

## PHOTOFRAGMENT ENERGY DISTRIBUTION AND ROTATIONAL ANISOTROPY FROM EXCITATION OF $\text{HN}_3$ AT 266 nm

K.-H. GERICKE, R. THEINL and F.J. COMES

*Institut für Physikalische und Theoretische Chemie, Niederurseler Hang,  
D-6000 Frankfurt am Main 50, Federal Republic of Germany*

Received 31 July 1989; in final form 13 October 1989

The photodissociation dynamics of hydrazoic acid at 266 nm has been analyzed by high-resolution Doppler spectroscopy. The NH fragment carries most of the available energy as translation,  $f_T(\text{NH})=0.32$ , and only 3% as rotation;  $\text{N}_2$  is mainly internally excited,  $f_{\text{int}}(\text{N}_2)=0.48$  with fairly low translational motion,  $f_T(\text{N}_2)=0.17$ . The rotational distribution is Gaussian-like, peaking at  $J_{\text{NH}}\approx 5-6$ . Previously published rotational state distributions are perturbed by rotational relaxation. The  $A$  doublets are populated statistically. The alignment of NH rotation versus the transition dipole moment of the parent is low ( $A_0^{(2)}\leq 0.19$ ). The vector correlation between the translational ( $v_{\text{NH}}$ ) and rotational ( $J_{\text{NH}}$ ) motion of the NH fragment is positive, indicating a preferential parallel alignment of  $v_{\text{NH}}$  and  $J_{\text{NH}}$ .

### 1. Introduction

The tetra-atomic molecule hydrazoic acid is interesting for the study of the dynamics of a photo-fragmentation process because a double bond is excited and several upper electronic surfaces may be involved in the dissociation process. The absorption spectrum of  $\text{HN}_3$ , onseting at 325 nm with the first maximum at 265 nm, is entirely continuous with very small modulations [1,2] indicating a fast dissociation process. Primary products are the NH and  $\text{N}_2$  molecules although there may be another (minor) fragmentation channel where a hydrogen atom and a  $\text{N}_3$  molecule are generated [3-6]. Detailed investigations have been carried out at an excitation wavelength of 193 nm where most NH fragments are formed in their singlet states ( $a^1\Delta$ ,  $b^1\Sigma^+$ , and  $c^1\Pi$ ) and only a small part in the  $A^3\Pi$  triplet state. The quantum yield of formation of  $\text{NH}(X^3\Sigma^-)$  ground state products was found to be less than 0.2%, the detection limit of the experiment [3].

At 248 and 266 nm the NH products are generated exclusively in the  $a^1\Delta$  state with low rotational excitation,  $f_R(\text{NH})=3.7\%$  at 248 nm [3] and  $f_R(\text{NH})=3.9\%$  at 266 nm [1,7]. The rotational product state distribution of  $\text{NH}(^1\Delta, v=0)$  pro-

duced by photolysis of  $\text{HN}_3$  at 266 nm was stated to be a Boltzmann distribution with a temperature parameter of  $T=1200$  K [7]. That internal state distribution was deduced from the observed line intensities without considering the effect of rotational alignment which also influences the line intensities and consequently the calculated populations. From the experimental conditions used in the early study [1,7] it can be expected that the reported rotational state distribution may be not completely nascent in character. Any rotational relaxation process would influence the population of low rotational states and any inversion in the rotational state distribution would vanish.

In the present study, the measurement of the photodissociation of hydrazoic acid has been repeated under collision-free conditions and the results indicate the influence of rotational relaxation on the population of the different rotational states.

In order to elucidate the dynamics of the fragmentation process, the rotational anisotropy has been determined, i.e. the vector correlation between the transition dipole moment of  $\text{HN}_3$  and the rotation of the NH product. Furthermore, the line profiles for a P and Q transition have been analyzed with sub-Doppler resolution and a qualitative alignment be-

tween the translational and rotational motion of the fragment was established. From the width of these lines the translational energy of NH and the average internal energy of the other product,  $N_2$ , was deduced.

## 2. Experimental

The scalar and vector properties were measured by a fast photofragmentation and detection technique where nascent NH radicals resulting from photoexcitation of  $HN_3$  were analyzed by sub-Doppler laser-induced fluorescence measurements. The photolysis pulse at 266 nm was delivered by a frequency-quadrupled Nd:YAG laser (Quanta Ray, DCR 1) operating at a repetition rate of 10 Hz. The typical pulse energy was about 15 mJ at a pulse length of 6 ns. The radiation was slightly focused into an aluminium cell which was equipped with a series of light baffles to reduce the influence of stray light from the walls and the entrance and exit window. The NH products were probed by a frequency-doubled dye laser (Lambda Physik, FL 2002E) which was pumped by a second frequency-doubled Nd:YAG laser (Spectron SL2 Q). The delay between both Nd:YAG lasers can be varied up to several ms in 10 ns steps. The time jitter between the pump and probe laser pulse was below 5 ns.

With DCM dissolved in methanol as active laser material of the dye laser a tuning range of 308 to 330 nm was achieved which is sufficient to excite all rotational transitions of the (0, 0) band of the NH ( $c^1\Pi \leftarrow a^1\Delta$ ) electronic transition. The band width of the dye laser was  $0.5 \text{ cm}^{-1}$  in broadband operation and  $0.1 \text{ cm}^{-1}$  using a stepping motor tuned intracavity etalon. Both the photolyzing and the analyzing laser beam were linearly polarized and their planes of polarization could be rotated by  $\frac{1}{2}\lambda$  plates. The laser beam arrangement allowed experiments at three different probe geometries (geometry II, IV, VI as defined in ref. [8]).

The undispersed fluorescence signal was viewed perpendicular to the laser beams without considering polarization. The influence of scattered light was reduced by a 320 nm interference filter (10 nm fwhm). For averaging and normalization to constant photolysis and analysis laser output energies, the signals were fed into a boxcar integrator (Stanford Re-

search Systems, model SR 250) and after A/D conversion stored in a micro computer (PC AT 386/7).

Hydrazoic acid was generated in a vacuum line using  $NaN_3$  in excess of stearic acid [9]. When heated to  $80^\circ\text{C}$  sufficient amounts of  $HN_3$  evolved and were pumped directly into the observation cell. The  $HN_3$  pressure was about 0.66 Pa controlled by a capacitance manometer for the observation of nascent NH products. For relaxation measurements helium was bubbled through the  $NaN_3$ /stearic acid mixture at a variable total pressure in the range from 90 to 900 Pa.

## 3. Results and discussion

Photolysis of  $HN_3$  at 266 nm gives rise to NH exclusively formed in the  $a^1\Delta$  state. Only at high pulse energies some NH fluorescence in the range of 320 to 335 nm was observed, indicating a two-photon absorption which produces NH radicals in the  $c^1\Pi$  state. The NH( $^1\Delta$ ) product state distribution is probed by excitation of the  $c^1\Pi \leftarrow a^1\Delta$  band. Since each rotational level in both states consists of two closely spaced  $A$  doublets, each rotational transition is actually a pair of lines. At high  $J$ ,  $J \geq 5$ , this splitting is resolved which mainly reflects the spacing of  $A$  doublets of the  $c^1\Pi$  state which is much larger than that of the  $a^1\Delta$  state. However, the initial level of one line is of  $\Delta(A')$  symmetry while the other transition "starts" at a  $\Delta(A'')$  state [10]. Although the energy spacing between these two  $A$  levels is extremely small, any  $A$  doublet specificity always reflects a *dynamical* feature of the dissociation process.

A slight preference for  $\Delta(A')$  levels was found in IR dissociation experiments [11]. In the present UV photolysis experiment each pair of lines was recorded under high resolution ( $\Delta\nu \leq 0.1 \text{ cm}^{-1}$ ) and a sum of two Doppler profiles was fitted to the observed (and normalized) fluorescence signal. Thus, the relative population of each  $A$  doublet was obtained even if the line splitting is not completely resolved. The related integrated line intensities of each transition are found to be equal within the experimental error of a few percent. Therefore, the dissociation process does not distinguish between the formation of  $\Delta(A')$  or  $\Delta(A'')$  levels. The consequence of this result will be discussed in connection with the

observed correlation between the translational and rotational motion of the NH fragment.

The rotational state distribution in a direction-specific process can only be correctly measured by LIF, if vector properties are taken into account [12]. Fortunately, the integrated line intensities are only influenced by a correlation between the transition dipole moment of the parent,  $\mu$ , and the rotation of the fragment,  $J$ . This  $\langle \mu \cdot J \rangle$  correlation gives rise to a branch and geometry specific excitation probability and proper populations  $P(J)$  for a rotational state  $J$  can be determined from the fluorescence light  $I$ , if the expression

$$I \sim BP(J)(a_0 + a_1 A_0^{(2)})$$

is applied, where  $B$  is the transition probability. The parameters  $a_0$  and  $a_1$  depend on the transition and geometry which were used in the LIF experiment [13]. The alignment  $A_0^{(2)}$  is a quantitative measure of the  $\langle \mu \cdot J \rangle$  correlation. For high product rotation a limiting value of +0.8 corresponds to a parallel alignment between  $\mu$  and  $J$ , while a perpendicular alignment between both vectors demands the limiting value of  $A_0^{(2)} = -0.4$ .

The alignment was determined by measuring Q lines at two different geometries where the  $E$  vector of the analysing dye laser is either perpendicular (geometry II) or parallel (geometry IV) to the  $E$  vector of the photolyzing Nd:YAG laser beam [13]. The advantage of this procedure is a greater independence on long term intensity fluctuations of the lasers and variations of the  $\text{HN}_3$  pressure. Then the alignment  $A_0^{(2)}$  can be easily calculated by

$$A_0^{(2)} = \frac{a_0^{\text{II}} I^{\text{IV}} - a_0^{\text{IV}} I^{\text{II}}}{a_1^{\text{IV}} I^{\text{II}} - a_1^{\text{II}} I^{\text{IV}}}$$

The values obtained as a function of NH product rotation are shown in fig. 1. Obviously, the fragments exhibit only a slight alignment in the photodissociation of  $\text{HN}_3$  at 266 nm. Even the largest value observed,  $A_0^{(2)} = +0.2$ , is far from the limiting value of  $A_0^{(2)}(\text{max}) = 0.8$ . However, the positive alignment for all  $J > 2$  indicates a preferentially parallel alignment between the transition dipole moment of the  $\text{HN}_3$  and the rotational vector of the NH product.

The rotational state distribution  $P(J)$  was determined from R and Q lines taking the  $\langle \mu \cdot J \rangle$  correlation into account. Since the A doublets are popu-

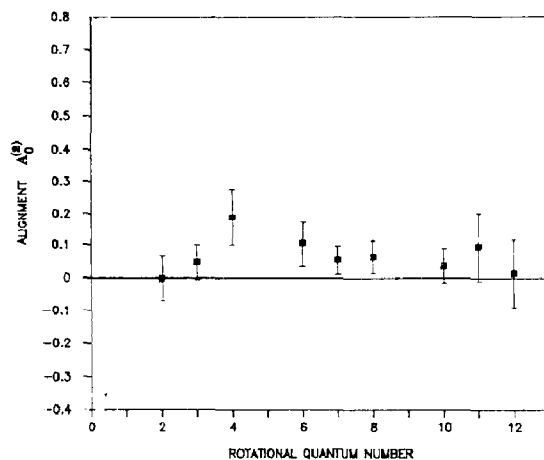


Fig. 1. Product alignment  $A_0^{(2)}(J)$  of  $\text{NH}(a^1\Delta, v=0)$  products in the photodissociation of  $\text{HN}_3$  at 266 nm. The small positive value indicates a more parallel orientation between the rotational vector of the fragment,  $J$ , and  $\mu$ , the transition dipole in the parent molecule.

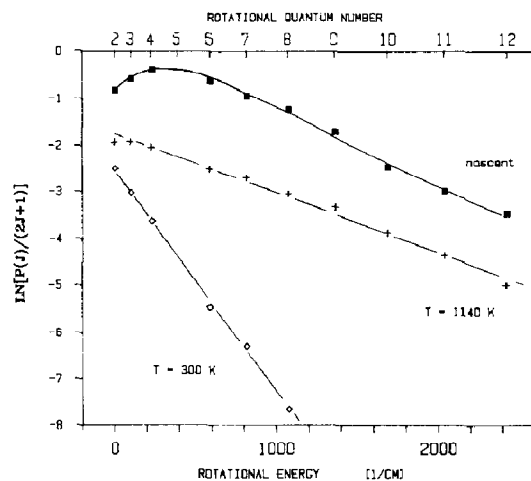


Fig. 2. Boltzmann plots for  $\text{NH}(a^1\Delta, v=0)$  fragments from the UV dissociation of  $\text{HN}_3$  at different experimental conditions. The upper distribution is nascent in character (0.65 Pa  $\text{HN}_3$  and 30 ns delay time between photolyzing analysing laser beam) while the other distributions are partly relaxed ( $T=1140$  K; 13 Pa  $\text{HN}_3$  and 300 ns delay time) or completely relaxed ( $T=303$  K; 10 Pa  $\text{HN}_3$  + 850 Pa He and 16  $\mu\text{s}$  delay time) and can be characterized by a rotational temperature  $T$ .

lated statistically, the integrated intensity of both A transitions was used. The data obtained are represented as a Boltzmann plot in fig. 2. If a plot of  $\ln[P(J)/(2J+1)]$  versus  $E_{\text{rot}}$  can be described by a

straight line, then the distribution is characterized by a single parameter  $T_{\text{rot}}$ , "the rotational temperature". The distribution observed can only be described by a straight line at high product rotations. For  $J < 5$  the values strongly deviate from this behavior and even show a population inversion.

This finding contradicts former observations of the NH product state distribution, where the population of all rotational states was described by a Boltzmann distribution with a temperature parameter  $T_{\text{rot}} = 1200$  K. The discrepancy between both observed distributions may be a result of the use of wrong transition probabilities at low  $J$ 's or an originally nascent distribution is already disturbed by rotational relaxation when it is observed.

In order to determine the reliability of transition probabilities, we set up an experiment where the produced NH radicals should be completely relaxed and the observed product state population should be described by an ambient temperature distribution around  $T = 300$  K. The lower part of fig. 2 shows the result of such an analysis where the total pressure in the observation cell was increased up to 860 Pa (10 Pa  $\text{HN}_3$  and 850 Pa He) and the delay between production of NH and observation was set to 16  $\mu\text{s}$  corresponding to a mean collision number of roughly 1200. The straight line in the lower part of this figure is the result of a least-squares fit of a Boltzmann distribution. The observed rotational temperature of  $T_{\text{rot}} = 303 \pm 7$  K strongly indicates the adequacy of the applied analysis technique.

When the total pressure in the reaction chamber and the delay time between both laser beams is reduced, one obtains a continuous change from the room temperature distribution to the nascent distribution shown in the upper part of fig. 2. The difference between the present observed and the former reported rotational state distribution is caused by the fast rotational relaxation process. The reported rotational distribution can be reproduced with a pressure of 13 Pa and a delay time of 300 ns between photolysis and analyzing laser beams which corresponds roughly to the former reported experimental conditions. A Boltzmann fit to the partly relaxed distribution gives a rotational temperature of  $T_{\text{rot}} = 1140$  K which is in agreement with the reported value of  $T_{\text{rot}} = 1200$  K.

In addition to the observed nascent NH fragment

rotational state distribution, Doppler profile measurements can give information about the product recoil velocity and further vector properties of the dissociation process [13,14]. The polarized photolysis laser beam excites preferentially those parent molecules which exhibit a transition moment parallel to the electric  $E$  vector. This anisotropy induced in the ensemble of randomly distributed  $\text{HN}_3$  molecules will be carried over to the photofragment motion if the dissociation of the parent is faster than the molecular rotation. For very slow fragmentation processes, the initial parent motion will dominate the measurable product translational anisotropy and rotational alignment with respect to the  $E$  vector of the dissociating laser light. An exception is the correlation between the recoil velocity  $v$  and the rotation  $J$  of the fragment. This  $\langle v \cdot J \rangle$  correlation only depends on product properties and is, therefore, independent on the lab frame, thereby permitting an insight into dissociation dynamics directly in the molecular frame.

This correlation between the translational and rotational motion of the fragment can easily be determined in a qualitative way by Doppler spectroscopy simply because the  $\langle v \cdot J \rangle$  correlation influences the line profile. Different Doppler-line profiles will be observed for P and Q or R and Q transitions. The  $\langle v \cdot J \rangle$  correlation is independent on a change in beam geometries or polarization directions.

Fig. 3 shows two Doppler profiles, both probing the  $J = 8$  rotational state of the NH ( $a^1\Delta, v = 0$ ) product. The experimental arrangement of the laser beams and their polarization were kept identical for both transitions. Then, according to the preceding paragraph a correlation between the translational and rotational motion is responsible for a change in the observed Doppler profiles [16]. Since the center of the Q line dominates the wings, in contrast to the P line where the intensity at the center is lowered in favor of the wings, the rotational vector  $J$  should be aligned more parallel to  $v^{\#1}$ . Therefore, we obtain the surprising result of a positive  $\langle v \cdot J \rangle$  correlation of the

<sup>#1</sup> This relation between the transition dipole moment and the rotation is derived from a one-electron system [15], but it can be shown that it is also valid for both  $A$  lines of a Q transition in a  $\Delta \rightarrow \Pi$  system [10,16].

## NH Doppler profiles

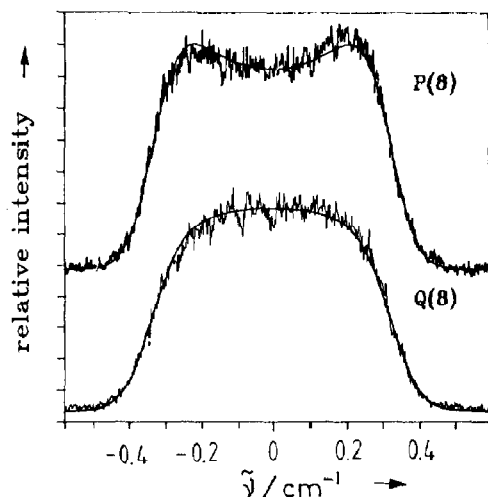


Fig. 3. Doppler profiles of nascent  $\text{NH}(a^1\Delta, J=8)$ . The enhanced intensity in the center of the Q transition in contrast to the P line indicates a more parallel orientation between recoil velocity and rotation of the product.

NH fragment in the UV dissociation of thermal hydrazoic acid.

The solid line in fig. 3 shows the best fit of the profile of the NH products with suitable convolution of a Gaussian profile [17] to account for probe laser linewidth, parent Doppler motion, and the internal energy distribution of the  $\text{N}_2$  partner fragment. The value found for the Doppler width is  $\Delta\nu_D = 0.34 \text{ cm}^{-1}$  which can be converted to an average NH recoil velocity of  $v_{\text{NH}} = \Delta\nu_D c / \nu_0 = 3340 \text{ m/s}$ , where  $\nu_0$  is the center frequency of the observed transition and  $c$  the speed of light. The effective parameter  $\beta_{\text{eff}}$  [13] is  $\beta_{\text{eff}} = 0.15$  for the Q(8) line and  $\beta_{\text{eff}} = -0.2$  for the P(8) line.

From the rotational state distribution and the linewidth measurement, the energy partitioning into the products can be determined. The total excess energy,  $E_{\text{av}}$ , which is available to the  $\text{NH}(a^1\Delta)$  products in  $v=0$  is determined by the photon energy,  $h\nu = 37590 \text{ cm}^{-1}$ , the dissociation energy [18] to form the fragment in its  $a^1\Delta$  state,  $D_a = 16450 \text{ cm}^{-1}$ , and the initial internal energy of the parent,  $E_{\text{int}}(\text{HN}_3) \approx 380 \text{ cm}^{-1}$ , which is mainly determined by rotation,  $E_{\text{vib}}(\text{HN}_3) \approx 70 \text{ cm}^{-1}$ :

$$E_{\text{av}} = h\nu + E_{\text{int}}(\text{HN}_3) - D_a = 21520 \text{ cm}^{-1}.$$

The fraction of energy which is transferred into the NH fragment in the  $v=0$  state is calculated in the usual way:

$$f_r(\text{NH}) = \sum_J P(J) E_r(J) / E_{\text{av}} = 0.03,$$

where  $P(J)$  is the normalized population of the rotational state  $J$  with the energy  $E_r(J)$ . The fraction of energy which is transferred into translational energy is calculated from the measured linewidth of the NH fragment:

$$f_T(\text{NH}) = E_T(\text{NH}) / E_{\text{av}} = \frac{1}{2} m_{\text{NH}} v^2 / E_{\text{av}} = 0.32.$$

The  $\text{N}_2$  partner product which is formed simultaneously with the observed  $\text{NH}(^1\Delta, v=0, J=8)$  fragment must exhibit the same linear momentum in the center of mass system. Thus, the kinetic energy of the  $\text{N}_2$  product molecule is

$$E_T(\text{N}_2) = (m_{\text{NH}} / m_{\text{N}_2}) E_T(\text{NH}) = 3670 \text{ cm}^{-1}$$

and

$$f_T(\text{N}_2) = 0.17.$$

The nitrogen molecule must have a significant amount of internal energy,  $E_{\text{int}}(\text{N}_2)$ , to fulfill the law of conservation of energy:

$$\begin{aligned} E_{\text{int}}(\text{N}_2) &= E_{\text{av}} - E_{\text{int}}(\text{NH}) - E_T(\text{NH}) - E_T(\text{N}_2) \\ &= 10300 \text{ cm}^{-1} \end{aligned}$$

and

$$f_{\text{int}}(\text{N}_2) = 1 - f_{\text{int}}(\text{NH}) - f_T(\text{NH}) - f_T(\text{N}_2) = 0.48.$$

The  $\text{N}_2$  product molecule is generated with a great amount of internal excitation in the photodissociation of  $\text{HN}_3$  at 266 nm in contrast to the  $\text{NH}(a^1\Delta)$  fragment which is only weakly rotationally excited.

Hydrazoic acid is a planar molecule in the electronic ground state. The three nitrogen atoms are almost linear (N-N-N angle  $\approx 171^\circ$ ) and the angle between the hydrogen atom and the  $\text{N}_3$  chain is close to  $110^\circ$ . The rotational vector of NH is aligned slightly parallel to symmetry and the first excited state exhibits  $A''$  symmetry. If excited to this  $A''$  state, transition dipole moment - related to the long wavelength end of the absorption spectrum - is perpendicular to the NNN-H plane. Zero-point motion of

the NNH  $\nu_4$  bending vibration can be transferred into product rotation when the upper potential surface is only weakly dependent on the bending angle. A simple calculation, where the terminal nitrogen atom is regarded as a mere spectator, shows that  $575 \text{ cm}^{-1}$  of zero-point energy will be released as NH rotation [16]. The plane of fragment rotation would be in the plane of the parent and, thus  $\mathbf{J}_{\text{NH}}$  should be parallel to  $\mu_{\text{HN}_3}$  which would result in a strong positive alignment  $A_0^{(2)}$ . A positive value of  $A_0^{(2)}$  is observed; however, NH rotation generated via this type of  $\text{HN}_3$  motion results in a perpendicular alignment between  $\mathbf{J}$  and  $\mathbf{v}$ , in contrast to the experimental observations of the Doppler profiles for  $J=8$ .

Initial parent rotation will also influence the observed product rotation and has to be considered in the discussion of the dissociation dynamics. Parent rotation about the two axes of inertia which are almost perpendicular to the N-N-N chain will be transferred almost exclusively into orbital angular momentum of the  $\text{N}_2$ -NH system, thereby slightly affecting the recoil velocity. Only parent rotation about the axis of inertia which is essentially along the nitrogen chain can be transferred into NH product rotation. The resulting  $\mathbf{J}$  will point in the recoil direction,  $\mathbf{J} \parallel \mathbf{v}$ .

If we assume a mean thermal rotational energy of  $\frac{1}{2}kT$  for each rotational degree of freedom, then at room temperature  $2-3\hbar$  of initial  $\text{HN}_3$  rotation will be found as NH fragment rotational motion. These few quanta of rotation are comparable to the rotation of the nuclei,  $N_{\text{R}}$ , of the product when the two units of electronic angular momentum modified by parent rotation to a more parallel alignment between the translational and rotational motion of the parent.

Other out-of-plane motions, like the  $\nu_6(a'')$  wagging vibration, would also give rise to vibrational angular momentum aligned along the  $\text{N}_3$  chain. But the initial planar electronic ground state geometry of the  $\text{HN}_3$  molecule at equilibrium is not necessarily conserved in the dissociation process. A bending motion of the NN...NH system may result in a configuration where the potential energy will become dependent on the dihedral angle. In that case  $\text{HN}_3$  distorts to a non-planar structure before fragmentation. This is consistent with a linear-bent electronic transition for the NNN framework.

Another hint for the complexity of the fragmen-

tation process is the population of the  $A$  doublets. Hydrazoic acid is excited to the  $A^1A''$  state which has an antisymmetric wavefunction with respect to reflection in the (body-frame) plane of rotation. If the  $\text{HN-N}_2$  molecule remains planar during the dissociation process, i.e. the  $\text{N}_2$  and NH bond axis will always lie in the plane of the parent, then the wavefunction of the NH fragment should also be antisymmetric with respect to reflection because the wavefunction of the  $\text{N}_2(X^1\Sigma_g^+)$  is symmetric. Thus, one would expect those  $A$ -doublet levels of the  $\text{NH}(^1\Delta)$  fragment to be preferentially populated which are of  $\Delta(A'')$  geometry, because the wavefunction of this state is antisymmetric with respect to reflection in the plane of rotation. However, in the present work no experimental evidence for a preferred population of either the  $\Delta(A'')$  or the  $\Delta(A')$  state is found. Following this argument, the basic assumption of a planar dissociation process seems questionable, especially when the more parallel alignment between  $\mathbf{v}$  and  $\mathbf{J}$  is taken into account.

The influence of parent rotation during the fragmentation process can be eliminated by studying the dissociation dynamics in a supersonic molecular beam. Furthermore, the measurement of all vector properties, like the correlation between the transition dipole moment of the parent and the recoil velocity of the products, as a function of NH rotation will give the necessary support to characterize the geometry of the process and to elucidate the complete fragmentation dynamics. Results of such an investigation in combination with the internal energy distribution of the  $\text{N}_2(X^1\Sigma_g^+)$  partner fragment will be presented in a forthcoming paper.

### Acknowledgement

The work has been performed as part of a program in the "Sonderforschungsbereich" of the Deutsche Forschungsgemeinschaft. Financial support is gratefully acknowledged.

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