# Velocity-map ion-imaging of the NO fragment from the UV-photodissociation of nitrosobenzene

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Received 27th February 2003, Accepted 2nd May 2003 First published as an Advance Article on the web 27th May 2003

The velocity and angular distribution of NO fragments produced by UV photodissociation of nitrosobenzene have been determined by velocity-map ion-imaging. Excitation of the S<sub>2</sub>-state by irradiation into the peak of the first UV absorption band at 290.5 nm leads to a completely isotropic velocity distribution with Gaussian shape. The average kinetic energy in both fragments correlates with the rotational energy of the NO fragment and increases from 6% of the excess energy for j = 6.5 to 11% for j = 29.5. A similar isotropic distribution albeit with larger average velocity is observed when the ionization laser at 226 nm is also used for photodissociation, corresponding to excitation into a higher electronic state S<sub>n</sub> ( $n \ge 3$ ) of nitrosobenzene. It is concluded that photodissociation occurs on a timescale much slower than rotation of the parent molecule, and after redistribution of the excess energy into the vibrational degrees of freedom.

## 1. Introduction

Many nitroso compounds are prone to efficient photodissociation leading to the comparatively stable radical NO. The mechanism of this photodissociation has been studied extensively for the classes of aliphatic C-nitroso compounds R-NO and nitrites RO-NO.<sup>1-23</sup> Detailed investigations of the product state distributions of the rotational and vibrational states of NO by LIF or REMPI as well as measurements of the alignment and the Doppler profiles have been performed. The results indicate that the dissociation follows either of two mechanisms. The statistical mechanism, which is observed for most aliphatic nitroso compounds, leads to a quasi thermal population and velocity distribution with little or no anisotropy. The other mechanism involves very fast dissociation on a repulsive potential surface and is frequently observed with the aliphatic nitrites. In all these aliphatic compounds the photodissociation is initiated by excitation into the first excited singlet state which is of  $n\pi^*$ -character.

Nitrosobenzene is so far the only aromatic nitroso compound whose photodissociation has been studied in a similar fashion.<sup>24–29</sup> In this case the excitation energy of the first n $\pi$ \*-transition is not sufficient to break the C–NO bond. The energy gap between  $S_1$  and  $S_2$  is very large, but excitation to  $S_2$  does not lead to fluorescence but to efficient fragmentation. The origin of the  $S_0 \rightarrow S_2$  transition could be resolved in an argon matrix<sup>30</sup> and a supersonic jet,<sup>25</sup> and the homogeneous linewidth of this transition indicates a lifetime of 60–90 fs for the excited state.

Although this fact might point to a very fast dissociation reaction, LIF measurements showed a quasi thermal population of the rotational and vibrational levels of NO.<sup>26,27</sup> The Gaussian shape of the Doppler profiles is consistent with an isotropic and thermal velocity distribution. However, a deviation from an isotropic distribution can be observed in the Doppler profiles only for specific arrangements of the beam and polarization directions. The critical dip in the lineshape could easily be overlooked or be washed out when the distribution of velocities is very broad. Such a broad distribution was indeed proposed by a study in which the angularly resolved

time-of-flight distributions of both fragments were measured.<sup>28</sup> This study came to the conclusion that the velocity distribution is anisotropic with an anisotropy parameter  $\beta = -0.64$ . A negative anisotropy parameter indicates fast dissociation and preferred perpendicular arrangement of the transition dipole and the recoil velocities. It was rationalized by the assumption that the initially excited state has  $n\pi^*$ -character.

Since our investigations lead us to a different conclusion, namely that photodissociation is slow compared to rotation of the parent molecule, we decided to apply the technique of velocity-map ion-imaging<sup>31,32</sup> to the photodissociation of nitrosobenzene. This method measures a 2D projection of the 3D fragment velocity distribution. If this distribution is cylindrically symmetric around an axis parallel to the image plane, the 3D distribution can be reconstructed by Abel inversion. During the ten years since the development of this method it has been applied to the study of many fragment atoms and some diatomic fragment molecules. The NO fragment from the photodissociation of NO<sub>2</sub> has been monitored in an early study,<sup>33</sup> but larger nitroso compounds have not been studied by this technique until very recently.

The photophysical and photochemical processes exploited in our experiment are indicated in the level diagram in Fig. 1. Nitrosobenzene is excited into one of its UV bands leading to population of the states  $S_2$  and above. These states are well above the dissociation threshold of  $E_{\rm D} = 18955 \text{ cm}^{-1} \text{ }^{34}$  and the fragment radicals NO and phenyl will be created with high efficiency. A second laser ionizes the NO fragment via 1+1 **REMPI** resonant with the  $A^2\Sigma^+$   $(v' = 0) \leftarrow X^2\Pi_{1/2,3/2}$ (v'' = 0) transition. These ions are accelerated towards a position-sensitive detector (multichannel plate, MCP) by a static electric field. The ions impinging on the detector create a projected image of the velocity distribution which is monitored by a CCD camera interfaced to a computer. Analysis of these data allows the reconstruction of the complete three-dimensional velocity distribution since it is axially symmetric around the polarization axis of the photolysis laser.

We have built an apparatus for the measurement of these ion images and report here first results. In order to assess the performance of the new machine we give data for the well

Phys. Chem. Chem. Phys., 2003, 5, 2799–2806 2799



Fig. 1 Energy level scheme for the photodissociation of nitrosobenzene and the ionization of NO by 1+1 REMPI.  $E_D = 18\,955$  cm<sup>-1</sup> marks the dissociation energy of the C–N-bond of nitrosobenzene.  $D_0$  and  $D_1$  indicate the two lowest doublet states of the phenyl radical.

known photodissociation of  $NO_2$  for comparison. Application of the method to the photodissociation of nitrosobenzene from  $S_2$  shows convincingly that the velocity distribution is completely isotropic and has a Gaussian shape.

## 2. Experimental

### 2.1. Chemicals

Nitrosobenzene (98%) was obtained from Fluka and purified by vacuum sublimation at 65 °C. Nitrogen monoxide and nitrogen dioxide (99.5 + %) were obtained from Aldrich and used without further purification.

#### 2.2. Vacuum chambers and molecular beam

The vacuum apparatus consists of a sequence of three chambers which serve for the generation of the cold supersonic beam of educt molecules, the photofragmentation and ionization of the fragments, and the field free flight region for the ions, respectively. The main components of the setup are shown schematically in Fig. 2 (not to scale). The supersonic beam was created by expansion of helium through a pulsed nozzle (General valve No. 9, 0.5 mm orifice) into a cylindrical stainless steel chamber of 28 cm diameter pumped by the combination of an oil diffusion pump (DN 250 ISO-K,  $3000 \text{ l s}^{-1}$ , Leybold), a roots pump (RUVAC WAU 251, 253 m<sup>3</sup> h<sup>-1</sup> , Leybold) and a rotary pump (TRIVAC D40B, 40  $m^3 \ h^{-1},$ . Levbold) to a final pressure of  $10^{-6}$  mbar. Nitrosobenzene was seeded into the beam by heating it to 60 °C in an oven adjacent to the nozzle. Beams seeded with NO or NO<sub>2</sub> were produced by expanding through the nozzle a mixture with helium (5: 95) prepared in a steel cylinder. The molecular beam is collimated by a skimmer with an opening of 1 mm diameter before it enters the ionization chamber. The skimmer was made by



Fig. 2 Schematic setup of the ion imaging apparatus.

electrodeposition of copper onto a stainless steel mold as described in 25. The shape of the skimmer was originally designed as light baffle for optimized stray light rejection.<sup>35</sup> For the beam skimmer we used a radius of 30 mm and an opening of 1 mm diameter, resulting in an asymptotic aperture angle of 25°.

#### 2.3. Ion imaging apparatus

The ion imaging apparatus was constructed in our laboratory in analogy to a similar setup published by Wrede et al.<sup>36</sup> in 2001 and is described here for the first time. The molecular beam enters the photolysis and ionization chamber through a hole in the repeller electrode. This chamber is pumped by a turbomolecular pump (EXT250H, BOC Edwards) to a pressure of 10<sup>-7</sup> mbar. Halfway between repeller and extractor electrode the molecular beam is intersected perpendicularly by two counterpropagating, linearly polarized dye laser beams. One laser photolyses the sample molecules, the second stateselectively ionizes the NO fragments by 1+1 REMPI. Both lasers are focused into the region of overlap with the molecular beam by quartz lenses (f = 400 mm, Linos Photonics). The ions are accelerated by a static electric field between repeller and lens electrode towards the field free drift region of 500 mm length, which is pumped by an additional turbomolecular pump (EXT70, BOC Edwards). After passing the drift region the ions impinge upon the position sensitive detector which consists of two multichannel plates (Proxitronic), coupled to a phosphor screen (P43, 40 mm active diameter). These images are recorded by a CCD camera (Imager 3, 1280 × 1024 pixel, LaVision) through an objective (Schneider-Kreuznach XENON 25/0,95) and processed on a PC with the DAVIS 6.0 Software. In a typical experiment about 5000 laser shots were accumulated. If the ionization laser also dissociates the parent molecules a background image caused by the ionization laser alone was accumulated for the same number of shots and subtracted from the data image. If the probability of ionization of the fragments is independent from the relative orientation of the fragment velocity and the polarization of the ionizing laser beam, the recorded ion-images are projections of the three dimensional velocity distribution of the neutral fragments.

In addition to the ion imaging measurements, 1 + 1 REMPI spectra of the NO fragments can be recorded with the same apparatus. For this purpose the CCD camera was replaced by a photomultiplier (Thorn Emi RFIB289) and the probe laser was scanned through the rotational transitions of interest of the NO fragments while the photolysis wavelength was fixed. The integral emission of the phosphor screen was detected by the photomultiplier and processed on a gated boxcar integrator (SRS 245, Stanford Research Systems) and a PC.

The optimum voltage ratios for velocity mapping were determined by simulations with the Simion 6.0 program<sup>37</sup>

and the geometry of the electrodes as input. The best focussing was found for the ratio of 1:2:2.45 of the voltages at the lens electrode  $(V_1)$ , the extractor electrode  $(V_e)$ , and the repeller electrode  $(V_r)$ , with the electrode at the beginning of the drift region at ground potential. The total voltage was adjusted so that the image filled a large fraction of the MCP detector. For NO<sub>2</sub> a voltage of  $V_r = 1200$  V was used, for nitrosobenzene a voltage of  $V_r = 2000$  V. Calibration was based on simulations of trajectories of NO fragments with different recoil energies and different voltages Vr. Plots of the simulated image diameter versus the initial recoil velocities are well fitted by straight lines for fixed repeller voltages. This fact was used to translate pixel positions into velocities. The velocity distribution for the photodissociation of NO<sub>2</sub> obtained in this way is in very good agreement with that published previously<sup>33</sup> (see results section). We also observe the expected linear relationship when the experimentally determined image diameter is plotted versus the inverse of the square root of the acceleration voltage.

#### 2.4. Laser and data acquisition

The two dve lasers (Lambda Physik LPD 3002 and FL 3002) used for the photolysis of nitrosobenzene/NO2 and the ionization of the NO fragments were pumped by a single XeCl excimer laser (Lambda Physik Lextra 200). The probe laser was optically delayed by about 10 ns. The typical laser pulse energy was about 20-40 µJ for both lasers. The polarisation direction of the photolysis laser was rotated parallel to the vertical axis of the detector surface by a double-Fresnel rhomb (Halle). The ionization laser was polarized parallel to the photolysis laser and operated in the spectral region of the  $A^{2}\Sigma^{+}$   $(v' = 0) \leftarrow X$  ${}^{2}\Pi_{1/2,3/2}$  (v'' = 0) transition of NO near 226 nm by frequency doubling the output of the coumarin 120 dye with a BBO I crystal. The fundamental wavelength was removed by a set of 4 Pellin-Broca prisms or a filter (Schott UG 5). For the photolysis of NO<sub>2</sub> the second laser was tuned to 360 nm. Nitrosobenzene was studied at the photolysis wavelengths 290.5 nm and 226 nm. In the first case the photolysis laser was operated with the dye rhodamine 6G and frequency doubled with a KDP crystal. In the second case, a single laser was used for photolysis and ionization of the fragments.

The nozzle, lasers and CCD camera were synchronized with suitable delays by a home built trigger unit. The repetition rate was kept below  $\approx 2$  Hz to avoid an increase of the pressure in the ion drift chamber above  $10^{-6}$  mbar. Typically 5000 laser shots were taken for each image, and the CCD camera read out after every shot.

#### 2.5. Data analysis

The image produced on the CCD camera is a two dimensional data array B(x,z), where the axis z is parallel to the polarization of the photolysis laser, and x is perpendicular to it. This image is the projection of a three dimensional distribution function F(x,y,z) onto the (x,z)-plane. If this distribution function is cylindrically symmetric, *i.e.* if it depends only on the distance  $r = \sqrt{x^2 + y^2}$  from the z-axis, it can be regained from the projection by the inverse Abel transform <sup>38</sup>

$$Q(r,z) = F(r,0,z) = -\frac{1}{\pi} \int_{r}^{\infty} \frac{\partial B}{\partial x} \frac{\mathrm{d}x}{\sqrt{x^2 - r^2}} \tag{1}$$

Since this transform does not depend on the value of the *z*-coordinate, it can be performed for each line in B(x,z) separately. Several algorithms have been proposed for the numerical implementation of this integral transform.<sup>39</sup> We have chosen the matrix method as described in 39 and apply the transform to each line of the image separately.

For the analysis of the Abel inverted image Q(r,z) in terms of a velocity distribution and an angular distribution, we found it convenient to transform to another distribution function defined by

$$C(\nu,\zeta) = 2\pi\nu^2 Q(\nu\sqrt{1-\zeta^2},\nu\zeta)$$
<sup>(2)</sup>

In this expression,  $v = \sqrt{r^2 + z^2}$  is the absolute value of the velocity, and  $\zeta = z/v = \cos \theta$  measures the angle between the velocity vector and the *z*-axis. The velocity distribution G(v) and the angular distribution  $H(\zeta)$  are obtained by the integrations

$$G(v) = \int_{-1}^{1} \mathrm{d}\zeta \ C(v,\zeta) \tag{3}$$

$$H(\zeta) = \int_0^\infty \mathrm{d}\nu \, C(\nu, \zeta) \tag{4}$$

which correspond to summing over all rows or all columns, respectively, in the matrix  $C(v,\zeta)$ . A photodissociation initiated by a one-photon absorption is usually described well by a distribution function of the form:<sup>40–42</sup>

$$P(\nu,\theta) = \frac{1}{2}p(\nu)[1 + \beta \mathscr{P}_2(\cos\theta)], \qquad (5)$$

where  $\mathcal{P}_2$  is the second Legendre polynomial. This distribution function is normalized according to<sup>†</sup>

$$1 = \int_0^{\pi} \sin \theta \, \mathrm{d}\theta \int_0^{\infty} \mathrm{d}v \, P(v, \theta) \tag{6}$$

Analysis of an ion image resulting from this distribution with the method outlined above yields

$$G(v) = p(v) \tag{7}$$

$$H(\zeta) = 1 + \beta \mathscr{P}_2(\zeta) \tag{8}$$

This separates the velocity distribution from the angular distribution. A fit of a parabola to  $H(\zeta)$  yields the anisotropy parameter  $\beta$ .

### 3. Results and analysis

#### 3.1. NO from the photodissociation of NO<sub>2</sub>

The photodissociation of NO<sub>2</sub> has been studied by a number of groups with various experimental methods. The angular distribution of the NO and O fragments and the partitioning of the excess energy onto the states of the NO products are known for many different photolysis wavelengths.<sup>42–48</sup> Early ion imaging experiments by Houston *et al.* show a strongly anisotropic distribution of the NO fragments (anisotropy parameter  $\beta = 1.46 \pm 0.20$ ) formed in the photodissociation at 355 nm.<sup>33,49</sup> Because of this high anisotropy and the large number of former measurements, nitrogen dioxide is well suited for testing our newly built ion imaging apparatus.

Fig. 3a shows the velocity-map ion-image of NO formed in the  ${}^{2}\Pi_{1/2}$  (v = 0, j = 13.5) state by photodissociation of NO<sub>2</sub> at 360 nm. This corresponds to an excess energy of  $\approx 2650$ cm<sup>-1</sup> above the threshold for dissociation.<sup>50</sup> The fragments were ionized by 1 + 1 REMPI resonant with the P<sub>21</sub>,Q<sub>11</sub> transition. The image size is  $360 \times 360$  pixel. Most of the intensity lies along the vertical axis parallel to the polarization direction of the photolysis laser. This indicates a positive correlation between the transition dipole moment  $\vec{\mu}$  of the parent molecule and the velocity vector  $\vec{v}$  of the NO fragments. Most of the fragments recoil along  $\vec{\mu}$ , *i.e.* the dissociation process has predominantly parallel character. A large anisotropy of this kind can only be observed if the time constant for photodissociation is

 $<sup>\</sup>dagger$  Note that in contrast to the usual convention for integration in spherical coordinates the factor  $v^2$  is already included in the distribution function.



**Fig. 3** (a) Ion velocity image of NO fragments from the photolysis of NO<sub>2</sub> at 360 nm. A frequency doubled dye laser tuned to the P<sub>21</sub>,Q<sub>11</sub>(13.5) line of the  $A^{2}\Sigma^{+}(v'=0) \leftarrow X^{2}\Pi_{1/2}(v''=0)$  transition of NO at 226 nm was used as probe beam. (b) Abel inverted image of (a). (c) Transformation of the Abel inverted image to the distribution function  $C(v,\zeta)$  in the orthogonal coordinates v and  $\zeta = \cos \theta$ . For details see text.

short compared to the rotational period of the parent molecule. Based on their data of alignment and anisotropy from TOF measurements, Mons and Dimicoli have previously estimated an upper limit of 250 fs for the lifetime of the excited <sup>2</sup>B<sub>2</sub> state.<sup>45</sup>

The velocity distribution Q(r,z) obtained by Abel inversion of these data is shown in Fig. 3b. This image corresponds to a cut through the three-dimensional velocity distribution along the polarization axis of the photolysis laser. Transformation of these data according to eqn. (2) leads to the representation shown in Fig. 3c, in which the velocity and the angular coordinates are orthogonal. Summation of all columns yields the velocity distribution integrated over all angles, as shown in the upper part of Fig. 4. This velocity distribution peaks at 740 m s<sup>-1</sup> corresponding to a kinetic energy of 687 cm<sup>-1</sup> of the NO fragments. This peak velocity is close to the value of 729 m s<sup>-1</sup> found by Houston *et al.*<sup>33</sup> by ion imaging of NO in the state  ${}^{2}\Pi_{1/2}(v = 0, j = 25.5)$  formed by photodissociation of NO<sub>2</sub> at 355 nm. The full width at half maximum of the velocity distribution in Fig. 4 is  $\approx 125$  m s<sup>-1</sup>, which is narrower



**Fig. 4** Velocity distribution p(v) and angular distribution  $H(\cos \theta)$  for the NO fragment from the photolysis of NO<sub>2</sub>, calculated from the Abel inverted image of Fig. 3.

than the value of  $\approx 230 \text{ m s}^{-1}$  that appears in the work by Houston *et al.*.

Summation of all rows of  $C(v,\zeta)$  in Fig. 3c in the velocity range from  $v \approx 650-850$  m s<sup>-1</sup> results in the angular distribution shown in the lower part of Fig. 4. The latter is well fitted by a parabola with the anisotropy parameter  $\beta = 1.35 \pm 0.05$ . The values for the mean velocity, the width of the distribution, and the anisotropy measured with our new apparatus are in good agreement with values reported from earlier experiments.<sup>33,42,44</sup>

#### 3.2. Ion imaging of NO from the photolysis of nitrosobenzene

Cooling of molecules seeded into a supersonic beam can lead to the formation of Van der Waals dimers or higher aggregates. The tendency for dimer formation increases with the polarity and polarizability of the molecules and their partial pressure in the expansion. For example, with t-butylnitrite a sharp onset of cluster formation has been reported when the fraction of this compound in the gas mixture exceeds 5%.8 The rotational distribution of the NO fragments produced from photolysis of these clusters is quite different from that of the monomers. Drucker and Flade<sup>51</sup> have reported the vapor pressure of solid nitrosobenzene in the temperature range 25-66 °C. We have measured the absorbance of the absorption band at 212 nm in this temperature range in vapor cells with 1 cm and 0.2 cm length, with some solid nitrosobenzene at the bottom. For this absorption band, which peaks at 218 nm in mixtures of ethanol and n-heptane, an extinction coefficient of  $\varepsilon = 6480 \ 1 \ M^{-1} \ cm^{-1}$  and a constant shape has been reported independent of the solvent composition.<sup>52</sup> In contrast to this, the first two UV absorption bands show a strong solvent dependence. Assuming the same extinction coefficient for the vapor phase, we obtain vapor pressures of 10 mbar at 50 °C, 24 mbar at 60 °C, and 49 mbar at 69 °C, in good agreement with the early measurements of Drucker and Flade.<sup>51</sup> In our ion-imaging measurements we



Fig. 5 1+1 REMPI spectrum of NO fragments from the 290.5 nm photolysis of nitrosobenzene. The spectrum was measured in the ion imaging apparatus by integration of the whole image area while tuning the probe laser.

used a stagnation pressure of 2500 mbar and observed no change in the ion images in the temperature range of 50–60 °C. Hence we believe that our data are not affected by cluster formation.

In our previous measurements of Doppler profiles of the NO fragments from the photodissociation of nitrosobenzene we used the photolysis wavelengths 290, 266, and 255 nm. The two latter wavelengths excite into parts of the absorption spectrum with higher absorption cross section and hence lead to larger signals. However, these wavelengths fall already into the second UV absorption band, *i.e.* the initially prepared excited state is  $S_3$  or even higher. Since we are mainly interested in the mechanism of photodissociation following excitation into the  $S_2$ -state, we have concentrated on the photolysis wavelength of 290 nm in the present study.

Fig. 5 shows part of the 1 + 1 REMPI spectrum of the NO fragments produced by 290.5 nm photodissociation of jetcooled nitrosobenzene. It was measured by integration of the whole ion signal on the phosphor screen by a photomultiplier while the ionization laser was scanned. After assignment of the transitions several well isolated lines with reasonable intensity in the range of j = 6.5-29.5 were chosen for the ion imaging experiments.

The wavelength of the ionization laser near 226 nm falls close to a minimum of the absorption spectrum between the second and the third UV band. Nevertheless we observed that this laser produced a considerable amount of fragments by itself. The experiment with the photolysis laser tuned to 290.5 nm resonant with the maximum of the first UV band hence yields an ion image which has contributions from photodissociation with photons of 226 and 290.5 nm. These two components were separated by subtraction of an ion image measured with the same number of laser shots but only the ionization laser at 226 nm operating. In all experiments with 290.5 nm photolysis the intensity of the ionization laser was attenuated to such an extent that the contribution by this laser alone was small compared to the signal due to both lasers. Two ion images, representing the velocity distributions of NO in the state  ${}^{2}\Pi_{1/2}(v = 0, j = 14.5)$  produced by photodissociation at 226 and 290.5 nm, are shown in the upper and lower part of Fig. 6.

Both images appear to be completely isotropic, with the highest intensity in the center. The projections of these images onto the horizontal and vertical axes, corresponding to the summation of all rows or all columns in the data array, are very well fitted by Gaussians. Fig. 7 shows these projections and the Gaussian fits for a photolysis experiment at 290.5 nm. Six of these measurements yielded the average width of



**Fig. 6** (a) Ion velocity image of NO fragments from the photolysis of nitrosobenzene at 226 nm. A frequency doubled dye laser tuned to the P<sub>21</sub>,Q<sub>11</sub>(14.5) line of the  $A^2\Sigma^+(\nu'=0) \leftarrow X^2\Pi_{1/2}$  ( $\nu''=0$ ) transition was used simultaneously as photolysis and probe beam. (b) Ion velocity image of NO fragments from the photolysis of nitrosobenzene at 290.5 nm. The probe laser was tuned to the same transition as in (a).

 $486 \pm 12 \text{ m s}^{-1}$ . (The small difference in the widths for the analysis of the columns and the rows can partly be accounted for by the fact that the ionization volume extends more into the horizontal direction, *i.e.* the propagation direction of the laser beams.) The corresponding analysis for six images of the photolysis at 226 nm yields the average width of  $594 \pm 20$  m  $s^{-1}$ . It was checked that not only the total projection but also individual horizontal lines of each image were fitted by a Gaussian with the same width. In this special situation the image is proportional to its own Abel inverse, as shown in the appendix. Making use of this fact we have integrated the images directly and obtained the velocity and angular distributions shown in Fig. 8. This avoids artifacts, which are produced by the matrix method (and other methods too) of Abel inversion due to amplified noise, in particular near the symmetry axis of the velocity distribution. As a consequence of the Gaussian nature of the projection onto one coordinate, the total velocity distribution is a Maxwell Boltzmann distribution with  $v_{\rm rms} = 840 \text{ m s}^{-1}$  for photolysis at 290.5 nm and  $v_{\rm rms} = 1030 \text{ m s}^{-1}$  for photolysis at 226 nm. The angular distributions found for both photolysis wavelengths are almost horizontal lines. The anisotropy parameters obtained from the fits are close to zero. The simulated shape for an angular distribution with  $\beta = -0.64$  is shown for comparison.

Measurements of ion images have been performed for several rotational states of the NO fragment in the  ${}^{2}\Pi_{1/2}(\nu = 0)$ state. In all cases an isotropic and Gaussian velocity distribution was found. The mean velocities, average kinetic energies



**Fig. 7** Integration of Fig. 6b along all columns (a), and along all rows (b). This corresponds to the distribution of the velocity component perpendicular (a) or parallel (b) to the polarization vector of the photolysis light. Both curves are well fitted by Gaussians.

of the fragments, the fraction of excess energy converted to kinetic energy, and the anisotropy parameters are collected in Table 1. Apparently the average kinetic energy of the NO fragment increases with the rotational energy.



**Fig. 8** (a) Normalized velocity distribution p(v) and (b) angular distribution  $H(\cos \theta)$  of NO fragments in the state j = 14.5 from the photolysis of nitrosobenzene at 290.5 nm (left scale) and 226 nm (right scale). The simulated angular distribution for an anisotropy parameter  $\beta = -0.64$  is also shown (left scale).

**Table 1** Analysis of ion imaging data for nitrosobenzene. Mean velocities  $v_{\rm rms}$  of NO fragments obtained by analyzing the rows and the columns of the data matrix were used to calculate the average translational energies ( $E_{\rm tr}$ ) of the NO and the phenyl fragments. The last two columns present the fraction of the excess energy converted to kinetic energy and the anisotropy parameter  $\beta$ . Errors are the standard deviations from six measurements

$\lambda_{ m ph}/$ nm	J	$\frac{v_{\rm rms}({ m NO})}{{ m m~s}^{-1}}$	$\frac{E_{\rm tr}({ m NO})}{{ m cm}^{-1}}$	$\frac{E_{\rm tr}({\rm phenyl})}{{ m cm}^{-1}}$	$E_{\rm tr}/E_{\rm exc}$	β
225.96	14.5	$1029\pm35$	$1328\pm90$	$517\pm35$	0.073	+0.05
290.50	6.5	$753\pm20$	$711 \pm 37$	$277 \pm 15$	0.064	+0.00
290.50	12.5	$873\pm24$	$956\pm52$	$372\pm20$	0.086	+0.01
290.50	14.5	$842\pm21$	$889\pm44$	$346 \pm 17$	0.080	-0.04
290.50	22.5	$943\pm27$	$1114\pm 64$	$433\pm25$	0.100	-0.05
290.50	29.5	$995\pm32$	$1243\pm80$	$483\pm31$	0.112	+0.03

## 4. Discussion

## 4.1. NO<sub>2</sub>

For an instantaneous photodissociation a value of the anisotropy parameter of  $\beta = 2\mathscr{P}_2(\cos \alpha)$  is expected, where  $\alpha$  is the angle between the transition dipole moment and the vector for the recoil velocity in the center of mass frame of the molecule. The extremal values are  $\beta = 2$  and  $\beta = -1$  if these vectors are parallel or perpendicular. With increasing duration of the photodissociation process the anisotropy will decay towards  $\beta = 0$ . The transition dipole  $\vec{\mu}$  for the  ${}^{2}A_{1} \rightarrow {}^{2}B_{2}$  transition lies along the line connecting the two oxygen atoms. Values of 134° and 102° have been reported for the ONO bond angle in the ground state  ${}^{2}A_{1}$  and the excited state  ${}^{2}B_{2}$ , respectively.53 Hradil and coworkers have chosen the geometry of the ground state and the velocity vector along the breaking NO bond.<sup>49</sup> The result  $\alpha = 23^{\circ}$  and  $\beta = 1.54$  have subsequently been used by others.<sup>48</sup> With the geometry of the excited state the same choice for the velocity vector results in  $\alpha = 39^{\circ}$  and  $\beta = 0.81$  which is smaller than the experimental value and hence not reasonable. Alternatively one could assign the velocity vector pointing from the dissociating O atom towards the center of mass of the NO fragment. This choice assigns all the angular momentum to the rotation of NO and none to the relative motion of the two fragments. In this case  $\alpha = 7.4^{\circ}$  or 13.8° and  $\beta = 1.83^{\circ}$  or 1.95° for the geometry of the ground state or the excited state.

Due to the finite lifetime  $\tau_D$  of the excited state, the initial anisotropy will decay by the rotation of the parent molecule after excitation and before dissociation. We can model the instantaneous velocity distribution at time *t* after the photolysis by

$$P(\nu, \theta, t) = \frac{\exp(-t/\tau_{\rm D})}{2\tau_{\rm D}} p(\nu) [1 + \beta(t)\mathscr{P}_2(\cos\theta)], \qquad (9)$$

Assuming an exponential decay of the anisotropy with a characteristic rotational time constant  $\tau_{R}$ ,

$$\beta(t) = \beta_0 \, \exp(-t/\tau_R),\tag{10}$$

the time-integrated velocity distribution will have the form of eqn. 5 with

$$\beta = \beta_0 \left( 1 + \frac{\tau_D}{\tau_R} \right)^{-1} \tag{11}$$

The ratio of the observed value of  $\beta = 1.35$  and the initial anisotropy  $\beta_0$  can thus be used to calculate the ratio  $\tau_D/\tau_R$ of the dissociation and rotation times. The result depends on the choices made for the initial geometry of the dissociating molecule and the direction of the velocity vector. Above we have discussed three choices, namely (i) ground state geometry and velocity along the NO bond, (ii) ground state geometry and velocity along the line connecting the O atom and the center of mass of the NO fragment, and (iii) excited state geometry and velocity as in (ii). For these three cases the ratio of the time constants  $\tau_D/\tau_R$  is 0.14, 0.36, and 0.44.

#### 4.2. Nitrosobenzene

Nitrosobenzene exhibits three strong absorption bands in the UV with peaks at 34 500, 37 000, and 46 500 cm in the gas phase.<sup>26</sup> The corresponding excited states can be phenomenologically assigned to  $S_2$ ,  $S_3$ , and  $S_4$ . However, many more electronic states are expected for an organic molecule of this size in this energy range. Indeed, semiempirical calculations indicated a number of states with a large contribution of doubly excited configurations.<sup>30</sup> These will carry little oscillator strength but might gain intensity *via* vibronic coupling to higher electronic states. The fact that the intensity of the first UV-band strongly increases with the polarity and the polarizability of the solvent could be due to such a state mixing.

Although we can not exclude the presence of more than one electronic state in the range of  $31\,000-36\,000$  cm<sup>-1</sup>, the maximum-entropy deconvoluted spectrum in argon matrix<sup>30</sup> and the spectrum in the supersonic jet<sup>25</sup> measured indirectly by monitoring the product yield of NO could both be analyzed into progressions of five vibrations built on a single electronic origin. The homogeneous line width of this origin band led us to conclude a lifetime of 60–90 fs for the S<sub>2</sub>-state.

In our previous investigations on the photodissociation of jet-cooled nitrosobenzene we have studied Doppler profiles and product state populations of the NO fragment produced by photodissociation with photons of 320, 308, 290, 266, and 250 nm wavelength.<sup>26,29</sup> All these data were consistent with a statistical mechanism of photodissociation. The primarily populated S<sub>2</sub>-state decays through internal conversion within 60–90 fs into the S<sub>1</sub> or S<sub>0</sub> state, and dissociation occurs on the potential surface of the lower state on a much longer time scale.

Such a mechanism leads to Gaussian lineshapes for the Doppler profiles of individual rotational lines of the NO fragment. On the other side, a very fast dissociation would lead to an anisotropic velocity distribution which could be detected by the observation of dips in Doppler profiles measured with specific polarization conditions. However, such a dip might be obscured even in the presence of a considerable anisotropy if the spread of velocities is large.<sup>29</sup> Quantitative evaluation of Doppler profiles requires deconvolution of these lineshapes since the laser linewidth is of the same order of magnitude as the Doppler width. In contrast to Doppler profile measurements, ion imaging obtains the complete velocity distribution and no deconvolution is required.

The increase of the average velocity with the rotational quantum number of the NO fragments indicates that these two degrees of freedom are not statistically independent. A similar tendency was already observed in our previous study of Doppler widths.<sup>29</sup> A small line broadening could, however, also be explained by the increase of the A-splitting with increasing rotational quantum number. A rigorous mechanistic analysis of this correlation would require quantum dynamical wavepacket calculations on the potential energy surface involved, a task which is far beyond the scope of the present work. In a simplified classical picture such a correlation could be the result of an impulsive torque at the N end of NO. If the center of mass of the NO fragment remains in the plane of the phenyl radical, the dissociation coordinate will be a linear combination of the C-N stretch, the CNO and CCN bending modes, and the CCNO torsional mode. These four coordinates define the relative position of the two fragments and will, after dissociation, describe four degrees of freedom of relative motion. The latter are the two components of the velocity vector (constrained to the plane of the phenyl radical) and the two rotational degrees of freedom of the NO radical. If the CNO bending mode or the CN stretch have a large contribution in the reaction coordinate, they will be highly excited in the moment of dissociation. This could lead to a correlation of vand J. This is not a contradiction to the absence of alignment (*i.e.* a correlation of J and the transition moment  $\mu$ ) found in ref. 29.

A negative anisotropy of  $\beta = -0.64$  has recently been reported as the result of a study of 266 nm photodissociation by angularly resolved time-of-flight measurements of the neutral fragments.<sup>28</sup> These data are at variance with our findings, and possible reasons for this should be discussed. From the photolysis of nitrites it is known that NO fragments formed in the dissociation of clusters have different rotational and vibrational populations and lower anisotropy than the fragments ejected from monomers.<sup>54</sup> At the temperature of 60°C the vapor pressure of nitrosobenzene is ca. 24 mbar. With a stagnation pressure of 2.5 bar the concentration of nitrosobenzene is far below the critical value of 5% observed for cluster formation with nitrites. The higher anisotropy has been reported for the experiment with the higher concentration of nitrosobenzene. Hence it is unlikely that the difference was caused by the presence of clusters in one of the two experiments.

In ref. 28 a focused Nd:YAG laser beam with pulse energies of 40 mJ at 226 nm was used for photodissociation of nitrosobenzene. Assuming a cross section at the focus of one square millimeter and a typical pulse duration of 4 ns, the average intensity is  $I \approx 10^9$  W cm<sup>-2</sup>. It has been shown that intense laser fields can trap and align neutral molecules in the gas phase. Efficient alignment of CS<sub>2</sub> followed by multiphoton dissociation and ionization has been achieved with 35 ps light pulses at 532 nm and intensities in the range  $10^{12}$ – $10^{14}$  W cm<sup>-2,55,56</sup> Larsen and coworkers succeeded in aligning 3,4dibromothiophene along all three axes by elliptically polarized light at 1064 nm and intensities of  $10^{11}$ – $10^{12}$  W cm<sup>-2.57</sup> The alignment is proportional to the anisotropy of the polarizability. The latter is strongly enhanced when the frequency of the electric field is resonant with an electronic transition. If this resonance enhancement is of the order of  $10^2$ – $10^3$ , the light pulses used by Huang and coworkers might be strong enough to align nitrosobenzene.

Since light at 266 nm is resonant with a strong absorption band of nitrosobenzene, multiphoton excitation should also be considered. The electronic state initially populated by UV excitation decays very quickly (≈60 fs) by internal conversion to either the  $S_1$  or the  $S_0$  state. The isotropic distribution of the fragment velocities indicates that dissociation occurs on a much slower timescale, probably in the range of 10-100 ps. During this time the system can absorb a second photon. If internal conversion leads to the  $S_1$  state, absorption of a second photon will populate electronic states at  $\approx 6.1$  eV above the ground state. The potential energy surfaces of these states could be repulsive, leading to an anisotropic velocity distribution of the fragments generated via this two-photon dissociation. The yield of this process relative to that of one-photon dissociation depends on the ratio of the rate constant k of dissociation of the hot  $S_1$  state and the rate  $\sigma F$  of the transition  $S_1 \rightarrow S_n$  excited by the second photon. The intensity of  $I = 10^9$  W cm<sup>-2</sup> corresponds to a photon flux of  $F = 1.3 \times 10^{27}$  photon cm<sup>-2</sup> s<sup>-1</sup>. With an estimated cross section of  $\sigma = 10^{-17} \text{ cm}^2$  for excited-state absorption the excitation rate will be  $\sigma F = 1.3 \times 10^{10} \text{ s}^{-1}$ . Since  $k \approx 10^{10} \text{ s}^{-1}$  is of similar magnitude, a substantial fraction of the molecules could be pumped into this two-photon dissociation channel. Rotational relaxation will be essentially complete before the second photon is absorbed. The anisotropy of the fragment velocities will hence reflect the orientation of the transition dipole of the excited-state absorption. If the latter is perpendicular to the molecular plane, as is expected for a transition from a  $n\pi^*$  state to a  $\pi\pi^*$  state, it will be perpendicular to the velocity vector, and negative anisotropy will be observed.

## 5. Conclusions

Applying the technique of velocity-map ion-imaging we have determined the three-dimensional velocity distribution of NO fragments from the photodissociation of jet-cooled nitrosobenzene. Photolysis was performed at 290.5 nm and 226 nm, corresponding to excitation of S2 and a higher singlet state, respectively. The ion images presented here are completely isotropic and can be modelled very well by a Maxwell-Boltzmann distribution. The negative anisotropy of  $\beta = -0.64$  recently reported from a study of 266 nm photodissociation might be an artifact produced by the high laser intensity applied. A strong light field could either align and trap the nitrosobenzene molecule, or lead via two-photon excitation to a different very fast dissociation channel.

#### Appendix: Invariance of the Gaussian with 6. respect to Abel transformation

Application of the Abel inversion to a Gaussian with mean 0, standard deviation  $\sigma$ , and area A,

$$f(x) = \frac{A}{\sigma\sqrt{2\pi}} \exp\left(-\frac{x^2}{2\sigma^2}\right),$$
 (12)

yields the integral expression

$$F(r) = \frac{A}{\sigma^3 \sqrt{2\pi^3}} \int_r^\infty dx \exp\left(-\frac{x^2}{2\sigma^2}\right) \frac{x}{\sqrt{x^2 - r^2}}.$$
 (13)

This can be solved with the substitution  $y = \sqrt{x^2 - r^2}$ , leading to

$$F(r) = \frac{A}{\sigma^3 \sqrt{2\pi^3}} \int_0^\infty dy \exp\left(-\frac{r^2 + y^2}{2\sigma^2}\right)$$
(14)

$$=\frac{A}{\sigma^2\pi}\exp\left(-\frac{r^2}{2\sigma^2}\right).$$
 (15)

Hence the Abel inverse F(r) of f(x) is a Gaussian with mean 0 and the original standard deviation, but with the scaled area

$$\tilde{A} = \frac{A}{\sigma} \sqrt{\frac{2}{\pi}}.$$
(16)

#### Acknowledgements

TJO gratefully acknowledges a fellowship from the Fonds der Chemischen Industrie.

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