Photodissociation dynamics of HN₃.
The N₃ fragment internal energy distribution

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The H-atom velocity distribution of the photofragmentation of HN₃ at 243 nm has been characterized using resonant enhanced multiphonon ionisation (REMPI) in combination with time-of-flight (TOF) measurements. The internal energy distribution of the N₃ fragment has been determined from the experimental results. The structures in the N₃ internal energy distribution were assigned to the excitation of the N₃ symmetric stretching mode. The relative population of the (000):(100):(200):(300):(400) modes was found to be 0.09:0.19:0.28:0.29:0.15. The means of the vibrational and rotational energies are \( \langle E_{\text{vib}} \rangle = 2970 \text{ cm}^{-1} \) and \( \langle E_{\text{rot}} \rangle = 720 \text{ cm}^{-1} \). The excitation of the symmetric stretching mode indicates the dominating influence of the N-N₂H, N₂-NH, and N₂-H coordinates of the upper potential energy surface (PES) on the N₃ internal energy distribution.

1. Introduction

The photodissociation of HN₃ has been object of extensive studies by several groups [1–9]. In an infrared multiphoton dissociation experiment Casassa et al. [1–3] observed the NH product in the \( \chi^3 \Sigma^- \) and the \( \chi^1 \Delta \) quantum state depending on the applied IR wavelength. Several studies [4–9] were carried out by excitation of the \( \chi^1 \Delta^* \) state of the HN₃ molecule using various UV wavelengths. Scalar properties as well as vector correlations have been determined giving a detailed view into the dissociation dynamics of the reaction

\[
\text{HN}_3 + h\nu \rightarrow \text{NH}(\chi^1 \Delta) + \text{N}_2(\chi^1 \Sigma^+) .
\]

Another reaction channel leading to H atoms has recently been verified [10] by the detection of nascent H atoms using photolysis wavelengths of 193 and 248 nm. Two reaction paths leading to the separation of a H atom are energetically possible, although the second one is spin-forbidden:

\[
\begin{align*}
\text{HN}_3 + h\nu & \rightarrow \Pi(\chi^2 \Sigma) + \text{N}_2(\chi^2 \Pi) , \\
\text{HN}_3 + h\nu & \rightarrow \text{H}(\chi^2 \Sigma) + \text{N}(\chi^4 \Sigma) + \text{N}_2(\chi^1 \Sigma^+) .
\end{align*}
\]

In a recent study some scalar properties as well as the asymmetry \( \langle \mu \cdot \nu \rangle \) correlation of the nascent H atom have been determined at photolysis wavelengths of 248 and 193 nm using the sub-Doppler laser-induced fluorescence (LIF) technique [11]. If the available energy is increased by decreasing the photolysis wavelength, the additional energy is released as internal energy of the N₃ fragment. The strongly negative \( \langle \mu \cdot \nu \rangle \) correlation suggests that the fragments are ejected in the molecular plane. The N₃ fragment is believed to be highly vibrationally excited but rotationally cold since the N₃ chain in the HN₃ is elongated compared to the free N₃ radical. In the present work, we intend to classify which internal modes are excited in the dissociation process in order to determine which molecular coordinates are involved in this elementary reaction.

The N₃ radical has already been observed by the LIF technique [12,13] as a product of the photolysis of HN₃. But it was believed to be produced by the secondary reaction \( \text{HN}_3 + \text{NH}(\chi^1 \Delta) \rightarrow \text{NH}_2 + \text{N}_3 \) [12]. Unfortunately the \( \chi^3 \Sigma \) state of the N₃ molecule used for the LIF detection is predissociative [12,14], and so the sensitivity of this experimental technique is drastically reduced, making it difficult to detect low N₃ concentrations. Other than this, several thousand rovibronic states can be populated by the N₃ fragment within a range of 5000 cm⁻¹ internal energy [15], so the expected concentration per
quantum state is low. Moreover, only a few of the vibrational bands [12,13,16] have been resolved until now. Thus the LIF technique is not an appropriate tool for investigating the nascent N3 product.

The easiest way to obtain information about the population of quantum states of the N3 fragment is the determination of the H atom kinetic energy distribution which reflects the internal energy distribution of the N3 fragment.

2. Experimental

The H-atom velocity distribution is analyzed with the (2 + 1)-REMPI-TOF technique [17-19] as a diagnostic tool. Because the influence of initial parent molecule motion has to be minimized, the use of supersonic expansion in a molecular beam is necessary. The reaction chamber is made of stainless steel and evacuated by two baffled 500 l/s oil diffusion pumps to a base pressure of 10^{-4} Pa. The home-built TOF spectrometer is mounted inside the reaction chamber and evacuated by a 360 l/s turbomolecular pump (Leybold Heraeus 360 CSV).

HN3 is generated by dropwise addition of phosphoric acid to NaN3 under vacuum and stored in a glass bulb at a maximum pressure of 10^{-4} Pa. The HN3 is expanded through a pulsed nozzle (General Valve) into the reaction chamber. The molecular beam is collimated by a skimmer before it enters the TOF spectrometer, where it is intersected by the photolyzing/analyzing laser beam. During the measurements the background pressure is 10^{-3} Pa in the TOF tube.

The (2+1) REMPI process uses the H(2^2S) → H(1^2S) resonant transition as an intermediate step. The photolyzing and analyzing light is delivered by an excimer laser pumped (LPX 605i Lambda Physik) dye laser system with SHG (LPD-3000 Lambda Physik) and focused tightly into the spectrometer by a 6 cm quartz lens. The laser power is carefully controlled to avoid space charge effects and is typically kept below 1 mJ. H ions are detected by a double stage multichannel plate (MCP) assembly (Galileo).

The TOF spectrometer (fig. 1) is designed for maximum kinetic energy resolution. All metal parts inside the spectrometer are gold plated to avoid disturbing electric fields due to anisotropic work functions [11]. The spectrometer is divided into three parts: a 9 cm long drift region, a 10 cm long acceleration region, and a second 38 cm long drift region which is separated from the acceleration region and the MCP assembly by two gold plated stainless steel meshes. TOF drift profiles were obtained by applying an electric field between the last six electrodes, so that the H ions are produced in a field free region. Therefore, only ions which initially fly directly towards the detector will hit the detector. In this operation mode only a few ions will reach the MCP assembly, resulting in a weak H ion signal. Therefore an amplifier/discriminator unit (7011 FAST) in combination with a multihit time to digital converter (7885 FAST) has been used to process the signal. The TOF signal is obtained by adding over a large number (10^3–10^5) of laser shots. The advantage of this operation mode is a high resolution of the H atom recoil velocity distribution.

To compensate for any systematic errors due to inhomogeneous electric fields inside the TOF spectrometer, the H atom velocities were calibrated by observing H atoms produced in the following reaction:

HI + hν(243 nm) → H(2^2S) + I(2P_{3/2})
HI + hν(243 nm) → H(2^2S) + I^*(2P_{1/2}).

Since the dissociation energy [20] of HI and the spin orbit splitting of the I atom are well known it is possible to calculate the two discrete H atom recoil velocities belonging to the different I states.

3. Results and discussion

To obtain precise information on the H atom ve-
velocity distribution which represents the \( \text{N}_3 \) internal energy distribution, several TOF drift profiles were recorded. A typical TOF drift profile is shown in fig. 2 which was obtained by accumulation over \( 5 \times 10^5 \) laser shots.

The relation between the H atom velocity and the measured time of flight is given to a good approximation by

\[
t(\upsilon_H) = t_c + \frac{d}{\upsilon_H},
\]

where \( d \) is the distance between the laser focus and the beginning of the acceleration region. The constant \( t_c \) accounts for the time of flight between the beginning of the acceleration region and the MCP assembly. In our experiment \( t_c \) is assumed to be independent of \( \upsilon_H \) since the additional kinetic energy of the acceleration (109 eV) is much larger than the kinetic energy release in the photodissociation (\( \approx 1 \) eV).

The system is calibrated with HI as a standard to evaluate the constant \( t_c \). The conversion of the TOF drift profile into a H atom kinetic energy spectrum is shown in fig. 3 where the following equation has been used:

\[
E_{\text{kin}}(H) = \frac{1}{2} m_H \left\{ \frac{d}{[t(\upsilon_H) - t_c]} \right\}^2.
\]

The intensity normalization was carried out using the relation \( f(E) \, dE = f(t) \, dt \).

Since linear momentum has to be conserved, the total kinetic energy of both fragments is given by

\[
E_{\text{kin}}(\text{tot}) = E_{\text{kin}}(H) \left(1 + \frac{m_H}{m_{\text{N}_3}}\right).
\]

So the internal energy distribution of the \( \text{N}_3 \) fragment can be calculated from the total kinetic energy distribution to be

\[
E_{\text{int}}(\text{N}_3) = E_{\text{av}} - E_{\text{kin}}(\text{tot}).
\]

\( E_{\text{av}} \) is the available energy for the products, \( E_{\text{av}} = h\nu + E_{\text{int}}(\text{HN}_3) - E_{\text{diss}} \), where \( E_{\text{diss}} \) is the dissociation energy of the H–\( \text{N}_3 \) bond, and \( E_{\text{int}}(\text{HN}_3) \) is the internal energy of the parent molecule which is negligible since \( \text{HN}_3 \) is cooled in a molecular beam.

It can be seen from fig. 3 that the observed H atom kinetic energy distribution consists of five nearly equally spaced maxima which are well fitted by the sum of five Gaussian functions of the same width:

\[
I = B + \sum_{i=0}^{4} A_i \exp \left[ -4 \ln 2 \left( \frac{E_{\text{kin}}(H) - E_{\text{kin},i}(H)}{\Delta E_{\text{kin}}(H)} \right)^2 \right].
\]

\( B \) is the height of the baseline, the factors \( A_i \) are the intensities, \( E_{\text{kin},i}(H) \) are the center positions, and \( \Delta E_{\text{kin}}(H) \) is the common width (fwhm) of the five...
Gaussian functions. The results of the fitting procedure are summarized in table 1.

The tail of fast H atoms in fig. 3 with kinetic energy of more than 11 000 cm$^{-1}$ can be assigned to a minor secondary dissociation of NH(a' A) fragments into N(2D) and H(2S). However, the internal state distribution and the kinetic energy distribution of the NH(a' A) product from the 248 nm photolysis [8,21] suggest an almost constant background signal of H atoms due to secondary processes in the kinetic energy range under consideration falling off to zero at 3000 cm$^{-1}$ respectively at 14 000 cm$^{-1}$. Therefore the height of the baseline $B$ is set approximately equal to the value at the edge of the profile of fig. 3 at 11 000 cm$^{-1}$. This procedure is justified by the fact that within the experimental error it yields the same values for the mean fragment energies as the preceding experiments by Lock et al. [11] where secondary dissociation can be excluded.

In order to obtain the dissociation energy $E_{\text{diss}}$(II–N$_3$) it is necessary to determine the maximum H atom kinetic energy $E_{\text{kin, max}}$(H) from these fitted spectra. Since the data shown in fig. 3 are a convolution of the H atom kinetic energy spectra with the response function of the TOF spectrometer, one has to consider the width of the response function for a correct evaluation of the maximum H-atom kinetic energy. Assuming the response function to be Gaussian with a width of $\Delta E_{\text{resp}}$ and the kinetic energy distribution to be described by eq. (5), the maximum H-atom kinetic energy is given by

$$E_{\text{kin, max}}(H) = E_{\text{kin,0}}(H) + (1 + 1/\sqrt{e})\sigma,$$

where $E_{\text{kin,0}}(H)$ is taken from the fitting procedure (eq. (5)) and $\sigma$ is given by

$$\sigma = [(\langle \Delta E_{\text{kin}}(H) \rangle^2 - \langle \Delta E_{\text{resp}}^2 \rangle)/(4 \ln 2)]^{1/2}. \quad (7)$$

Since the dissociation of jet-cooled HI leads to monoenergetic H atoms, the observed signal can directly be regarded as the response function of the spectrometer. The width of the response function was determined to be $\approx 950$ cm$^{-1}$ by evaluating the width of the H atom calibration signal from the HI photolysis. A value of 10 270 cm$^{-1}$ was obtained for $E_{\text{kin, max}}(H)$. Assuming that H atoms with maximum kinetic energy can be correlated with N$_3$ fragments having zero internal energy and, if furthermore no internal energy for the HN$_3$ molecule is considered, we can write

$$E_{\text{diss}}(H-N_3) = h\nu - E_{\text{kin, max}}(H)(1 + m_H/m_{N_3}). \quad (8)$$

The value obtained for $E_{\text{diss}}(H-N_3) = 30 850 \pm 400$ cm$^{-1}$ is in good agreement with previous measurements [11]. The error is mainly due to the response function regarded as Gaussian shaped which is a fairly crude approximation.

The H atom kinetic energy distribution can be converted into the N$_3$ internal energy distribution (fig. 4) using eq. (4). The detected structure in the N$_3$ internal energy distribution already gives a hint on the energy release, e.g., the internal motion of the N$_3$ fragment. First of all, the measured energy dis-
tribution can hardly be attributed to pure rotational excitation of N₃, because we would not expect to see structure unless well separated selected groups of rotational states would be populated, which is unlikely. It remains that the observed structure is essentially from vibrational excitation of the N₃ product. Here again, pure excitation of the degenerated ν₂ bending mode cannot be attributed to the observed N₃ energy distribution, because one quantum of vibrational energy of the ν₂ mode carries 457 cm⁻¹ [13] which is also far too low to be resolved in this experiment. Thus, only the N₃ stretching modes are responsible for the structured N₃ internal energy distribution. In order to discriminate between the symmetric stretch, ν₁ = 1320 cm⁻¹, and the asymmetric stretch, ν₃ = 1644 cm⁻¹, a quantitative analysis of the TOF spectra is necessary.

With the positions of Ekin(H) and the intensities Aᵢ of the five maxima of the kinetic energy distribution (fig. 3) one can calculate the position and the height of each maximum (table 1) in the N₃ internal energy distribution (fig. 4). The energy differences between the peaks are indicative for the type of stretching mode. Table 2 lists the possible vibrational modes, their energy and the remaining rotational energy of each maximum of the N₃ internal energy distribution [15]. Excitation of the asymmetric stretching mode (table 2, record 1) cannot explain the internal energy distribution of the N₃ fragment, since in that case the vibrational energy exceeds the observed N₃ internal energy. By the same argument, excitation of a combination mode consisting of a bending mode and several symmetric stretching vibrations (table 2, record 2) can be excluded. Only the excitation of the symmetric stretching mode (table 2, record 3) leads to a reasonable energy for the N₃ rotation. However, it should be mentioned that excitation of at most one quantum of the ν₁ mode (table 2, record 4) cannot be excluded. So it is evident that excitation of the ν₁ mode is responsible for the structures of the N₃ internal energy distribution. The population of the symmetric stretching mode is shown in fig. 5. If we assume an exclusive excitation of the ν₁ mode, then the mean vibrational energy is given by:

Table 2

<table>
<thead>
<tr>
<th>Record</th>
<th>Vib. mode (ν₁ν₂ν₃)</th>
<th>E_vib</th>
<th>E_rem(N₃)</th>
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<td>000</td>
<td>35</td>
<td>860</td>
</tr>
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<tr>
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<td>260</td>
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<td>310</td>
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</tr>
<tr>
<td></td>
<td>301</td>
<td>5500</td>
<td>370</td>
</tr>
</tbody>
</table>

Fig. 5. The relative population of the ν₁ mode of the N₃ fragment generated by the photolysis of HN₃ at 243.12 nm.
The mean remaining rotational energy \( \langle E_{\text{rot}}(N_3) \rangle \) is determined to be 720 cm\(^{-1}\) where the values of record 3 in table 2 have been used. The partitioning of the available energy is calculated to be: \( f_{\text{trans}} = 0.64 \), \( f_{\text{vib}} = 0.29 \), and \( f_{\text{rot}} = 0.07 \).

A significant amount of rotational motion will broaden the width \( \Delta E_{\text{kin}}(H) \) of the kinetic energy distribution. If we compare the value \( \Delta E_{\text{kin}}(H) = 1270 \) cm\(^{-1}\) obtained by the fitting procedure with the width of the response function \( \Delta E_{\text{resp}} \), we can estimate the width of the rotational energy distribution \( \Delta E_{\text{rot}} \):

\[
\Delta E_{\text{rot}} = \left[ \Delta E_{\text{kin}}(H)^2 - \Delta E_{\text{resp}}^2 \right]^{1/2}
\]

\( \approx 840 \) cm\(^{-1}\),

where the response function and the internal energy distribution of a single stretching mode are assumed to be Gaussian.

For dynamical calculations it is of advantage to use Jacobian coordinates to describe the photodissociation process. However, the upper PES can be visualized easier when normal modes are used for a qualitative description of the fragmentation process of HN\(_3\). The rotational excitation of the N\(_3\) product is related to initial motion of the parent and to the torque provided by the gradient of the upper PES with respect to the NNH bending angle which describes the \( \nu_4 \) mode of the parent. A strong N\(_3\) rotation could be induced by a \( \nu_4 \) bending motion of the NNH frame. Since the energy release in rotation is relatively low, the NNH bending angle dependence of the upper PES should be similar to that of the ground state. This is confirmed by ab initio calculations [22].

If the upper PES causes only a separation of the two products, i.e. the dissociation process is characterized by the Franck-Condon limit, then the release of the available energy in kinetic and internal energy of the N\(_3\) fragment is determined by the quantum state distribution of the HN\(_3\) parent molecule in its ground state and the internal energy distribution of the N\(_3\) fragment should be nearly independent of the photolysis wavelength. Thus any additional available energy should be released as kinetic energy of the fragments. Since the N\(_3\) fragment is a linear and symmetric molecule (N–N bond length 118 pm) and the HN\(_3\) molecule has two different N–N bonds (113 and 124 pm), one would also expect an excitation of the N\(_3\) asymmetric stretching mode from this asymmetrically elongated N\(_3\) frame. Comparison of the experimental results with the predictions of the Franck-Condon limit indicates that the dissociation process cannot be described by the Franck-Condon limit because:

1. the N\(_3\) fragment is strongly excited [11],
2. any additional available energy is released as internal energy of the N\(_3\) fragments [11], and
3. the symmetric stretching mode of the N\(_3\) fragment is excited.

Thus the experimental data suggest that the photofragmentation process can be described by the strong coupling case, i.e. the motion of the fragments is essentially determined by the upper PES of the \( \tilde{A} \rightarrow \tilde{A}' \) state and only to a minor extent by the ground state distribution of the HN\(_3\) parent. So we expect steep gradients along the coordinates which lead to excitation of the \( \nu_1 \) mode.

The fragmentation process is governed by anharmonic coupling phenomena on the upper PES. In a simplified mechanistic picture of the dissociation process this may be described in such a way that the original N\(_1\)–N\(_2\) bond length of 113 pm is prolonged to 124 pm, or the N\(_2\)–N\(_3\) bond length is compressed to 113 pm before complete fragmentation into H + N\(_3\) in order to explain the observed N\(_3\) symmetrical stretching vibration in the dissociation of the asymmetrical elongated N\(_1\)–N\(_2\)–N\(_3\) chain of the N\(_1\)–N\(_2\)–N\(_3\)–H parent. The observed \( \nu_1 \) vibrational distribution is centered around \( \nu_1 = 2 \). A quantum-mechanical calculation of the maxima of the \( | \Psi |^2 \) function, describing harmonic N\(_3\) vibrations, shows that the N–N bond length of the free N\(_3\) molecule is changed by about 6 pm for \( \nu_1 = 2 \) relative to the \( | \Psi |^2 \) maximum of the \( \nu_1 = 0 \) state. This shift in the bond length is necessary when the N\(_1\)–N\(_2\)–N\(_3\) frame of the parent is “transformed” into the free N\(_3\) product. The dissociation process may be visualized as follows:

While the H atom is recoiling from the neighboring N atom, this N atom approaches the N\(_1\)–N\(_3\) frame to a distance of about 113 pm. During this approach the length (113 pm) of the strong N\(_1\)–N\(_2\) bond should
not be changed significantly. When the symmetrical configuration of the \(N_1-N_2-N_3\) frame is reached the influence of the recoiling hydrogen becomes negligible resulting in symmetrical vibrational motion of the \(N_3\) product. Less likely is a fragmentation process which involves lengthening of the \(N_1-N_2\) bond length to about 124 pm while the \(N_2-N_3\) bond length remains essentially unchanged when the H atom is leaving the excited HN\(_3\) complex. The influence of the hydrogen becomes unimportant for the fragmentation process when a symmetrical \(N_1-N_2-N_3\) configuration is reached and the \(\nu_1\) mode of the product is excited.

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References