Short Communication

Laser photodissociation of NO_2 at 248 nm and production of $NO(A\ ^2\Sigma^+ \rightarrow X\ ^2\Pi)$ fluorescence

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With the development of high power UV excimer lasers multiphoton excitation (MPE) has been used as a means of bypassing several of the problems of vacuum UV photochemistry and consequently, through the analysis of fluorescence from electronically excited photofragments, to investigate the dynamics of the photodissociation of polyatomic molecules. The role of the intermediate state in MPE is of particular interest [1], *i.e.* whether it is a virtual state in a *simultaneous* MPE process or whether it is a real state, bound, unbound or predissociated, in a *sequential* MPE process. In the latter case, if the state is unbound or predissociated there will be competition between the up-pumping process and dissociation into photofragments. The photofragments may then absorb another photon to produce laser-induced fluorescence, a process which has increased probability when relatively broad band excimer lasers are used. The outcome of this competition will ultimately depend upon the intensity of the laser and the strength of the predissociation or the degree of repulsion in the intermediate state. The laser photolysis of NO_2 at 248 nm is reported in this communication. The laser line overlaps the (000–000) band of the $NO_2(\widetilde{B}\ ^2B_2 \leftarrow \widetilde{X}\ ^2A_1)$ transition at 249.1 nm which, owing to predissociation, has a lifetime of 42 ± 5 ps [2].

A cross-shaped static fluorescence cell fitted with Spectrosil windows of diameter 5 cm was filled with various mixtures of NO_2 (47 - 532 N m^{-2}) and N_2 (0 - 89 kN m^{-2}). The rear window of the cell was at an angle such that scattered light from the laser beam was directed into a Wood horn. A transverse discharged excimer laser (Lambda Physik EMG500) operating at 248.4 nm (KrF) with a bandwidth of about 0.35 nm was used as the excitation source. The beam was focused first by a cylindrical lens ($f = 25$ cm) and secondly by a convex lens ($f \approx 10$ cm) so that the cross-sectional area at the observation point was about 0.04 cm^2; photon fluxes of the order of 10^{26} - 10^{27} photons cm^{-2} s^{-1} (*i.e.* 10^{18} - 10^{19} photons cm^{-2} per pulse) were readily

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achieved. Fluorescence was observed at right angles to the laser beam using a Jobin–Yvon HRS2 monochromator with a grating blazed for 300 nm and an EMI9781B photomultiplier. The output of the photomultiplier was connected to a Brookdeal 2415 linear gate (1 μs) and subsequently to a chart recorder.

Fluorescence from $NO(A\,^2\Sigma^+ \rightarrow X\,^2\Pi)$ in the region 195 - 290 nm was detected when NO_2 was irradiated by KrF laser light at 248.4 nm. The intensity of the $NO(A \rightarrow X)$ fluorescence was proportional to the laser energy raised to the power 1.6 ± 0.1. For NO_2 pressures of about 0.5 kN m^{-2} fluorescence from $NO(A\,^2\Sigma^+, v' = 3, 2, 1, 0)$ was observed, with the $v' = 3$ progression by far the strongest (Fig. 1). At lower pressures (about 47 N m^{-2}) the $v' = 2, 1, 0$ progressions were barely detectable, indicating that vibrational relaxation of $NO(A\,^2\Sigma^+, v' = 3)$ by NO_2 was responsible for the fluorescence from $NO(A\,^2\Sigma^+, v' < 3)$ at higher pressures. On addition of a large amount of N_2 (about 89 kN m^{-2}) to 0.5 kN m^{-2} of NO_2, the majority of the fluorescence resulted from the $v' = 0$ progression (Fig. 2) with the relative
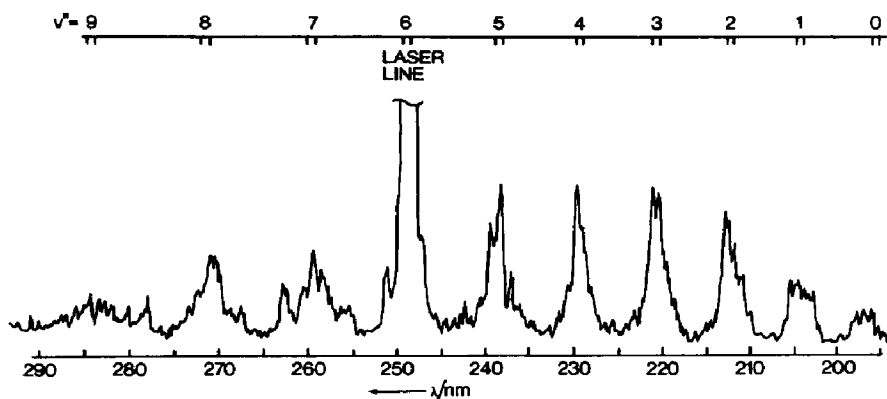

Fig. 1. Laser-induced fluorescence from NO following photolysis of NO_2 at 248 nm ($P_{NO_2} = 0.5$ kN m^{-2}; laser energy, 25 mJ). Bands originating from the $v' = 3$ level of the $NO(A\,^2\Sigma^+ \rightarrow X\,^2\Pi)$ system are indicated.
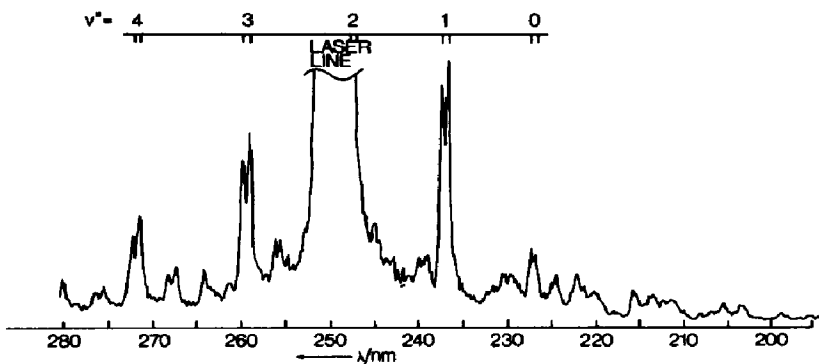

Fig. 2. Laser-induced fluorescence from NO following the photolysis of NO_2 ($P_{NO_2} = 0.5$ kN m^{-2}) at 248 nm in the presence of a large excess of N_2 ($P_{N_2} = 89$ kN m^{-2}; laser energy, 50 mJ). Bands originating from the $v' = 0$ level of the $NO(A\,^2\Sigma^+ \rightarrow X\,^2\Pi)$ system are indicated.

intensities of the $v' = 1, 2, 3$ progressions decreasing in that order owing to vibrational relaxation of $NO(A\ ^2\Sigma^+, v' = 3)$ by N_2 [3]. When smaller amounts of N_2 were added (8 - 66 kN m^{-2}) the intensities of the $v' = 1, 2, 3$ progressions relative to the $v' = 0$ progression increased as P_{N_2} decreased.

These observations can be rationalized as follows. $NO_2(\widetilde{X}\ ^2A_1)$ absorbs one photon of 248 nm radiation and undergoes a transition to the $\widetilde{B}\ ^2B_2$ state†. The $\widetilde{B}\ ^2B_2$ state is rapidly predissociated (lifetime, 42 ± 5 ps at about 249.7 nm) [2] to produce $NO(X\ ^2\Pi, v'' \leqslant 8)$ and $O(^3P)$. The vibrationally hot ground state NO then absorbs another 248 nm photon to undergo the resonant transition $NO(A\ ^2\Sigma^+, v' = 3 \leftarrow X\ ^2\Pi, v'' = 6)$ and hence produces $NO(A\ ^2\Sigma^+, v' = 3 \rightarrow X\ ^2\Pi, v'' = n)$ fluorescence by a laser-induced fluorescence process. It is interesting to note that the $NO(A\ ^2\Sigma^+, v' = 0 \leftarrow X\ ^2\Pi, v'' = 2)$ transition overlaps the extreme wing of the laser line at about 247.9 nm, but the $v' = 0$ progression is not observed despite a favourable Franck–Condon factor for the (0, 2) band. Unfortunately no assessment of the relative populations in the $v'' = 2$ and $v'' = 6$ levels can be made at this stage as a knowledge of the rotational distribution in these two levels would be needed to determine the overlap of the relevant transitions with the laser line.

A small contribution due to the two-photon sequential excitation of NO_2, which produces an upper state which subsequently dissociates to produce NO fluorescence, cannot be entirely ruled out. However, our spectra do not display detectable amounts of $NO(B\ ^2\Pi, C\ ^2\Pi, D\ ^2\Sigma \rightarrow X\ ^2\Pi)$ fluorescence, and this suggests that two-photon excitation of NO_2 to produce excited NO is a minor process since Lenzi and Okabe [4] observed emission from the B, C and D states for $\lambda < 129$ nm in single-photon vacuum UV photodissociation of NO_2. In addition, two photons of 248 nm radiation produce states above the ionization limit of NO_2 (ionization potential, 9.78 eV) and ion formation may be a competing channel. Although single-photon vacuum UV studies [5] indicate that the quantum yield for ions at about 124 nm is less than 2% the selection rules for single- and two-photon transitions differ and it may be that ionization is a more significant process with two-photon excitation. It is our intention to investigate this further and to examine the nascent $NO(X\ ^2\Pi)$ vibrational and rotational distributions using a dye laser as a probe in order to provide information on the dynamics of the photodissociation process. A similar study has been carried out by Zacharias *et al.* [6] using a nitrogen laser at 337 nm and a dye laser as a probe in which the rotational and vibrational populations were shown to deviate strongly from an equilibrium distribution, indicating a non-statistical decay mechanism. This contrasts with the results of Busch and Wilson [7, 8] at 347 nm (doubled ruby laser line) who used mass spectrometry detection of the

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†NO may also be formed by absorption into a weak continuum of B_2 vibronic symmetry [2] which lies in this region. The concentration of N_2O_4 is very low under the conditions used and photolysis of this species is not expected to yield significant amounts of NO.

photofragments and time-of-flight measurements to obtain the product energy distribution. Their results were interpreted theoretically by Quack and Troe [9] as following a decay mechanism with a statistical distribution of the excess energy.

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