Vector correlations in the photofragmentation of HN\textsubscript{3}

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Hydrazoic acid was excited to its lowest electronic excited state $\tilde{A} \, { }^1A^+$ and the fragments were analyzed by high resolution Doppler spectroscopy. The NH fragment is rotationally cold, while N\textsubscript{2} is strongly internally excited $f_{\text{int}}(N_2) = 0.48$. The $\Lambda$ doublets are populated statistically. The alignment of NH rotation vs the transition dipole moment of the parent is low ($\beta_{\mu \nu} < 0.14$). The vector correlation between the translational ($v_{\text{NH}}$) and rotational ($J_{\text{NH}}$) motion of the NH fragments is positive and increases with increasing $J_{\text{NH}}$, indicating a preferential parallel alignment of $v_{\text{NH}}$ and $J_{\text{NH}}$ ($\beta_{\mu \nu} = 0.40$). The observed correlation between the transition dipole moment of the parent and the NH($^1A$) recoil velocity is negative at low NH rotations [$\beta_{\mu \nu}(J_{\text{NH}} = 2) = -0.4$] and increases to positive values with increasing $J_{\text{NH}}$. The HN\textsubscript{2} disturbingly from a nonplanar configuration after excitation of a linear-bent electronic transition in the NNN framework, resulting in a strong N\textsubscript{2} rotation and relatively weak NH rotation. The upper potential surface must be dependent on the torsional angle of the NN–NH system.

I. INTRODUCTION

The four atomic molecule hydrazoic acid is an interesting molecule for the study of the dynamics of a photofragmentation process because a double bond ($N = N$) is excited. 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 for formation of NH($^1A \, ^3\Sigma^-$) ground state products was found to be less than 0.2%, the detection limit of the experiment.\textsuperscript{1}

The absorption spectrum of HN\textsubscript{3} in the region of its first maximum at 265 nm is entirely continuous with very small modulations,\textsuperscript{2,3} indicating a fast dissociation process. The primary products NH and N\textsubscript{2} have been studied; but there may be another (minor) fragmentation channel where a hydrogen atom and a N\textsubscript{3} molecule are generated.\textsuperscript{4,5} At 248 and 266 nm, the NH products are generated exclusively in the $a \, ^1\Delta$ state\textsuperscript{1,6} with low rotational excitation $f_k$(NH) = 3.7% at 248 nm\textsuperscript{1} and $f_k$(NH) = 3% at 266 nm.\textsuperscript{7} The nascent rotational product state distribution of NH($^1\Delta, \nu = 0$) produced by photolysis of HN\textsubscript{3} at 266 nm is a non-Boltzmann distribution peaking at $J_{\text{NH}} = 5$–6.

In the present study, the photodissociation dynamics of hydrazoic acid has been analyzed under collision-free conditions by observation of scalar and vectorial properties of the NH product. The vector correlations between the transition dipole moment of HN\textsubscript{3} and the rotation, as well as the translation of the NH product, have been analyzed with sub-Doppler resolution since the quantitative determination of the ($\mu$-$\nu$), ($\mu$-$\nu^*$), ($\nu$-$\nu$), and ($\mu$-$\nu$-$\nu$) correlation gives a detailed picture of the fragmentation process.

II. EXPERIMENTAL

The scalar and vector properties in the photoexcitation of HN\textsubscript{3} were analyzed by sub-Doppler laser-induced fluorescence measurements of nascent NH products under different detection and polarization geometries. Details of the experimental setup have been published elsewhere.\textsuperscript{7,8} In short, 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 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 was kept constant at 30 ns with a time jitter below 5 ns.

The tuning range of the dye laser (308–330 nm) is sufficient to excite all rotational transitions of the (0,0) band of the NH (c $\nu' = a$ $\Delta$) electronic transition. The bandwidth of the dye laser in the UV was 0.1 cm\textsuperscript{-1} using a stepping motor tuned intracavity etalon. Both the photolyzing and the analyzing laser beams were linearly polarized and their planes of polarization can be rotated by $\lambda / 2$ plates. The laser beam arrangement allowed experiments at three different probe geometries (geometry II, IV, and VI as defined in Ref. 9).

The undispersed fluorescence signal was viewed perpendicular to the laser beams regardless of polarization. The influence of scattered light was reduced by an interference filter [peak transmission at 327 nm with 10 nm full width at half-maximum (FWHM)]. For averaging and normalization to photolysis and analysis laser output energies, the signals were fed into a boxcar integrator (Stanford Research 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\textsubscript{3} in excess of stearic acid.\textsuperscript{10} When heated to 75–85 °C sufficient amounts of HN\textsubscript{3} evolved and were pumped directly into the observation cell. The HN\textsubscript{3} pressure was about 0.6 Pa controlled by a capacitance manometer for the observation of nascent NH products. For measurements in a supersonic jet, helium was bubbled through the NaN\textsubscript{3}/stearic acid
mixture at a total pressure of $2 \times 10^4$ Pa. The pulsed nozzle with a diameter of 0.5 mm operated with a pulse length of less than 300 $\mu$s.\(^{11}\)

### III. RESULTS

The detailed knowledge of the correlated vector properties of a molecular photoproduct can provide a three-dimensional picture of the fragmentation process. Such experimental examinations in the dissociation of HN\(_3\) were accomplished by the use of sub-Doppler polarization spectroscopy. The vectors of interest in these experiments are the HN\(_3\) parent molecule transition dipole moment $\mu$, the NH fragment recoil velocity vector $v$, and the NH rotational angular momentum $J$.

The theoretical framework required to convert the laboratory frame experiments of line profiles into the required bipolar moments that characterize the correlated $(\mu, v, J)$ distribution has been described by Dixon\(^{12}\) for laser-induced fluorescence (LIF) and emission experiments. It has meanwhile been extended by Docker for $(n + m)$ LIF experiments\(^{13}\) and by Mons and Dimicoli\(^{14}\) for multiphoton ionization spectroscopy in connection with time-of-flight analysis of the ionized product. The fluorescence intensity for a single recoil velocity $v = \Delta \nu_D/c/v_0$ can be expressed as a function of the relative Doppler shift $[x_D = (v - v_0)/\Delta \nu_D]$ from line center $v_0$ in terms of bipolar moments.

$$I(x_D) = C \sum_{i=0}^{n} g_{2,i} \cdot P_{2,i}(x_D)$$

(1)

when linearly polarized photons are applied, where the possible value of $i$ and the number of bipolar moments are determined by the number of photons $n$ in the photolysis and the absorption fluorescence sequence [$n = 3$ for conventional photolysis and $(1 + 1)$ LIF analysis]. The terms $g_{2,i}$ are linear combinations of bipolar moments $\beta^2(k_1,k_2)$ which parametrize the $(\mu, v, J)$ correlations. The coefficients of these linear combinations depend on the polarization, the photolysis detection geometry, and the rotational branch which is used for analyzing the photoproducts.

Fortunately, one can simplify Eq. (1) for $(1 + 1)$ LIF according to Ref. 9 and neglect all but the first two terms in the line shape function. The line profile function\(^{15}\)

$$I(x_D) \sim \frac{1}{\Delta \nu_D} [1 + \beta_{\text{eff}} P_2(x_D)]$$

(2)

with $\beta_{\text{eff}} = g_{2,0}/g_{0,0}$ is fitted to the experimentally recorded Doppler line shapes with suitable convolution of the laser bandwidth, parent molecule translational motion, and N\(_2\) velocity distribution. The N\(_2\) velocity distribution is very well characterized by a Gaussian function which was determined by a high resolution pulsed dye laser system ($\Delta \nu_f = 50$ MHz) when jet cooled HN\(_3\) was photolyzed at 248 nm. The higher photolysis energy in that experiment in comparison to the 266 nm excitation should not significantly change the shape of the N\(_2\) velocity distribution, since the same electronic transition is excited. Furthermore, the exact form of the velocity distribution does not strongly influence the line profile.

The anisotropy parameter $\beta_{\text{eff}}$ contains information on the vector properties in the dissociation process

$$\beta_{\text{eff}} = \frac{b_0 \beta_{\mu \nu} + b_0 \beta_{\mu J} + b_0 \beta_{\nu J}}{b_0 + b_0 \beta_{\mu \nu}}.$$  

(3)

The multipliers $b_0 - b_0$ of the bipolar moments $\beta_{\mu \nu}, \beta_{\mu J},$ and $\beta_{\nu J}$ include the excitation detection geometry and angular momentum coupling factors. The numerical values of the multipliers $b_0$ to $b_0$ were calculated for $P, Q, R$ transitions and for all the different geometries I–IV defined in Ref. 10. The fact of observing undispersed fluorescence without using a polarizer has been taken into account. Transition probabilities were taken from the literature.\(^{16,17}\)

We have measured the values of $\beta_{\text{eff}} (J_{\text{NH}})$ for three different geometries and for all nonoverlapping $P, Q,$ and $R$ transitions. The system of Eq. 3 was solved with a least-squares procedure and the bipolar moments and their rotational dependence were determined. In Figs. 1–4, the evaluated bipolar moments $\beta_{\mu \nu}, \beta_{\mu J},$ and $\beta_{\nu J}$ are shown as functions of $J_{\text{NH}}$ within their theoretically defined range $-1 < \beta_{\mu \nu} < 0.5$ and $-0.5 < \beta_{\nu J} < 1.0$ for the remaining bipolar moments.

The alignment of the fragments, i.e., the correlation between $\mu$ and $J$, has only an indirect influence on the line profile. The integral of the line profile depends only on $g_{0,0}$:

$$\int I(dv) = g_{0,0} + b_0 \beta_{\mu \nu}.$$  

(4)

The value of $\beta_{\mu \nu}$, which is the renormalized rotational alignment parameter $A_{\mu}^{(2)} = \beta_{\mu \nu}$, has been determined by measuring the integrated line intensities for different geometries and excitation branches. The rotational dependence of $\beta_{\mu \nu}$ is shown in Fig. 1. The NH$(a' \Delta)$ products exhibit only a minor alignment in the photofragmentation at 266 nm which does not significantly change with fragment rotation. However, the positive values of $\beta_{\mu \nu}$ for all $J_{\text{NH}} > 2$ indicate a preferentially parallel alignment between the transition dipole moment of the HN\(_3\) and the rotational vector of the NH product.
The influence of $\beta_{\mu J}$ on the evaluation of the other bipolar moments is not important because of its low value. The second bipolar moment $\beta_{\mu v}$ (Fig. 2) describes the spatial anisotropy of the photoproducts and is proportional to the classical anisotropy parameter $\beta = 2\beta_{\mu v}$. The negative value of $\beta_{\mu v}$ for the lowest rotational state [$\beta_{\mu v}(J_{NH} = 2) = -0.4$] indicates a preferentially perpendicular alignment between $\mu$ and $v$. However, $\beta_{\mu v}$ increases with increasing $J_{NH}$ and becomes positive for high product rotations ($J_{NH} > 9$).

The mutual correlation of the photofragment translational and rotational vector $v_{NH}$ and $J_{NH}$ is described by the bipolar moment $\beta_{\mu J}$. Since this moment is independent of the lab frame, $\beta_{\mu J}$ permits an insight into fragmentation dynamics directly in the molecular frame. Perfect alignment in the high $J$ limit between $v$ and $J$ is given when $\beta_{\mu J} = +1$ or $\beta_{\mu J} = -0.5$ indicating that $v$ is either parallel or perpendicular to $J$. We observe a positive ($vJ$) correlation (Fig. 3) which increases with increasing $J_{NH}$. At high $J$, we obtain a value of $\beta_{\mu J} \approx 0.40$ indicating the preference for a parallel alignment between $v$ and $J$.

The last observed bipolar moment $\beta_{\mu vJ}$ describes the mutual correlation between the $HN_3$ transition dipole moment $\mu$, the translational, and the rotational motion of the NH fragment. Since only a low correlation between $\mu_{HN_3}$ and $J_{NH}$ as well as between $\mu_{HN_3}$ and $v_{NH}$ for high $J_{NH}$ is observed, a strong three vector correlation is not expected. Thus the low value of $\beta_{\mu vJ}$ for all $J_{NH}$ is not surprising (Fig. 4). We assume a value of $\beta_{\mu vJ} = 0.0 \pm 0.05$ independent of fragment rotation.

**IV. DISCUSSION OF THE DISSOCIATION PROCESS**

The molecular structure of $HN_3$ in the electronic ground state is shown in Fig. 5. The planar $HN_3$ molecule consists of an almost linear $N_3$ chain ($\alpha_{NNN} = 171.3^\circ$) and a strongly bent NH bond ($\alpha_{NNH} = 108.8^\circ$). The NH distance in the $HN_3$ parent does not differ significantly from the NH($^1\Delta$) bond length of the free molecule $r_{NH} = 1.034$ Å. Also the bond length between the terminating nitrogen atoms is comparable with the $N_2$($^2\Sigma_g^+$) equilibrium distance $r_{NN} \approx 1.098$ Å.

Near the ground state geometry $\bar{X}^1A'$, only singlet states of $A'$ or $A''$ geometry can be excited to a significant amount. The transition probability to the $^3A'$ or $^3A''$ states...
will be lower by several orders of magnitude. If we neglect the influence of the terminating H atom on the electronic transitions, then we expect to see two electronic excited states of \( ^1A' \) and \(^1A''\) geometry both at the same energy. The transition moments to these states will be aligned perpendicular to the \( N_3 \) chain and in the molecular plane for one transition, but perpendicular to the plane for the other one. In this case, the photoexcitation of \( \text{HN}_3 \) will not strongly align the parent molecule in the lab frame and the ejected NH fragments should show a spatial isotropic distribution, i.e., a vanishing \( \langle \mu \rangle \) correlation with \( \beta_{\mu \nu} = 0 \). However, for the lowest rotational state of the \( \text{NH}(^1\Delta) \) product, a value of \( \beta_{\mu \nu} = -0.4 \) is observed which is close to the theoretical limit of \( \beta_{\mu \nu}(\text{max}) = -0.5 \) for a perfect perpendicular alignment between the transition dipole moment of the parent and the recoil velocity. Thus, only the \(^1A'\) state of \( \text{HN}_3 \) will be populated.

\textit{Ab initio} calculations of Meier and Staemmler\textsuperscript{18,19} demonstrate that five of the six singlet states (\( ^3A' \) and \( ^3A'' \)) of the \( \text{HN}_3 \) in its equilibrium geometry of the ground state correlate with \( N_3(\Sigma_+^0) \) and different NH states: \( \text{NH}(a' \Delta) \) with \( \tilde{X}^1A' \) and \( ^1A'' \), \( \text{NH}(b' \Sigma^+) \) with \( \tilde{B}^1A' \), and \( \text{NH}(c' \Pi) \) with \( C^1A' \) and \( D^1A'' \). In the photolysis of \( \text{HN}_3 \) at 248, 266, and 308 nm, all NH products are formed exclusively in the \(^1A'\) state.\textsuperscript{10,21} Therefore, one would expect to excite only the \(^1A'\) state of the \( \text{HN}_3 \) parent molecule. Furthermore, the vertical excitation energies were calculated to be 4.96 eV for the \( \tilde{X}^1A' \rightarrow \tilde{X}^1A' \) transition and 6.57 eV for the \( \tilde{B}^1A' \rightarrow \tilde{X}^1A' \) transition.\textsuperscript{19} Experimentally, one observed 4.68 and 6.2 eV for the corresponding transitions.\textsuperscript{3} Thus, at wavelengths \( > 248 \) nm, only the \(^1A'\) state will be excited and the transition dipole moment \( \mu(\tilde{A}^1A' \rightarrow \tilde{X}^1A' \) must be aligned \textit{perpendicular} to the \( \text{HN}_3 \) plane (Fig. 5). At higher excitation energies (\( \tilde{B}^1A' \rightarrow \tilde{X}^1A' \) ) also NH products in the \( b' \Sigma^+ \) state can be generated as observed in the experiment at 193 nm.\textsuperscript{1}

In order to discuss the origin of NH rotation, we will first consider the influence of initial vibrational motion of the parent. At room temperature, the NH stretch \( [v_3(a') = 3336 \text{ cm}^{-1}] \), the NNN asymmetric stretch \( [v_5(a') = 2140 \text{ cm}^{-1}] \), the NNN symmetric stretch \( [v_5(a') = 1274 \text{ cm}^{-1}] \), and the NH bent \( [v_6(a') = 1150 \text{ cm}^{-1}] \) vibrational modes are not excited. Only the NNN in plane bend \( [v_3(a') = 522 \text{ cm}^{-1}] \) and the NNN out-of-plane bend \( [v_3(a') = 1274 \text{ cm}^{-1}] \) vibrational excited levels are populated to a small extent. The total initial vibrational energy of the parent \( E_{\text{vib}} (\text{HN}_3, T = 300 \text{ K}) = 76 \text{ cm}^{-1} \) is negligibly small.

From all normal modes of \( \text{HN}_3 \), only zero point motion of the NH \( v_4 \) bending vibration can induce NH rotation. Zero point motion of the other modes will essentially be released as NH translation. If the upper potential surface of \( \text{HN}_3 (\tilde{A}^1A' \) ) is only repulsive along the \( R \) coordinate (see Fig. 5) and does not induce any torque in the NH rotor, i.e., the anisotropy of the upper surface is zero, then the distribution of final rotational states \( P(J) \) in the energy sudden approximation is determined by the expansion of the ground-state wave function \( \Psi_{gs} (\gamma) \) in terms of the free rotor eigenstates \( Y_\gamma (\gamma, 0) \)\textsuperscript{22}:

\[ P(J) = \left| a_J \right|^2 \sum |a_J|^2 \]

with the expansion coefficients

\[ a_J = \langle \Psi_{gs} | Y_J \rangle = 2\pi \int_0^\pi d\gamma \sin \gamma \Psi_{gs} (\gamma) Y_J (\gamma, 0) \]  

Since the parent molecule is initially in its \( v_4 \) vibrational ground state, the distribution of angles \( \gamma \) is a narrow Gaussian type function centered at the NNH equilibrium angle \( \gamma_0 = 108.8^\circ \).

Using Jacobian coordinates, this angle will be transformed to an equilibrium angle of \( \gamma_r = 113.5^\circ \) for repulsion along the \( R \) coordinate. Figure 6 shows the calculated product state distribution (circles) in comparison to the experimental data squares. The electronic momentum of the \(^1A'\) state is added to the nuclear motion. The pronounced structure of the calculated distribution [Eq. (5)] will vanish when the distribution of initial parent rotational states is taken into account.\textsuperscript{23}

If final state interaction is negligible, the product state distribution should be identical to that prepared in the first step. In the Franck-Condon limit, the final distribution is a direct reflection of the parent nuclear wave function. Since the observed product rotation is hotter than in the FC limit, final state interaction is responsible for the observed distribution.

The \( \langle \nu J \rangle \) correlation contains detailed information about the origin of product rotation. We observe a positive \( \beta_{\omega J} \) parameter which increases with increasing \( J_{\text{NH}} \) (Fig. 3). For high \( J \), we assume it to be \( \beta_{\omega J} \approx + 0.45 \). It is well understood that an alignment between \( \nu \) and \( J \) strongly influences the Doppler line profile. For \( \nu \parallel J \) the center of the \( Q \) lines will show increasing intensity in favor of the wings, whereas the \( P \) and \( R \) lines behave in just the opposite direction that the center of the lines decreases in intensity in favor of the wings. The reason for this behavior is the relation between the transition dipole moment \( \mu \) of the product with the fragment rotation \( J \). In the high \( J \) limit, \( \mu \) is parallel to \( J \) for \( Q \) lines, whereas \( \mu \) is perpendicular to \( J \) for \( P \) and \( R \) lines.

\[ \text{FIG. 6. Rotational product state distribution of } \text{NH}(a' \Delta) \text{ in the photodissociation of } \text{HN}_3 \text{ at 266 nm (filled squares). The circles represent the Franck-Condon limit without considering the electronic structure of } \text{NH}(a' \Delta). ] \]
In the one electron $\Sigma \rightarrow \Pi$ transitions, the $Q$ transition probes one $\Lambda$ doublet $\Pi (A')$, while $P$ and $R$ lines probe the other $\Lambda$ component $\Pi (A'')$. In the analysis of NH products, the two-electron $^1\Delta$ state is excited to a $^1\Pi$ state. Each rotational transition consists of a pair of lines. The initial level of one line is of $\Delta (A')$ symmetry, while the origin of the other line is the asymmetric $\Delta (A'')$ state. For an understanding of the line profiles, it is important to know the orientation of the transition dipole moment for these line pairs. In Fig. 7, the $P$, $R$, and $Q$ branches for the NH $^1\Pi \rightarrow ^1\Delta$ transition are shown. Right to the energy levels the symmetry of the electrons with respect to reflection of the spatial coordinates in the plane of rotation is shown.

The $\Delta (A')$ and $\Delta (A'')$ states are linear combinations of two $\pi$ electrons which are identified by indices 1 and 2 in Fig. 7. The symmetry of $\Pi$ states for a $\pi^e$ electron is directly given by its symmetry. $\pi$ lobe in the plane of rotation for $^1\Pi (A')$ and $\pi$ lobe parallel to $J$ for $^1\Pi (A'')$.

The possible transitions and the direction of the transition dipole moment $\mu$ is obtained by the matrix elements considering the parity rules $++ \rightarrow --$. $\rightarrow +$:

\[
\langle \Delta (A') | \mu (A') | ^1\Pi (A') \rangle = P \text{ branch \ } \mu || J;
\]

\[
\langle \Delta (A') | \mu (A') | ^1\Pi (A'') \rangle = P, R \text{ branch \ } \mu \perp J;
\]

\[
\langle \Delta (A'') | \mu (A'') | ^1\Pi (A') \rangle = Q \text{ branch \ } \mu || J;
\]

\[
\langle \Delta (A'') | \mu (A'') | ^1\Pi (A'') \rangle = P, R \text{ branch \ } \mu \perp J. \quad (7)
\]

Here $\mu (A'')$ represents a transition dipole moment perpendicular to the plane of rotation and $\mu (A')$ is the transition moment in the plane of rotation. The other transitions are forbidden:

\[
\langle ^1\Delta (A') | \mu (A') | ^1\Pi (A'') \rangle = \langle ^1\Delta (A') | \mu (A'') | ^1\Pi (A') \rangle = 0.
\]

Thus both transition dipole moments for the $Q$ lines probing different $\Lambda$ levels are parallel to $J$ and the transition dipole moments for $P$ and $R$ lines are perpendicular to $J$. In the analysis of the Doppler profile, both $\Lambda$ levels are treated equally and the observed vector correlations as a function of product rotation represent the average of the $^1\Delta (A')$ and $^1\Delta (A'')$ states.

Since we observe a dip in the line profiles of $P$ or $R$ lines and an increased intensity in the center of the line when $Q$ transitions are excited, $v$ and $J$ are aligned preferentially parallel to one another. In the high $J$ limit, the average angle $\theta_{\omega v}$ between $v$ and $J$ is given by

\[
\beta_{\omega v} = \langle P_z (\cos \theta_{\omega v}) \rangle.
\]

With $\beta_{\omega v} = +0.40$, we obtain an average angle of $\langle \theta_{\omega v} \rangle \approx 39^\circ$. If the influence of initial parent rotation on the dissociation dynamics is negligible, then a parallel alignment between the translational and rotational motion of the NH product can only be generated by a torsional motion of the NH–N$_2$ system due to conservation of angular momentum.

The fraction of rotational energy induced by torsion $f_{\text{torsion}} = \langle E_{\text{torsion}} \rangle / E_{\text{rot}}$ or bending motion $f_{\text{bend}} = \langle E_{\text{bend}} \rangle / E_{\text{rot}}$ is given by

\[
f_{\text{torsion}} = (1 + 2\beta_{\omega v}) / 3 \approx 60\% ,
\]

\[
f_{\text{bend}} = 2(1 - \beta_{\omega v}) / 3 \approx 40\%. \quad (8)
\]

Thus the major part of rotational energy is induced by a nonplanar (torsional) motion of the NH rotor during the fragmentation process.

The influence of parent rotation on $J_{\text{NH}}$ can be estimated by simple classical calculation where parent rotation about the three axes of inertia will be transferred into fragment internal rotation or orbital angular momentum. In the case of HN$_2$ ($kT / 2 = 104$ cm$^{-1}$ for each degree of freedom), $J_{\text{NH}} = 2.2$ $\hbar$ will be transferred into NH rotation where the rotational vector is aligned along the recoil $R$ axis and $J_{\text{NH}} = 0.4$ $\hbar$ for a perpendicular alignment between $v$ and $J$. Since much more product rotation is generated in the dissociation process (see Fig. 6), the observed positive ($\text{vJ}$) correlation is not caused by parent rotation, but mainly by the dynamics of the fragmentation process. This is confirmed by the analysis of Doppler broadened NH lines in the photodissociation of HN$_2$ at 248 nm in a molecular beam, where the initial parent motion is significantly reduced to a rotational energy of less than 10 K. Since in this beam experiment a positive ($\text{vJ}$) correlation is also observed, the product rotation must be generated via a nonplanar motion of the NH rotor.

Another hint for the nonplanarity of the dissociation process is the population of the $\Lambda$ doublets. HN$_2$ is excited to the $^1A'$ state which has an antisymmetric wave function.
with respect to reflection in the molecular plane. For a planar fragmentation, i.e., the $N_2$ and NH bond will always lie in this plane, the wave function of the NH fragment should also be antisymmetric with respect to reflection, since the wave function of the $N_2(X^2\Sigma^+_g)$ is symmetric. Thus, the $\Delta (A^*)$ levels of the NH($a^1\Delta$) product should be preferentially populated, because the wave function of this state is antisymmetric (Fig. 7). However, no preferred population has been found within the experimental error of 10%.

While the vector correlation between $v$ and $J$ is independent of the dissociation lifetime, since $v$ and $J$ are only produced at the moment of fragmentation, the vector correlation between the transition dipole of the parent $\mu$ and the recoil velocity $v$ depend on the time scale of the dissociation process for a rotating parent, since $\mu$ is aligned with $E$, the electric field vector of the photolyzing laser beam, at $t = 0$, but the velocity is determined at the moment of separation and is analyzed for a period of time much longer than the fragmentation lifetime

$$\beta_{\mu v} = \langle P_2(\mu_{i=0} \cdot v_{t=\infty}) \rangle. \tag{9}$$

Only the $A^1\Delta$ electronic transition is excited, where the transition dipole moment is perpendicular to the plane of the parent.\cite{18,19} If this planar geometry is conserved during the fragmentation process, $\beta_{\mu v}$ should be negative (and close to $-0.5$) for all product rotations. However, the observed increase of the $\langle \mu \cdot v \rangle$ correlation with increasing fragmentation rotation to positive values implies a motion of the direction $\mathbf{R}$ towards the $\mathbf{E}$ vector during fragmentation. Since $\mu$ is perpendicular to the initial plane of the parent $HN_3$ molecule, this motion corresponds to an out-of-plane wagging vibration comparable to the $v_6(a^3\Delta)$ mode. Thus a linear-bent electronic transition in the NNN frame is excited and the $HN_3$ distorts from a NN--NH bent configuration.

A pictorial view of the photofragmentation of hydrazoic acid is shown in Fig. 8. The NNN frame is bent and the direction of repulsion is given by the dissociation coordinate $R$. The average angle of $\beta_{\mu v} = 49.8^\circ$ is calculated from the observed $\beta_{\mu v}$ value at high NH rotations $\beta_{\mu v} = \langle P_2(\cos \theta_{\mu v}) \rangle$.

Since the mass of the terminating hydrogen atom is much lower than that of the nitrogen atoms, the bending vibration is essentially determined by the NNN framework. Consequently, the $N_2$ fragment should exhibit a much higher rotational excitation than the NH fragment. The internal energy of the $N_2$ product can be measured by (2 + 2) REMPI, or by an accurate measurement of the velocity $v_{NH}$ of the NH partner fragment which is generated in the same dissociation process\cite{20}

$$E_{int}(N_2) = E_{av} - E_{int}(NH) - \frac{1}{2} m_{NH} v_{NH}^2 / \mu_{N,NH}, \tag{10}$$

in which $E_{av}$ is the available energy and $\mu_{N,NH}$ is the reduced mass of the $N_2$--NH system. Figure 9 shows the mean internal energy of the $N_2$ partner fragment as a function of NH rotation obtained by linewidth measurements of the $\tilde{c}^1\Pi \rightarrow a^1\Delta$ transitions. Final resolution of the dye laser and residual Doppler motion of the parent has been considered. The internal energy of the $N_2$ product shows only a minor dependence on the rotation of the NH fragment. The average value of internal $N_2$ energy is extremely high $\langle E_{int}(N_2) \rangle = 9900$ cm$^{-1}$.

The exact shape of the $N_2$ internal energy distribution could not be determined because of the remaining $HN_3$ Doppler motion, the resolution of the dye laser, and the narrow energy spacing of $N_2$ rotational quantum states. However, high resolution experiments ($\Delta \nu < 50$ MHz) in a molecular beam at a photolysis wavelength of 248 nm show no structure in the line profile which is to be interpreted as $N_2$ vibrational energy. Therefore, we conclude that in the photodissociation of $HN_3$ at 266 nm, the $N_2$ products are generated with extremely high rotational excitation. The product state distribution is fitted to a Gaussian distribution. The average rotational energy of 9900 cm$^{-1}$ corresponds to a mean $N_2$ rotation at quantum number of $\langle J_{N_2} \rangle = 70$. The width $\Delta J$ of the rotational state distribution $P(J_{N_2})$ is determined by the width of the fitted Gaussian velocity distribution.

![FIG. 8. A pictorial view of the fragmentation of hydrazoic acid at 266 nm. A linear-bent electronic transition within the NNN frame is excited and $HN_3$ becomes distorted from a strongly bent configuration.](image)

![FIG. 9. Mean internal energy of the $N_2$ partner product as a function of NH rotation.](image)
\[ P(J_{N_2}) \sim \exp \left[ -\frac{(J - \langle J_{N_2} \rangle)^2}{\Delta J} \right] \quad 4 \ln 2 \]  
with \( \Delta J = 15 \) (FWHM).

These observations are supported by the results of (2 + 2) REMPI measurements performed by Dagdigian and co-workers\(^{25}\) where high power laser beams \( \approx 283 \) nm were used to photolyze HN\(_3\) and to analyze the N\(_2\) product through its \( a'1\)T state with the same light pulse. The N\(_2\) products were found to be vibrationally cold, but highly rotationally excited with an average rotational excitation of \( \approx 6.400 \text{ cm}^{-1}\). A lower rotational excitation in the REMPI work can be expected since a lower HN\(_3\) excitation energy is used. The N\(_2\) product state distribution in the photodissociation of HN\(_3\) at 283 nm is roughly Gaussian shaped with the most probable N\(_2\) rotation at \( \langle J_{N_2} \rangle = 56 \) and a width of \( \Delta J = 13 - 14 \) (FWHM).\(^{25}\) The results at 283 and 266 nm photolysis wavelength indicate that the increase of HN\(_3\) excitation energy will essentially be transferred into N\(_2\) rotation.

A rough estimation of the lifetime of the dissociation process can be extracted from the \( \beta_{\mu\nu} \) value at the lowest rotational state. We start with the model assumption that the parent molecule become distorted in a plane. For an instantaneous planar dissociation with \( \mu \) perpendicular to the molecular plane the limiting value of \( \beta_{\mu\nu} = -0.5 \) is expected. A deviation from this value can be attributed to a deflection of the recoil velocity by the tangential velocity \( v_\rho \) of the rotating parent and to a HN\(_3\) rotation through an angle \( \delta = \omega \tau \) before fragmentation where \( \omega \) describes the angular velocity and \( \tau \) the lifetime of the parent in the excited state.\(^{27}\) Since the tangential velocity is very small \( (\omega \approx 290 \text{ m/s}) \) in comparison to the recoil velocity \( (v \approx 3000 \text{ m/s}) \), the value of \( \beta_{\mu\nu} \) is reduced mainly by the finite time of dissociation (angle of deflection \( \approx 5^{\circ} \)). Following the work of Bush and Wilson,\(^{27}\) we obtain for the first order decay the upper limit for the fragmentation time \( \tau \ll 100 \text{ fs} \). This short dissociation time on the femtosecond time scale is in accordance with the broad and only weakly modulated HN\(_3\) absorption spectrum. However, the value of \( \tau \) can only be interpreted as an upper limit because the strong NNN bending motion mainly influences the \( \beta_{\mu\nu} \) parameter as can be seen for high NH product rotations where \( \beta_{\mu\nu} \) becomes positive (Fig. 2). As a consequence, the dissociation geometry becomes dependent on the dissociation lifetime. This can also be seen when the ratio of the \( \langle \mu \nu \rangle \) and the \( \langle \mu \lambda \rangle \) correlation is considered. Corresponding to Eq. (9) \( \beta_{\mu\nu} \) can be written in the classical limit

\[ \beta_{\mu\nu} = \langle P_2(\mu_{\nu, 0} \cdot \mu_{\lambda, 0}) \rangle. \]

Following the work of Dockert et al.\(^{28}\) and the azimuthally averaged addition theorem described by Barnwell et al.\(^{29}\) we can separate the complete fragmentation process into two parts, one part before dissociation has started (up to time \( \tau \)) and the other part after dissociation has begun:

\[ \beta_{\mu\nu} = \langle P_2(\mu_{\nu, 0} \cdot \mu_{\lambda, 0}) \rangle P_2(\mu_{\nu, \tau} \cdot \mu_{\lambda, \tau}) \];

\[ \beta_{\mu\nu} = \langle P_2(\mu_{\nu, \tau} \cdot \mu_{\lambda, \tau}) \rangle P_2(\mu_{\nu, 0} \cdot \mu_{\lambda, 0}). \]

If the dissociation geometry is independent of the fragmentation lifetime, then the ratio of the two expressions cancels the lifetime factor

\[ \frac{\beta_{\mu\nu}}{\beta_{\mu\nu}} = \frac{\langle P_2(\mu_{\nu, 0} \cdot \mu_{\lambda, 0}) \rangle}{\langle P_2(\mu_{\nu, \tau} \cdot \mu_{\lambda, \tau}) \rangle}. \]

This "geometry index" \( \beta_{\mu\nu}/\beta_{\mu\nu} \) should be approximately independent of the lifetime if the dissociation geometry is independent of the time of separation. Since we observe a low \( \beta_{\mu\nu} \) value independent of \( J_{NH} \), but a strongly increasing \( \beta_{\mu\nu} \) parameter with increasing \( J_{NH} \), the fragmentation geometry should depend on the dissociation lifetime.

From the knowledge of the NH\(^{('A')}\) and N\(_2\)(\(^{1}S^+\)) product pair rotation information about the orbital angular momentum \( L_{N_2-NH} \) and the impact parameter \( b \) can be extracted. In general, conservation of angular momentum limits the range of the orbital angular momentum for a nonrotating HN\(_3\) parent to

\[ J_{N_2} + J_{NH} > L_{N_2-NH} > |J_{N_2} - J_{NH}|. \]

Furthermore, the available phase space is also limited by energy conservation

\[ L_{N_2-NH} = b^2 \langle 2\mu_{N_2-NH} [E_{av} - E_{rot}(N_2) - E_{rot}(NH)] \rangle, \]

where the relation

\[ L_{N_2-NH} = \mu_{N_2-NH} b_{N_2-NH} \]

is used, with \( b_{N_2-NH} \) being the relative velocity of the products N\(_2\) and NH\(^{('A')}\).

Since the NH partners exhibit only low rotational excitation and the N\(_2\) fragments are formed with high rotation [even for a nonrotating NH\(^{('A')}\) partner fragment at \( J_{NH} = 2 \), see Fig. 9], the orbital angular momentum is essentially characterized by N\(_2\) rotation.\(^{30}\) For \( L_{N_2-NH} = \langle J_{N_2} \rangle = 70 \) and \( v_{NH} = 3300 \text{ m/s} \), we obtain an impact parameter of \( b \approx 0.9 \text{ Å} \) which is not strongly dependent on \( J_{NH} \) rotation. This impact parameter is larger than the distance between the N\(_2\) center-of-mass and the HN\(_3\) center-of-mass in its equilibrium position \( (d = 0.64 \text{ Å}) \). A completely different situation is observed in the photodissociation of H\(_2\)O\(_2\), where the rotational vectors of the OH products are oriented essentially in the opposite direction and an extremely low value for the orbital angular momentum is observed.\(^{11}\)

The range of the impact parameter \( \Delta b \) is essentially given by the spread of the observed recoil velocity and one obtains \( \Delta b = 0.26 \text{ Å} \). The correlation of product quantum states as indicated in Fig. 9 gives some further hints on the impact parameter distribution. If more energy is released into internal product excitation, the translational energy slightly decreases (Fig. 9). If \( b \) is constrained, a lower velocity of \( b_{N_2-NH} \) results in less orbital angular momentum [Eq. (17)] and therefore in less N\(_2\) rotation \( L_{N_2-NH} \approx |J_{NH} + J_{NH}| \). In this case, rotationally excited NH products correlate with N\(_2\) partner fragments in lower rotational states.

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15This parameter \( \beta_{\text{me}} \) incorporates already the term \( \hat{P}_2(\cos \theta) \) which sometimes is written explicitly in the line profile function (Ref. 9).
18V. Staemmler and U. Meier (private communication).
25P. J. Dagdigian (private communication).
30Transfer of initial parent rotation into \( \text{N}_2 \) product rotation is also negligible, because from classical calculations one concludes that less than five quanta of \( \text{HN}_2 \) rotation (essentially from the \( A \) and \( B \) axis of inertia) will be found as \( \text{N}_2 \) rotation.