NO($A^2\Sigma^+$) PRODUCTION BY PHOTODISSOCIATION OF NITRITES AND OF CF_3NO IN THE 1200 - 1700 Å REGION

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Summary

The fluorescence of NO($A^2\Sigma^+$), produced by the photodissociation of deuteromethyl nitrite, ethyl nitrite, isopropyl nitrite and trifluoronitrosomethane, was studied using synchrotron radiation as the source of excitation in the 1200 - 1700 Å spectral region. The relative quantum yield for NO($A^2\Sigma^+$) production at 1400 Å was measured; fluorescence excitation spectra for NO(A, $v' = 0$ and $v' = 1$) are reported and are compared with the absorption spectra. The results are discussed in terms of a statistical energy distribution among the fragments, with particular emphasis on possible deviation from RRKM predictions in the case of vibrational energy disposal.

1. Introduction

The main primary photodissociative process for simple alkyl nitrites (RONO) or nitroso compounds (RNO) in the gas phase is the formation of nitric oxide (NO) and either an alkoxy or an alkyl radical [1].

Most of the photochemical studies on these compounds have been performed at wavelengths exceeding 2000 Å and are mainly concerned with the analysis of final products. In the case of alkyl nitrites a fraction of the RO radicals has been found to be vibrationally excited and to undergo a subsequent unimolecular decomposition. More recently Johnson *et al.* [2] have reported that photodissociation of these compounds at 1470 and 1236 Å yields electronically excited NO which fluoresces before being deactivated by collisions. In contrast, the emission of RO excited radicals has been obtained [3] in the photolysis of alkyl nitrites using iodine (2062, 1876 Å) and mercury (1849 Å) lamps.

In a previous investigation [4] we have studied the photodissociation of methyl nitrite (CH_3ONO) in the vacuum UV using the synchrotron radiation

of the electron storage ring at Orsay as the source of excitation. Electronically excited NO fragments in different electronic and vibrational states $(A^2\Sigma^+, v' = 0, 1, 2, 3; C^2\Pi, v' = 0; D^2\Sigma^+, v' = 0)$ have been identified from the study of emission spectra and decay time measurements.

The production efficiency of the NO excited fragment in the A, C and D states has been determined as a function of the incident wavelength; the energy distribution in $NO(A^2\Sigma^+, v = 0, 1, 2)$ in the photolysis of CH_3ONO has been explained in terms of a statistical energy partition between the products CH_3O and NO.

In order to obtain more information on the role of the radical associated with NO in the photodissociation mechanism we extended our studies to a series of organic nitrites (deuteromethyl nitrite (CD_3ONO), ethyl nitrite (C_2H_5ONO) and isopropyl nitrite (i-C_3H_7ONO)) and to nitrosotrifluoromethane (CF_3NO).

2. Experimental

C_2H_5ONO and i-C_3H_7ONO were prepared from the reaction of sodium nitrite on ethanol or isopropanol in a sulphuric acid medium. CD_3ONO was prepared by the same method using methanol-D_4, D_2SO_4 and D_2O. The samples, the purities of which were checked by vapour phase chromatography and mass spectrometry, were degassed and stored in the dark.

CF_3NO is a commercial product (PCR) and was used without further purification.

The synchrotron radiation of the Orsay Collision ring ACO (τ = 1 ns, 13 MHz repetition rate) was used for excitation after being passed through a specially designed monochromator [5].

The photolysis gas cell, which was made of stainless steel, was provided with three MgF_2 windows, the fluorescence being observed at right angles to the exciting beam. The relative photon flux passing through the gas cell was measured by a combination of a photomultiplier and a sodium salicylate screen the quantum efficiency of which was assumed to be constant in the range 1200 - 2000 Å. Using conventional procedures the absorption spectra were deduced from the intensity of the transmitted light in the presence and in the absence of the compound.

The fluorescence was spectrally analysed using a home-built vacuum monochromator [6]. Photon-counting techniques and correlated single-photon-counting techniques (for decay time measurements) were used with an RTC 56 SBUVP solar blind photomultiplier as the detector (dark counting level of about 5 counts s^{-1}).

The gas pressure was measured by means of a Pirani gauge calibrated with an MKS Baratron manometer.

Fig. 1. Vacuum UV absorption spectra of CD$_3$ONO (————), i-C$_3$H$_7$ONO (— — —) and CF$_3$NO (— · — ·).

3. Results and discussion

3.1. Vacuum UV absorption spectra

The far-UV absorption spectra of the nitrites and of CF$_3$NO are composed of broad diffuse bands without any sharp features. The spectra of CD$_3$-ONO, i-C$_3$H$_7$ONO and CF$_3$NO in the range 1200 - 1700 Å are shown in Fig. 1 ($\Delta\lambda$ = 2 Å). As expected, the spectrum of CD$_3$ONO is very similar to that of CH$_3$ONO. The presence of methyl groups instead of hydrogen in the alkoxy group leads to a shift of the absorption band towards longer wavelengths, with the maximum going from 1390 Å for CH$_3$ONO to 1530 Å for i-C$_3$H$_7$-ONO. In this spectral region several excited states can be involved: Rydberg states as well as valence shell excitations. From the photoelectron spectrum of i-C$_3$H$_7$ONO determined by Dewar et al. [7] the first two ionization potentials are located at 10.5 and 12.5 eV (vertical ionization potentials). Thus the transitions from these highest occupied orbitals to a 3s Rydberg orbital can be calculated (taking a quantum defect δ = 1) at 1750 Å and 1380 Å respectively. These Rydberg transitions are probably overlapped by an intense absorption which may correspond to a $\pi\pi^*$ transition localized on the nitroso group, as suggested by Tanaka et al. [8].

The absorption spectrum for CF$_3$NO between 1100 and 1700 Å consists of two broad bands with maxima at about 1410 and 1200 Å. According to Robin [9] the 1410 Å peak may be assigned to the $\pi \rightarrow \pi^*$ transition on the N=O double bond. In fact, the similarity between CH$_3$ONO and CF$_3$NO in this region suggests that the same chromophoric NO group is involved in both cases.

3.2. Quantum yields of the NO excited fragment in the $A^2\Sigma^+$ state

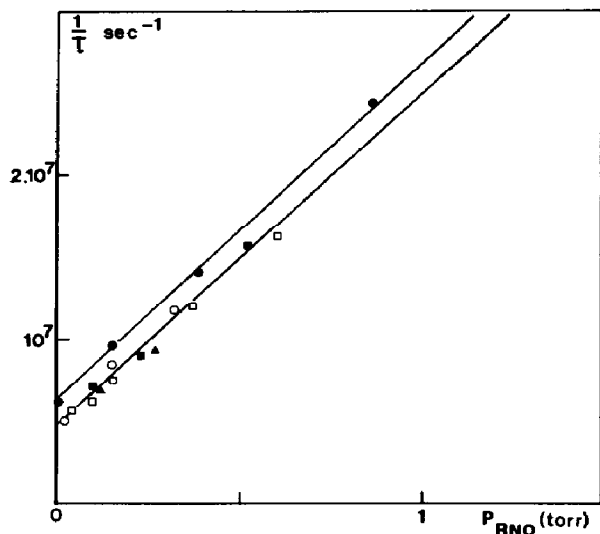The fluorescence spectra resulting from the photolysis of CD$_3$ONO, C$_2$H$_5$ONO and i-C$_3$H$_7$ONO in the long-wavelength region of the vacuum UV

Fig. 2. A Stern–Volmer plot of the fluorescence quenching of $NO(A^2\Sigma^+)$ by nitrites and by CF_3NO (nitrites, $\lambda_{exc} = 1400$ Å, $\lambda_{obs} = 2360$ Å; $CF_3NO + NO$ ($P = 0.1$ Torr), $\lambda_{exc} = 2260$ Å, $\lambda_{obs} = 2360$ Å): □, CH_3ONO; ○, CD_3ONO; ▲, C_2H_5ONO; ■, i-C_3H_7ONO; ●, CF_3NO.

spectrum are identical with that previously observed in the case of CH_3ONO photodissociation and can be assigned mainly to emission from the $NO(A^2\Sigma^+)$ excited fragment. This result is corroborated by fluorescence life-time measurements for RONO excited at $\lambda_{exc} = 1400$ Å and by $NO(A^2\Sigma^+)$ fluorescence observed selectively at 2360 Å ($\gamma(0,1)$ band). Under these conditions the decay curves observed are purely monoexponential, indicating no overlap with other possible emissions. A lifetime τ_0 at zero pressure of 200 ns can be deduced for the fluorescence product from the intercept of the Stern–Volmer plot (Fig. 2). This value is in good agreement with the known lifetime of $NO(A^2\Sigma^+)$. The quenching rate constant of $NO(A, v' = 0)$ by the nitrites, which was calculated from the slope of the Stern–Volmer plot, is close to the hard sphere collision rate constant:

$$k_{RONO} = (6 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

For CF_3NO the intensity of the emission from the photoproducts is lower than that for the nitrites and the energy-resolved spectra are hardly observable. Nevertheless, the main features of the fluorescence spectra between 2000 and 3000 Å can be identified as belonging to the NO $A^2\Sigma^+ \rightarrow$ X system. In this case, because of the very low level of the counting rate (approximately 25 counts s^{-1} for the most intense band at 2360 Å), lifetime measurements were not performed under selective narrow band observation conditions; this was carried out only for the nitrites. However, the time decay of the total fluorescence produced from CF_3NO photolysis is clearly non-exponential and shows a very long component which is probably due to the

formation of the NO B state. The quenching rate constant of $NO(A^2\Sigma^+)$ by CF_3NO was measured by exciting NO ($P = 100$ mTorr) directly in the zeroth vibrational level at $\lambda = 2260$ Å in the presence of CF_3NO. The quenching rate constant obtained this way can be compared with those obtained for the nitrites:

$$k_{CF_3NO} = (6 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

The quantum yields for $NO(A^2\Sigma^+, v' = 0)$ production were determined relative to that of CH_3ONO at $\lambda_{exc} = 1400$ Å. (These results can be converted to absolute values by using the quantum yield of $NO(A^2\Sigma^+)$ from the CH_3ONO photolysis determined in our previous work [4] : $\phi_{P\{NO(A,v'=0)\}}^{CH_3ONO} = 0.14$ at $\lambda_{exc} = 1400$ Å.)

$\phi_{P\{NO(A,v'=0)\}}^{RNO}$ is proportional to the experimental quantity $Y_{F\{NO(A,v'=0)\}}^{RNO}$ defined by

$$Y_{F\{NO(A,v'=0)\}}^{RNO} = \frac{I_F\{(0,1)\}(1 + k_{RNO}\tau P_{RNO})}{I_{0\lambda_{exc}}(1 - T)}$$

where $I_F\{(0,1)\}$ is the measured intensity of the $\gamma(0,1)$ emission band, $1 + k_{RNO}\tau P_{RNO}$ is the correction factor for the quenching of NO(A) by RNO (k_{RNO} has been determined previously), $I_{0\lambda_{exc}}$ is the relative primary photon flux at the wavelength of excitation (as measured from the fluorescence of the scintillator screen in the incident light beam) and $T = 10^{-\epsilon\lambda_{exc}lc}$ is the transmission of RNO for the path length of the incident photon beam viewed by the photomultiplier ($l = 0.9$ cm) at the excitation wavelength λ_{exc}.

The following values were obtained:

$$\phi_{P\{NO(A,v'=0)\}}^{CD_3ONO} \big/ \phi_{P\{NO(A,v'=0)\}}^{CH_3ONO} = 1.1$$

$$\phi_{P\{NO(A,v'=0)\}}^{C_2H_5ONO} \big/ \phi_{P\{NO(A,v'=0)\}}^{CH_3ONO} = 0.65$$

$$\phi_{P\{NO(A,v'=0)\}}^{i-C_3H_7ONO} \big/ \phi_{P\{NO(A,v'=0)\}}^{CH_3ONO} = 0.40$$

$$\phi_{P\{NO(A,v'=0)\}}^{CF_3NO} \big/ \phi_{P\{NO(A,v'=0)\}}^{CH_3ONO} = 0.19 \quad (\lambda_{exc} = 1450 \text{ Å})$$

From these results it can be seen that deuteration does not affect the quantum yield of production of NO(A); however, the substitution of hydrogen by one or two methyl groups leads to a decrease in the $NO(A^2\Sigma^+)$ production yield. This result is not surprising from a statistical point of view if we consider that an important fraction of the excess energy should go into the more complex of the two products and that this fraction should increase as more and more degrees of freedom are involved. Thus, the production of NO(A) from RONO at 1400 Å (requiring about 80% of the excess energy used as electronic energy to excite NO) becomes less and less probable as the size of RO increases.

For CF_3NO such a simple explanation for the low measured quantum yield is not sufficient. The dissociation energies of the F_3C—NO [10] and
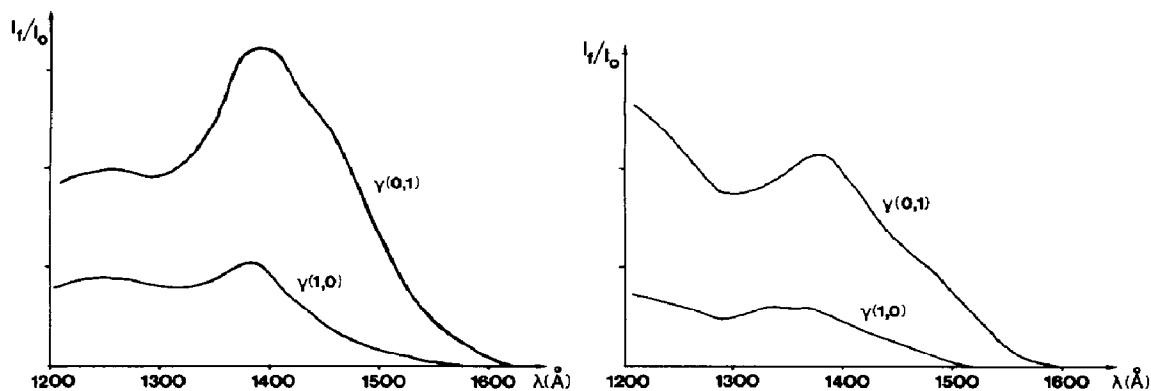
Fig. 3. Excitation spectra of $NO(A^2\Sigma^+)$ produced from CD_3ONO photodissociation.

Fig. 4. Excitation spectra of $NO(A^2\Sigma^+)$ produced from C_2H_5ONO photodissociation.

RO—NO [11] bonds are nearly identical and the excess energy available is similar. It should be noted, however, that $NO(A^2\Sigma^+)$ is not the only excited product; the $NO(B^2\Pi)$ fragment has also been detected at 1470 Å [2]. Thus the photodissociation processes are less selective and the excess energy is spread over more channels than in the case of the nitrites where no $NO(B)$ emission has been found.

3.3. Excitation spectra of NO(A)

In Figs. 3 - 5 are shown the excitation spectra of $NO(A, v' = 0, 1)$ resulting from the photolysis of CD_3ONO, C_2H_5ONO and $i\text{-}C_3H_7ONO$ ($p = 0.3$ Torr). These spectra were obtained by monitoring the emission intensity I_F at $\lambda_{obs} = 2360$ Å ($\gamma(0,1)$) and $\lambda_{obs} = 2150$ Å ($\gamma(1,0)$) as a function of the incident wavelength. The emission intensity I_F, weighted by the contribution of the $\gamma(0,1)$ and $\gamma(1,0)$ bands to the total emission from $NO(A, v' = 0)$ and $NO(A, v' = 1)$ respectively [12], was corrected for the relative incident flux at each excitation wavelength. No correction for pressure effects was applied since it is known that vibrational relaxation is very inefficient in the NO $A^2\Sigma^+$ state [13] and that both vibrational levels are quenched at the same rate by the nitrites, as has been shown in the case of CH_3ONO [4].

Several conclusions can be drawn from these spectra.

(1) The threshold wavelengths required to give $NO(A^2\Sigma^+)$ fluorescence (1610 ± 10 Å for $v' = 0$ and 1550 ± 10 Å for $v' = 1$) are identical for all the nitrites. This result indicates that the bond dissociation energies $D_0(RO—NO)$ for CH_3ONO, CD_3ONO, C_2H_5ONO and $i\text{-}C_3H_7ONO$ are the same. This value can be evaluated:

$$D_0(RO—NO) \leqslant E_{h\nu} - E\{NO(A^2\Sigma^+)\} = 2.2 \text{ eV}$$

where $E\{NO(A^2\Sigma^+)\} = 5.48$ eV for $v' = 0$ and $E\{NO(A^2\Sigma^+)\} = 5.77$ eV for $v' = 1$. It should be noted that the $NO(A, v' = 1)$ threshold wavelength is
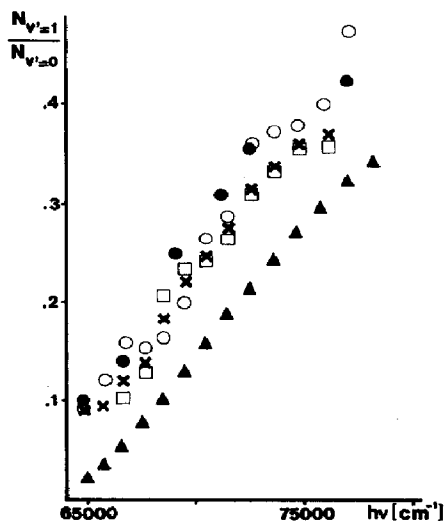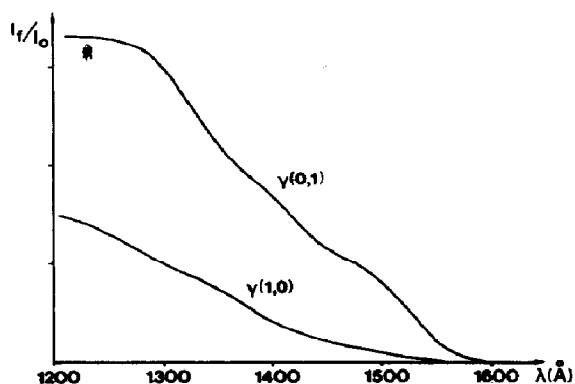
Fig. 5. Excitation spectra of NO($A^2\Sigma^+$) produced from i-C$_3$H$_7$ONO photodissociation.

Fig. 6. Relative population of NO(A, $v' = 1$)/NO(A, $v' = 0$) as a function of the excitation energy: ●, CH$_3$ONO; ○, CD$_3$ONO; □, C$_2$H$_5$ONO; ×, i-C$_3$H$_7$ONO; ▲, statistical calculation for CH$_3$ONO.

shifted relative to that for NO($v' = 0$) by 0.3 eV = 2400 cm^{-1} which corresponds to the vibrational frequency of NO in the $A^2\Sigma^+$ state.

This result is slightly higher (approximately 0.4 eV) than the dissociation energy of the RO—NO bond (1.8 ± 0.04 eV) determined recently using a thermochemical method [11]. This discrepancy seems to be too important to be attributed to the inaccuracy of the experiment. The extinction coefficients for CD$_3$ONO and C$_2$H$_5$ONO are very low at the calculated threshold wavelength (1700 Å) and the difference could be due to the difficulty in detecting very low fluorescence intensities under these conditions. However, because of the shift of the absorption spectrum towards longer wavelengths, the absorption for i-C$_3$H$_7$ONO is not negligible at 1700 Å and NO($A^2\Sigma^+$) should have been detected in this case. More probably this result shows that some kinetic and internal energy is released in the fragments at the observed threshold.

(2) The excitation spectrum of NO(A) for CD$_3$ONO mirrors the absorption spectrum quite well, particularly in the region of the 1400 Å absorption band. This result shows that the quantum yield for production of NO($A^2\Sigma^+$) is constant over the range 1300 - 1600 Å. The same behaviour has been obtained for CH$_3$ONO photodissociation and seems to suggest a correlation between the initial and the product excited states.

However, the NO($A^2\Sigma^+$) production efficiency in the photolysis of isopropyl nitrites exhibits a completely different behaviour. The excitation spectrum does not reproduce the absorption bands. Instead a smooth and regular increase of the NO($v' = 0$ and $v' = 1$) population with excitation wavelength is obtained. In this case it can be concluded that the total energy

input in the reactant seems to be the dominant factor inducing the formation of NO(A) and the branching ratio between this process and other competitive unidentified pathways is markedly dependent on the excess energy.

(3) The relative population $NO(A^2\Sigma^+, v' = 1)/NO(A^2\Sigma^+, v' = 0)$ can be evaluated as a function of the available excess energy in the particular channel $RONO \rightarrow RO + NO(A)$. It can be seen in Fig. 6 that the vibrational energy distribution of the $NO(A^2\Sigma^+)$ fragment follows the same energy dependence for CH_3ONO [4], CD_3ONO, C_2H_5ONO and i-C_3H_7ONO. This result is not expected if we assume a statistical energy distribution in the fragments. In fact we should obtain an enhanced vibrational excitation in the RO fragment associated with a corresponding reduction in the vibrational energy deposited in NO(A) with substitution of hydrogen atoms by heavier atoms (CD_3O rather than CH_3O) or with substitution by methyl groups (($CH_3)_2CHO$ or CH_3CH_2O rather than CH_3O) because of the increase in density of the vibrational states in the RO radical. We have shown previously that the vibrational energy distribution in $NO(A^2\Sigma^+)$ for CH_3ONO photodissociation can be explained in terms of a not totally equilibrated redistribution which would favour the excitation of preferential modes in CH_3O. The present data give a confirmation of the incomplete randomization of the energy in this specific photodissociation pathway.

4. Conclusions

We have observed that the vacuum UV photodissociation of polyatomic NO derivatives leads to the formation of $NO(A^2\Sigma^+)$. The NO(A) production efficiency seems to be associated with a specific transition in the parent molecule for the smaller members of the series (CH_3ONO, CD_3ONO) but this behaviour tends to disappear as the parent compound becomes more and more complex. In the case of i-C_3H_7ONO statistical considerations seem to be predominant in explaining the low quantum yield of $NO(A^2\Sigma^+)$ and its dependence on excitation energy.

If we consider the vibrational energy distribution in the photodissociation channel giving rise to NO(A), it is striking that the fraction of excess energy which appears as vibrational excitation of NO(A) does not vary with the number of available vibrational modes in the RO fragment. This result emphasizes the necessity to take deviations from assumptions used in the RRKM theory into account in the photodissociation of polyatomic molecules.

Acknowledgments

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