Vibrational emission from electronic quenching

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Introduction

This report presents the results of an investigation applying time-resolved Fourier Transform Infrared (FTIR) spectroscopy to study the quenching of electronically excited nitric oxide and the hydroxyl radical. The first excited electronic states of NO and OH are prepared by laser excitation at 226 nm and 308 nm, respectively, as denoted in equation (1) and the fate of the electronic energy is determined from the observation of IR emission from vibrationally excited NO/OH(X) and products Q formed by quenching, described in equation (2),

$$\mathrm{NO/OH}(X^2\Pi, v=0) + h\nu \rightarrow \mathrm{NO/OH}(A^2\Sigma^+, v=0) \qquad (1)$$

$$\mathrm{NO/OH}(A^2\Sigma^+, v=0) + Q \rightarrow \mathrm{NO/OH}(X^2\Pi, v') + Q \qquad (2)$$

This study aims to determine how much of this energy appears as vibrational excitation in the ground state NO/OH species and how much energy appears as internal excitation of the quencher Q. Time resolved FTIR emission spectroscopy has the advantage that emission from all vibrationally excited levels of NO/OH can be observed simultaneously. In addition when the collision partner has IR active modes, we can observe energy partitioning into it. The collisional transfer of energy from one species to another is an atmospherically important and intriguing aspect of fundamental gas phase chemical dynamics; however despite both fundamental and applied interest, there is not a great deal of discussion in the literature concerning internal energy distributions following energy transfer from electronically excited states.

Results and discussion

1. Quenching of NO(A) by SF_6

A variety of pathways for energy disposal from the NO A state exist when SF_6 is the quenching molecule, including uptake into the vibrational modes of NO(X, v'), into the vibrational modes of SF_6 and also there is the possibility of reactive quenching to produce F atoms, which has never been observed previously. Figure 1 shows a spectrum produced in the NO overtone region when SF_6 is used as a quencher. Despite the low quantum yield of quenching ($\Phi_{SF6} = 0.1$), reasonable vibrational excitation of NO (X) is seen with population in levels as high as $v' = 19$, which represents 72% of the available energy in the system. A nascent vibrational distribution of NO (X, v') has been determined for this pressure and in the future, with our new laser system, we plan to investigate a larger range of pressures of SF_6 so that we can determine the population in NO (X, v') produced by quenching by SF_6 alone.

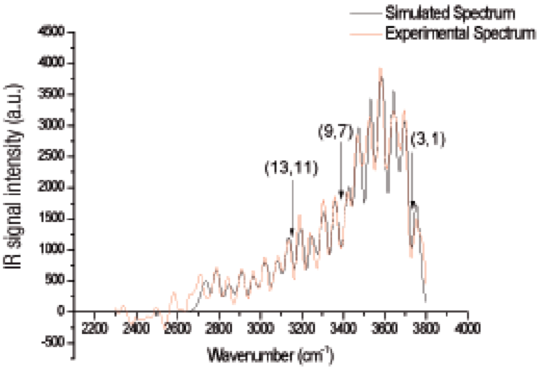

Figure 1. NO X $^2\Pi$ ($\Delta v' = -2$) emission spectrum following 226.257 nm pumping of 50 mTorr NO in the presence of 50 mTorr SF_6 and 50 Torr Ar. Selected band origins are shown.

To investigate whether a reactive pathway to produce F atoms was in operation, H_2 was added to the system to sequester any free F atoms to produce HF, as shown in (3).

$$F + H_2 \rightarrow HF + H \qquad (3)$$

This a well studied reaction,[1,2,3] and HF is a very strong IR emitter, with vibrational Einstein coefficients up to 10 times larger than those for NO,[4] and so is easily detectable. Figure 2 shows a survey contour plot of emission from 1800 cm^{-1} - 4000 cm^{-1}. The strong, structured features between 3500 cm^{-1} - 4000 cm^{-1} are from HF. Populations have been extracted and a nascent vibrational distribution determined and is shown in Figure 3. Also shown are the distributions by a variety of research groups for the vibrational distribution of HF produced from reaction (3). These agree well and indicate that F atoms are produced directly from the reaction of NO (A) with SF_6. To avoid overlap between emission features of NO and HF, D_2 was used which allowed the analysis of the NO and DF populations.

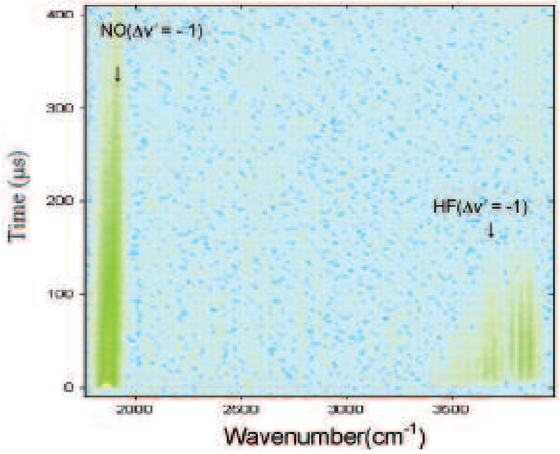

Figure 2. Contour plot of IR emission following pumping of 50 mTorr NO, 4.5 Torr SF_6, 15 mTorr H_2 and 50 Torr Ar with 226.257 nm radiation. Orange denotes high intensity and blue denotes low intensity.

The emission intensity at 50 μs from DF was compared to that of NO (X, Δv' = -2) and the respective A factors were accounted for. This gave a ratio of quantum yields of 1:100, suggesting that the production of F atoms is a relatively insignificant pathway.

We also observe evidence of the production of FNO, as a short-lived emission feature lying on top of the NO fundamental emission at 1860 cm^{-1}. This can be seen in Figure 3. Populations have been extracted and are shown for various time-slices in Figure 4. This emission appears regardless of whether H_2 is present and appears to result from direct reaction of NO (A) with SF_6.

2. Quenching of NO by Ethene and Ethyne

Reactive as well as non reactive pathways are available for energy disposal in quenching by ethene and ethyne. Reactive pathways have been observed previously by a variety of groups,[5,6] but the time dependence of the reaction products and the vibrational state distributions have not previously been determined. With quenching by ethene, we have seen evidence of reactive quenching to produce ethyne, which is highly vibrationally excited. This emission is centred on 3200 cm^{-1} and can be seen in Figure 5. It is efficiently relaxed by Ar and C_2H_4 and a clear vibrational cascade is evident. We do not however see any uptake into the vibrational modes of C_2H_4. Furthermore, a cold NO (X, v') distribution is produced, with population in NO (X) up to v = 7 observed, in contrast to the case of SF_6 as outlined above. With ethyne as the quenching molecule, we observe a similarly cold NO (X, v') distribution but unlike the C_2H_4 case we see uptake of energy into the vibrational modes of the ethyne. The quenching molecule used clearly has an effect of the resultant pathways for energy disposal.

3. Quenching of OH(A, v = 0,1)

Unlike NO (A), OH (A) offers a very different system in that its Franck Condon factors are dominated by

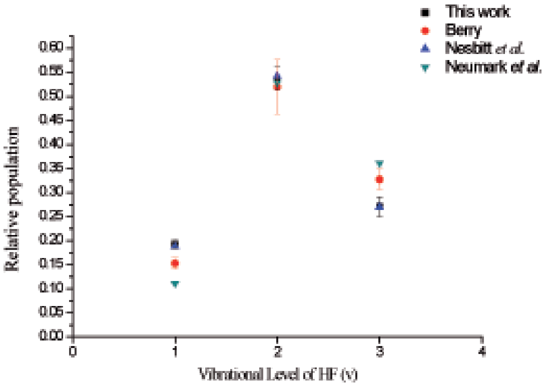

Figure 3. Averaged nascent vibrational populations of HF, normalised for the first three levels, as found in this work and by Nesbitt *et al.*,[i] Neumark *et al.*[ii] and Berry.[iii] Error bars are plotted where available (this work and Berry). (References shown below).

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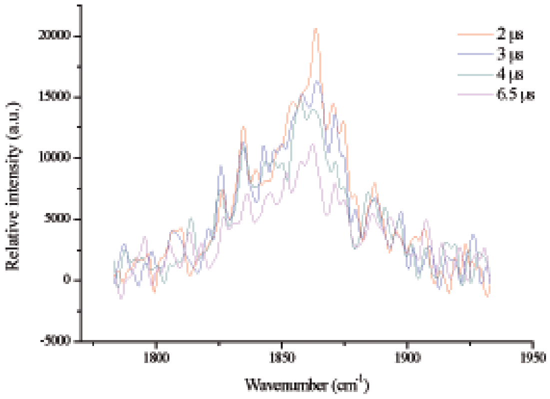

Figure 4. Emission spectra in the region of NO fundamental emission obtained from pumping 50 mTorr of NO, 500 mTorr SF_6 and 50 Torr Ar. Emission collected with InSb detector operating at 2 cm^{-1} resolution.

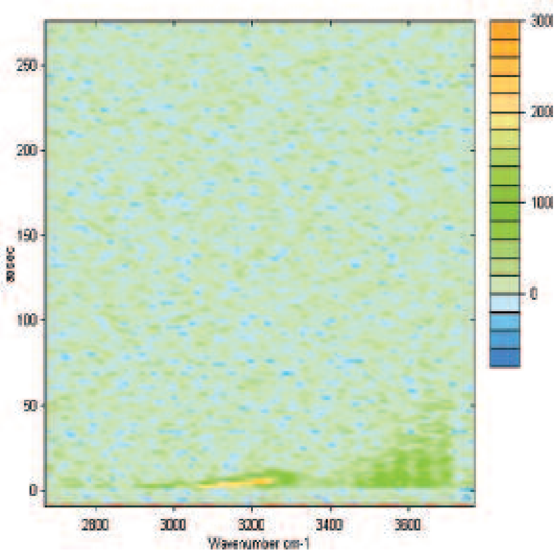

Figure 5. Contour plots of IR emission in region 2600 cm^{-1} to 3940 cm^{-1} resulting from pumping of 50 mTorr NO to its A state in the presence of 920 mTorr C_2H_4 and 50 Torr Ar. The resolution is 20 cm^{-1}.

OH A→X Δv = 0 transitions and so any IR emission following excitation of the (0 – 0) band would be purely a result of quenching. We have recorded the total IR emission whilst scanning the wavelength and found that it tracks the expected LIF excitation spectral simulation. We are currently measuring population changes as a function of pressure of HNO_3 (the OH precursor), and are starting to determine the energy transfer quantum yields to form OH ($X\ ^2\Pi$, $v>0$). Our preliminary indicate that with HNO_3 as a quenching molecule, OH(X, v') is populated up to $v = 4$. We hope to study the quenching by a variety of other molecules including O_2. Interestingly, upon excitation to OH (A, $v = 1$) we have also been able to observe unexpectedly strong infrared vibrational emission within the A state.

References

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