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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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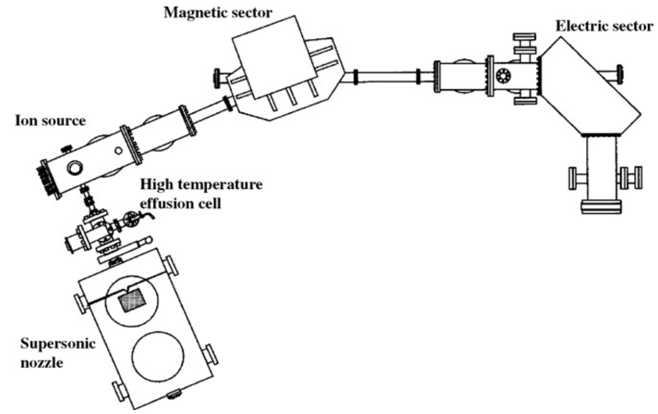

Fig. 1. Schematic diagram of the apparatus.

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

$$E^* = \frac{m_2 z_1}{m_1 z_2} E_0 \tag{1}$$

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].

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]

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

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,

$$X_n^+ \rightarrow X_{n-1}^+ + X \tag{3}$$

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

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

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

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

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:

$$T^{\#} = \frac{< \mathrm{KER} >}{1.5 k_{\mathrm{B}}} \tag{6}$$

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

$$T_{\mathrm{b}} = T^{\#} \frac{\exp(\gamma/C - 1) - 1}{\gamma/C - 1} \tag{7}$$

where C is the classical vibrational heat capacity in units of k_{B} and γ is defined by the equation

$$\gamma = \ln\left(\frac{A}{k(T)}\right) = \frac{E_{\mathrm{a}}}{k_{\mathrm{B}} T_{\mathrm{b}}} \tag{8}$$

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 $\mathrm{Ar}_n{}^+$ cluster ions, where the data exhibited a more or less smooth progression from $n = 4$ through to $n = 60$ [6].