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Time-dependent size distribution of xenon-cluster ions

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The evaporation of monomers following electron-impact ionization causes a significant enhancement of the intensity anomalies ("magic numbers") in mass spectra of xenon clusters. The dissociation rates are measured on a microsecond time scale for clusters containing between 10 and 79 atoms. The highest dissociation probability, 99(1)%, is found for $Xe_{57}{}^+$, which is two atoms larger than a closed-shell icosahedral cluster. Each anomaly in the dissociation rates corresponds to an intensity anomaly (magic number) in the mass spectrum. Recent Monte Carlo simulations for $Xe_n{}^+$, $n \leq 30$, are in full agreement with our experimental results.

The intensity anomalies in mass spectra of neutral rare-gas clusters ionized by electron impact have been the object of many experimental and theoretical efforts in the last few years.[1-8] Recently, the important role of fragmentation caused by the ionization process has been shown for small argon clusters.[9] Analyzing the kinematically different behavior in a scattering experiment in which the neutral-cluster beam is crossed by a helium beam, the probability for direct fragmentation of the argon trimer has been found to be nearly 100%. Additionally, the metastable dissociation of argon-cluster ions up to cluster size $n = 25$ has been measured with a double-focusing mass spectrometer[10] and with a modified single-focusing instrument.[11] In a preliminary work we tried to measure the dissociation of small xenon-cluster ions ($n \leq 25$) in the field-free drift tube of our time-of-flight mass spectrometer,[12] but the dissociation probabilities were too small for a quantitative analysis. After significant improvement of the ion intensity and the mass resolution as well as the energy resolution of the ions, we can now present the first information about the dissociation of larger xenon cluster ions up to cluster size 79 on a microsecond time scale.

Neutral clusters are formed by adiabatic expansion, ionized by a pulsed electron beam (energy 28 eV) and mass analyzed in a time-of-flight (TOF) mass spectrometer. The conventional TOF technique probes the size distribution of the cluster ions effectively at the end of the acceleration gap. Decompositions of the ions occurring in the subsequent field-free drift tube cannot be detected, because the daughter ions nearly maintain their velocity and thereby their total time of flight. In order to measure these decompositions we analyze the kinetic energy of the ions at the entrance of the detector with the help of a barrier potential U_b. If a singly charged ion (charge e_0) with mass m_p dissociates in the field-free drift tube into a daughter ion m_d and a neutral fragment, the kinetic energy of the daughter ion will be given by

$$e_0 U_d = e_0 U_0 m_d / m_p$$

(neglecting the energy released in the dissociation, which is small in comparison with the energy of the parent ions: $e_0 U_0 = 2$ keV). This experimental method allows us to exclude ions which dissociate during their time of flight in the drift tube by raising the barrier voltage U_b to values higher than U_d. The background pressure in the drift tube (length 1 m) is kept below 10^{-7} mbar during the experiment in order to avoid collision-induced dissociations. Nevertheless, collisions between the accelerated ions and the atoms in the neutral jet may occur, because the ions are accelerated collinearly in our setup. From the total target thickness (jet plus background gas) we calculate that only a small fraction of the observed dissociations is induced by collisions. More experimental details are described elsewhere.[12,13]

Figure 1 shows two representative mass spectra of xenon clusters recorded with different barrier voltages. The upper spectrum displays the cluster ion distribution at the entrance to the drift tube. All ions contributing to this spectrum have been stable during their acceleration ($t_{14} = 9$ μs, $t_{55} = 17$ μs for the 14-atom and 55-atom cluster, respectively), but they may be product ions formed after electron ionization within less than 1 μs, because we apply a pulsed acceleration field.[13] The subensemble of the cluster ions in the upper spectrum, which additionally stay stable during their total time of flight to the detector ($t_{14} = 75$ μs, $t_{55} = 147$ μs), constitutes the lower spectrum. In this case the barrier voltage is set high enough ($U_b = 0.99 U_0$) to reflect and therefore exclude all product ions formed by dissociations in the drift tube. The occurrence of dissociation processes will therefore cause a loss in intensity for unstable

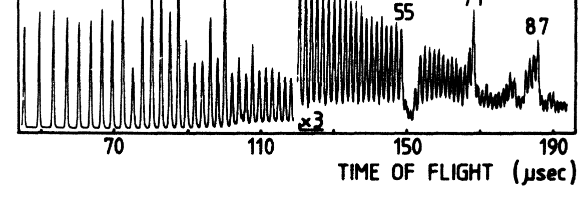

FIG. 1. Sections from time-of-flight mass spectra of xenon clusters. Top, conventional setup; bottom, product ions from dissociations in the drift tube are excluded.

cluster ions. The most striking example is the ion Xe_{57}^+, which dissociates with a probability of 99(1)% in the drift tube. The exclusion of product ions additionally enhances the intensity steps after $n=13$, 19, 23, 25, and 29.

For a careful analysis of the dissociation probabilities more than two mass spectra with different barrier voltages had to be recorded, because the kinetic-energy distribution of a product ion from a big cluster will partially overlap the distribution of its precursor ion. Knowing the energy distribution for a stable ion, we can calculate the probability for the various dissociation channels (loss of one or two or more monomers) by solving the corresponding set of linear equations. The evaporation of single monomers turns out to be the main dissociation process. For clusters bigger than 50 atoms a small but increasing probability for the evaporation of more than one monomer becomes detectable in our time window. Especially, those cluster ions which could reach a particularly stable ion configuration show higher probabilities for multiple evaporation processes. For example, the ion Xe_{57}^+ has a relatively high dissociation probability for the evaporation of two monomers, because it can reach a closed-shell, icosahedral structure with 55 atoms, which is energetically favored.[14]

The time of flight for the cluster ions in the drift tube increases with the square root of their mass because of the fixed acceleration voltage in a TOF experiment. Comparing the dissociation probabilities of cluster ions over a wide mass range might be misleading because of this mass dependence of the time window for dissociations. Therefore, we calculate total effective dissociation *rates* for the cluster sizes 10 to 79, starting with the total dissociation probability (including all dissociation channels) and assuming an exponential decay within the time window. These rates are displayed in Fig. 2. The curve shows a striking maximum after $n=55$ and a broader minimum at $n=71$. The dissociation rates for smaller cluster ions are magnified in the inset, revealing a maximum for $n=14$ and minima for $n=19$, 23, and 25. Each of these features corresponds to an intensity anomaly in the upper mass spectrum in Fig. 1 presenting the cluster ion distribution directly after the acceleration. Comparing the mass spectra with the dissociation rates, it becomes obvious that the intensity steps after 13 and 55 (complete first and second shells of an icosahedron[14]) are caused by *high* dissociation rates of the next biggest cluster ions $n=14$ and $n=56$, 57, and 58. On the other hand, the relatively high intensities for $n=19$, 23, 25, 29, and 71 in the upper mass spectrum in Fig. 1 are caused by the *low* dissociation rates of these ions themselves. Starting with a closed shell of an icosahedron and putting one and two additional caps (on opposite ends) on it, one ends up with clusters of 19 and 25 atoms for the first-shell icosahedron and 71 and 87 atoms for the second-shell icosahedron.[1] Somewhat similar structures can be reached with 23 and 29 atoms.[4] These compact structures cause an increased binding energy. The differences in the dissociation rates reflect the stability of these ions. The numbers of particularly stable ions are in full agreement with a recent Monte Carlo simulation[8] on argon and xenon cluster ions up to cluster size 30.

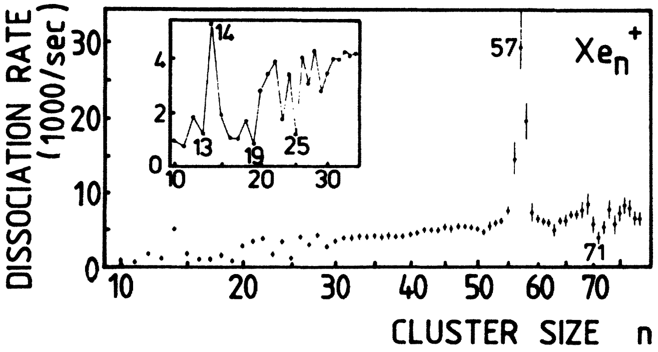

FIG. 2. Total effective dissociation rates for xenon custer ions in the field-free drift tube.

Comparing our result for xenon clusters to a recent work on cold argon clusters (growth of clusters on ions),[15] there is full agreement for cluster sizes smaller than 30. The only exception is the maximum for $n=26$ in the case of argon, whereas xenon has a maximum at $n=25$. This difference is due to the different distortions produced by the dimer ion.[6,8,16] The main difference in the distributions of xenon and argon cluster ions occurs in the size range $n=30$–54. The argon clusters show a rich structure in intensity, whereas xenon has no intensity anomaly at all. This is the size range where two different, mutually exclusive cluster structures, both being supported by the icosahedral core ($n=13$), are expected to compete energetically.[15] In one of these structures, which gives rise to the anomalies at $n=19$, 23, 25 or 26, and 29, the number of bonds with the core will be maximized. In the other structure, which finally yields the complete-shell icosahedron at $n=55$, the number of bonds within the second shell will be maximum. In the case of argon cluster ions the break-even point for these two structures occurs between $n=35$ and 40, as indicated by the absence of intensity anomalies.[15] In the case of xenon, the two structures can apparently compete with each other over a much wider size range. We cannot definitely rule out that the different methods being used for cluster ion *preparation* (growth of clusters on ions for argon,[15] ionization of neutral clusters for xenon) contribute to the differences in this size range, $n=30$–54. This seems less likely, however, because in both cases the cluster ions are thought to be initially hot,[6,8,15] while ample time for cooling via evaporation of monomers[17] is given in the low-pressure environment of the mass spectrometer.

In the case of water and carbon dioxide clusters, we have previously shown[12,13] that the intensity anomalies in the size distributions will only evolve *after* the cluster ions have cooled down sufficiently, because the calculated stability of *molten* clusters versus size does not show any "magic numbers."[18] Therefore, an alternative explanation for the absence of anomalies in our experimentally determined dissociation rates might be thought to arise from insufficient cooling of the xenon cluster ions in the size range $n=30$–54. This hypothesis, however, appears to be very unlikely, because intensity anomalies in our mass spectra of xenon clusters do occur for larger sizes, especially at $n=55, 71, 74, 81, 87, \ldots$. The same anomalies are found in the argon spectra, and they are of comparable magnitude. Also, the available time for the evaporative cooling of the cluster ions is 0.1–0.2 ms in both experiments, and the relatively low dissociation rate of our xenon cluster ions for $n \leq 55$ also indicates a low internal temperature. We therefore conclude that the residual excitation energy of the xenon cluster ions is about the same as in the argon cluster ions, if scaled to the relevant bond energies.

In summary, the measured anomalies in the dissociation rates completely agree with theoretical models of cluster ion stability based on icosahedral structures for $Xe_n{}^+$, $n \leqslant 30$.[8] The main difference between argon and xenon cluster ions occurs in the size range $n = 30-54$, where the second icosahedral shell is completed. This is attributed to the different amount of distortions being introduced by the different weight of atom-atom versus atom-ion interaction strength. Each anomaly in the dissociation rates corresponds to an intensity anomaly (magic number) in the mass spectrum. Thus the explanation of the magic numbers in mass spectra of xenon clusters is given by the stability of the ions.

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