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Rotational distribution of N_2^+ fragments from 355 nm photolysis of N_4^+

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Abstract

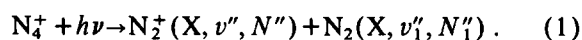
The vibrational and rotational status of $X^2\Sigma_g^+ N_2^+$ fragments from the 355 nm photolysis of N_4^+ has been assessed using two complementary experimental techniques. Evidence from both methods suggests that the N_2^+ photofragments are predominately in the $\nu=0$ vibrational level of the electronic ground state and can possess considerable rotational energy (up to 3000 cm^{-1}).

1. Introduction

This Letter presents the first rotationally resolved spectra of molecular fragments from the photolysis of an ionic complex. Kinetic energy distributions of radical ion photofragments from complexes such as N_4^+ [1], and $(NO)_2^+$ [2] have been measured previously and while these provide information on the situation and symmetry of electronic states, and in some cases on fragment vibrational energies (e.g. for KrO_2^+ [3]), the inherent resolution of the technique is insufficient to probe the *rotational* state of the ionic or neutral fragments. Contrast this with the current situation for neutral species where spectroscopic measurements of fragment vibrational states, angular momenta and velocities have illuminated dynamical details of molecular photodecompositions [4].

The focus of the present work is the photodecomposition of N_4^+ . Thermochemical [5], matrix [6,7] and ab initio [6,8] studies present a consistent view of the precursor N_4^+ as being a symmetric linear spe-

cies ($^2\Sigma_u^+$ ground state), with a D_0 for dissociation into N_2^+ ($X^2\Sigma_g^+$) and N_2 ($X^1\Sigma_g^+$) of approximately 1 eV. Lying some way above the ground electronic state is a $^2\Sigma_g^+$ repulsive surface, so that irradiation with light between 670 and 260 nm results in the direct production of ground electronic state N_2^+ and N_2 fragments [1,8–10],



Our concern is with the energy disposal in the photodissociation reaction (1). Neglecting the possibility for fragment electronic excitation, there are five degrees of freedom amongst which the energy can be distributed – rotational and vibrational motion for each fragment and relative translational motion. That is

$$\begin{aligned} h\nu &= D_0 + E_{\text{vib}}(N_2^+) + E_{\text{rot}}(N_2^+) + E_{\text{vib}}(N_2) \\ &\quad + E_{\text{rot}}(N_2) + E_{\text{trans}} \\ &= D_0 + E_{\text{avail}} , \end{aligned}$$

where D_0 is the $N_2-N_2^+$ binding energy. Fragment

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translational energy distributions for N_4^+ photolysis have been measured at several fixed wavelengths. In these measurements the average E_{trans} is generally considerably less than E_{avail} [1]. For instance at 488 nm (assuming $D_0 \approx 1$ eV) the available energy is 1.5 eV, yet the peak in the fragments' kinetic energy distribution occurs at around 0.45 eV, proving that considerable energy is shared between the remaining degrees of freedom [1]. The latter authors conclude that most of this energy is probably deposited in the fragment vibrational motion, with the peak in the kinetic energy distribution corresponding to 4 N–N stretch quanta (ω_e for N_2 and N_2^+ is 2358.6 and 2207.0 cm^{-1} [11]), although the absence of resolved vibrational structure in the kinetic energy release distribution suggested a lower limit of 0.15 eV for product rotational energy [1].

In a more recent study, the vibrational energy of N_2^+ photofragments produced at several different wavelengths (266, 315, 396, 532 and 630 nm) was assessed by allowing them to react with Ar buffer gas [12]. The technique relies upon the fact that while N_2^+ ions in the ground vibrational state ($v=0$) have a small cross section for charge transfer with Ar, the higher vibrational levels react rapidly to produce Ar^+ . Surprisingly these data showed that 60%–70% of the N_2^+ fragments were in the $v=0$ level, almost independent of the photolysis wavelength, prompting the proposal that the fragments may acquire considerable rotational energy as they traverse the dissociative surface [12].

To further explore energy partitioning in the N_4^+ photodissociation reaction (1) we have in this work appraised the vibrational and rotational state of the N_2^+ fragments from the 355 nm photodissociation of cold N_4^+ (20–40 K) using two spectroscopic techniques – laser-induced fluorescence (LIF) and laser-enhanced charge transfer with Ar buffer gas. The results provide evidence that N_2^+ photofragments from cold N_4^+ are indeed mostly in the $v=0$ state and can have up to 3000 cm^{-1} of rotational energy, findings which are discussed in the light of the earlier kinetic energy release experiments [1].

2. Experimental details

In the charge transfer experiment, N_4^+ ions formed

in an electron-beam crossed-supersonic expansion [13] were selected with a quadrupole mass filter and injected into an octopole ion trap where they were irradiated with light in the 350–360 nm range (pulse energy 1 mJ, pulse duration 10 ns, beam diameter = 3 mm). Besides photolysing N_4^+ , light in this region is capable of exciting the N_2^+ B←X (1–0) transition lying near 358 nm. A single laser pulse serves both to dissociate N_4^+ and excite N_2^+ fragments. Following the pulse, N_2^+ photoproducts are trapped within the octopole for 10 ms with $\approx 10^{-5}$ Torr of Ar buffer gas. The cross section for the charge transfer reaction $N_2^+(X^2\Sigma_g^+, v) + Ar \rightarrow N_2 + Ar^+$ depends sensitively upon the vibrational state of N_2^+ [14], rising from 0.28 \AA^2 for $v=0$ to 26.3 \AA^2 for $v=1$ and 22.9 \AA^2 for $v=2$ at a collision energy of 1.2 eV [15]. By scanning the photolysis laser across the N_2^+ B←X (1–0) band, the population of N_2^+ in the different vibrational states change slightly (due to radiative relaxation of N_2^+ (B, $v=1$) into vibrationally excited levels of the X manifold). This effect can be discerned by sampling the relative fractions of Ar^+ and N_2^+ present at the end of the trap period. Full details of the experimental arrangement have been published previously [10].

The second LIF experiment yielded spectra with improved S/N, although without the advantage of mass selectivity. Again, N_4^+ ions were synthesized by crossing a pulsed expansion of neat N_2 (backing pressure ≈ 3 –4 bar) with electrons from twin filaments. Approximately 20 mm ($X/D=25$) from the nozzle orifice, the plasma was crossed with spatially and temporally overlapping outputs of a dye laser (< 40 $\mu\text{J}/\text{pulse}$, 3 mm beam diameter, 0.3 cm^{-1} bandwidth) and the third harmonic of a Nd:YAG laser (355 nm, 15 ns, ≈ 10 mJ/pulse, 3 mm beam diameter). Given a 355 nm photodissociation cross section of $\approx 10^{-17}$ cm^2 , the photolysis pulse should fragment up to 80% of the N_4^+ [10]. However, because of non-ideal beam overlap, the probe laser may not sample the entire photolysed volume. LIF from the plasma was collected with a 50 mm quartz lens and filtered to transmit the N_2^+ B→X (0–1) band in the 428 nm region. The plasma composition was monitored with a TOF mass spectrometer ≈ 200 mm downstream. In this experiment N_4^+ and N_2^+ signals were comparable, with the concentration of larger $(N_2)_n^+$ clusters at least an order of magnitude lower.

Data acquisition involved collecting LIF signals for 10 laser shots with the photolysis laser, then 10 shots without the photolysis laser, followed by a step in the probe laser wavelength.

3. Results and discussion

A spectrum of N_2^+ fragments from photolysed N_4^+ obtained using the charge transfer technique is shown in the upper trace of Fig. 1. To date this appears to be the only spectrum of an ionic photofragment from a mass selected ionic complex. The P branch head in the $B \leftarrow X$ (0–0) band occurring at $N'' \approx 13$ (at ≈ 358.2 nm) is clearly apparent. For comparison an N_2^+ $B \leftarrow X$ spectrum obtained by injecting N_2^+ (rather than N_4^+) into the octopole and monitoring the Ar^+ production is shown in the lower part of the trace. The poor S/N ratio (2:1) in the fragment spectrum is a consequence of a large background signal arising from the substantial fraction of N_2^+ photofragments ($\approx 40\%$) with $\nu > 0$, that react with Ar to produce Ar^+ irrespective of whether the laser is tuned to an N_2^+ ($B \leftarrow X$) resonance [12].

A clearer picture of the fragment N_2^+ rotational distribution comes from Fig. 2 where the sum (upper) and difference (lower) LIF spectra are reproduced. Observation of the difference spectrum re-

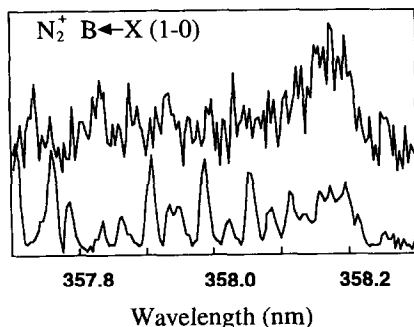


Fig. 1. The N_2^+ $B \leftarrow X$ (1–0) band near 358 nm. The lower and upper spectra were obtained by introducing N_2^+ and N_4^+ , respectively, into an octopole ion guide filled with $\approx 10^{-5}$ Torr of Ar . The ion population was irradiated and the $[Ar^+]/([Ar^+] + [N_2^+])$ fraction was monitored as a function of laser wavelength. The technique relies upon the substantially larger charge transfer cross section for N_2^+ in $\nu'' > 0$ vibrational levels. For N_4^+ , the same laser pulse is responsible for photolysis and N_2^+ $B \leftarrow X$ (1–0) fragment excitation. The N_2^+ population used to obtain the lower spectrum was deliberately warmed to make the P branch head more apparent.

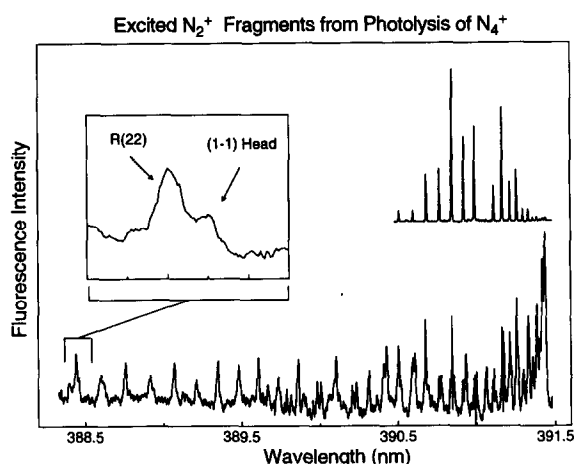


Fig. 2. The N_2^+ $B \leftarrow X$ (0–0) band near 391 nm obtained using LIF in an electron beam crossed supersonic expansion of neat N_2 . The free jet was intersected at $X/D=20$ by a 355 nm photolysis beam collinear with the probe laser beam. The lower spectrum is the difference between the signal obtained with and without photolysis laser and represents the rotational status of the N_2^+ photofragment from photolysis of N_4^+ . For comparison, the sum of photolysis laser on/off signals, representing the background N_2^+ LIF spectrum, is displayed in the top trace. Note the significant rotational population in the P branch head (near 391.44 nm) for the N_2^+ photofragment. The inset displays an expanded region near the (1–1) head.

quires the presence of the photolysis pulse, good spatial overlap between photolysis and probe beams, and proper adjustment of the ion source to produce N_4^+ . On the basis of this evidence we propose that the difference spectrum reflects the rotational distribution of N_2^+ photofragments from N_4^+ . As in the charge transfer spectrum, the P branch head of the (0–0) band is the most prominent feature.

Whereas the rotational population distribution in the upper spectrum in Fig. 2 corresponds to a temperature of ≈ 20 K, the N_2^+ population responsible for the lower spectrum is considerably more energetic. Although the S/N ratio is not sufficient to precisely determine a rotational level distribution we note that fragments with N'' between 4 and 38 are distinguishable, with the distribution peaking at around $N'' = 20$.

The P branch head of the (1–1) hot-band is discernible (position marked with an arrow in Fig. 2 inset) allowing us to estimate the fraction of N_2^+ fragments in the $\nu = 1$ level by comparing the heights of the two heads. To minimize errors, the relative inten-

sity of the heads was assessed by comparing the heights of the (1–1) head with the adjacent (0–0) R(22) line and the (0–0) head with the nearby (0–0) P(22) line. The intrinsic strengths of the R(22) and P(22) lines should be almost identical. Assuming unsaturated transitions, identical rotational distributions for $\nu=0$ and $\nu=1$ populations, and making allowances for Franck–Condon factors for excitation and emission in the 428 nm range [16] the $[\text{N}_2^+(\nu=1)]/([\text{N}_2^+(\nu=0)] + [\text{N}_2^+(\nu=1)])$ ratio is estimated as $40 \pm 15\%$. This is consistent with the earlier charge transfer measurements which suggested that $40 \pm 10\%$ of N_4^+ complexes photolysed in the 300–400 nm region produce vibrationally excited N_2^+ photofragments [12]. We have searched without success for the (2–2) P branch head.

Of some concern in the LIF experiments is the possibility of charge transfer between the nascent N_2^+ photofragments and N_2 molecules in the supersonic expansion. The cross section for $\text{N}_2^+ + \text{N}_2$ charge transfer for 0.3–0.5 eV collision energy has been reported as 43 \AA^2 [17]. With a stagnation pressure of 3–4 bar and a fragment kinetic energy of ≈ 1 eV, approximately 10% of the nascent fragments may have exchanged charge with background N_2 during the 10 ns laser pulse. Thus, the difference spectrum shown in Fig. 2 may be slightly ‘contaminated’ by contributions from ‘secondary’ N_2^+ . By varying the delay between pump and probe lasers it is possible to follow the rotational distribution of the excess N_2^+ charge carriers. For small delays (10–50 ns) the rotational distribution does not differ appreciably from the zero delay one. Scattering studies of low energy $\text{N}_2^+ + \text{N}_2$ collisions ($E_{\text{c.m.}} \leq 1.0$ eV) indicate the importance of complex formation with efficient distribution of the collision energy into vibrational or rotational degrees of freedom [18], and there is the possibility that the result of such collisions is a rotational distribution that does not differ greatly from the nascent one. With greater delay times ($> 1 \mu\text{s}$), a noticeable rotational cooling of the excess N_2^+ population is observed.

The N_2^+ rotational distribution provides information on both the ground and excited state potential surfaces. Schinke [4] has discussed the fragment rotational distribution arising from direct photodissociation processes in terms of a rotational reflection principle, whereby an electronic transition causes the ground state vibrational wavefunction to be reflected

onto the repulsive upper surface. Fragment rotational distributions can be predicted by calculating a series of classical trajectories on the upper state surface with initial conditions chosen to represent the reflected vibrational wavefunction. Thus the final rotational distribution is governed by the anisotropy of the upper dissociative surface in the Franck–Condon allowed region. If the vibrational temperature of our N_4^+ is the same as the rotational temperature of the coexpanded N_2^+ (≈ 20 K) only the lowest bending vibrational levels should be populated. The observation of an energetic fragment rotational distribution implies the existence of zero-point excursions in the ground state and significant torques in near linear configurations of the repulsive surface.

How do the results obtained in the present work relate to the kinetic energy release data reported in Ref. [1] which indicate that at 488 nm on average only around 35%–40% of the available energy appears in fragment translation? Can the present results which suggest modest vibrational energy in the N_2^+ fragments and an N_2^+ rotational distribution extending from $N''=4$ to 38 (corresponding to E_{rot} between 0.005 and 0.350 eV) be reconciled with these earlier measurements? In addressing these questions it is proper to recognize that we have no direct experimental information on the vibrational or rotational energy content of the neutral N_2 . However, for the sake of argument, let us assume that dissociation proceeds such that the N_2 neutrals have the same vibrational and rotational energy distributions as do the N_2^+ . With this assumption we have modelled fragment kinetic energy distributions and have found that by taking vibrational excitation probabilities that are consistent with the charge transfer data [12] and also the present work (e.g. $P(0, 0)=0.4$, $P(0, 1)=P(1, 0)=0.25$ and $P(1, 1)=0.1$ – where $P(m, n)$ is the probability that the N_2^+ and N_2 molecules have m and n vibrational quanta, respectively) and Gaussian rotational distributions peaking at around $N''=38$ and with fwhm of ≈ 15 , one can fit the kinetic energy release spectra reported in Ref. [1] reasonably well. Without significantly higher vibrational energy in the fragments it is impossible to simultaneously fit both sets of results with rotational distributions that peak at much lower N'' and certainly not with a rotational distribution that has a maximum at $N''=20$ as indicated by the present experiments.

One solution to this apparent dilemma could lie in the different *vibrational* temperatures of N_4^+ samples used in the various studies. We note that N_4^+ ions employed in the kinetic release studies [1] were generated in an ion source at 193 K and that while no evidence was presented concerning their temperature, in later work on the ArN_2^+ cluster it was suggested that internal energies between 0.1 and 0.2 eV were possible [19]. Under these circumstances it is possible that the two doubly degenerate low frequency bending modes, which should lie well below the low frequency stretch vibration ($\omega_e \approx 430 \text{ cm}^{-1}$ [7]), will be excited. For vibrationally excited ions, the sampled portion of the repulsive surface will depart further from the linear configuration, with consequent changes in the effective torques and fragment rotational distributions [4]. Consistency of the kinetic energy release data, the charge transfer data and the results reported here requires that the fragment rotational distribution shifts to higher N'' as the N_4^+ temperature increases. If our line of reasoning is correct, one can predict that the kinetic energy release distribution for N_4^+ ions at 20 K will be quite different from the one at higher temperatures and that as the N_4^+ temperature is reduced there should be a shift in the average translational kinetic energy to higher values.

Finally it should be noted that there are several precedents for highly rotationally excited diatomic fragments which have little vibrational energy arising from the direct photodissociation of linear neutral species [4,20,21]. For example, the maximum in the CN rotational distribution resulting from C1CN photolysis at 193 nm ($E_{\text{avail}} = 2.133 \text{ eV}$) lies at $N'' = 60$ [21]. Only 10%–20% of the fragments are vibrationally excited and for the CN ($v=0$) about 40% of the available energy is in rotation.

4. Conclusions

The present work demonstrates the use of two spectroscopic techniques to extend understanding of energy disposal accompanying direct photodissociation of N_4^+ . In doing so we hope to provide impetus for the development of accurate ab initio surfaces for ionic complexes usable in predictive dynamical calculations. From the experimental side it appears

worthwhile to measure fragment kinetic energies of *cold* N_4^+ in order to assess to what extent excitation of the low frequency bending vibrations influences product rotational and translational energy distributions. Particularly desirable would be a measurement of the velocity distribution of N_2^+ fragments in particular (v'' , N'') levels thereby gaining information on the energy distribution of both diatomic fragments.

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