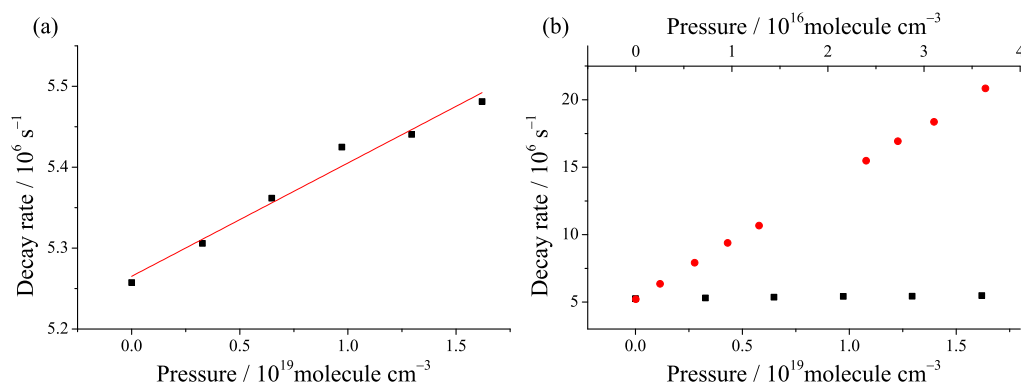


Figure 5.4: (a) Measured decay rate of NO A $^2\Sigma^+$ LIF signal as a function of pressure of Ar (■). A linear fit to the data is also shown (red). The decay rate constant obtained from this particular experiment was $(1.4 \pm 0.1) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. (b) Plot showing the same decay rate data as a function of pressure of Ar as presented in (a) (■). Also shown for comparison is the decay rate of NO A $^2\Sigma^+$ as a function of pressure of CO_2 (●). Note the CO_2 data correspond to the upper x-axis.

to that of quenching by CO_2 (the same data as presented in Figure 5.2). This comparison serves to highlight just how inefficient the noble gases are at quenching electronically excited NO. Even with a partial pressure three orders of magnitude larger than was employed in the CO_2 experiments, the observed change in the

5.3. Results

decay of the LIF signal from electronically excited NO is an order of magnitude less. The results for the noble gases are displayed in Table 5.1. The rate constants

Table 5.1: Measured quenching rate constants of NO A $^2\Sigma^+(\nu = 0)$ by the noble gases.

Quenching partner	Quenching rate constant / $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
He	2.0 ± 0.5
Ne	1.7 ± 0.4
Ar	1.2 ± 0.4
Kr	1.8 ± 0.2
Xe	1.6 ± 0.2

for the different noble gases are very similar. It was mentioned in Section 5.2 that a desorption rate of $3.3 \times 10^{-6} \text{ mbar s}^{-1}$ was measured for the cell. If this rate was due solely to water vapour, then during the course of an experiment 3 mTorr of water vapour would contribute $4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to the measured quenching rate constant. This value is only 3 to 4 times smaller than the values presented in Table 5.1. In light of this it is highly likely that the true quenching rate constants are smaller still, and thus the figures presented in Table 5.1 should be taken as upper limits. Indeed previous attempts to measure these quenching rate constants [17, 18] have presented the results as upper limits, reporting rates of the order of $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and below. The one exception is the measurement by Nee *et al.* of the quenching rate constant of NO A $^2\Sigma^+(\nu = 0)$ by Xe [11]. They reported a value of $1.38 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, two orders of magnitude larger than that measured in this work. The presence of impurities cannot be used to explain the discrepancy given that the purity was tested in the work of Nee *et al.* [11] by UV absorption spectra taken in the range 100 nm to 150 nm, which will have allowed detection of both oxygen and water vapour present in the gas. An explanation for the high value of the quenching rate

constant, as obtained by Nee *et al.* [11] is given by the technique employed. In Stern-Volmer analysis the reduction in fluorescence intensity as a function of the pressure of quenching partner is measured and used to calculate the quantum yield of quenching. This technique works well for fast quenchers where the pressures required to produce a significant quantum yield of quenching of the excited state are small. However, for inefficient quenchers, such as the noble gases, much larger pressures are required. The Stern-Volmer analysis procedure makes the assumption that the reduction in the fluorescence intensity is due solely to the reduced lifetime of the emitting state as a result of collisional quenching. If other reasons for the reduced intensity exist, then the measured quenching rate constant will be an over estimate. A necessary requirement then for Stern-Volmer analysis is that the amount of NO A $^2\Sigma^+(\nu = 0)$ generated must be constant. A cursory glance at Figure 5.3 (a) confirms that this is not the case because of pressure broadening; for a broadened absorption line the amount of NO A $^2\Sigma^+$ molecules generated will be less.

If the excitation radiation has sufficiently large bandwidth, then pressure broadening will not affect the number densities of NO A $^2\Sigma^+(\nu = 0)$ formed. The radiation employed by Nee *et al.* [11] had a bandwidth of 0.1 nm, which is broader than individual rotational lines at the pressures employed, but not broader than the whole vibrational absorption band, and thus the effects of pressure broadening cannot be neglected. One aspect which is evident from the experiments performed in this work is that the larger noble gases (Kr and Xe) cause, as expected, a greater degree of pressure broadening of the NO A-X (0,0) rotational lines. This can be seen clearly in Figure 5.5, which shows the nascent LIF intensity (obtained by extrapolation of the fitted single exponential functions) as

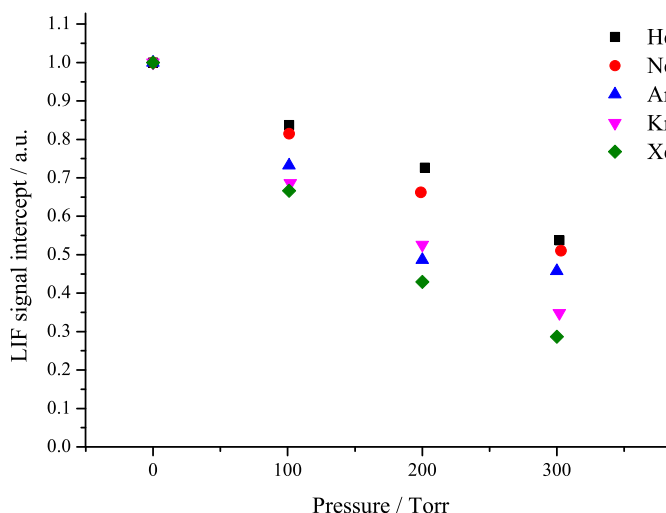


Figure 5.5: The $t = 0$ LIF signal as a function of pressure of quenching gas: He (■), Ne (●), Ar (▲), Kr (▼) and Xe (◆). The series have been scaled to according to the intercept at 0 Torr of quenching gas.

a function of partial pressure of the noble gases. The nascent LIF intensity is proportional to the number of NO $A^2\Sigma^+(\nu = 0)$ molecules generated and it can be seen that Xe has the largest effect, supporting the suggestion that pressure broadening may have contributed to the fast rate constant for quenching of NO $A^2\Sigma^+(\nu = 0)$ by Xe, as determined by Nee *et al.* [11].

In conclusion, despite great care having been taken to ensure accurate measurements of the quenching rate constants of NO $A^2\Sigma^+(\nu = 0)$ by the noble gases, the values obtained can only be viewed as an upper limits of the true value. There are two main limitations to the technique used. First, the range pressures of noble gas employed meant the maximum quantum yield of quenching was less than 0.1. The second limitation is the presence of impurities affecting the measurements. As was demonstrated in this work, even when gas purification

5.4. Implication for electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by Xe

filters are used, the experiment is still susceptible to leaks or gas desorbing from the cell walls. Heating the cell would be a method of removing as much gas as possible from the cell walls prior to each experiment.

5.4 Implication for electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by Xe

The electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by Xe has been investigated previously in the group using time-resolved FTIR emission spectroscopy and a nascent vibrational distribution of NO X $^2\Pi$ was reported [13]. The analysis was performed taking the rate constant for quenching of NO A $^2\Sigma^+(\nu = 0)$ to be $1.38 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, as measured by Nee *et al.* [11]. This meant that it was believed that 647 Torr of Xe afforded a quantum yield of quenching of 0.84, whereas using the rate constant present in Table 5.1, the quantum yield becomes 0.06. What is particularly interesting is the marked effect that Xe has on the resultant NO X $^2\Pi$ overtone emission spectrum, despite the low quantum yield of quenching, while similar pressures of the other noble gases have very little effect. An illustration of this can be seen in Figure 5.6, where the overtone emission spectra of NO, observed following the quenching of the NO A $^2\Sigma^+(\nu = 0)$ state by the noble gases are shown. As can be clearly seen, the spectrum recorded when Xe was present shows a much greater level of vibrational excitation in the NO X $^2\Pi$ molecule. In each of these cases, given the small quenching rate constants, the quantum yield of quenching is going to be around 0.06 or below. It is therefore not unexpected that the spectra recorded in the presence of He, Ar

5.4. Implication for electronic quenching of NO $A^2\Sigma^+(\nu = 0)$ by Xe

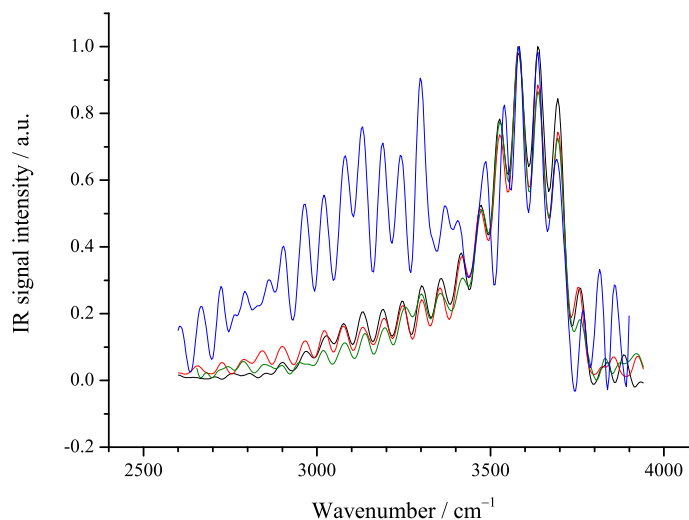


Figure 5.6: Emission spectra following excitation of 50 mTorr of NO to its $A^2\Sigma^+$ state in the presence of 595 Torr of He (black), 400 Torr of Ar (red), 240 Torr of Kr (green) and 647 Torr of Xe (blue). All spectra were detected by an InSb detector and were recorded at a resolution of 20 cm^{-1} . Spectra have been scaled according to their maximum value for clarity.

and Kr look very similar to that observed with only 50 mTorr of NO in the cell. There are two possible explanations for the observed emission in the presence of Xe. Either the quenching process preferentially populates these higher levels of NO, so much so that even when the quantum yield of quenching is only 0.06, the effect is significant. Alternatively there was an impurity, either in the sample or entering the cell another way, and strong emission observed from the higher vibrational levels of NO is a result of quenching by the impurity rather than Xe. As discussed in Section 5.2, oxygen and water are two molecules that as impurities could have a significant effect on the quenching of electronically excited NO. The electronic quenching of NO $A^2\Sigma^+(\nu = 0)$ by O_2 was studied in depth in Chapter 3, and some experiments have been performed on the electronic quenching of

5.4. Implication for electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by Xe

NO A $^2\Sigma^+(\nu = 0)$ by H₂O. Brief summaries of these two systems are presented below, with particular attention paid to any features which can identify their occurrence as impurities in the NO A $^2\Sigma^+ + \text{Xe}$ experiments.

5.4.1 NO quenching by O₂ impurity

First the observed emission spectra in the presence of Xe will be compared to the findings of Chapter 3, the quenching of NO A $^2\Sigma^+(\nu = 0)$ by O₂. It was found that while the is process produced a distribution of NO X $^2\Pi$ that was hotter than statistical, it was still a monotonically decreasing distribution, indicative of a long lived complex rather than a fast interaction. Another feature of quenching by oxygen was the extremely efficient relaxation of the vibrational levels $\nu = 12$ –15, which corresponds to emission in the region of 3000 cm⁻¹ to 3300 cm⁻¹ and has the effect that the emission spectrum attains a slight bimodal appearance at later time. Figure 5.7 shows a series of NO overtone emission spectra taken at 10 μs , 20 μs and 30 μs after the excitation pulse in the presence of oxygen and xenon separately to allow comparison of the spectral and temporal characteristics of the NO overtone emission between the two systems. The spectra presented in Figure 5.7 (a) were recorded under conditions such that quantum yield of quenching by O₂ was 0.5, and Figure 5.7 (b) shows spectra recorded after NO A $^2\Sigma^+(\nu = 0)$ is quenched by 647 Torr of Xe, which equates to a quantum yield of quenching of 0.06. Figure 5.7 (a) shows that, under conditions where quenching by O₂ is significant, a hot distribution is formed, as indicated by emission from the lower wavenumber region ($< 3400 \text{ cm}^{-1}$). However this distribution is not as hot as that obtained as a result of quenching by Xe, as shown in Figure 5.7 (b).

5.4. Implication for electronic quenching of NO $A^2\Sigma^+(\nu = 0)$ by Xe

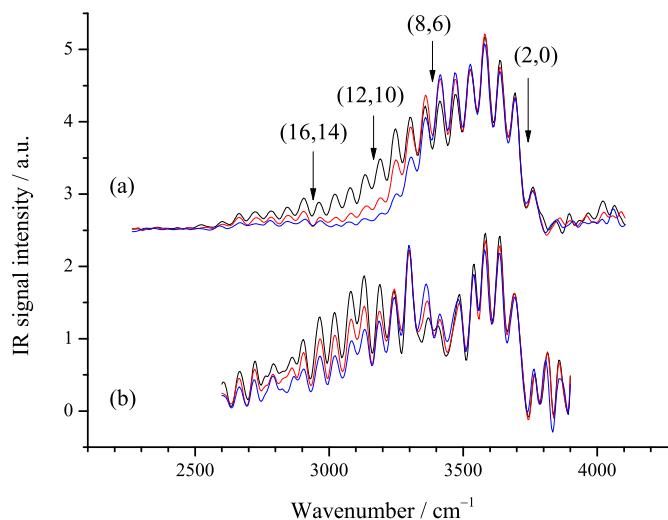


Figure 5.7: Emission spectra following excitation of 50 mTorr of NO to its $A^2\Sigma^+(\nu = 0)$ state in the presence of (a) 1.17 Torr of O_2 and (b) 647 Torr of Xe. In all cases the spectra shown are taken 10 μ s (black), 20 μ s (red) and 30 μ s (blue) after the excitation pulse. The spectra were obtained with an InSb detector and recorded at 20 cm^{-1} resolution. Selected band origins are shown.

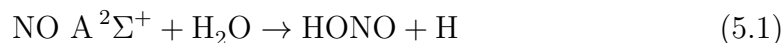
Another feature of the spectra observed in the Xe experiments is a slight bimodal nature, with the minimum at 3500 cm^{-1} , which is not apparent in any of the spectra from the oxygen experiments, and cannot be explained by the rapid relaxation of the emission in the region of 3000 cm^{-1} to 3300 cm^{-1} , indicative of the efficient relaxation of the vibrational levels $\nu = 12$ –15 by oxygen. This then suggests that oxygen cannot be responsible for the observed emission when 647 Torr of Xe was present.

5.4.2 NO quenching by H_2O impurity

The other molecule considered as a potential impurity responsible for the observed hot NO vibrational distribution is H_2O . The electronic quenching of NO

5.4. Implication for electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by Xe

A $^2\Sigma^+(\nu = 0)$ by H₂O has received minimal attention beyond the determination of the quenching rate constant and its temperature dependence [14]. The room temperature value has been reported to be between $7.51 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $9.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [14, 22, 25] meaning that it is an extremely efficient process. Work by Umemoto *et al.* [25] investigated the reactive channel of NO A $^2\Sigma^+$ with H₂O, observing the production of fast H(2S) atoms, indicating the presence of the reactive process shown in Equation 5.1.



Another example of a reaction between H₂O and electronically excited species is that shown in Equation 5.2, where NO₂^{*} represents an electronically excited state of NO₂.



This has been studied by Crowley *et al.* [26] and Li *et al.* [27], the latter reporting that the reaction proceeded with a quantum yield of OH formation of 0.001, which was sufficient to suggest the reaction a significant source of OH in the atmosphere. However this result has since been called into question by Carr *et al.* [28], who concluded that, unlike the reaction shown in Equation 5.1, this reaction only proceeded with significant quantum yield if two photon processes were involved.

Experiments were performed where 50 mTorr of NO was excited to its A $^2\Sigma^+(\nu = 0)$ state in the presence of 200 mTorr of water vapour, which gives a quantum yield of quenching to be ~ 0.5 . The emission observed in the NO overtone region from these experiments is displayed in Figure 5.8. These spectra appear very different from those shown in Figure 5.7. The earliest time spectrum in Figure 5.8 shows

5.4. Implication for electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by Xe

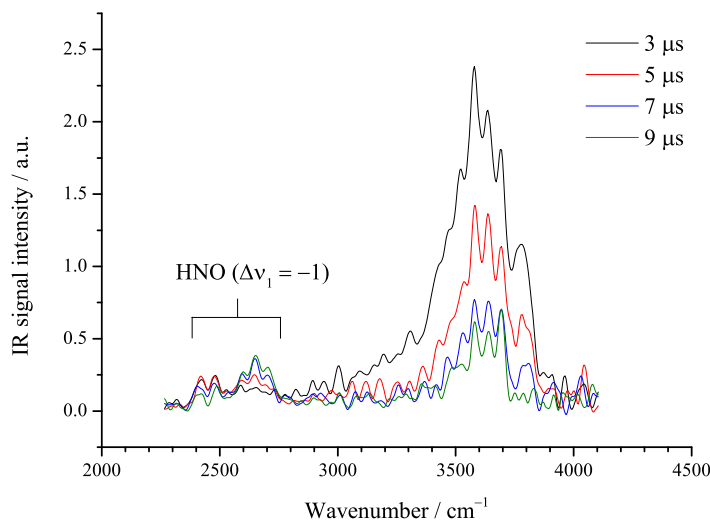
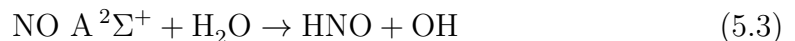


Figure 5.8: Spectra taken at 3 μs (black), 5 μs (red), 7 μs (blue) and 9 μs (green) following excitation of 50 mTorr of NO to its A $^2\Sigma^+(\nu = 0)$ state in the presence of 200 mTorr of H₂O and 50 Torr of Ar. Spectra were obtained with an InSb detector and were recorded at a resolution of 20 cm^{-1} .

intense, relatively unstructured emission around 3600 cm^{-1} which decays rapidly within the first 5 μs . Later time spectra at 7 μs and 9 μs after the excitation pulse show a more structured emission appearing. This implies that there is a short lived early time emission feature which decays in a matter of microseconds to reveal the underlying, weaker NO overtone emission. Channelling of the electronic energy of the NO A $^2\Sigma^+$ molecule into the vibrational modes of the quenching molecule has been observed for nearly all systems studied previously [12, 13, 29]. The $\Delta\nu_3 = -1$ emission band of H₂O lies at $\sim 3600 \text{ cm}^{-1}$, and given its large Einstein A factors [30] it is likely that this is the source of the intense, early time emission seen in Figure 5.8. Another possibility is that emission comes from a reaction product, such as OH or HONO, both of which emit in this region, and can be formed in the processes shown in Equations 5.1 and 5.3. The relative emission

5.4. Implication for electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by Xe

strengths of these molecules are a quarter and equal to that of the $\Delta\nu_3 = -1$ band of H₂O respectively.



In Figure 5.8 two additional emission features at 2400 cm^{-1} and 2600 cm^{-1} are apparent. The intensity of the lower wavenumber peak falls with time, while the reverse effect is seen with the higher wavenumber peak. The behaviour is typical of a cascading emission feature due to transfer of population from one state to another through vibrational relaxation. The frequency of the emission features correspond to the $\Delta\nu_1 = -1$ band of HNO. This band has been studied in emission by Setser and co-workers [31], and the two features seen in Figure 5.8 can be identified as the the $(2,0,0) \rightarrow (1,0,0)$ and $(1,0,0) \rightarrow (0,0,0)$ transitions. At the modest resolution used, it is not possible to determine the contribution of transitions where $\nu_2, \nu_3 > 0$. This then is evidence of the reactive quenching pathway shown in Equation 5.3. As a result of the overlapping emission features in the experiment, and the relatively weak contribution from the NO overtone, it is not possible to extract a nascent distribution with any confidence. Upon consideration of the spectra in Figure 5.7 (b), it is immediately obvious that no HNO $\Delta\nu_1 = -1$ emission, or the accompanying intense early time emission from H₂O/HONO is present. This leads to the conclusion that the experimental Xe quenching data show no features that suggest O₂ or H₂O are present as impurities and dominating the dynamics of the system. Either another impurity is present, or the emission observed is truly a result of the quenching of NO A $^2\Sigma^+(\nu = 0)$ by xenon.

5.4. Implication for electronic quenching of NO $A^2\Sigma^+(\nu = 0)$ by Xe

5.4.3 Re-analysis of Xe data

In light of the discussions presented in Sections 5.4.1 and 5.4.2, it seems probable that impurities are not affecting the observed emission, and a re-analysis of the data collected previously in the group [13] was performed, now taking the quantum yield of quenching of NO $A^2\Sigma^+(\nu = 0)$ to be 0.06. Time dependent

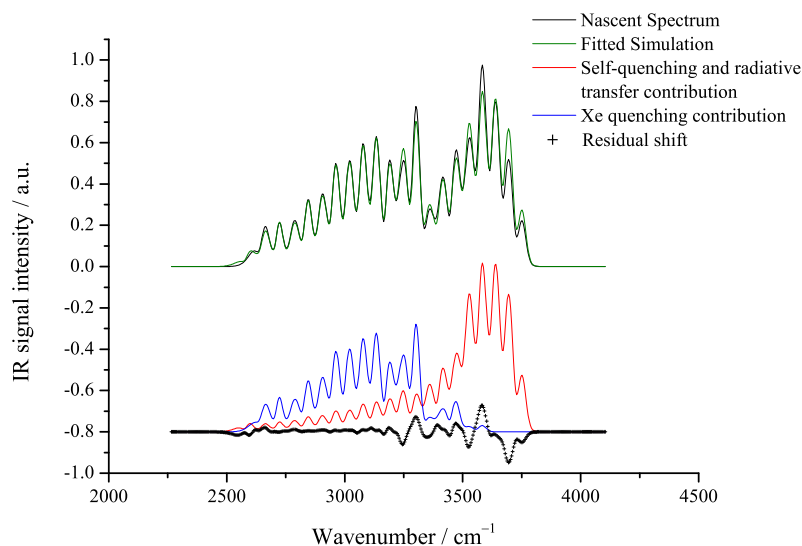


Figure 5.9: Spectrum of nascent emission following the pumping of 50 mTorr of NO to its $A^2\Sigma^+$ state in the presence of 647 Torr of Xe (black) along with the fitted spectral simulation (green). As described in the main text the ratio of NO $X^2\Pi(\nu)$ population resulting from quenching by Xe and the combined processes of self-quenching and radiative transfer was kept at 94:6. Also shown, and offset for clarity are the contributions to the fitted simulated spectrum from Xe quenching (blue) and NO self-quenching and radiative transfer combined (red). Residuals of the fit are also shown (+).

vibrational distributions of NO were obtained by fitting a spectral simulation to the spectra at each timeslice (of which three are shown in Figure 5.7 (b)). Extrapolating to zero time was achieved by fitting a kinetic simulation to the time dependent vibrational distributions. This nascent distribution will contain contributions from Xe quenching, self quenching and fluorescence. Under the ex-

5.4. Implication for electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by Xe

perimental conditions, fluorescence and NO self-quenching will account for 94 % of the removal of NO A $^2\Sigma^+(\nu = 0)$. The nascent distributions for these pro-

Table 5.2: Vibrational distributions of NO X $^2\Pi$ resulting from radiative transfer from NO A $^2\Sigma^+(\nu = 0)$ and by collisional quenching of the same state by NO and by Xe. The distributions are scaled according the their contribution to the fit of the nascent experimental spectrum acquired when NO A $^2\Sigma^+(\nu = 0)$ was quenched by 647 Torr of Xe and 50 mTorr of NO, as shown in Figure 5.9.

Vibrational level	Fluorescence	NO quenching	Xe quenching
0	16.47	0.79 $\pm$ 0.09	0.00 $\pm$ 0.00
1	24.31	0.74 $\pm$ 0.08	0.00 $\pm$ 0.00
2	20.41	0.79 $\pm$ 0.11	0.00 $\pm$ 0.45
3	12.90	0.63 $\pm$ 0.16	0.00 $\pm$ 0.53
4	6.85	0.52 $\pm$ 0.16	0.00 $\pm$ 0.32
5	3.25	0.71 $\pm$ 0.10	0.30 $\pm$ 0.19
6	1.42	0.48 $\pm$ 0.11	0.00 $\pm$ 0.10
7	0.59	0.43 $\pm$ 0.12	0.76 $\pm$ 0.11
8	0.23	0.46 $\pm$ 0.07	0.00 $\pm$ 0.10
9	0.09	0.25 $\pm$ 0.07	0.17 $\pm$ 0.13
10	0.03	0.31 $\pm$ 0.06	1.46 $\pm$ 0.15
11	0.01	0.19 $\pm$ 0.04	0.00 $\pm$ 0.15
12	0.00	0.21 $\pm$ 0.04	0.69 $\pm$ 0.14
13	0.00	0.19 $\pm$ 0.03	0.57 $\pm$ 0.12
14	0.00	0.22 $\pm$ 0.03	0.47 $\pm$ 0.09
15	0.00	0.13 $\pm$ 0.01	0.40 $\pm$ 0.06
16	0.00	0.10 $\pm$ 0.04	0.39 $\pm$ 0.05
17	0.00	0.10 $\pm$ 0.05	0.16 $\pm$ 0.04
18	0.00	0.07 $\pm$ 0.04	0.28 $\pm$ 0.04
19	0.00	0.04 $\pm$ 0.04	0.06 $\pm$ 0.02
20	0.00	0.03 $\pm$ 0.03	0.21 $\pm$ 0.02
21	0.00	0.00 $\pm$ 0.00	0.08 $\pm$ 0.01
22	0.00	0.00 $\pm$ 0.00	0.00 $\pm$ 0.00
Total	86.56	7.39 $\pm$ 1.48	6.00 $\pm$ 2.82

cesses are known [12, 32, 33], and for the experimental conditions employed can be scaled appropriately. From this distribution a spectrum was simulated, and was incorporated into a least squares fitting procedure, with a constraint that the ratio of the total population in the individual levels representing the contribution

5.4. Implication for electronic quenching of NO A $^2\Sigma^+(\nu = 0)$ by Xe

of Xe channel to the population associated with the self-quenching and fluorescence spectrum, was 6:94. The result can be seen in Figure 5.9, where the nascent spectrum, containing the contributions from all channels is shown in black. The contributions of the Xe quenching channel (blue) and combined self-quenching and fluorescence (red) are also shown. This NO X $^2\Pi$ vibrational distribution, along with the distributions resulting from radiative transfer and self-quenching are shown in Table 5.2, scaled according to the contributions as shown in the spectra in Figure 5.9. This then shows that it is possible for such a small quantum yield of quenching of NO A $^2\Sigma^+(\nu = 0)$ by Xe to produce a distribution of NO X $^2\Pi$ that is consistent with the experimentally observed emission. The fit is not perfect, particularly at the high wavenumber end of the emission spectrum, where the high quantum yield of fluorescence has resulted in an over prediction of the emission intensity from the low vibrational levels ($\nu = 2-3$). The distribution obtained for quenching by Xe is inverted with essentially no population in vibrational levels lower than $\nu = 7$. If correct, this means Xe is unique among all the quenching species previously studied by this research group [12, 13, 29, 32], where the NO X $^2\Pi$ vibrational distributions have been found to be near statistical in all cases. Experiments similar to those performed by Settersten *et al.* [34], monitoring the proportion of quenched molecules that are returned to the NO X $^2\Pi(\nu = 0)$ state would provide a simple test of the validity of the distribution presented in Table 5.2.

5.5 Conclusions

This chapter has produced upper limits for the quenching rate constants of the NO $A^2\Sigma^+(\nu = 0)$ state by the noble gases He, Ne, Ar, Kr and Xe. These were all found to be of the order of $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which is lower than most other previous measurements [11, 17]. However, it is still believed that impurities in the cell could account for up to 30 % of the observed quenching rate constants, and as such these should only be viewed as an upper limit. The observed emission when 647 Torr of Xe was present was compared to systems where quenching by O_2 and H_2O , likely candidates for impurities, was dominant. In both cases it was concluded that neither could be used to explain the observed emission. Hence it was concluded that quenching of NO $A^2\Sigma^+(\nu = 0)$ by xenon, despite the small quantum yield of quenching of 6 %, results in a marked population in the higher vibrational levels of NO $X^2\Pi$ and a distribution has been extracted from the experimental data collected previously in the group [13]. It is therefore felt that such a system would be a prime candidate for theoretical investigation, to bring insight into the dynamics of the quenching process that could cause such a non-statistical distribution.

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Chapter 6

Electronic quenching of OH

A $^2\Sigma^+(\nu = 0)$ by H₂

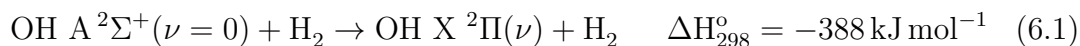
6.1 Introduction

The chemistry of the hydroxyl radical is of particular significance in the atmosphere, where it is intimately involved with the oxidising chemistry of both the troposphere and the stratosphere. As such it governs the lifetime of many species and therefore their contribution to climate change, air pollution and ozone formation. Hydroxyl radicals are also of importance in flame and combustion environments. Determining the concentration of OH within these environments is of great importance for probing of the chemistry taking place, and this is often achieved by laser induced fluorescence (LIF) using the OH A $^2\Sigma^+ - X^2\Pi$ band system [1]. Collisions of electronically excited OH with various molecular partners have been the focus of many investigations. The dependence of the quenching cross sections on the temperature and rotational and vibrational excitation of OH

$A^2\Sigma^+$ has been well documented [2–8]. The cross sections are found, in general, to decrease with increasing temperature, indicating that attractive forces govern the kinetics [5]. The decreasing quenching efficiency of the higher rotational states of the OH $A^2\Sigma^+$ molecule, as found for the case for a large variety of collisional partners, has been attributed to the anisotropy of the OH $A^2\Sigma^+ + M$ potential energy surfaces (PESs), signifying that certain orientations of the OH– M complex preferentially lead to quenching. A higher degree of rotational excitation within OH $A^2\Sigma^+$ will more effectively average over all relative orientations of the collision partners with the OH radical, thus reducing the contribution of the favourable configurations that lead to quenching [3]. Investigations of the non-quenching collisions that occur between electronically excited OH and various collisional partners have also been performed. Brouard *et al.* [9] have employed quantum beat spectroscopy to study the collisions of various rotational states of OH $A^2\Sigma^+(\nu = 0)$ with Ar. They observed a depolarisation rate that was much greater than the rate of rotational energy transfer within the electronically excited state. The rate of depolarisation was found to decrease for increasing level of rotational excitation.

Recently, attention has moved to exploring the dynamics of the electronic quenching of OH $A^2\Sigma^+(\nu = 0)$, identifying product state distributions and measuring the branching ratios between different channels. In particular, collisions with H_2 can remove population from the electronically excited OH $A^2\Sigma^+$ state by two competing channels, non-reactive and reactive quenching, as shown in

Equations 6.1 and 6.2,



The reactive quenching channel was the first to be investigated experimentally, by Lester and co-workers [10], who detected H atom products, confirming the presence of the reactive pathway. The velocity distribution of the H-atom products was bimodal, attributed to a direct and an indirect (statistical) reaction mechanism. It was also concluded that a significant fraction of the OH A $^2\Sigma^+$ electronic energy was channelled into internal excitation of the H₂O product. More recently experiments probing the quantum state distribution of the OH X $^2\Pi$ product from the non-reactive quenching channel have been performed [8, 11]. Process (6.1) was found to account for $(12 \pm 5)\%$ of the products [12]. Lester and co-workers employed a pump-probe LIF based technique to determine the internal energy distribution of OH X $^2\Pi$ products and it was found that OH X $^2\Pi$ products were formed vibrationally cold, with $> 70\%$ of the molecules in the lowest vibrational level [11]. In all vibrational levels probed, OH X $^2\Pi$ products were found to be highly rotationally excited, the distribution peaking around $N = 15$ and 16 in $\nu = 0$ and 1 respectively. Quantitative measurements of the population distributions of the products of quenching have significant importance with regard to LIF studies. As mentioned earlier one method for determining the concentration of OH radicals is to observe LIF from the OH A-X band. Collisional deactivation (quenching) of OH A $^2\Sigma^+$ fluorescence by neighbouring molecules in high pressure environments (such as flames or the atmosphere) can affect LIF measurements of

OH population distributions, by returning population to the pumped state within the timescale of the laser excitation pulse.

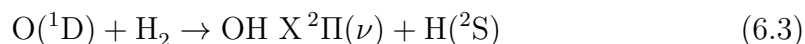
This chapter presents an experimental investigation of the collisional electronic quenching of OH A $^2\Sigma^+(\nu = 0)$ by molecular hydrogen, using time-resolved FTIR emission spectroscopy to investigate the products.

6.2 Generation of OH radicals

First it was first necessary to select a suitable method of OH X $^2\Pi$ radical generation. Early experimental studies of the collisional quenching of OH A $^2\Sigma^+$ employed reactive methods for producing hydroxyl radicals *in situ*, in particular the reaction between NO₂ and hydrogen atoms, produced in a microwave discharge in H₂ or H₂O [2, 3]. More recently, photolytic methods for generating OH have been employed, for example the UV photolysis of molecules such as H₂O₂ and HNO₃ [5–8]. In this section, two methods for producing OH radicals will be investigated for their suitability for the study of the electronic quenching of OH A $^2\Sigma^+$ using FTIR emission spectroscopy.

6.2.1 Reactive generation

The reaction between O(1D) and molecular hydrogen, process (6.3), was chosen as a potential method for the generation of OH radicals.



One particular advantage of this method of generating OH for study of the the electronic quenching of OH A $^2\Sigma^+$ by H₂ is that H₂ will already be present in the cell. This of course means that its suitability for investigating the effects of other quenching is severely reduced. Due to its key role in atmospheric chemistry, the reaction of O(1D) and H₂ has been extensively studied [13–16], proving to be an efficient process producing OH in vibrationally excited states [17].

The method chosen for the generation of O(1D) in this work was the photolysis of N₂O at 193 nm. At this wavelength there are four energetically feasible pathways, as illustrated in Equations 6.4, 6.5, 6.6 and 6.7 where the long wavelength limits indicated are the thermochemical thresholds for each pathway [18].



Photodissociation between 185 nm and 229 nm under collisionless conditions proceeds almost exclusively along pathway (6.5) [19], with a dissociation energy of $(351.0 \pm 1.8) \text{ kJ mol}^{-1}$. While the formation of ground state oxygen atoms, process (6.4), is energetically more favourable, with a dissociation energy of only $161.5 \text{ kJ mol}^{-1}$, it is spin-forbidden and has a negligible quantum yield of 0.005 at 193 nm [20]. Such selectivity makes N₂O as a suitable precursor for the generation of O(1D) atoms—particularly in view of the chemical inertness of the partner fragment N₂—ensuring no other photolysis initiated reactions would occur.

Experiments were first performed to confirm the formation of OH radicals. A

6.2. Generation of OH radicals

flowing sample of N_2O was photolysed at 193 nm, in the presence of H_2 and Ar, each with a partial pressure of 1.7 Torr. The rate constant for reaction (6.3) is reported as $(2.7 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which under the experimental conditions employed means that by $0.7 \mu\text{s}$ the reaction will be 86 % complete. Figure 6.1 (a) presents the fundamental emission spectrum of OH $\text{X}^2\Pi(\nu)$ ob-

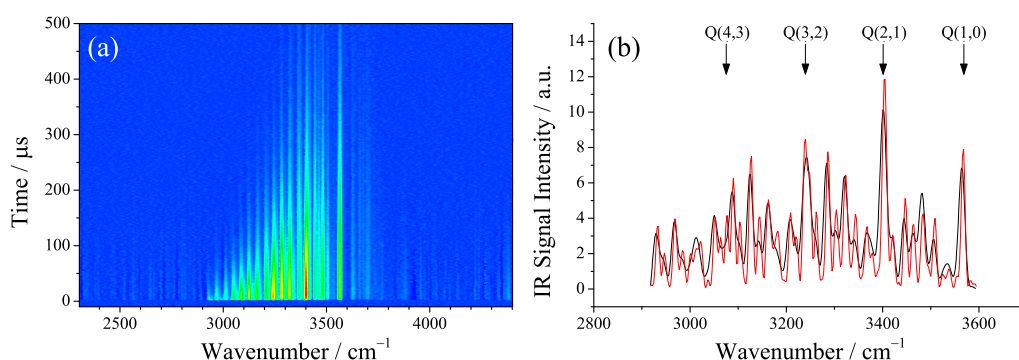


Figure 6.1: (a) Contour plot of OH $\text{X}^2\Pi(\nu)$ emission observed following the photodissociation of 330 mTorr of N_2O in the presence of 1.7 Torr of H_2 and 1.7 Torr of Ar. Plot obtained at 10 cm^{-1} resolution using an InSb detector. Red denotes high intensity and blue denotes low intensity. (b) IR emission observed at $5 \mu\text{s}$ following the photolysis laser pulse (black). OH $\text{X}^2\Pi$ fundamental emission simulation overlaid (red).

served following the photolysis of N_2O and subsequent reaction with H_2 . Marked on Figure 6.1 (b) are the positions of the Q branches for the fundamental transitions, $\Delta\nu = -1$, originating in $\nu = 1-4$. Also shown is a best-fit spectral simulation with the vibrational populations treated as adjustable parameters; a 300 K rotational distribution was assumed for all vibrational levels. The vibrational distribution obtained at $5 \mu\text{s}$ following the photolysis pulse is broad, with approximately equal populations in the first three vibrational levels and a smaller population in the fourth. This slightly inverted distribution closely resembles the nascent distribution reported by Sloan and co-workers [17], as presented in Table 6.1.

6.2. Generation of OH radicals

Table 6.1: Normalised vibrational distribution of OH X $^2\Pi$ formed following the photodissociation of N₂O at 193 nm in the presence of H₂ and Ar.

OH X $^2\Pi(\nu)$	$\nu = 1$	$\nu = 2$	$\nu = 3$	$\nu = 4$
This work	0.27 ± 0.03	0.28 ± 0.02	0.27 ± 0.02	0.19 ± 0.02
Sloan and co-workers [17]	0.29	0.32	0.25	0.13

Experiments were subsequently performed exciting OH X $^2\Pi$ to the A $^2\Sigma^+$ state using radiation at 307.935 nm, pumping the overlapped Q₁(1) and P₂₁(1) rotational lines, which both excite population only from the $N = 1$ state. Generation of OH A $^2\Sigma^+$ was confirmed by detecting LIF from the OH A $^2\Sigma^+(\nu = 0) \rightarrow$ X $^2\Pi(\nu = 1)$ band at 345 nm with a PMT positioned above the reaction cell. Figure 6.2 presents the integrated LIF intensity as a function of delay between the photolysis and pumping lasers. The LIF intensity is proportional to the number of OH molecules excited up to the A $^2\Sigma^+$ state, and thus it can be seen that the maximum number density occurs when the delay between the two lasers is 600 μ s. The lower number density at shorter laser delays is a result of process (6.3) forming OH X $^2\Pi$ in vibrationally excited states, as shown by the distribution in Table 6.1. Thus as vibrational relaxation of the OH X $^2\Pi(\nu > 0)$ molecules occurs, the population in the ground vibrational level increases, and so more molecules can be excited up to the A $^2\Sigma^+$ state. The fall in number density of OH at longer laser delays is caused by the diffusion of OH molecules out of the laser beam path. However, even with the time delay between the laser pulses set to the optimum value, the IR signal detected after collisional deactivation of OH A $^2\Sigma^+$ exhibited a poor signal-to-noise ratio, indicating that insufficient quantities of OH X $^2\Pi$ were present in the reaction chamber for these purposes. Therefore, despite the relatively clean nature of the system, another method of generating OH radicals must be used.

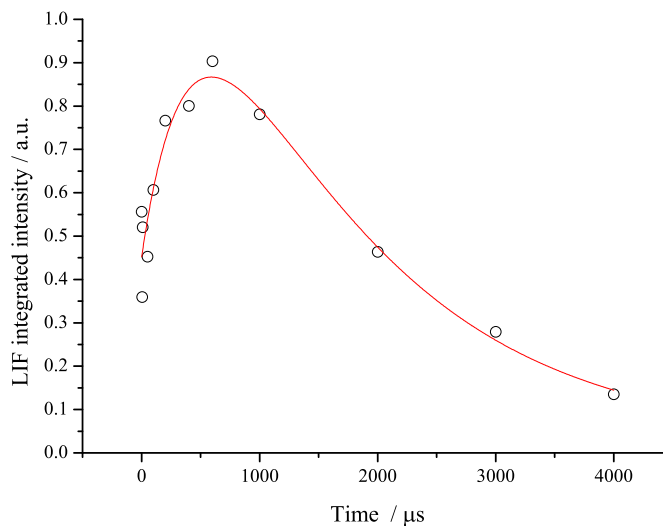


Figure 6.2: Integrated LIF intensity of the OH $A^2\Sigma^+(\nu = 0) \rightarrow X^2\Pi(\nu = 1)$ emission band plotted as a function of delay between the photolysis and pumping lasers ($\circ$). Also shown is double exponential fit to the experimental data (red).

6.2.2 Photolytic generation of OH

Nitric acid and hydrogen peroxide are two molecules that have been widely used as photolytic precursors for OH radicals. Both processes are of key atmospheric significance, with HNO_3 and H_2O_2 acting as reservoirs of OH, and hence the solar photolysis of these species is intimately involved with governing the OH concentrations in the atmosphere. The various photolytic channels are well identified and competing efficiency of these as a function of photolysis wavelength has been the focus of many investigations [21–26]. Of particular significance to the present work is the achievable number density of OH radicals, which in turn depends upon absorption cross sections and quantum yields. The 193 nm photolysis of

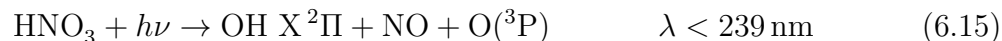
H_2O_2 is dominated by two pathways:



The quantum yield for the generation of OH X $^2\Pi$ radicals following photodissociation of H_2O_2 is reported to be between 1.2 and 1.6 [21, 22], with up to 15 % of the OH formed in a vibrationally excited state. Photolysis of HNO_3 produces a lower quantum yield of OH, reported to lie between 0.33 and 0.6 [24, 27]. However, despite the favourable quantum yield for hydroxyl production *via* hydrogen peroxide photolysis, the absorption cross section of H_2O_2 at 193 nm is two orders of magnitude lower than for HNO_3 [24]. The number density of OH radicals is of primary importance for the experiments in this chapter. Previous experiments in the group attempted to use H_2O_2 [28], but with no success, and it is clear that photolysis of nitric acid is the preferable choice for OH generation. There are many thermally accessible photolysis channels following the absorption of 193 nm photons [22, 29], as shown below in Equations (6.10)-(6.16).



6.2. Generation of OH radicals



At 193 nm, the processes shown in (6.10) and (6.14) form the major dissociation pathways [22, 24, 27, 29], with pathway (6.11) providing a small contribution [30]. However, there exists some disagreement over the branching ratio between formation of OH and HONO products, with the reported values for the quantum yield of OH formation showing considerable spread. Values of 0.33 ± 0.06 , 0.47 ± 0.06 and 0.6 ± 0.1 have been reported by Turnipseed *et al.* [24], Schiffman *et al.* [22] and Felder *et al.* [27] respectively. Each work employed a different experimental technique, which could account for some of the discrepancy. Myers *et al.* [30] investigated dissociation channel (6.10) using photofragment translational spectroscopy (PTS) and observed the NO_2 fragment formed in two electronic states, $\text{NO}_2(1^2\text{B}_2)$ and an unidentified state NO_2^* , in the ratio of 1:2.2. They determined that the NO_2^* was unstable and underwent secondary dissociation *via* the process (6.17).



The OH fragment is known to be formed both electronically and vibrationally cold, with no more than 5% formed with vibrational excitation [26]. However, despite the discrepancy of the reported branching ratios, all works are in agreement that the formation of OH radicals is a major dissociation pathway following the 193 nm photolysis of HNO_3 .

An understanding of the IR emission following the 193 nm photolysis of HNO_3 is required in order to ensure that the photolysis step does not interfere with emis-

6.2. Generation of OH radicals

sion resulting from electronic quenching of the OH $A^2\Sigma^+$ state. A flowing sample of HNO_3 (70 % w/w solution) was photolysed at 193 nm, and Figures 6.3 and 6.4 show the time-resolved emission spectra obtained with the InSb and HgCdTe detectors, respectively. A number of emission features are evident in Figure 6.3.

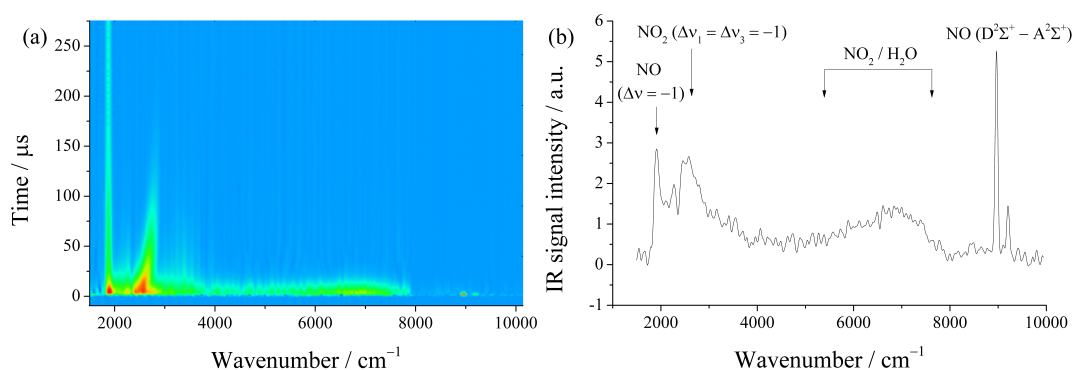


Figure 6.3: (a) Contour plot of emission observed in the region of 1850 cm^{-1} to 10000 cm^{-1} following the dissociation of 70 mTorr of HNO_3 at 193 nm. The emission above 8000 cm^{-1} has been reduced by a factor of 5 to allow sufficient colour resolution for the low wavenumber emission. Spectra were obtained at a resolution of 40 cm^{-1} using a liquid nitrogen cooled InSb detector. Red represents high intensity and blue represents low intensity. (b) Spectrum of emission observed, summed from $0\text{ }\mu\text{s}$ to $10\text{ }\mu\text{s}$ following the photolysis laser pulse. Band assignments are marked.

The intense doublet appearing at $\sim 9000\text{ cm}^{-1}$ is identified as the P and R branch of the $\text{NO } D^2\Sigma^+(\nu = 0) \rightarrow A^2\Sigma^+(\nu = 0)$ electronic transition. This has been observed by Yeh *et al.* [23] and is the result of a two photon process involving the absorption of a second photon by highly rotationally excited states of nascent $\text{NO } X^2\Pi(\nu = 1)$, a secondary fragment produced *via* pathway (6.17). The weak, long-lived feature present in Figure 6.3 (a) below 2000 cm^{-1} is assigned to fundamental emission from vibrationally excited $\text{NO } X^2\Pi$, further confirming the presence of this species. The weaker, broadband emission spanning the range 6000 cm^{-1} to 8000 cm^{-1} in Figure 6.3 is attributable to electronic emission from NO_2 . Finally, the feature peaking at 2750 cm^{-1} is due the NO_2 ($\Delta\nu_1 = \Delta\nu_3 = -1$)

emission band. A feature which cannot be clearly seen in Figure 6.3 (but will be discussed in the following section) is the long-lived, weak emission from OH $X^2\Pi(\nu)$ formed as a result of the $O(^1D) + HNO_3$ reaction. Figure 6.4 shows the time-resolved emission spectra obtained with the HgCdTe detector, showing copious emission appearing in the region 800 cm^{-1} to 1850 cm^{-1} . First, the three

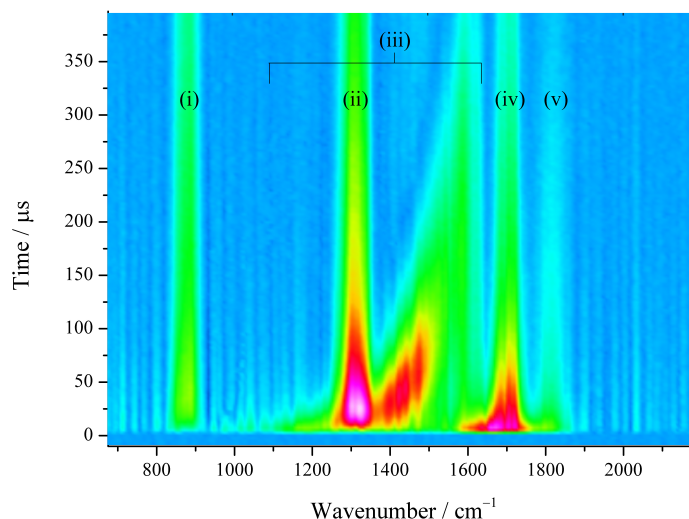


Figure 6.4: Contour plot of IR emission following the photodissociation of 30 mTorr of HNO_3 at 193 nm. Plot obtained at 10 cm^{-1} resolution using an HgCdTe detector. Red denotes high intensity and blue denotes low intensity.

narrow bands of long-lived emission, (i), (ii) and (iv), may be attributed either to vibrationally excited HNO_3 itself, formed following vibrational energy transfer (VET), or to HONO formed directly as a product of the photolysis. Secondly, the feature between 1200 cm^{-1} to 1600 cm^{-1} , labelled (iii), and seen to cascade rapidly to higher wavenumbers with time is assigned to highly vibrationally excited $NO_2(\nu_3)$. Finally, the weakest feature apparent in Figure 6.4 just above 1800 cm^{-1} , labelled (v), is assigned to emission from the fundamental transitions

6.2. Generation of OH radicals

of NO X²Π. That this feature should be weak is attributed to the low pass optical filter, with a cut-off at 1850 cm⁻¹, employed to prevent the strong NO₂ $\Delta\nu_1 = \Delta\nu_3 = -1$ emission band at ~ 2750 cm⁻¹ from aliasing. Figure 6.5 (a) examines the kinetic behaviour of emission features (i), (ii) and (iv), and clearly reveals that two of the three exhibit a rise-time, suggesting that these two bands, (i) and (ii), may be attributed to non-nascent species. Feature (i) is assigned to the HO–N stretch of HNO₃, vibrationally excited *via* VET, and feature (ii) to the symmetric –NO₂ stretch of HNO₃, excited in a similar manner. Experiments performed under lower pressure conditions found the rise-time of these features to increase. Feature (iv) is attributed to the nascent species, HONO, formed directly from the photolysis with excitation in the –N=O stretching mode. For

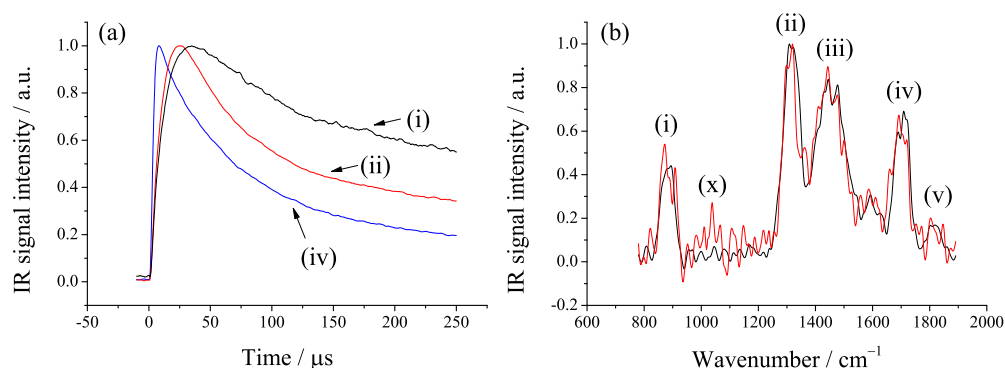


Figure 6.5: (a) Temporal profiles of IR emission in the region corresponding to emission feature (i) (black), (ii) (red) and (iv) (blue), as labelled in Figure 6.4, following the photodissociation of 30 mTorr HNO₃ at 193 nm. (b) Plot of total IR emission summed between 175 μs and 300 μs (late time) following the photolysis laser pulse. Emission following photodissociation of HNO₃ (black) and following photodissociation of 30 mTorr of DNO₃ (red).

further confirmation of the assignments, experiments photolysing the deuterated counterpart, DNO₃, were performed. Figure 6.5 (b) presents a comparison between the late time IR emission following the 193 nm photolysis of HNO₃ and

DNO_3 . The labelling of the emission features is consistent between Figure 6.4 and Figure 6.5 (b). Features (i) and (ii), assigned to vibrationally excited HNO_3 , would be expected to shift only marginally to lower wavenumbers with DNO_3 . Emission feature (iv), attributed to HONO excited in the $-\text{N}=\text{O}$ stretching mode, is also barely expected to shift. This proves to be the case, as demonstrated by Figure 6.5 (b), giving confidence in the assignment of the emission features is correct. An additional feature appears following the 193 nm photolysis of DNO_3 , as labelled (x). This feature is assigned as the $\text{D}-\text{O}-\text{N}$ bend of either DNO_3 , similarly excited through VET or DONO . The emission is too weak and broadened to confidently distinguish between the two possibilities. The corresponding $\text{H}-\text{O}-\text{N}$ bend of both molecules would appear in the emission region of feature (ii) in Figure 6.4, and would not be discernible from the HNO_3 emission. Efficient vibrational energy transfer processes are occurring following the photodissociation of HNO_3 ; the rise-time of the HNO_3 emission in Figure 6.5 (a) implies a VET rate constant of $\sim 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This would require a close energy match between the vibrational spacing of the donor and acceptor molecules. HONO , vibrationally excited in the $-\text{N}=\text{O}$ stretching mode, is formed following the photolysis of nitric acid. Nitric acid has an equivalent vibrational mode, with a very similar frequency, so it is likely that VET between these modes of HONO and HNO_3 would be a fast process. It is clear that the 193 nm photolysis of HNO_3 affords an array of photoproducts detectable by FTIR emission spectroscopy, including NO_2 , HONO , and NO , in agreement with the literature. While $\text{OH } X^2\Pi$ was not detected directly, due to strong emission from other photoproducts in the OH fundamental region, together with the low quantum yield for forming vibrationally excited OH, its co-product, NO_2 , has been detected, and thus we

can be confident of large number densities of OH being generated.

6.3 Excitation spectrum

An excitation spectrum of OH was obtained in the presence of H₂ to confirm that the IR emission detected following the laser pulse at 308 nm was a result of quenching of the OH A ²Σ⁺ state, and not due to any undesired processes such as photolysis of other photoproducts (eg HONO and NO₂) or two-photon processes. A flowing sample of HNO₃ (100 %, fuming) was photolysed at 193 nm, in the presence of H₂ and Ar, typical of the experiments performed in this chapter. The UV output from the Nd:YAG pumped dye laser was subsequently employed, after a delay of 2 ms following the photolysis pulse, to scan across a wavelength region 307.091 nm to 309.087 nm containing a number of rotational lines of the OH transition. LIF on the OH A ²Σ⁺(ν = 0) → OH X ²Π(ν = 1) band at ~345 nm was collected with a photomultiplier tube (PMT) and IR emission measured using an InSb detector, in the region 2700 cm⁻¹ to 4000 cm⁻¹, as a function of excitation wavelength. A photodiode was used to confirm the laser intensity remained constant throughout the wavelength scan. Figure 6.6 displays the excitation spectrum of OH as recorded by an InSb detector and PMT, alongside a spectral simulation. The positions of individual rotational lines seen in the experimental spectra correlate well with those predicted by the LIFBASE spectral simulation [31]. In this instance, the OH transition is saturated, and thus the relative line intensities of the LIFBASE simulation and the experimental LIF spectra are not seen to correlate well. Whilst this aspect is not of concern, it is important that the relative intensity of the features in the LIF and IR spectra are consistent.

6.4. Setting up for IR emission experiments

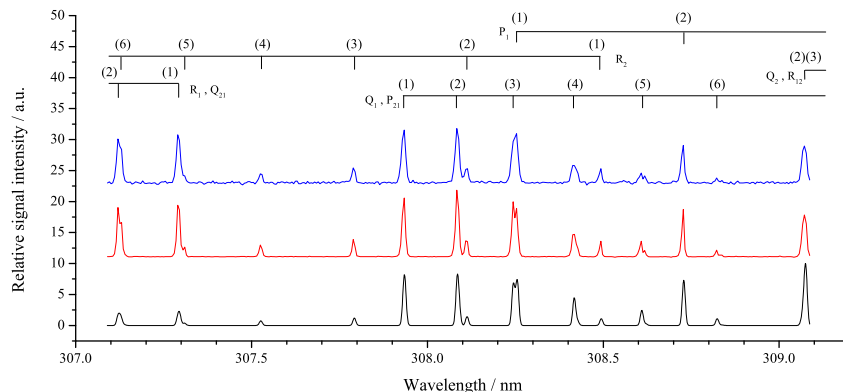


Figure 6.6: Excitation spectrum of OH following 193 nm photolysis of 35 mTorr of HNO_3 , in the presence of 410 mTorr of H_2 and 1.0 Torr of Ar, and subsequent excitation of OH $X^2\Pi$ radicals in the region 307.091 nm to 309.087 nm, as recorded by an InSb detector (blue) and PMT (red). Spectrum as predicted by LIFBASE [31] database is also displayed (black). Spectral assignments are shown, according to the nomenclature described in Chapter 1. For clarity certain bands have been grouped together, as the difference in line positions for equivalent N is <0.015 nm.

This behaviour is observed in Figure 6.6, confirming that all the IR emission is directly dependent on the number density of OH $A^2\Sigma^+$ molecules, and that the presence of additional photolysis products, such as NO_2 and HONO, does not interfere with the experiment.

6.4 Setting up for IR emission experiments

Attention is now turned to investigating the electronic quenching of OH $A^2\Sigma^+$ by H_2 . OH radicals, generated *in situ* by the 193 nm photolysis of nitric acid, are excited up to the $A^2\Sigma^+(\nu = 0)$ state by pumping the overlapped $Q_1(1)$ and $P_{21}(1)$ rotational lines of the OH A-X (0,0) transition. This represents a more complex experimental procedure than was needed for studying the collisional quenching of NO $A^2\Sigma^+$ as described in Chapters 3, 4 and 5. Certain modifications to the data

6.4. Setting up for IR emission experiments

collection procedure are required as a result. First, the method for normalising the IR signal for the laser intensity is no longer appropriate. For a single laser experiment, this is a facile process, whereby a small fraction of the laser beam is monitored by a photodiode, and the recorded IR trace is normalised accordingly on a shot-by-shot basis. However, in the current experiment where two lasers are required, normalisation to either one in the manner described above would be incorrect. It was necessary instead to normalise to the OH A $\rightarrow$ X LIF signal, which is proportional to the number of OH A $^2\Sigma^+$ molecules generated. The OH A-X (0,1) emission band was chosen as this could be separated from the laser scatter. The Franck-Condon factor for this transition is several orders of magnitude weaker than the OH A-X (0,0) transition, and a careful arrangement of a focusing lens and a monochromator, positioned in-between the cell and the PMT, were required to achieve sufficient scatter free signal.

There are certain caveats to using the above procedure, due to the nature of the system; a two laser experiment means that there are two points in time that IR emission is initiated. In Figures 6.3 and 6.4 it can be seen that there are certain emission features which have long lifetimes, namely the HNO₃, HONO and NO emissions at 1300 cm⁻¹, 1700 cm⁻¹ and 1900 cm⁻¹ respectively. If these emissions have not fully relaxed before the pump laser is initiated, then the IR emission due to quenching of the A $^2\Sigma^+$ state of OH will be superimposed upon emission from the photolysis of nitric acid. Normalising the IR traces to the OH A-X LIF emission will correctly scale the intensity of the emission from quenching products, but this does not take into account any IR emission from photo-products that are detected at the same time. Such a procedure would lead to a source of variation of IR signal intensity observed at the detector which is not a function of the path

6.4. Setting up for IR emission experiments

difference induced by the interferometer, which will manifest itself as noise upon Fourier transformation. This issue will only arise if emission from photolysis products is detected alongside the emission from quenching of OH A $^2\Sigma^+$. As stated above the only long lived emission features which would cause this are all below 2000 cm^{-1} , and fortunately do not interfere spectrally with the emission from OH at $\sim 3500\text{ cm}^{-1}$, and so optical filters can be employed to remove them.

The nascent intensity of the photolysis initiated emission is several orders of magnitude larger than the emission observed following quenching of OH A $^2\Sigma^+(\nu = 0)$. The typical InSb detector output corresponding to the emission observed in the region 2300 cm^{-1} to 4500 cm^{-1} following the quenching of OH A $^2\Sigma^+(\nu = 0)$ is around 2.5 mV . The digitisation procedure requires the signal to be $> 100\text{ mV}$ and so an amplification with a gain of $+30\text{ dB}$ is used. However, this degree of amplification of the electronic signal immediately following the photolysis laser overloads the amplification system, which leads to artifacts appearing in the data. Figure 6.7 (a) shows a contour plot recorded following the photolysis of 40 mTorr of $\text{HNO}_3/\text{H}_2\text{O}$ mixture in the presence of Ar and H_2 . The OH photoproduct was subsequently pumped to its A $^2\Sigma^+(\nu = 0)$ state after a delay of $120\text{ }\mu\text{s}$. The contour plot, as well as showing emission in the region of the OH fundamental, shows a strong, invariant feature between 2500 cm^{-1} and 2800 cm^{-1} . This region corresponds to the NO_2 ($\Delta\nu_1 = \Delta\nu_3 = -1$) emission band, but the observed feature is an artifact in the data. As can be seen in Figure 6.3 (a) the NO_2 emission feature has relaxed by $120\text{ }\mu\text{s}$, and given the presence of H_2 in the experiment, the relaxation of this NO_2 will be faster. Figure 6.7 (b) shows a comparison between a late time spectrum taken from Figure 6.3 (a), which shows the relaxed spectrum of NO_2 , and a spectrum of the artifact feature. Evidently the two spectra do

6.4. Setting up for IR emission experiments

not match. If the feature in Figure 6.7 (a) was real emission from NO_2 , either it would be expected to appear at higher wavenumbers, peaking at $\sim 2900\text{ cm}^{-1}$, or be seen to shift to higher wavenumbers as a function of time as vibrational relaxation occurs. The artifact appears because the amplifier was being overloaded, and a ringing effect occurs which lasts much longer in time than the emission. The intensity of the ringing effect is not constant but depends on the intensity of the input signal, which in turn is dominated by the early time emission from vibrationally excited NO_2 . As such the artifact that appears in the data takes the appearance of the early time emission from the NO_2 $\Delta\nu_1 = \Delta\nu_3 = -1$ band. The amplification system was modified to clamp the signal midway through the amplification process to avoid overloading the electronics. This removed the artifact from the data, and thus allowed observation of emission appearing within this region (2500 cm^{-1} to 2800 cm^{-1}) which had not been previously possible [28].

The final consideration that was necessary for these experiments was the photolysis-pump laser delay time. Experiments monitoring the intensity of the OH A-X LIF signal as a function of delay time between the photolysis and the pumping laser pulses revealed that the largest signal corresponded to a delay time of $\sim 100\text{ }\mu\text{s}$. This is a much shorter delay than was found for the reactive generation experiment, as can be seen in Figure 6.2. This is because the OH $X^2\Pi$ product from the photolysis of HNO_3 at 193 nm is formed vibrationally cold. However, using such a short delay time meant emission from photolysis products interfered with the emission from quenching products, as can be seen in Figure 6.7. Choosing a delay time required a compromise between intensity of the post-quenching IR emission and the long lived photolysis initiated emission,

6.4. Setting up for IR emission experiments

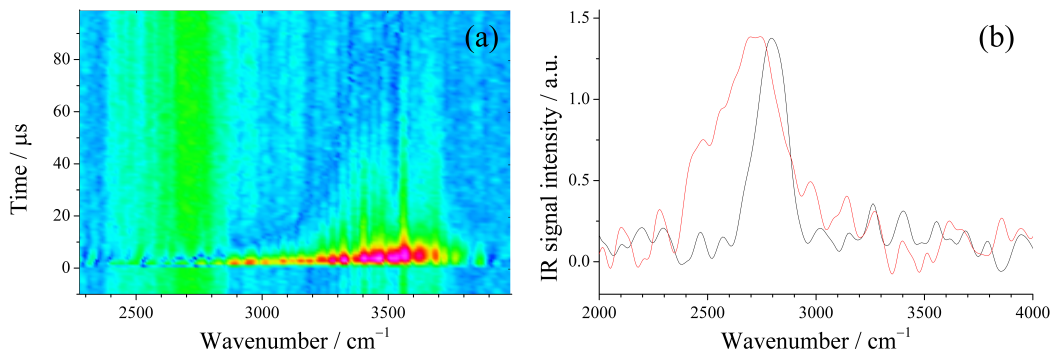


Figure 6.7: (a) Contour plot of emission following the photolysis of 40 mTorr of HNO_3 solution in the presence of 800 mTorr of Ar and 1.2 Torr of H_2 , and subsequent pumping of the OH photoproducts at 308 nm. Emission was detected with a liquid nitrogen cooled InSb detector, and was collected at 20 cm^{-1} resolution. The delay between with photolysis and pumping lasers was $120\text{ }\mu\text{s}$. Red represents high intensity and blue represents low intensity. (b) Spectrum taken at $85\text{ }\mu\text{s}$ following pumping laser from (a) (red), shown with a spectrum of emission at $120\text{ }\mu\text{s}$ following the photolysis laser in the experiment shown in Figure 6.3 (a) (black).

which will be referred to as pre-pumping emission. Even with a delay of 2 ms there was still a weak pre-pumping signal, and delaying any longer resulted in an increasingly small post-quenching IR signal, as the density of OH molecules in the laser beam path drops through diffusion. In general, delay times of between 1 ms and 2 ms were used. Although pre-pumping signals were still apparent, they were weak, and showed minimal spectral variation with time. Figure 6.8 presents a contour plot of IR emission observed following the quenching of OH $\text{A}^2\Sigma^+(\nu = 0)$ by H_2 . The pre-pumping emission exhibits clear structure, which corresponds well to the rotational lines of the OH $\text{X}^2\Pi(\Delta\nu = -1)$ emission band. It is unlikely that this emission is from the OH photoproduct, since vibrationally excited OH has a negligible quantum yield in the 193 nm photolysis of HNO_3 [26]. Rather the reaction between the $\text{O}(^1\text{D})$ fragment with surrounding H_2 and HNO_3 , producing vibrationally excited OH is responsible. Similar emission is observed

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

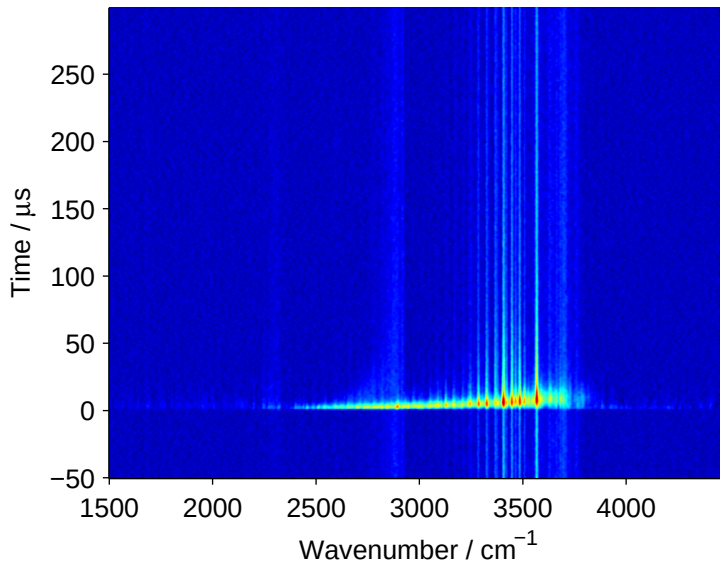


Figure 6.8: Contour plot of IR emission following pumping of the overlapped Q₁(1) and P₂₁(1) rotational lines of the OH A-X (0,0) transition in the presence of 40 mTorr of HNO₃, 1.1 Torr of Ar and 400 mTorr of H₂. The delay between the photolysis laser and the pumping laser was 1.1 ms. Plot obtained at 10 cm⁻¹ resolution using an InSb detector. Red denotes high intensity and blue denotes low intensity.

in the absence of H₂, albeit weaker. This emission can be successfully subtracted from the data by using IR traces obtained without the pumping laser firing to scale the photoysis-initiated emission appropriately prior to subtraction.

6.5 Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

Photolysis of nitric acid at 193 nm was the method of generation of OH radicals adopted for the quenching experiments presented in this chapter. This was the method employed in a previous study on the collisional quenching of OH A $^2\Sigma^+$ performed in the group [28], where a HNO₃ (70 % w/w solution) was employed as the precursor, the vapour of which is a mixture of HNO₃ and H₂O in a 1:1 ratio

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

[32]. Emission from H₂O was observed following the quenching by the vapour of the HNO₃ solution, and it was not possible to discern whether the vibrationally excited H₂O was a reaction product, or whether it was formed from the non-reactive quenching of OH A $^2\Sigma^+$ by the H₂O vapour in the cell. For the present work 100 %, fuming, nitric acid was used. A consequence of using a precursor for the generation of OH radicals is that collisional quenching of OH A $^2\Sigma^+(\nu = 0)$ by HNO₃, the precursor, will occur for whatever quencher, M , is studied. The expression therefore for the quantum yield of quenching of OH A $^2\Sigma^+$ by a given collision partner, M is given in Equation 6.18.

$$\Phi_M = \frac{k_M[M]}{k_f + k_M[M] + k_{\text{HNO}_3}[\text{HNO}_3] + k_{\text{Ar}}[\text{Ar}]} \quad (6.18)$$

Although conditions can be chosen to ensure the desired process will dominate, the quenching by nitric acid cannot be ignored, particularly as it has been found to be an efficient quencher of OH A $^2\Sigma^+$ [6], with a rate constant of $(5.56 \pm 0.60) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The contribution of this quenching channel will be discussed in detail in Section 6.5.1.

Experiments were first performed to investigate the electronic quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂. A flowing sample of HNO₃ (100 %, fuming) was photolysed at 193 nm, in the presence of H₂. Partial pressures, 40 mTorr of HNO₃, 1.1 Torr of Ar and 400 mTorr H₂, were chosen such that the quantum yield of quenching by H₂ was around 0.6 with the ratio $\Phi_{\text{H}_2}:\Phi_{\text{HNO}_3} = 4:1$. A more favourable ratio could be achieved by either increasing the partial pressure of H₂ or reducing the partial pressure of HNO₃. Using lower pressures of HNO₃ results in smaller signal sizes, while H₂ was found to efficiently collisionally quench the

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

observed post-quenching infrared signal, so having a greater partial pressure of H₂ will prevent nascent distributions from being observed. OH photofragments were excited by laser radiation, tuned to resonance with the overlapped Q₁(1) and P₂₁(1) rotational lines of the OH transition at 307.935 nm. Experiments were performed in the presence of Ar in order to rotationally thermalise products formed following collisional quenching of OH A $^2\Sigma^+$, thus enabling a rotational temperature of 300 K to be used in spectral simulations. In light of the findings of Lester and co-workers [12], it is expected that the majority of emission will be attributable to vibrationally excited H₂O, formed as a result of reactive quenching. Only a minor contribution is expected from OH X $^2\Pi(\nu)$. Pure HNO₃ was employed for the generation of OH X $^2\Pi$, rather than an HNO₃ solution so that any H₂O detected in emission will be evidence of reactive quenching, and not of energy transfer from OH A $^2\Sigma^+$ to H₂O already present in the cell. Figure 6.9 presents a series of emission spectra in the region from 2200 cm⁻¹ to 4000 cm⁻¹ recorded following quenching of OH A $^2\Sigma^+(\nu = 0)$. The pre-pumping OH emission from the O(¹D) + H₂ reaction, as seen in Figure 6.8 has been subtracted. The early time emission (Figure 6.9 (a)) is broad, relatively unstructured and seen to shift rapidly to higher wavenumbers as a function of time. This emission relaxes rapidly, and reveals a weak structured emission feature, an example of which is shown in Figure 6.9 (b). This emission is assigned as the OH X $^2\Pi$ fundamental emission band, confirmed by the excellent agreement seen between the experimental spectrum and the fitted OH X $^2\Pi$ fundamental simulation. However, at early time the experimental emission spectrum does not resemble that of OH. The work performed by Lester and co-workers [10, 12] show that hydrogen abstraction by OH A $^2\Sigma^+$ radicals to form H₂O dominates when OH A $^2\Sigma^+(\nu = 0)$

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

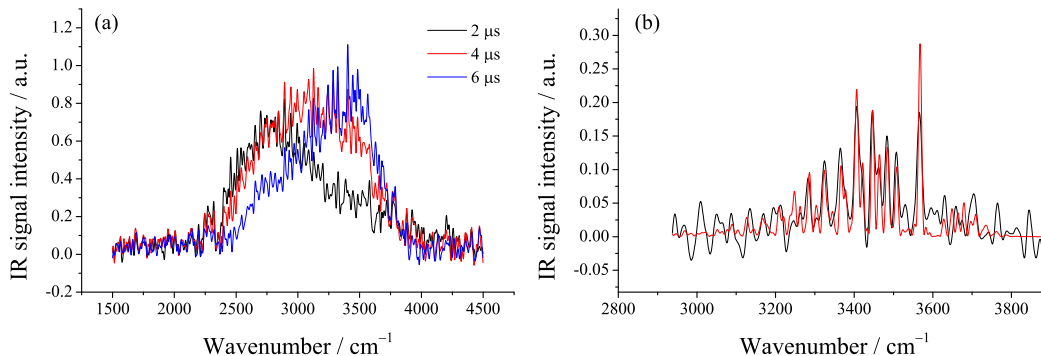


Figure 6.9: (a) Emission observed at 2 μ s (black), 4 μ s (red) and 6 μ s (blue) following pumping of the overlapped Q₁(1) and P₂₁(1) rotational lines of the OH A $\leftarrow$ X transition in the presence of 40 mTorr of HNO₃, 1.1 Torr of Ar and 400 mTorr H₂. (b) Spectrum of IR emission recorded at 45 μ s following pumping laser pulse (black) with fitted OH X $^2\Pi(\nu)$ fundamental simulation (red) overlaid. All spectra obtained at 10 cm⁻¹ resolution using an InSb detector. N.B. Pre-pumping emission has been subtracted.

is quenched by H₂. Therefore the early time emission is likely to originate from vibrationally excited H₂O formed *via* a reactive quenching channel (6.2).

6.5.1 Quenching of OH A $^2\Sigma^+(\nu = 0)$ by HNO₃

The previous section demonstrated that collisional quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂ produces both vibrationally excited H₂O and OH. Under these experimental conditions, OH A $^2\Sigma^+$ may be quenched not only by the molecular partner of choice, H₂, but also similarly by HNO₃, *via* both reactive and non-reactive pathways. As stated above, $\Phi_{\text{H}_2}:\Phi_{\text{HNO}_3} = 4:1$. So before a more detailed analysis of the emission spectra was performed, the quenching of OH A $^2\Sigma^+(\nu = 0)$ by HNO₃ was investigated.

Partial pressures were chosen so that the quantum yield of quenching by nitric acid was ~ 0.5 ; higher pressures of HNO₃ were associated very short lifetimes

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

of the emission features. Argon was present also to rotationally thermalise the quenching products. Figure 6.10 (a) shows a contour plot of the emission (with the pre-pumping signal subtracted) in the OH fundamental region that was detected following the generation of OH A $^2\Sigma^+(\nu = 0)$ molecules and Figure 6.10 (b) shows an early and a late time emission spectrum, recorded 2 μs and 45 μs following the excitation laser pulse. These show that there are a number emission features, which overlap at early time. The late time emission spectrum shows two features, at 2900 cm^{-1} and 3600 cm^{-1} , which are assigned as the $\Delta\nu_3 = \Delta\nu_1 = -1$ band of NO₂ and the fundamental emission of OH respectively. The early time spectra shows emission throughout the whole region of 2200 cm^{-1} to 4000 cm^{-1} . The emission above 2900 cm^{-1} , which cannot be from NO₂, does not resemble fully the well structured emission of the OH fundamental transition, indicating that another emission feature is present, overlapping with the OH and NO₂ emissions. It is noticed that the early time emission exhibits distinct similarity with the early time emission spectra observed following quenching of OH A $^2\Sigma^+$ by H₂, shown in Figure 6.9 (a), suggesting that vibrationally excited water is formed following the quenching of OH A $^2\Sigma^+$ by HNO₃. Observation of emission from NO₂ and H₂O shows that reactive processes are occurring. A proposed reaction scheme for this is shown in Equations 6.19 and 6.20



The reactive process (6.19) produces NO₃ which given the large amount of energy

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

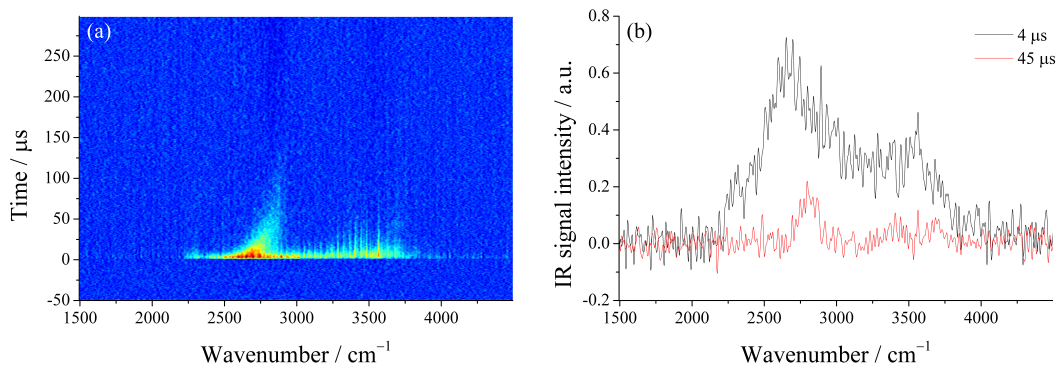


Figure 6.10: (a) Contour plot of emission following the pumping of the overlapped Q₁(1) and P₂₁(1) rotational lines of the OH A-X(0,0) transition in the presence of 75 mTorr of HNO₃ and 1.3 Torr Ar. Red represents high intensity and blue represents low intensity. (b) Emission spectra from the same experiment recorded at 4 μs (black) and 45 μs (red) following the laser excitation pulse. The delay between the pump and probe lasers was 1.5 ms. The spectra were recorded at a resolution of 10 cm⁻¹ with a liquid nitrogen cooled InSb detector.

available can be formed with sufficient energy to subsequently dissociate. The photodissociation of NO₃ has been well studied [33–37]. The two channels, shown by Equations 6.20 and 6.21 both have similar activation energies, which lie below the energy available as a result of process (6.19). For photodissociation of NO₃ at wavelengths that exceed the energy threshold for both channels, dissociation to give NO₂ dominates, with a quantum yield of around 0.7 [33]. Experiments were performed attempting to observe NO₃ emission bands at ~1500 cm⁻¹ were unsuccessful due to the interference from the intense long lived emissions from HNO₃ and HONO as seen in Figure 6.4. However, it was noticed that the intensity of the NO fundamental emission band exhibited an increase upon firing of the 308 nm pumping laser. This could be attributed to process (6.21), but other pathways for the generation of NO X²Π(ν) exist, such as the photolysis of the NO₂ photoproduct. To distinguish between these two possibilities, a series of experiments were performed where the intensity of the NO fundamental emission following

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

the 308 nm laser pulse was measured as a function of (i) pumping wavelength and (ii) quantum yield of quenching by HNO₃. It was found that the intensity of the NO emission was highly dependent on the pumping wavelength, and that as the Φ_{HNO_3} was reduced (by adding H₂), the intensity of the NO signal, correctly normalised for OH A-X LIF, was also reduced in a linear fashion. This is taken as confirmation that vibrationally excited NO observed following the 308 nm pump laser is a product of the quenching of OH A $^2\Sigma^+(\nu = 0)$ by HNO₃, as shown in pathway (6.19). The NO₃ formed in this manner then subsequently dissociates *via* both channels, (6.20) and (6.21) to form vibrationally excited NO₂ and NO respectively.

Now the early time emission following quenching of OH A $^2\Sigma^+(\nu = 0)$ by HNO₃ is known, its contribution to the emission following the quenching by H₂ (shown in Figure 6.9) can be removed by a subtraction procedure. In this way, product state distributions for H₂O formed from the reactive quenching of OH A $^2\Sigma^+$ by H₂ may be examined. To this end, experiments were conducted pumping OH X $^2\Pi$ radicals, firstly in the presence of HNO₃ and Ar, then secondly in the presence of HNO₃, Ar and H₂. Figure 6.11 (a) presents the early time IR emission spectra observed in each experiment as a result of collisional quenching of the OH A $^2\Sigma^+(\nu = 0)$ state. As mentioned previously, these spectra exhibit remarkable similarity, showing that H₂O is formed as a reaction product in both cases. Each emission spectrum was subsequently scaled according to measurements of the relative IR emission intensity for the two systems, obtained using a narrowband optical filter, as presented in Figure 6.11 (b). This experiment indicates that upon addition of H₂ to the gas mixture (which was accompanied by a reduction in the partial pressure of HNO₃ by about half), the emission intensity is seen to increase.

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

This therefore gives confidence that the observed emission following quenching by H₂ is dominated by processes involving H₂, and not HNO₃. The emission observed following collisional quenching of OH A $^2\Sigma^+$ by HNO₃ was then scaled according to its contribution to the emission following the collisional quenching of OH A $^2\Sigma^+(\nu = 0)$ by both HNO₃ and H₂, calculated to be 20 %. Finally, this contribution, as displayed red in Figure 6.11 (c), was then subtracted from the experimental data to reveal the emission resulting purely from the collisional quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂.

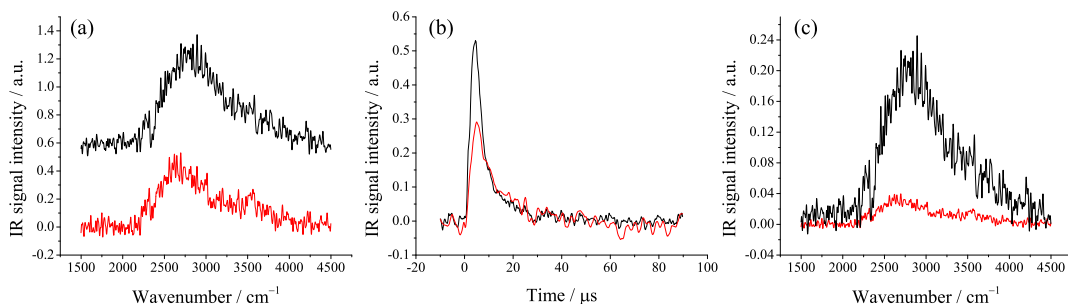


Figure 6.11: (a) Emission observed at 2 μ s following pumping of the overlapped Q₁(1) and P₂₁(1) rotational lines of the OH A $^2\Sigma^+(\nu = 0) \leftarrow$ OH X $^2\Pi(\nu = 0)$ transition in the presence of (i) 75 mTorr of HNO₃ and 1.3 Torr of Ar (red) and (ii) 40 mTorr of HNO₃, 1.1 Torr of Ar and 400 mTorr H₂ (black). Spectra obtained at 10 cm⁻¹ resolution using an InSb detector, arbitrarily scaled and offset for clarity. (b) Temporal profiles of IR emission (normalised to LIF) in the region 2980 cm⁻¹ to 3125 cm⁻¹ following formation of OH A $^2\Sigma^+(\nu = 0)$ as under the same conditions as described for (a). (c) Emission observed at 2 μ s following the formation of OH A $^2\Sigma^+(\nu = 0)$ as described for (a). The red trace has been scaled according to the IR emission intensity ratio shown in (b) and quantum yield considerations.

6.5.2 Reactive collisional quenching

Attention is now paid to the analysis of H₂O emission feature. At this stage, it is noted that the earliest time for which experimental data may be obtained is

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

2 μ s following the pumping pulse. In order to ascertain whether significant relaxation of the nascent H₂O product state distribution may have occurred by this time, experiments were performed at a lower total pressure (where vibrational relaxation would be slower). Although the data obtained in these experiments exhibit lower signal-to-noise ratios, and are therefore not used in the analysis, a comparison of the 2 μ s spectra is shown in Figure 6.12 and confirms that minimal relaxation has occurred in the higher pressure experiments. Thus, it is concluded that the 2 μ s data presented herein form an accurate representation of nascent H₂O vibrational excitation. The current experiments provide the first direct ob-

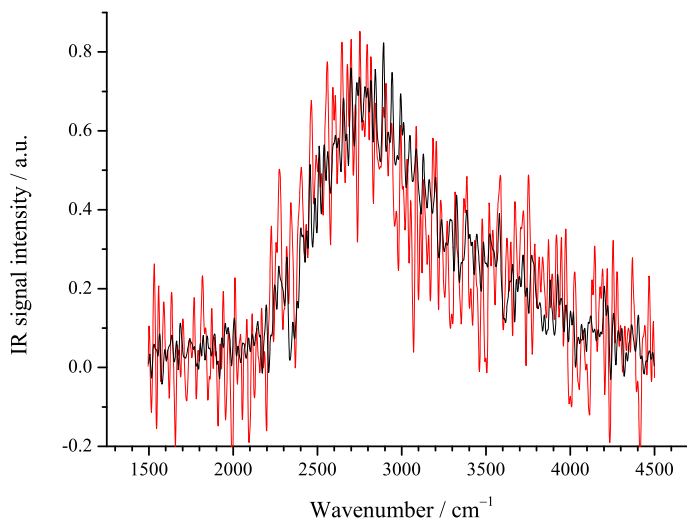


Figure 6.12: An early time emission spectra, recorded 2 μ s following pumping of the overlapped Q₁(1) and P₂₁(1) rotational lines of the OH A-X(0,0) transition in the presence of (i) 40 mTorr of HNO₃, 1.1 Torr of Ar and 400 mTorr H₂ (black) (ii) 14 mTorr of HNO₃, 340 mTorr of Ar and 144 mTorr H₂ (red).

servations of the nascent H₂O vibrational excitation following reactive quenching of OH A $^2\Sigma^+$ by H₂. The maximum of the early time emission spectrum appears at around 2900 cm⁻¹, which, when compared to the emission frequency of the

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

H₂O (0,0,1) state at 3750 cm⁻¹, indicates a high degree of internal excitation. Bowman and co-workers [38] have recently reported full-dimensional, electronically adiabatic PESs for the ground (1 A') and excited (2 A') states of OH₃, together with a *quasi*-classical trajectory study of the vibrational state distribution of H₂O. They present three vibrational distributions: ($\nu_1, 0, 0$), ($0, \nu_2, 0$) and ($0, 0, \nu_3$). The distributions for the ν_1 (symmetric stretch) and ν_3 (asymmetric stretch) modes are very similar, with approximately equal population in $\nu_{1,3} = 1$ –4 with the probability of population in higher quanta decreasing steadily up to $\nu_1 = 8$ and $\nu_3 = 9$. As was noted by Zittel and Masturzo [39] in their discussion of the vibrational relaxation of H₂O, the relaxation rate between the nearly energy resonant ν_1 and ν_3 stretching modes of H₂O is approximately gas kinetic, and after an initial rapid equilibration, these levels will relax together as a single reservoir. The distribution of the bending mode is, however, quite different. A rather broad and inverted distribution is predicted, peaking at $\nu_2 = 13$ and with population observed up to $\nu_2 = 19$. Very recently Bowman and co-workers have performed a more extensive set of calculations to obtain a full vibrational-state resolved distribution [40]. The distributions in this instance are extracted from the *quasi*-classical calculations by a Gaussian binning method based on exact quantum energies of the H₂O vibrational states. Comparison between the experimental data with both sets of theoretical distributions will be made.

First a full vibrational distribution is estimated from the published distributions for the ($\nu_1, 0, 0$), ($0, \nu_2, 0$) and ($0, 0, \nu_3$) modes of H₂O. This is done by assuming that these distributions are independent; Equation 6.22 was used to

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

calculate the probability, $P(\nu_1, \nu_2, \nu_3)$, of each nascent vibrational state.

$$P(\nu_1, \nu_2, \nu_3) = P(\nu_1, 0, 0) \times P(0, \nu_2, 0) \times P(0, 0, \nu_3) \quad (6.22)$$

Any state possessing energy above the energetic threshold was subsequently discarded. Using this distribution, generated from Equation 6.22 a spectral simulation of H₂O is calculated, as detailed in Appendix A from which a set of quantum state resolved populations have been obtained.

Figure 6.13 presents a comparison between the experimental and both sets of theoretical data. Experimental data above 3570 cm⁻¹ have not been displayed as the detector sensitivity is significantly reduced in this region. Very good agreement is observed between the experimental data and the H₂O spectrum simulated from the published theoretical distributions [38]. However, this distribution is reliant on an assumption which is unlikely to be true. The theoretical distribution

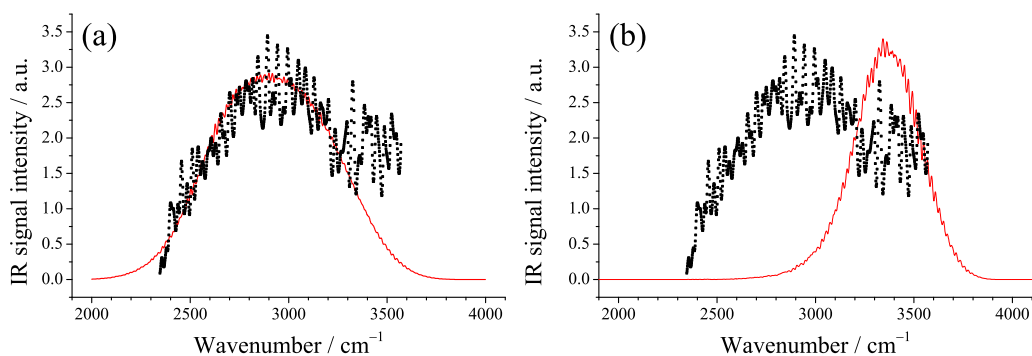


Figure 6.13: (a) Emission observed at 2 μ s following pumping of the overlapped Q₁(1) and P₂₁(1) rotational lines of the OH A-X (0,0) transition in the presence of 40 mTorr of HNO₃, 1.1 Torr of Ar and 400 mTorr H₂; quenching contribution by HNO₃ subtracted (■). Theoretical H₂O simulation calculated from published distributions [38] overlaid (red). (b) The same experimental data are presented, along with the simulation calculated from the recently obtained complete vibrational distribution of H₂O [40] (red).

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

used to generate the simulation shown in Figure 6.13 (a) accounts for 92 % of the available energy (as quoted in Equation 6.19). The agreement is less good between the experimental data and the full quantum state distribution, which only accounts for 58 % of the available energy. These observations confirm the predictions made by Lester and co-workers [10] regarding a high degree of internal excitation in the H₂O product. Bowman and co-workers expect that their calculation will under predict the degree of vibrational excitation [40]. Nevertheless careful checks were made as to the reliability of the H₂O simulation, to remove any doubt that the cause for the discrepancy lies there. As detailed in Appendix A the H₂O simulation is generated by taking the (0,0,1) $\rightarrow$ (0,0,0) emission spectrum from the HITRAN database [41]. Hot-band emission simulations are then obtained by red shifting the fundamental emission according to the relative energies of the vibrational states involved (a ν_3 term in the intensity calculation is included on the basis of the harmonic approximation). Therefore any error in the calculation of the energy of the higher vibrational states will affect the simulation. These energies were calculated in the same manner as described in the review of IR chemiluminescence from H₂O formed in reactions by Butkovskaya *et al.* [42], using the molecular constants reported by Benedict *et al.* [43]. Many databases of both experimentally determined and calculated levels of exist [41, 44, 45], but no single set provided information on all the vibrational states required to generate the simulations. The BT2 list of H₂O transitions [44] was the most extensive, and comparisons were made between energies reported in this dataset and the energy calculated in this work using the molecular constants of Benedict *et al.* [43]. In general the agreement was good, with discrepancies rarely exceeding ± 5 %. The transitions energies calculated from the BT2 list and

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

the molecular constants of Benedict *et al.* show that the latter generally produces lower values than the BT2 list. Therefore any error in the simulation presented in Figure 6.13 (b) will result in a hotter spectrum.

It has been assumed during the analysis thus far that the rotational distribution of the H₂O molecule is 300 K. However, the pressure of Ar is less than was employed in Chapters 3 and 4, due to the flowing nature of the experiment. Employing higher pressures of Ar, while desirable for the rotational thermalisation, were not possible. If a higher flow rate of Ar was used, in order to ensure a suitable partial pressure of HNO₃ (and therefore signal size) the pumping efficiency of the reaction cell had to be reduced by such an extent, that over the course of an experiment, the build up of products from photolysis and reaction within the cell were detectable. Static samples were also attempted, but the photolysis of HNO₃ reduced its partial pressure, and therefore the signal size, to unusable levels within the time of one experiment. The effect of rotational temperature was tested using the spectral simulation. While higher rotational temperatures increased the intensity of the intensity of the P and R branches, the Q branch remained strong, and the simulated emission from the vibrational distribution obtained by Bowman and co-workers [40] with a rotational temperature of 3000 K was found to increase the width of the emission but only have marginal shift on the peak. Previous investigations on the spectra of rotationally hot H₂O [46] have found that the HITRAN database underestimates the absorption cross sections on the P branch for the higher rotational levels at high temperatures. This would increase the width of the simulated emission spectrum, and could shift the peak to lower wavenumber, bringing the vibrational distribution of Bowman and co-workers into closer agreement with the experimental spectrum.

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

It is clear that the observed emission spectrum of H₂O represents a high degree of internal excitation, which is in agreement with the conclusions of Lester and co-workers [12] and Bowman and co-workers [38]. In order to accurately compare the theoretical vibrational distributions of Bowman and co-workers, the rotational excitation of the H₂O needs to be known. It is calculated that an H₂O molecule will undergo ~ 30 collisions with Ar molecules present in the cell by 2 μ s, and so while a certain degree of rotational relaxation will have occurred within the first 2 μ s it cannot confidently be assumed that it has thermalised. The extent that this would effect the simulation of the theoretically vibrational distributions will depend on the rotational temperature at 2 μ s for which more experimental work is required.

6.5.3 OH X $^2\Pi(\nu)$ fundamental emission

Attention is now turned to the emission from the OH quenching products, which is seen clearly at late time in Figure 6.9. The non-reactive quenching channel, (6.1), for the quenching of OH A $^2\Sigma^+(\nu = 0)$ + H₂ system was reported to have quantum yield of $(12 \pm 5) \%$ [12], of which 27.5 % of OH X $^2\Pi$ products are formed with vibrational excitation. Consideration of the relative Einstein A coefficients for H₂O and OH IR emission [47, 48], less than 3 % of the total nascent emission should be attributable to OH X $^2\Pi(\nu)$. An attempt to quantify the contribution of OH X $^2\Pi(\nu)$ to the observed nascent emission was made as follows. Spectral simulations of OH X $^2\Pi(\nu)$ fundamental emission were fitted to the experimental data at each microsecond by varying the vibrational state populations; the rotational temperature was fixed at 300 K. This yielded a time-dependent vibra-

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

tional distribution of OH X $^2\Pi(\nu)$, to which a kinetic model was then fitted. This model assumes only single quantum step transitions, similar to those employed in Chapters 3 and 4. The fitting process involved varying both the initial populations of each vibrational state and their decay constants. Only data from 50 μs onwards was included in the fit as by this time the H₂O product had relaxed, and the remaining emission is attributed solely to the OH X $^2\Pi(\nu)$ fundamental band. Figure 6.14 (a) shows the experimentally determined vibrational distributions together with the results of the fitted kinetic model. As displayed in

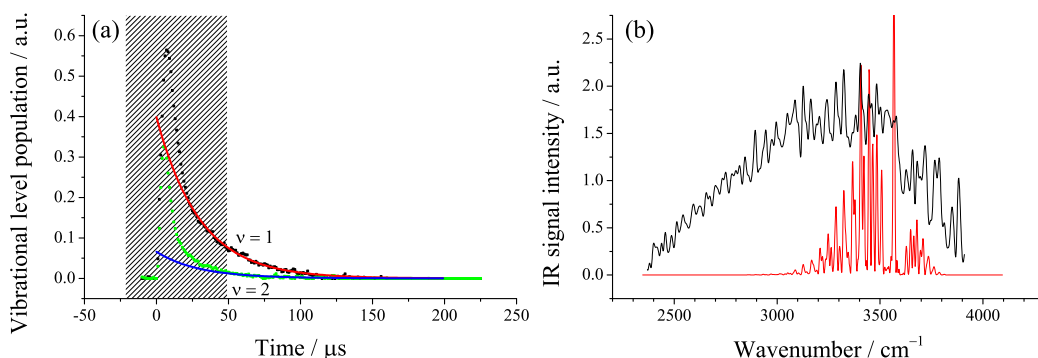


Figure 6.14: (a) Time dependence of the population in the vibrational levels of OH X $^2\Pi$. Experimentally determined $\nu = 1$ (■) and $\nu = 2$ (■) are shown with corresponding kinetic fits (red and blue respectively). Note the shaded region denotes data not included in the fit. (b) Emission observed at 4 μs following pumping of the overlapped Q₁(1) and P₂₁(1) rotational lines of the OH A-X (0,0) transition in the presence of 40 mTorr of HNO₃, 1.1 Torr of Ar and 400 mTorr of H₂ (black). OH X $^2\Pi(\nu)$ nascent fundamental simulation, calculated from kinetics fits in (a), overlaid (red).

Figure 6.14 (b), such an extrapolation predicts that the nascent OH X $^2\Pi$ fundamental emission represents a significant percentage of the whole emission feature. The emission coefficients of H₂O are around an order of magnitude larger than those of OH [47, 48], which means vibrationally excited OH dominates over H₂O if the spectra shown in Figure 6.14 (b) are correct. This conflicts with the conclusions of all other studies of the system [12, 38, 40] that vibrationally excited

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

H₂O is the major product following collisional quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂. It is therefore concluded that the extrapolation procedure is in error. Ravishankara and co-workers [49] have measured the rate coefficient for the removal of OH X $^2\Pi(\nu = 1)$ by HNO₃ as $2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, at 295 K. Despite incorporating this value into the kinetic model, the OH X $^2\Pi(\nu)$ contribution is still much greater than expected. In order to reconcile the data at late times with the expected early-time OH emission—which according to the results of Lester and co-workers [12] will be negligible—it is clear that vibrationally excited OH X $^2\Pi$ must increase in concentration within the first 50 μs following the pumping pulse prior to its decay. Figure 6.15 presents experimental spectra observed within the first 3 μs to 9 μs following the pumping pulse. The spectral region shown corresponds to the emission bands of the low vibrational levels of H₂O and OH. The observed increase of emission intensity across the whole region as a function of time is due to the rapid vibrational relaxation of H₂O from higher levels, and not a detector rise-time effect. Marked on Figure 6.15 is the position of the Q branch of the OH X $^2\Pi(\nu = 1) \rightarrow (\nu = 0)$ transition. This spectral feature is clearly non-nascent and is seen to grow in, relative to the neighbouring emission. This indicates that the population of the low rotational levels of the OH X $^2\Pi(\nu = 1)$ state (which dominate the Q branch emission) is increasing rapidly in the first 10 μs . As discussed, Lester and co-workers [8] report that OH X $^2\Pi$ products are formed primarily in the lowest vibrational level with a negligible amount formed in states where $(\nu > 1)$. It is therefore unlikely that vibrational relaxation from the OH X $^2\Pi(\nu = 2)$ level is can explain the observed increase of the OH X $^2\Pi(\nu = 1 \rightarrow 0)$ Q branch emission. A more plausible explanation is rotational relaxation; Lester and co-workers report the nascent OH X $^2\Pi(\nu = 1)$

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

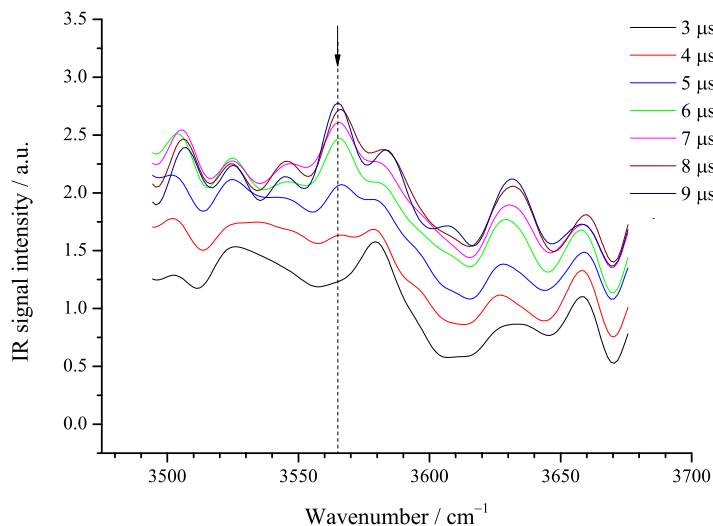


Figure 6.15: Early time emission observed following pumping of the overlapped Q₁(1) and P₂₁(1) rotational lines of the OH A-X (0,0) transition in the presence of 40 mTorr of HNO₃, 1.1 Torr of Ar and 400 mTorr of H₂. Position of the Q branch for OH X $^2\Pi(\nu = 1) \rightarrow (\nu = 0)$ fundamental transition is indicated.

state possesses a non-thermal rotational distribution, peaking at $N = 16$, whose relaxation would be accompanied by an increase in the Q branch emission intensity. However, the rate coefficients for the rotational relaxation of OH X $^2\Pi$ upon collisions with both Ar and HNO₃ indicate that, under the present experimental conditions, such a process would take place in less than 1.5 μs [50]. It is therefore concluded that OH X $^2\Pi(\nu = 1)$ is generated by an efficient vibrational energy transfer (VET) process between excited H₂O molecules and OH X $^2\Pi(\nu = 0)$, present following the 193 nm photolysis of HNO₃ but not excited to the electronic A $^2\Sigma^+$ state. VET affords a growing population of vibrationally excited OH X $^2\Pi(\nu = 1)$, particularly within the first 20 μs following the pumping pulse during which the majority of vibrationally excited H₂O is seen to decay. Within this time period it is not possible, at the resolution employed in Fig-

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

ure 6.15, to disentangle the emission due to vibrationally excited OH X $^2\Pi$ from that attributable to H₂O.

6.5.4 Quenching by D₂

As discussed in the previous section, the OH X $^2\Pi(\nu)$ nascent vibrational distribution was unable to be measured because of the branching ratios between reactive and non-reactive channels, and the unfavourable Einstein A coefficients for OH compared to H₂O. However, making an isotopic substitution, and performing experiments to investigate the quenching the A $^2\Sigma^+(\nu = 0)$ state of OH by D₂ instead, allowed this channel to be observed with greater success. According the results of Lester and co-workers [11, 12], the formation of vibrationally excited OH X $^2\Pi$ molecules, following quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂ has a quantum yield of 3.3 %, compared to 4.7 % when D₂ is the collisional partner. In addition, the energy partitioning in the HOD reaction product is expected to exhibit much greater selectivity. In the case of quenching by D₂ it is expected energy will be preferentially channelled into the ν_1 mode, corresponding to the O–D stretch on the reasoning that this is the new bond formed during the collision. A molecular beam study on the reaction of OH X $^2\Pi$ with D₂, performed by Strazisar *et al.* [51], observed excitation of the O–D bond, with the O–H bond behaving as a spectator during the collision. In light of this it can be assumed that, following the reaction between D₂ and OH A $^2\Sigma^+(\nu = 0)$, the majority of the vibrational excitation of the HOD product will be in the O–D stretching mode. The relative emission strengths of the $\Delta\nu_1 = -1$ band of HOD is around a fifth of that of the $\Delta\nu_3 = -1$ band, which itself is approximately the same as the equivalent band

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

in H₂O [42]. Therefore the strong IR emission from vibrationally excited H₂O that was overlapping with the OH fundamental emission following quenching of electronically excited OH by D₂ will be red shifted (the $\Delta\nu_1 = -1$ band lies at around 2700 cm⁻¹) and reduced in intensity. Together with the expectation that more vibrationally OH X $^2\Pi$ will be formed means confidence can be had that the non-reactive quenching channel can be investigated.

6.5.4.1 Experiments

Experiments were performed with partial pressures such that $\Phi_{D_2} \sim 0.55$. Higher pressures of D₂ than H₂ were required to achieve this as D₂ is a slower quencher of the OH A $^2\Sigma^+(\nu = 0)$ state [2]. The observed IR emission in the region of 2200 cm⁻¹ and 4500 cm⁻¹ were weaker than were found from equivalent conditions in the H₂ experiments, as expected. Pre-pumping signal was still observed, but with a different spectral signature. While there was still weak emission in the OH region, originating from the reaction of O(¹D) with HNO₃, emission was also observed in the OD fundamental stretching region, formed by the reaction of O(¹D) with D₂, thus confirming the earlier assignment of the origin of the pre-pumping signal. Experiments were performed employing an optical filter to transmit light in the region of 2900 cm⁻¹ to 4000 cm⁻¹ only, thus allowing greater amplification of the signal due to OH. Figure 6.16 shows three early time spectra from such an experiment. It is first noted that the emission spectra do not resemble the OH X $^2\Pi$ fundamental emission band. Despite the advantages of the D₂ system for observing the nascent OH spectra, early time emission from other molecules was still present. This emission was either from H₂O formed *via* reactive quenching of OH A $^2\Sigma^+$ by HNO₃, a process that has a quantum yield of

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

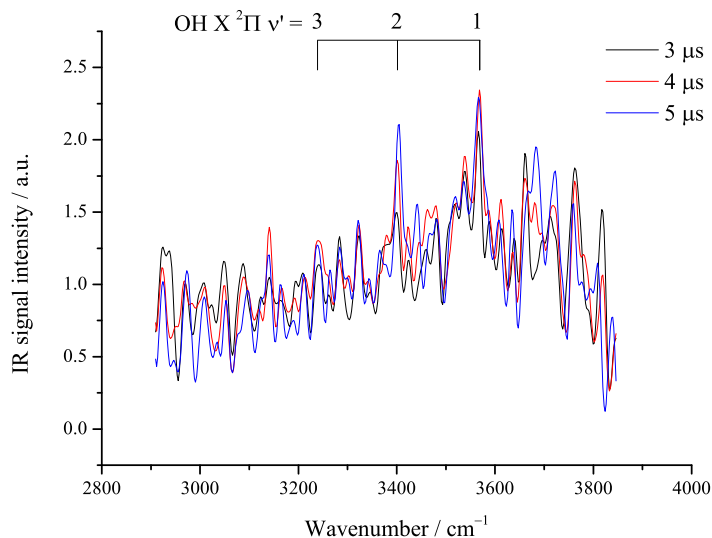


Figure 6.16: Emission observed following pumping of the overlapped Q₁(1) and P₂₁(1) rotational lines of the OH A-X (0,0) transition in the presence of 40 mTorr of HNO₃, 1.2 Torr of Ar and 560 mTorr of D₂. Spectra are shown at 3 μs, 4 μs and 5 μs following excitation as marked. Also shown is the position of the Q branches of the OH X $^2\Pi$ fundamental vibrational transition. Spectra were obtained with the InSb detector at a resolution of 10 cm⁻¹.

around 0.15, or it could be emission from HOD, with excitation in the ν_3 mode and dominantly in low values of ν_3 emitting near 3700 cm⁻¹. Although this mode is expected to be predominantly in the ground level in nascent HOD, the emission coefficient for the $\Delta\nu_3 = -1$ is five times larger than for the ν_1 emission band, and thus the experiment has a greater sensitivity for this mode. Nevertheless, information on the nascent OH emission is able to be obtained. Marked on the figure are the positions for the Q branches of the (3,2), (2,1) and (1,0) vibrational transitions within the OH X $^2\Pi$ state. While there is no resolvable feature able to be ascribed to the (3,2) Q branch with any confidence, it is evident that there is nascent emission from both the OH X $^2\Pi(\nu = 1-2)$ states. Both features show some increase with time, most notably the (2,1) Q branch. Comparing this figure

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

with the spectra presented in Figure 6.15 it is clear that the OH X $^2\Pi(\nu = 1 \rightarrow 0)$ Q branch appears promptly in the presence of D₂ compared to H₂. This slow rise time of the OH emission for the H₂ quenching experiments was explained as vibrational energy transfer (VET) from the highly excited H₂O reaction product. This process is expected to be much less efficient in the current system, as most of the excitation of the HOD reaction product lies in the ν_1 mode which is red shifted with respect to the OH fundamental transitions by around 1000 cm⁻¹, so any vibrational energy transfer will be slow. This leaves the question of what causes the observed rise. One explanation is rotational relaxation. Lester and co-workers [11] found that the OH X $^2\Pi$ post quenching fragments were formed with a greater degree of rotational excitation, for all vibrational states, upon quenching of OH A $^2\Sigma^+$ by D₂ compared to H₂. This means rotational thermalisation will take longer, and this reasonably could explain the observed rise in the OH X $^2\Pi(\nu = 1 \rightarrow 0)$ Q branch between 3 μ s and 4 μ s. It is unlikely, however, that this could also explain the much greater rise of the (2,1) Q branch, since Lester and co-workers predict that the rotational distribution of the $\nu = 2$ will only be marginally hotter than for the lower vibrational levels, and so cannot account for such a large difference in behaviour between the two Q branches.

It is clear that as before, in order to obtain an indication of the nascent emission from OH X $^2\Pi$, an extrapolation is going to have to be performed from later time. The emission from H₂O/HOD was relaxed by around 25 μ s, allowing the OH simulation to be fitted. Figure 6.17 shows the vibrational distributions for the first two vibrational levels of OH as a function of time. A kinetic model was fitted to the data in an attempt to obtain a nascent distribution. Data within the first 25 μ s (shaded in Figure 6.17) were not included in the fit as

6.5. Quenching of OH A $^2\Sigma^+(\nu = 0)$ by H₂

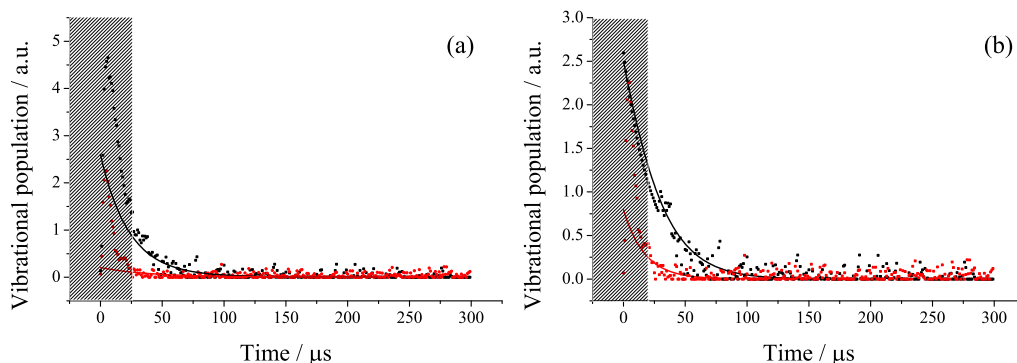


Figure 6.17: (a) Temporal behaviour of vibrational distributions of OH X $^2\Pi(\nu = 1)$ (■) and $(\nu = 2)$ (■) following the non-reactive quenching of OH A $^2\Sigma^+(\nu = 0)$ by D₂. Also shown as lines are the results of the fitted kinetic model, fitted to all data points after 25 μs ; data within shaded region was not considered in the model. (b) Re-analysis of the same time dependent distributions. In this case all data points after 20 μs are included in the fit. The $\nu = 1$ populations before 25 μs are substituted by the fit shown in (a), as described in the main text.

emission from H₂O or HOD was still present. The ratio of nascent population for the two vibrational levels is 12.5:1. The value reported by Lester and co-workers for this ratio was much smaller: 4.5:1 [11]. This value was not directly measured, but involved the assumption the total population in $\nu = 0$ and 1 were the same for both the H₂ and D₂ systems. However, it is believed that the ratio calculated above is wrong, especially considering the clearly resolved OH X $^2\Pi(\nu = 2 \rightarrow 1)$ Q branch evident in Figure 6.16 at early time, which cannot be explained by such a small population in $\nu = 2$. The rationale for rejecting data in the first 25 μs is that emission from H₂O/HOD persists. However, it does not persist equally at all frequencies. The emission is longest lived at higher wavenumber (corresponding to the lower vibrational states of H₂O/HOD), which overlaps predominantly with the (1,0) band of OH X $^2\Pi$. Therefore it can be argued that the measured populations for $\nu = 2$ become reliable at an earlier time than those for $\nu = 1$. However, the populations cannot be taken separately.

The emission bands from the two vibrational levels overlap and so in any fitting procedure they are connected. Therefore if there is still H₂O/HOD emission underlying the (1,0) emission band, a higher population will in this level will be ascribed to fit it, and this can then cause a lower fitted population term for the (2,1) band. Both of these points suggest that the obtained nascent OH X²Π($\nu = 2$) is an underestimate. Unfortunately it is not possible to remove the interference of the water, so the measured vibrational distribution cannot be improved. The kinetic model fitting was performed again with data as early 20 μ s included in the fit. In light of the discussion above, for these extra five time points, rather than using the measured $\nu = 1$ populations (which will be overestimates due to water emission), the results of the first kinetic model were used. The results of this second fit can be seen in Figure 6.17 (b), where the effect on the $\nu = 2$ level is immediately evident. The ratio now becomes 4.2:1, which is closer agreement with that reported by Lester and co-workers [11].

6.6 Conclusion

This chapter has presented an experimental investigation of the collisional quenching of OH A²Σ⁺($\nu = 0$) by H₂ using time-resolved FTIR emission spectroscopy. Quenching proceeds *via* two competing channels; namely, non-reactive quenching producing OH X²Π, and reactive quenching generating H₂O and H-atom products. Experiment has confirmed that the latter channel is highly dominant. Strong emission from H₂O was observed, exhibiting a large shift from its fundamental position, indicating a high degree of internal excitation. This provides the first direct observation of vibrationally excited H₂O following reactive quenching

of OH A $^2\Sigma^+(\nu = 0)$ by H₂. Near nascent experimental data have been compared to recent a theoretical distribution calculated by Bowman and co-workers [40]. This distribution represented 58 % of the energy released by the reactive quenching process (calculated using the molecular constants of Benedict *et al.* [43]). There was disagreement between simulated and the experimental spectra. It was determined that the H₂O simulation slightly under predicts the energy of transitions from high vibrational states, and thus this is not the source of the disagreement between the experimental and theoretical data. A more likely reason is persisting rotational excitation in H₂O, which will increase the width of the simulated spectrum and shift the peak to lower wavenumber. The extent of either effect could not be quantified without further experiments identifying the rotational temperature of the H₂O molecule. It can be confidently stated that the observed H₂O emission spectrum represents a significant percentage of the available energy, > 60 %, in accord with the conclusions of Lester and co-workers that this is the dominant channel [12].

Analysis of the OH X $^2\Pi$ vibrational distribution was complicated by low quantum yields and overlapping emission features. The strong OH X $^2\Pi(\nu = 1 \rightarrow 0)$ Q branch is evident at early time, and seen to increase within the first 10 μ s following the pumping laser, ascribed to efficient VET from the vibrationally excited H₂O products. However, the overlapping H₂O emission prevented confident determination of the nascent OH distribution. Experiments were performed with D₂ as the collision partner in an attempt to discern the nascent OH X $^2\Pi$ distribution. This proved moderately successful, although some of the issues experienced for the H₂ quenching system persisted in the D₂ case. The distribution obtained was found to be cold, in agreement with Lester and co-workers.

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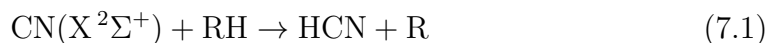
Chapter 7

Hydrogen atom abstraction reactions of the CN radical

7.1 Introduction

In the previous chapter, it was found that the interaction between electronically excited OH radicals with hydrogen containing molecules (such as nitric acid and molecular hydrogen) resulted predominantly in a hydrogen abstraction process, with efficient energy channelling into the vibrational mode of the product molecule that corresponded to the new bond formed. In this chapter, another hydrogen abstraction process is investigated; the reaction between the CN radicals and cyclohexane is studied, with specific attention paid to the vibrational energy distribution of the resulting product molecules. The CN radical is of great importance within combustion environments [1, 2], particularly due to its involvement in the generation of NO_x pollutants, from both fuel-fixed nitrogen, but also from ambient N₂ which becomes involved in the high temperature chemistry typical of

flame environments. In such a chaotic environment there are numerous pathways in operation, and many of those involving the CN radical are hydrogen atom abstractions, which can be generalised by Equation 7.1.



There have been many studies performed on the reaction of CN radicals with numerous organic and inorganic compounds, determining rate constants and their dependence on temperature. Tsang [3] presented a summary of the kinetics of many CN hydrogen abstraction reactions involved in combustion. Focusing on reactions with alkanes, Hess *et al.* [4] measured the temperature dependence of rate constants for the reaction of CN with ethane and propane. By a series of experiments of partially deuterated derivatives they were able to discern that a small barrier existed for the abstraction of primary hydrogen atoms while little or no barrier existed for abstraction from secondary site hydrogen atoms. Yu *et al.* [5] performed similar experiments for the reaction of CN with cycloalkanes, finding a positive temperature dependence for the case of cyclopropane, and slight negative dependencies for cyclopentane and cyclohexane. More recently attention has turned to the products state distributions of such reactions, in particular the vibrational energy distribution of the nascent HCN. The HCN molecule has three vibrational modes, which have been historically labelled as the C–N stretch (ν_1), a double degenerate bend, (ν_2) and the C–H stretch (ν_3). It is known that the barrier, such that it is, for hydrogen atom abstraction by CN is an early one, [6], meaning that the HCN product is formed with an extended C–H bond distance, and therefore energy is preferentially channelled into the ν_3 mode. This has been

observed experimentally. Jackson and co-workers [7, 8] investigated the reaction of CN with a range of small organic molecules with time-resolved FTIR emission spectroscopy. It was found for all cases that the HCN product was formed with the ν_3 mode in a vibrationally excited state with emission observed in the region of the C–H stretch around 3300 cm^{-1} . For all but two cases they report a population inversion between $\nu_3 = 2$ and $\nu_3 = 1$ levels. Work by Macdonald and co-workers [9, 10] on the reaction of CN with ethane, employing absorption spectroscopy, detected vibrational excitation of the bending motion of the HCN, but little excitation in the N–C bond.

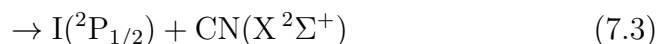
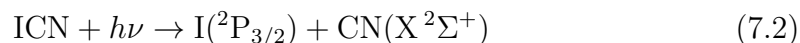
The relevance of the hydrogen atom abstraction by CN process is not limited to combustion. The CN radical, which is isoelectronic with Cl, is often viewed as a pseudo-halogen, and therefore is a logical extension of work, both theoretically and experimentally on the reaction dynamics of hydrogen abstraction by halogens, such as $\text{F} + \text{H}_2$ [11–13]. Most recently CN reactions have seen prominence in the field of solution based reactions [14–17] as the dynamics of reactions within this much more complex environment are investigated. Orr-Ewing and co-workers [15, 17] have used transient broadband IR absorption spectroscopy on a sub-picosecond time scale to observe the dynamics of the hydrogen-atom abstraction reactions of the CN radical with small organic molecules in solution with common chlorinated solvents. They find that dynamics similar to gas phase processes are exhibited, albeit with slightly colder vibrational distributions in the products. They also present the first molecular dynamics study of abstraction mechanisms for reactions of CN + polyatomic organic molecules in both the gas phase and a CH_2Cl_2 solvent, reporting calculated vibrational distributions of the vibrational modes of the HCN reaction product [16].

This chapter presents the investigations of the gas phase reaction of CN with cyclohexane, focusing on the partitioning of the reaction energy into the vibrational modes of the HCN product molecule. It is expected that the HCN will be formed with high vibrational excitation of the C–H bond, as this is the new bond that is formed during the reaction.

7.2 Generation of CN radicals

The method of choice for generation of CN radicals for the experiments presented in this chapter is the photodissociation of ICN at 266 nm. This is the method used by Orr-Ewing and co-workers for their solution phase experiments [15, 17], and in order to draw meaningful comparisons between the two systems, it is desirable that as many of the numerous experimental parameters are kept the same.

The photolysis of ICN in the $\tilde{A}$ continuum (210 nm to 320 nm) is a well studied process. It was found by early experimental investigations [18–20] that there are two possible exit channels, as shown by processes (7.2) and (7.3).



$\text{I}({}^2\text{P}_{3/2})$ is the ground electronic state of atomic iodine, and $\text{I}({}^2\text{P}_{1/2})$ is the first electronically excited state, often referred to as I and I* respectively. The relative efficiencies of the two dissociation channels, (7.2) and (7.3), show a dependence on the photolysis wavelength; the I*/I ratio is found to peak at 266 nm with a value of 1.7, decreasing to both higher and lower photolysis wavelengths [19, 21]. Studies

probing the nascent CN photo-fragments have found the rotational distributions to be non-statistical, with the I channel producing the hotter distributions [22, 23]. Early work, since found to be in error [18], reported that up to 60 % of CN fragments were formed in an electronically excited state, A $^2\Pi$, while the ground electronic state products were formed with an inverted vibrational distribution between $\nu = 2$ and $\nu = 3$. A LIF based series of experiments performed a year later by Baranovskii *et al.* [19], found that ≥ 98 % of the CN fragments were formed in the electronic and vibrational ground state; a conservative estimate that less than 0.1 % are formed in the electronically excited state was reported.

The literature provides overwhelming evidence that photolysis of ICN at 266 nm produces a high yield of ground state CN radicals. Nevertheless experiments were performed to observe the resulting IR emission, and to assess the potential occurrence of other pathways, such as two photon processes. Figure 7.1 shows a contour plot of emission observed in the region of 1800 cm^{-1} to $10\,000\text{ cm}^{-1}$ following photodissociation of ICN at 266 nm. The contour plot shows a number of intense emission features throughout the observed spectral region. There is strong, prompt but short lived emission spanning the region between 2000 cm^{-1} to 3000 cm^{-1} . Looking at higher wavenumbers there are two narrow features, at 7000 cm^{-1} and 9000 cm^{-1} , which exhibit slightly different kinetics to the lower wavenumber emission. Finally there are two long-lived emission features at 2000 cm^{-1} and 7600 cm^{-1} . Such a rich variety of emissions was unexpected in light of the literature of this process, where ≥ 98 % of CN products are formed in the ground vibrational and electronic states and are therefore undetectable *via* emission spectroscopy [19]. First the kinetics of the emissions will be considered. Figure 7.2 shows the temporal dependence of the emission features

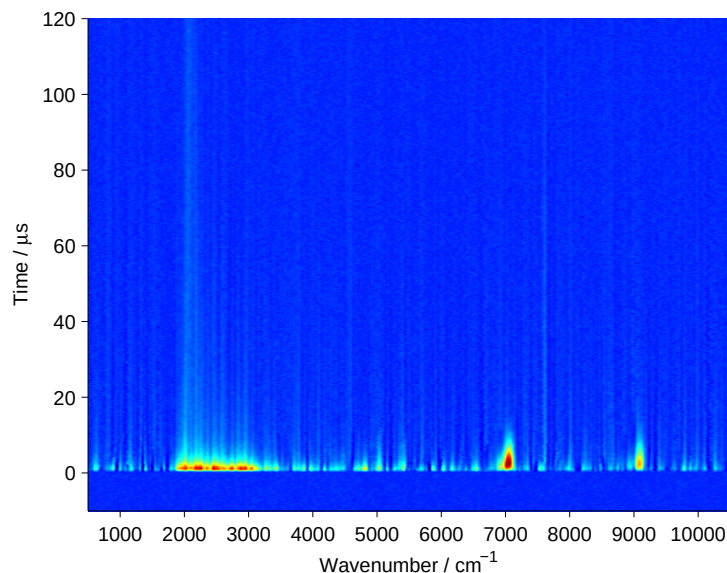


Figure 7.1: Contour plot of emission detected in the region 2000 cm^{-1} to $10\,000\text{ cm}^{-1}$ following the photodissociation of a flowing sample of 50 mTorr of ICN at 266 nm radiation. Emission was detected with the InSb detector at a resolution of 40 cm^{-1} . Red represents high intensity and blue represents low intensity.

at 7000 cm^{-1} , 9000 cm^{-1} and between 2000 cm^{-1} and 3000 cm^{-1} . The emission features at 7000 cm^{-1} and 9000 cm^{-1} show near identical kinetics, suggesting that they originate from the same state of CN. The emission between 2000 cm^{-1} and 3000 cm^{-1} exhibit faster kinetics. The limiting effect of the detection system rise time prevents meaningful quantitative analysis of these traces, but it is clear that the emission at 2000 cm^{-1} to 3000 cm^{-1} does not originate from the same state as the emission at 7000 cm^{-1} to 9000 cm^{-1} . The CN $A^2\Pi(\nu = 0) \rightarrow$ CN $X^2\Sigma^+(\nu = 0, 1, 2, 3)$ transitions lie at 9117 cm^{-1} , 7075 cm^{-1} , 5059 cm^{-1} and 3069 cm^{-1} respectively, with the frequencies of the first two corresponding well to the two emission features at 7000 cm^{-1} and 9000 cm^{-1} shown in Figure 7.1. The emission in the region between 2000 cm^{-1} to 3000 cm^{-1} is too broad to be simply the CN A-X (0,3) transition. Emission features originating from the higher

vibrational levels of the A $^2\Pi$ state are red shifted with respect to those originating from the $\nu = 0$ level. A recent work by Civiš *et al.* [24] have observed these sequence bands of the CN radical in the region from 1850 cm^{-1} to 3100 cm^{-1} , following a discharge through a sample of $(\text{CN})_2$ with time-resolved Fourier transform spectroscopy. They report spectroscopic analysis of seven newly observed bands from the $\Delta\nu = -3$ vibronic sequence, originating from vibrational levels $\nu = 0-6$ to within the CN A $^2\Pi$ state. While the frequency of this emission between 2000 cm^{-1} to 3000 cm^{-1} corresponds to that of the $\Delta\nu = -3$ vibronic transitions of the CN A-X band, consideration of the Einstein coefficients make such an assignment unlikely [25]; the emission coefficients of the $\Delta\nu = -3$ vibronic transitions between 2000 cm^{-1} and 3000 cm^{-1} are on average two orders of magnitude smaller than those for the CN A-X (0,0) and (0,1) emission lines. Even consideration of the wavelength dependence of the InSb sensitivity cannot explain the observed intensities if this emission was from the $\Delta\nu = -3$ vibronic transitions of CN. More importantly is that the $\Delta\nu = -2$ vibronic transitions have emission coefficients one order of magnitude larger, and thus if there was population in higher vibrational levels of the CN A $^2\Pi$ state, emission between 4000 cm^{-1} and 5000 cm^{-1} would be observed. The emission is clearly electronic in origin, as indicated by the fast nature of its temporal behaviour. A power dependence experiment found a non-linear relationship between the intensity of this emission and the laser power. As such it can only be stated that such emission is a result of a two photon process. Being electronic in nature it will have large associated Einstein emission coefficients, and thus, like the CN A-X emission at higher wavenumbers will not represent a large fraction of the photolysis products.

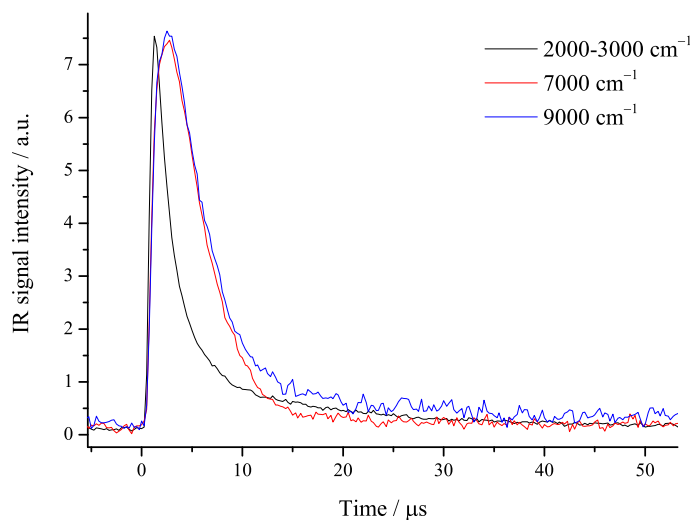


Figure 7.2: Temporal behaviour of emission features at specific wavenumber frequencies following the photolysis of a flowing sample of 50 mTorr of ICN at 266 nm radiation: 2000 cm^{-1} to 3000 cm^{-1} (black), 7000 cm^{-1} (red) and 9000 cm^{-1} (blue). These traces are scaled by their maximum values for clarity.

In addition to the short lived emission features, there are two much longer lived but weaker emission features at 2000 cm^{-1} and 7600 cm^{-1} visible in the contour plot shown in Figure 7.1. These are assigned to the CN $X^2\Sigma^+(\nu = 1 \rightarrow 0)$ transition and the $I(^2P_{1/2}) \rightarrow I(^2P_{3/2})$ transition. Their comparative weakness can be readily explained: Baronavski *et al.* reported that the branching ratio for vibrationally excited CN $X^2\Sigma^+$ photofragments following the dissociation of ICN at 266 nm was 0.012 [19], and the electronic transition between the two lowest electronic states of I is forbidden. A comparison of the intensities of this emission feature with that of the CN A-X (0,1) emission at 7000 cm^{-1} reveal how minor the channel to produce electronically excited CN is. The Einstein A coefficient for the CN A-X (0,1) electronic transition is three orders of magnitude larger than for the transition between the two lowest spin-orbit states of I. $I(^2P_{1/2})$ is generated

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by around 60 % of the photolysis events, which means that if the emission features were the same intensity the branching ratio for production of CN A $^2\Pi$ molecules would be 0.06 %. An exact branching ratio cannot be determined due to lack of an accurate detector response function at such high wavenumbers. Nevertheless it is evident that the generation of electronically excited CN radicals is a minor channel and should not adversely affect the subsequent reactions of CN. However, a more significant implication of such emission is the potential for overlapping of spectral features, which will hinder the analysis processes. This issue was negated by the addition of a high pressure of Ar into the cell. The rate of collisional quenching of CN A $^2\Pi$ by Ar has been measured [26], and it is calculated that the addition of 50 Torr of Ar will reduce the lifetime of the CN A $^2\Pi(\nu = 0)$ state from around 10 μs to 1.6 μs . An additional benefit of the presence of Ar, is that it will efficiently rotationally thermalise the reaction products, removing the need for the rotational temperature to be an additional parameter in the fitting procedure.

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The previous section has confirmed that the photolysis of ICN is a suitable method of generating CN radicals for use in the experiments presented below. Now attention is turned to the reaction of CN radicals with cyclohexane, as shown Equation 7.4 .



The CN radicals, as discussed above, were generated by photolysis of a static sample of 50 mTorr of ICN at 266 nm radiation. This was performed in the

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presence of 50 mTorr of cyclohexane and 50 Torr of Ar. The rate constant for this reaction has been measured as $2.66 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1}$ [5], which means the reaction time, under the conditions employed in this work, was $\sim 2 \mu\text{s}$. Such conditions afforded the a good compromise between a fast reaction time, while ensuring vibrational relaxation of reaction products was not too fast, allowing accurate determination of nascent distributions. Experiments were performed to observe any emission within the spectral regions corresponding to both the C–N and the C–H stretching modes of HCN. There was no signal distinct from experimental noise for the former case, while for the latter, strong IR emission was detected. A contour plot of emission observed from such an experiment is presented in Figure 7.3. At early times it is still possible to see the CN A-X

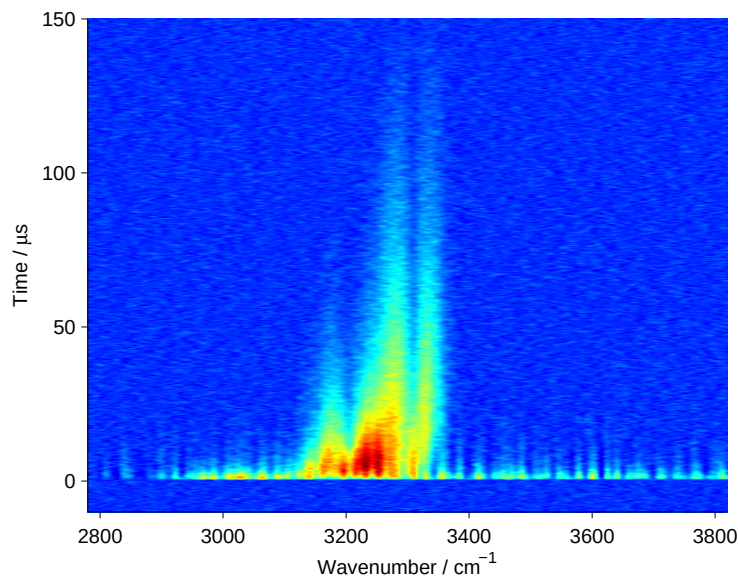


Figure 7.3: Contour plot of emission observed following the photo-dissociation of a static sample of 50 mTorr of ICN at 266 nm and subsequent reaction of the CN photo-fragment with 50 mTorr cyclohexane in the presence of 50 Torr of Ar. Spectra were obtained at a resolution of 10 cm^{-1} with the InSb detector. Red denotes high intensity, blue represents low intensity.

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electronic emission, but this can be subtracted to reveal the emission resulting solely from the reactive process (note emission below 2900 cm^{-1} is cut out by an optical filter placed in front of the InSb detector). The emission from HCN (3100 cm^{-1} to 3400 cm^{-1}) shows a cascade effect with time from low to high wavenumber, typical of vibrational relaxation processes. Another feature that is apparent from the contour plot is the appearance of structure within the emission band at late time. This can more clearly be seen in Figure 7.4 which shows the development of the emission spectrum as a function of time. The positions of the

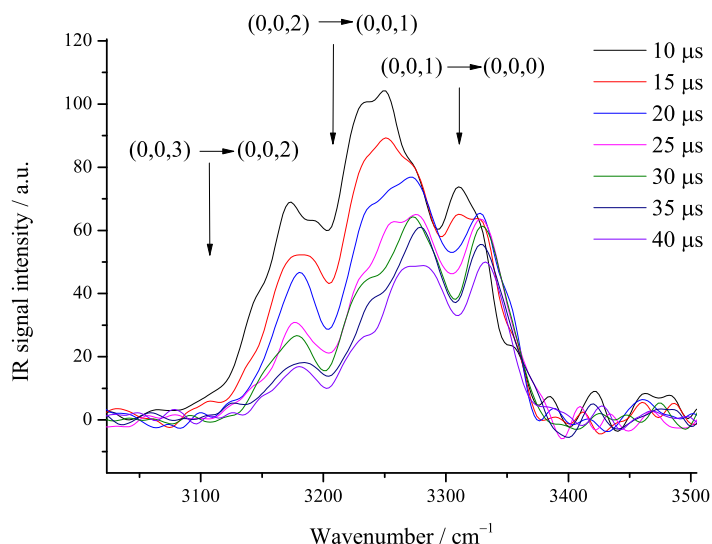


Figure 7.4: HCN emission spectra observed following the reaction between CN radicals (generated *via* photo-dissociation of ICN at 266 nm radiation) and cyclohexane. Spectra are taken at $5\text{ }\mu\text{s}$ intervals following the photolysis laser pulse as indicated on the figure. Marked on the figure are the locations of three $\Delta\nu_3 = -1$ fundamental transitions of HCN. All spectra are taken at 10 cm^{-1} resolution with the InSb detector.

$(0,0,\nu_3) \rightarrow (0,0,\nu_3 - 1)$ transitions for $\nu_3 = 1-3$ are marked. These transitions, being Σ - Σ , have a simple P and R branch structure. First, it is evident that the $\nu_3 = 3$ level is not populated, and therefore only the states with $\nu_3 \leq 2$ need

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be considered. At late time the emission can be well described by these levels, with the troughs between the P and R branches aligning well with the marked positions. At early time, these troughs in the emission are red shifted and this is explained by there being population in the other two modes.

Before a spectral simulation of the $\Delta\nu_3 = -1$ band was fitted to the data, the states that can be thermally populated following the reaction need to be identified. In a study of the reactions of CN with various alkanes (including cyclohexane) by Huang *et al.* [6] it was implied that the energy release is 118 kJ mol^{-1} . This was confirmed by using a Hess cycle for the reaction. The difference in the enthalpy of formation of the cyclohexyl product and cyclohexane was calculated from the C–H bond dissociation enthalpy at 298 K, $(402.5 \pm 1.3) \text{ kJ mol}^{-1}$ [27], and the standard enthalpy of formation of the hydrogen atom, $218.0 \text{ kJ mol}^{-1}$. Combining this appropriately with the standard enthalpies of formation of CN and HCN ($435.14 \text{ kJ mol}^{-1}$ and $135.14 \text{ kJ mol}^{-1}$ respectively, both taken from the NIST thermodynamic database) gives an enthalpy change of reaction of $-115.5 \text{ kJ mol}^{-1}$, which is equivalent to 9655 cm^{-1} , and similar to that obtained from the work of Huang *et al.* [6]. This is sufficient to populate levels as high as 3, 14 and 3 in ν_1 , ν_2 and ν_3 respectively. However, this is not taking into account the cycloalkyl product. In experiments performed in this work it was not possible to assess how much energy is channelled into the vibrational modes of this product, but is very unlikely to be minimal simply on the observation from Figure 7.4 that no emission from $\nu_3 = 3$ was observed. Huang *et al.* [6] observed the cC_6H_{11} alkyl product ion by imaging following reaction of CN and cyclohexane and determined that some energy was channelled into the alkyl product internal modes. In light of a study of hydrogen abstraction reactions by $\text{O}(^3\text{P})$ from a variety of

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alkanes [28] it was concluded that between 17 kJ mol^{-1} and 21 kJ mol^{-1} of the available energy was taken up by the alkyl product, and is not available for the HCN product. The argument for this was that the process was ‘vertical’ rather than adiabatic, meaning the nascent cC_6H_{11} product will be formed in a geometry dictated by that of the parent cC_6H_{12} molecule. It was assumed that a similar amount of energy was channelled into the cC_6H_{11} product, leaving 8250 cm^{-1} of energy available to the HCN product. In the theoretical work on this system by Glowacki *et al.* [16], it was suggested that minimal energy was channelled into the translational and rotational modes of the HCN product, which means that the majority of the 8250 cm^{-1} will go into the vibrational modes of HCN. This allows all the thermally allowed vibrational states of nascent HCN to be identified.

The spectral simulation was then fitted to the experimental data for each microsecond in an unconstrained least squares manner, returning a weighted contribution for each of the states of HCN (ν_1, ν_2, ν_3) included in the fit. Summation of the contributions from these states for each quantum in each mode provides a vibrational distribution for $\nu_1 = 0\text{--}2$, $\nu_2 = 0\text{--}6$ and $\nu_3 = 1\text{--}2$, which are shown in Figure 7.5. The distributions shown exhibit vibrational excitation in all three modes. While excitation of the C–H stretch and possibly the bending motion (depending on the geometry of the transition state) is expected, the C–N bond is predicted to be formed with negligible vibrational excitation, typical of spectator bonds. The degree with which the observed emission defines a particular distribution of a given mode is related to the shift that is associated with excitation in that mode. As the emission corresponds to the $\Delta\nu_3 = -1$ band it is expected that the ν_3 mode will be best defined. The shift in the emission band associated with excitation in the ν_1 , ν_2 and ν_3 is around 15 cm^{-1} , 20 cm^{-1} and 100 cm^{-1}

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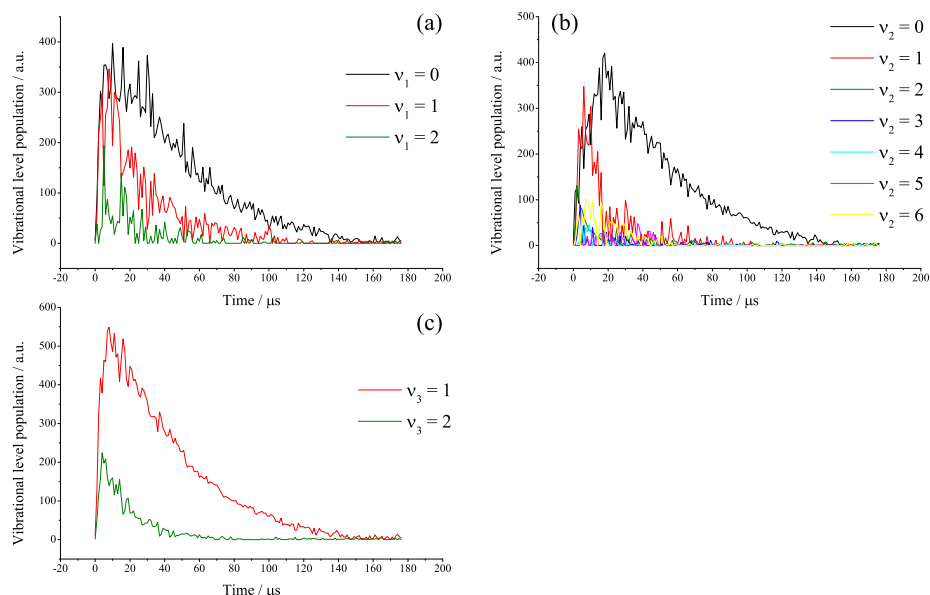


Figure 7.5: Time dependent vibrational population distributions for ν_1 (a), ν_2 (b) and ν_3 (c) modes of HCN, obtained by an unconstrained least squares fit of spectral simulations from all states of HCN (ν_1, ν_2, ν_3) that can be populated by 8250 cm^{-1} of energy.

respectively. Before these distributions are accepted, the reliability of the fitting procedure must be considered. To obtain confirmation of the vibrational distributions of the ν_1 and ν_2 , the emission from the fundamental band of these modes needs to be considered. However, no appreciable IR signal was observed in the ν_1 fundamental emission region, and emission from the ν_2 mode could not be observed due to lack of a suitable detector. The fitting procedure employed is over parametrised, meaning that many combinations of the different emissions bands will provide a satisfactory fit to the experimental data, and therefore the distribution returned by the least square fitting algorithm may not necessarily be the correct distribution. In addition the fitted distribution of vibrational modes are not independent. For example emission from HCN (0,6,1) overlaps with that

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from HCN (0,0,2), and so the contributions of each state will be dependent on each other. So even though the primary interest of this work was the ν_3 distribution, potential inaccuracies in the ν_1 and ν_2 modes cannot be ignored. Therefore the distributions of these two modes were constrained in accordance with the theoretical distributions reported by Orr-Ewing and co-workers [16, 29]. (This distribution is presented later in Figure 7.8 (b)). Figure 7.6 shows the fit achieved by both unconstrained and constrained fitting methods. As can be seen both simulations describe the experimental data well, affording us confidence in the constraining processes is able to produce distributions that are consistent with the experimental data. The fitting procedure was then repeated, this time plac-

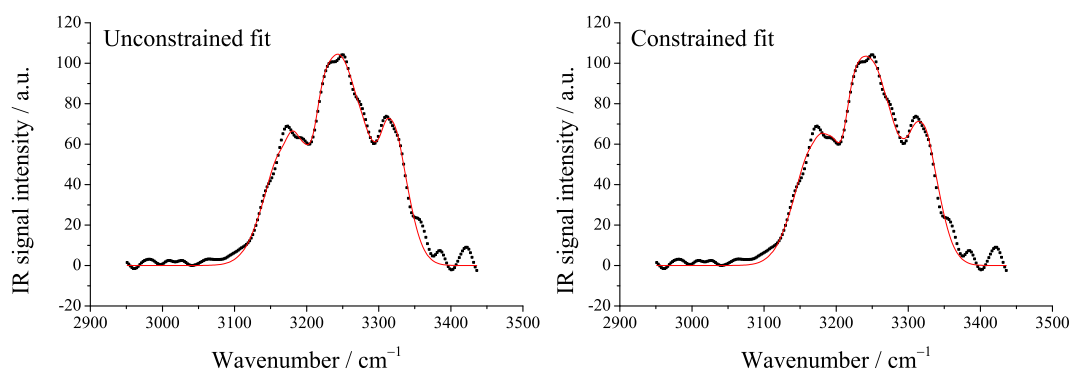


Figure 7.6: Spectra of HCN emission observed in the region of the $\Delta\nu_3 = -1$ fundamental transitions, recorded 10 μs after the initiation laser pulse (■). The best fit simulated spectrum is also shown (red). Two cases for the simulation fitting are shown, unconstrained and constrained, as described in the main text.

ing an upper limit on the ratio of $\nu : \nu - 1$ for $\nu = 1$ in the C–N stretching mode and $\nu = 3\text{--}6$ in the bending mode. As before time dependent vibrational distributions for each mode were obtained, which are shown in Figure 7.7 (a), (b) and (c). It is noted that despite considerable difference in the distributions for the ν_1 and ν_2 modes as a result of the constraining procedure, the ν_3 mode is relatively

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unaffected. In order to determine the nascent vibrational distribution of HCN, a kinetic model was fitted to these temporal vibrational populations. While each mode could be fitted independently, it was decided to perform a global fit due the interconnectivity of the modes. In particular, the ‘decay’ rate of $\nu_1 = 0$ and $\nu_2 = 0$ levels, which are only seen to decay because (0,0,1) level is detectable while the (0,0,0) level is not. Therefore the ‘decay’ rates of these two states were tied to that of the $\nu_3 = 1$ state. The model employed a single quantum cascade process with the nascent populations and decay rate constants as the fitting parameters. Figure 7.7 (a) illustrates the time-dependence of vibrational level populations of the C–H stretching mode and Figure 7.7 (b) and (c) show the same for the for the bending and C–N stretching mode. The nascent populations for each mode,

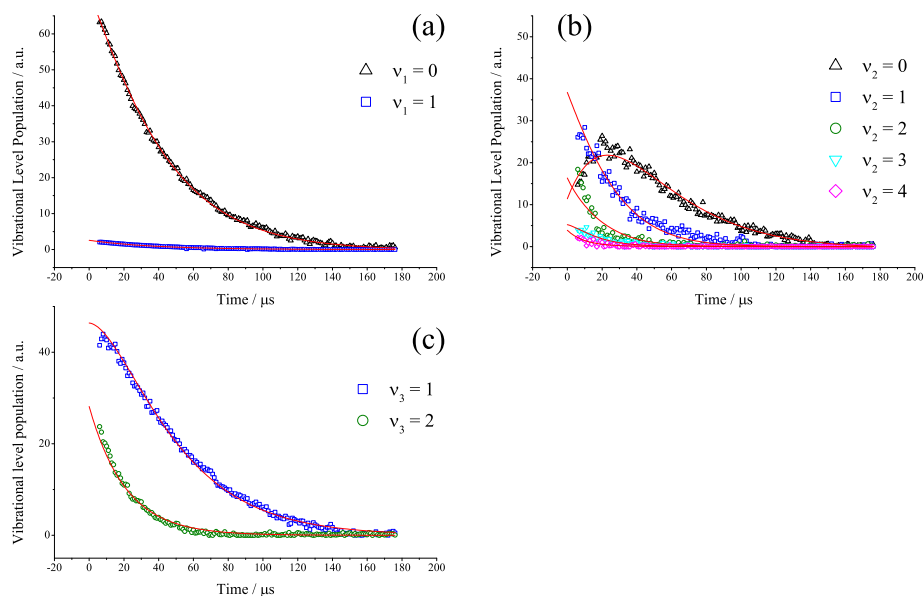


Figure 7.7: Time dependent vibrational population distributions for ν_1 (a), ν_2 (b) and ν_3 (c) modes of HCN. For each mode, data corresponding to zero quanta, one quanta and two quanta are represented by the symbols Δ , $\square$ and $\circ$ respectively. The results of the global kinetic fit are also shown (red).

obtained from the kinetic fit described above, are shown in Table 7.1. However, it is noted that this does not represent the full distribution as only states with $\nu_3 > 0$ were able to be measured.

Table 7.1: Nascent populations distribution for the three modes of HCN, following the reaction of CN with cyclohexane. Values in italics have been constrained during the fitting procedure as described in the main text.

Vibrational Quanta	ν_1 C–N stretch	ν_2 Bend	ν_3 C–H stretch
0	0.97 $\pm$ 0.04	0.15 $\pm$ 0.07	–
1	<i>0.04</i> $\pm$ <i>0.02</i>	0.50 $\pm$ 0.08	0.62 $\pm$ 0.05
2	0	0.22 $\pm$ 0.04	0.38 $\pm$ 0.04
3	0	<i>0.07</i> $\pm$ <i>0.02</i>	0
4	0	<i>0.05</i> $\pm$ <i>0.01</i>	0
5	0	<i>0.01</i> $\pm$ <i>0.01</i>	0

7.4 Discussion

The distributions presented in Table 7.1 are now discussed in light of recent theoretical work on this system by Glowacki *et al.* [16]. They performed quasi-classical and classical non-equilibrium molecular dynamics simulations of the reactions of CN + cyclohexane in both the gas phase and in a CH₂Cl₂ solvent. Energy partitioning into the translational, rotational and vibrational degrees of freedom was performed by normal mode analysis, and they presented normalised distributions of energy deposited into each degree of freedom of the HCN reaction product for both the gas phase and the solution phase calculations. These distributions show that the nascent HCN has excitation in both the C–H stretching and HCN bend beyond that expected for a 298 K thermal distribution, without accompanying translational and rotational excitation.

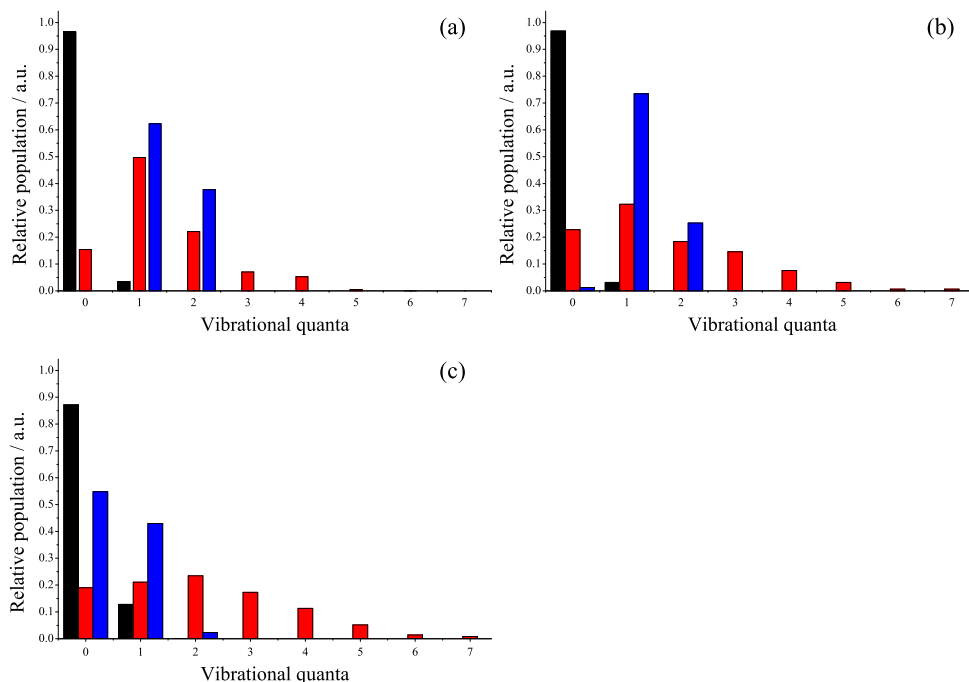


Figure 7.8: (a) Nascent distributions for the three vibrational modes of HCN, ν_1 (black), ν_2 (red) and ν_3 (blue), obtained by extrapolation of the of the experimental data shown in Figure 7.7. Also shown are the theoretically determined nascent distributions for the three vibrational modes of HCN, ν_1 (black), ν_2 (red) and ν_3 (blue) resulting from: (b) the gas phase reaction and (c) solution phase reaction. Both distributions were calculated by Glowacki *et al.*[16, 29].

Comparison is now made between the experimentally determined distributions and the theoretical distributions obtained by Glowacki *et al.* [16], both shown in Figure 7.8. As mentioned above, the higher vibrational levels of the ν_1 and ν_2 mode were constrained in the fitting procedure, and so discussion will focus on the ν_3 mode. The C–H stretching distribution as found by theory and experiment show good agreement. Both show excitation in this mode with up to the second vibrationally excited level, although a slightly hotter distribution was found from the experimental data, with the ratio between the populations of the $\nu_3 = 1$ and

$\nu_3 = 2$ level around two thirds larger than that found from the theoretical study. Figure 7.8 (c) shows the nascent vibrational distribution of HCN for the solution phase reaction, as calculated by Glowacki *et al.* [16]. This shows a very similar distribution in both the ν_1 and ν_2 modes is expected, while the ν_3 is somewhat colder than the gas phase distribution.

While it should not be forgotten that the distribution obtained by experiments described in this chapter is only a partial distribution, as all $(\nu_1, \nu_2, 0)$ states cannot be detected, the low fraction of products formed with $\nu_3 = 0$ (1.3% as determined from theoretical results shown in Figure 7.8 (b)) indicates that to a good approximation the experimental results can be considered a complete distribution. The observation contrasts directly with the conclusions of Jackson and co-workers [7, 8], that hydrogen abstraction from organic compounds by CN results in vibrationally excited HCN product with a population inversion between the $\nu_3 = 1$ and $\nu_3 = 2$ levels. Most of the molecules included in the study contained only primary hydrogen atoms (neopentane, isobutane), and as cyclohexane (not included in the study) contains only secondary hydrogen atoms, this might be the cause of the discrepancy. However, a more likely explanation comes from the analysis procedure employed by Jackson and co-workers. The ratio of $\nu_3 = 1$ and $\nu_3 = 2$ was extracted from their data by comparing the emission intensity of the R branch of the HCN $(0,0,1)-(0,0,0)$ transition, for $J = 12-20$, with that from the P branch of the HCN $(0,0,2)-(0,0,1)$ transition for the same upper state rotational levels. Crucially the contribution from other states with $\nu_1, \nu_2 > 0$ were ignored. The theoretical calculation by Glowacki *et al.* [16] and experimental evidence of Macdonald and co-workers [9, 10] for similar hydrogen abstraction processes show that this assumption is clearly not

appropriate. The contribution of states with excitation in the other modes will red shift emission from HCN (0,0,1) level, which will decrease the intensity in the region of the R branch of this transition, and if the excitation in the other modes is great enough, will increase the emission intensity in the region of the P branch of the HCN (0,0,2)-(0,0,1) emission band. Comparison of the experimental emission spectra presented by Jackson and co-workers with the spectra shown in Figure 7.4 reveal similar limits to the feature. Therefore it is concluded that their identification of a population inversion between the $\nu_3 = 1$ and $\nu_3 = 2$ levels of HCN following hydrogen abstraction from small hydrocarbons is incorrect.

The obtained vibrational distribution of the ν_3 mode represents 4523 cm^{-1} of energy, accounting of 47 % of the total available energy. The equivalent value from the theoretical data, shown in Figure 7.8 (b) is 42 %. Assuming that the excitation of translational and rotational degrees of freedom of excitation of HCN is minimal [16], the total energy deposited into the HCN molecule is 5600 cm^{-1} , leaving 4000 cm^{-1} unaccounted for. This is greater than the value that was ascribed initially to the internal excitation of the cC_6H_5 product. Either this value could be an underestimate, or the calculated value for energy released by the reaction is an overestimate. The calculation relies on the energy of the C–H bond in cyclohexane, which has a large spread in the literature, and so has a relatively large degree of uncertainty.

Comparison of the experimental distribution to the solution phase work of Orr-Ewing and co-workers [15] demonstrates that even in the complex condensed phase environment, many features of the dynamics of the gas phase process are relatively well maintained. It was found that the potential energy surface of the reactive process was very similar for both gas and solution phase [16], leading to

similar deposition of energy in the vibrational modes of the HCN product. An inverted distribution was observed in the C–H stretching mode at early time, with the majority of HCN products formed with one quanta of excitation in this mode. The highest observed vibrational state in solution was (0,2,1), compared to (0,1,2) for the gas phase reaction. The theoretical calculations of the solution phase reaction [16] suggest that higher vibrational states are formed, which undergo initial rapid relaxation by the spatially close alkyl co-product before the HCN can diffuse away.

7.5 Conclusion

The dynamics of hydrogen abstraction reaction between the CN radical and cyclohexane in the gas phase have been studied using time-resolved FTIR emission spectroscopy. HCN reaction products were formed, and were found to be substantially vibrationally excited. Experiments have demonstrated the efficient channelling of energy into as many as two quanta of the C–H stretching mode. Limited information was able to be obtained about the excitation in the C–N stretching mode and the bending mode, due to the relative insensitivity of the experiment to excitation in these modes. Therefore these distributions were constrained during the fitting procedure. Nascent vibrational level populations have been presented for each of the three vibrational modes of HCN, which support theoretical calculations of Glowacki *et al.* [16]. The HCN reaction product formed by reaction (7.4) does not exhibit a population inversion between the $\nu_3 = 1$ and $\nu_3 = 2$ vibrational levels, which also supports the calculations of Orr-Ewing and co-workers, although this is discordant with the findings of Jackson and co-workers [7, 8].

The dynamics of the reactions of CN radicals with cyclohexane also have many features in common with their liquid phase counterparts. The HCN reaction products are formed with high degrees of vibrational excitation. This degree of vibrational excitation is, as one would expect, higher than has been reported for comparable reactions in the liquid phase. This indicates partial dampening of the developing HCN vibrational motion after the transition state in the liquid phase.

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Appendix A

Spectral simulations

Infrared emission spectra for NO, OH, CO₂, H₂O and HCN were simulated by the procedures detailed in this appendix. For most cases a thermal Boltzmann rotational distribution was assumed, on account of the large pressure of Ar present in the experiments described in this thesis ensuring rapid thermalisation of rotational levels. For each molecule the general procedure for generating the spectral simulation remains the same. First, the line positions for all rotational transitions of a given vibrational band are obtained from the literature, either from experimental measurements or calculated from reported vibrational and rotational molecular constants using formulae described by Herzberg [1, 2]. Secondly the intensity of each rotational line is calculated, which is done using Equation A.1

$$I(\nu' J', \nu'' J'') = \frac{hc\bar{\nu}_{\nu' J', \nu'' J''}^4 S_{J'} A_{\nu', \nu''} N_{\nu' J'}}{(2J' + 1)\bar{\nu}_{\nu', \nu''}^3} \quad (\text{A.1})$$

where $\bar{\nu}_{\nu J, \nu', J'}$ is the transition energy for the specific rotational line, S_J is the line strength term, $A_{\nu, \nu'}$ is the rotation-less Einstein A coefficient and $\bar{\nu}_{\nu, \nu'}$ is the

rotation-less transition energy. $N_{\nu'J'}$ is the population of the specific rovibrational state, which can be separated into factors $N_{J'}$ and $N_{\nu'}$. $N_{J'}$ is calculated according to the Boltzmann distribution.

$$N_{J'} = \frac{(2J' + 1)}{Q_{rot}(\nu')} \exp \left[-F(J') \frac{hc}{kT_{rot}} \right] \quad (\text{A.2})$$

T_{rot} is the rotational temperature and $Q_{rot}(\nu')$ is the rotational partition function, which for molecules with a small rotational spacing (i.e. not hydride diatomics) can be approximated as:

$$Q_{rot}(\nu') = \frac{kT_{rot}}{hcB_{\nu'}} \quad (\text{A.3})$$

$N_{J'}$ is the vibrational state population, and it is allowed to vary as the fitting parameter. Thus the least squares fitting procedure returns a vibrational distribution. The expressions for the line strengths, $S_{J'}$ (Höln-London factors), for the P,Q and R branch transitions are shown below in Equations A.4, A.5 and A.6, where Λ is the quantum number for the projection of the orbital angular momentum onto the internuclear axis.

$$S_{J'}^P = \frac{(J' + 1 + \Lambda)(J' + 1 - \Lambda)}{J' + 1} \quad (\text{A.4})$$

$$S_{J'}^Q = \frac{(2J' + 1)\Lambda^2}{J'(J' + 1)} \quad (\text{A.5})$$

$$S_{J'}^R = \frac{(J' + \Lambda)(J' - \Lambda)}{J'(J' + 1)} \quad (\text{A.6})$$

Finally, the stick spectrum was convoluted with a sinc^2 function of appropriate width to match the line shape of the interferometer and the spectral resolution of the experimental data.

A.1 NO simulations

There were four different spectral simulations of the NO molecule used in this thesis: The NO X²Π fundamental and first overtone bands, the fundamental of the NO A²Σ⁺ state and the Ogawa bands (transition between the NO a⁴Π and NO b⁴Σ⁻ states). For all cases the energy of the rovibrational states were calculated with the aid of PGOPHER simulation software [3] using constants taken from the literature, which are presented in Table A.1. The transition

Table A.1: Molecular vibrational and rotational constants of NO for the X²Π, A²Σ⁺, a⁴Π and b⁴Σ⁻ states. Values are in units of cm⁻¹.

Molecular constant	NO X ² Π[4]	NO A ² Σ ⁺ [5]	NO a ⁴ Π [6]	NO b ⁴ Σ ⁻ [6]
$\bar{\nu}_{00}$	0	44200.3	38267.2	46171.8
ω_e	1904.13455	2374.372	1016.214	1262.354
$\omega_e x_e$	14.088358	16.159	10.313	14.797
$\omega_e y_e / 10^{-2}$	1.00467	3.73	-2.59	4.23
$\omega_e z_e / 10^{-3}$	0.115331	-	-6.41	-
B_e	1.70488847	1.995586	1.11677	1.3594
$\alpha_e / 10^{-2}$	1.754158	1.8714	1.485	2.002
$\gamma_e / -4$	0.14886	-0.478	-2.2	-1.9

energies were then simply calculated by taking the energy difference between appropriate rovibrational states. The rotation-less Einstein A coefficients were required for the NO X²Π fundamental and first overtone transitions as well as those for the Ogawa band system. These have been reported in the literature and the values used in this thesis are listed in Table A.2. There are no published values for emission coefficients for transitions within the A²Σ⁺ state of NO, and so these were calculated from the dipole moment functions. This is described in detail in the main thesis (Section 4.3.2). The spin-orbit coupling constants for the NO X²Π and a⁴Π were taken from experimentally determined values reported by Amiot [4] and Huber *et al.* [6] respectively and are listed below in Table A.3.

Table A.2: Einstein A coefficients for the fundamental and first overtone transitions of NO X²Π, and for the Ogawa band transitions, both calculated by Langhoff *et al.* [7, 8]. The Ogawa bands involve two electronic states of NO: the b⁴Σ⁻ and a⁴Π. All values are in s⁻¹.

ν	NO X ² Π		NO b-a (0 → ν)
	($\nu \rightarrow \nu - 1$)	($\nu \rightarrow \nu - 2$)	
0	-	-	12300
1	12.074	-	16100
2	22.863	0.786	11800
3	32.441	2.271	6220
4	40.889	4.363	2600
5	48.253	6.967	876
6	54.607	9.976	230
7	60.006	13.335	-
8	64.511	16.926	-
9	68.17	20.688	-
10	71.06	24.54	-
11	73.22	28.427	-
12	74.712	32.302	-
13	75.582	36.101	-
14	75.865	39.789	-
15	75.604	43.321	-
16	74.824	46.661	-
17	73.548	49.786	-
18	71.803	52.663	-
19	69.608	55.278	-
20	66.975	57.628	-
21	63.907	59.717	-
22	60.398	61.557	-
23	56.462	63.146	-
24	52.138	64.462	-

Table A.3: Spin-orbit coupling constants for the NO X $^2\Pi$ and a $^4\Pi$ states.

ν'	A / cm^{-1}	A / cm^{-1}
	NO X $^2\Pi$ [4]	NO a $^4\Pi$ [6]
0	123.1336110	-41.53
1	122.8891850	-41.62
2	122.6348510	-41.7
3	122.3693690	-41.78
4	122.0914500	-41.85
5	121.8002900	-41.91
6	121.4941600	-
7	121.1704500	-41.99
8	120.8282800	-41.99
9	120.4644500	-
10	120.0764500	-
11	119.6632700	-
12	119.2194100	-
13	118.7418100	-
14	118.2258100	-
15	117.6677000	-
16	117.0596000	-
17	116.3986900	-
18	115.6759400	-
19	114.8828500	-
20	114.0136000	-
21	113.0540600	-
22	112.0009500	-

A.2 CO₂ ($\Delta\nu_3 = -1$)

The program for simulating the CO₂ ($\Delta\nu_3 = -1$) emission band was developed by a visitor the the research group, M. Burgos. For this it was assumed that only transitions of the from $(\nu_1, \nu_2(\ell_2), \nu_3) \rightarrow (\nu_1, \nu_2(\ell_2), \nu_3 - 1)$ occurred. Each band was represented by three branches, a P and R branch, separated by $\sim 25 \text{ cm}^{-1}$, and a Q branch, which only occurred for transitions between levels for which $\ell_2 > 0$, where ℓ is the azimuthal quantum number, which represents the angular momentum associated with the doubly degenerate bending motion. ℓ can take values of $\nu_2, \nu_2 - 2, \nu_2 - 4 \dots 1$ or 0. The energies of the states were calculated according the Herzberg [2], and were compared with those measured by Bailly *et al.* [9] for conformation. The intensity of each band was calculated using Equation A.7.

$$I(\nu_1, \nu_2, \nu_3) = P^0(\nu_1, \nu_2, \nu_3) \left[\frac{\bar{\nu}(\nu_1, \nu_2, \nu_3)}{\bar{\nu}(0, 0, 1)} \right]^4 \nu_3 A_{001} N_{PQR} \quad (\text{A.7})$$

A_{001} is the Einstein A coefficient for the ν_3 fundamental transition, which was calculated by integrating the intensity of the $(0,0,1) \rightarrow (0,0,0)$ transition from the HITRAN database [10] and using the relations detailed in a publication by Gamache and Rotham [11]. $\bar{\nu}$ the frequency of the $\Delta\nu_3 = -1$ transition and N_{PQR} is a factor taking into account the relative intensities of P, Q and R branches. The quartic term allows for the dependence of the spontaneous emission coefficient on the transition frequency, and the ν_3 quantum number dependence assumes harmonic oscillator behaviour. Fermi resonance between ν_1 and ν_2 was considered for levels with $\nu_1 < 10$ and $\ell_2 = 0, 1$ using the relation for perturbed energy given

by

$$E = E_{\text{NI}} \pm \frac{1}{2} \sqrt{(4|W_{\text{NI}}|^2 + \Delta^2)} \quad (\text{A.8})$$

where E_{NI} is the mean of the unperturbed states, Δ is the energy separation of the unperturbed states, and W_{NI} is the matrix element for the perturbation. A value of 50.4 cm^{-1} was used for W_{NI} , which corresponds to the $W_{100,020}$ element [2, 12].

A.3 OH X $^2\Pi$ fundamental band

To simulate OH X $^2\Pi$ fundamental spectra, both line positions and emission coefficients were taken from the work of van der Loo *et al.* [13, 14]. This thorough resource covered the range of required vibrational and rotational states, so no calculation was required to generate energy levels of states. Again Equation A.1 was used to generate the line intensities, prior to convolution to obtain the correct spectral resolution.

A.4 $\text{H}_2\text{O}(\Delta\nu_3 = -1)$

The method for generating H_2O emission simulations was based on that described by Setser and co-workers [15] in the excellent review on H_2O chemiluminescence following water-forming reactions. The method also corresponds to the general procedure for generating simulations described at the beginning of this appendix. First the H_2O $(0,0,1) \rightarrow (0,0,0)$ emission band was simulated. Line positions for the individual rotational lines of this transition were taken from the HITRAN database [10], as were the rotationally resolved Einstein emission coefficients,

which were calculated from the absorption cross sections [16], and then Equation A.1 was used to calculate the intensity of each line, with a thermal Boltzmann rotational distribution assumed. In order to simulate the hot bands, this fundamental emission spectrum was simply red shifted according to the relative rotation-less transitions energies of the respective vibrational transitions. This is shown in Equation A.9, where Δ is the shift in cm^{-1} , and is always negative representing a red shift of the emission as a result of the anharmonicity of the potential.

$$\Delta = G(\nu_1, \nu_2, \nu_3) - G(\nu_1, \nu_2, \nu_3 - 1) - [G(0, 0, 1) - G(0, 0, 0)] \quad (\text{A.9})$$

These vibrational energies were calculated using the constants presented by Benedict *et al.* [17], presented in Table A.4. The only correction for intensity was the inclusion of a ν_3 term, which is in accordance with the harmonic oscillator approximation.

Table A.4: Table presenting the molecular vibrational constants for H_2O . All values are in cm^{-1} .

Molecular constant	H_2O
ω_1	3832.17
ω_2	1648.47
ω_3	3942.53
$x_1 1$	-42.576
$x_2 2$	-16.813
$x_3 3$	-47.566
$x_1 2$	-15.933
$x_1 3$	-165.824
$x_2 3$	-20.332

A.5 HCN($\Delta\nu_3 = -1$)

The spectroscopy of the HCN molecule has received greater attention in the literature than H₂O. Consequently there is a greater body of measured and calculated rovibrational energy levels, and so the method for simulating the HCN emission spectra is more reliable than H₂O. An extensive work by Mellau and co-workers [18, 19] provided experimental values for vibrational energy levels, $G(\nu_1, \nu_2, \nu_3, \ell)$ and state resolved rotational constants B_ν , D_ν and H_ν . The rovibrational line positions for each vibrational band were calculated using the PGOPHER simulation software package [3]. The intensity of each line was calculated using Equation A.1, with rotationless A factors as reported by Botschwina [20] and presented in Table A.5. A more complete set of emission coefficients is not available, and so the values presented in Table A.5 were used for all transitions for a given ν_3 .

Table A.5: Einstein A coefficients for the $(0,0,\nu_3) \rightarrow (0,0,\nu_3 - 1)$ transitions in HCN as reported by Botschwina [20]. All values in s⁻¹.

HCN transition	Emission coefficient
$(0,0,1) \rightarrow (0,0,0)$	77.2
$(0,0,2) \rightarrow (0,0,1)$	135.6
$(0,0,3) \rightarrow (0,0,2)$	177.4
$(0,0,4) \rightarrow (0,0,3)$	205.4

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Appendix B

Surprisal analysis

The nascent vibrational distributions of NO X $^2\Pi$ that were obtained in Chapters 3, 4 and 5 were to compared to the Prior distribution for the quenching process. This enabled determination of whether a distribution was hotter or colder than statistical, and also provide a method for estimating the population in the low vibrational levels ($\nu = 0,1$) for the experiment does not provide reliable direct observations.

B.1 The Prior distribution

This describes the distribution of energy among the internal degrees of freedom of products of given process, such as reaction of photodissociation. The Prior energy distribution, P^0 , assumes that the population within each group of energetically available product states, a_n , is proportional to the number of states in that group. In calculating this distribution it is assumed that there are no dynamical effects in the process and that the only constraint is the conservation of energy. Therefore

B.1. The Prior distribution

the probability of populating of an energetically allowed group of states, a_n , is proportional to the degeneracy of that state, $g(a_n)$, and is shown below in Equation B.1, where $\rho(E_{tr})$ is the density of translational states at E_{tr} .

$$P^0(a_n) = \frac{g(a_n)\rho(E_{tr})}{\sum_n g(a_n)\rho(E_{tr})} \quad (\text{B.1})$$

For a total energy E , the equation becomes:

$$P^0(a_n : E) = \frac{g(a_n : E)\rho(E - E(a_n))}{\sum_n g(a_n : E)\rho(E - E(a_n))} \quad (\text{B.2})$$

where $E(a_n)$ is the energy of the group a_n . The prior distribution for a subset, a_m of the a_n quantum states can be defined as shown in Equation B.3.

$$P^0(a_m : E) = \frac{\sum_{i \neq m} g(a_i : E)\rho(E - E(a_i) - E(a_m))}{\sum_i g(a_i : E)\rho(E - E(a_i))} \quad (\text{B.3})$$

If it is assumed that the product species are well described by the rigid-rotor harmonic oscillator model, and that the internal energy is a continuous function, then the prior distribution for a particular class of products can be derived from the analytical expressions for the vibrational, rotational and translational density of states (degenecies) by using the continuous approximation of Equation B.3 [1].

$$P^0(a_m : E) = \frac{\iiint_{a_i \neq a_m} g(a_i : E)\rho(E - E(a_i) - E(a_m)) da_i}{\iiint_{a_i} g(a_i : E)\rho(E - E(a_i)) da_i} \quad (\text{B.4})$$

B.1. The Prior distribution

Finally the density of translational states can be expressed in terms of the translational energy E_{tr} . For simple cases where no dissociation occurs, the relationship is described by Equation B.5 [2, 3], where $\rho_{2,tr}$ is the number of states per unit volume per unit interval in E_{tr} and μ is the reduced mass.

$$\rho_{2,tr}(E_{tr}) = \frac{\mu^{3/2}}{\sqrt{2}\pi^2(h/2\pi)^3} E_{tr}^{1/2} = \alpha_2 E_{tr}^{1/2} \quad (\text{B.5})$$

The prior distributions that were required for the analysis performed in this thesis are derived below, using the methods outlined by Muckermann [4].

B.1.1 AB(ν_{AB} J_{AB}) + CD(ν_{CD} J_{CD}) products

This case includes the NO A $^2\Sigma^+(\nu = 0) + \text{O}_2 \rightarrow \text{NO X } ^2\Pi + \text{O}_2$ system and the NO A $^2\Sigma^+(\nu = 1) + \text{NO X } ^2\Pi(\nu = 0) \rightarrow \text{NO X } ^2\Pi + \text{NO X } ^2\Pi$ system studied in Chapters 3 and 4 respectively. In this situation the total density of product states, $\rho(E)$ can be found using the denominator expression of Equation B.4:

$$\rho(E) = \iiint\int (2J_{AB} + 1)(2J_{CD} + 1)(E - E_{int})^{1/2} d\nu_{CD} dJ_{CD} d\nu_{AB} dJ_{AB} \quad (\text{B.6})$$

$E_{int} = E_{R_{AB}} + E_{\nu_{AB}} + E_{R_{CD}} + E_{\nu_{CD}}$, the sum of the rotational and vibrational energy of both AB and CD product molecules, and the $(2J+1)$ terms represent the degeneracy of the rotational level the molecule. A change of variable from

B.1. The Prior distribution

quantum number to energies be performed by using the definitions shown below:

$$\begin{aligned}
 E_R &= BJ(J+1) \\
 \frac{dE_R}{dJ} &= B(2J+1) \\
 E_\nu &= \omega(\nu + \frac{1}{2}) \\
 \frac{E_\nu}{d\nu} &= \omega
 \end{aligned} \tag{B.7}$$

Upon the change of variables Equation B.6 becomes Equation B.8.

$$\rho(E) = \iiint \frac{(E - E_{int})^{1/2}}{\omega_{AB}\omega_{CD}B_{AB}B_{CD}} dE_{\nu_{CD}} dE_{R_{CD}} dE_{\nu_{AB}} dE_{R_{AB}} \tag{B.8}$$

The integral limits are defined below.

$$\begin{aligned}
 E_{\nu_{CD}} &= 0 \quad \text{to} \quad E - E_{R_{AB}} - E_{\nu_{AB}} - E_{R_{CD}} \\
 E_{R_{CD}} &= 0 \quad \text{to} \quad E - E_{R_{AB}} - E_{\nu_{AB}} \\
 E_{\nu_{AB}} &= 0 \quad \text{to} \quad E - E_{R_{AB}} \\
 E_{R_{AB}} &= 0 \quad \text{to} \quad E
 \end{aligned} \tag{B.9}$$

Solving Equation B.8 reveals the total density of states to be $k \frac{16}{945} E^{9/2}$, where k is a constant including the various molecular constants. The Prior expectation probability for individual state of the system, $P^0(E_{R_{AB}}, E_{\nu_{AB}}, E_{R_{CD}}, E_{\nu_{CD}})$ can be expressed as shown in Equation B.10.

$$P^0(E_{R_{AB}}, E_{\nu_{AB}}, E_{R_{CD}}, E_{\nu_{CD}}) = \frac{945}{16kE^{9/2}} (E - E_{R_{AB}} - E_{\nu_{AB}} - E_{R_{CD}} - E_{\nu_{CD}})^{1/2} \tag{B.10}$$

B.1. The Prior distribution

The Prior distribution for a single degree of freedom (such as the vibrational mode of one of the product, which has particular relevance to this the work in this thesis) is then the sum (or the integral) over all the other degrees of freedom. Therefore the Prior probability for the AB vibrational mode, $P^0(\nu_{AB})$ is calculated using Equation B.11.

$$P^0(\nu_{AB}) = \iiint \frac{945}{16kE^{9/2}} (E - E_{RAB} - E_{\nu_{AB}} - E_{RCD} - E_{\nu_{CD}})^{1/2} dE_{\nu_{CD}} dE_{RCD} dE_{RAB} \quad (\text{B.11})$$

Solving this equation using the integration limits defined in (B.9), results in an expression in terms of the total energy available to the products. Prior distributions are often expressed as a fraction of the energy, and both forms are shown in Equation B.12, where N is simply a normalisation factor.

$$P^0(\nu_{AB}) = \frac{9}{2kE^{9/2}} (E - E_{\nu_{AB}})^{7/2} = N(1 - f_{\nu_{AB}})^{7/2} \quad (\text{B.12})$$

B.1.2 AB(ν_{AB} J_{AB}) + CDE(ν_1 ν_{2a} ν_{2b} ν_3 J_{CDE}) products

This system is appropriate for the analysis performed in Chapter 4 on the quenching process $\text{NO A } ^2\Sigma^+(\nu = 0) + \text{CO}_2 \rightarrow \text{NO X } ^2\Pi + \text{CO}_2$. The methodology is exactly the same as was presented in detail in the previous section. The only difference is that the CDE product now contains four internal degrees of freedom, include a doubly degenerate bending motion. Therefore, the expression for the total density of states, $\rho(E)$, is different.

$$\rho(E) = \frac{128k}{155925} E^{15/2} \quad (\text{B.13})$$

B.1. The Prior distribution

Equation B.14 shows the general expression for the Prior expectation for a specific state of the system, expressed in terms of fraction of energies.

$$P^0(f_{AB}f_{CDE}) = \frac{155925}{128k}(1 - f_{AB} - f_{CDE})^{1/2} \quad (\text{B.14})$$

In Chapter 4, both the Prior distribution for the vibrational mode of NO and for CO₂ were calculated. To calculate the former, the vibrational Prior of the diatomic product is straight forward, and simply requires integration over the remaining degrees of freedom, J_{AB} , ν_1 , ν_{2a} , ν_{2b} , ν_3 , and J_{CDE} which is shown in Equation B.15.

$$P^0(f_{\nu_{AB}}) = N(1 - f_{\nu_{AB}})^{13/2} \quad (\text{B.15})$$

First, the Prior distribution as defined in Equation B.14 is summed over the vibrational and rotational modes of the diatomic product and the rotational mode of the triatomic product. This leaves the Prior probability for separate vibrational modes of CDE, as shown in Equation B.16.

$$P^0(f_{\nu_1}f_{\nu_{2a}}f_{\nu_{2b}}f_{\nu_3}) = \frac{19305}{16k}(1 - f_{\nu_1} - f_{\nu_{2a}} - f_{\nu_{2b}} - f_{\nu_3})^{1/2} \quad (\text{B.16})$$

Then a new variable is defined thus:

$$f_{\nu_{CDE}} = \nu_1 + \nu_{2a} + \nu_{2b} + \nu_3 \quad (\text{B.17})$$

This is substituted for any of the vibrational modes of the CDE product (ν_1 is arbitrarily chosen).

$$P^0(f_{\nu_{\text{CDE}}} f_{\nu_{2a}} f_{\nu_{2b}} f_{\nu_3}) = \frac{19305}{16k} (1 - f_{\nu_{\text{CDE}}})^{1/2} \quad (\text{B.18})$$

Summation of this distribution over the ν_{2a} , ν_{2b} and ν_3 modes reveals the Prior distribution of $f_{\nu_{\text{CDE}}}$, as defined in Equation B.17, which is presented below in Equation B.19.

$$P^0(f_{\nu_{\text{CDE}}}) = N f_{\nu_{\text{CDE}}}^3 (1 - f_{\nu_{\text{CDE}}})^{7/2} \quad (\text{B.19})$$

B.2 Surprisal analysis

In the statistical limit, all quantum states are populated equally following a given process. However measured distributions are often found to deviate from this Prior distribution, and in these cases, Surprisal analysis is performed, which allows quantification of the deviation of the measured distribution from statistical (prior), the basis of which is detailed below.

The entropy for a series of final states is given by [3]:

$$S = - \sum_f P(f) \ln P(f) \quad (\text{B.20})$$

where $P(f)$ is the probability of forming state f . The entropy defined in this manner is dimensionless. Considering the vibrational levels of a diatomic molecule, if

a given distribution of $g(\nu)$ states has the probability $P(\nu)$ then:

$$P(f) = P(\nu)/g(\nu) \quad (\text{B.21})$$

and

$$S = - \sum_f (P(\nu)/g(\nu)) \ln[P(\nu)/g(\nu)] \quad (\text{B.22})$$

This expression is summed over f and since there are $g(\nu)$ terms for each value of ν and each term has the same value (statistical), Equation B.22 becomes:

$$S = - \sum_{\nu} P(\nu) \ln[P(\nu)/g(\nu)] \quad (\text{B.23})$$

Within the Prior distribution all quantum states are equally probable, and therefore:

$$P^0(\nu) = g(\nu) / \sum_{\nu} g(\nu) \quad (\text{B.24})$$

The entropy of the system can be defined as the deviation of the measured distribution from statistical (Prior)

$$S = S_{\max} - DS \quad (\text{B.25})$$

where DS is the entropy deficiency, the degree that actual entropy is lower than the maximum value, which itself is define thus:

$$S_{\max} = \ln \left[\sum_{\nu} g(\nu) \right] \quad (\text{B.26})$$

Substituting Equation B.24 into Equation B.26 yields

$$S_{\max} = \ln[g(\nu)/P^0(\nu)] \quad (\text{B.27})$$

This equation is then substituted into Equation B.25 along with Equation B.23 to give:

$$-\sum_{\nu} P(\nu) \ln[P(\nu)/g(\nu)] = \ln[g(\nu)/P^0(\nu)] - DS \quad (\text{B.28})$$

which rearranges to give

$$DS = \sum_{\nu} P(\nu) \ln[P(\nu)/P^0(\nu)] \quad (\text{B.29})$$

For the situation that the measured distribution is the Prior distribution, DS will be zero. Given a measured distribution, $P(\nu)$, either the integral measure of the specificity, DS , or the local measure, $I(\nu)$ can be considered in order to quantify the deviation from Prior. $I(\nu)$ is defined below.

$$I(\nu) = -\ln[P(\nu)/P^0(\nu)] \quad (\text{B.30})$$

It is often found that Surprisal are often well described by a straight line, despite measured distribution being qualitatively very different from predicted Prior distributions.

$$I(\nu) = -\ln[P(\nu)/P^0(\nu)] = \lambda_0 + \lambda_1 f_{\nu} \quad (\text{B.31})$$

λ_0 and λ_1 are the Surprisal parameters, which are described in detail in the thesis.

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