

Discrete UV absorption by $N_3^+-(N_2)_n$ clusters

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Abstract

Photoabsorptions by $N_3^+-(N_2)_n$ complexes have been observed near 282 nm by detecting both N^+ and N_3^+ photofragments. The absorptions occur near the recently characterized $A^3\Pi \leftarrow X^3\Sigma_g^-$ transition of the N_3^+ cation, implying that the larger complexes essentially consist of an N_3^+ core surrounded by electrostatically bound N_2 ligands. Two mechanisms for the photodissociation are proposed, one involving coupling of the A state of the N_3^+ chromophore to a dissociative $^3\Pi$ surface to produce N^+ fragments, the other beginning with $A \rightarrow X$ internal conversion followed by a series of N_2 ligand evaporations to leave only N_3^+ .

1. Introduction

Given their possible importance in aeronomic and plasma environments it is desirable to understand the spectroscopy and photophysical behaviour of the cationic nitrogen clusters. While the even nitrogen cluster cations (N_{2n}^+ complexes) have been the subject of considerable experimental attention [1–5], their odd cousins, the N_{2n+1}^+ series, have apart from one or two studies [1,6] been largely ignored. This is somewhat surprising, given that under some circumstances both series have comparable abundances. The even $(N_2)_n^+$ sequence appears to consist of an N_4^+ ionic core surrounded by electrostatically bound N_2 ligands and it is a bound-free $^2\Sigma_g^+ \leftarrow ^2\Sigma_u^+$ transition of the N_4^+ core that appears to be responsible for cluster absorptions and photodissociation occurring between 650 and 260 nm [2,3]. The odd N_{2n+1}^+ series, which in analogy with the even series might be suspected to have essentially an $N_3^+-(N_2)_n$ structure, seem to be somewhat more robust towards photodissociation in most of this wavelength range, and there-

do not appear to be any reports of their photodestruction.

For some time it has been known that N_3^+ is a relatively stable molecular ion ($D_0 \approx 3.53$ eV [7] compared to $D_0 \approx 1$ eV for N_4^+ [4]) and has been long recognized as a common constituent of nitrogen plasmas [8–11]. Recently we have observed rotationally resolved absorptions of N_3^+ in the 282 nm region corresponding to its $A^3\Pi \leftarrow X^3\Sigma_g^-$ transition [12]. These absorptions were detected by monitoring the production of N^+ ions as the wavelength of a tunable laser was scanned. Analysis of the rotational structure revealed that the molecule is linear and centrosymmetric in its ground state with little change in geometry accompanying the electronic transition. In this Letter, we show that larger N_{2n+1}^+ complexes absorb in the same spectral region, an observation that supports the conclusions of previous thermochemical measurements and ab initio calculations suggesting that N_{2n+1}^+ ions can be viewed as an N_3^+ core surrounded by electrostatically bound N_2 ligands [6].

2. Experimental methods

Our experimental arrangement has been described in detail elsewhere [13,14] and here we merely provide a condensed description. Photodissociation of mass selected N_{2n+1}^+ clusters is accomplished in a tandem mass spectrometer system consisting of a cluster ion source, a quadrupole mass filter for selecting the parent ion beam, an octopole ion guide where the laser beam interacts with the ions and finally a quadrupole mass filter tuned to transmit daughter fragment ions. The ion photofragment current (sensed with a Daly detector [15]) is measured as the pulsed laser wavelength (bandwidth 0.5 cm^{-1} , $\approx 100 \mu\text{J}/\text{pulse}$, 10 ns pulse width) is scanned. Measurements of the branching ratios for the production of the various ionic fragments were made using a gated counter with the second quadrupole mass filter under computer control and alternately tuned to the different possible fragment masses after every 30–60 laser shots.

The heart of the ion source is a conventional electromagnetic pulsed valve. Gas issuing from the nozzle orifice (diameter 0.8 mm) is crossed by electrons emanating from twin filaments positioned $\approx 5 \text{ mm}$ downstream. A diagram of the source may be found in Ref. [13]. To some extent, the chemistry taking place in the expansion can be controlled by adjusting the relative positions of the nozzle and the electron impact zone, by varying the electron energy, or by changing the composition and stagnation pressure of the expansion gas. In the experiments described in this Letter a pure nitrogen expansion with backing pressure of $\approx 4 \text{ bar}$ was used. The mass resolution of both quadrupole mass filters is easily sufficient to ensure that the primary ion beam consist essentially of one particular N_{2n+1}^+ or N_{2n}^+ species. Previous spectroscopic experiences with the $N_2^+ - \text{He}_n$ cluster series indicate that small molecular ions produced by the source have rotational temperatures in the 30–40 K range [14] but may sometimes possess considerable energy in their higher frequency vibrational modes.

3. Results

Illumination of mass selected N_{2n+1}^+ complexes near 280 nm results principally in N_3^+ photofragments, although for N_5^+ , N_7^+ and N_9^+ there is also some production of N^+ . No larger photofragments (e.g. N_5^+ , N_7^+ , etc.) were observed. In line with previous observations a small fraction of the clusters were metastable with respect to the loss of a single N_2 ligand [1]. Spectra of N_{2n+1}^+ ($n=2-7$) recorded by monitoring the N_3^+ fragment intensity as a function of laser wavelength in the 280 nm region are displayed in Fig. 1. For N_3^+ the transition shown in Fig. 2 is the lowest energy member of a series of bands

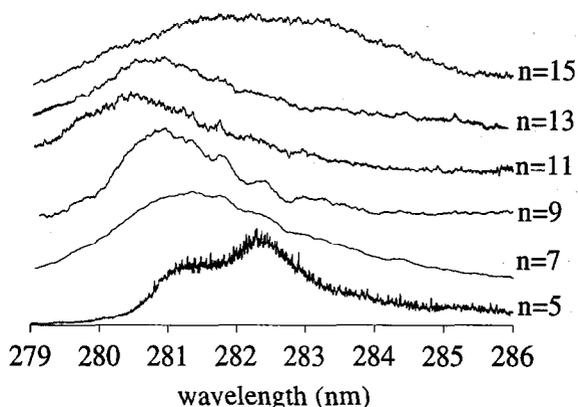


Fig. 1. Photodissociation spectra of N_{2n+1}^+ cations ($N_5^+ - N_{15}^+$) in the 280 nm region recorded by monitoring the N_3^+ photofragment intensity as laser wavelength was scanned. The spectra are normalized with respect to laser power.

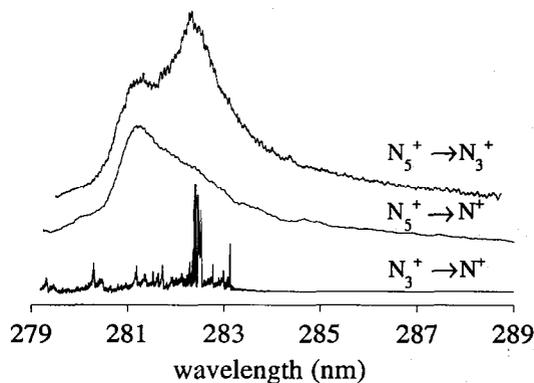


Fig. 2. Photoyield spectra of N_5^+ and N_3^+ near 280 nm. The N_5^+ spectra were measured by monitoring both N_3^+ (upper trace) and N^+ (lower trace) fragments.

extending to shorter wavelength [12], the next prominent transition lying some 1300 cm^{-1} to higher energy. For N_3^+ we hunted unsuccessfully for other transitions within a range extending from 3500 cm^{-1} below to 1400 cm^{-1} above the energy of the band shown in Fig. 1.

Powder dependence studies, where the light flux was varied over an order of magnitude (5 to $100\text{ }\mu\text{J}/\text{cm}^2$ per pulse) show production of both N^+ and N_3^+ from N_3^+ , N_7^+ , N_9^+ to be a linear function of laser power and thus presumably a one photon process. Distinctly different spectra were observed for N_3^+ depending upon whether the N^+ or N_3^+ photofragment was monitored (Fig. 2). The $\text{N}_3^+ + h\nu \rightarrow \text{N}_3^+ + \text{N}_2$ spectrum consists of two rather broad bands whose maxima are separated by $\approx 150\text{ cm}^{-1}$ while in contrast, the $\text{N}_3^+ + h\nu \rightarrow \text{N}^+ + 2\text{N}_2$ trace has a single maximum corresponding to the higher energy peak (Fig. 2). Spectra of the larger complexes (N_{2n+1}^+ , $n \geq 3$) measured by detecting the N_3^+ photofragment exhibit only a single broad band whose centre is more or less coincident with the higher energy band in the N_3^+ spectrum. With the laser tuned to 282.4 nm (approximately the peak of the $\text{N}_3^+ + h\nu \rightarrow \text{N}_3^+ + \text{N}_2$ photoyield curve) the $[\text{N}^+]/([\text{N}_3^+] + [\text{N}^+])$ ratio was 0.17, 0.06 and 0.01 for N_3^+ , N_7^+ and N_9^+ , respectively.

4. Discussion

Before embarking upon the discussion, it is worth emphasizing that spectra obtained in our studies are photodissociation spectra and therefore reflect a convolution of wavelength-dependent absorption and dissociation profiles. If there is no possibility for dissociation, a band strong in absorption need not necessarily appear in the resonance-enhanced photodissociation spectrum. For small, relatively strongly bound molecules, dissociation after excitation to a level with 'discrete character', often occurs when the bound potential energy surface is intersected by a dissociative surface. Dissociation probabilities, and thus the strength of bands seen in a spectrum recorded by monitoring a photofragment, may be quite sensitive to the position of the curve crossing.

For N_3^+ , we have analyzed and assigned one set of bands, lying $\approx 1300\text{ cm}^{-1}$ to higher energy from the one shown in Fig. 1, as the $\text{A } ^3\Pi_u(100) \leftarrow \text{X } ^3\Sigma_g^-$

(000) transition of a $\text{D}_{\infty h}$ molecule [12]. The nature of the electronic states involved is consistent with the ones expected from ab initio calculations [16,17], and the transition corresponds to ones observed in the isoelectronic species NCN [18] and CCO [19]. We suspect that the origin band of the $\text{N}_3^+ \text{A} \leftarrow \text{X}$ transition lies $\approx 282.5\text{ nm}$ but is absent from the spectrum recorded by monitoring the N^+ photofragment because of the low fragmentation yield of the $\text{A } ^3\Pi_u(000)$ level [12]. We have conjectured that N_3^+ transitions shown in Fig. 2 are most probably due to sequence bands of the type (010)–(010), (020)–(020), or possibly $^1\Pi \leftarrow ^1\Delta$ transitions [12] as none of them display the $^3\Pi_u \leftarrow \text{X } ^3\Sigma_g^-$ rotational structure expected for the origin transition. The conclusion that the N_3^+ origin does indeed lie close to 282.5 nm is supported by the fact that we do not observe other nearby transitions for the larger N_{2n+1}^+ complexes, and also by the observation of an isolated N_3^+ absorption in a neon matrix at 283 nm [20].

We have proposed that the photodissociation of N_3^+ following excitation of the $\text{A } ^3\Pi_u \leftarrow \text{X } ^3\Sigma_g^-$ transition is due to couplings between the $\text{A } ^3\Pi_u$ state and a dissociative $^3\Pi$ surface [12]. Both the $\text{X } ^3\Sigma_g^-$ and the repulsive $^3\Pi$ states are presumed to correlate with the same lowest-lying atom plus diatomic limit ($\text{N}^+(^3\text{P}) + \text{N}_2(\text{X } ^1\Sigma_g^+)$) [12] with the $\text{A } ^3\Pi_u$ state correlating *adiabatically* with a higher-lying dissociation limit. The lower-lying N_3^+ molecular states, dissociation limit and the proposed mechanism are illustrated schematically in Fig. 3. It appears that the (000) level of the $\text{A } ^3\Pi_u$ state lies below the point where the surfaces cross and is thus immune to fragmentation.

The proximity of the N_{2n+1}^+ absorptions shown in Figs. 1 and 2 to the $\text{N}_3^+ \text{A } ^3\Pi_u \leftarrow \text{X } ^3\Sigma_g^-$ bands, is strong evidence that the latter acts as a chromophore core in the larger complexes, a view that is consistent with previous experimental and theoretical investigations [6]. Restricted open-shell Hartree-Fock calculations of Hiraoka and Yamabe point to a linear $\text{C}_{\infty v}$ N_3^+ structure essentially consisting of an N_2 ligand electrostatically bound to N_3^+ [6]. Thermochemical data derived from the measurement of the clustering equilibria in the $\text{N}_3^+ - (\text{N}_2)_{n-1} + \text{N}_2 \leftrightarrow \text{N}_3^+ - (\text{N}_2)_n$ reactions show that bonding enthalpies for the first six ligands are 4.5, 4.1, 4.1, 3.67, 3.25 and 2.44 kcal/mol [6].

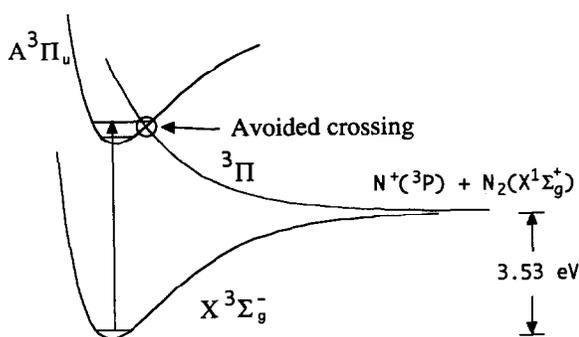


Fig. 3. Schematic illustration of the lower triplet electronic states of N_3^+ showing the proposed photodissociation mechanism from the $A^3\Pi_u$ state. When the system is confined to a linear configuration, the $N^+(^3P) + N_2(X^1\Sigma_g^+)$ dissociation limit gives rise to the $^3\Sigma_g^-$ ground state of N_3^+ and a $^3\Pi$ surface that is repulsive at long range. The $A^3\Pi$ state of N_3^+ correlates *adiabatically* with a higher-lying limit. For N_3^+ , fragmentation from the (000) level does not appear to occur (Ref. [12]), however addition of N_2 ligands may shift the repulsive curve down, leading to N^+ production from larger N_{2n+1}^+ complexes. The 3.53 eV D_0 for the $X^3\Sigma_g^-$ state of N_3^+ comes from Ref. [7].

If, as the calculations suggest, N_3^+ has a $C_{\infty v}$ $N_3^+ - N_2$ structure the electronic transition should again be a $^3\Pi \leftarrow ^3\Sigma^-$ one, with transitions to three $^3\Pi$ components (the spin-orbit splitting in N_3^+ is approximately 40 cm^{-1} [12]). However, its small rotational constant, the fact that for a $^3\Pi \leftarrow ^3\Sigma$ transition there should be 27 branches [12,21] and the presence of several low-frequency modes, probably conspire to make the N_3^+ spectrum appear as little more than a broadened hump, at least at the spectral resolution we command. It is possible that spectral measurements at higher resolution may resolve discrete rotational features, allowing a direct structural determination for N_3^+ , although the situation for larger complexes in this regard is less hopeful.

What then of photodissociation mechanisms for the larger complexes? The observation of N^+ photofragments from N_5^+ , N_7^+ and N_9^+ in this wavelength range is particularly intriguing as it seems that N_3^+ does not itself fragment from the (000) level of the $A^3\Pi_u$ state. One explanation for N^+ photoproduction by larger complexes is that addition of N_2 ligands lowers the crossing point of the two $^3\Pi$ potential energy surfaces shown in Fig. 3, so that the (000) level is efficiently coupled to the dissociative continuum. The diminishing fraction N^+ compared to N_3^+ photofragments

with increasing cluster size may then be due in part to the enhanced possibilities of an intracuster recombination of the nascent N^+ fragment with a N_2 ligand.

For the larger complexes, vibrational predissociation on the ground state surface after either fluorescence or internal conversion, may also constitute an important fragmentation mechanism. The branching ratio measurements help in deciding whether such processes indeed occur. Photoexcitation of all N_{2n+1}^+ complexes up to N_{15}^+ at 282.4 nm produces only N^+ or N_3^+ products (no larger ionic photofragments were detected). Fission of N_{15}^+ to give $N_3^+ + 6N_2$ requires around 7200 cm^{-1} of energy, making it extremely unlikely that vibrational predissociation takes place on the ground state surface following fluorescence. If post-fluorescence vibrational predissociation was important one would expect a good fraction of the complexes to radiate to vibrational levels where they have insufficient energy to cause complete cluster fission, but have merely enough to lose one or two ligands. This does not seem to occur and we do not observe other than N^+ and N_3^+ photofragments, even from N_{15}^+ . Thus we must look to internal conversion (or possibly to triplet-singlet intersystem crossing) occurring on a timescale shorter than the fluorescence lifetime for transformation of electronic to vibrational energy. In this regard it is conceivable that the low-frequency modes associated with core-ligand vibrations may help bridge energy defects and thereby expedite radiationless processes.

The only substructure apparent in the N_3^+ spectrum are the broad twin peaks spaced by around 150 cm^{-1} (Fig. 2). One explanation for these is that they arise from two distinct isomers. This has some appeal in that the higher band seems associated with the preferential production of N^+ rather than N_3^+ fragments. The isomer associated with the lower energy band may either have the N_2 ligand so disposed that the N^+ fragment ejected by the N_3^+ recombines to yield N_3^+ fragments or may be in a less propitious position to promote coupling between the bound and repulsive curves shown in Fig. 3. Another possibility is that the two bands are the first and second members of a vibrational progression. If the higher energy band corresponds to the excitation of the large amplitude bending vibration there is again the possibility for a less obstructed escape of an N^+ fragment.

However, the question then arises as to the whereabouts of the next member of the progression.

5. Conclusions

To summarize, we note that the situations for the even and odd nitrogen cation series are comparable in the sense that in the former, N_4^+ appears to be the core and acts as a chromophore in the visible/UV spectral region, while in the latter the N_3^+ molecular cation takes this role. In contrast to the even clusters, which have a broad photodissociation spectrum extending from 650 to 260 nm, the odd series has relatively narrow absorptions corresponding to the $N_3^+ A^3\Pi \leftarrow X^3\Sigma_g^-$ transition. Photofragmentation of the larger complexes appears to involve non-radiative relaxation followed by complete N_2 ligand loss to leave an N_3^+ core. Some fraction of the smaller complexes are postulated to fragment by a direct curve crossing process to give N^+ fragments.

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