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The dynamics of the photolysis of alkyl nitrites from a dielectric surface. A comparison with gas phase results

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Abstract

The alkyl nitrites, tert-butyl nitrite and iso-butyl nitrite have been photolysed at 351 nm on a dielectric surface. This involves excitation to the A $^1A''$ state with two quanta in the localized NO stretching mode of iso-butyl nitrite and three quanta in the case of tert-butyl nitrite. The vibrational, rotational and translational energy distributions of the NO product are compared with the results of previous gas phase work. The vibrational distributions mimic those in the gas phase, but the rotational distributions do not do so.

1. Introduction

Our objective in these experiments is to investigate the dynamics of the photolysis of small molecules adsorbed on dielectric surfaces. By comparing the energy distribution of the products of dissociation with that seen in the gas phase, an insight into the photochemistry of the adsorbate is gained.

We have selected the alkyl nitrites for which there exists an extensive body of work concerning their dissociation [1–13]. In addition, the NO produced may be detected with great sensitivity by laser-induced fluorescence (LIF) or by resonance-enhanced multi-photon ionisation (REMPI) spectroscopy.

In the gas phase, all the alkyl nitrites show a similar UV absorption spectrum. In the range 300–400 nm, a well-resolved vibrational progression is seen, corresponding to the A $^1A'' \leftarrow$ X $^1A'$ ($\pi^* \leftarrow n$) transition with simultaneous excitation of the localized NO stretching mode, ν_3. No rotational fine structure is seen. The positions of the vibrational bands are shifted slightly along the series of alkyl nitrites. Once the nitrite has been excited to the A $^1A''$ state, dissociation to the alkoxy fragment, RO, and NO follows in less than 400 fs [14].

In gas phase studies, non-Boltzmann distributions of vibrational and rotational energies of the NO fragment have been measured. The vibrational distributions are closely linked with the number of vibrational quanta present in the ν_3 mode of the electronically excited state. Thus, excitation of $v = 2$ of the NO stretching vibration in the parent molecule leads to a vibrational distribution in the product NO molecule which peaks at $v = 1$, while excitation of $v = 3$ of the parent nitrite leads to a vibrational distribution in the product NO molecule with the greatest population in the $v = 2$ and $v = 1$ levels. These data are shown in Table 3. An approximately Gaussian rotational distribution is seen, the exact distribution varying from molecule to molecule. Moreover, when the same number of quanta is pres-

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ent in the ν_3 mode, the vibrational distributions seen in the NO product are very similar for different nitrites [1].

The nitrites are excellent candidates for comparisons between gas phase and surface phase photolysis because it is easy to see whether, following photolysis on a dielectric surface, the NO is born highly rotationally excited and, more importantly, whether the NO is born vibrationally excited. If the NO is born vibrationally excited it will be important to see whether or not the degree of vibrational excitation in the product NO is dependent on the number of quanta in the N=O stretching vibration in the parent nitrite. The rapid dissociation of the nitrites in the gas phase gives the possibility that the dissociation and desorption of the NO product will be sufficiently fast to compete favourably with energy transfer processes which remove energy from the excited N=O group.

By changing the molecule studied whilst keeping the excitation frequency constant, the degree of excitation in the NO stretching vibration may be varied. The N=O stretching mode of iso-butyl nitrite, $(CH_3)_2CHCH_2ONO$, and tert-butyl nitrite, $(CH_3)_3CONO$, was excited to $v = 2$ and $v = 3$ respectively, as shown in Fig. 1. Since the vibrational state of the NO(v, J) product molecule is governed primarily by the number of vibrational quanta in the N=O vibration of the RONO molecule rather than the size of the RO group, it is to be expected that these two nitrites will give different vibrational distributions in the NO product molecules provided that there is no significant vibrational relaxation preceding desorption.

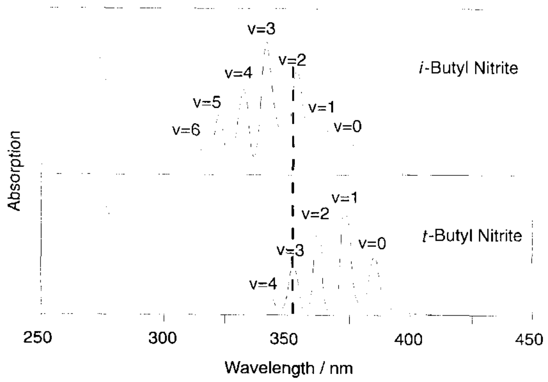

Fig. 1. Ultraviolet absorption spectra of iso- and tert-butyl nitrite in the 300–400 nm region.

2. Experimental

Much of the experimental apparatus and techniques used is described elsewhere [15–17]. The experiments were performed in an ultra high vacuum (UHV) chamber with a base pressure of $\leqslant 5 \times 10^{-11}$ Torr. A MgF_2 surface was used, which is transparent to the laser radiation. The desorption laser fluence was kept sufficiently low that molecules transparent to the laser radiation and bound less strongly than the nitrites were not desorbed. The single crystal MgF_2 surface used is 15 mm in diameter and 0.5 mm thick. It is mounted on a probe cooled by liquid He. The temperatures of the copper block on which the crystal is mounted and of the crystal surface itself are monitored with Lakeshore diodes.

The tert- and iso-butyl nitrite were supplied by Aldrich with a specified purity of 97%. The samples were used following freeze–pump–thaw cycles and are introduced on to the crystal surface by a microcapillary array fed from a 2 μm pinhole. This doser has been calibrated for CO by observing the formation of monolayer and multilayer peaks in the temperature programmed desorption (TPD) spectra of CO desorbed from a W(111) surface [17]. Unfortunately, this procedure is not possible for nitrites since individual features attributable to the formation of monolayers and multilayers are not clearly resolved in the TPD spectra. The slower rate of effusion of the nitrite through the doser is more than compensated for by its greater size compared with CO and we estimate that the conditions which led to monolayer coverage for CO produce about five layers for the nitrites.

The investigation of laser-induced processes on surfaces requires that, in order to minimize thermal effects, a laser beam of uniform fluence over a large area is available. This cannot be achieved with a frequency-doubled dye laser source, and so a fixed frequency excimer source, a Lambda Physik 105i excimer operating at 351 nm, was used for the photolysis. The central portion of the beam was used to illuminate a mask, which was imaged onto the crystal face to give a spot of 5 mm diameter coincident with the dosed area [16]. An NO_2 attenuating cell was used to control the incident laser power, to give a fluence of 0.5 mJ cm^{-2} on the surface.

TPD spectra were taken using a 1 kW heater, providing a heating rate of 2 K s^{-1} on the surface of the crystal. Previous studies on $(NO)_2$ have shown that NO is desorbed from a MgF_2 surface at 57 ± 3 K. The crystal face was held at 77 K throughout the experimental runs, ensuring that all NO produced by the photolysis is desorbed. TPD spectra showed that the surface coverage was essentially constant during the experiments. Constant surface conditions were achieved without the need for re-dosing during the experimental runs.

The desorbed NO molecules were ionised using a Lambda Physik 3002 dye laser pumped by a Lumonics HX460 XeCl excimer laser. The dye laser output was frequency doubled using a β-barium borate crystal. The ionisation laser power was constant to within ±20%. The ion counting scheme incorporates a Gallileo multi-channel plate (MCP) and an ion deflection scheme based on a Wiley McLaren design [18].

Time of flight (TOF) spectra were taken by varying the delay between the photolysis laser and the ionisation laser. This gives individual spectra for each vibrational state of NO.

3. Data analysis

The translational energies for the desorbed NO fragment were obtained from the TOF spectra. The spectra could not be fitted exactly with either single or double Maxwell–Boltzmann distributions. This is in contrast to earlier work on non-dissociative desorption and energy transfer of medium-sized organic molecules [15,16], but mirrors our findings on dissociative desorption of $(NO)_2$ [17]. Since Maxwell–Boltzmann distributions could not be used to describe the data, a mean kinetic energy for each TOF spectrum was obtained. An error of ±20% was assigned to each energy; the errors in the mean energies were calculated using the procedures of Cvetanović et al. [19].

The REMPI system was first calibrated against a room temperature sample of NO, introduced into the chamber at a partial pressure of 10^{-9} Torr. A spectrum of the (0, 0) band of the $A\,^2\Sigma^+ \leftarrow X\,^2\Pi$ transition was taken and assigned using the published one-photon spectrum of Deészi [20].

The signal of the $Q_1 + P_{21}$ (7/2) transition of the spectrum was found to be linear with NO pressure up to 1×10^{-8} Torr, above which the detector is saturated.

For each band the signal was linear with the REMPI laser power. The observed ion current is therefore proportional to the population of the ground state [21] and, together with the assigned spectra, can be used to calculate the population of rotational levels [21]. By plotting $\ln[I_J/(2J+1)]$ versus rotational energy, an estimate of the rotational temperature of the NO may be made. We calculate room temperature to be 280 ± 20 K. For the NO produced from the surface photolysis the data are usually well fitted by Boltzmann distributions, with observed temperatures in the range 300–450 K.

The vibrational populations were calculated by fitting a Maxwell–Boltzmann distribution, at the characteristic temperature found in the rotational analysis, to a plot of I_J against J for each band of each molecule. The ratios of the integrated distributions for the same bands in the different vibrational levels then gave the ratios of the vibrational populations. This method reduces the errors caused by scatter in the intensities of different lines.

In a similar way, the population of the two $X\,^2\Pi$ states may be found. By comparing the ratio of the integrated distributions, for example of the Q_1 and

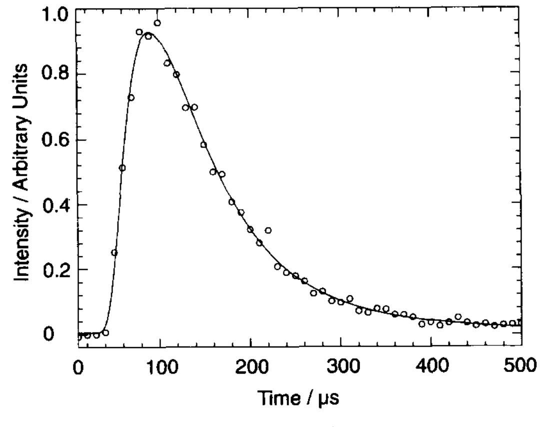

Fig. 2. A typical TOF spectrum; the (0, 3) band of NO formed from tert-butyl nitrite.

Table 1
Variation of NO kinetic energy with v''

Vibrational band	Mean kinetic energy (cm^{-1})	
	tert-butyl nitrite	iso-butyl nitrite
(0, 0)	240 ± 50	200 ± 40
(0, 1)	330 ± 70	430 ± 90
(0, 2)	230 ± 50	260 ± 50
(0, 3)	250 ± 50	230 ± 50
mean over all bands	250 ± 90	240 ± 80

the Q_2 bands of NO, a ratio of the population in the two states may be found.

4. Results

TOF and REMPI spectra were taken for the (0, 0), (0, 1), (0, 2), (0, 3) and (1, 4) bands of the $A\ ^2\Sigma^+ \leftarrow X\ ^2\Pi$ of the desorbed NO molecules. The translational, rotational and vibrational distributions derived from these spectra are given below.

4.1. Translational distribution

A typical TOF spectrum is shown in Fig. 2. The kinetic energies for each vibrational band for the two molecules are given in Table 1.

4.2. Fast molecules

A small fraction of the desorbed NO arrived at the detector after only 30 μs, in contrast to the majority, which arrived after 130 μs. The small yield precluded a detailed analysis of the rotational distribution of these molecules, although it could be seen that the degree of rotational excitation was high. The average kinetic energy of these fast molecules was around 2300 cm^{-1}. This Letter concentrates on the slower molecules which form the major species.

Table 2
Rotational temperatures

Vibrational band	Rotational temperatures (K)	
	tert-butyl nitrite	iso-butyl nitrite
(0, 0)	400 ± 100	400 ± 100
(0, 1)	390 ± 90	400 ± 100
(0, 2)	380 ± 60	500 ± 200
(0, 3)	330 ± 90	300 ± 200
mean over all bands	400 ± 100	400 ± 100

Table 3
Vibrational population distributions compared with those found in gas phase studies

Molecule	Fraction of population in vibrational level				Total vibrational energy (cm^{-1})
	$v = 0$	$v = 1$	$v = 2$	$v = 3$	
surface studies					
iso-butyl nitrite ($v = 2$) [b]	0.1	0.6	0.3	~ 0.01	2300
tert-butyl nitrite ($v = 3$) [b]	0.01	0.4	0.4	0.2	3350
gas phase studies					
methyl nitrite ($v = 2$) [a]	0.20	0.50	0.30	< 0.05	2100
tert-butyl nitrite ($v = 3$) [c]	0.02	0.35	0.42	0.21	3500

[a] Ref. [22]. [b] This work. [c] Ref. [7].

4.3. Rotational distribution

The rotational temperatures for the different vibrational bands of each molecule are given in Table 2; no differences were found between rotational bands of the two spin states.

4.4. Vibrational distribution

The vibrational population distributions for the two alkyl nitrites studied are given in Table 3, together with the total vibrational energy. Some signal was seen from $v = 4$ for tert-butyl nitrite, however, the spectra were very weak and the population is negligible compared to those in the lower vibrational levels.

In these experiments the fluence of the photolysis laser was held constant to better than 10%, the dosing conditions were easily reproducible, and the coverage was constant to within a few percent during laser runs. The largest uncertainty is in the fluence of the ionisation laser. It is considered that this could give errors of ± 20% in the vibrational energy distributions given in Table 3.

4.5. Population of spin states

Our spectra show that the population of the lower $X\ ^2\Pi_{1/2}$ state is 1.5 ± 0.5 times greater than that of the upper state. This result is similar to that in the gas phase and clearly shows that the spin states are not equilibrated with the surface temperature.

5. Discussion

The most striking feature of our results for the photolysis of these two physisorbed nitrites is that the vibrational distributions of the NO(v, J) are qualitatively different for the two molecules, but very closely mimic those seen in the gas phase, as seen in Table 3. There are no gas phase data for iso-butyl nitrite, however, the similar spectra of methyl and iso-butyl nitrites justifies a comparison of vibrational distributions for these two molecules. It is clear that the nascent vibrational distributions in the NO molecule are not relaxed by the surface, by co-adsorbed molecules or by collisions in the gas phase as the molecules leave the surface. The last condition is shown by the small population in $v = 0$ in the NO formed from the butyl-nitrites since the (VV) exchange processes

$$\mathrm{NO}(v = n) + \mathrm{NO}(v = 1) \rightleftharpoons \mathrm{NO}(v = n + 1) + \mathrm{NO}(v = 0)$$

are known to be very efficient, requiring less than 100 collisions, and collisional energy transfer would lead to a large population of $v = 0$.

The striking similarity between the vibrational distributions in the gas phase and surface photolysis experiments implies that the potential energy surface in the region of the shallow well from which dissociation occurs must be very similar in both cases.

The recent experiments on NOCl by Ferkel et al. [23], in which both gas phase and surface studies have been made, provides no information on vibrational distributions since in both cases the NO is formed predominantly in $v = 0$. Their results on the translational and rotational distributions differ from ours in that they conclude that the rotation probably accommodates with their surface temperature of 90 K whereas we find rotational temperatures of about 400 K from the surface held at 70 K. This difference may be connected with how the molecules pack on the surface in these two cases, but this has yet to be established.

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