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Measurements of kinetic energy release and binding energy following the unimolecular fragmentation of molecular cluster ions

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ABSTRACT

High resolution mass spectrometry has been used to record the fragmentation patterns of size-selected carbon dioxide, carbon disulphide and protonated acetonitrile cluster ions that have been produced by electron impact ionization of a beam of neutral clusters. From the shapes of fragment ion peaks it has been possible to extract information about the kinetic energy that is released in the decay reaction. Average kinetic energies have been recorded and using finite heat bath theory these data have been used to calculate the binding energies of single molecules to the decaying cluster ions.

1. Introduction

Mass spectrometric studies of the unimolecular (metastable) fragmentation of cluster ions have attracted considerable interest in the recent years. Measurements taken from peak profiles following metastable decay can provide kinetic energy release (KER) data, which in turn can yield important information concerning the structures of ions, reaction energetics, and decay dynamics [1]. Extending these ideas to cluster ions takes the study one step further, in that measurements over a size range might provide evidence of systematic trends. For example, the average kinetic energy release recorded from argon clusters ions, Ar_n^+, might be expected to vary as a function of the number of degrees of freedom ($3n$-6). The first such measurements on cluster ions were made by Stace and Shukla using a single focusing (magnetic field only) mass spectrometer to study carbon dioxide [2]. Bowers and coworkers also presented results from small complexes generated by ion-molecule reactions [3,4]. Subsequent measurement on argon cluster ions [5] were used to suggest that any excess energy present in the ions is partitioned in a statistical manner. These results were later extended and refined using a double focusing sector field instrument [6], and the link with statistical energy partitioning verified through computer simulation [7]. KERs measurements on protonated ammonia and methanol clusters by Lifshitz et al. were correlated with the appearance of magic numbers [8,9].

An increasingly active part of the analysis of KERs has been the deconvolution of unimolecular lifetime and average kinetic energy release into a determination of the binding energy of a monomer to a cluster. Using existing experimental data [4,5], Engelking determined the binding energies of carbon dioxide and argon cluster ions using a QET/RRK type model [10]. Likewise, Castleman et al. applied the same model to determine the binding energies of ammonia cluster ions [11], and subsequently the same group used a *finite heat bath theory*, as developed by Klots [12], to determine the binding energies of ammonia and xenon cluster ions [13,14]. Further to this analysis, Lifshitz and Louage proposed that the average kinetic energy associated with a monomer leaving a cluster is a measure of the temperature of the transition state [15]; an approach that was subsequently used to determine the binding energy of fullerene cluster ions by Lifshitz and Märk [16]. More recently, Märk et al. have measured kinetic energy releases and determined binding energies for rare gas cluster ions [17,18] and oxygen cluster ions [19] by applying finite heat bath theory to KERs measured on two and three sector mass spectrometers [20]. A quantitative link between kinetic energy release and temperature, as proposed by Lifshitz [15], has been demonstrated quite nicely in a series of experiments where kinetic energy releases were measured following the single photon infrared excitation of cluster ions [21].

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In the present study we have measured kinetic energy releases and from these extracted binding energies for carbon dioxide, carbon disulfide and acetonitrile cluster ions. The measurements on carbon dioxide have been repeated both for the purposes of correcting an error that was highlighted earlier [5], and because the current experimental setup offers improvements in energy resolution over that available in an earlier experiment [2].

2. Experimental

The apparatus consists of a high resolution reversed geometry mass spectrometer (VG Analytical ZAB-E) coupled with a supersonic expansion nozzle for generating neutral clusters. The supersonic nozzle system consists of two differentially pumped chambers; an expansion chamber which houses a pulsed nozzle and a collimation chamber which is separated from the former by a skimmer 1 mm in diameter. Neutrals clusters of interest were generated by an expansion of gas or vapor/argon mixture through a 200 μm diameter conical nozzle, 5 mm in length and with an opening angle of 30°. The gas flow is pulsed by a Bosch fuel injector valve driven by a 0–12 V square wave pulse at a frequency of between 10 and 20 Hz. A 3 mm diameter cap, covered in a disc of Kalrez fitted onto the injector needle seals against the nozzle when the voltage pulse is low. To generate neutral $(CO_2)_n$ clusters a premixed cylinder consisting of 1% CO_2 in argon was used. For generating molecular clusters from liquids and vapours (carbon disulfide, acetonitrile), argon was passed through the liquid contained in a reservoir cooled in an ice bath.

The neutral clusters in the beam were ionized by 70 eV electrons and the resulting ion beam was then extracted from the source at 5 kV into the flight tube of a sector mass spectrometer. The mass-analyzed ion kinetic energy (MIKE) technique [22] has been used to study cluster ion fragmentation occurring in the second field free region (2nd *ffr*) of the mass spectrometer between the magnetic and electric sector. A particular cluster ion of charge (z_1) and mass (m_1) was selected using the magnet and the electric sector field voltage was scanned while the accelerating voltage and magnetic field remained constant. The following equation provides a means of identifying fragment ions from the magnitude of the electric sector voltage necessary to transmit them

$$E^* = \frac{m_2 z_1}{m_1 z_2} E_0 \qquad (1)$$

E_0 is the initial parent ion kinetic energy (5000 eV in the present experiment), E^* is the kinetic energy after fragmentation and m_2 and z_2 are the mass and charge of the fragment ion. The detection system consists of a Daly scintillation detector [23] that has been modified to extend the sensitivity range by enabling photon counting techniques to be used in conjunction with gated photon counting. Ion counting is achieved using a fast photomultiplier (EMI 9324) at a cathode voltage of −1 kV in conjunction with a photon counter (Stanford Research SR 400). During the course of these experiments, the background pressure in the 2nd *ffr* remained $<1 \times 10^{-7}$ mbar, which ensured minimal interference from collision induced fragmentation [6].

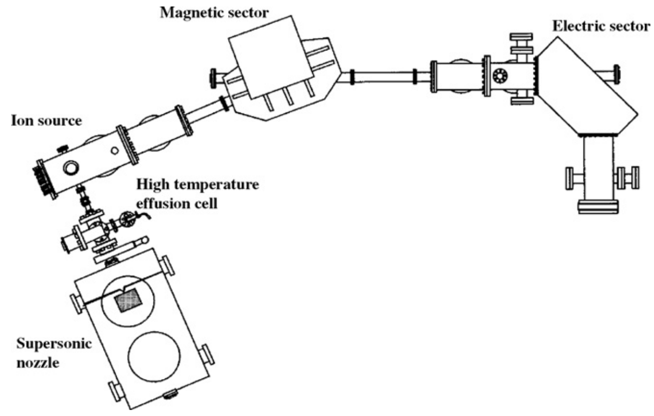

Fig. 1. Schematic diagram of the apparatus.

3. Results and data analysis

For the purposes of analyzing MIKE spectra it has been assumed that both the fragment and parent ion peaks have Gaussian profiles. Furthermore, the measured peak widths can be corrected for the effects of translational energy spread in the parent ions by using the relationship [24]

$$(\Delta E)^2 = (\Delta E^*)^2 - \left(\frac{m_2 \Delta E_0}{m_1}\right)^2 \qquad (2)$$

where ΔE^* and ΔE_0 are the measured full widths at half maximum (FWHM) of the fragment and parent ions, respectively and ΔE is the corrected width. For a unimolecular dissociation reaction,

$$X_n^+ \rightarrow X_{n-1}^+ + X \qquad (3)$$

the relationship between laboratory-frame energy spread and average kinetic energy release <KER> [25] at 5 kV is given by

$$< \mathrm{KER} >= \frac{n^2 \Delta E^2}{8 \times 10^4 (n-1)} \qquad (4)$$

If the laboratory-frame peak profiles are Gaussian in shape and ΔE is full width at half maximum (FWHM), then Eq. (4) becomes [25]

$$< \mathrm{KER} >= \frac{n^2 \Delta E^2}{8 \times 10^4 (n-1)} \times 2.16 \qquad (5)$$

The experimentally determined average kinetic energy release in the center of mass frame, yields the transition state temperature, $T^{\#}$, of an evaporative ensemble of decaying cluster ions [26,27], and for a Gaussian peak $T^{\#}$ may be obtained from the equation:

$$T^{\#} = \frac{< \mathrm{KER} >}{1.5 k_B} \qquad (6)$$

where k_B is Boltzmann constant. $T^{\#}$ can be related to the isokinetic temperature, T_b, of a canonical ensemble by the equation [26]

$$T_b = T^{\#} \frac{\exp(\gamma/C - 1) - 1}{\gamma/C - 1} \qquad (7)$$

where C is the classical vibrational heat capacity in units of k_B and γ is defined by the equation

$$\gamma = \ln\left(\frac{A}{k(T)}\right) = \frac{E_a}{k_B T_b} \qquad (8)$$

k is the unimolecular decay rate constant, A is the pre-exponential factor in the Arrhenius relation, and E_a is the binding energy for the loss of a monomer unit. If an evaporative ensemble of cluster ions is sampled after excitation, then according to [27] if $k \sim 1/t$ and $t \sim 10$ μs and $A = 1.6 \times 10^{15}$ (which is often used for atomic/molecular clusters irrespective of monomer mass and cluster size), then $\gamma = 23.5$. Thus from Eqs. (5)–(8) the binding energy of a monomer to a cluster ion can be calculated (Fig. 1).

It has been suggested in the literature (see for example [20]) that the unimolecular decay of clusters containing fewer than 10 atoms may not be purely *via* vibrational predissociation. No evidence to this effect was seen in earlier measurements on Ar_n^+ cluster ions, where the data exhibited a more or less smooth progression from $n = 4$ through to $n = 60$ [6].

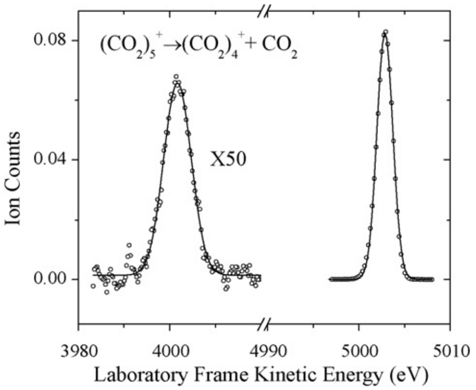

Fig. 2. MIKE scans following the metastable decay of $(CO_2)_5^+ \rightarrow (CO_2)_4^+ + CO_2$. The solid lines indicate least-squares fits of Gaussian profiles to each of the data sets.

4. Results and discussion

4.1. CO_2 cluster ions

Fig. 2 shows a representative MIKE spectrum showing a precursor ion, $(CO_2)_5^+$, and the fragment, $(CO_2)_4^+$, formed following unimolecular decay. All other clusters ions exhibited virtually the same shape. The solid lines represent Gaussian fits from which FWHM were measured for both the fragment and parent ions. If there were no kinetic energy released during unimolecular decay, the fragment ion peak would have the same width as the parent ion peak, only reduced by the ratio of electric sector voltage E^*/E_0. The resolution that could be achieved for the parent ion is not quite as good as that recorded in previous experiments on the same machine; the reason being that an intermediate slit has been removed to facilitate photodissociation experiments.

Fig. 3b shows a plot of experimental <KER> values for the unimolecular loss of one carbon dioxide molecule from each of the $(CO_2)_n^+$ cluster ions in the range $n = 4–15$. Also shown is a result taken from the measurements of Bowers et al. [4], for which there is good agreement with the current results. In contrast, there is a large discrepancy between these data and those shown in Fig. 3a that are from an earlier experiment on $(CO_2)_n^+$ cluster ions [2], and which are now known to be too large by a factor of n [5]. There are several discontinuities in the data, with the most pronounced being at $(CO_2)_{13}^+$. The thermodynamic and structural properties of neutral $(CO_2)_n$ clusters have been investigated by Etters et al. [28], and for $(CO_2)_{13}$ they predicted a distorted isoscahedron. However, the interactions that determine the structures of ions are, at short range, quite different from those applicable to a collection of neutral molecules. Although, similar magic number structures are known for rare cluster ions, those containing 13 atoms are usually built around a single central atomic ion and do not feature prominently in mass spectra [29]. In contrast, the comparatively high binding energy for $(CO_2)_2^+$ [4] would probably lead to a central dimer core and so the resultant 13-molecule structure is unlikely to be icosahedral.

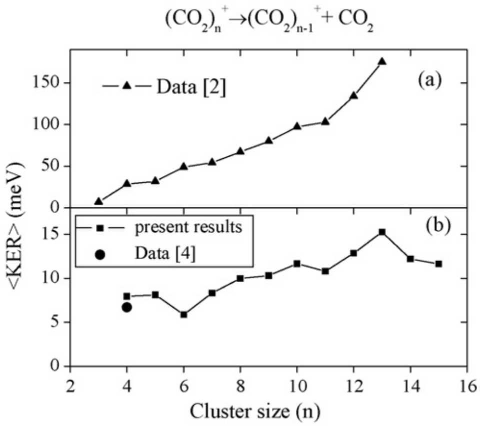

Fig. 3. Average kinetic energy release recorded for the loss of a carbon dioxide molecule from each of the $(CO_2)_n^+$ cluster ions plotted as a function of the number of molecules in the parent ion. The solid triangles in 3a are taken from [2]. The solid squares in lower panel are the present data and the solid circle is taken from [4].

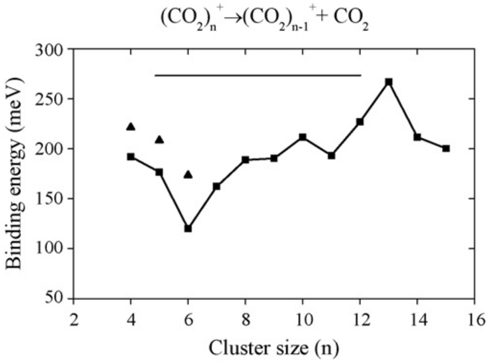

Fig. 4. Solid squares: binding energies of CO_2 molecules derived from the kinetic energy release measurements and plotted as a function of n in $(CO_2)_n^+$. Solid triangles: enthalpy changes measured for the corresponding association reaction [30]. Shown as a straight line is the bulk enthalpy of sublimation [31].

From these values for <KER> the binding energies have been derived using Eqs. (6)–(8) and the results summarized in Fig. 4 (solid square). Based on the data available and the underlying assumptions behind the theory, we were able to derive binding energies only beyond the tetramer. As might be expected, the binding energy data show the same trend observed in the <KER> data, with the most prominent value being for $(CO_2)_{13}^+$. Our binding energy data for cluster size 4, 5, and 6 are comparable with the data of Hiraoka et al. [30] (solid triangles in Fig. 4), even though the latter are derived from an entirely different type of experiment. The small variations seen for other cluster sizes are probably within the error limits of our measurements. One further comparison is possible and that is with the bulk enthalpy of sublimation for CO_2 (270 meV [31]), which is represented by the solid line in Fig. 4. As can be seen, the trend in the BE data for the larger clusters is towards this value.

4.2. CS_2 cluster ions

MIKE spectra have been recorded for CS_2 cluster ions from which the <KER> shown in Fig. 5 have been derived. Fig. 6 shows the corresponding binding energies that have been calculated from these data. Since there are no previous results available for a comparison of molecular interactions, the nearest link that can be made is with the bulk enthalpy of vaporization (280 meV [31]). This value is represented by a straight line in Fig. 6, where is can be seen there is reasonable agreement with the experimental binding energy data.

4.3. Acetonitrile cluster ions

Fig. 7 shows the experimental <KER> values measured for $(CH_3CN)_nH^+$ cluster ions for n in the range 2–12. There is some evidence of an odd-even effect out as far as $n = 8$, which can also be seen in Fig. 8 where the data have been transformed into binding energies (because of its very large value, the data point for $n = 2$ has been omitted from Fig. 8). A similar odd-even effect has been seen in molecular dynamics simulations of neutral acetoni-

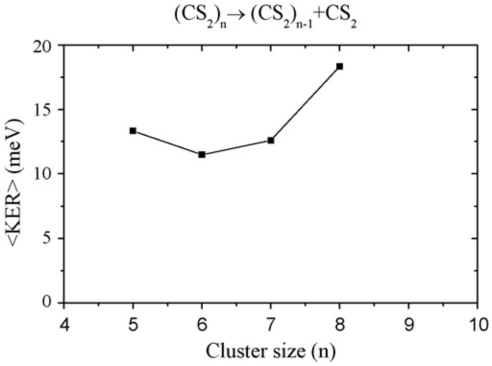

Fig. 5. Average kinetic energy release recorded for the loss of a CS_2 molecule from each of the $(CS_2)_n{}^+$ cluster ions plotted as a function of the number of the molecules in the parent ion.

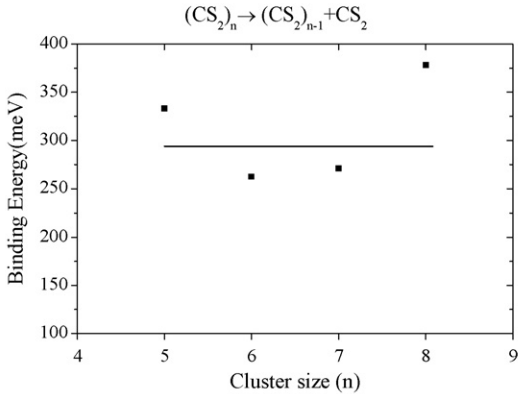

Fig. 6. Solid squares: binding energies of CS_2 molecules derived from the kinetic energy release measurements and plotted as a function of n in $(CS_2)_n{}^+$. Shown as a straight line is the known enthalpy of vaporization of the bulk material [31].

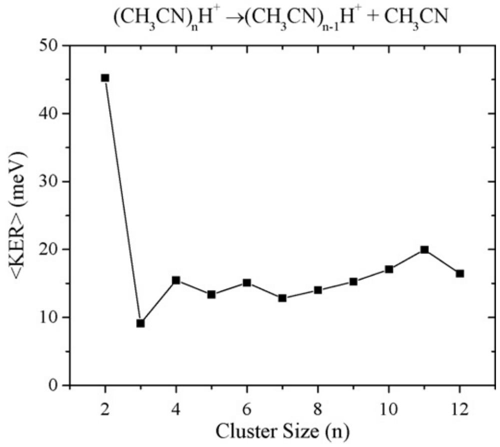

Fig. 7. Average kinetic energy release recorded for the loss of a CH_3CN molecule from each of the $(CH_3CN)_nH^+$ cluster ions plotted as a function of the number of molecules in the parent ion.

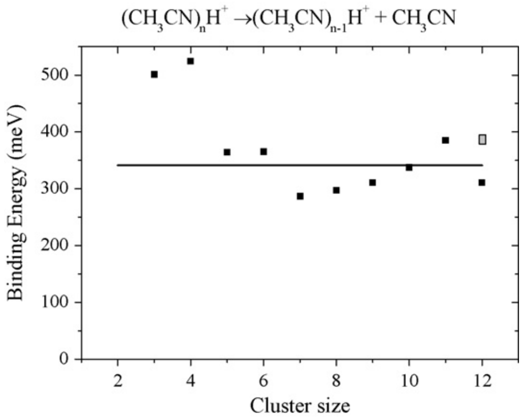

Fig. 8. Full squares: binding energies of CH_3CN molecules derived from the kinetic energy release measurements and plotted as a function of n in $(CH_3CN)_nH^+$. Shown as a solid line is the enthalpy of vaporization of the bulk material [31], and the open square is taken from a calculation of individual molecular binding energies for 12 CH_3CN molecules bound to a central ion [33].

trile clusters and was attributed to a pairing of molecules in even sized clusters [32]. The high dipole moment associated with neutral acetonitrile (3.92 D) gave rise to a stable head-to-tail geometry, which meant that complexes consisting of pairs of molecules were calculated to have high boiling/vaporization temperatures [32]. The trend extends to $n = 9$ through the formation of a stable 3 × 3 lattice structure. Whether or not similar behaviour can be attributed to protonated structures remains to be seen; however, the binding energy data shown in Fig. 8 do support an odd-even trend.

The expected trend in binding energies predicted from the bulk enthalpy of vaporization (340 meV [31]) has also been plotted in Fig. 8, where it can be seen there is good agreement with the results derived from the <KER> data. Nguyen and Peslherbe [33] have calculated the binding energies of individual CH_3CN molecules clustered to the central ions Na^+, Cs^+ and I^-, and although there are considerable differences between the two positive ions when the clusters are small, the BE values do converge at around $n = 11$–12. Since the central ion here is H^+ large discrepancies with the alkali metal ions might be expected in the small clusters; however, the calculated binding energy for $n = 12$ [33] has been plotted in Fig. 8, where it can be seen that it is in good agreement with the experimental results.

5. Conclusion

A comprehensive and systematic investigation of the unimolecular decay of three different types of cluster ions has been presented in this work. These results are consistent with a statistical partitioning of internal energy and where comparisons with other data can be made the agreement is good. For two of the systems studied, carbon dioxide and acetonitrile, the experimental binding energies at large n are a close match to the bulk enthalpies of sublimation/vaporization, which should be the case in the limit of very large clusters. At a more qualitative level the magnitudes of the measured binding energies in the larger clusters also follow the trend in boiling points: CO_2 (216 K), CS_2 (319 K) and CH_3CN (355 K).

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