

Electronically Excited Nitric Oxide by Vacuum Ultraviolet Photodissociation of Nitroso-compounds and Nitrites

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The gas-phase photolysis of CF_3NO and EtONO at 123 and 147 nm and of Bu^tNO at 147 nm gives rise to electronically excited nitric oxide which fluoresces. The strongest emission is that of the $A^2\Sigma^+ - X^2\Pi$ transition (γ -bands), although other transitions are also observed. The vibrational level populations in the $\text{NO}(A^2\Sigma^+)$ state show some correlation with the energy of the incident radiation and the strength of the R-NO bond. Addition of helium to the CF_3NO or EtONO produces an enhancement of emission from the $\nu' = 2$ and 3 levels of the $A^2\Sigma^+$ state, while emission from $\nu' = 0$ and 1 is almost unchanged. Addition of low pressures of N_2 and H_2 also gives some enhancement of the $\nu' = 2$ and 3. These observations are discussed in terms of the possible excited states of NO produced during the photolysis, and the deactivating effects of the added gas. Photolysis of ONCN at 147 nm yields electronically excited cyanide radicals and the ($B^2\Sigma^- - X^2\Sigma$) violet bands are observed. There is evidence for considerable rotational excitation of the CN radical, an effect well known in the vacuum u.v. photolysis of other cyanides, e.g. ICN.

THERE have been a considerable number of studies of the electronically excited nitric oxide molecule. Most of these studies involve either low pressure discharge tubes, or direct excitation of pure nitric oxide with u.v. light. The review of Heicklen and Cohen¹ summarises much of the data. Combination of N and O atoms in low pressure flow systems^{2,3} and electron impact⁴ have also been used to excite nitric oxide fluorescence. There are very few reports on work in which the electronically excited nitric oxide is produced by the photodissociation of an NO containing molecule. Photodissociation of N_2O leads to NO fluorescence, but it has been established that secondary processes involving N and O atoms are the source of the fluorescence.^{5,6} Photodissociation of NO_2 at wavelengths <130 nm and of NOCl at wavelengths <170 nm has been shown to produce electronically excited nitric oxide.⁷ The only report of NO fluorescence in the photodissociation of polyatomic molecules is that of Style and Ward,⁸ who observed NO emissions when methyl and ethyl nitrite were excited through a fluorite window with a hydrogen arc. No details of the NO emission were given.

The work reported here is concerned with the observation of electronically excited NO produced in the vacuum u.v. photodissociation of some nitroso-compounds and nitrites, and supplements the data given in our previous communication.⁹

EXPERIMENTAL

A conventional greaseless mercury-free vacuum system was used for all gas handling. The microwave-powered resonance lamps were attached to the photolysis cell with 64/40 O ring joints. The krypton (123 nm) and xenon (147 nm) lamps were fitted with 2 mm thick LiF windows. In some cases a second window was attached to the lamp. Use of a CaF_2 window eliminates the 116 nm krypton line, while a sapphire window eliminates the 129 nm xenon line. There was no significant change in the relative intensities of

¹ J. Heicklen and N. Cohen, *Adv. Photochem.*, 1968, **5**, 157.

² R. R. Reeves, G. Manella, and P. Harteck, *J. Chem. Phys.*, 1960, **32**, 946.

³ I. M. Campbell, S. B. Neal, M. F. Golde, and B. A. Thrush, *Chem. Phys. Letters*, 1971, **8**, 612.

⁴ M. Jeunehomme and A. B. G. Duncan, *J. Chem. Phys.*, 1964, **41**, 1692.

⁵ K. H. Welge, *J. Chem. Phys.*, 1966, **45**, 166.

the NO emission bands when the higher energy resonance line was eliminated, and as the main resonance line was itself attenuated by almost an order of magnitude by the addition of the respective second window, experiments were usually carried out using the LiF windows only. Some experiments were carried out using a flow lamp,¹⁰ fitted with a 1 mm thick silica window. This was used to produce the following atomic lines: (i) $\text{Br}(^4P_{3/2} \rightarrow ^2P_{3/2})$ at 163.4 nm (Br_2 in He); (ii) $\text{N}(^2P \rightarrow ^2P_0)$ at 174.3 and 174.5 nm (N_2 in He); (iii) $\text{C}(^1P^0_1 \rightarrow ^1D_2)$ at 193.1 nm (CH_4 in He). The intensities of the C and Br atom lines were much less than those of the inert gas lamps, or the N atom lamp.

The photolysis cell (ca. 350 cm³) was constructed as a double Wood's horn, fluorescence being viewed at right angles to the incident radiation through a 3 mm thick LiF window by a 1 m evacuable monochromator fitted with an EMI 9789 QB 13-stage photomultiplier operated in photon counting mode. The 600 line mm⁻¹ grating was blazed at 150 nm. The quartz window of the photomultiplier tube transmitted radiation >160 nm. Sodium salicylate was used to extend the response to 120 nm when necessary. Experiments were carried out using slit widths of 0.2–0.4 mm (bandpass ca. 0.3–0.6 nm). All photolyses were carried out at ambient temperature, with sample pressures of 0.05–0.25 Torr (Pirani gauge). At these sample pressures polymer built up on the lamp windows which required regular cleaning.

The nitrites were prepared by the standard method,¹¹ stored at low temperatures over desiccant, and shielded from light. Trifluoronitrosomethane and 2-methyl-2-nitrosopropane dimer were commercial samples. We are indebted to Dr. C. M. Keary for providing a sample of nitrosyl cyanide.

RESULTS AND DISCUSSION

Photolysis of Pure Compounds.—Photolysis of pure nitric oxide at 123 and 147 nm resulted in extremely weak fluorescence. Fluorescence was also weak with the C and Br atom lines, but stronger using the N atom lamp. This is in agreement with the literature.^{1,7} Experiments were also carried out in which small amounts (ca.

⁶ H. Okabe, *J. Chem. Phys.*, 1967, **47**, 101.

⁷ K. H. Welge, *J. Chem. Phys.*, 1966, **45**, 1113.

⁸ D. W. G. Style and J. C. Ward, *Trans. Faraday Soc.*, 1953, **49**, 999.

⁹ C. A. F. Johnson, V. Freestone, and J. Giovanacci, *J.C.S. Chem. Comm.*, 1976, 590.

¹⁰ D. Davis and W. Braun, *Applied Optics*, 1968, **7**, 2071.

¹¹ W. A. Noyes, *Org. Synth.*, 1936, **16**, 7.

0.02 Torr) of NO were added to the sample. No significant change in intensity or type of emission was observed. Therefore the observations described here cannot be due to secondary photolysis of NO, formed unexcited in the primary act, nor to transfer of energy from excited molecules to ground state NO.

Trifluoronitrosomethane. Photolysis at 123 and 147 nm resulted in strong fluorescence, the emission consisting of a large number of bands extending from below 200 to over 350 nm. At 147 nm the dominant emission was that of the nitric oxide ($A^2\Sigma^+ \rightarrow X^2\Pi$) γ -band system, the more intense bands belonging to the $v' = 0$ and 1 progressions, while the weaker $v' = 2$ and 3 progressions could also be observed. Emission spectra were identified using the extensive wavelength data of Wallace.¹² Other weak bands at 300–370 nm belonged to the $v' = 0$ and 1 progressions of the nitric oxide ($B^2\Pi \rightarrow X^2\Pi$) β -band system. Weak bands underlying the γ -band system at wavelengths <250 nm were apparently transitions from higher v' levels of the $B^2\Pi$ state, with possibly a contribution from $C^2\Pi$, $v' = 0$ and $D^2\Sigma^+$, $v' = 0$ (δ and ϵ bands). Using literature data,¹³ we estimate the number of molecules emitting from the $B^2\Pi$ state to be less than one tenth of those emitting from the $A^2\Sigma^+$ state.

At 123 nm the NO γ -band system was again important, with the $v' = 1$ –3 levels all showing increased populations (relative to $v' = 0$). We have estimated the populations of the $A^2\Sigma^+$ vibronic levels (relative to $v' = 0$) using literature Franck–Condon data,¹³ and these are given in the Table. Some other bands were observed underlying

Relative populations of NO($A^2\Sigma^+$) vibronic levels					
Substrate	λ/nm	$v' = 0$	$v' = 1$	$v' = 2$	$v' = 3$
CF ₃ NO	147	1.0	0.7	0.13	0.10
CF ₃ NO	123	1.0	1.05	0.6	1.05
EtONO	163	1.0	0.05		
EtONO	147	1.0	0.2	0.045	0.015
EtONO	123	1.0	0.35	0.25	0.25
Bu ^t ONO	123	1.0	0.36	0.21	0.20
Bu ^t NO	147	1.0	0.38	0.30	0.18

the γ -band system. These could be fitted to β -band emissions, with v' at least up to 6, which progression closely overlaps the γ -band $v' = 3$ progression. Some δ - and ϵ -bands were also present.

No evidence for emission from $A^2\Sigma$, $v' = 4$ was obtained, implying the population ratios $v' = 4 : v' = 0 < 0.005$ at 147 nm and < 0.02 at 123 nm. No other emissions due to electronically excited NO could be identified at wavelengths of 125–185 nm.

Nitric oxide γ -band emission was just detected when radiation at 163 nm was used, but the 174 nm lamp gave no emission.

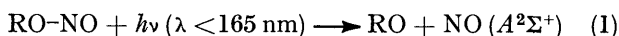
2-Methyl-2-nitrosopropane. Photolysis at 147 nm gave rise to nitric oxide γ -band emission, although at lower intensity than that from CF₃NO. The $v' = 0$ –3 progressions were all identified but no $v' = 4$ emission

was observed. Data on the relative populations are included in the Table. Some very weak δ - and ϵ -bands were observed at wavelengths <220 nm. Photolysis at 123 nm gave rise to only very weak NO fluorescence. As the quantum energy at 123 nm is 10 eV, and the ionization potential of 2-methyl-2-nitrosopropane has been reported¹⁴ as ca. 8 eV, it is possible that photoionization is the dominant process at this wavelength.

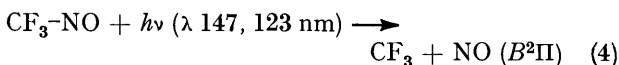
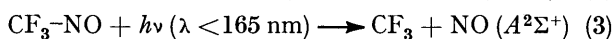
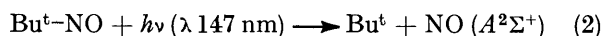
Ethyl nitrite. Photolysis at 123 and 147 nm also gave rise to nitric oxide γ -bands. The emission intensity was about five times greater than for CF₃NO under comparable experimental conditions. The relative populations of the $v' = 1$ –3 levels were significantly less than in the case of the nitroso-compounds, and emission from lower v' levels of the β -bands was very weak. Some very weak emission at wavelengths <220 nm could have been due to δ - and ϵ -bands. Weak γ -band emission was observed when the Br atom line at 163 nm was used. In this case the $v' = 0$ progressions predominated, with the $v', v''(1,0)$ band just observable. The data are summarised in the Table. Photolysis using the 174 nm lines of the N atom lamp gave no observable fluorescence.

Both isopropyl and t-butyl nitrites, when photolysed at 123 and 147 nm gave rise to nitric oxide γ -band emissions, with vibrational populations similar to those observed with ethyl nitrite, but with intensity decreasing with increasing molecular weight. Therefore detailed investigation of these compounds was not pursued.

Some general conclusions may be drawn from the data presented in the Table. In the photolysis of nitrites at wavelengths shorter than 165 nm one of the primary processes produces nitric oxide in the $A^2\Sigma^+$ electronic state [reaction (1)]. Similar processes occur in the

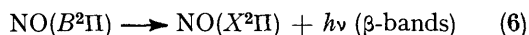
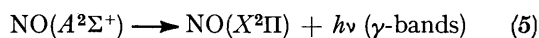


photolysis of the nitroso-compounds [reactions (2) and (3)]. In the case of CF₃NO an additional process yields nitric oxide in the $B^2\Pi$ state [reaction (4)]. Processes



analogous to (4) either do not occur with the nitrites and Bu^t-NO, or are not fast enough to produce a detectable fluorescence.

Fluorescence is observed from both the *A* and *B* states of NO [reactions (5) and (6)]. The data in the Table



demonstrates that the relative vibrational excitation of the emitting NO molecule increases at shorter incident wavelengths for both CF₃NO and EtONO, although at the shorter wavelengths there are increasing amounts of energy unaccounted for. The same qualitative trend is

¹² L. Wallace, *Astrophys. J. Suppl. Series*, 1962, **7**, 165.

¹³ H. A. Ory, A. P. Gittleman, and J. P. Madox, *Astrophys. J.*, 1964, **139**, 346.

¹⁴ R. Egdell, J. C. Green, C. N. Rao, B. G. Gowenlock, and J. Pfab, *J.C.S. Faraday II*, 1976, 988.

observed with decreasing bond strength in the dissociating molecule, where $D(\text{EtO}-\text{NO}) > D(\text{Bu}^t-\text{NO}) > D(\text{CF}_3-\text{NO})$. The RO-NO bond in simple alkyl nitrites¹⁵ is *ca.* 170 kJ mol⁻¹. With radiation at 163 nm, corresponding to an energy of 734 kJ mol⁻¹, there are 564 kJ mol⁻¹ available for excitation of the NO molecule, if the alkoxy radical is produced with no excess energy. The $A^2\Sigma^+$, $v' = 1$ level of NO is 557 kJ mol⁻¹ above ground state (ignoring rotational energies), and is observed in fluorescence weakly. The unobserved $v' = 2$ level exceeds the available energy by *ca.* 30 kJ mol⁻¹. At 147 nm the available energy is 644 kJ mol⁻¹, allowing the $v' = 4$ level (639 kJ mol⁻¹) to be excited in principle, although the $v' = 3$ level (611 kJ mol⁻¹) is the highest observed. At 123 nm, the available energy is *ca.* 800 kJ mol⁻¹, although there was no evidence for NO fluorescence from levels higher than $A^2\Sigma^+$, $v' = 3$. The very weakly observed $D^2\Sigma^+$, $v' = 0$ level (ϵ bands) lies only 26 kJ mol⁻¹ above $A^2\Sigma^+$, $v' = 3$, and below $A^2\Sigma^+$, $v' = 4$.

The reported values^{16,17} for $D(\text{Bu}^t-\text{NO})$ vary from 146 to 162 kJ mol⁻¹, and for CF_3NO a value of 130 kJ mol⁻¹ has been reported.¹⁸ Thus the available energy will be a little higher for these compounds, but the $A^2\Sigma^+$, $v' = 3$ level was the highest observed. In the case of CF_3NO the $B^2\Pi$, $v' = 6$ level lies only 3.6 kJ mol⁻¹ above $A^2\Sigma^+$, $v' = 3$. The $B^2\Pi$, $v' = 7$ and 8 levels are thought to be strongly predissociative,¹⁹ so it is unlikely emission would be observed from $B^2\Pi$, $v' > 7$ in our system, even if populated. The only comparable data reported is that of Welge,⁷ for the photolysis of NOCl at 123 and 147 nm. γ -Band emission from $v' = 0-3$ was reported, together with some weak unidentified bands below 250 nm. Relative populations of $v' = 0-2$ were found to be 1.0:0.75:0.1, which are very like those found by us for CF_3NO . It should be noted that $D(\text{N}-\text{O})$ in nitric oxide is 632 kJ mol⁻¹ (189 nm). Fluorescence from levels higher than $A^2\Sigma^+$, $v' = 4$; $B^2\Pi$, $v' = 6$; and $C^2\Pi$, $v' = 0$ is very weak or unobserved due to predissociation, although fluorescence from higher electronic states can be observed.

It is of interest to compare the results of this work with our earlier data obtained using end product analysis.²⁰ In the photolysis of Bu^tONO at 147 and 123 nm, no evidence was obtained for stable Bu^tO radicals. At 147 nm, the difference between the available energy (644 kJ mol⁻¹) and the highest level observed in fluorescence ($A^2\Sigma^+$, $v' = 3$ at 611 kJ mol⁻¹) is 33 kJ mol⁻¹, while $D[(\text{CH}_3)_2\text{C}(\text{O})-\text{CH}_3]$ ²¹ is only 29 kJ mol⁻¹. Thus it is not surprising that essentially all the t-butoxy radicals decompose. The photolysis of Bu^t-NO at 147 nm yields t-butyl radicals that are sufficiently stable to undergo abstraction reactions.²⁰ $D[(\text{CH}_3)_2\text{CCH}_2-\text{H}]$ ²²

is thought to be *ca.* 170 kJ mol⁻¹. Therefore at 147 nm there is insufficient energy both to excite NO to the $A^2\Sigma^+$ state and decompose the t-butyl radical, hence stable Bu^t radicals are consequential to the observation of process (2) above.

Fluorescence in the Presence of Other Gases.—A number of studies into the quenching effect of gases on the $\text{NO}(A \rightarrow X)$ emission have been reported (see *e.g.* p. 180 of ref. 1). Generally, the quenching effect of gases such as He, Ar, or N_2 is small, while gases such as CO_2 ,

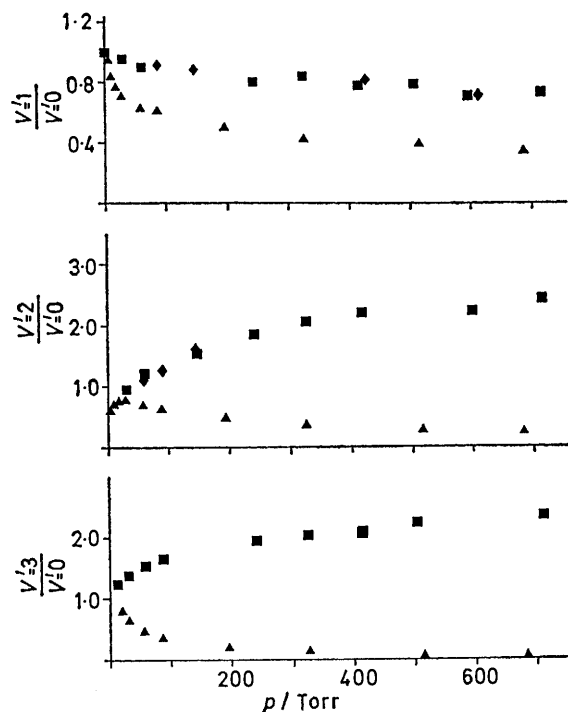


FIGURE 1 Changes in relative vibrational populations of NO ($A^2\Sigma^+$) with added gas in the photolysis of CF_3NO at 123 nm: ■, He; ▲, N_2 ; ◆, Ar

H_2O , or C_2H_4 quench the fluorescence rapidly. In the present work the effect of added gases on the NO fluorescence was unexpected. Addition of He to CF_3NO and EtONO produced an increase in intensity of the $v' = 2$ and 3 progressions of the γ -band system, while changes in the $v' = 0$ and 1 progressions were small. The effect was greater for CF_3NO than for EtONO , and was greater at 123 than at 147 nm with both compounds. Figures 1 and 2 are plots of relative populations of the vibronic levels with added gas, for CF_3NO at 123 nm and EtONO at 147 nm. Also included are some data with added H_2 and N_2 . Nitrogen gave some enhancement at low pressures, but at higher pressures there was an increase in $v' = 0$ and a decrease in the intensities of the higher vibronic levels. The effect of hydrogen was similar to N_2 , while Ar behaved more like He.

¹⁹ T. Hikida, N. Washida, S. Nakajima, S. Yagi, T. Ichimura, and Y. Mori, *J. Chem. Phys.*, 1975, **63**, 5470.

²⁰ P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *J.C.S. Perkin II*, 1973, 2019.

²¹ S. W. Benson, *J. Chem. Educ.*, 1965, **42**, 502.

²² J. A. Kerr, *Chem. Rev.* 1966, **66**, 465.

¹⁵ L. Batt and R. T. Milne, *Internat. J. Chem. Kinetics*, 1977, **9**, 141.

¹⁶ P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *Internat. J. Chem. Kinetics*, 1972, **4**, 339.

¹⁷ K. Y. Choo, G. D. Mendehall, D. M. Golden, and S. W. Benson, *Internat. J. Chem. Kinetics*, 1974, **6**, 813.

¹⁸ P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *J.C.S. Perkin II*, 1973, 1853.

It is possible that in the vacuum u.v. photolysis of these compounds, NO is also being produced in an excited state other than the $A^2\Sigma^+$ state, and that collisions induce an electronic transition into the $A^2\Sigma^+$ state at $v' 2$ and 3 . Vibrational deactivation of the $A^2\Sigma^+$ state in Ar or He is slow,²³ hence fluorescence from $v' 0$ is increased only slowly by vibrational cascade. Inspection of the NO potential energy curves, as given by Gilmore,²⁴ shows that the $A^2\Sigma^+$ state is crossed by the $a^4\Pi_i$, $b^4\Sigma^-$, and $B^2\Pi$ states in the region of interest, the latter two states also intersecting. Thus collisional perturbation may be effective in inducing crossover, the more so as NO is paramagnetic.²⁵ Hikida *et al.*¹⁹ have reported similar behaviour when pure NO is excited at 184.9 nm. At low pressures of NO only very weak $v' 9$ β -band emission is observed, addition of He (50 Torr) giving strong $v' 4$ γ -band emission. At He pressures >100 Torr the lower v' γ -band emissions begin to appear due to vibrational deactivation. In the present study, the excited NO from the primary photochemical act is likely to have a distribution of energies, and thus the $A^2\Sigma^+$ state is populated both at $v' 3$ and 2 . If the $B^2\Pi$ state is the precursor, then the $\beta(v' 6-8)$ would

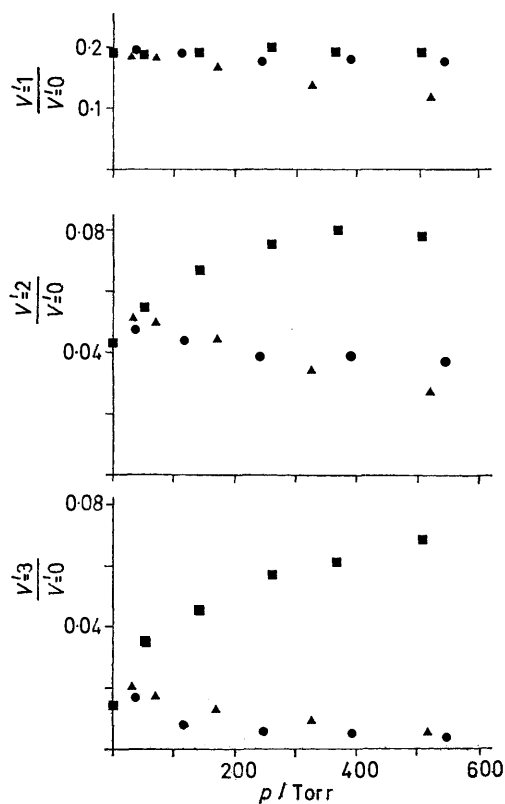


FIGURE 2 Changes in relative vibrational populations of NO ($A^2\Sigma^+$) with added gas in the photolysis of EtONO at 147 nm: ■, He; ▲, N_2 ; ●, H_2

populate $\gamma(v' 3)$, and $\beta(v' 4,5)$ would populate $\gamma(v' 2)$. β -Bands are observed more strongly with CF_3NO than

²³ A. B. Callear and I. W. M. Smith, *Trans. Faraday Soc.*, 1963, **59**, 1735.

²⁴ F. R. Gilmore, *J. Quant. Spectroscopy Radiative Transfer*, 1965, **5**, 369.

EtONO, and more strongly at 123 than 147 nm. This is in qualitative agreement with the extent of enhancement observed. Figure 3 shows portions of spectra obtained

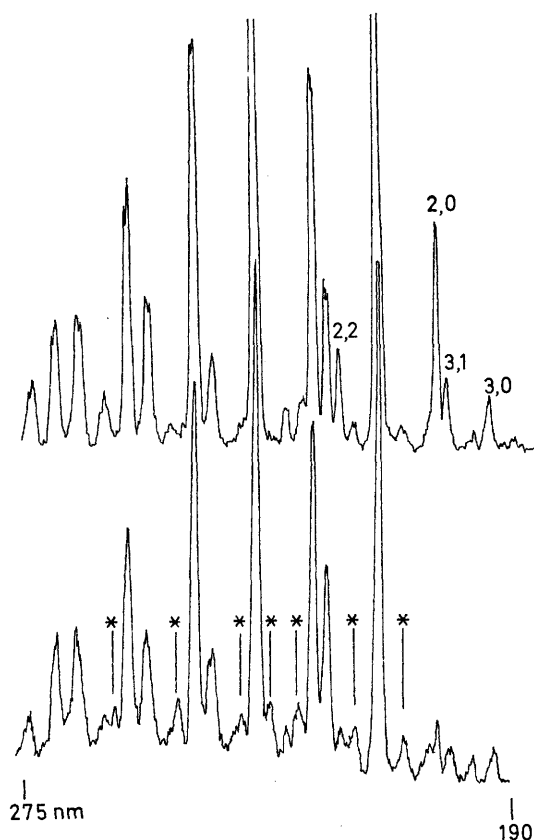


FIGURE 3 Spectra (uncorrected for system response) of NO γ -bands obtained in the 147 nm photolysis of CF_3NO . Lower: 0.2 Torr CF_3NO . Upper: 0.2 Torr CF_3NO + 300 Torr He. In the upper spectrum the increase in intensity of bands due to $v' 2,3$ may be noted, while other bands (*) have decreased

with CF_3NO at 147 nm, in the presence and absence of helium. The increase in intensity of $\gamma(v' 2,3)$ can be seen, together with a decrease in some of the weaker bands marked. Neither the $C^2\Pi$ nor $D^2\Sigma^+$ states are likely to be the precursor state, as it is known that quenching of these states with Ar does not lead to an increase in intensity of any γ -bands.^{26,27}

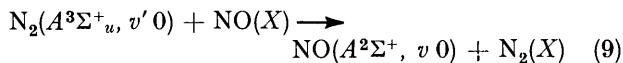
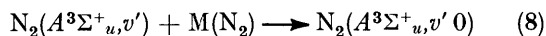
Nitrogen is known to cause rapid vibrational deactivation of the $A^2\Sigma^+$ state, but to be extremely inefficient at electronic deactivation,²³ and this we observe. It has been suggested^{19,26} that N_2 deactivates the $B^2\Pi$ and $C^2\Pi$ states to $A^2\Sigma^+$, $v' = 0$ through the intermediacy of the $N_2(A^3\Sigma^+_u)$ state [reactions (7)–(9)]. In this work, this mechanism probably accounts for only a fraction of the enhancement of NO($A^2\Sigma^+$, $v' 0$), because of the small concentration of NO in relation to sample molecules. Our observations imply that vibrational deactivation of

²⁵ C. S. Burton and W. A. Noyes, jun., in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1969, vol. 3.

²⁶ A. B. Callear and I. W. M. Smith, *Trans. Faraday Soc.*, 1965, **61**, 2383.

²⁷ A. B. Callear, M. J. Pilling, and I. W. M. Smith, *Trans. Faraday Soc.*, 1968, **64**, 2296.

the $A^2\Sigma^+$ state by N_2 is faster than the induced crossover at the higher pressures.



Reports on the quenching efficiency of hydrogen towards $NO(A^2\Sigma^+)$ differ. Broida and Carrington²⁸ and Kleinberg and Terenin²⁹ both report very slow quenching, whereas Basco *et al.*³⁰ reported that at pressures below 20 Torr, H_2 efficiently reduces emission by chemical reaction. For pressures >20 Torr a small emission remains, which is gradually reduced by increasing H_2 concentration. Hecklen,³¹ by monitoring photochemical product formation, has also derived a very fast quenching rate constant. Our data show that H_2 is as ineffective as N_2 or He in reducing the overall intensity of the γ -band emission, and thus support the lower values of quenching efficiency. There is a small but significant difference between the action of H_2 and N_2 , suggesting (a) H_2 is not as efficient at vibrational deactivation of the $NO(A)$ state and (b) H_2 is not as efficient at inducing crossover into the $NO(A)$ state, or may remove the precursor state in a competing process. This can be seen in Figures 1 and 2.

The effect of added gas on the NO fluorescence in Bu^tNO photolysis at 147 nm differs. Addition of He, N_2 , or H_2 produces an increase in intensity of all the γ -bands, with the enhancement in the $v' 0$ progression being greater than that for the other progressions. The increase in intensity of the $v' 0,2$ emissions is shown in

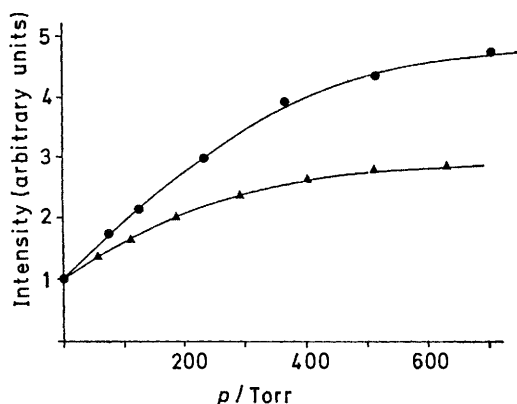


FIGURE 4 Increase in intensity of the $NO(A^2\Sigma^+)$ bands due to addition of He in the photolysis of Bu^tNO at 147 nm: ●, $v' 0$; ▲, $v' 2$

Figure 4 for the addition of He, while Figure 5 summarises the data as population relative to $v' 0$. Vibrational cascade is again much more evident with N_2 or H_2 than with He.

²⁸ H. P. Broida and T. Carrington, *J. Chem. Phys.*, 1963, **38**, 136.

²⁹ A. V. Kleinberg and A. N. Terenin, *Doklady Akad. Nauk. S.S.S.R.*, 1955, **101**, 1031.

The fluorescence intensity from Bu^tNO is much less than that from $EtONO$ or CF_3NO , and it is probable that process (2) is only one of a number of competing processes. Product analysis shows²⁰ that reaction (10),

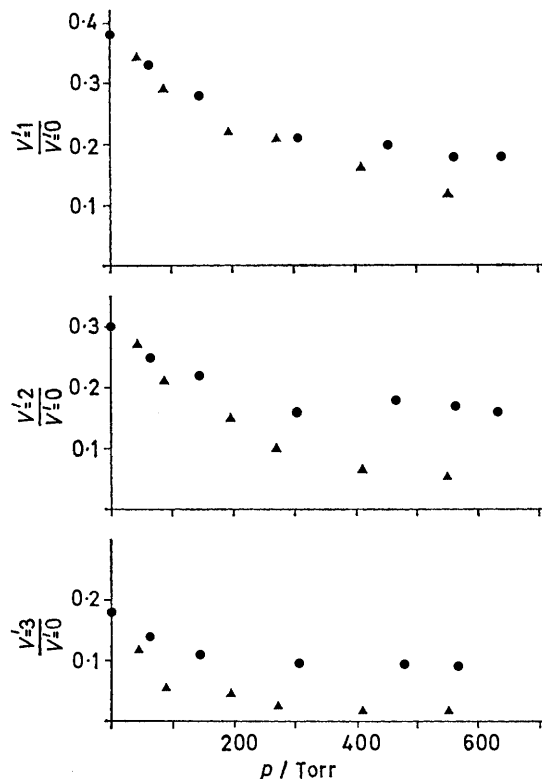
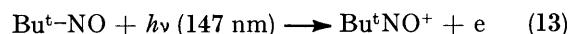
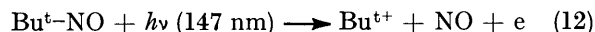
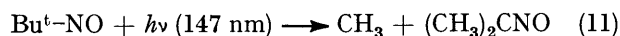
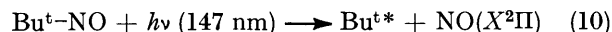


FIGURE 5 Changes in relative vibrational populations of $NO(A^2\Sigma^+)$ with added gas in the photolysis of Bu^tNO at 147 nm: ●, He; ▲, N_2

producing 'hot' Bu^t radicals, and reaction (11) are important. It may also be necessary to consider ionization processes, *e.g.* (12) and (13). The ionization



potential of the Bu^t radical³² is ≤ 6.93 eV, which together with a $D(Bu^t-NO)$ value of 1.5 eV (146 kJ mol⁻¹) gives a threshold wavelength for (12) of *ca.* 147 nm (8.44 eV). There is uncertainty about the ionization potential of Bu^t-NO . The molecular ion is not observed in electron impact, implying the minimum in the ion ground state photoelectron curve is very small, or displaced to sufficiently large bond length that normal ionization processes lead to dissociation. A value of 7.99 eV for the first ionization band maximum has been obtained by photoelectron spectroscopy,¹⁴ but it is now

³⁰ N. Basco, A. B. Callear, and R. G. W. Norrish, *Proc. Roy. Soc.*, 1962, **A260**, 459.

³¹ J. Hecklen, *J. Phys. Chem.*, 1966, **70**, 2456.

³² F. P. Lossing and G. P. Semeluk, *Canad. J. Chem.*, 1970, **48**, 955.

thought possible the spectrum observed was that of the dimer.³³ During some earlier electron impact work,¹⁸ we obtained a photoelectron spectrum of Bu^tNO, and this showed only one ionization band below 11.5 eV. In this respect our spectrum is similar to that obtained by Bergman and Bock³⁴ for nitrosomethane, and leads to a value of 8.91 eV for the first band maximum, and an ionization threshold at *ca.* 8.42 eV, almost identical to the estimated threshold for process (12). We have no way of detecting whether photoionization is occurring, but energetically, both (12) and (13) appear possible. The overall effect of adding non-reactive gas to the photolysis is to increase the probability of (2), presumably at the expense of one or more of the competing processes. Any selective enhancement of *v'* 2 or 3 as occurs with EtONO or CF₃NO is masked by this overall increase in total fluorescence intensity.

Other Emissions.—Trifluoronitrosomethane. When CF₃NO was photolysed at 123 nm in the presence of He or N₂, two pairs of bands were observed at *ca.* 353 and 358 nm. The intensity of these bands increased with increasing pressure. Figure 6 shows the result of adding He (200 and 550 Torr) to CF₃NO (*ca.* 0.2 Torr), and also the absence of these bands when no gas is added. The same bands are observed weakly using the Xe lamp with LiF window, but are absent when a sapphire window is added, implying it is the 129.5 nm Xe line that is responsible. These bands were not observed with either

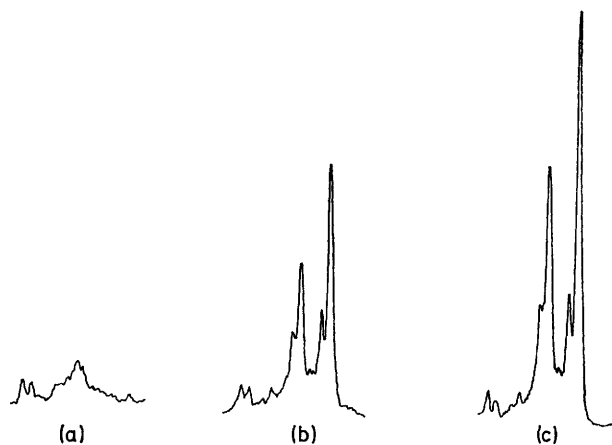


FIGURE 6 Spectra obtained in the photolysis of CF₃NO at 123 nm. (a) 0.2 Torr CF₃NO; (b) 0.2 Torr CF₃NO + 200 Torr He (c) 0.2 Torr CF₃NO + 550 Torr He. The largest and next largest bands occur at 352.8 and 357.7 nm

the nitrites or Bu^tNO, and could not be correlated with known NO emissions or electronic states. The energy threshold of <924 kJ mol⁻¹ implies that, if NO were the emitting species, the lower state must be X²Π or a⁴Π. In addition these bands were quenched by low pressures of H₂ and CO. The quenching half-pressures at a total pressure (He) of 470 Torr were 0.61 Torr for H₂ and 0.39 Torr for CO. The latter value may be compared with

³³ J. Pfab, personal communication.

³⁴ H. Bergman and H. Bock, *Z. Naturforsch.*, 1975, **30b**, 629.

³⁵ H. S. Johnston and H. J. Bertin, jun., *J. Mol. Spectroscopy*, 1959, **3**, 683.

³⁶ P. Venkateswarlu, *Phys. Rev.*, 1950, **77**, 676.

values of 7 and 28 Torr for the CO quenching half-pressures for the NO γ- and δ-bands respectively.²⁶ Thus it seems unlikely these bands are due to NO. Other

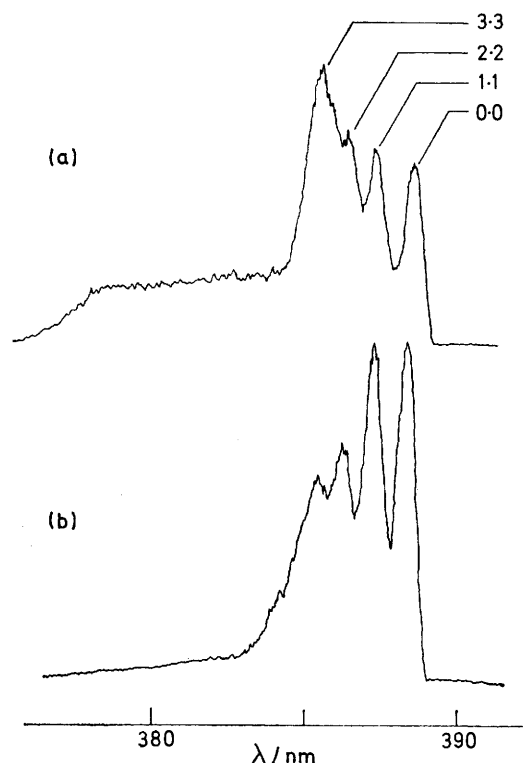


FIGURE 7 Spectrum of CN(*B*²Σ-*X*²Σ) violet bands (Δv 0) obtained in photolysis at 147 nm of (a) 0.3 Torr ONCN; (b) 0.3 Torr ONCN + 50 Torr N₂

possible emitters are FNO and CF₂. Johnston and Bertin³⁵ have observed the u.v. absorption spectrum of FNO at 260–335 nm, and also a chemiluminescent continuum at 510–640 nm from F + NO. There are no obvious correlations between these data and the bands observed by us.

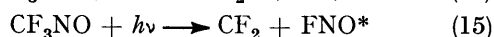
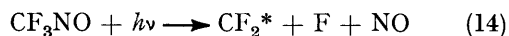
CF₂ fluorescence is easily excited in a discharge through fluorocarbons.^{36,37} The strongest emission system occurs at 240–325 nm, although a considerable number of weak bands have been observed at 325–420 nm. The emitter(s) giving rise to these longer wavelength bands has not been proven to be CF₂. It should be noted that all gas-phase studies on CF₂ emission have been carried out at low pressure (<1 Torr) at which pressure we do not observe these bands, although a low temperature matrix study³⁸ yielded no fluorescence at wavelength >345 nm. It is unlikely these bands are due to the CF₃ radical, since its only known absorption band lies in the vacuum u.v. at <165 nm.³⁹ Thus the identity of the species emitting the bands shown in Figure 6 remains uncertain. Thermochemically, process (14) is possible

³⁷ L. Marsigny, J. Ferran, J. Lebreton, and R. Lagrange, *Compt. rend.*, 1968, **266C**, 9, 507.

³⁸ C. E. Smith, M. E. Jacox, and D. E. Milligan, *J. Mol. Spectroscopy*, 1976, **60**, 381.

³⁹ N. Basco and F. G. M. Hathorn, *Chem. Phys. Letters*, 1971, **8**, 291.

at 129 nm, but not at 147 nm, if the CF_2 species emits to its ground state, with the 0,0 band at *ca.* 350 nm. It would not be possible to produce the known fluorescent state of CF_2 , even at 123 nm, unless FNO was eliminated as a molecule. Process (15) would be energetically possible at wavelengths < 176 nm, assuming the emission at 350 nm were to ground state FNO.



Nitrosyl cyanide. The behaviour of ONCN when photolysed at 147 nm differed from that of the other NO containing compounds studied in that emission of the nitric oxide γ -bands was extremely weak. Instead, strong emission of the $\text{CN}(B^2\Sigma^+ - X^2\Sigma^+)$ 'violet' bands was observed. These bands have been reported in the vacuum u.v. photodissociation of a number of X-CN compounds, where X = F, Cl, Br, I, H, CN, CH_3 , C:CH.⁴⁰⁻⁴⁴ The general appearance of our spectra obtained from ONCN is in agreement with that for ICN.^{41,42} The spectral resolution (*ca.* 0.3 nm) only resolves the vibrational bands of the CN fluorescence, although the long tail to shorter wavelengths implies there is considerable rotational excitation. It has been shown⁴¹ that no vibrational population inversion is produced by photodissociation of ICN, but that the apparent inversion is due to the population of very high K values in the zeroth vibrational level of the excited state. Figure 7(a) shows

the fluorescence observed with ONCN itself, while Figure 7(b) shows the effect of adding nitrogen. The rotational quenching is apparent, and so ONCN behaves much like ICN, the 0,0 band growing with increasing pressure. The 1,1 band also increases and so $v' 1$ may also be rotationally excited, although the extent is uncertain due to overlap with the 0,0 band. Vibrational deactivation will also become important as the pressure increases, and at N_2 pressures above 60 Torr electronic quenching becomes evident, and the integrated band intensity falls off with increasing pressure. Due to the bunching up of the bands for $v' > 4$, we cannot determine whether any levels with $v' > 4$ were populated. Some very weak bands on the long wavelength side of the $\Delta v 0$ sequence could have been tail bands with $v' > 10$, although identification is uncertain. If it is assumed that the $\text{CN}(B^2\Sigma^+)$ state is produced with $v' < 4$, then a considerable amount of energy is unaccounted for, and is presumably carried off by vibrationally excited ground state NO. Assuming $D(\text{ON-CN}) 125 \text{ kJ mol}^{-1}$ ⁴⁵ then the $\text{CN}(B^2\Sigma^+)$ state could be produced in principle in vibrational levels as high as $v' 17$.

By comparison with other X-CN compounds, one might also expect to observe the $\text{CN}(A^2\Pi - X^2\Sigma^+)$ 'red' bands, but these are emitted at wavelengths beyond the 520 nm limit of our monochromator grating and could not be observed.

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⁴⁰ D. D. Davis and H. Okabe, *J. Chem. Phys.*, 1968, **49**, 5526.

⁴¹ A. Mele and H. Okabe, *J. Chem. Phys.*, 1969, **51**, 4798.

⁴² W. M. Jackson and J. L. Faris, *J. Chem. Phys.*, 1972, **56**, 95.

⁴³ H. Okabe and V. H. Dibeler, *J. Chem. Phys.*, 1973, **59**, 2430.

⁴⁴ G. A. Chamberlain and J. P. Simons, *J.C.S. Faraday II*, 1975, 2043.

⁴⁵ B. G. Gowenlock, C. A. F. Johnson, C. M. Keary, and J. Pfab, *J.C.S. Perkin II*, 1975, 351.