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Photodissociation of methyl nitrite in the vacuum ultraviolet. II. Excitation energy dependence of the NO fluorescent fragments

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The production efficiency of NO excited fragments in $A\,^2\Sigma^+$ $v'=0,1,2,3$, $C\,^2\Pi$ $v'=0$, $D\,^2\Sigma^+$ $v'=0$ states resulting from the photolysis of methyl nitrite in the far UV has been measured as a function of incident wavelength using the synchrotron radiation of the electron storage ring of Orsay as the source of excitation. The experimental energy threshold to produce each NO excited state is in agreement with a bond dissociation energy of CH_3O–NO of 1.8 eV. The excitation spectra of electronically excited NO $A\,^2\Sigma^+$, $C\,^2\Pi$, $D\,^2\Sigma^+$ are discussed in relation with the absorption spectrum of the parent molecule. The vibrational energy distribution in NO $A\,^2\Sigma^+$ $v'=0,1,2$ can be explained by a statistical energy partition between CH_3O and NO products provided some restrictions on the activated modes of the CH_3O fragment. NO $A\,^2\Sigma^+$ $v'=3$ population shows an anomalous behavior which can be indicative of a half-collision effect due to the interaction of NO $C\,^2\Pi$ and $D\,^2\Sigma^+$ primary product with CH_3O.

INTRODUCTION

Recent experimental and theoretical studies have focused attention on the dynamics of molecular photofragmentation of polyatomic species.[1] One of the most fruitful sources of information on the primary photochemical event is the analysis of the detailed quantum states in which the fragments are produced before collisions relax the initial populations.

In a previous paper[2] we have undertaken an investigation of the photofragmentation of methyl nitrite in the vacuum ultraviolet. The production of electronically excited NO fragments in different electronic and vibrational states ($A\,^2\Sigma^+$ $v'=0, 1, 2, 3$, $C\,^2\Pi$ $v'=0$, and $D\,^2\Sigma^+$ $v'=0$) have been evidenced from the study of emission spectra and decay time measurements. The quantum yields of the dissociation channels leading to the fluorescent fragments have also been measured at several wavelengths.

Apart from the study of photoproducts states distribution at a given excitation energy, it is of interest to investigate the photolysis wavelengths dependence of individual products state population since this information may provide valuable insight into the fundamental problems of photodissociation dynamics. The basic questions concern the following:

(1) the dissociative pathway (i.e., direct photodissociation or predissociation),

(2) the correlation of electronically excited photoproducts with the nature of the parent molecule initial states,

(3) the factors governing the vibrational energy disposal within the separating fragments (statistical or Franck–Condon type factors?).

Recently, several theoretical models have been developed to describe the dynamics of photodissociation in simple linear triatomic molecules.[3] These theoretical descriptions range from simple golden rule calculations to more sophisticated quantum mechanical models. The main feature of these models is the derivation of Franck–Condon type factors to estimate the final distribution over the vibrational states in the photofragments. However, in the case of complex polyatomic molecules the energy disposal is thought to be more likely statistical. A theoretical information approach based on the observation of deviation of real distributions from a pure statistical behavior (surprisal analysis) has also been applied to polyatomic systems.[4] The experimental data which allow one to test these different theoretical approaches are very scarce. The case of methyl nitrite photolysis for which the formation of several electronic and vibrational product states has been observed with relatively high quantum yields may provide a good example to examine how these models can apply in an intermediate size molecule. Because of its interesting properties (repetitive pulsed source with a continuous spectrum in the far UV region) the synchrotron radiation offers a unique tool to investigate the excitation wavelength dependence of the energy disposal in the photodissociation of CH_3ONO.

EXPERIMENTAL AND RESULTS

Methyl nitrite was prepared from reaction of nitrous acid on methanol in sulfuric acid medium. The sample whose purity was checked by gas chromatography and mass spectrometry was stored in the dark. The experimental setup was basically the same as before.[5] The synchrotron radiation of the Orsay collision ring (ACO) ($\tau = 1$ ns, 13 MHz repetition rate) was used for excitation through a specially designed monochromator. The exciting beam was focused in the center of the fluorescence gas cell equipped with three MgF_2 windows. The relative intensity of the excitation light as a function of wavelength was measured by detecting the fluorescence of a

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sodium salicylate screen on the exit window of the cell, the emission yield being assumed constant with λ between 1100 and 2000 Å.

The fluorescence was spectrally analyzed by a home built vacuum monochromator.[6] Photon counting and correlated single photon counting techniques (for decay time measurements) were used with an RTC 56 SBUVP solar blind photomultiplier as detector (Cs–Te photocathode on a fused silica window–spectral response extending from 1600 Å to 3500 Å–low noise <5 cps.)

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

The excitation spectra of the different fluorescent NO fragments $A\,^2\Sigma^+\ v'=0,1,2,3$, $C\,^2\Pi\ v'=0$, and $D\,^2\Sigma^+\ v'=0$ produced by CH_3ONO photolysis were recorded by monitoring the emission intensity at selected observation wavelengths ($\Delta\lambda \sim 20$ Å). The fluorescence signal intensity at a given observation wavelength λ_{obs} can be expressed as follows:

$$I^F = FN(\lambda_{exc})\phi(\lambda_{exc})\,A(\lambda_{exc})P^F\frac{1}{1+k_Q\tau p}\ , \qquad \text{(I)}$$

where F is an experimental factor related to the sensitivity of the detection (F was evaluated by comparing the relative intensity of the emission bands of pure NO in $A\,^2\Sigma^+$ and $D\,^2\Sigma^+$ states with their theoretical values known from the literature[7]), $N(\lambda_{exc})$ is the relative incident photon flux at excitation wavelength λ_{exc}, $\phi(\lambda_{exc})$ is the quantum yield for production of the observed species from CH_3ONO photolysis at λ_{exc} and extrapolated at zero-pressure, $A(\lambda_{exc})$ is the percentage of incident light absorbed by CH_3ONO over the length of the cell viewed by the detector, P^F the relative emission probability of electronically excited NO at λ_{obs} is proportional to Y_F, $q_{v'v''}/\lambda^3_{obs}$ with Y_F being the zero pressure fluorescence quantum yield of the NO species under investigation, $q_{v'v''}$ the Franck–Condon factor for the observed emission band,[8] $1/(1+k_Q\tau p)$ represents the correction factor for pressure quenching where τ is the zero pressure lifetime of the species under investigation,[9] p the pressure of CH_3ONO, and k_Q the quenching rate constant of this species by CH_3ONO.[2]

In a first series of experiments, the fluorescence signal intensity I^F has been meausred as a function of λ_{exc} at $\lambda_{obs}=2360$, 1914, and 1880 Å corresponding, respectively, to $\gamma(0,1)$, $\delta(0,0)$ and $\epsilon(0,0)$ emission bands. The signal intensity was then extrapolated at zero pressure to take into account the pressure quenching effect. Furthermore, the $A\,^2\Sigma^+\ v'=0$ state of NO can be populated either directly in the photodissociation of CH_3ONO or in a secondary process by the radiative cascade from $C\ v'=0$ and $D\ v'=0$. Thus, the intensity of $\gamma(0,1)$ band was corrected for the contribution due to $C\ v'=0$ and $D\ v'=0$ formation in the CH_3ONO photolysis using the relative intensity of the $\gamma(0,1)$ to $\delta(0,0)$ and $\epsilon(0,0)$ bands determined from the fluorescence spectra of directly excited NO $C\,^2\Pi\ v'=0$ and $D\,^2\Sigma^+\ v'=0$ states and extrapolated at zero pressure. From these data, the excitation spectra of NO $A\,^2\Sigma^+$, $C\,^2\Pi$, and $D\,^2\Sigma^+$ in the zeroth vibrational level resulting from CH_3ONO photolysis are obtained.

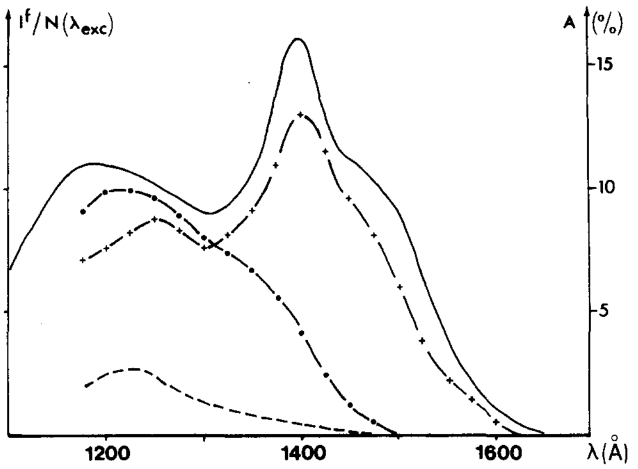

FIG. 1. Relative efficiency for the production of NO electronically excited fragment from CH_3ONO photolysis as a function of incident wavelength. + — + — $A\,^2\Sigma^+\ v'=0$, 1, 2, 3; • — • — $C\,^2\Pi\ v'=0$; – – – $D\,^2\Sigma^+\ v'=0$. The full line (—) represents the absorption A of the CH_3ONO sample ($p=170$ mTorr) in the part of the cell from which the fluorescence is observed (right hand scale).

On the other hand, the $A\,^2\Sigma^+$ excited NO fragment has been shown previously to be produced in several vibrational levels $v'=0,1,2,3$. Because of the weakness of the fluorescence signal these vibronic species were studied at observation wavelength corresponding to emission bands with the highest Franck–Condon factor $\gamma(0,1)$, $\gamma(1,0)$, $\gamma(2,0)$, $\gamma(3,0)$. However, decay time measurements show that $\gamma(0,1)$ emission follows a single exponential decay whereas $\gamma(1,0)$, $\gamma 2,0)$, $\gamma(2,0)$ decays show deviations from exponentiality with a long component corresponding to the NO $A\,^2\Sigma^+$ emission and a short one which can be assigned to contributions from $C\,^2\Pi$ or $D\,^2\Sigma^+$ emissions. In fact, from comparison of the experimental spectra of NO directly excited in $A\,^2\Sigma^+\ v'=0,1,2,3$, $C\,^2\Pi\ v'=0$, and $D\,^2\Sigma^+\ v'=0$, it can be seen that with the observation bandwidth used in the study ($\Delta\lambda \sim 20$ Å) the $\gamma(3,0)$ band at 1957 Å is partially overlapped by $\epsilon(0,1)$ (1947 Å), the $\gamma(2,0)$ at 2047 Å by $\delta(0,2)$ (2057 Å), and $\gamma(1,0)$ at 2148 Å by $\delta(0,3)$ (2138 Å) or $\epsilon(1,5)$ (2157 Å).

In order to obtain the $A\,^2\Sigma^+$ emissions free from most of the contribution of the short lifetime emission, a second set of spectra have been recorded taking only the long part of the fluorescence by means of a time resolved technique. In these experiments, only the photons emitted with a delay Δt($t=30$ ns, $t+\Delta t=60$ ns) after the exciting pulse were counted with a single channel analyzer receiving the output of the time amplitude converter. From the excitation spectra of each vibronic level of NO $A\,^2\Sigma^+$ obtained in these conditions, one can deduce the relative vibrational population of NO $A\,^2\Sigma^+$ photofragment (from the quantity I^F/P^F) and calculate the total yield of $A\,^2\Sigma^+$ as a function of incident wavelength.

The results of these experiments are shown in Figs. 1–3. The excitation spectra of each electronically excited NO $A\,^2\Sigma^+\ v'=0,1,2,3$, $C\,^2\Pi\ v'=0$, and $D\,^2\Sigma^+\ v'=0$ where $I^F/N(\lambda_{exc})$ is plotted against λ_{exc} and the absorption

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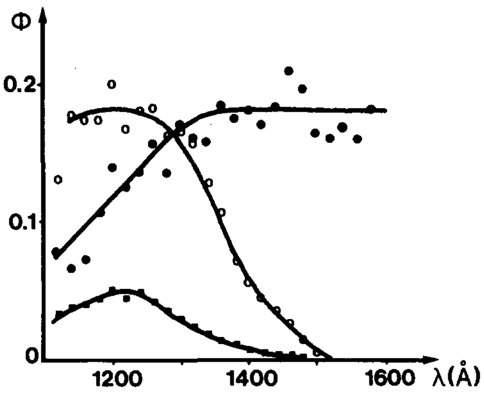

FIG. 2. Excitation energy dependence of the quantum yield for production of NO electronically excited fragments. ● NO $A\,^2\Sigma^+$ $v'=0, 1, 2, 3$; ○ NO $C\,^2\Pi$ $v'=0$; ■ NO $D\,^2\Sigma^+$ $v'=0$.

spectra $A(\lambda_{exc})$ of the CH_3ONO sample are shown in Fig. 1. According to Eq. (I) the quantity $I^F/N(\lambda_{exc})$ is proportional to $\phi(\lambda_{exc})A(\lambda_{exc})$. The absolute quantum yields $\phi(\lambda_{exc})$ for NO $A\,^2\Sigma^+$ at $\lambda_{exc}=1440$ Å, NO $C\,^2\Pi$ at $\lambda_{exc}=1380$ Å, and NO $D\,^2\Sigma^+$ at λ_{exc} at 1200 Å known from a previous study[2] were used to scale the spectra one relative to the other in order to obtain comparative data for the efficiency of production of each electronically excited species as a function of incident wavelength.

Figure 2 shows the incident excitation wavelength dependence of the quantum yields $\phi(\lambda_{exc})$ of NO $A\,^2\Sigma^+$ $v'=0,1,2,3$, $C\,^2\Pi$ $v'=0$, $D\,^2\Sigma^+$ $v'=0$ fragments.

In Fig. 3 are shown the excitation spectra of individual vibronic species NO $A\,^2\Sigma^+$ $v'=0,1,2,3$ (obtained by the time resolved technique) corrected for the incident photon flux and for the emission probability of each observed emission band [$I^F/F\,N(\lambda_{exc})\,P^F$ is plotted against λ_{exc}]. As the relative intensity of NO $\gamma(0,1)$ $\gamma(1,0)$ $\gamma(2,0)$, and $\gamma(3,0)$ does not depend on the pressure of CH_3ONO between 0.05 and 1 Torr, it can be concluded that in our experimental conditions ($P_{CH_3ONO}=100$ mTorr) there is no vibrational relaxation. Besides, the rate constants for quenching of NO $A\,^2\Sigma^+$ by CH_3ONO have been shown previously from lifetime measurements to be independent of the excited vibrational level. Thus, from these excitation spectra, one can deduce immediately the relative vibrational population of the NO $A\,^2\Sigma^+$ fragment at each excitation wavelength.

DISCUSSION

Electronically excited NO fragments formation

Threshold energies

The bond dissociation energy of CH_3ONO has been determined by a thermochemical method to be 1.81 eV.[10] The energy of the excited states of NO and CH_3O which can be reached by the photodissociation of CH_3ONO are

NO $A\,^2\Sigma^+=5.48$ eV ,

NO $B\,^2\Pi=5.64$ eV ,

NO $C\,^2\Pi=6.49$ eV ,

NO $D\,^2\Sigma=6.61$ eV ,

CH_3O $^1A_1=4.07$ eV (Ref. 11) ,

NO $B'\,^2\Delta=7.43$ eV ,

NO $E\,^2\Sigma^+=7.55$ eV .

Table I summarizes the thermochemical threshold energies of the different dissociation channels accessible in the excitation wavelength range used in this work. The experimental threshold energies for the observed excited fragment are also given in Table I. From comparison of the two sets of values, it can be concluded that NO $A\,^2\Sigma^+$ $v'=0$ formation coincides with the onset of the absorption of CH_3ONO in that region (~1650 Å) which is slightly higher in energy than the thermochemical threshold whereas NO $C\,^2\Pi$ $v'=0$ and $D\,^2\Sigma^+$ $v'=0$ fragments appear for an excitation wavelength corresponding exactly to the thermochemical threshold. In the case of NO $A\,^2\Sigma^+$ the small difference between the calculated value and the observed one can be due to difficulty in determining very weak fluorescence intensity

TABLE I. Threshold energies for the production of electronically excited fragments in the photodissociation of CH_3ONO.

Reactions	E_{calc} (eV)	λ_{calc} (Å)	λ_{obs} (Å)
$CH_3ONO \rightarrow CH_3O\ X\,^2E + NO\ X\,^2\Pi$	1.81		
$\rightarrow CH_3O\ ^1A_1 + NO\ X\,^2\Pi$	5.9	2060	2060
$\rightarrow CH_3O\ X\,^2E + NO\ A\,^2\Sigma^+$, $v'=0$	7.30	1698	1650
$v'=1$	7.58	1635	1600
$v'=2$	7.87	1575	1540
$v'=3$	8.15	1521	1500
$\rightarrow CH_3O\ X\,^2E + NO\ B\,^2\Pi$	7.45	1664	
$\rightarrow CH_3O\ X\,^2E + NO\ C\,^2\Pi$ $v'=0$	8.29	1496	1500
$\rightarrow CH_3O\ X\,^2E + NO\ D\,^2\Sigma^+$ $v'=0$	8.41	1475	1475
$\rightarrow CH_3O\ X\,^2E + NO\ B\,^2\Delta$ $v'=0$	9.24	1342	
$\rightarrow CH_3O\ X\,^2E + NO\ E\,^2\Sigma$	9.42	1316	

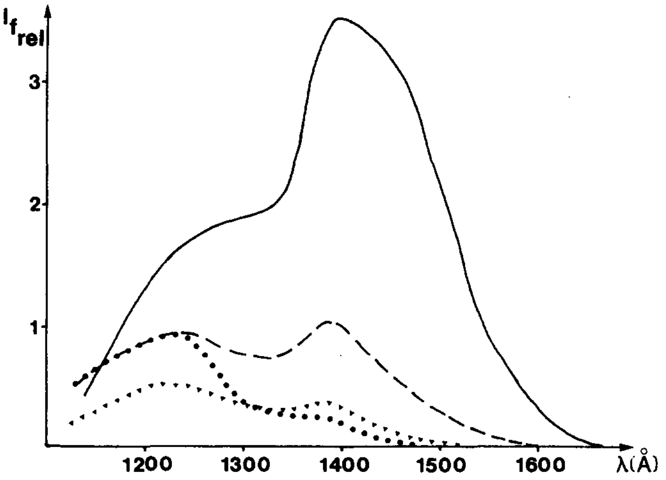

FIG. 3. Excitation spectra of vibronically excited NO $A\,^2\Sigma^+$ fragment from CH_3ONO photolysis. — NO $A\,^2\Sigma^+$ $v'=0$; – – – NO $A\,^2\Sigma^+$ $v'=1$; ▼▼▼ NO $A\,^2\Sigma^+$ $v'=2$; ●●● NO $A\,^2\Sigma^+$ $v'=3$.

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because of a very weak absorption in the 1600–1700 Å region.

The agreement between the thermochemical threshold energies and the experimental ones can be interpreted as indicative of a predissociation mechanism rather than a direct photodissociation. In the latter case where the dissociation takes place from directly excited repulsive state, the fragments are not expected to be produced at the thermochemical threshold. On the other hand, numerous excited states may participate to the absorption of CH_3ONO in the region 1150–1600 Å and in the case where these states are predissociated the system will always have some probability to dissociate at the threshold because of the complexity of the potential hypersurfaces for polyatomic molecules.

In fact, the appearance of the fluorescence from excited photofragments when the energy input in the parent molecule is just sufficient to break the bond and to excite the fragment is frequently observed for strongly absorbing polyatomic molecules and this property has been widely used to determine the bond dissociation energy of numerous compounds.[12] Hence, these experiments give a confirmation of the known value of CH_3O–NO bond energy.

It should be pointed out that since the absorption spectrum of CH_3ONO in the 1150–1650 Å range is diffuse and does not show any structure even in the long wavelength part, no information can be obtained from spectroscopic data on the kind of predissociation involved in the system.

Excitation energy dependence of electronically excited NO *fragment yields*

The observation that excited states of NO are produced as soon as enough energy is available for their formation indicates that there are no severe correlation rules between the initially excited states of the parent molecule and the dissociation products. Nevertheless, several characteristic features which reveal a specific behavior in the CH_3ONO photochemical processes can be noted:

(1) The absolute quantum yields (Fig. 2) for production of electronically excited fragments are higher by about one order of magnitude than those generally obtained in the photodissociation of polyatomic molecules.[13] In large molecules it is expected that the probability to obtain a given product decreases when the complexity of the molecule increases because of the increasing number of dissociation channels open.

(2) It is striking that the $B\,^2\Pi$ state of NO has not been detected in our experiments. Although the reason for this could be as suggested before[2] the efficient quenching of NO $B\,^2\Pi$ by CH_3ONO due to its long radiative lifetime, this result may reflect some forbidden process from the reactive excited state of CH_3ONO.

(3) The quantum yield for NO $A\,^2\Sigma^+$ production is constant within the error limits in the 1600–1400 Å excitation range ($\phi = 0.18 \pm 0.03$). In this region NO $A\,^2\Sigma^+$ is the main observed fluorescent fragment and this result indicates that the probability of NO $A\,^2\Sigma^+$ formation relative to the other competitive processes does not vary with the excess energy available for its formation over a wide range extending from 3000 to 13 000 cm^{-1}.

(4) In the part of the absorption spectrum between 1350 and 1150 Å for which $C\,^2\Pi$ and $D\,^2\Sigma^+$ NO states are produced as well as $A\,^2\Sigma^+$ state, the branching ratio $C\,^2\Pi\ v'=0/D\,^2\Sigma^+\ v'=0$ is approximately constant ($C/D \simeq 4$). Thus, the energy dependence for the production of NO $C\,^2\Pi$ and $D\,^2\Sigma^+$ does not reproduce a statistical behavior: The $C\,^2\Pi$ state which is only 1000 cm^{-1} lower in energy than the $D\,^2\Sigma^+$ state is ~4 times more populated than $D\,^2\Sigma^+$ for an overall excess energy $[E_{h\nu} - D(CH_3O\text{–}NO)$ between 60 000 and 70 000 $cm^{-1}]$.

All these observations suggest that the electronic configuration of the initially dissociating reactant states may play an important role in determining the nature and the yields of the products. On the basis of these arguments it would be interesting to correlate some CH_3ONO transition with excited NO products as it has been suggested by Okabe and Lenzi in the case of NOCl.[14] It can be possible that Rydberg states of CH_3ONO which are predicted to be located at 1600 Å ($n \to 3s$) and 1410 Å ($n \to 3p$) from photoelectron spectra would lead preferentially to NO $A\,^2\Sigma^+$ and $C\,^2\Pi$ Rydberg states. Although experimental data do not allow to make any precise conclusion on this point, simple theoretical orbital and state correlation diagrams could be helpful to have a better understanding of the photodissociation pathway in CH_3ONO.

Vibrational energy disposal in the NO $A\,^2\Sigma^+$ fragment

In the present discussion we are only concerned with the dissociation channel:

$$CH_3ONO \xrightarrow{h\nu} CH_3O\ X\,^2E + NO\ A\,^2\Sigma^+ \ ,$$

The experimental vibrational state populations of NO $A\,^2\Sigma^+$ produced in the photolysis of CH_3ONO between 1200 and 1600 Å are reported in Table II. Figure 2 also shows the excitation spectra of $v' = 0, 1, 2, 3$. From these data several features can be noted:

(1) The experimental threshold energies for each vibrational level are close to the calculated thermochemical threshold (see Table I).

(2) In the first part of the excitation spectra (1600–1350 Å) the $v'=0$ is the most populated level, higher vibrational levels $v' = 1, 2, 3$ population increasing smoothly with increasing excitation energy.

(3) In the second part of the excitation spectrum the $v' = 3$ level shows an anomalously high population relative to that of the other vibrational levels.

In order to analyze the vibrational distribution, it is interesting in a first step to compare it with an *a priori* distribution. For this purpose we will use the usual statistical assumption that all product quantum states allowed by energy conservation are equally probable. Thus, the probability to observe a given vibrational state of NO $A\,^2\Sigma^+$ fragment for an excess energy $E = E_{h\nu} - D_0 - E_{NO(A\,^2\Sigma^+)v'=0}$ can be expressed by

$$P^0 = \rho(E, v) \Big/ \sum_{v=0}^{v_{\max}} \rho(E, v) \ ,$$

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TABLE II. Relative population of NO $A\,^2\Sigma^+$ vibronic levels.

		Experiments			Model I			Model II			Best fit	
λ_{exc} (Å)	E (eV)	$\frac{N\,v'=1}{N\,v'=0}$	$\frac{N\,v'=2}{N\,v'=0}$	$\frac{N\,v'=3}{N\,v'=0}$	$\frac{N\,v'=1}{N\,v'=0}$	$\frac{N\,v'=2}{N\,v'=0}$	$\frac{N\,v'=3}{N\,v'=0}$	$\frac{N\,v'=1}{N\,v'=0}$	$\frac{N\,v'=2}{N\,v'=0}$	$\frac{N\,v'=3}{N\,v'=0}$	$\frac{N\,v'=1}{N\,v'=0}$	$\frac{N\,v'=2}{N\,v'=0}$
1200	10.33	0.60	0.35	0.59	0.44	0.18	0.065	0.738	0.5321	0.37	0.574	0.31
1240	10	0.57	0.31	0.55	0.40	0.14	0.043	0.71	0.4875	0.317	0.53	0.27
1300	9.54	0.42	0.19	0.20	0.32	0.088	0.019	0.658	0.41	0.284	0.465	0.185
1340	9.25	0.35	0.15	0.13	0.267	0.057	0.09	0.566	0.352	0.176	0.41	0.147
1400	8.85	0.31	0.09	0.056	0.184	0.023	0.015	0.538	0.252	0.09	0.32	0.08
1440	8.61	0.25	0.05	0.02	0.129	0.009		0.472	0.178	0.04	0.25	0.043
1500	8.26	0.14	0.02		0.052	0.002		0.343	0.068	0.016	0.14	
1540	8.05	0.10						0.234	0.014	0.007		

where $\rho(E, v)$ is the density of states with total energy E.[15] As we have no information on the CH_3O internal energy distribution nor on the rotational excitation of NO $A\,^2\Sigma^+$, the total density of states can be expressed by

$$\rho(E, v)=\sum_{J=0}^{J_{\max}}(2J+1)\int_{E_I=0}^{E-E_v^{NO}-E_J^{NO}}\rho_I(E_I^{CH_3O})\rho_T\,dE_I\ .$$

ρ_T is the density of translational states of relative motion of the products and is proportional to $E_T^{1/2}$, with $E_T=E-E_v^{NO}-E_J^{NO}-E_I^{CH_3O}$. $\rho_I(E_I^{CH_3O})$, the vibrational–rotational density of states of CH_3O, has been computed by means of the Laplace transform method.[16] The vibrational frequencies of CH_3O used for this calculation were 1015 cm^{-1} (C–O stretching), 1182 cm^{-1} (degenerate CH_3 rocking), 1380 and 1460 cm^{-1} (CH_3 deformation), and 2930 and 3000 cm^{-1} (CH stretching). The rotational constants calculated for the predicted geometry of CH_3O[17] [prolate symetric top molecules: $r_{CH}=1.08$ Å, $r_{CO}=1.44$ Å, A(O–C–H)$=109°$] are $A\simeq 5$ cm^{-1} and $B\simeq 1$ cm^{-1}.

The computed values of the internal density of vibrational–rotational states of CH_3O show that in the range $5000<E<20\,000$ cm^{-1} ρ_I can be approximated by

$$\rho_I=E_I^{5.5}\ .$$

Thus,

$$\rho(E, v)=\sum_{J=0}^{J_{\max}}(2J+1)\times\int_0^{E-E_v^{NO}-E_J^{NO}}E_I^{5.5}(E-E_v-E_J-E_I)^{0.5}dE_I\ ,$$

which can be transformed by substitution of the reduced variable $E_I/(E-E_v-E_J)$ and integrated

$$\rho(E, v)\propto\sum_{J=0}^{J_{\max}}(2J+1)(E-E_v-E_J)^7\ .$$

Replacement of the sum by an integral over dE_J gives the final expression

$$\rho(E, v)\propto(E-E_v)^8\ .$$

This case corresponds to a complete energy randomization in the reaction (model I). On the other hand, a simplifying approximation which consists in neglecting vibration in the CH_3O fragment can be made. This assumption corresponds to the limiting case of no rapid vibrational redistribution (model II). The density of states is then expressed by

$$\rho(E, v)\propto(E-E_v)^3\ .$$

In Table II are given the relative vibrational populations in the two limiting cases for $v'=1$, $v'=2$, $v'=3$ relative to $v'=0$. If we except the anomalous behavior of $v'=3$ which is obvious from excitation spectrum, the comparison of the *a priori* distribution with the experimental ones shows that neither of the models agrees with the observed distributions. It can be deduced that neither the vibration of CH_3O can be neglected nor all the degrees of freedom of CH_3O have to be taken into account to match the experimental results.

If the experimental populations are empirically assumed to follow a n power dependance on the excess energy $[P_v^{exp}\propto(E-E_v)^n]$, a plot of log P_v^{exp} as a function of $\log(E-E_v)$ gives an empirical value of 5.5 for n. Such a result would be consistent with the approximation that CH_3O can be described by three effective modes of frequency ~1000 cm^{-1}. It seems thus that although an important part of the excess energy goes in the CH_3O fragment, there is a noncomplete randomization of energy in this system. On the other hand, it should be pointed out that the fact that the observed vibrational distributions can be matched with a statistical treatment does not imply that intrafragment coupling (i.e., the Franck–Condon factors associated with the optical excitation and the predissociation) as predicted by the theoretical models of Band and Freed[18] and Mukamel and Jortner[19] will not give a good fit with experimental results. In the case of CH_3ONO however, such models could be difficult to test because of the complexity of the molecules and of our lack of knowledge on the nature and geometry of the reactive excited states.

As noted before the NO $v'=3$ level does not follow the main conclusions drawn in the previous section. The excitation spectrum shows an anomalously high population in the short wavelength excitation range. This behavior can be explained if we consider the excitation spectrum of NO $D\,^2\Sigma^+$ $v'=0$ and $C\,^2\Pi$ $v'=0$ in the same spectral region. The comparison of the excitation spectra shows that NO $A\,^2\Sigma^+$ $v'=3$ production efficiency is very similar to that of NO $C\,^2\Pi$ $v'=0$ and $D\,^2\Sigma^+$ $v'=0$. This can be interpreted if we suppose that the interaction

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between CH_3O and NO nascent fragments may relax the primarily formed $C\,^2\Pi\ v'=0$ and $D\,^2\Sigma^+\ v'=0$ NO species to the closely lying $A\,^2\Sigma^+\ v'=3$.

We have no direct proof for this interpretation but this assumption is supported by the study of the effect of helium on NO $C\ v'=0$ and $D\ v'=0$ fluorescence. The results of this study will be reported elsewhere[20] but we observed a very efficient collision induced relaxation of NO $D\ v'=0$ and $C\ v'=0$ specifically towards NO $A\,^2\Sigma^+\ v'=3$. A high population of $A\,^2\Sigma^+\ v'=3$ has also been observed by Johnson[21] in the photodissociation of pure C_2H_5ONO and CF_3NO.

The effect of interfragment coupling is considered to to be in most of the cases negligible to account for the vibrational energy distribution in photodissociation.[22] Nevertheless, a very high probability of relaxation of NO $C\,^2\Pi$ and $D\,^2\Sigma^+$ to $A\,^2\Sigma^+\ v'=3$ could be the reason for this exceptional behavior.

CONCLUDING REMARKS

The present work represents the first systematic study of the excitation dependance of individual quantum states fragments resulting from the photodissociation of a polyatomic molecule. The main conclusions that can be drawn from the results can be summarized as follows:

(1) The products appearance threshold corresponds to the threshold energy calculated from the known value of CH_3ONO bond energy

$$D^0(CH_3ONO)=E^0_{h\nu}-E(NO_{A,C,D}) \quad ,$$

where $E^0_{h\nu}$ is the onset of the excitation spectrum. This observation makes improbable the photodissociation from a directly excited repulsive state for the mechanism of photofragmentation in CH_3ONO.

(2) The total quantum yield of detected excited fragments is relatively high ($\phi=0.4$) at 1200–1250 Å and the branching ratio of the electronic states seems to be very specific. Besides the fluorescent NO fragments studied in this work, a number of other electronically excited species which have not been looked at (NO $B'\,^2\Delta$, $E\,^2\Sigma^+$) or which are nonfluorescent ($A\,^2\Sigma^+\ v'>4$, $C\,^2\Pi\ v'>1$) could have been formed. It is thus possible that a favorable population inversion exists in this system and it would be interesting to look at the possibility of lasing action in highly excited CH_3ONO.

(3) The vibrational energy distribution in the NO $A\,^2\Sigma^+$ state seems to be nearly statistical. It can be deduced from this result that an important part of the excess energy goes in the CH_3O excited fragment. This is in agreement with the results of near UV photolysis of higher organic nitrites.[23] In the case of ethyl, isopropyl, and *t*-butyl nitrite the alkoxy fragment was shown to carry a sufficient amount of internal energy to allow an important proportion of the excited radical to undergo a subsequent unimolecular decomposition. One can expect in fact that a large fraction of the excess energy goes into the more complex of the two fragments. From that point of view, it will be interesting to look at the vibrational energy distribution in the case of the photodissociation of other XNO compounds where the nature of X (size and mass) would be varied.

(4) The final state interaction (interfragment coupling) could play an important role in affecting the vibronic state distribution as suggested by the $A\,^2\Sigma^+\ v'=3$ population. The effect of the X substituant would give valuable information to assess the importance of interfragment coupling.

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