PHOTODISSOCIATION OF NO₂. INTERNAL ENERGY DISTRIBUTION AND ANISOTROPIES IN THE FRAGMENTS

Michel MONS and Iliana DIMICOLI

CEN Saclay, DESICP, Département de Physico-Chimie, 91191 Gif-sur-Yvette Cedex, France

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The near-UV photodissociation of NO₂ has been investigated at excess energies from -600 up to 1700 cm^{-1} above the NO X $v=1+O^{3}P$ dissociation limit. A complete analysis of the NO X v=1 fragment, including internal and translational energy as well as the angular properties of its vectorial parameters, has been carried out using REMPI combined with TOF mass spectrometry. The high-precision state-selective measurements of the NO fragment velocity have been used to evaluate the internal energy of the O atoms formed in coincidence. Concerning the internal energy of the NO X v=1 fragment, two types of final state distributions of the fragments have been found; the difference depending upon the excess energy with respect to the NO X $v=1+O^{3}P$ dissociation limit. Above the threshold, statistical rotational behaviour with nonvanishing anisotropies has been observed. Below the threshold, an efficient R→V transfer, allowed by a significant molecular distortion, was detected. The influence of the parent rotation on the NO fragment rotational distribution is discussed.

1. Introduction

Molecular photodissociation is one of the most fundamental photochemical processes and presents a key for the understanding of further complex chemical events. A complete description of this process involves the determination of both the internal and translational energies and their partitioning between the fragments [1,2] as well as the measurement of the vector correlations (velocity and angular momentum) in the fragments [3,4].

Various methods have been applied in the last decade in order to partially resolve one of the aspects of this problem. In previous communications [5,6], we have discussed the advantages of the resonance enhanced multiphoton ionization (REMPI) as probe technique. Briefly, this probe method is based on the time-of-flight (TOF) measurement of laser ionized fragments detected in a time-of-flight mass spectrometer (TOF MS). It is thus possible to obtain, in the same experiment, information about the internal energy distribution in the photofragments as well as, for each probed fragment, the magnitude of the velocity and the rotational and translational anisotropies. Since the TOF depends linearly on the ion velocity projection along the spectrometer axis, the TOF spectra are images of these projections. The kinetic resolution we obtain is about three times better than those reported by LIF Doppler spectroscopy [7,8], the main concurrent method in this field. Thus the REMPI TOF MS method is a tool for deriving highresolution state-selective data concerning the final state of the dissociative systems and especially for the investigation of their near-threshold behaviour.

In this paper are reported results on the photodissociation dynamics of the NO_2 molecule, excited around its first dissociation limit. A considerable number of studies have been carried out on this species [9-21]. They can be summarized as follows:

The nitrogen dioxide molecule is known to exhibit predissociation in the near UV. The infrared-visible absorption system, which extends as far as this UV region, is composed of ill-defined vibronic structure superimposed on a substantial background [9]. The onset of the predissociative process has been determined at about 25125 cm⁻¹, in fair agreement with the thermodynamical data [10]. These results were corroborated by several O atom [11,12] and fluorescence [13] quantum yield measurements after photoexcitation. The observation of fragments at an energy below the dissociation threshold (-1400 cm^{-1}) has shown the availability of some initial internal en-

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The first investigation of the internal energy distribution in the fragments formed from the NO₂ photolysis was performed by Busch and Wilson, using time-of-flight photofragmentation spectroscopy [15]. Their experiments documented the formation of both NO X v=0 and 1 fragments, formed at an excitation energy of 28810 cm^{-1} . A translational anisotropy analysis [16] allowed them to determine the symmetry of the main state responsible for the photoexcitation (NO₂ $\tilde{A}^{2}B_{2}$) and to give an upper limit of the excited state lifetime (200 fs). More recently, LIF detection of the NO fragment performed by Welge's group at different energy excess [17,18] has shown the importance of the fragment rotational energy, whose distribution covers the whole energetically accessible domain. On the other hand, the NO dissociation product of jet-cooled molecules has been shown to be rotationally cold [19]. A precise value of the first dissociation limit of NO₂, $D_0 = 25130.6 \pm 0.6$ cm^{-1} , has been obtained from these experiments.

Our investigations on the photopredissocation of NO_2 were motivated by different reasons:

Firstly, the nature of the dissociation process – a fast predissociation – which provides an opportunity to observe the angular distribution of velocity and angular momentum of the fragments at their formation threshold as well as to perform state-selective measurements of the translational anisotropy for fragments of kinetic energy down to 600 cm^{-1} .

Secondly, our ability to ionize selectively through a 2+1 REMPI process the NO fragments and to derive from an intensity analysis of their REMPI and TOF spectra the rotational and kinetic anisotropies as well as the angular v-J correlation [6].

Finally, the high resolution obtained in the velocity measurement makes possible the first observation of interfragment correlations between the NO fragment and the O atom formed in coincidence.

We present, in this paper, a complete characterization of the NO X v = 1 fragment formed in the photodissociation of NO₂ at energy excess from -627(default energy) up to 1710 cm^{-1} above the NO X $v = 1 + O^{3}P$ dissociation threshold. In the first part of this work, we discuss the internal energy deposited in the diatomic fragment and its determination by REMPI spectroscopy. The velocity measurement for each NO rotational level obtained by the shape analysis of the TOF peak, which yields information about the internal energy of the O atom formed simultaneously, is described in the second part. The angular properties of both velocity and angular momentum as well as their correlation is given. Finally the experimental results are compared with the theoretical predictions and a probable state-selective picture of the dissociation process close to the threshold is presented.

2. Experimental procedure

The photodissociation study has been performed in a two-color experiment using two excimer-pumped nanosecond dye lasers (Lambda-Physik FL 2002 and EMG 102) and a TOF mass spectrometer. The apparatus has been described in detail previously [5,22]. A first laser pulse (pump or dissociation), propagating perpendicularly to the spectrometer axis, is roughly focused (f=250 mm) on the thermal jet of NO₂ molecules (Messer-Griesheim product) in the interaction chamber of the TOF MS. The residual pressure is kept smaller than 0.1 mPa during operation. After an electronically controlled delay of about 30 ns, a second laser pulse (probe), propagating anticollinearly to the pump beam is focused (f=200)mm) on the photolysis region and induces the NO 2+1 REMPI probe process. The laser polarization was achieved using Glan polarizers. The ions are detected after their flight by multichannel plates (RTC 12.5-25). The mass-selected ion signal can be collected as a function of the scanned wavelength after averaging over a variable number of laser shots. The data are processed and the experiment monitored, using a microcomputer. The temporal shape of the mass-selected ion current is recorded on a Tektronix

R7912 transient analyser. The dyes used are PTP, butyl PBD, BBQ and PBBO for the photolysis light (spectral domain: 345-395 nm; pulse energy 500μ J, spectral width 0.2 cm^{-1}) and BBQ for the probe beam (energy of about 300μ J; similar spectral width).

Three kinds of experiments have been performed:

(i) The REMPI spectra are obtained by scanning the probe laser frequency over a two-photon transition of the NO fragment, keeping fixed the frequency of the dissociation laser.

(ii) Production spectra of well-defined quantum states of the NO fragment (probe laser wavelength fixed) are recorded by scanning the photolysis laser frequency.

(iii) Time-of-flight spectra of the NO fragments in a well defined quantum state are measured at fixed dissociation wavelengths.

The present mass spectrometer consists of two acceleration regions and a field-free region. The timeof-flight of the ions depends on the initial conditions of their formation (velocity v_z and position z along the Oz axis) and can be expressed as a function of z, v_z and the geometrical and electrical parameters of the spectrometer. The electric fields are chosen in order to obtain satisfactory signal-to-noise ratios: $E_1 = 100 \text{ V}/0.72 \text{ cm}$ and $E_2 = 800 \text{ V/cm}$. The timevelocity equivalence is given by the linear relation between time-of-flight T and velocity projection along Oz, the spectrometer axis [5]:

$$T(v_z) = T_0 - av_z, \quad \text{with } a = m/qE_1. \tag{1}$$

With these operating parameters the dispersion coefficient was for NO⁺ ions a=2.36 ns per 100 m/s, which corresponds to a kinetic resolution of about 260 m/s.

3. Internal energy of the NO X v=1 fragment

The photodissociation of NO₂ has been investigated around the NO X v=1+O ³P dissociation limit $(E=27006 \text{ cm}^{-1})$. Above this limit and up to 1800 cm⁻¹ of excess energy both NO X v=0 and v=1 fragments are thermodynamically accessible. The vibrationally excited species have been found, however, to be dominating [18]. We choose to focus our attention on the NO X v=1 fragment which furthermore exhibits two interesting advantages. First, the measurements on the probed fragment are not influenced by the presence of NO, one of the major impurities of NO₂ since the fraction of NO X v=1 is negligible. Concerning the other impurity, the NO₂ dimer, its fragmentation into NO₂+NO(v=1)+O needs an additional energy of about 4800 cm⁻¹, corresponding to the estimated dissociation energy of the dimer [23]. Secondly, the probe-laser wavelengths for the REMPI process are located in a spectral domain (384–391 nm) where the excitation of the parent NO₂ molecule is possible but does not allow the formation of the NO X v=1 species.

The internal energy distributions in the NO fragment have been determined at various excitation energies above and below the dissociation threshold and the role of the internal energy of NO_2 has been examined.

3.1. Internal energy of thermal nitrogen dioxide

The rotational energy distribution $W(\epsilon)$ of thermal molecules of NO₂ can be evaluated using the semi-classical formula for polyatomics [16]:

$$W(\epsilon) \propto \sqrt{\epsilon} \exp(-\epsilon/kT),$$
 (2)

or directly by computing the density of the quantum states, using a symmetric top model. Fig. 1 shows the small differences existing between both distributions. The most probable energy is located around 130 cm⁻¹ and differs from the average value (≈ 305



Fig. 1. Rotational energy of thermal NO_2 molecules. Classical (---) and quantum-mechanical (---) distributions.

 cm^{-1}). A long rotational tail is observed.

The vibrational energy of the thermal NO₂ is low since the frequencies [24] of the three vibrational modes are significantly higher than kT. Table 1 indicates the relative population of the first vibrational levels. The most populated excited state (0, 1, 0), corresponding to a single quantum in the bending mode, has a normalized population of about 2.4%.

The internal energy of NO_2 molecules can thus be considered as composed of rotation and vibration. The evaluation of the energy distribution after photoexcitation has to be analyzed.

Considering the quasi-continuum characteristics of the NO₂ absorption spectrum above the dissociation limit, as well as the excitation laser spectral width (0.2 cm^{-1}), which is much larger than the Doppler profile of the molecules, one can say that our laser beam induces simultaneously a great number of rovibronic transitions. Since the characteristics of the transitions (energy, type, ...) only depend on the complex rovibronic structure of the molecule, P, Q and R branches should statistically occur with the same frequency. Since the sum of the intensities for P, Q and R branches does not vary significantly in the symmetric top model [24] and since the $\Delta J=0, \pm 1$ selection rules ensure a small rotational energy variation, if the rotational constants are of the same order of magnitude between ground and excited state, one can deduce that the rotational energy distribution of the ground state should be transferred by photoexcitation to the excited state without any serious distortion.

The case of the vibrational energy distribution, however, is less simple. The vibrational population in the excited state is a function of both the ground state population and the photoexcitation oscillator strength. No measurements of the absorption proba-

Table 1

Relative populations of the first vibrational levels of $NO_2\,\tilde{X}$ at room temperature

(n_1, n_2, n_3)	Population (%)			
(0,0,0)	97.3			
(0, 1, 0)	2.43			
(1, 0, 0)	0.15			
(0, 2, 0)	0.06			
(0, 0, 1)	0.04			

bility in this region have been reported in the literature. Recently, Calvert et al. [14] have explained the temperature dependence of the oxygen quantum yield from NO₂ in the excitation region about 404 nm by assuming an excitation process five times more important for the (0, 1, 0) state than for the ground (0, 0, 0) state. If the same tendency is present in our excitation region, the relative population of excited NO_2 molecules formed from (0, 1, 0) is increased to 11%. Consequently, it seems more convenient, in estimating the internal energy distribution in the excited state, to consider separately the NO₂ excited species (NO_2^{**}) formed from the state (0, 1, 0) and those (NO_2^*) from the vibrational ground state. The energies deposited in these species are indeed of quite different natures: the extra energy, coming from vibrational energy in the ground electronic state for the NO^{**} molecules, can be directly involved in the dissociation process since it is of vibronic nature, whereas the rotational internal energy of both NO^{*}₂ and NO^{**} species must first be transferred to the vibrational motion in order to allow the bond breaking. This difference is assumed to play a decisive role in the dissociation process at low excess energies or in case of thermodynamical energy default. In the following, the average thermal ground state energy, transferred by photoexcitation to the NO^{*}₂ and NO₂^{**} species, will be noted $\langle E_{\rm th}^* \rangle$ and $\langle E_{\rm th}^{**} \rangle$ respectively.

3.2. NO Xv = 1 rotational population above the threshold

The rotational population distribution in the NO X v=1 fragment has been measured at 15, 391, 692 and 1712 cm⁻¹ of energy excess (E_{exc}) above the NO X v=1 formation threshold, corresponding to photoexcitation wavelengths from 370 down to 348.13 nm. Fig. 2 shows a part of the 2+1 REMPI spectra of the NO(D $v=0 \leftarrow X v=1$) two-photon transition. Owing to the low excess energies and to the relatively broad probe laser linewidth, no Doppler broadening was detected. An increase in the rotational excitation is observed when the excess energy increases. The rotational level populations n(J) deduced from the spectra analysis are given in fig. 3 for each electronic angular momentum projection $\Pi_{1/2}$ and $\Pi_{3/2}$. The limiting values of the thermodynamically accessible



Fig. 2. Part of the 2+1 REMPI spectrum of the NO photofragment (O₁₁ branch of the NO(D $v=0 \leftarrow X v=1$) transition) obtained at different excess energies above the (NO X v=1+O ³P) dissociation limit of NO₂.

rotational levels $\bar{J}_{\rm lim}$ and $J_{\rm lim}$ have been estimated with and without taking into account the average thermal energy of NO₂ in the calculation of the average available energy $\langle E_{\rm avl} \rangle$ defined as $\langle E_{\rm avl} \rangle = E_{\rm exc} + \langle E_{\rm th}^{\rm NO_2} \rangle$,

$$E_{\rm rot}^{\rm NO}(J_{\rm lim}) = E_{\rm exc}, \quad E_{\rm rot}^{\rm NO}(\bar{J}_{\rm lim}) = \langle E_{\rm avl} \rangle. \tag{3}$$

The populations have been found to be identical, within the experimental error, for each Λ -doubling component. The rotational distributions are larger than the thermodynamically accessible domain and appear similar to those observed by Welge et al. [17] in this energy region (355 nm). The main part of these distributions is however spread inside the [1/2, J_{lim}] domain, which could be an indication of the influence of the parent rotational energy. Additional measurements, discussed in section 3.3 have been performed in order to prove this hypothesis and to eliminate the possible influence of parent vibrational thermal motion.



Fig. 3. Rotational distributions of the NO X v=1 fragment obtained from the analysis of the REMPI spectra. The J limiting values corresponding to the thermodynamical limit (see text) have been indicated, when taking into account (!) or not (!) the average thermal energy of the NO₂ molecules.

The $\Pi_{3/2}/\Pi_{1/2}$ population ratio, which vanishes at threshold (see table 2) for reasons of thermodynamical access, increases monotonically up to 37% as soon as E_{exc} reaches 1700 cm⁻¹. The average NO rotational energies $\langle E_{\text{rot}}^{\text{NO}} \rangle$ are defined as:

$$\langle E_{\rm rot}^{\rm NO} \rangle = \sum_{J} n(J) E_{\rm rot}(J) / \sum_{J} n(J).$$

These energies have been computed for each NO X Π_{Ω} species and reported in table 2. From these values, it can be shown that the main part of the average available energy $\langle E_{avl} \rangle$ flows into the NO rotational degree of freedom at threshold ($\approx 60\%$) and decreases slightly to 40% at excess energies of 1700 cm⁻¹. The remaining available energy must thus be shared between internal energy of the O atom and

λ _{air} (nm)	E _{exc}	$\langle E_{\rm avi} \rangle$	$\langle E_{ m rot}^{ m NO}(\Pi_{1/2}) angle$	$\langle E_{ m rot}^{ m NO}(\Pi_{3/2}) angle$	$\Pi_{3/2}/\Pi_{1/2}$ population ratio (%)	
370	15	337	184			
364.91	391	713	386	287	25	
360.95	692	1014	465	407	35	
348.13	1712	2032	861	810	37	

Table 2 Average rotational energies (cm⁻¹) of the NO X v=1 fragment as a function of the excess energy

translational energy. This partition is depicted in fig. 4 for the O X $\Pi_{1/2} v=1$ species, showing the major contribution of NO rotation at E_{exc} below 500 cm⁻¹.

3.3. NO X v = 1 rotational population below the threshold

The study of the dissociation products formed at negative excess energies, i.e. in the case of energy default, is directly linked to the question of the nature of the internal energy which allows the dissociation to occur. The main advantage of such experiments is that they make possible a selection among the excited molecules, according to their internal – rotational or vibrational – energy.

The NO rotational distribution has been probed for both e and f A-doubling components of the NO X $\Pi_{1/2} v=1$ fragment obtained at excess energies of 15, -203, -417, -627 cm⁻¹ (corresponding to air wavelengths of 370, 373, 376 and 379 nm). Fig. 5 shows these distributions, found to be identical for both e and f components and non-sensitive to the ex-



Fig. 4. Energy partition in the dissociation channel (NO X $\Pi_{1/2}$ v=1+O ³P) as a function of the average excess energy.



Fig. 5. Rotational distributions of the NO X $\prod_{1/2} v = 1$ fragment obtained from the analysis of the REMPI spectra. The dots indicate the rotational distribution of the thermal NO molecule.

citation energy. Their shape is well reproduced using a Boltzmann population distribution characterized by temperatures of about $T=275\pm15$ K.

In order to rule out spurious effects, the production spectra of some quantum states of the NO X $\Pi_{1/2} v=1$, J species have been recorded in the threshold spectral region centered about 370 nm. Fig. 6 shows the NO $J=8\frac{1}{2}$ fragment intensity as a function



Fig. 6. Yield of the NO X $\Pi_{1/2} v=1 J=8\frac{1}{2}$ photofragment as a function of the photodissociation wavelength. The reported production spectrum is corrected from the spectral variations of the laser intensities.

of the excitation wavelength. The decrease to zero of the fragment production, as the default energy goes up, allows us to exclude the possible contribution of thermal NO v=1 molecules. The shape of the spectrum is similar to the O atom [11,12] or NO₂ fluorescence [13] quantum yield curves obtained in the spectral range around the NO X v=0+O ³P dissociation limit (≈ 400 nm). The observation of fragments, at energies where the dissociation channel is closed, is a direct proof of the involvement of the internal energy of the parent molecule in the process leading to the N-O bond breaking.

The average NO rotational energies $\langle E_{\text{rot}}^{\text{NO}} \rangle$ are reported in table 3 for each excitation wavelength. They are close to the thermal value for a diatomic molecule $E = kT \approx 205 \text{ cm}^{-1}$. Thus, whereas the parent molecules are under deficit conditions they dissociate and produce fragments with substantial rotational energy. The total "missing energy" defined as $(E_{\text{exc}} - \langle E_{\text{rot}}^{\text{rot}} \rangle)$ can only be balanced by the initial

thermal energy of the parent molecules. As shown in table 3, the average thermal energy in either NO^{*}₂ or NO^{**}₂ species is sufficient for this purpose. However more precise information can be obtained if the nature of the NO₂ molecules which lead to the formation of the NO X v=1 fragments was known. There are reasons for suggesting that only the NO^{*}₂ species are precursors of the observed fragments in the investigated spectral region.

From the results obtained above the threshold, we have seen that the NO₂ molecule exhibits some propensity for yielding NO fragment rotational distributions covering the whole accessible domain. Since these domains differ substantially for NO^{*}₂ and NO^{*}₂, and since, according to ref. [14], the relative population of NO^{*}₂ would increase from 11% at threshold up to nearly 50% at 379 nm, one could expect some changes in the shape of the NO fragment rotational distribution, and for instance, in the location of its maximum. This effect was not detected (fig. 5).

Secondly, the production spectra recorded for several NO X v=1, J fragments provide some quantitative arguments. Since the rotational distribution of the NO fragment does not vary with the excitation wavelength, the production spectrum of a state-selected fragment can be considered as the spectrum of the whole NO X v=1 species. At threshold (370 nm), the NO^{*}₂ is the main dissociative species. At 380 nm, at default energies around 690 cm⁻¹, the fragment can be generated from all the NO^{*}₂ molecules as well as from 8% of the NO^{*}₂ species, i.e. those sufficiently excited to undergo dissociation. The ratio of the intensities at these two wavelengths ($\approx 5\%$) in the spectrum of fig. 6 is an upper limit of the value of the population of the NO^{*}₂ species yielding the NO X

Table 3

Average rotational energy of the NO X $\Pi_{1/2} v=1$ fragment below the threshold ($\langle E_{rot}^{NO} \rangle$); energy balance deficits ($E_{exc} - \langle E_{rot}^{NO} \rangle$) and comparisons with the average thermal energies transferred by photoexcitation in both NO^{*}₂ and NO^{**}₂ species. All the energies are expressed in cm⁻¹

λ_{air} (nm)	E _{exc}	$\langle E_{\rm rot}^{ m NO} angle$	$E_{\rm exc} - \langle E_{\rm rot}^{\rm NO} \rangle$	$\langle E_{ m th}^{*} \rangle$	$\langle E_{ m th}^{ m **} angle$	$\begin{array}{c} E_{\rm exc} + \langle E_{\rm th}^* \rangle \\ - \langle E_{\rm rot}^{\rm NO} \rangle \end{array}$	
370	15	184	- 169	305	1055	136	
373	-203	173	-376	440	1055	64	
376	-417	178	- 595	625	1055	30	
379	-627	182	-809	826	1055	17	

v=1 fragment expressed relatively to the total NO₂ population yielding NO X v=1 at threshold. The value obtained is smaller than that proposed by Calvert et al. (11%). These results, however, are not necessarily in contradiction; firstly, because the excitation energy range is somewhat different and is supposed to be dependent on the Franck-Condon factors; secondly because the "missing" NO₂^{**} molecules can dissociate towards the NO X v=0 channel, which is not detected in our experiment.

Consequently, we will suppose that the NO₂^{*} species is the major precursor of the observed NO X v=1 fragment below the threshold. The thermal energy in the NO₂^{*} molecules is rotational. As a consequence, the difference (table 3) between the average available energy, $\langle E_{avl} \rangle$ and the NO rotational energy $\langle E_{rot} \rangle$, is small (<100 cm⁻¹) and decreases steeply as the energy deficit goes up.

Considering the energy balance, this difference is an estimation of the sum of two positive quantities: (i) the average total translational energy $\langle E_T^{\text{tot}} \rangle$ and (ii) the average internal energy of the O fragment $\langle E_{int}^0 \rangle$. The low values indicate very small fragment velocities ($v_{NO} \ll 200 \text{ m/s}$) as well as small internal excitations of the ground state O atoms produced in coincidence with the NO X v=1 fragments. The ground configuration of the O atom (O ^{3}P) is split into three spin-orbit components, ${}^{3}P_{J}$, with J=2, 1and 0 of respective energies 0, 159 and 227 cm^{-1} [25]. The average internal energy of the O fragment will thus vary between 0 and 227 cm^{-1} , depending on the relative populations of the three spin-orbit levels, with the noticeable value of 81 cm^{-1} corresponding to a statistical distribution according to the degeneracies.

Thus we can conclude that the O fragment formed in the photodissociation of NO₂ below its NO X v=1+O ³P threshold is preferentially in the lowest ground state (³P₂). The evaluation of the oxygen atom internal energy, when the fragmentation takes place with positive energy excess, needs the measurement of the translational energy for each quantum state of the NO fragment. This will be discussed in section 4.

4. Velocity measurements

The NO fragment velocity has been obtained following to the procedure described previously [5]. The time-of-flight spectra of the ionized NO fragment have been recorded at different excitation wavelengths (360, 355 and 348 nm) and for a series of quantum states of the fragment (fig. 7). The stateselective determination of the NO translational energy could thus allow us to directly derive the internal energy of the O fragment and to observe for the first time a correlation between fragments formed in coincidende near the threshold.

Considering the energy balance of the photodissociation for the channel leading to the well-defined state of NO X $\Pi_{1/2} v = 1$ (electronic energy $E_{el}^{NO} = 0$; rotational energy E_{vol}^{NO} ; vibrational energy $E_{vib}^{NO} =$ one quantum):



Fig. 7. Time-of-flight spectra (——) and TOF simulations (…) of several NO X $\Pi_{1/2} v=1$ fragments formed at 348 nm. The fragments were ionized through the O_{11} branch of the NO($D v=0 \leftarrow X v=1$) two-photon transition, with a singly magic polarization arrangement (ϵ_D parallel to the TOF spectrometer axis *S*; ϵ_P tilted to the magic angle). The time-to-velocity scale is 2.36 ns for 100 m/s.

$$\bar{E}_{exc} = h\nu + \bar{E}_{th}^{NO_2} - (D_0 + E_{vib}^{NO})
= E_{rot}^{NO} + \bar{E}_T^{NO} + \bar{E}_T^{O} + \bar{E}_{int}^{O},$$
(4)

where D_0 is the dissociation energy, \bar{E}_{1h}^{NO2} is the average thermal energy in the NO₂ parent molecules which dissociate to the NO X $\Pi_{1/2} v = 1 + O$ ³P dissociation channel, \bar{E}_{exc} is the average excess energy for the considered channel, \bar{E}_{int}^{O} is the average internal energy of the O atoms formed simultaneously with the NO fragment in the considered quantum state, \bar{E}_{T}^{NO} and \bar{E}_{T}^{O} are respectively the average translational energies of the NO and O fragments.

Using the measured average translational energy (\bar{E}_T^{NO}) in the center-of-mass frame for the quantum states of NO, the average total kinetic energy $(\bar{E}_T^{iot} = \bar{E}_T^{NO} + \bar{E}_T^O)$ has been obtained from the con-



Fig. 8. Plots of (total translational energy+rotational energy of NO) versus (rotational energy of NO) for each probed rotational state of NO X $\Pi_{1/2} v=1$, formed at (a) 360, (b) 355, (c) 348 nm. The vertical scale can be compared (cq. (5)) to the average available energy minus the different internal energies deposited in the O fragment.

servation of the linear momentum. Fig. 8 shows for each NO X $\Pi_{1/2} v=1$, J probed fragment the value of $\bar{E}_{T}^{tot} + E_{rot}^{NO}$ as a function of E_{rot}^{NO} , which has been calculated using the formula of ref. [25] and the rotational constants from ref. [24] ($B_{v=1}=1.6785$ cm⁻¹). From eq. (4), it can be shown that:

$$\bar{E}_{\rm T}^{\rm tot} + E_{\rm rot}^{\rm NO} = (E_{\rm exc} + \bar{E}_{\rm th}^{\rm NO_2} - \bar{E}_{\rm int}^{\rm O}),$$
 (5)

where E_{exc} is defined as $h\nu - (D_0 + E_{\text{vib}}^{\text{NO}})$.

In order to evaluate the internal energy deposited in the O fragment, the variability of the average thermal energy $\bar{E}_{th}^{NO_2}$ has to be examined.

Two kinds of NO₂ molecules can dissociate in this region: NO^{*}₂ and NO^{**}₂ with an average internal energy of 305 and 1055 cm⁻¹ respectively. Considering the procedure used to simulate the ion current shapes and the high precision of the velocity measurement method, precise information about the thermal energy content of the parent molecule is expected.

In fact, the velocity distribution for the simulation of the TOF spectra is assumed monokinetic and the derived velocity value is the most probable one. As the thermal energy difference between the two kinds of parent molecules is 750 cm⁻¹, the velocity difference between fragments due to NO2 and NO2*, at an excess energy of $E_{\rm exc} \approx 1700 \, {\rm cm^{-1}}$ for instance, should be typically 300 m/s for $J \approx 20\hbar$. The velocity measurement allows us to distinguish between NO fragments due to NO^{**}₂ or NO^{*}₂ molecules. One can even detect the intermediate case (NO from either NO^{*}₂ or NO_2^{**}), since it should occur with a large increase of the apparatus function during the simulation process. No anomalous broadening of the apparatus function width has been seen during the simulation. We can thus conclude that the observed fragments have been formed exclusively from NO₂^{*} or from NO^{**} dissociation.

With this in mind and considering the results reported in fig. 8, it can be shown that:

(i) No NO fragment exclusively formed from NO₂^{**} molecules could be detected, since for this species, the sum $E_{\text{exc}} + \langle E_{\text{th}}^{**} \rangle$ would reach about 2700 cm⁻¹.

(ii) Rotationally excited NO fragments $(J \ge 20\hbar)$ cannot be formed from cold NO^{*}₂ molecules. However, since these fragments represent the main part of the products, one can consider them as dissociation products of NO^{*}₂ molecules with an average thermal energy of $\frac{3}{2}kT$. The velocity measurements are then indicative of a dissociation process leading mainly to the ${}^{3}P_{2}$ ground state of the O atom, however compatible with a statistical weighted distribution.

(iii) Concerning the less excited NO fragments $(J \leq 20\hbar)$, their formation appears to be compatible with an O atom cofragment in any of its states, with however a propensity for the ground state $({}^{3}P_{2})$ if these fragments are originated from rotationally cold NO₂^{*} molecules.

These conclusions can be derived for either of the three experiments carried out above the dissociation threshold, showing a general trend of the system to yield O atoms with the ${}^{3}P_{2}$ internal state as a favoured channel.

5. Angular properties of the NO fragment velocity and angular momentum

The REMPI TOF MS technique has allowed us to observe the vectorial anisotropy of the fragments in the laboratory frame, i.e. the relative orientation of the three vectors involved in the photodissociation process: μ the transition moment in the parent molecule, v the velocity and J the angular momentum of the NO fragment.

5.1. Rotational anisotropy in the NO fragment

Like any optical process, resonance enhanced multiphoton ionization is sensitive to the angular distribution of the probe molecule angular moment [6,26]. If the ionization transition in the REMPI process can be made very probable [6], the ion signal depends only on the intensity of the first two-photon step. Under such conditions, it can be shown that the intensity of a photofragment probe process can be expressed as:

$$\mathscr{J} \propto \mathscr{J}_0[1 + q_2 \mathscr{A} P_2(\cos \chi)], \tag{6}$$

where \mathscr{A} is the alignment parameter defined as $\mathscr{A} = \langle 2P_2(\boldsymbol{\epsilon}_{\mathrm{D}}, \boldsymbol{J} \rangle, q_2 \text{ is a coefficient which depends}$ on the nature of the probe process, and specifically on the line and on the rotational branch of the probe transition, χ is the angle between the pump and probe laser polarisations $\boldsymbol{\epsilon}_{\mathrm{D}}$ and $\boldsymbol{\epsilon}_{\mathrm{P}}$, and $P_2(x)$ is the second-order Legendre polynomial. As P_2 vanishes when χ is fixed to the value of about 54.7° (magic angle), we can perform REMPI spectra free of any alignment effects. Thus the populations can be derived without any corrections. On the other hand, the comparison between photofragment REMPI spectra performed at different χ angles allows us to measure the alignment parameter from ratio intensities.

The intensity of a transition probing a J fragment and belonging to a (Br) branch can be expressed as a function of \mathcal{A} , χ , q_2 and S(Br) its Hönl-London factor:

$\mathscr{J}(\mathbf{Br}) \propto S(\mathbf{Br}) [1 + q_2 P_2(\cos \chi) \mathscr{A}].$

The intensity ratio of two lines probing the same fragment but belonging to different branches (1) and (2) is given by

$$R_{\rm P} = \frac{\mathscr{I}(1)}{\mathscr{I}(2)} = \frac{S(1)}{S(2)} \frac{1 + q_2(1)\mathscr{A}}{1 + q_2(2)\mathscr{A}} \tag{7}$$

when $\chi = 0$ (parallel polarizations geometry), and by

$$R_{\rm M} = \frac{\mathscr{J}(1)}{\mathscr{J}(2)} = \frac{S(1)}{S(2)}$$
(8)

when $\chi = 54.7^{\circ}$ (magic angle geometry).

Finally the *A* parameter is derived from the following relation:

$$\mathscr{A} = \frac{1 - \mathscr{R}}{\mathscr{R}q_2(2) - q_2(1)},\tag{9}$$

where \Re is defined as the ratio $\Re = R_P/R_M$. The values of the q_2 coefficient for the REMPI process have been already reported elsewhere [6].

The present method helps to avoid two important sources of error: (i) laser intensity variations which can be important when the lines wavelengths differ by several nanometers (the use of the *#*ratio allows us to work on the uncorrected spectra), (ii) the uncertainty in the Hönl-London factors.

We here report the first measurements of \mathscr{A} for the NO X $\Pi_{1/2} v = 1$ fragment, in the spectral region located above the NO X $v = 1 + O^{-3}P$ dissociation limit (fig. 9). The rotational anisotropy is weak ($\mathscr{A} \approx 0$), except for rotational levels close to the thermodynamical limit (J_{lim} ; eq. (3)), for which $\mathscr{A} \approx -0.2$. This appears clearly in the experiment carried out with the largest excess energy ($\lambda_{\text{D}} = 348$ nm, $E_{\text{exc}} \approx 1700$



Fig. 9. Rotational alignment parameters \mathscr{A} of some rotational states of the NO X $\prod_{1/2} v=1$ fragment formed at (a) 365, (b) 360, (c) 346 nm.

cm⁻¹), and to a lesser extent at $\lambda = 360$ nm, $E_{exc} = 700$ cm⁻¹. No rotational alignment could be seen at lower excess energies.

The values obtained are all negative, which indicates the propensity of the angular momentum of the fragment to be oriented perpendicularly to the polarization of the dissociation laser.

5.2. Translational anisotropy of the fragments

The translational properties of the NO fragment have been measured from the analysis of the TOF spectra. It has previously [5] been shown that the TOF spectra can be considered as a good image of the velocity profile of the neutral fragments, with an effective anisotropy parameter β_{eff} . We have more recently reported [6] calculations of β_{eff} as a function of the anisotropy parameters (A and β) and of \mathscr{C} , the v-J angular correlation coefficient. Among the interesting probe geometries encountered, a singly magic geometry (ϵ_D parallel to the spectrometer axis S and ϵ_P at the magic angle with respect to ϵ_D), for which the effective parameter β_{eff} coincides with β , has been seen. The values obtained (fig. 10a) for the anisotropy parameters measured at an excitation wavelength of 348 nm are close to 0.6 ± 0.1 , with a significant decrease observed for the rotationally excited fragments located in the vicinity of the thermodynamical limit. Measurements carried out at an excitation wavelength of 355 nm have yielded similar values of β . These results are in good agreement with those obtained for NO X v=1, by Busch and Wilson [16] in their photofragment spectroscopy experiments ($\beta=0.46$) performed at an excess energy of 1800 cm⁻¹ and by Kawasaki et al. [27] ($\beta=0.48$ at $E_{\rm exc}=1650$ cm⁻¹ without correction from the v-Jcorrelation effects).

5.3. Angular correlation between velocity and angular momentum in the NO fragment

The analysis of the TOF spectra of NO X $\Pi_{1/2} v = 1$ fragments recorded in different pump-probe geometries has allowed us to measure the first-order v-Jcorrelation coefficients, defined as $\mathscr{C} = \langle P_2(v, J) \rangle$. A detailed description of the procedure used has been given elsewhere [6]. The \mathscr{C} values for the NO X v=1fragments have been found to be weak $(\mathscr{C} \approx -0.2 \pm 0.1)$ even at excess energies around 1700 cm^{-1} (fig. 10b). The negative values can be explained by a slight preferential orientation of v perpendicularly to J. At lower excess energies, the v-Jcorrelation tends to vanish: at $E_{\rm exc} = 1160 {\rm cm}^{-1}$, one gets $\mathscr{C} = -0.05 \pm 0.05$.



Fig. 10. Angular properties of the NO X $\Pi_{1/2} v = 1$, J fragments formed at 348 nm: (a) translational anisotropy parameters β , (b) first-order v-J correlation parameters \mathscr{C} .

In order to obtain information on the NO X v=0fragment, some one-color dissociation-probe experiments, in fully parallel geometry, have been carried out on this species. At $E_{\rm exc} \approx 1495 \, {\rm cm}^{-1}$, the comparison between profiles recorded on different rotational branches of the (D $v=0 \leftarrow X v=0$) transition, assuming rotational alignment values similar to those observed on the NO X v=1 species in the same excess energy region, yields for NO X $\Pi_{1/2} v = 0, J = 19\frac{1}{2}$: $\mathscr{C}_{v=0} = -0.15 \pm 0.05$. At higher excess energies $(E_{\rm exc} \approx 2500 \text{ cm}^{-1})$, the $\beta_{\rm eff}$ value obtained (1.45) for NO X $\Pi_{1/2}$, v=0 $J=18\frac{1}{2}$ (O₁₂ band head of the $(D v=1 \leftarrow X v=0)$ two-photon transition) is indicative of an important correlation effect. Using the β value proposed by Bush and Wilson ($\beta \approx 0.9$) at an excess energy of 3600 cm^{-1} [16], one gets, under the same assumption as made previously, $\mathscr{C}_{t=0} =$ -0.33 ± 0.05 . These results, reported in fig. 11, show an important increase of the correlation as soon as the excess energy reaches 1500 cm^{-1} .

6. Discussion

6.1. Lifetime and symmetry of the excited state

The absorption spectrum is generally considered as indicative of the dynamical properties of the excited state. However, in the case of NO_2 , the absence of spectral structures cannot be considered as an evidence for a fast relaxation process, since the absorption spectrum in the visible-near UV region is known to be congested [9].

The anisotropies detected in the fragments, the β parameter as well as \mathscr{A} the rotational alignment of NO,



Fig. 11. v-J correlation parameter for NO X $\prod_{1/2} v$, $J \approx 18\hbar$ fragments as a function of the excess energy. The curves are theoretical calculations (see text) assuming a v-J correlation lowering due to (a) v alone, (b) v and J together.

are more useful since they allow us to compare the lifetime of the photoexcited state with the average rotational period T of the parent excited molecules [16,28-30]. T can be estimated from the period of the thermal ground state, assuming that the effects of the geometry changes can be neglected. Following Busch and Wilson [16], one obtains $T \approx 2.0$ ps, which gives a rough upper limit of τ . A better limiting value requires more attention to the signs of the anisotropies.

Our results on both translational and rotational anisotropies appear coherent assuming the excitation towards a B_2 symmetry state in the C_{2y} configuration. Since the anisotropy parameters are connected to the angular correlations existing in the molecular frame between μ and v or between μ and J, their measurement yields information about the location of μ in the molecular frame, if the general trends of v and Jcan be estimated. The case of a triatomic molecule is very favourable, if the effects of the molecular rotational motion can be neglected, since the fragment velocity should lie in the molecular plane and the angular momentum of the diatomic fragment, generated by the recoil torque exerted between both fragments, should be normal to this plane (fig. 12). The negative values of the alignment parameter $(\mathscr{A} \approx -0.2)$ indicate that φ , the average angle between μ and ν , is nearly a right angle ($\phi \ge 54.7^{\circ}$) whereas the positive values of the β parameter $(\beta \approx 0.5)$ show that χ , the average angle between μ and J, should be small ($\chi \leq 54.7^{\circ}$). These results are only consistent with a predominant contribution of excited states formed through parallel type transitions, i.e. the transition moment μ lies in the molecular plane. Since the in-plane components of μ belong to the A1 and B2 symmetries and since the ground state $\mathbf{\tilde{X}}$ is of A_1 symmetry, it can be concluded that the photoexcited state is of A_1 or B_2 symmetry. However since no A_1 state is known in this region (vide infra), the predominant contribution comes from the



Fig. 12. Geometrical arrangement of μ , v and J in the molecular frame of a non-rotating NO₂ molecule.

 \tilde{A} ²B₂ state. This result already derived by Busch and Wilson [16] is clearly corroborated by our alignment measurement.

The comparison between the measured value of the alignment ($\mathcal{A} = -0.2$) for the rotationally excited NO fragments and its maximum value ($\mathcal{A}_{iim} = -0.4$), demonstrates the effects of the finite parent lifetime or the contribution of parent motion to the fragment rotation. However, assuming that the molecular lifetime is the only effect responsible for the lower alignment, we can deduce from the calculated curves of Nagata et al. [30] a maximum value τ_{max} of the lifetime expressed as a fraction of the average rotation period T. One gets $\tau_{max}/T \approx 0.8$; hence $\tau \leq 250$ fs. This value slightly higher than these found by Busch and Wilson (220 fs [16]), indicates a significant contribution of the parent rotation to the lowering of the alignment parameter. These intermediate lifetimes, between direct dissociation and vibrational predissociation time scales, should cause a significant line broadening (15 cm^{-1}) which, together with the rovibronic density lines in this region [31,32], could explain the structureless fragment production spectra.

6.2. Internal state of the fragments at excitation energies above the NO $X v = 1 + O^{3}P$ limit

The rotational energy of the NO X v=1 fragment represents an important part of the average available energy above the NO X v=1+O ³P channel. The spread of the NO distribution over the whole accessible domain of rotation as well as the time scale of the deduced lifetimes suggest to compare these experimental distributions (fig. 13) with those obtained from the statistical "prior" model [33], taking into account all internal and translational degrees of freedom in the fragments as well as the initial internal energy of the NO₂ molecules.

Fair agreement between experimental and calculated data is obtained separately for each spin-orbit component of NO, at excess energies above 500 cm^{-1} . This result supports the vibrational predissociation mechanism and is not in contradiction with our observations on the internal energy of the O atom. Indeed, the above calculation predicts relative populations of the O ${}^{3}P_{J}$ states close to their degeneracies (2J+1) and hence favours greatly the production of the O atom ground state ${}^{3}P_{2}$. The discrepancies, observed close to the threshold, at excess energies smaller than 500 cm^{-1} , between experiment and model should be ascribed to the influence of parent motion.

The spread of the rotational distributions (fig. 3) beyond the limit, due to the energy conservation (rotational tail), must be assigned to hot NO₂ molecules (thermal energy greater than $\langle E_{\rm th}^{\rm NO_2} \rangle$). However, the probability of observing rotationally excited fragments above this limit falls off very rapidly. This shows that there is no specificity for the excited NO₂ molecules to yield rotationally supported by the NO fragment velocity measurement, which shows that for each probed NO X, v=1 J+O channel the average initial internal energy of NO₂ was detected in the total energy balance.

Finally, the statistical features of the NO X v=1+Ochannel are clear when fig. 4 is examined. It can be seen that the energy flowing into NO rotation and total translational motion is respectively 40% and 60% of the average available energy, as soon as $E_{\rm exc}$ reaches 500 cm⁻¹, which is in accordance with the ratio of the corresponding degrees of freedom: 2/5 and 3/5. This could be considered as the result of an efficient energy redistribution among the different degrees of freedom of the system. This should be effective within a short time (250 fs), slightly greater than the vibrational period of the parent excited molecule (≈ 40 fs). It should be pointed out here that the nonvanishing anisotropies observed are not in disagreement with the statistical behavior. A typical statistical system, characterized by a long lifetime compared to its rotation period can however exhibit translational anisotropies since at least one component of the parent angular momentum is preserved [16,29,30].

6.3. Interfragment correlations

The population ratio of both spin-orbit components of NO X, showing clearly that the formation of the X $\Pi_{1/2}$ species is favored, can be considered as the consequence of the complex interfragment coupling occurring during the half-collision. Its effects are also apparent, when considering the internal states correlation between NO X $\Pi_{1/2}$ and O ${}^{3}P_{J}$. The dominant contribution of the ground state of the O fragment, which is compatible with a statistical popula-



Fig. 13. Comparison between experimental results (\bullet) and statistical prior model predictions (|) on the rotational distributions of the NO X v=1 fragments formed at different excess energies above the dissociation threshold. The normalizations have been performed separately on both spin-orbit components.

tion ratio, indicates either a propensity rule yielding the ground state or strong mixing effects leading to a statistically weighted final distribution.

6.4. Dissociation dynamics of thermal NO₂ species excited below the NO X $v = 1 + O^{-3}P$ dissociation limit

From the analysis of the NO REMPI spectra, it has been shown that the rotational energy, originally present in the NO₂ molecules, plays a major role in the dissociation process at low excess energies, and more dramatically under conditions of energy deficit. It will be shown that both of the observed characteristics of the fragments, the thermal rotational distribution of the NO fragment and the low recoil velocities, are connected. The former will appear as a consequence of the latter.

If one considers that the excess energy of the NO_2 excited molecules (fig. 14) flows mostly into the NO rotational energy, the dissociation will yield the most rotationally excited fragment compatible with the energy conservation. The remaining energy will thus be shared between the translational motion and the



Fig. 14. Illustration of the below threshold dissociation model, in which the main part of the available energy is transferred to the NO rotational energy.

internal energy of the O atom if the excited states are accessible. Since the shape of the NO_2 internal energy distribution (fig. 1) is mainly due to the exponential behavior (eq. (1)), the rotational distribution of the fragments predicted by this simple model would also exhibit an exponential behavior characterized by a thermal temperature. The prediction of this model, depicted in fig. 15, is in fair agreement with the experimental data, and corroborates our conclusions of



Fig. 15. Rotational distribution of the NO X $\Pi_{1/2}$ fragment obtained under conditions of default energy; predictions of a simple model assuming that the internal energy of the NO₂ molecules is totally transferred into the rotational motion of the diatomic fragment (see text).

section 3.3 concerning the respective roles of both NO₂^{*} and NO₂^{**} species. In addition, this model indicates low values of kinetic energies: about $\frac{1}{2}B_{\text{NO}}J$ for the NO X v=1, J fragment, compatible with the translational energy data.

In conclusion, it can be noticed that, below the threshold, the excited state of the molecules exhibits a large tendency to use its rotational motion as an energy supply in order to break the -N-O bond, when the vibronic energy is not sufficient to allow this. The process, responsible for the R-V energy transfer should be very efficient. It occurs, even when another channel exists, which does not need this transfer. As an example, when the molecule is excited below the NO X v+O threshold, the NO X v fragment is observed, whereas the NO X (v-1)+O channel is open with an excess energy of about 1800 cm⁻¹.

Two fundamental questions must thus be answered: (i) how the rotational energy of the excited molecules can be transferred to the vibronic motion in order to allow the dissociation, and (ii) how the important rotational energy and low kinetic energy of the fragments can be explained.

One of the first processes capable of inducing the R-V energy transfer could be the ν_2 degenerate vibrational motion (bending) of a linear electronic state. Indeed, in such a configuration, this vibrational motion is strongly coupled to the rotational motion around the O-O axis (a axis in the ground state of NO_2) in the bent conformation. However, the average energy initially located in this motion, ranging from 96 cm⁻¹ at threshold up to 270 cm⁻¹ for the excited molecules capable to dissociate, is not sufficient to make up the energy balance. On the contrary, a drastic change in the molecular geometry would provide an efficient way for the transfer to occur. For instance, a significant elongation of one of the N-O bonds would increase the moment of inertia I of the molecule, and thus lower a part of its rotational energy $(\frac{1}{2}(J^2/I + K^2/I'))$. Energy conservation would thus require that the remaining energy flows into the vibrational motion. This interpretation, already suggested in ref. [12], is supported by the low kinetic energies measured for the fragment formed below the threshold. The velocities derived from these values are smaller than the estimated velocity of the NO moiety in the thermal NO₂ molecule in rotation. Assuming that the molecules first distort to a well-defined geometry before dissociating and lead to fragments of kinetic energy only due to rotational motion of this critical configuration, one can infer much, concerning the geometry, from the velocity measurements. Whereas, in a pseudodiatomic model, the ground state geometry of the NO₂ molecule is equivalent to a NO-O diatomic, with a 1.95 Å bond length, the velocity data obtained at the threshold and at default energies of 400 cm⁻¹ yield 2.7 and 5.2 Å respectively for the bond length of the critical configuration. These values, like those of Quack et al. [34] (≥ 3 Å) in their statistical calculations, thus confirm the necessary deformation of the molecule in order to reach the dissociation continuum.

The remainder of the rotational energy of the excited NO_2 molecules, i.e. the rotational energy in the critical configuration, should, at least partially, be transferred to the NO fragment rotational motion. Assuming the same simple model as used previously i.e. deformation followed by bond breaking without

recoil torque (the motion of both fragments is thus only dependent on the rotational motion of the parent) one can establish a relationship between the dissociative geometry and both parent (J) and fragment *j* angular momentum [35]. From $\langle J^2 \rangle$ calculated for the NO^{*}₂ species and from $\langle j^2 \rangle$ obtained from the rotational distributions of fig. 15, we deduce (table 4) the NO-O bond length of the critical configuration, in two limiting cases: the T-shaped molecule ($L_{\rm T}$, fig. 16a) and the linear molecule ($L_{\rm lin}$, fig. 16b). These results indicate a general trend which allows us to conclude that a significant elongation of the molecule occurs before the bond breaking. The data obtained appear slightly larger than those obtained from the analysis of the velocities. This can be explained by the crude approximations used throughout this model, namely neglecting the influence of K.

6.5. Influence of the parent rotation of the NO fragment rotational motion

The rotational motion of the NO fragment can essentially be ascribed to two different sources:

Firstly, the recoil torque, exerted during the dissociation process, which produces the angular momentum of NO normally oriented with respect to the molecular axis (fig. 12).

Secondly, the rotational motion of the parent molecule, which induces a rotation of the NO moiety, even if no recoil torque occurs.

The parent thermal rotational motion $(\langle E_{rot}^{NO2} \rangle = 305 \text{ cm}^{-1})$, indeed, presents a wide range of rotational excitations (fig. 1). The probability distribution of the J quantum number has its maximum value at about $22\hbar$ and is still appreciable at excitations as high as $40\hbar$. Its effects on the fragment motion are largely observed at the threshold where no

torque occurs on NO. The rotational distributions (fig. 5) are useful in order to quantify the parent to fragment rotational transfer: $\sqrt{\langle J_{NO}^2 \rangle} \approx 9-10\hbar$, previously explained by the stretching of one of the N–O bonds.

This transfer also occurs at higher excess energies. Two features support this observation: the tails of the NO rotational distribution and the values of the v-Jcorrelation coefficient.

The rotational tails observed above the threshold, beyond the thermodynamical limit for the rotational energy of the NO fragment, are most easily seen at low excess energies, at which a small increase in the excess energy opens new dissociation channels corresponding to increasing rotational energy of the NO fragment. This is clear for the NO X v=1 fragment in our experiments (fig. 3) as well as in those reported by Welge et al. [17] at 355 nm on the NO X v=2 fragment. All of these tails exhibit a Boltzmann thermal behavior and can thus be explained by the same model as already used for distributions obtained below the threshold. In this case, the parent to fragment energy transfer does not participate in the N-O bond breaking (as observed below the threshold), but permits the formation of rotationally excited NO fragments. Whereas this extra energy could flow in any degree of freedom of the system, the efficiency of the transfer, supported by the internal dynamics of the excited NO₂ molecule, causes this energy to be transferred into the NO rotational motion.

A second proof of this transfer can be found in the analysis of the v-J correlation coefficients (%) measured above the threshold (fig. 11). As underlined previously [6], the specific case of the NO₂ molecule allows us to evaluate the in-plane component of the NO angular momentum. For this triatomic molecule, a strong perpendicular orientation of v with respect to J is expected (fig. 12, % = -0.5). The v-J corre-

Table 4

Rotational energy transfer in the dissociation below threshold; bond length of the critical configuration assuming a total (linear molecule; L_{lin}) or a partial (T-shaped molecule; L_{T}) energy transfer

$E_{\rm exc}~({\rm cm}^{-1})$	$\langle J^2 angle (\hbar^2)$	$\langle j^2 angle (\hbar^2)$	L _{lin} (Å)	$L_{\rm T}$ (Å)	
 15	470	99	2.1	1.5	
-203	710	93	2.6	1.9	
-417	1000	96	3.1	2.2	
- 627	1320	98	3.3	2.3	



Fig. 16. Influence of the NO₂ rotational motion (J) on the rotation of the NO fragment (j), (a) for a T-shaped molecule, (b) for a linear molecule.

lation, which is not sensitive to the lifetime of the excited molecule, can be lowered by two distinct sources: (i) the out-of-plane component of v induced by the parent rotational motion, (ii) the in-plane component of J induced by the rotational transfer discussed above.

The curve (a) of fig. 11 has been obtained, assuming that the first process (i) alone is involved in the lowering of the *v*-J correlation. The velocity is calculated in the pseudo diatomic model, with a molecular shape similar to the ground state geometry. The impact of this velocity decreases when the excess energy goes up, since it becomes thus negligible compared to the recoil velocity. Although the general trends of the & coefficient are correctly reproduced, the (a) curve has to be shifted in order to fit the experimental data. A good agreement is obtained (curve (b)) in fig. 11, when taking into account an in-plane component (J_{ν}) of J (ii) equal to $6\hbar$ over the whole considered energy range. This value confirms the occurrence of the parent to fragment rotational transfer, all over the investigated dissociation range as well as for any rotational excitation range in the fragment.

6.6. Nature of the dissociation process

Numerous studies have been carried out in order to investigate the excited \tilde{A} state of the NO₂ molecule. Below the dissociation threshold, an important question was that of the lifetime. Anomalous lifetimes (microsecond scale) were detected [36]. This effect (Douglas effect) was interpreted as resulting from the strong vibronic coupling between the \tilde{A}^2B_2 excited state and the vibrationally excited levels $|\tilde{X}, v^{\dagger}\rangle$ of the ground state [37,38]. Jackels and Davidson [39] have shown that these states are coupled by the b_2 vibrational motion through a process similar to the Jahn–Teller effect. They should be considered as two different parts of a single electronic state of ²A' symmetry (according to the C_s symmetry group) connected by a conical intersection. The classical C_{2v} potential curves should thus be considered as sections of this A' surface; the minimum of the B₂ potential curve being actually a saddle point on the A' surface.

Concerning the dissociation process, theoretical investigations [40,41] seem to indicate that the \tilde{A} B₂ state is correlated to the NO $X+O^{1}D$ dissociation limit ($\approx 40850 \text{ cm}^{-1}$ [20]), whereas the ground state is known to lead to the first limit: NO $X + O^{3}P$. The dissociation of the photoexcited \tilde{A}^2B_2 state is thus necessarily indirect. This point is confirmed by the order of magnitude of the estimated lifetime (250 fs). The molecule is predissociated either through an electronic predissociation towards a repulsive state correlated to the NO $X + O^{3}P$ limit or through an internal conversion followed by a vibrational predissociation process. The last assumption requires an efficient conversion process, which seems unlikely in a small molecule with a low number of degrees of freedom and hence low densities of states. This problem can, however, be solved by considering the strong \tilde{A} B₂- \tilde{X} A₁ coupling. Since both states belong to the C_{2v} state A', the system can flow from \tilde{A} to \tilde{X} through the conical intersection, more efficiently than in a classical non radiative transition. In such a case, the statistical features observed in the rotational distribution of NO can be interpreted as a consequence of the decay of $|\tilde{X}, v^{\dagger}\rangle$, the highly vibrationally excited levels of \tilde{X} . The non-statistical distributions observed by Welge et al. [17,18] in the vibrational motion of the NO fragment would be thus explained by the specific dynamics of the $\tilde{A} B_2 \rightarrow \tilde{X} A_1$ radiationless transition. Finally, the $R \rightarrow V$ transfer as well as the significant distortions occurring below the threshold, can be assigned to the same $|\tilde{\mathbf{X}}, v^{\dagger}\rangle$ state. This assumption is supported by the chaotic behavior suspected by several authors for the ground state in this energy region [31,32]. The resulting state, mixture of several levels with different internal characteristics, could be the source of the observed behavior.

7. Conclusion

Data have been presented about the photodissociation of NO₂ around its NO X v=1+O ³P threshold. The determination of the internal energy of the NO fragment by REMPI is performed in the same measurement as its translational energy by TOF mass spectrometry. Laboratory frame state-selective anisotropies are inferred from the intensity analysis of the 2+1 REMPI spectra (rotational alignment \mathscr{A}) and from the TOF shape of the ionized fragments (anisotropy parameter β) as well as the *v-J* angular correlation existing in the molecular frame.

The new results reported in this paper can be summarized as follows:

The lifetime (≤ 250 fs) and the symmetry (\tilde{A}^2B_2) of the excited NO₂ state have been estimated from the anisotropies.

The statistical rotational behavior found experimentally above the threshold suggests that we only observe the vibrational predissociation of the highly vibrationally excited levels of the ground state of NO₂.

The rotational energy of the parent molecule has been shown to play a dominant role in the dissociation process under energy deficit conditions. A simple model, assuming a drastic change in the molecular geometry, explains the efficient $R \rightarrow V$ transfer observed, the thermal rotational distribution and the low kinetic energy (<100 cm⁻¹) in the NO fragment.

Finally, first measurements of a correlation between quantum states of fragments formed in coincidence at low excess energies ($<1700 \text{ cm}^{-1}$) have been reported.

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