

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. Specifically, the first excited electronic state of NO is prepared by laser excitation at 226 nm as denoted in equation (1) and the fate of the electronic energy is determined from the observation of IR emission vibrationally excited of NO(X) formed by quenching, described in equation (2),



Quenching from the A to X state of NO releases some 529 kJ mol⁻¹ of energy and this study aims to determine how much of this energy appears as vibrational excitation in the ground state NO molecule and how much energy appears as internal excitation of the quenching species. The technique used, time resolved FTIR emission spectroscopy, has the advantage that emission from *all* vibrationally excited levels of NO can be observed at the same time. 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 of the molecules in the system following energy transfer from electronically excited states. Similarly, theoretical understanding of electronic state changing collisions is still inadequate.

Experimental

The technique of step-scan FTIR emission spectroscopy has been described in several reviews^[1,2,3] and the basic methodology therefore is summarized here. Radiation of wavelength 226 nm from a frequency doubled pulsed tuneable dye laser from the Laser Loan Pool (SIRAH PRSC-LG-24 (2 mJ pulse⁻¹, 10 Hz) pumped by a Quanta-Ray PRO-290-30 Nd:YAG laser) was directed into a stainless steel reaction vessel equipped with a multi-pass mirror system (6 passes of the UV beam) and Welsh collection optics^[4]. This radiation pumped the Q₁₁ band head of the A²Σ⁺-X²Π transition of NO and, following collisions with a chosen partner, IR emission from NO (X²Π, v') was observed. This emission was collected by a series of parabolic mirrors, focused into an FTIR spectrometer (Bruker IFS/66), and detected with an InSb

(Graseby IS-2) detector, operating in the range 1-5.5 μm. Time-resolved data, averaged over several laser shots (typically 20), were acquired at a fixed path difference. A moveable mirror was then stepped and the time resolved emission recorded at a series of path differences to form an interferogram, which then underwent Fourier Transformation to produce time-resolved spectra. The resulting spectra can then be used, for example in the determination of vibrational state distributions, energy transfer rates, product determination and product branching ratios. In the experiments described here, 50 Torr of Ar was present in the cell to ensure rotational thermalisation without affecting the nascent product vibrational distribution.

Results and discussion

1. Self Quenching of NO

The electronic self-quenching of NO was investigated and populations in ground state NO(v) up to v=20 were found, equivalent to some 80% of the available energy. The populations were found to be well described by a surprisal analysis, with a distribution slightly hotter than prior, but with some oscillations in populations clearly present and reproducible. A preliminary report has been published in PCCP^[5]. Since then we have looked at a variety of different quenchers, including CO, CO₂, N₂O and Xe.

2. N₂O as a quencher

Figure 1 shows a sample vibrational overtone spectra of NO recorded 10 μs after the pump pulse for the cases where N₂O is used as a quencher and when NO is self-quenched under equivalent conditions of quenching quantum yields. It is evident from this figure that the collisional quenching of NO (A²Σ⁺, v=0) with N₂O preferentially populates lower vibrational levels, and this is confirmed from the nascent vibrational distributions obtained. The population in the lower vibrational levels may be a result of dissociation of N₂O into N₂(¹Σ_g⁺) and either O(³P) or O(¹D). This is thermodynamically feasible since there is 529 kJmol⁻¹ of energy in the A state of NO and the dissociation thresholds for N₂O to O(³P) and O(¹D) are 163.3 kJmol⁻¹ and 350.7 kJmol⁻¹, respectively^[6]. The dissociation thresholds for channels producing O(³P) and O(¹D) therefore permits population up to NO (X²Π, v' = 18) and NO (X²Π, v' = 8), respectively. The formation of O(¹D) may be consistent with results in Figure 1, which show some bimodality in the distribution around this vibrational level. Above this threshold, population in higher vibrational levels of NO could be produced in conjunction with vibrationally excited N₂O (which we

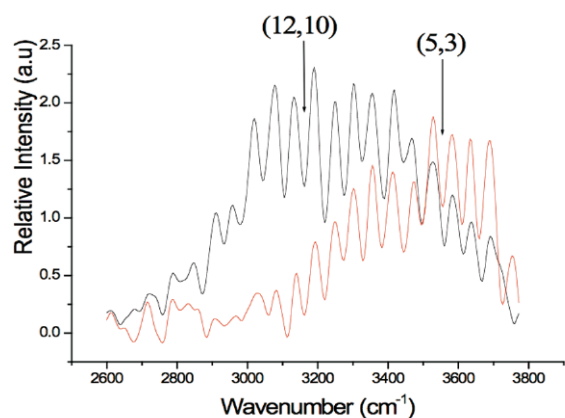


Figure 1. NO ($\Delta v' = -2$) emission spectrum at 10 μs following irradiation of 50 mTorr of NO on its A state resonance in the presence of 3.5 Torr of N_2O ($\Phi_{\text{N}_2\text{O}} = 0.9$, red) and 5 Torr of NO ($\Phi_{\text{NO}} = 0.9$, black). Selected band origins have been shown.

observe) or from the dissociation into ground state $\text{O}(^3\text{P})$. In the absence of N_2O we observe its emission, which we attribute to a small contribution from the reaction of $\text{NO}(\text{A})$ with $\text{NO}(\text{X})$:



The reaction enthalpy is sufficiently exothermic (261 kJ mol^{-1}) to produce vibrationally excited $\text{N}_2\text{O}^{(6)}$.

We can also track the emission from the vibrationally excited N_2O , as is evident in figure 2, which shows a 3-dimensional data set, with wavenumber on the horizontal axis, time on the vertical axis and emission intensity indicated by colours, which represent points of equal intensity. Blue represents low intensity and orange represents high intensity. N_2O clearly appears with both a nascent 'hot' component as well as a colder component, which grows in over a period of $\sim 75 \mu\text{s}$. The cold component appears to come from energy transfer from vibrationally excited NO, whereas the hot species are produced directly by the quenching process (2).

3. Xe as a quencher

Quite different results are obtained when xenon is the quencher. From figure 3, it is evident that the distribution produced by Xe is bimodal. This figure also shows the distribution produced when NO is self-quenched with $\Phi_{\text{NO}} = 0.1$. Under these conditions the nascent vibrational distribution is governed predominantly by radiative transfer to low vibrational levels. Thus we conclude that the low vibrational level component present in both distributions is due to radiative transfer while the higher vibrational level component is produced by collisional energy transfer from the Xe. Unlike Ar, another monatomic quencher, which does not change the $\text{NO}(\text{X})$ distribution from that governed by fluorescence at appreciable pressures⁽⁷⁾, Xe has a more significant effect as expected.

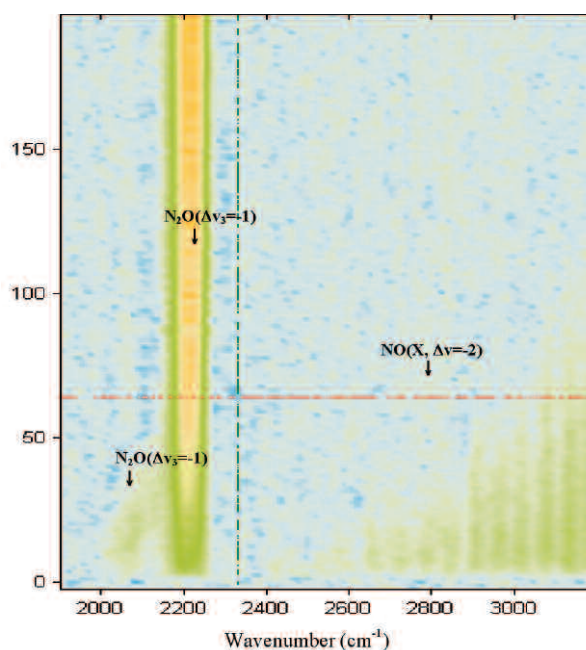


Figure 2. Contour plot of spectra recorded at a resolution of 20 cm^{-1} following pumping of $\text{NO}(\text{X})$ (total pressure: 500 mTorr) to its A state in the presence of 50 mTorr N_2O ($\Phi_{\text{N}_2\text{O}} = 0.07$).

At early time some very strong emission features are present when Xe is the quencher. These have a markedly different time dependence to the NO emission and have a much shorter lifetime of $\sim 10 \mu\text{s}$, as shown in figure 4, compared to $\sim 130 \mu\text{s}$ for NO ($\text{X}, \Delta v = -2$). Furthermore their intensities show a squared dependence on the uv laser power. Because there is no visible P/R branch overlap these emission lines are clearly not due to nitric oxide and have been assigned to be mid-IR Xe emissions from $5p^5(^2P^0_{1/2})6p$, which is excited via a two photon absorption process in NO, consistent with the time dependence of the

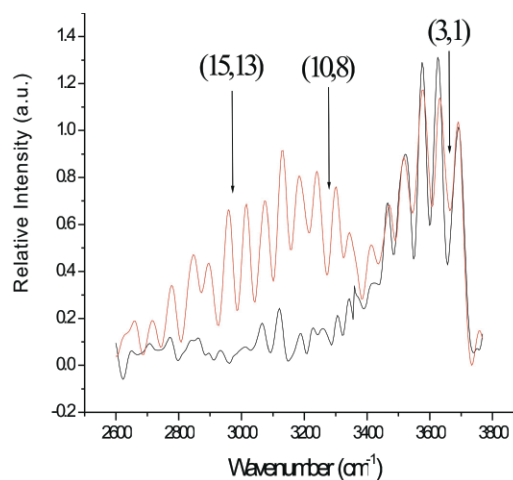


Figure 3. NO ($\Delta v' = -2$) emission spectrum at 10 μs following 226 nm irradiation of 50 mTorr of $\text{NO}(\text{X})$ in the presence of 120 Torr of Xe ($\Phi_{\text{Xe}} = 0.5$, red). Also shown is self-quenching by NO, which has a Franck Condon distribution ($\Phi_{\text{NO}} = 0.1$, black). Selected band origins are shown.

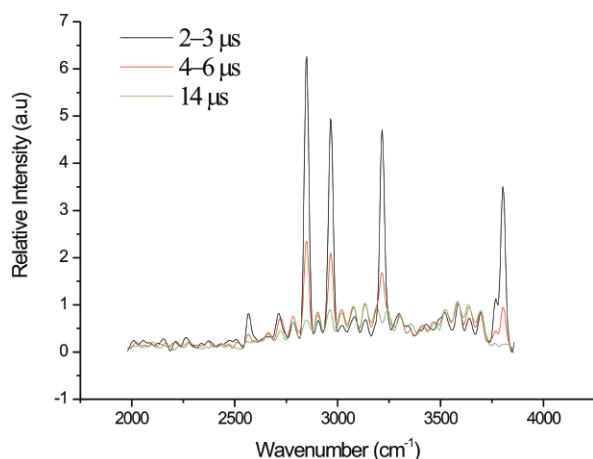


Figure 4. Emission spectra over time following the pumping of NO to its A state (total pressure: 50 mTorr) in the presence of 120 Torr of Xe ($\Phi_{\text{Xe}} = 0.5$).

signals and the line positions. It should be noted that the presence of NO is required to see these IR Xe signals at 226 nm and hence these Xe lines must be a result of an interaction between Xe and NO. To ascertain whether Miller's mechanism^[8] is in operation, i.e. a Van der Waals complex between NO and Xe is being formed and then excited by 2 photons and then falls apart or whether the population of this Xe energy level is as a result of a two photon excitation of NO, which is then collisionally transfers energy to Xe, an excitation spectrum was performed and is shown in figure 5. This shows the variation of signal intensity with pump wavelength for IR emission at early and late time. The early time data show two large Xe signals, which appear regardless of whether or not NO is present and are well known two photon excitations in Xe^[9]. This and the fact that no prominent [NO-Xe] features are observed in the excitation spectrum gives weight to the idea that these lines are a result of collisional energy transfer between NO** and Xe. Further experiments are being carried out to observe the distribution of nascent electronic levels populated.

4. Quenching by CO₂

Copious emission from vibrationally excited CO₂ has been observed in both fundamental and combination band regions. The nascent signals in the $\Delta v_3 = -1$ band are between 2300 and 1700 cm⁻¹, indicating the presence of highly vibrationally excited CO₂ formed by collisional quenching. Overtone bands such as those seen for pure NO in figure 1 are swamped by the intense combination bands for the strong CO₂ emitter, but rapid quenching of this species by Ar has enabled nascent distributions in NO to be estimated.

5. Excitation at 215 nm

NO ($v = 1$) in the A state has been produced by pulsed excitation at 215 nm. At low pressures where radiative quenching is dominant the nascent NO(X) distribution follows that expected from the emission coefficients. The more rapid quenching of this level with Ar in comparison with that for $v = 0$ has allowed the nascent distribution in

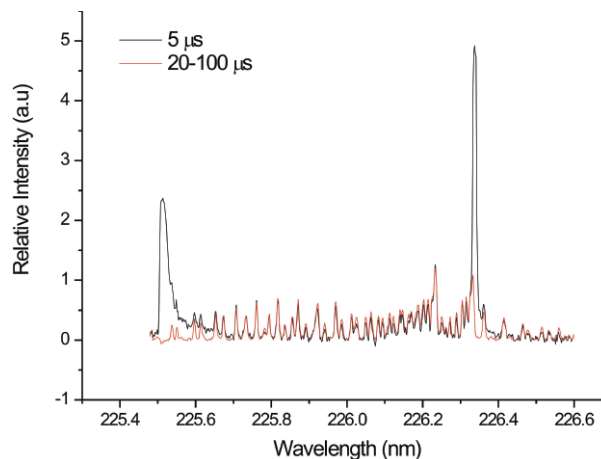


Figure 5. Variation of the intensity of IR emission from NO($\Delta v = -2$) in the region 2500-4000 cm⁻¹ pumping of 50 mTorr of NO in the presence of 120 Torr Xe and 50 Torr Ar across the wavelength range 225.5-226.6 nm, shown at early and late time.

high vibrational levels of NO to be observed, and this is being compared with that from quenching by Xe. Preliminary data for quenching by CO₂ has shown that CO is a product (the reaction to break the C-O bond in CO₂ becomes exothermic for $v = 1$).

Conclusions

It has been shown that FTIR spectroscopy can be applied to novel and interesting systems to provide a significantly greater quantity of information than has been previously found. Different quenching molecules clearly have rather different effects on the vibrational distribution of NO(X). FTIR makes it possible to observe all IR transitions in the region being acquired, and has resulted in structured emission from the quenchers N₂O and CO₂ together with electronic emission features in the Xe system, which can be explained in terms of collisional energy transfer between excited NO and Xe.

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