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Binding Energies of cluster ions

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1. Introduction

The evolution of crystalline structure in small elemental clusters, and the convergence of their binding energy towards the bulk value, have been central topics in cluster science. Neutral inert gas clusters have served as model systems because the low computational power that was available decades ago restricted searches for the minimum energy structure to systems with pair-wise additive interaction potentials [1, 2]. Early mass spectrometric analysis of xenon clusters [3] revealed intriguing qualitative agreement with computational work, but it was soon realized that those mass spectra revealed properties of charged, rather than neutral, clusters [4, 5]. The binding energy of charged clusters may be measured by analyzing the kinetic energy released in the metastable decay of mass selected parent ions. In the present work we use finite heat bath theory to determine the binding energies of argon, neon, krypton, oxygen and nitrogen clusters from their respective average kinetic energy releases.

2. Experimental

Details of the experimental arrangement have been published elsewhere [6]. In brief, the apparatus consists of a high-resolution double focusing two-sector field mass spectrometer of reversed Nier-Johnson type geometry. The clusters are produced by expanding the gas from a stagnation chamber with a pressure of about 1-10 bar through a nozzle (diameter 10 μm or 20 μm) into a vacuum of about 10^{-7} torr. The ensuing neutral clusters are ionised by an electron beam of variable energy and current. The cluster ions are then extracted by an electric field and accelerated by 3 kV into the spectrometer. They pass through the first field free region, are then momentum-analyzed by a magnetic sector field, enter a second field-free region (length 33.3 cm), pass through a 90° electric sector field and are finally detected by a channeltron.

MIKE (mass-analyzed ion kinetic energy) spectra are measured to investigate decay reactions of mass-selected ions [7]. Spectra are 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

$$U_d = \frac{m_d}{m_p} U_p \quad (1)$$

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 that 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 scaled by the ratio of the electric sector field voltages U_d/U_p . However, any kinetic energy release (KER) in the reaction will 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 the width of the daughter ion ΔU has to be corrected for the finite width of the parent ion by deconvoluting the fragment ion signal with the parent ion signal.

$$\langle KER \rangle = \frac{z_d^2 m_1^2 U_{av}}{16 z_p m_2 m_3} \left(\frac{\Delta U}{U_p} \right)^2 \times 2.16 \quad (2)$$

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. The cluster ions are produced with a distribution of internal energies in the ion source, but only a distinct sub-ensemble of these ions will decay in the experimental time window of about 20 to 60 μ s which we sample by the MIKE scan technique, depending on the mass of the selected cluster ion. At this 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 [8].

3. Results and discussion

The smallest cluster ion for which we observe here statistical driven metastable monomer evaporation is five. The shape of the metastable peaks observed in this work is Gaussian hence the average kinetic energy release in the center-of-mass system $\langle KER \rangle$ is extracted from the width of the peaks with help of eq. 2. Given the KER and the fact that the KER distributions are Gaussian we can apply finite heat bath theory to derive the transition state temperatures and the dissociation energies of the cluster ions. (for details see Ref. [8-13]).

In Fig.1 we show as an example binding energy values for neon, argon and krypton cluster ions. The solid dots are derived by using a constant Gspann factor of $\gamma = 23.5$. Also shown (as a solid line slightly above the solid dots) are binding energies obtained with a more carefully chosen, size-dependent Gspann factor. The latter binding energies are 10 to 15 % larger than the former, depending on cluster size n and monomer mass. The corresponding deviations in the Gspann factor from the commonly accepted value of $\gamma = 23.5$ [11] are smaller, but they exceed the uncertainty of 6 % that Klots had suggested for γ for small and medium-sized clusters, for a variety of different systems and $k = 10^5 \text{ s}^{-1}$ [12]. Hence, the common practice of using a constant Gspann factor for different cluster sizes, monomer masses and mass spectrometers is questionable.

Included in Fig. 1 are binding energies of argon cluster ions recently measured in our lab [13]. The reader is referred to that report for a comparison with experimental results obtained by Stace and co-workers [14,15], and for a detailed comparison with Engelking's alternative procedure [16] to derive binding energies from average KER values.

For the inert gases Ne, Ar and Kr, the binding energies initially decrease with increasing size n and then level off at a value above the enthalpy of vaporization of the condensed phase [17] which is indicated in Fig. 1 as a solid horizontal line. Beyond this general decrease, there are no features that are common to all three systems. The local variations for larger cluster sizes are probably statistical. It should be noted, though, that neither the geometric structure of small inert gas cluster ions nor the size dependence of their stabilities are expected to follow a common trend. For example, the size distributions observed after electron impact ionization

of neutral clusters are notably different in this size range [18-21]. Experiments and computations at various levels of sophistication suggest that the structure of the ionic core may well be different for neon, argon, krypton and xenon cluster ions [22-27]. Results for calculated binding energies (Ne [27] and Ar [24]) are designated by the dotted lines in Fig. 1.

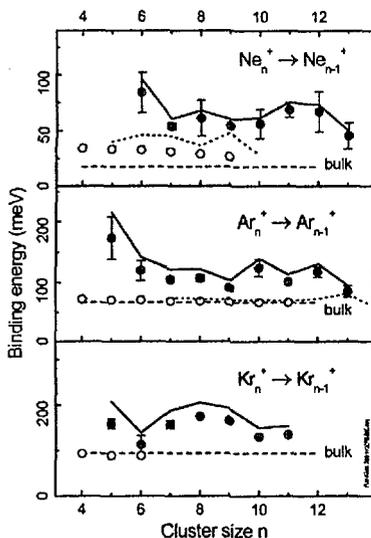


Fig.1: Full dots: Binding energies of Ne, Ar and Kr cluster ions calculated from the average KER with finite heat bath theory and a constant Gspann factor of $\gamma = 23.5$. Solid line: Same, but with a more appropriate, size-dependent Gspann factor. Open dots: Results from high-pressure gas phase experiments [28]. Dashed horizontal line: Enthalpy of vaporization of the bulk [17]. Dotted lines: Binding energies calculated for Ne_n^+ [27] and Ar_n^+ [24].

Also shown in Fig. 1 are thermochemical stabilities (ΔH^0 values, open dots) determined by Hiraoka and Mori from van't Hoff plots of ionic clustering equilibria in a high-pressure mass spectrometer source [28]. These values are significantly below the values obtained by us. However, as pointed out by Klots [12], these measurements are subject to systematic errors which arise from evaporation of cluster ions before mass analysis is accomplished.

We have applied the same method in order to measure kinetic energy release for decaying N_2 and O_2 clusters ions and derived binding energies from the kinetic energy release data of these metastable decay reactions. Both, average kinetic energy release $\langle KER \rangle$ data derived from the peak shapes and the time dependence of the metastable fractions of stoichiometric oxygen cluster ions show a characteristic dependence on cluster size (U-shape) indicating a change in the metastable fragmentation mechanism when going from the dimer to the dekamers ion. The binding energy results obtained are in fair agreement with previous results based on gas phase ion equilibria measurements and the corresponding bulk value.

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