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Decay reactions of rare gas cluster ions: Kinetic energy release distributions and binding energies

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Abstract. We have carried out measurements on metastable fragmentation of mass selected argon cluster ions which are produced by electron impact ionization of a neutral argon cluster beam. From the shape of the fragment ion peaks (MIKE scan technique) one can deduce information about the distribution of kinetic energy that is released in the decay reaction. In this study, for Ar_5^+ to Ar_{15}^+, it is Gaussian and thus we can calculate from the peak width the mean kinetic energy release ⟨KER⟩ of the corresponding decay reactions. Using finite heat bath theory we calculate from these data the binding energies of the decaying cluster ions.

PACS. 36.40.Qv Stability and fragmentation of clusters – 33.15.Fm Bond strengths, dissociation energies – 34.30.+h Intramolecular energy transfer; intramolecular dynamics; dynamics of van der Waals molecules

1 Introduction

Mass spectrometric studies of spontaneous (metastable) decay reactions and of dissociative reactions of mass-selected cluster ions induced by photons, electrons or surface collisions have provided a wealth of information about structure, stability and energetics of these species (see the review on this subject [1]). Surprisingly few studies, however, have been reported concerning measurements of the kinetic energy release (KER) distribution for the decay of metastable, weakly bound atomic (rare gas) or molecular cluster ions. Exceptions to this are the measurements by Stace and co-workers of the average kinetic energy release ⟨KER⟩ of carbon dioxide [2] and argon [3] cluster ions. The ⟨KER⟩ was derived from metastable peaks arising from decays in the field free region between the ion source and an analyzing magnetic sector field. In a later paper Stace and co-workers repeated the argon measurements with a double focusing sector field instrument employing the mass analyzed ion kinetic energy (MIKE) scan technique [4]. This method had already been used before by Bowers and co-workers [5,6] to obtain ⟨KER⟩ values for small cluster ions (mainly dimers) of water, ammonia and carbon dioxide, and by Lifshitz and co-workers for protonated ammonia and methanol cluster ions up to size $n = 8$ [7,8]. Moreover, Castleman and co-workers employed a reflectron-type time-of-flight mass spectrometer to determine the energy release of decaying protonated ammonia clusters from the arrival time peak shapes [9]. In addition to these studies the ⟨KER⟩ has been measured for metastable and electron induced carbon cluster ion decay reactions [10–12].

Vibrational predissociation is a very likely mechanism for the dissociation of metastable cluster ions [1]. Lifshitz *et al.* [7] have argued that results obtained on the dependence of ⟨KER⟩ on cluster size in the case of ammonia demonstrates indeed the statistical nature of the dissociations. Whether vibrational predissociation is the dominating channel at all times is not known, nevertheless the kinetic energy release as a function of cluster size has been modeled with statistical theories. In a pioneering study Engelking [13] showed that the binding energy of a cluster constituent within a cluster may be determined within a QET/RRK type statistical model from the measurement of cluster evaporative lifetime and average kinetic energy release. Whereas stringent demands are placed on the accurate determination of the ⟨KER⟩, only moderate demands are placed on the lifetime. Engelking has applied this method to calculate binding energies for argon and carbon dioxide cluster ions using the ⟨KER⟩ data from [2, 3]. Castleman and co-workers [9] applied the same model to their own data to obtain binding energies for ammonia cluster ions.

Moreover, evaporation from small particles has been treated theoretically by Klots [14] in the so-called finite heat bath theory. He showed that the *relative* binding energies of a series of cluster ions can be calculated by fitting

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measured decay fractions with estimated heat capacity and Gspann parameter. Castleman and co-workers [9,15] applied this method to ammonia and xenon cluster ions. Other researchers applied it to negative cluster ions [16] and carbon cluster ions [17,18]. Furthermore, it has been proposed [7] that the average kinetic energy with which a monomer leaves the cluster is a measure of the temperature in the transition state. The reaction coordinate as a molecular thermometer has been discussed by Klots [19]. This has been combined by Lifshitz and co-workers to calculate the ⟨KER⟩ as a function of cluster size and to compare results with experimental data, thereby also yielding *absolute* values for the binding energies [7]. This procedure has been recently extended to the calculation of the binding energy of fullerene ions [11].

Based on our previous work [11] we present new experimental data pertaining to the kinetic energy release distribution (KERD) of argon cluster ions to derive activation energies for monomer evaporation. The KERDs are obtained from high-resolution mass analyzed ion kinetic energy spectra using a specially improved experimental set-up [10]. We apply extensive numerical modeling of the ion trajectories in order to determine the effect of instrument geometry, slit widths, beam divergence etc., on the shape of MIKE spectra. The aim of the present paper is the determination of the evaporation energies using the finite heat bath approach. These results are compared with binding energies obtained by applying the Engelking model to the present and earlier experimental ⟨KER⟩ data [3,4].

2 Experimental

The apparatus consists of a high-resolution double focusing two-sector field mass spectrometer of reversed Nier-Johnson type geometry. Rare gas cluster ions, including also excited species, are produced by expanding the rare gas under study from a stagnation chamber with a pressure of about 1-10 bar through a nozzle orifice (nozzle diameter 10 μm for Ne and 20 μm for Kr) into a vacuum of about 10^{-7} torr. The ensuing neutral clusters are ionized by an electron beam of variable energy and current. The cluster ions are then extracted by an electric field and accelerated by $U_{acc} = 3$ kV into the spectrometer. They pass through the first field free region (1ff), are then momentum-analyzed by a magnetic sector field, enter a second field-free region (2ff, length 33.3 cm), pass through a 90° electric sector field and are finally detected by a channeltron.

In order to analyze decay reactions of mass-selected cluster ions we use the MIKE (mass-analyzed ion kinetic energy) scan technique [20]. MIKE spectra are usually recorded as follows: The magnet is tuned to the mass of the parent ion, m_p, while the electrostatic sector field voltage U is scanned. Stable singly charged ions will have a kinetic energy of 3 keV and pass at the nominal sector field voltage of $U_p = 510$ V. Daughter ions (mass m_d), formed in the 2ff in a spontaneous decay reaction, will then pass at a voltage

$$U_d = \frac{m_d}{m_p} U_p. \tag{1}$$

This equation relates the position of a daughter ion peak to the position of the parent ion peak in a MIKE spectrum. In practice, the parent ion peak will have a finite width and a distinct shape which will also be imposed on the daughter ion peak. If no kinetic energy were released in the decay reaction the daughter ion peak would have the same shape as the parent ion peak, only changed by the ratio of electric sector field voltages U_d/U_p. However, any kinetic energy release (KER) in the reaction will further modify the peak shape of the daughter ion. If the MIKE peak is strictly Gaussian, then the average kinetic energy can be extracted from its full width-at-half-maximum, ΔU, from

$$\langle \mathrm{KER} \rangle = \frac{2.16 z_2^2 m_p^2 U_{acc}}{16 z_1 m_d (m_p - m_d)} \left(\frac{\Delta U}{U_p} \right)^2 . \tag{2}$$

The width of the daughter ion, ΔU, has first to be corrected for the finite width of the parent ion by deconvoluting the fragment ion signal with the parent ion signal.

Gaussian peaks are observed when the decaying ensemble is (i) prepared in a way that the internal energy is equally partitioned over all degrees of freedom, and (ii) no reverse activation barrier prevents the production of ions with low kinetic energies, thus leading to fragmentation reactions with kinetic energy releases ranging from zero to a maximum value. Such a situation is present in the case of monomer evaporation from a larger cluster ions. The cluster ions are produced with a distribution of internal energies in the ion source, but only a distinct part of these ions will decay in the experimental time window of about 10 to 50 μs which we sample by the MIKE scan technique. At this late time the excess energy is uniformly distributed among all degrees of freedom and thus we can model the decay reactions with statistical theories. Details of the data analysis have been presented elsewhere [11].

3 Results and discussion

The smallest argon cluster ion for which we observe statistical metastable monomer evaporation is Ar_5^+. Delayed dissociation of the dimer, trimer and tetramer ion have been observed as well, but this reaction is not due to vibrational predissociation; the results will be discussed elsewhere. The shape of the metastable peaks observed in this work is Gaussian (except for the dimer ion and decays involving non-statistical decay reactions); hence the average kinetic energy release in the center-of-mass system, ⟨KER⟩, is extracted from the width of the peaks with help of eq. (2). The results of the analysis are shown in Fig. 1 (full dots). The ⟨KER⟩ increases with increasing cluster size n from less than 2 meV to some 5 meV. The solid line is drawn to guide the eye. The error bars indicate the *rms* standard deviation of the results, computed from three to five independent data sets for each cluster size. Given the

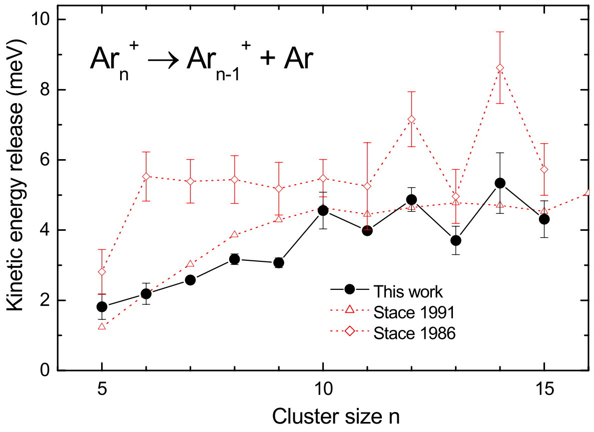

Fig. 1. Full dots: Average kinetic energy release in the center-of-mass system for metastable monomer evaporation of Ar cluster ions. The error bars indicate the *rms* standard deviation calculated from 3 to 5 separate experimental runs. Open diamonds and open triangles: Average KER obtained by Stace and co-workers [3,4].

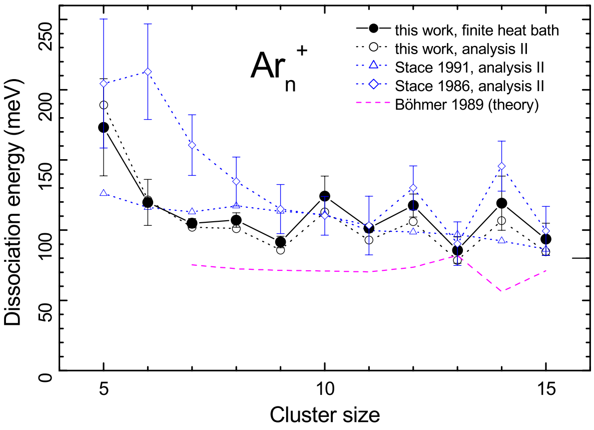

Fig. 2. Full dots: Dissociation energy of Ar cluster ions calculated from the average KER obtained in this work using finite heat bath theory. Open symbols: Our data (open dots) and data published by Stace *et al.* [3,4], analyzed as suggested by Engelking [13]. Dashed line: Dissociation energy calculated by Böhmer and Peyerimhoff assuming a trimeric ion core [26].

indicated uncertainties of our data, the local anomalies beyond $n = 10$ appear to be statistically significant.

Also shown in Fig. 1 are data published by Stace and co-workers in 1986 (open diamonds) and 1991 (open triangles) [3,4]. Their earlier data deviate significantly from ours, but the overall trend in their more recent data agrees with our findings. On the other hand, the size-dependence of their more recent $\langle \mathrm{KER} \rangle$ values is very smooth, in stark contrast to our findings. Unfortunately, in their more recent work no estimate of experimental uncertainties is given. Remarkably, in their earlier work they reported the same pattern of anomalies that we observe here beyond $n = 10$.

Given the $\langle \mathrm{KER} \rangle$ and the fact that the KER distributions are Gaussians we can apply finite heat bath theory to derive the transition state temperatures and the dissociation energies of the cluster ions, as explained in section 2 [7,11,14]. The results of this analysis are shown in Fig. 2 (solid dots). Initially the dissociation energy decreases to some 100 meV and then slowly converges towards the bulk value of 80 meV which is indicated as a horizontal bar on the ordinate to the right.

We wish to compare these dissociation energies with values that Engelking [13], applying phase space theory, derived from the KER values reported by Stace [3]; these are shown as open diamonds in Fig 2. For the sake of better comparison, we have analyzed our present KER data by the same procedure (open circles). Specifically, we do not consider the size dependences of the collision cross section, the degeneracy factor and the transit time of the cluster ions through the field-free region relative to their formation in the ion source. The only modification is that we use an average transit time of 38 μs, appropriate for mid-sized Ar cluster ions decaying in the second field-free region of our instrument. This is more than an order of magnitude larger than the value given by Stace [3] and adopted by Engelking in his analysis [13], but those earlier data were, in fact, recorded in the first field-free region of a magnetic spectrometer. Likewise, we derive dissociation energies from the more recent $\langle \mathrm{KER} \rangle$ data measured by Stace and co-worker [4] in the second field-free region of their magnetic spectrometer. In this work the authors did not specify the transit time of the cluster ions. We estimate them to be $\sqrt{3/8}$ of those in our instrument, taking into account that their instrument operates at a higher accelerating voltage of 8 kV. The results of this analysis are shown in Fig. 2 as open triangles. Comparing the data in Fig. 2 one notices that

- The Engelking model increases the dissociation energy for Ar_5^+ by about 10% and decreases it by about the same amount for the largest clusters. Incorporating the size dependence of the transit time and the collision cross section would reduce these differences to a few percent.
- The large differences between the $\langle \mathrm{KER} \rangle$ values of Stace's earlier work and our current data do not produce equally large differences between the dissociation energies. That is, one reason for the large $\langle \mathrm{KER} \rangle$ values in Stace's earlier work is caused by the relatively short transit time in his instrument.

Dissociation energies of argon cluster ions have been calculated by Kuntz and Valldorf [25] and Böhmer and Peyerimhoff [26]. In Fig. 2 we show, as a dotted line, the values obtained by Böhmer *et al.* [26]. The dissociation values are lower than the experimental ones; they show a local maximum at $n = 13$. However, the results of the MRD-CI calculations [26] depend on the structure of the ion core and on the vibrational temperature of the cluster. The values shown in Fig. 2 apply to a trimeric core and

$T = 10$ K. In the experiment, evaporative cooling will provide for a temperature of, roughly, 40 K [27]. Photoabsorption experiments indicate that the charge in argon cluster ions of this size localizes on a tetramer [28].

Also, earlier experimental data that might suggest anomalies in the stability of argon cluster ions are contradictory. This information can be derived from the appearance of intensity anomalies in mass spectra, or from unimolecular decay rates [29–33], but in most cases the data suggest that Ar_{14}^{+} rather than Ar_{13}^{+} has a relatively high dissociation energy. This would be in agreement with our present findings.

In conclusion, we have presented kinetic energy release data for argon cluster ions; dissociation energies have been derived from these data by applying the finite heat bath method. Although the overall trend in the size dependence of the dissociation energies agrees with other experimental data and with theory, there are significant discrepancies in the detail. We believe that the current data are more accurate than earlier data, that their uncertainties are assessed more reliably, and that the method chosen to analyze them is more appropriate.

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