

Metastable decay of $N_2^+-He_n$ ($v = 1$) ($1 < n \leq 6$) clusters¹

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Abstract

Laser and mass spectroscopic techniques have been combined to explore the fragmentation processes of metastable $N_2^+-He_n$ ionic clusters. It has been found that clusters possessing a single quantum of the $N \cdots N$ stretching vibration decay on the $100 \mu s$ time scale. The rate for the relaxation of the $N \cdots N$ stretching vibration in larger $N_2^+-He_n$ complexes has been determined by measuring the relative intensities of hot bands involving the $N \cdots N$ stretch vibration in the $B \leftarrow X$ spectra and comparing with the hot-band intensity for the N_2^+-He complex for which a lifetime for the $v = 1$ state of $220 \pm 30 \mu s$ has been previously measured. While for the smaller complexes ($n = 1-3$) the relaxation rate is proportional to ligand number there appears to be some saturation for the larger species ($n = 4-6$). The roughly linear increase in dissociation rate with ligand number and the ionic fragment size distribution are consistent with a two-step fragmentation process whereby a single He atom collides inelastically with the vibrationally excited core with the recoiling N_2^+ undergoing intracluster collisions with the other ligands leading to further He evaporations.

Key words: Nitrogen–helium clusters; Metastable decay

1. Introduction

For some time we have been concerned with the spectroscopy and dynamics of ionic complexes, particularly those consisting of an N_2^+ core attached to one or more He or Ne ligands. Investigation of such ionic systems enjoys the practical advantage that both primary cluster mass selection and determination of the fragment size distribution are straightforward using mass spectroscopic techniques. In addition, the ease with which ions can be steered, stored, trapped and

detected facilitates the characterisation of relatively slow dynamic processes. Our studies of the $N_2^+-He_n$ complexes have been carried out in a tandem mass spectrometer system and have entailed observation of resonance-enhanced photodissociation after excitation of the $B \leftarrow X$ electronic transition of the N_2^+ chromophore.

Of some initial surprise in our studies was the appearance in the N_2^+-He electronic spectrum of vibronic bands arising from transitions in complexes possessing one quantum of the $N-N$ stretch vibration [1]. It appears that complexes with $\approx 2200 \text{ cm}^{-1}$ of internal energy survive the $100-200 \mu s$ journey from ion source to laser interaction region

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¹Dedicated to Professor Christoph Ottinger on the occasion of his 60th birthday.

even though the $\text{He} \cdots \text{N}_2^+$ binding energy is of the order of 100 cm^{-1} . Recently we have determined a dissociation lifetime of $220 \pm 30 \mu\text{s}$ for the $\text{N}_2^+-\text{He}(v=1)$ complex [1]. This determination relied on the measurement of the ratio of 1_1^+ hot band and origin transitions intensities as the delay between ion creation and dissociation was varied. Such measurements are difficult as they involve altering the potential of the ion source and the field axis potential of the first quadrupole, changes which in our apparatus must be accompanied by adjustment of 15 or so electrostatic lens potentials. Therefore we have adopted a somewhat different strategy, entailing comparison of the intensity ratios of the 1_1^+ hot band and origin transitions with that of N_2^+-He . If the initial proportion of N_2^+-He_n with ($v=1$) is independent of cluster size, differences in the relative intensities of the origin and 1_1^+ transitions at a specific time after formation reflect differing rates of vibrational predissociation. Knowing the rate for the $\text{N}_2^+-\text{He}_1(v=1)$ decay one is able to deduce rates for the larger species.

There are several precedents for slow vibrational predissociation/metastable decay processes in neutral and ionic systems. For instance, recent time-of-flight measurements in a pulsed nozzle FT microwave spectrometer put a lower limit of 1 ms on the lifetimes of the (10^0_0) level of $\text{Ar} \cdots \text{HCl}$ and $\text{Kr} \cdots \text{HCl}$ [2]. Another example involves the $(\text{N}_2)_n^+$ clusters, where vibrational metastability occurs on the microsecond to millisecond time scale and is due to the intracuster relaxation of a high-frequency N–N stretching vibration followed by loss of a specific number of N_2 ligands [3–5]. In addition, a lower bound of $10 \mu\text{s}$ has been determined for $\text{NeCl}_2(X^1\Sigma_g^+, v''=1)$ [6].

On the basis of the calculated and measured strength of the $\text{He} \cdots \text{N}_2^+$ bond ($\approx 100 \text{ cm}^{-1}$) a single quantum of the N–N vibration (2200 cm^{-1}) should be energetically sufficient

to remove up to 20 helium ligands. Nevertheless, for clusters up to N_2^+-He_6 the dominant fragmentation channels involve loss of only one or two ligands, although an appreciable fraction of the complexes lose more ligands. In this paper it is argued that together with the dissociation rate data, the product ion distribution is consistent with a two-stage dissociation mechanism whereby primary relaxation of the N_2^+ vibration occurs in a half collision with a single He ligand with subsequent evaporations from a hot nascent $\text{N}_2^+-\text{He}_{n-1}$ complex responsible for further He loss.

2. Experimental methods

The N_2^+-He_n clusters were investigated in a tandem mass spectrometer system equipped with a cluster ion source. As previous papers give a complete description of the experimental arrangement [1, 7, 8] here we merely summarise the details most relevant to the vibrational predissociation/metastable fragmentation experiments. Cluster ions are created by electron bombardment of a 1:1000 N_2/He gas mixture issuing from the orifice of a pulsed nozzle (stagnation pressure 4–5 bar, nozzle diameter = 0.8 mm, electron energy $\approx 200 \text{ eV}$). The resulting plasma is skimmed and positive ions are focused into a quadrupole mass filter where mass selection of the desired N_2^+-He_n cluster ion is accomplished. After deflection through 90° by an electrostatic quadrupole bender the ions are injected into an r.f.-octopole ion guide where they encounter the output of a pulsed dye laser. A second quadrupole mass filter is set to transmit N_2^+ photofragment ions. Spectra are recorded by monitoring the fragment ion intensity as the laser wavelength is scanned. In all instances photon absorption resulted in complete cluster fission, with N_2^+ the only observable photofragment. The

laser power was sufficient to saturate the $B \leftarrow X$ absorption of N_2^+ (2.5 mJ pulse⁻¹ with a beam diameter of 3–5 mm). Spectra of $N_2^+-He_n$, $n = 1-6$ were recorded in consecutive scans with no change in ion-source conditions or laser operating parameters.

The effective age of the $N_2^+-He_n$ complexes decides the ratio with $v = 1$ and $v = 0$ N_2^+ cores. Usually a 20–30 μ s bunch of ions was created by pulsing the accelerating voltage for the ionising electron beam. The laser pulse was timed to fire when the bulk of the ions were in the octopole ion guide, the age of the ions being the difference in the electron beam and laser beam firing times. Several series of $N_2^+-He_n$ spectra were recorded with flight times ranging from 90 to 140 μ s.

For metastable fragmentation experiments, $N_2^+-He_n$ clusters were mass selected by the first quadrupole with the second quadrupole set to transmit the $N_2^+-He_{n-1}$, $N_2^+-He_{n-2}$ etc. masses. With an octopole field axis potential of ≈ 3 V we observe metastable decay in an ≈ 80 μ s time window beginning when the $N_2^+-He_n$ ions enter the octopole $\approx 90-120$ μ s after their formation in the ion source. Branching ratio measurements were also made for $N_2^+-He_n$ ($n = 2-4$) ions trapped in the octopole for one millisecond before being released for mass analysis and single ion counting. Counting of fragment ions was accomplished using a photon counter. To minimise mass discrimination effects a strategy was adopted whereby the ratios of counts for adjacent fragment masses were measured. For example for $N_2^+-He_3$ the ratios $[N_2^+-He_2]/[N_2^+-He_1]$ and $[N_2^+-He]/[N_2^+]$ were ascertained. As the difference between the adjacent fragment masses is small compared to the total mass, collection efficiencies should be similar. In order to further guard against discrimination effects, the resolution of the second quadrupole mass filter was adjusted to have an effective ΔM of ≈ 1.5 u, sufficient to

separate the various fragments but broad enough to maximise collection efficiency.

To gauge the importance of collision-induced dissociation (CID) Ar was introduced into the octopole ion guide and the ratio of fragment N_2^+ to parent N_2^+-He counts was measured as a function of pressure. These data are displayed in Fig. 1. For pressures less than 10^{-6} Torr CID is a minor process compared to collisionless metastable decay. The metastable dissociation experiments described in this paper were conducted with pressures of 2×10^{-7} Torr or lower. Due to the presence of other ions with $m = 32$ u in the primary beam (e.g. O_2^+), the y -axis intercept in Fig. 1 represents a lower limit for the metastable N_2^+-He fraction.

There may be some concern that $N_2^+-He_n$ complexes with $v > 1$ also contribute to the metastable fragmentation. Two observations counter this possibility. First we have been unable to observe the 1_2^2 hot band in spectra of $N_2^+-He_n$ complexes which, given the signal-to-noise ratio attainable with the apparatus, implies that the population of the $v_1 = 2$ level in the octopole is less than 5–10% of the $v_1 = 1$ level. Furthermore the metastable branching ratios were independent of the ion energy in the octopole region intimating that if the $v_1 = 2$ level is populated it has a similar

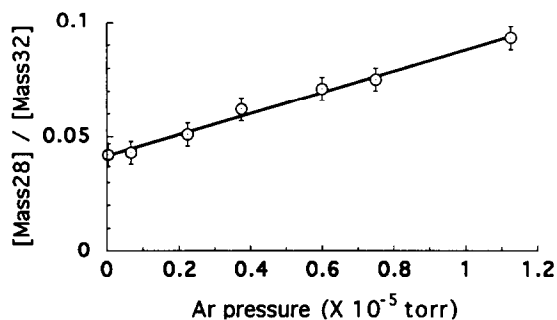


Fig. 1. Fragmentation of N_2^+-He complexes caused by introducing Ar into the octopole ion guide. The ratio of the mass 28 signal to the mass 32 signal is plotted as a function of Ar pressure. Due to the presence of O_2^+ impurities in the primary ion beam the y -axis intercept represents a lower limit for the metastable N_2^+-He fraction.

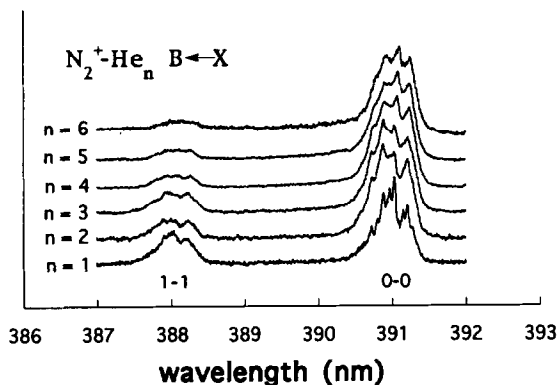


Fig. 2. Spectra of $N_2^+-He_n$ ($n = 1-6$) complexes near 390 nm displaying both the $B \leftarrow X$ origin and the 1_1^+ N-N stretch hot band.

fragmentation pattern to the $v_1 = 1$ level. It appears most likely that the initial population of $N_2^+-He_n$ ($v_1 = 2$) complexes is small enough and the metastable fragmentation rate is sufficiently rapid for the population to be effectively zero by the time the complexes reach the octopole.

3. Results

A series of $N_2^+-He_n$ ($n = 1-6$) spectra including the $B \leftarrow X$ origin and the 1_1^+ hot-band transitions collected under identical experimental conditions is shown in Fig. 2. As the number of He ligands increases there is a broadening of the bands and a diminishing of the relative size of the 1_1^+ peak compared to the origin peak. We note that if the ions are trapped within the octopole for more than a few hundred microseconds the hot band disappears entirely whilst the more intense origin band remains. The spectra for $N_2^+-He_n$ ($n = 1-3$) shown in Fig. 2 are similar to the ones reported previously [8], though in the current experiments to maximise the signal-to-noise ratio, the transition was intentionally saturated and consequently power broadened.

Our assertion is that the decrease in the relative size of the 1_1^+ peak as the cluster

becomes larger reflects an increase in the vibrational relaxation/predissociation rate. If the following assumptions are valid it is possible to determine the relative decay rates of the various $N_2^+-He_n$ ($v = 1$) clusters by comparing the intensities of the origin and 1_1^+ hot-band peaks.

(i) The formation rate for $N_2^+-He_n$ clusters does not depend on the vibrational state of the N_2^+ core, that is, in the source region at $t = 0$ the relative concentration of $N_2^+-He_n$ ($v = 1$) compared to $N_2^+-He_n$ ($v = 0$) clusters is independent of n . This does not seem unreasonable for a situation where the N-N stretching coordinate is poorly coupled to the low-frequency $He \cdots N_2^+$ coordinates. Predissociation is sluggish, so that the reverse association process should not depend strongly on the vibrational state of the core and thus N_2^+ ($v = 1$) should combine with He ligands in three-body processes equally as well as N_2^+ ($v = 0$). Even if the initial N_2^+-He complexes are formed through associative ionisation (Hornbeck-Molnar process), the ease with which further ligand addition occurs should be independent of the vibrational state of the N_2^+ core. It is not possible, to discount the possibility that $N_2^+-He_2$ for example, may be formed directly through an ionising association process involving a metastable helium dimer and a nitrogen molecule and that the $N_2^+-He_2$ formed in this way may have a different vibrational state distribution than it would if formed via association of N_2^+-He with a He atom. However, if the distribution amongst the various vibrational levels of N_2^+ depends primarily on the Franck-Condon factors linking neutral and ion, similar vibrational distributions should result from ionising association of both He^* and He_2^* with N_2 .

(ii) The ratio of the intrinsic $B \leftarrow X$ absorption and dissociation cross-sections for the origin and 1_1^+ hot-band transitions is independent of the number of heliums in the cluster.

Table 1

Total predissociation decay rates and fragment size distribution (percent) for $N_2^+-He_n$ ($1 \leq n \leq 6$) clusters. The branching ratio measurements were taken with the ions having an energy of ≈ 3 eV in the octopole and reflect dissociation occurring in an $\approx 80 \mu\text{s}$ time window beginning $\approx 100 \mu\text{s}$ after formation (see the Experimental section for more details)

Cluster	Rate (10^4 s^{-1})	Rate per He ligand (10^4 s^{-1})	Branching ratio %					E_{int} (cm^{-1})
			N_2^+	$N_2^+-He_1$	$N_2^+-He_2$	$N_2^+-He_3$	$N_2^+-He_4$	
$N_2^+He_1$	0.45	0.45						
$N_2^+-He_2$	1.1	0.55	45	55				30
$N_2^+-He_3$	1.4	0.46	22	34	44			56
$N_2^+-He_4$	1.7	0.42	9	19	36	36		75
$N_2^+-He_5$	1.9	0.38	4	11	18	34	33	90
$N_2^+-He_6$	2.0	0.33						108

Errors for the rates and ratios are estimated as $\pm 10^3 \text{ s}^{-1}$ and $\pm 5\%$ respectively. Also listed in the last column of the table is the internal energy of the nascent $N_2^+-He_{n-1}$ complex calculated using Eq. (6).

This assumption appears to be reasonable given that there is only mild interaction between core and ligand ($\approx 100 \text{ cm}^{-1}$ binding energy). We note the $B \leftarrow X$ absorption leads to total cluster disintegration with only N_2^+ fragments for all $N_2^+-He_n$ clusters that we have studied.

(iii) The time decay of the $N_2^+-He_n$ ($v = 1$) population $N_{v=1}^n(t)$ is exponential and can be represented as

$$N_{v=1}^n(t) = N_{v=1}^n(0) \exp(-k_n t) \quad (1)$$

where k_n is the predissociation rate. This assumption may initially appear suspicious as the $N_2^+-He_n$ ($v = 1$) population is in fact composed of sub-populations with various amounts of energy in overall rotation and the other two internal vibration/internal rotation coordinates. Each state will have a different dissociation rate and by integrating over the entire 1_1^1 band we are in effect averaging over these rates. However, we note that for all complexes, ratios of band areas are equal within experimental error to ratios of band heights, suggesting that quantum numbers other than v do not greatly influence dissociation rates.

If the above three assumptions are valid then the dissociation rate for the $N_2^+-He_n$ complex is given by:

$$k_n = 1/t_f \ln(R_1/R_n) + k_1 \quad (2)$$

Here k_1 is the disintegration rate of the $N_2^+-He_1$ ($v = 1$) complex and R_n is the ratio of the hot band to the origin band at time t_f for the $N_2^+-He_n$ cluster. In our experiment t_f is the time between ion formation and interrogation by the laser and is equal to the sum of the times taken for the ions to travel from the nozzle to the skimmer, from the skimmer to the octopole entrance and from the octopole entrance to the middle of the octopole where the bulk of the ions meets the laser pulse.

The rates determined by integrating over the bands in Fig. 2 and inserting the resulting ratio in Eq. (2) with the previously determined value for $k_1 = 4.5 \times 10^3 \text{ s}^{-1}$ [1] are listed in Table 1

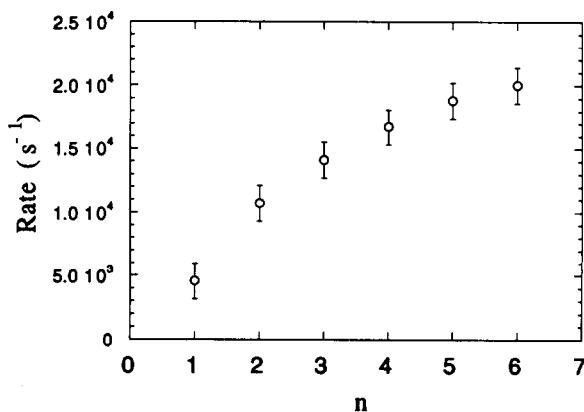


Fig. 3. Dissociation rates for $N_2^+-He_n$ ($v = 1$) complexes as a function of n . Rates were inferred from the relative sizes of the origin and hot-band transitions shown in Fig. 1.

and displayed graphically in Fig. 3. Inspection of Fig. 3 reveals that although the relaxation rate is approximately proportional to n for the smaller N_2^+-He_n ($v=1$) complexes ($n=1-3$), for larger clusters ($n=4-6$) there is some saturation (note also the third column of Table 1 where the rate per He atom is listed). Branching ratios for loss of various numbers of He atoms from N_2^+-He_n clusters as they pass through the octopole ion guide are also given in Table 1.

To understand at what stage a complete solvation shell develops about the N_2^+ core we have determined likely N_2^+-He_n equilibrium geometries representing the potential surface as the sum of pairwise interactions. The $\text{He}\cdots\text{N}_2^+$ interactions were described using the ab initio potential-energy surface of Miller et al. [9] and $\text{He}\cdots\text{He}$ interactions were represented with the free-atom 12–6 Lennard–Jones potential ($\epsilon = 7.1 \text{ cm}^{-1}$, $\sigma = 2.58 \text{ \AA}$ [10]). While there may be doubts about using the sum of pairwise interactions for the construction of potential-energy surfaces for larger complexes, equilibrium geometries determined by these means should at least provide a guide to structures, though non-additive three-body terms may also be of some consequence [11, 12]. The calculated ab initio $\text{He}\cdots\text{N}_2^+$ surface has only a small barrier ($< 10 \text{ cm}^{-1}$) to free internal rotation and a D_e of $\approx 139 \text{ cm}^{-1}$ [9].

The results of the calculations show that at least six helium atoms may be comfortably positioned next to the N_2^+ core. Figure 4 illustrates one of the lower-energy configurations for N_2^+-He_6 , although there are many other isomers with similar energies. The helium atoms occupy what is in essence an equipotential moat surrounding the ion core. The $\text{He}\cdots\text{He}$ attraction is sufficiently weak for there to be little tendency for the He atoms to clump together, though such an inclination would be countered by zero-point motions.

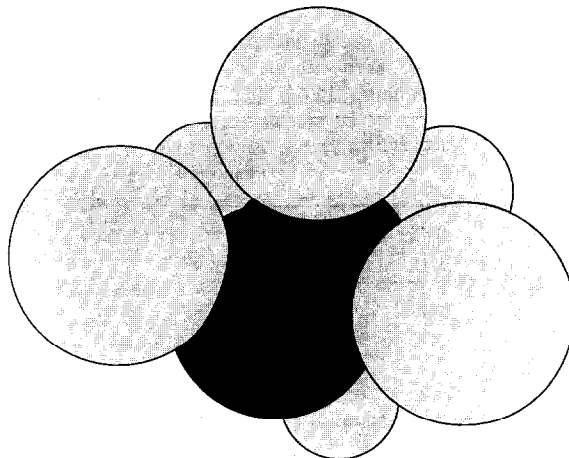


Fig. 4. One of the lower-energy structures for the N_2^+-He_6 complex determined by minimising a pairwise additive potential function. The $\text{He}\cdots\text{N}_2^+$ interactions were described using the ab initio potential from Ref. 9 and the $\text{He}\cdots\text{He}$ interactions were modelled by a Lennard–Jones potential with parameters taken from Ref. 10. It can be clearly seen that six He atoms fit comfortably about the N_2^+ core.

At 30–40 K, approximately the temperature of the clusters from our source, it is likely that the helium atoms are evenly distributed. Even in the lower-energy levels, He atoms should be relatively unconstrained in their exploration of the available angular space. Interactions between He atoms do not contribute significantly to the cohesion of the cluster, though the repulsive part of their potential is important in deciding their relative dispositions.

4. Discussion

4.1 General

Consideration of the relaxation of N_2^+-He_n complexes profits from a brief review of previous experimental and theoretical work. Miller et al. [9] have conducted ab initio calculations of the $\text{He}\cdots\text{N}_2^+$ potential-energy surface showing that although the equilibrium value of the $\text{He}\cdots\text{N}_2^+$ bond distance depends upon the angle θ , the depth of the well is

almost independent of orientation. The minimum of the calculated surface was reported as -139.36 cm^{-1} in a configuration where the N–N bond was tilted by 45° with respect to a line joining the He atom to the midpoint of the N–N bond. Minimum energies in the T-shaped and linear configurations are calculated as -133.12 cm^{-1} and -134.36 cm^{-1} respectively. The same authors used the ab initio surface to determine rovibrational energy levels which were eventually fitted to the expression

$$E(n\nu_s, j, l) = n\nu_s + Bj(j+1) + C_n l(l+1) \quad (3)$$

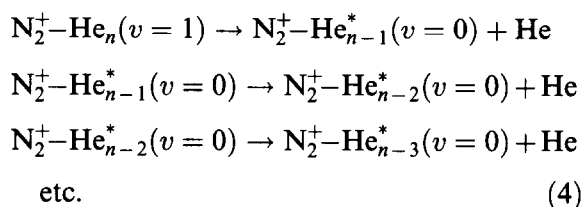
with $B = 1.879 \text{ cm}^{-1}$, $1\nu_s = 55.231 \text{ cm}^{-1}$, $2\nu_s = 83.404 \text{ cm}^{-1}$, $3\nu_s = 92.491 \text{ cm}^{-1}$, $C_0 = 0.477 \text{ cm}^{-1}$, $C_1 = 0.370 \text{ cm}^{-1}$ and $C_2 = 0.254 \text{ cm}^{-1}$.

The success of the fit indicates that the $\text{N}_2^+ \cdots \text{He}$ system in its ground electronic state is close to being a free internal rotor. Though strictly only the total angular momentum J and the parity of the wavefunctions are good quantum numbers the quantum number j pertaining to the internal rotation of the N_2^+ is also nearly conserved. This conclusion is supported by the $\text{B} \leftarrow \text{X}$ spectra of $\text{N}_2^+ - \text{He}$ that exhibits structure resembling in coarse detail the free N_2^+ spectrum. In loose terms, the N_2^+ core is only vaguely aware of the He ligand and exciting the $\text{B}^2\Sigma_u^+ \leftarrow \text{X}^2\Sigma_g^+$ electronic transition in the core leads to $\Delta j = \pm 1$ changes in the quantum number pertaining to its internal rotation.

Features reminiscent of the P and R branch transitions of the N_2^+ core are apparent in the spectra of all the $\text{N}_2^+ - \text{He}_n$ complexes, suggesting that even in the larger species the core is unbound in an angular sense and that the $\text{B} \leftarrow \text{X}$ electronic transition is accompanied by $\Delta j = \pm 1$ changes in the effective internal rotation quantum number.

4.2 Vibrational relaxation rates

Perhaps the simplest physically reasonable model for the fragmentation of $\text{N}_2^+ - \text{He}_n$ ($v = 1$) involves a two-stage mechanism whereby relaxation of the $\text{N}_2^+(v = 1)$ core is accomplished via an inelastic half collision with a single He ligand. The vibrational energy is partitioned between the recoiling He atom and the N_2^+ core which can undergo further intracluster collisions with the remaining He atoms. These secondary collisions increase the cluster's internal energy and can result in further evaporative He ligand loss. The overall process can be summarised as:



There are two justifications for such a two-step process. First of all, because the $\text{He} \cdots \text{He}$ interactions are extremely weak it seems unlikely that channels where the energy of the $\text{N} \cdots \text{N}$ stretching vibration is simultaneously shared between two He atoms are important. Secondly, the apparent near proportionality between ligand number and dissociation rate for the smaller complexes can be seen as evidence for the primary $\text{N}_2^+(v = 1)$ relaxation event involving only a single He atom. While the rate of cluster fission is determined by the slow initial relaxation process, the ultimate ionic fragment size, the subsequently occurring evaporation processes and hence the branching ratios will depend upon the amount of energy delivered into the nascent $\text{N}_2^+ - \text{He}_{n-1}^*$ complex.

In many ways the proposed model is consistent with previous experimental studies of the vibrational predissociation of diatomics bound to several He atoms. For instance in the original investigations of the $\text{I}_2 - \text{He}_n$ system,

where vibrational predissociation from high-lying vibrational levels of the B state was studied, a propensity for the loss of one diatomic vibrational stretch quantum per dissociated He atom was noted even though a single quantum is energetically sufficient to dissociate more than one He atom [13]. Such behaviour was rationalised by supposing that cluster fragmentation proceeds via a sequence of independent relaxation/dissociation steps with dynamic rather than energetic constraints being of primary importance.

In accord with our work, which for the smaller complexes ($n = 1-3$) indicates a roughly linear increase in the relaxation rate with ligand He number, studies of the vibrational predissociation of neutral halogen-rare gas (Hal-Rg_n) complexes with one and two rare gas ligands (Cl₂-Ne_n, Ref. 14, and I₂-Ne_n, Refs. 15 and 16) have generally concluded that the rate for the vibrational predissociation of the first ligand from Hal-Rg₂ complexes occurs at around twice the rate of loss from Hal-Rg₁ complexes.

If there is no orientational dependence for the relaxation of the N₂⁺($v = 1$) core by helium ligands one might expect the rate to scale linearly with ligand number until the first solvation shell is completed. Interactions between the N₂⁺ core and He atoms in the second and subsequent solvation shells should be less efficient in relaxing the vibrational motion. Even if there is an orientational dependence of the coupling between the N₂⁺($v = 1$) core and the ligands, as long as the He···N₂⁺ potential does not have pronounced anisotropies and the He ligands are evenly distributed about the core, the total relaxation rate may be expected to increase linearly with ligand number.

What then is the cause of the apparent saturation of the dissociation rate for the $n = 4-6$, complexes? As Fig. 4 shows, six He ligands fit easily about the N₂⁺ core making it

difficult to imagine that the less than linear behaviour in the relaxation rate is due to completion of the first solvation shell. It is possible however that the nature of the He···N₂⁺ interaction changes slightly as more ligands are added. In their original treatments of the vibrational predissociation of atom-diatom complexes Beswick and Jortner [17] and Ewing [18] developed expressions for the vibrational predissociation rate that emphasised the importance of the translational energy or momentum of the fragment pair. If the atomic-diatomic interaction can be described by a Morse potential with a range parameter a , the basic expression for the vibrational predissociation rate k_{vp} is

$$k_{vp} \propto \exp \left\{ -\pi \left[\frac{(2\mu E_t)^{1/2}}{a\hbar} \right] \right\} \quad (5)$$

where μ is the reduced mass and E_t the translational energy of the fragments. The expression summarises the reluctance of atom-diatom systems to dissociate into channels with large translational energy release. The relaxation/predissociation rate given by Eq. (5) is quite sensitive to the range parameter a such that even relatively small changes result in significantly different relaxation rates. For example, consider the case if one takes a to be 2.24 \AA^{-1} , a value consistent with both the calculated He···N₂⁺ potential of Miller et al. and with the data for the vibrational relaxation of N₂⁺($v = 1$) by He [19]. Reduction of the range parameter by only 1% leads to a 15% variation in the relative relaxation rate predicted by Eq. (5). Clearly small changes in the interaction potential can have considerable effects on relaxation/dissociation rates.

One of the many-body contributions to the total cluster energy that might be important in lowering the relaxation rate per He ligand for the larger complexes, may arise from the repulsive interaction between charge-induced

dipoles on the He atoms. (For a discussion of the structural importance of many-body interactions in K^+Ar_n complexes, including those arising from induced dipole–induced dipole forces see Ref. 11.) One can estimate the magnitude of this effect by calculating the interaction energy of the dipoles induced on two He atoms by a charge 2.9 \AA away (approximately the ab initio $He \cdots N_2^+$ equilibrium distance in a T-shaped geometry). If the $He \cdots He$ displacement is also 2.9 \AA (the distance for the $He \cdots He$ Lennard-Jones well minimum [10]) and a He polarizability of 0.2 \AA^3 is assumed [20], the repulsive energy contribution amounts to $2\text{--}3 \text{ cm}^{-1}$. Although this may seem insignificant, it is of the same order as the calculated anisotropy in the well depth of the $He \cdots N_2^+$ interaction potential and is $\approx 2\text{--}3\%$ of the $N_2^+ \text{--} He$ D_0 . In smaller complexes such as $N_2^+ \text{--} He_2$ and $N_2^+ \text{--} He_3$ the He atoms should be able to avoid one another so that induced dipole–induced dipole effects should be of little consequence. However for larger complexes where closer approach of He atoms will occur, the repulsive contribution to the energy should result in an increase in the effective solvent-shell volume and consequently a decrease in the interaction of each He ligand with the ion core.

4.3 Branching ratios

We now turn to a discussion of the ion fragment size distribution resulting from metastable decay of $N_2^+ \text{--} He_n$ complexes. Apart from vibrational predissociation with the fragmentation energy originally localised in the $N \cdots N$ bond other mechanisms may also be important. Energy in excess of the dissociation energy may be stored in electronic, vibrational or rotational degrees of freedom (or any combination of these). Mechanisms that may need to be considered and which have been observed previously in mass spectroscopic studies of ionic complexes

include tunnelling through a rotational barrier (seen in Ar_3^+ Ref. 21), dissociation due to energy localised in high- or low-frequency vibrations (seen in $(N_2)_n^+$ complexes Refs. 3–5) and fragmentation due to the release of electronic energy stored in one of the constituents (seen in $(N_2)_n^+$ complexes Ref. 3). Each of these processes will be characterised to some extent by the number of ligands that are lost when the stored energy becomes available for the evaporation of ligands and by the rate at which this stored energy is liberated. Thus depending upon the constitution of the initial population and the time window during which the mass spectroscopic observations of the fragments are made, differing branching ratios may be measured. A useful discussion of the roles of various energy storage mechanisms and fragmentation processes in ionic clusters can be found in Ref. 22.

In the past, branching ratio measurements have been employed by Magnera et al. to deduce the origin of the fragmentation energy in metastable $(N_2)_n^+$ clusters [3]. In these complexes, which appear to be best viewed as an N_4^+ core solvated by N_2 ligands, the dominant fragmentation process, involving up to 80% of the complexes, was due to the relaxation of an $N_2(v = 1)$ ligand and involved the loss of a characteristic number of N_2 ligands. A smaller proportion (1–9%) of the complexes lost a single N_2 ligand, a process attributed to evaporation, with the required energy coming from low-frequency cluster vibrations. It is also possible that single-ligand loss may come about via tunnelling through a rotational barrier as appears to occur in the metastable decay of Ar_3^+ [21]. A much smaller fraction (0.1–1%) of the complexes underwent complete or almost complete fragmentation to yield N_2^+ or N_4^+ fragments, a process conjectured to accompany the non-radiative relaxation of metastable electronic states of either the N_4^+ core or N_2 ligands with the accompanying conversion of between 2.1 and

3.7 eV of electronic energy to vibrational energy.

Analogous fragmentation processes to those observed in the $(\text{N}_2)_n^+$ clusters are likely to occur for N_2^+-He_n , though for these smaller species with a limited number of ligands, branching ratios may not provide an unambiguous guide to the operative fragmentation mechanisms. For example in the smaller complexes such as N_2^+-He_n ($n = 1, 2$) both vibrational predissociation and rotational tunnelling can lead to the loss of a single He ligand. For the larger complexes complete cluster fission can result from either vibrational predissociation or possibly from electronic relaxation. While differentiation of distinct mechanisms may be possible with selective excitation of the complexes this was not possible in our experiments. In addition, as mentioned above, different processes will usually have different rates so that the measurement of branching ratios in different effective time observation windows may yield clues as to whether one or more processes are important.

The branching ratio measurements reported in Table 1 were taken with the ions having an energy of ≈ 3 eV in the octopole and reflect dissociation occurring in an $\approx 80 \mu\text{s}$ time window beginning $\approx 100 \mu\text{s}$ after formation. For N_2^+-He_n ($n = 2-4$) measurements were also made for ions that were trapped within the octopole for 1 ms. Branching ratios measured with this enlarged time window did not differ significantly from those listed in Table 1, constituting some evidence that either there is one dominant fragmentation process occurring after $80 \mu\text{s}$ or that if several processes are important they have similar characteristic rates.

To get an idea of the fragmentation losses likely to accompany the two-stage vibrational predissociation/evaporation process (reaction (4)) it is helpful to consider the internal energy delivered into the nascent $\text{N}_2^+-\text{He}_{n-1}$ complex

following the ejection of a single He ligand. For smaller complexes the He atom that relaxes the $\text{N}\cdots\text{N}$ stretch vibration will be ejected from the complex without significant interactions with other He ligands. The recoiling N_2^+ can then undergo secondary intra-cluster collisions with other He ligands leading to energization of the $\text{He}\cdots\text{N}_2^+$ bonds with subsequent He evaporations. Classical arguments based on the conservation of energy and linear momentum suggest that the eventual internal energy of the nascent $\text{N}_2^+-\text{He}_{n-1}$ fragment will be

$$E_{\text{int}} = E_{\text{avail}} \frac{m_{\text{He}}}{(m_{\text{He}} + m_{\text{N}_2})} \frac{(n-1)m_{\text{He}}}{[(n-1)m_{\text{He}} + m_{\text{N}_2}]} \quad (6)$$

where E_{avail} is the energy of the $\text{N}-\text{N}$ stretch quantum minus the binding energy of the He atom. The internal energies of the nascent $\text{N}_2^+-\text{He}_{n-1}^*$ complexes calculated using Eq. (6) are given in the last column of Table 1.

It is also possible that internal rotations of the N_2^+ core are excited during the initial impulsive half collision, so that the E_{int} values listed in Table 1 which are deduced by considering conservation of linear momentum should probably be taken as lower limits for the internal energy of the nascent $\text{N}_2^+-\text{He}_{n-1}^*$ complexes.

From Table 1 we see that following the vibrational relaxation of N_2^+-He_2 ($v = 1$) the nascent N_2^+-He^* should have at least an additional 30 cm^{-1} in the low-frequency stretching coordinate. Thus depending upon the internal energy in the low-frequency motions ($\text{He}\cdots\text{N}_2^+$ stretching vibrations, internal rotations) before the $\text{N}_2^+(v = 1)$ core relaxation, an additional He ligand may be lost. Given that the N_2^+-He_n ions have internal temperatures of the order of 40 K and that the N_2^+-He D_0 is close to 100 cm^{-1} [8, 9] it is surprising that delivery of only $\approx 30 \text{ cm}^{-1}$ of

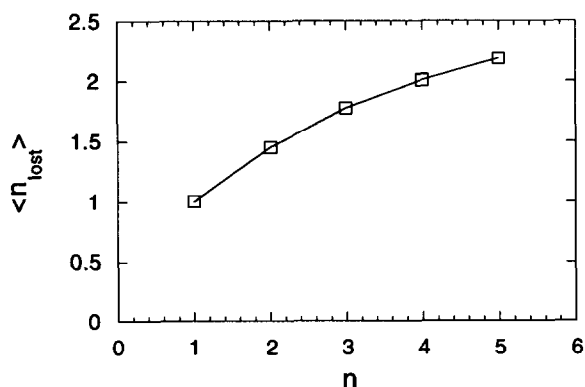


Fig. 5. Average number of He ligands lost ($\langle n_{\text{lost}} \rangle$) from metastable N_2^+-He_n complexes as a function of n . The average number of He ligands lost in metastable fragmentation in the octopole is calculated as $\langle n_{\text{lost}} \rangle = \sum_{i=1}^n f_i i$ where f_i is the fraction of metastable N_2^+-He_n complexes losing i helium ligands.

energy into the $\text{He} \cdots \text{N}_2^+$ bond leads to almost half of the complexes losing a second He ligand. As mentioned above there is some possibility of exciting N_2^+ internal rotations as the first He is kicked off and this may be the source of the necessary additional internal energy.

The internal energy delivered into the nascent $\text{N}_2^+-\text{He}_{n-1}^*$ fragment by the recoiling N_2^+ should increase with cluster size leading one to expect more extensive fragmentation for larger species. This trend is apparent in Fig. 5 where the average number of ligands lost is plotted as a function of the original cluster size

$$\langle n_{\text{lost}} \rangle = \sum_{i=1}^n f_i i \quad (7)$$

where f_i is the fraction of metastable N_2^+-He_n complexes losing i helium ligands, and in Table 1 where it can be seen that a steadily decreasing fraction of complexes lose only one He ligand. It is not unlikely that some of the complexes that shed a single ligand are cooling evaporatively.

It comes as a surprise that a small fraction of the N_2^+-He_5 complexes ($\approx 4\%$) lose all five He ligands to yield N_2^+ fragments. If

this total disintegration arises from a two-step vibrational relaxation/predissociation (Eq. (4)) one is forced to conclude that quite large amounts of energy ($\approx 300\text{--}400\text{ cm}^{-1}$) can be deposited in the N_2^+ internal rotation in the primary He ejection. It is also possible that total fragmentation comes about with the release of electronic energy stored in either the N_2^+ core or He ligands.

5. Conclusions

The present work details our indirect determinations of the vibrational relaxation/predissociation rates of N_2^+-He_n ($v=1$) ($n=2\text{--}6$) complexes. To our knowledge there are no comparable studies for either neutral or ionic systems where the dependence of chromophore vibrational relaxation rate on ligand number has been explored for clusters with more than two solvent atoms. While there appears to be a roughly linear increase in the relaxation rate for the first two to three He ligands, thereafter there is some saturation in the rate, well before the completion of the first solvent shell. The diminishing relaxation rate per He ligand for $n=4\text{--}6$ may be due to subtle changes in the potential-energy function governing the interaction between the $\text{N}_2^+(v=1)$ core and He atoms as cluster size increases. The branching ratio and relaxation rate data are consistent with a two-stage relaxation/decay mechanism with an impulsive encounter between a vibrationally excited N_2^+ core and a single He ligand, the formation of a hot nascent $\text{N}_2^+-\text{He}_{n-1}^*$ complex followed by subsequent He evaporations. Details of these intracluster collisions are obviously complicated and it might prove useful to model the evaporations using a molecular dynamics approach. To some extent this work complements previous studies of the metastable decay of $(\text{N}_2)_n^+$ complexes that demonstrate metastable fragmentation on the $100\text{ }\mu\text{s}$ time

scale due to energy stored in N···N stretching vibrations [3–5].

The weakness of the present work is that it relies on the comparison of hot-band intensities for the various sized complexes and is based upon assumptions concerning the independence of the initial vibrational state of the N₂⁺ core on the number of He solvent atoms. Better and less ambiguous would be to directly excite IR-active vibrations in mass-selected complexes allowing direct determinations of both vibrational predissociation/relaxation rates and fragmentation patterns.

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