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Photodestruction of NO_2^- using time resolved multicoincidence detection photofragment spectroscopy

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Abstract

We present an experiment on the photodestruction of the NO_2^- anion at 266 nm. We have quantified the competition between photodetachment and photodissociation and have identified the nature of the photodissociation process from the photofragment angular distribution. This study involves a novel technique; time resolved multicoincident detection photofragment spectroscopy. A three-dimensional double exposure CCD camera is employed. The system provides the position (x, y) and the relative arrival time (t)of all fragments. In the case of photodissociation events, NO and O⁻ fragments are detected for each event. The detection of multiple events per laser shot is made possible by using center-of-mass selection. © 2004 Elsevier B.V. All rights reserved.

1. Introduction

Molecular dynamics has witnessed large progress because of detector developments in the last decades. The study of dissociation, ionization and detachment processes requires special detectors, since optical spectra become devoid of characteristic structures. A multihit detector with the capability of sorting the fragments resulting from multiple dissociation events per laser shot is the ideal tool for such studies by allowing the largest possible counting rate when using relatively low repetition rate lasers. The ideal three-dimensional (x, y, t) detector measures the arrival time and the position of a large number of particles with good time and position resolution and no recovery times. In the last two decades several time- and position-sensitive detectors have been developed, which were more or less suitable for multiparticle detection, but rarely for multievent detection. Around 1982, de Bruijn and Los [1] presented a timeand position-sensitive detector suitable for detection in coincidence of two particles. Each particle is detected on a microchannelplate (MCP) equipped with separate

multianode employing capacitive charge division for position determination. Such a position-sensitive element can only handle one fragment at the time. Charge division-based detectors (resistive anodes, wedge-andstrip anodes, delay line anodes) have the advantage of good temporal and spatial resolution, but they do not allow simultaneous detection. Alternatively, multielement segmented anodes were made for multihit detection, often with a limited spatial resolution or dynamic range [2-4]. Recently, a number of groups have used delay line anodes together with microchannelplates. These systems combine high spatial resolution with a relatively short dead time for multihit detection (few nanoseconds) [5,6]. Zajfman and co-workers have introduced a hybrid system by combining the microchannelplate detector with a phosphor screen, such that each arriving particle gives a short flash. These short flashes are recorded on a high spatial resolution CCD camera, whereas with the aid of a beam splitter, a number of photomultiplier tubes (PMTs) also observe the same flashes. By working close to saturation, the PMT obtains a high time-resolution with crude position resolution. The advantage is that the combination of PMT and CCD camera allows multihit detection with good time- and position-resolution and essentially no

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dead time. The drawback of this setup is the limitation in the maximum number of particles that can be detected [7]. A similar approach for the time measurement has been made by drawing a number of gold strips using vapor deposition on the back of the MCPs to function as independent timing devices [8].

A new concept in the three-dimensional (3D) detection was introduced by Strasser et al. [9]. Inside the vacuum, they used a combination of a MCP and a phosphor screen. The back of the phosphor screen was imaged onto two correlated cameras, taking two images of the same event with a fixed time delay. The timing determination uses the fact that the time profile of the phosphorescence is highly reproducible. From the intensity ratio of the each spot in each of the two images, the arrival time of the particles can be retrieved. This system allows multihit 3D detection with no dead time and very good time and position resolution. The limitation of this system is in the short dynamic range of the timing measurement (limited by the characteristic decay time of the phosphor screen). Instead of employing two CCD cameras, the same principle was used in a single double exposure CCD camera (LaVision, modified Imager3 VGA). The camera retrieves the (x, y) coordinates of the spots (\sim 80 µm resolution) and the arrival time of the particles (~ 1 ns resolution) [10].

We present the use of this detection system in a fast beam experiment on the photodestruction of NO_2^- . In general, the photodestruction of molecular anions has not been studied in detail because of experimental difficulties. Photodestruction is the sum of two competing processes: photodetachment and photodissociation. With sufficiently energetic photons, or in weakly bound systems, also dissociative photodetachment is possible [11,12]. By using the same MCP detector for the detection of all molecular products, i.e., fragments from photodissociation as well as neutral molecular products from photodetachment, absolute branching ratios can be determined. The branching between the different processes is important under many conditions in very dilute plasmas, such as our own atmosphere. The products of photodetachment, free electrons and neutrals have different reactivity and affect the plasma in a very different way than the photodissociation products. The photodestruction of NO_2^- plays a role as intermediate in the chemistry of the D-region of the ionosphere [13]. Nitrogen dioxide has a very large electron affinity EA ~ 2.275 eV [14]. The anion and the neutral molecule have similar N–O internuclear separations (1.15 A for NO_2^- and 1.19 Å for NO_2) [14]. The attached electron induces a small bond length contraction. The bond angle for the ground state NO₂⁻ (X¹A₁), $\theta = 117.5^{\circ}$ is smaller than the bond angle of the neutral ground state $\theta = 135.1^{\circ}$ [15]. The dissociation energy is ~4 eV [19], which is more than that of the neutral parent molecule by about 0.8 eV. Most experiments have concentrated

on the photodetachment channel for this anion. When photodestruction was studied, no distinction was made between photodissociation and photodetachment. A number of experiments have concentrated on the existence of possible peroxide isomers with energies close to that of the anion ground state.

In this paper, we present two new aspects of our experiment. First, we describe in detail the use of a double exposure CCD camera in a fast beam experiment for the coincidence detection of fragments resulting from multiple dissociation events. From the (x, y, t) data the full 3D dissociation kinematics is deduced. In the second part, we present new results on the photodestruction of NO₂⁻. Here, we determine for the first time the competition between the two destruction channels at a photon energy where both pathways are fully open. Moreover, we provide kinetic energy release distribution and photofragment anisotropy information for the photodissociation channel.

2. Method

2.1. Experimental setup

The nitrogen dioxide anion, NO_2^- , is produced in a hollow cathode discharge ion source filled with O_2 and N_2 gas in proportions of 5:1. The discharge is maintained at 600 V and 20 mA. The negative species are extracted at 5 kV and the NO_2^- ions are mass selected by a Wien filter. The continuous molecular ion beam of NO_2^- is introduced into a fast beam setup (see Fig. 1). By



Fig. 1. (a) Scheme of the experimental setup. A continuous molecular ion beam of NO_2^- is crossed with a 25 Hz laser pulse (266 nm). Photodissociation and photodetachment occur leading to NO_2 , NO and O^- fragments. The use of the beam dump is optional as well as the use of deflection plates after the laser interaction region. The Imager CCD camera measures the position (*x*, *y*) and the arrival time *t* of the fragments on the detector. (b) Schematic of the dissociation process. The direction of dissociation is indicated by \vec{v} .

means of four deflection plates the beam is guided through the apertures of the apparatus. Two Einzel lenses are used to focus the beam through the exit aperture of the ion source region and to reduce the radial size of the beam in the region of interaction with the laser. The NO₂⁻ anion beam is intersected at 90° by ultraviolet laser radiation. The laser system used for this experiment was a 50 Hz Spectra Physics Nd-YAG laser. The 532 nm output of the Nd-YAG laser is frequency doubled in a BBO non-linear crystal and the energy of the UV laser pulse, measured after the interaction region is ~10 mJ. The polarization of the laser is chosen parallel to the detector surface, along the *y*-axis (see Fig. 1). The two processes we investigate are photodetachment and photodissociation of NO₂⁻

$$NO_2^- + hv \to NO_2 + e^- \tag{1}$$

$$\rightarrow NO + O^{-}$$
 (2)

The photodetachment signal consists of neutral NO₂ molecules flying in the same direction as the initial NO_2^- beam. The photodissociation signal, on the other hand, consists of NO and O- fragments flying away from the parent beam direction with velocities related to the kinetic energy released in the dissociation process. Other possible dissociation channels such as $N + O_2^-$ are energetically closed. After a time-of-flight of ~ 8.47 µs the fragments reach the detector consisting of two MCPs and a P46 phosphor screen. For a good signal-to-noise ratio, the detector is gated with respect to the firing of the laser. The voltage on the front of the MCP is raised to the optimum value (2 kV difference over the MCP stack) when the laser induced fragments are expected to arrive. The detection gate is open for 400 ns. Between laser shots, the voltage on the front of the MCP is decreased by 800 V to a value that does not permit particle detection.

Outside the vacuum system a so-called 3D double exposure CCD camera (LaVision, modified Imager3 VGA) records images of the phosphor screen. The principle of the 3D camera is described in detail elsewhere [9,10]. In brief, the camera records the image of the phosphor screen and the intensity of the spots corresponding to individual particles. Due to the fast interline transfer of the CCD chip, the camera is capable of taking two successive images of the same phosphor decay for each single laser pulse. Subsequently, the arrival time can be found for each particle from the ratio of intensities measured in both images [16]. The detection system retrieves the (x, y) coordinates of the spots with $\sim 80 \ \mu m$ resolution and the arrival time of the particles with ~ 1 ns resolution. This information is used to reconstruct the orientation of the molecule at the moment of dissociation and to calculate the kinetic energy released (KER) in the process

$$\operatorname{KER} = \frac{E_0}{L^2} \frac{m_1 m_2}{\left(m_1 + m_2\right)^2} \left(D^2 + v_0^2 \Delta t^2\right) \left(1 + 2\frac{m_1 - m_2}{m_1 + m_2} \frac{v_0 \Delta t}{L}\right),\tag{3}$$

$$\theta = \arctan \frac{\sqrt{(\Delta y)^2 + (v_0 \Delta t)^2}}{\Delta x}, \quad \Phi = \arctan \frac{v_0 \Delta t}{\Delta y}, \quad (4)$$

where m_1 and m_2 are the masses of the two fragments NO and O⁻, $D = \sqrt{(\Delta x)^2 + (\Delta y)^2}$ is the distance between them on the detector, Δt is the arrival time difference of the fragments, L = 1.25 m is the distance between the reaction region and the detector, E_0 is the kinetic energy of the fast beam (5 keV), and v_0 is the translational velocity of the NO₂⁻ anions (~1.5×10⁵ m/s). The angle θ is defined with respect to the laser polarization axis (see Fig. 1(b)).

The camera provides the master clock of the experiment and it controls the firing of the laser and the gating of the MCPs. The acquisition rate is limited by the camera to 25 Hz.

2.2. Multicoincident detection

This detection system providing (x, y, t) coordinates of the particles allows detection of multiple dissociation events. The data is taken and analyzed for each laser shot separately. The maximum number of fragments detected per laser shot is in principle only limited by the finite resolution of the camera chip, 640×480 pixels and the size of the spots, 3×3 pixels. In case of a coincident measurement, when the fragments must be correlated as coming from the same parent molecule, the maximum number of particles that can be resolved depends strongly on the experimental conditions, namely the size of the parent molecular beam.

The correlation is performed by center-of-mass selection. In the case of a homonuclear diatomic molecule, the two fragments have identical mass and the center-ofmass calculation is straightforward. The calculation is performed for each combination of two particles. Only those pairs having their center-of-mass inside a confined region defined by the size of the parent beam are considered true coincidences. In principle, the narrower the molecular beam is, the higher is the number of dissociation events that can be resolved. In this particular experiment where the fragments have different mass (30 and 16 amu) the nature of the fragments must be identified prior to center-of-mass calculation.

During a coincident measurement, we can detect all photodissociation products, neutrals and ions. For each laser shot up to 10 fragments are recorded. This number is determined by experimental conditions (molecular beam intensity, laser intensity). We avoided the use of any electric field after the interaction with the laser such that the negatively charged fragments can travel undisturbed towards the detector. We placed a circular beam dump ($\phi = 1$ mm) after the laser interaction region to stop the parent beam, which otherwise would saturate the detector in the central region. We detect only fragments resulting from photodissociation processes which have enough kinetic energy (>0.5 eV) and a sufficient velocity component in the (x, y) plane to escape the beam dump. The raw (x, y) data, as it is recorded by the camera over 180,000 laser shots at a photon energy of 4.66 eV is shown in Fig. 2. In the middle of the detector there are no counts due to the presence of the beam



Fig. 2. Photodissociation signal of NO_2^- at 266 nm. The two rings D_1 and D_2 indicate the presence of two different masses. The ratio D_2/D_1 is 1.85, a value in good agreement with a mass ratio of 30/16. The central arrow shows the direction of the laser polarization.

dump. Around the shadow of the beam dump, two main rings can be distinguished, the outer limit being shown by the two circles D_1 ($\phi = 300$ pixels) and D_2 ($\phi = 560$ pixels). The fragments detected inside the D_1 circle are mostly fragments having the high mass (NO fragments), while those detected outside this ring must have a lighter mass (O fragments).

We can also determine which one of the fragments carries the charge. For this purpose, we have applied an electric field after the laser interaction region to assure that the only fragments that reach the detector are neutral species. We do not use any beam dump since the ionic parent beam is also deflected. The raw (x, y) data integrated over 30,000 laser shots at a photon energy of 4.66 eV is shown in Fig. 3. The histograms of particles coordinates show a narrow strong peak in the middle of the image, corresponding to the NO₂ photodetachment signal. The size of the peak, $\phi \simeq 30$ pixels, indicates the size of the parent beam on the detector $D_{\rm CM}$ ($\phi \simeq 3$ mm). Most of the fragments resulting from a dissociation process and having a velocity component in the plane of the detector are confined inside the ring D_1 . From the size of the ring, it is clear that neutral fragment has a higher mass than the ionic fragment. We conclude that the charge is taken by the oxygen fragment and we identify the photodissociation products as NO and O⁻ fragments.

For a coincidence measurement, we analyze the images taken at each laser shot separately. Fig. 4 is a selected example of an image taken during a single laser shot. Ten particles are detected in this image. From the (x, y) position of the fragments, we assign them as being



Fig. 3. Photodestruction signal of NO_2^- at 266 nm. Only the neutral fragments are detected. The central peak represents NO_2 photodetachment signal while the rest of the counts, distributed around the central peak are NO fragments from photodissociation. From the *x* and *y* histograms, the branching between the two processes can be determined. The upper right plot shows the estimated radial distribution of the neutral NO calculated with respect to the center of the parent beam.



Fig. 4. Sample of the images taken during laser shots. Ten fragments are detected; from their position we identify the nature of each fragment: NO (\bullet) and O⁻ (\blacksquare). For each pair of NO and O⁻ the center of mass is calculated. We plot only those center of mass that lie inside the inner ring D_{CM} . Uncorrelated fragments are represented by (\bigcirc).

NO, if they lie inside D_1 ring, or as O⁻ fragments if they are found in between the D_1 ring and the D_2 ring. Once the mass of the fragment is know, we calculate the center-of-mass position for every pair of NO and O⁻. If the center-of-mass lies inside the D_{CM} ring, the pair is a true coincidence and their center-of-mass is plotted. Out of 10 fragments detected, eight were successfully correlated, while two of them were not. The two uncorrelated fragments are very likely to originate from a dissociation event of which the other fragment has not been detected. It is important to stress here that since the detection efficiency of the MCPs is ~50%, only in 25% of the cases both fragments are detected. In two-body break-up studies, the possibility to detect unlimited number of particles increases the detection rate considerably.

In Fig. 5, we present the center-of-mass distributions for two data sets taken at very different count rates, one corresponding to a low molecular beam intensity and another one corresponding to a high molecular beam intensity. The data has been taken in coincidence by allowing all fragments, ions and neutrals to reach the detector (similar to the data presented in Fig. 2) while blocking the central beam with the flag. From the histogram of number of particles detected per laser shot, the low count rate data set (see Fig. 5(a)) is characterized by a detection of mostly two particles per laser shot



Fig. 5. Center-of-mass determination for two different data sets: (a) low ion beam intensity; (b) high ion beam intensity. The position histograms of the center-of-mass for each combination of NO and O^- particles are shown. The fragments resulting from the same molecule appear in the central peaks.

while for the high count rate data set (see Fig. 5(b)) up to 10 particles are detected. The mass of each fragment is identified and the center-of-mass position for all combinations of NO and O⁻ fragments are calculated. The results are plotted in x_{CM} and y_{CM} histograms. The central peaks are a direct measure of the size of the molecular parent beam at the detector. In Fig. 5(b), the width of the center-of-mass peak is larger than the one seen in Fig. 5(a). This reflects the fact the size of the ion source exit aperture that defines the maximum size of the parent beam was increased from 400 to 1150 µm. The shoulders visible around 180 and 450 pixels in Fig. 5(b) are due to false coincidences obtained by calculating the center-of-mass for pairs of NO and O⁻ resulting from different parent molecules. These false coincidences are easily avoided by center-of-mass selection. The condition for a coincidence to be real is that both x_{CM} and y_{CM} belong to the center-of-mass peak.

Of course, it is possible that fragments resulting from different molecules give the correct center-of-mass position. These events cannot be differentiated from the real events and they contribute to the background. We estimate $\sim 5\%$ of the pairs are accidental coincidences. In the case of low count rate data less than 2% of the events are accidental coincidences. It is obvious that the narrower the center-of-mass peak is, the higher is the accuracy in the determination of real coincidences.

In Fig. 6, we compare the kinetic energy release spectra for the two data sets. From the low beam intensity data set, we analyze only those laser shots where two particles are detected. We compare this KER spectrum with the one obtained from analyzing the high beam intensity data set by selecting only the laser shots where at least eight particles are detected. The two spectra show no qualitative difference proving that by allowing higher count rate, the quality of the data is preserved. The cut-off around 500 meV is due to the flag



Fig. 6. Kinetic energy release spectrum. No significant difference can be observed by analyzing separately laser shots with maximum two particles detected (black curve) and laser shots contributing with more than eight particles (grey curve).



Fig. 7. Histograms of *x*-coordinates of the fragments before correction (grey curve) and after the 10 pixels correction of the O^- *x*-coordinates (black curve).

 $(r \sim 85 \text{ pixels})$ which intercepts also fragments with small recoil velocities.

For coincidence detection, we avoided the use of any electric field. Since the O- fragment is negatively charged, its trajectory is slightly perturbed by residual fields and the Earth's magnetic field. The observed displacement along the x-axis is approximately 10 pixels (~1 mm on the phosphor screen) and 15 pixels along y. Since most of the O⁻ fragments are isolated from the NO fragments, it is possible to correct the coordinates of the O⁻. For illustration, in Fig. 7, we present two histograms of all x-coordinates of all fragments detected during a coincidence measurement (data set presented in Fig. 2), before and after correction. The two inner peaks correspond to the NO signal, while the outer peaks are O⁻ fragments. It can be seen that, the two projected rings have their center displaced by ~ 10 pixels. The KER distribution is generated after the correction of the (x, y) coordinates for the O⁻.

3. Photodestruction of NO₂⁻

3.1. Branching between photodetachment and photodissociation

The photodestruction of the NO_2^- takes place via photodetachment and photodissociation processes. For measuring the branching between the two processes we detect only the neutral NO₂ molecules and NO fragments as it is shown in Fig. 3. In order to have an accurate estimate of the branching, we lowered the molecular beam intensity such that mostly one fragment is detected per laser shot (92% of the cases). This is necessary since the photodetachment signal is confined in a much smaller region on the detector than the photodissociation signal. By lowering the count rate to one fragment, we avoid overlapped photodetachment counts that cannot be resolved. This experiment is nearly background free and all signal detected is related to the presence of the laser. The particles detected in the center of the detector, confined in a circular region ($\phi = 30$ pixels) are neutral NO₂ from photodetachment process, while the particles distributed around it are NO fragments from the photodissociation process. We found that 7.5% of the excited NO_2^- decay via photodissociation. This result is the most important new physical result of this work. We note, that the photon energy (4.66 eV) is not so much larger than the binding energy (3.96 eV). The nature of the electronic excited state is unknown other than that the transition occurs along a parallel transition (see below). In view of the limited excess energy, photoexcitation may well take place via quasi-bound states with a certain vibrational lifetime, which may then undergo enhanced photodetachment. We note that this experiment does not provide the information whether the photodetachment signal is due to a direct photodetachment process or the result of photoexcitation of the anion to an excited state that undergoes autodetachment. A photoelectron energy spectrum would be more revealing for this distinction than the present experiment, which only measures the neutral fragment yield. The photoelectron spectrum is sensitive to the changing overlap between the anion ground state and the anion excited state with the different neutral product states. In the case of photodetachment of the excited molecular state, at higher photon energies and larger recoil velocities, the photodissociation branching may well be significantly larger.

3.2. Kinetic energy release spectrum and angular distribution

In Fig. 6, we present the kinetic energy release spectrum for the photodissociation of NO_2^- induced by a 266 nm (4.66 eV) photon. The kinetic energy release for each dissociation event is calculated according to Eq. (3). Since the dissociation energy is ~4 eV [19], assuming that no energy is stored as internal energy (neither in the parent molecule nor in the photodissociation products), the expected KER is ~0.66 eV. The experimental data shows a large distribution of KER centered on 0.8 eV. The conservation of energy during dissociation of NO_2^- , taking into account the internal energies reads

$$E_{\text{int}}^{\text{NO}_{2}^{-}} + hv - D_0 = E_{\text{avl}} = E_{\text{int}} + \text{KER}.$$
(5)

Eq. (5) expresses that the final observed kinetic energy release (KER) of the fragments increases with the internal energy of the anion and with photon energy. The

KER decreases if the molecular (NO) and atomic (O⁻) fragments end up internally excited. In the molecular fragment, energy can be stored in the form of rotational and vibrational energy. As will be described below, energy stored in fragment rotation influences the photofragment anisotropy. During the recoil, if the force is along the NO bond direction in the bent NO₂⁻ geometry, a significant fraction of available energy has to end up in rotation of the NO fragment. Another reason for rotational excitation is a possible large change in binding angle in going from the molecular ground state to the dissociative state. Vibrational energy may be added by the recoil force or by the contraction or extension of the NO-bond in going from the NO₂⁻ anion to the dissociation products.

We note that the coincidence KER spectrum of Fig. 6 lacks signal below 500 meV. As mentioned before, this is due to the presence of the beam dump. The broad radial distribution of the NO fragments detected in the absence of the beam dump (see Fig. 3) suggests that most events will escape the flag and reach the detector. Still, there are events appearing at radial distances smaller than 85 pixels (KER_{pos} < 500 meV), that in a coincidence detection are stopped by the beam dump. These low KER values suggest that the NO fragment can convert a big part of the energy from the dissociation process into internal energy. Busch and Wilson [17] developed a model to predict the energy partitioning in the photodissociation of neutral NO₂. Taking into account the smaller bond angle of NO₂⁻, we find that 24% of the E_{avl} would appear as rotational energy of the NO fragment and 76% as KER.

It is more important to realize that surprisingly large KER values are observed in the spectrum, which implies contribution of rovibrationally excited NO₂⁻ anions in the negative ion beam, indicating a non-thermal process in the ion source. The absence of clear structure in the KER spectrum, makes it impossible to say anything about the internal energy distribution in the initial ion beam. It is noteworthy that no autodetachment signal was observed in this experiment. The autodetachment channel would point at a part of the ion beam with a significant internal energy of more than 2.5 eV. It has been mentioned in the literature [18,19] that in the hollow cathode discharge ion source filled with O_2 and N_2 , vibrationally excited states may also be produced. In these reports, an onset of the photodetachment signal was observed at about 1.8 eV, indicating internal energies exceeding 0.5 eV. Our observation of KER values around 1 eV are in agreement with even larger internal energies as we expect some 25% of the excess energy at least to end up in NO rotation.

The product angular distribution (see Fig. 8) is described by

$$I(\theta) \sim [1 + \beta P_2(\cos \theta)], \tag{6}$$



Fig. 8. The angular distribution of the fragments in the detector plane with respect to the laser polarization (see Eq. (4)). Fitting the histogram (thick curve) the anisotropy parameter $\beta = 1.4$ is obtained.

where θ is angle defined by the orientation of the molecule during dissociation with respect to the laser polarization and $P_2(\cos\theta)$ is the second Legendre polynomial. The histogram of the angular orientations of the fragments shows a large anisotropy parameter $\beta = 1.4 \pm 0.1$. Clearly, the electronic transition is a parallel transition. The predictive value of the anisotropy parameter in triatomics is smaller than in the case of diatomic molecules. For diatomics, a parallel transition yields an anisotropy parameter of $\beta = 2$. If the excited state has a finite lifetime larger than the rotational period, the anisotropy parameter reduces to $\beta = 1/2$. In triatomics, other phenomena influence the resulting anisotropy parameter. For molecules with a bent geometry, such as NO_2^- , the dipole moment is not parallel to the bond that breaks. In the case of axial recoil, implying a repulsive force along the bond direction, the maximum anisotropy parameter is reduced to

$$\beta \sim 2P_2(\cos \alpha),$$
 (7)

with α the angle between the bond axis and the transition dipole moment. For a bond angle of 135° as in the case of neutral NO₂, this yields an anisotropy parameter of 1.54, close to the value reported in [21]. We note that this does not imply that the NO fragment is without rotational excitation. In fact, axial recoil, as defined above, results in rotational excitation of the fragment depending on the molecular geometry. For the present case with an equilibrium angle of the NO₂⁻ of 117.5°, an anisotropy parameter results of, $\beta = 1.2$, which is in fact smaller than the measured value in this work. In the case that the transition occurs between states with different equilibrium geometries, in particular the equilibrium angle, the excited state molecule will be formed with a considerable amount of bending excitation. The competition between the torque related to the bending motion and the axial recoil force determines the final anisotropy. The effect of the torque may be expressed in an angle ψ , which weighs the radial kinetic energy release. The anisotropy parameter is written as $\beta = 2P_2[\cos(\alpha + \psi)]$ [20]. If a transition takes place towards a state with a more linear geometry than the ground state geometry, the combination of forces along the rupturing bond and in radial direction may in fact lead to an increase in the anisotropy parameter. In our case our anisotropy parameter would imply a value of $\psi = -5^{\circ}$. In general, however, large torques result in a further reduction of the anisotropy parameter. In fact, the shape of the excited state potential determines the lifetime of the excited state and the distribution of the forces over bending and recoil motion. This result in a correlation between the fragment rotational energy and the observed anisotropy parameter. As in diatomics, a lifetime of the excited complex, that is comparable to the rotational period of the parent anion, also reduces the anisotropy parameter.

In our experiments, we find that the kinetic energy release spectrum contains dominantly values from 500 meV to more than 1 eV. The magnitude of the observed KER values implies the necessity of considerable excitation energy in the parent anion. It is unlikely that most of the available energy ends up in rotational energy of the NO fragment. The magnitude of the anisotropy parameter indicates a short lifetime of the excited state. Finally, the value of $\beta = 1.4$ suggests that the excited anion state may have a more linear geometry than its parent anion state. It is of interest to note that the possible presence of an autodetachment channel in the excited state may affect the anisotropy parameter. For example, long-lived anionic excited states, which would reduce the anisotropy parameter, may more prone to the autodetachment process and do not contribute to the photofragment channel.

The anion of nitrogen dioxide is a species that is important in the upper atmosphere. This molecular anion is more stable than its parent neutral, an unusual situation. The excess electron is captured in a bonding orbital. In view of its stability, photodestruction will be an important channel for removal of these species in the ionosphere. To the best of our knowledge the photodestruction of the NO_2^- has not been determined in much detail. This work provides the branching of the two pathways (7.5% photodissociation versus 92.5% photodetachment). As important, this research shows that coincident detection of molecular fragments from photodissociation in order to obtain high-resolution KER information is possible also when using relatively low repetition rate lasers. The combination of a detector that can determine the arrival position and arrival time of many particles and a setup with well-defined beam properties ensures this possibility.

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