Fluorescence in the Vacuum Ultraviolet Photolysis of Some Nitric Oxide-containing Compounds

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Summary Fluorescence from electronically excited nitric oxide has been observed during the photolysis at 147 and 123 nm of alkyl nitrites, trifluoronitrosomethane, and 2-methyl-2-nitrosopropane, while photolysis of NOCN leads to electronically excited cyanide radicals.

During studies into the vacuum u.v. photochemistry of NO-containing compounds, we have detected fluorescence from electronically excited species produced during photolysis. The gaseous sample, at a pressure of 0·1—1 Torr, was photolysed at wavelengths of 123 and 147 nm using microwave powered rare-gas resonance lamps. Fluorescence was monitored at right angles to the photolysis beam through a LiF window, using a 1 m normal incidence evacuable grating monochromator, fitted with a 9789 QB 13 stage photomultiplier, operated in the photon counting mode.

In the photolysis of ethyl nitrite at 147 and 123 nm a series of bands were observed between 190 and 300 nm, and identified[1] as belonging to the γ-system of NO. Similar emissions were observed in the photolysis of isopropyl nitrite and t-butyl nitrite, although the intensity of the emission decreased a little in the order Et > $\mathrm{Pr^i}$ > $\mathrm{Bu^t}$. The overall process may be written as in equations (1) and (2). Photolysis of 2-methyl-2-nitrosopropane (nitroso-t-butane) at 147 nm led to emission of NO γ-bands, the fluorescence being of reduced intensity compared to the nitrites. At 123 nm very weak emission of the nitric oxide γ-band system was observed.

$$\mathrm{RONO} + h\nu\ (147\text{ or }123\text{ nm}) \rightarrow \mathrm{RO} + \mathrm{NO}(A^2\Sigma^+) \quad (1)$$

$$\mathrm{NO}(A^2\Sigma^+) \rightarrow \mathrm{NO}(X^2\Pi) + h\nu\ (\gamma\text{-bands}) \quad (2)$$

Photolysis of trifluoronitrosomethane at 147 nm also led to emission of the NO γ-bands. The $v = 1$ level of the $A^2\Sigma^+$ state was considerably more populated than with the nitrites. Additional weak bands were observed at 280—380 nm, and identified as belonging to the nitric oxide β-system [equation (3)]. Photolysis of CF_3NO at 123 nm produced emission largely attributable to NO γ-bands, with the $v' = 0$, 1, 2, and 3 progressions being of comparable intensitites. In addition there was observed weak bands closely overlapping the $v' = 3$ progression of the γ-system. These bands could originate in the $v' = 6$ or $v' = 8$ levels of the $B^2\Pi$ state, or in the $v' = 0$ level of the $D^2\Sigma^+$ state of nitric oxide. The resolution used in these experiments (0·3—0·4 nm) is not sufficient to resolve these bands. It should be noted that none of these observations are attributable to secondary photolysis of NO, formed unexcited in the primary act.

$$\mathrm{NO}(B^2\Pi) \rightarrow \mathrm{NO}(X^2\Pi) + h\nu\ (\beta\text{-bands}) \quad (3)$$

During the photolysis of NOCN (nitrosocyanide) at 147 nm, a very weak emission of NO γ-bands was observed. A much more intense emission due to the cyanide 'violet' band system ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) was observed, the $\Delta v = 0$ sequence at 360—390 nm being the most intense. Levels at least to $v' = 3$ were populated, and considerable rotational excitation was in evidence. These observations complement observations on other cyanide containing compounds.[2]

The vibrational distributions in the emitting $\mathrm{NO}(A^2\Sigma^+)$ state vary both with the compound photolysed, and with wavelength. We have used the Franck–Condon factors of Nicholls, Fraser, and Jarmain[3] to obtain an estimate of the relative numbers of emitting molecules in each vibrational level. These estimations are in the Table, all relative to $N_{v'=0} = 1{\cdot}0$. In no case could emission from the $v' = 4$ level of the $\mathrm{NO}(A^2\Sigma^+)$ state be positively identified. The Table demonstrates that the vibrational excitation of the $\mathrm{NO}(A^2\Sigma^+)$ state is greater with increasing incident photon energy, and also with decreasing X–NO bond strength [$D(\mathrm{RONO}) > D(\mathrm{Bu^t{-}NO}) > D(\mathrm{CF_3{-}NO})$]. There is still, however, a considerable amount of energy not accounted for. The incident photons at 123 and 147 nm correspond to energies of 968 and 814 kJ mol^{-1}, respectively, while the $\mathrm{NO}A^2\Sigma^+$, $V = 3$ state corresponds to an energy of 611 kJ mol^{-1}. The excess energy could be carried away by the non-NO containing fragment, or could excite the NO to levels higher than $A^2\Sigma^+$, $V = 3$. No fluorescence attributable to excited NO was observed at wavelengths shorter than 185 nm. The wavelength region from about 190 nm to less than 150 nm showed the rapid appearance of $\mathrm{CO}(A^1\Pi \rightarrow X^1\Sigma^+)$ fourth positive system emission during each experiment due to the direct excitation of CO formed during the photolysis. This is most marked in the nitrite photolysis, but occurs also with the nitroso-compounds, and makes the detection of weak bands in this wavelength region difficult.

Table. Relative populations of $\mathrm{NO}(A^2\Sigma^+)$ vibronic levels

Substrate	λ/nm	He/Torr	$v' = 0$	$v' = 1$	$v' = 2$	$v' = 3$
CF_3NO	147	—	1·0	0·7	0·13	0·10
CF_3NO	147	690	1·0	0·7	0·43	0·15
CF_3NO	123	—	1·0	1·05	0·6	0·9
CF_3NO	123	620	1·0	0·8	2·3	2·3
EtONO	147	—	1·0	0·2	0·06	0·03
EtONO	147	580	1·0	0·2	0·1	0·09
EtONO	123	—	1·0	0·35	0·25	0·25
EtONO	123	620	1·0	0·4	0·8	0·9
$\mathrm{Bu^tNO}$	147	—	1·0	0·4	0·35	0·25
$\mathrm{Bu^tNO}$	147	540	1·0	0·2	0·17	0·10

There is indirect evidence for the production of NO in an excited state other than the $A^2\Sigma^+$ in the CF_3NO and ethyl nitrite photolysis. Addition of He leads to an enhancement of the $A^2\Sigma^+$, $V = 2$ and $V = 3$ emissions, without significantly affecting the $V = 0$ and $V = 1$ emissions, until at pressures approaching atmospheric vibrational deactivation becomes significant. Examples of these observations are included in the Table. The effect is greater for CF_3NO than for the nitrite, while in nitroso-t-butane, vibrational deactivation of $\mathrm{NO}(A^2\Sigma^+)$ appears to be the most significant process. These observations suggest that, in the photolysis of CF_3NO and ethyl nitrite, NO is produced in the $A^2\Sigma^+$ state which fluoresces, and also in an excited state which does not itself fluoresce at low pressures, perhaps undergoing predissociation, but which populates the $V = 2$ and $V = 3$ vibronic levels of the $A^2\Sigma^+$ state in the presence of He. Inspection of the potential energy curves of NO as given by Gilmore[4] indicates that the $B^2\Pi$, $v' = 6$, 7, or 8 states would all populate the $A^2\Sigma^+$, $v' = 3$ state, while the $B^4\Sigma^-$ would populate the $V = 2$ level of the $A^2\Sigma^+$. The NO($B^2\Pi$, $v' = 7,8$) are known to be strongly predissociative.[5]

Nitrogen addition also gives some enhancement of the NO($A^2\Sigma^+$, $v' = 2,3$) emission, but the effect is complicated by considerable vibrational deactivation and the possible occurrence of electronic energy transfer to nitrogen as observed by Callear and Smith in the deactivation of NO($A^2\Sigma^+$)[6] and NO($C^2\Pi$)[7] by N_2. We are currently extending these studies in an attempt to identify the predissociating state of nitric oxide involved.

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