Multiply Charged Neon Clusters: Failure of the Liquid Drop Model?

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We have analyzed the stability and fission dynamics of multiply charged neon cluster ions. The critical sizes for the observation of long-lived ions are $n_2 = 284$ and $n_3 = 656$ for charge states 2 and 3, respectively, a factor 3 to 4 below the predictions of a previously successful liquid-drop model. The preferred fragment ions of fission reactions are surprisingly small ($2 \leq n \leq 5$); their kinetic energy distributions peak at 200 meV or below. The size of these fragments and their average kinetic energies are much less than predicted by the liquid-drop model.

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Multiply charged atomic clusters are prone to charge separation by Coulomb explosion [1,2]. The process happens spontaneously when the cluster reaches the Rayleigh limit ($X = 1$) [3], or it can be induced in clusters with fissilities below $X = 1$ by collisional excitation or heating by photoexcitation [4,5]. Coulomb explosion occurs after electron or photon ionization of clusters [5–7], collisions with high energy transfer [8], or collisions with highly charged ions [9–11]. A novel Auger-like mechanism, interatomic Coulomb decay (ICD) by which electronic vacancies are rapidly filled by valence electrons from neighboring atoms, has been suggested to explain the surprisingly efficient formation of multiply charged van der Waals clusters by electron or photon ionization [12]. Furthermore, nuclear fusion has been induced by Coulomb explosion of deuterium clusters in intense laser fields [13].

Coulomb explosion raises several intriguing questions: For what size-to-charge ratio will the fission barrier vanish? How does the cluster deform from its spherical equilibrium shape at this point? Is electron tunneling involved in fission? What is the role of competing channels? How does the energy release partition between kinetic energy and vibrational energy? What are the size and kinetic energy distributions of the emitted fragment ions?

Rayleigh's prediction that highly charged liquids are emitted in the form of very fine jets when the fissility reaches $X = 1$ was recently confirmed by direct imaging of micron-sized droplets [14]. For smaller atomic clusters, mass spectrometry has successfully been applied to characterize fissioning of metallic [1,6,11,15] and van der Waals systems [4,6,7,10] and fullerenes [9,16].

The weak binding between the neutral constituents in van der Waals clusters implies instability for charge states as small as $z = 2$ unless the cluster contains tens or even hundreds of monomers. A large body of experimental data has been collected for these systems; they have been explained satisfactorily within a liquid-drop model [7,17]. Agreement to better than $\approx 30\%$ has been achieved between the calculated and experimentally observed critical sizes for more than 20 systems, and the asymmetric size distribution of fission fragments from metastable $(CO_2)_n^{3+}$ cluster ions (i.e., clusters near $X \approx 1$) has been rationalized. However, the van der Waals systems investigated so far feature relatively large binding energies and correspondingly small critical sizes, $n_2 < 100$, for doubly charged clusters. Critical sizes have not yet been reported for the most weakly bound systems, namely, helium, neon, and hydrogen. Furthermore, the prediction that cluster ions with fissilities greatly exceeding $X = 1$ favor symmetric fission has not yet been tested.

Here we report critical sizes for doubly and triply charged neon clusters, and the kinetic energy distributions of fission fragments. Isotopically pure neon was used for an unambiguous identification of Ne_n^{2+} for which the liquid-drop model predicts $n_2 = 868$. The model is at variance with our results: The experimental critical size is a factor 3 smaller, fission is highly asymmetric, and the kinetic energy is surprisingly small (≤ 200 meV).

Neutral clusters are produced by expanding neat neon from $T_0 = 40$ K and a pressure of typically 8 bar through a pin-hole nozzle of 5 μm diameter into vacuum. Either neon with natural isotopic abundance (purity 99.999%) or ^{20}Ne enriched to 99.95% are used. Clusters are ionized by electron impact. The ions are extracted by an electric field and accelerated into a high resolution double focusing mass spectrometer of reversed Nier-Johnson type geometry [18]. They pass through the first field-free region, are momentum analyzed by a magnetic sector field, enter a second field-free region, pass through a 90° electric sector field, and are detected by an ion detector.

Metastable (spontaneous) reactions of ions and the kinetic energy distribution of fragment ions (KED) may be recorded by mass-analyzed ion kinetic energy (MIKE) scans [18]. However, MIKE scans probe reactions that happen a long time after ionization (within $89 \leq t \leq 114$ μs for Ne_{284}^{2+}, the smallest observed doubly charged neon cluster). We did not observe spontaneous fission of doubly charged neon cluster ions on this time scale, in agreement with previous studies of doubly charged van der Waals clusters [4,7]. The absence of metastable (delayed) fission has been rationalized by the large energy

that is initially concentrated in a compression mode of the cluster ion. This energy, once dissipated, leads to monomer evaporation rather than fission [7,17,19].

We have chosen an alternative technique, namely, analysis of the z-deflection profile of the ion beam in the ion source [20]. The kinetic energy of an ion in the z direction is proportional to the square of the deflection voltage in that direction. The first derivative of the ion signal as a function of the deflection voltage yields the kinetic energy distribution (KED) after transformation of the energy scale. The ion deflection method covers a much earlier time window than the MIKE technique and it includes prompt reactions. For Ne_{284}^{2+} the window spans $0 \leq t \leq 6$ μs. However, with this technique it is not possible to determine the mass-to-charge ratio of the parent ion.

A mass spectrum of neon cluster ions, formed by expansion of ^{20}Ne and ionization at $E_e = 120$ eV, is shown in Fig. 1(a). The dominant ion peaks correspond to Ne_n^+; the abscissa has been labeled by the size-to-charge ratio n/z. A series of ions is observed between the main peaks starting at $n/z = 143.5$; these ions arise from odd-sized Ne_n^{2+} $n \geq 287$.

Figure 1(b) shows a spectrum of cluster ions formed in an expansion of neon with natural isotopic composition ionized at 120 eV. The large number of isotopomers makes it impossible to resolve individual cluster ions. Still, at a

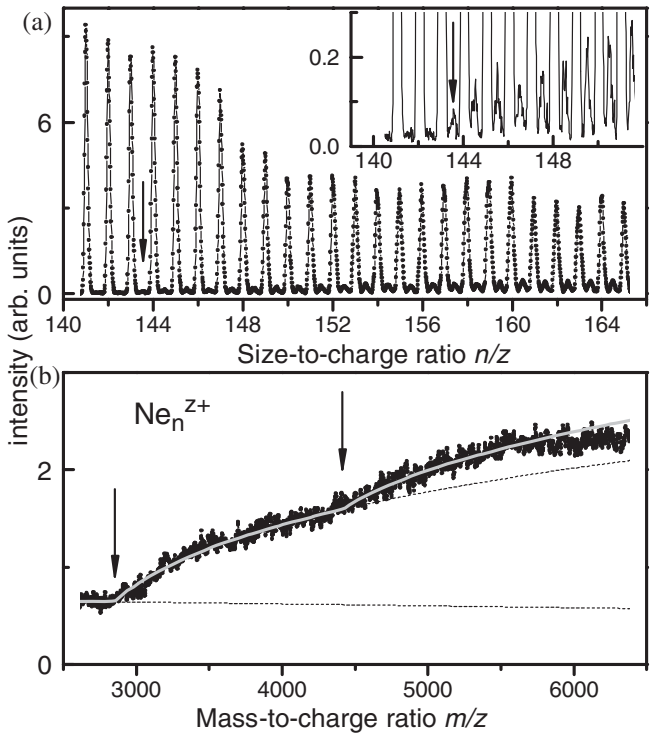

FIG. 1. (a) Mass spectrum of isotopically pure ^{20}Ne cluster ions. Arrows indicate the smallest observable doubly charged cluster, Ne_{287}^{2+}. (b) Cluster ions formed from isotopically mixed neon. The stepwise intensity increases at $m/z \approx 2875$ and 4425 arise from doubly and triply charged cluster ions above their critical sizes $n_2 \approx 284$ and $n_3 \approx 656$, respectively.

mass-to-charge ratio of $m/z = 2875 \pm 80$ (with ^{20}Ne set to 20 u) we see a stepwise increase of the ion intensity; another step occurs at $m/z = 4425 \pm 120$. The steps have been determined by fitting a sum of power laws shown as a solid gray line. These steps are characteristic of multiply charged clusters beyond their critical size. They are not observed at $E_e = 40$ eV which is not sufficient to form multiply charged cluster ions. Assigning charge states $z = 2$ and 3 to the values of m/z given above, we calculate critical sizes $n_2 = 284 \pm 8$ and $n_3 = 656 \pm 12$, respectively, using an average monomer mass of 20.25 u which takes into account the enrichment of ^{22}Ne in the cluster ions [21]. The n_2 value agrees with the value determined in the resolved spectrum of isotopically pure ^{20}Ne.

However, the observed critical sizes are much smaller than the values $n_{2,\mathrm{theo}} = 868$ and $n_{3,\mathrm{theo}} = 2950$ computed from a liquid-drop model for neon clusters [7]. Although the model is fairly crude, it successfully explains the critical sizes of many atomic and molecular van der Waals and hydrogen-bound clusters and the observed size distributions of their fission fragments. One of the largest discrepancies was observed for argon clusters where the computed critical size exceeded the observed value by 34%. In contrast, for neon clusters the predictions exceed our experimental values by a factor of 3.1 and 4.5 for charge states 2 and 3, respectively.

To gain more insight into the source of this discrepancy we have measured the z profiles of the ions; they reflect the kinetic energy distributions in the ion source. The narrow profiles in Fig. 2(a) represent Ne^+ formed by ionizing the collimated cluster beam at 40 and 120 eV; the broad profile is observed when neon is present as background gas. Symbols are experimental data; solid lines indicate the result of fitting a Gaussian centered at 0 V. Figures 2(b) and 2(c) display the profiles for Ne_2^+ and Ne_3^+. The 120 eV data are fit well by a Gaussian plus a smeared out step function. Figure 2(d) shows the profiles of larger cluster ions formed at 180 eV.

Figure 3 displays the KEDs derived from the fits shown in Fig. 2. The KED of Ne^+ formed by ionization of background gas is broad because of the random momentum directions of the neutrals. Ne^+ formed from the cluster beam has a much narrower KED (6 meV average, limited by the instrumental resolution). The value does not depend on the electron energy because monomer ions are ionization products of atoms; they do not carry the large recoil energy of cluster fragments [22].

The KEDs of Ne_2^+ and Ne_3^+ formed at 40 eV are much broader; they broaden even more at higher electron energy. The average KED values are 160 (30), 200 (15), 180, 105, 85, 66, 26, and 5 meV for $n = 2$, 3, 5, 10, 20, 30, 50, and 100, respectively, where values in parentheses refer to $E_e = 40$ eV.

The broadening at 40 eV, below the threshold for efficient formation of multiply charged ions, is due to ejection of one or more monomers from larger precursor ions. We

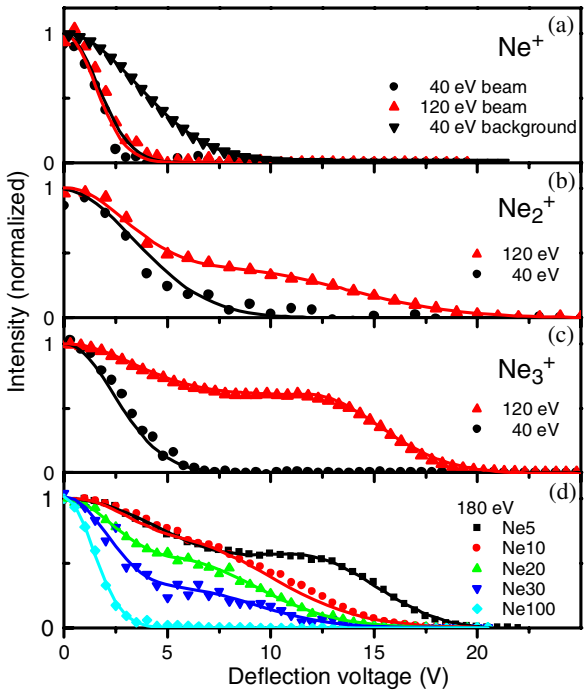

FIG. 2 (color online). Spatial profile of Ne^+, $Ne_2{}^+$, and $Ne_3{}^+$ formed at $E_e = 40$ and 120 eV, and larger cluster ions formed at $E_e = 180$ eV.

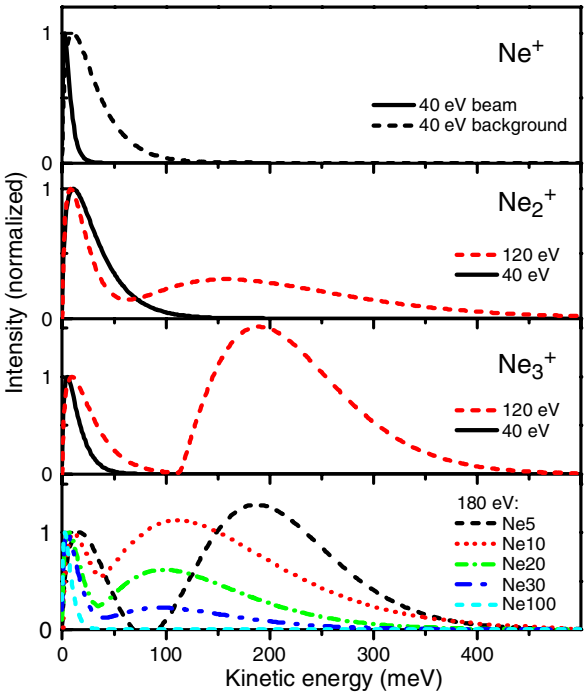

FIG. 3 (color online). KEDs of ions derived from the spatial profiles shown in Fig. 2.

have previously measured the total kinetic energy release (KER) for Ne evaporation from $Ne_n{}^+$. A value of 2 meV was found for $n \geq 10$ for events that occur ≈ 22 μs after ionization [18]. The much larger kinetic energies observed in the present work stem from several factors: (1) More than one evaporation is likely to occur during the experimental time window which includes $t = 0$ [23]; (2) during early times, nonstatistical processes including relaxation of long-lived electronic excitations (excitons) [24] may occur. A recent molecular dynamics study of neon cluster ions that includes nonadiabatic processes concludes that the preferred fragment of precursor ions with less than 15 atoms is the dimer ion, and that explosive fragmentation occurs mostly within the first 100 ps [23].

The KED becomes bimodal at $E_e \geq 120$ eV when formation of multiply charged cluster ions becomes possible. For $2 \leq n \leq 5$ we observe a second peak near 200 meV. For larger ions the peak becomes gradually less pronounced and shifts toward lower energies. For $n \geq 50$, the second maximum in the KED is barely visible. A large, narrowly defined component is the signature of Coulomb explosion into two charged fragments. Multifragmentation processes would not lead to such a narrow KED.

How symmetric or asymmetric is the reaction? An analysis reveals that $\approx 50\%$ of all light fission fragments end up as $Ne_2{}^+$ or $Ne_3{}^+$; another $\approx 20\%$ end up as $Ne_4{}^+$ or $Ne_5{}^+$. Some of these fragments may stem from very small precursor ions by more or less symmetric fission. On the other hand, the high intensity of large cluster ions in mass spectra recorded at 40 eV and the instability of doubly charged cluster ions below $n_2 = 284$ implies that the fission fragments arise from a broad range of precursor sizes. Together with the small size of preferred fragments ($n_f \leq 5$) we conclude that fission is extremely asymmetric.

Figure 4 shows the prediction using the liquid-drop model [7] for the fission barrier, the reverse fission barrier (= total reaction energy in the absence of nonadiabatic effects) and, plotted along the right ordinate, the size of the lighter of the preferred fragment ions, i.e., the one that minimizes the fission barrier. Lennard-Jones parameters and the dielectric constant of neon are from Ref. [7]. Vertical arrows in Fig. 4 highlight the discrepancy between the observed and calculated critical size for $Ne_n{}^{2+}$. Two other discrepancies are apparent: The model predicts (i) a reverse fission barrier exceeding 0.9 eV for fragment ions from $Ne_n{}^{2+}$, $n \leq 284$, and (ii) a preferred fragment size of $n_f \approx 70$ for doubly charged parent clusters around $n_p \approx 284$. n_f would further increase with decreasing n_p until fission becomes symmetric. Within the liquid-drop model, small fission fragment ions could arise only from fission of very small doubly charged clusters, below ≈ 10. However, in this case the computed reverse barrier would approach 3 eV, further increasing the discrepancy between the model and experiment.

The liquid-drop model used here [7] is rather simplistic. The total energy of a multiply charged cluster is written as the sum of a volume, a surface, and a Coulomb term. The fission barrier is estimated by considering the reverse reaction and determining the point at which the two spherical fragments make contact. The model does not consider the formation of a neck which will lower the fission barrier.

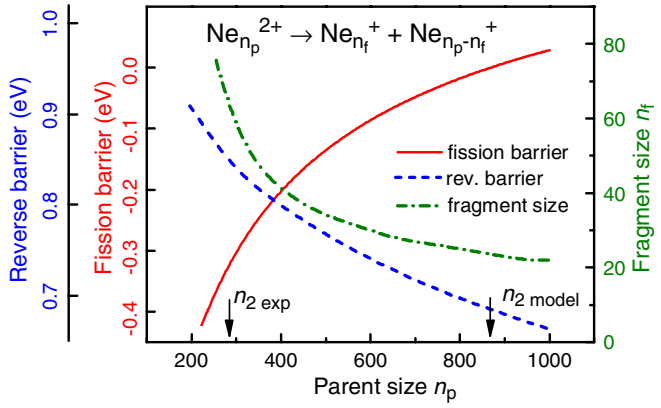

FIG. 4 (color online). Predictions calculated from the liquid-drop model [7] for Ne_n^{2+}. Left ordinate, solid and dashed lines: Height of the fission barrier and reverse fission barrier, respectively. Right ordinate, dash-dotted line: Size n_f of the (smaller) fragment ion.

However, a more refined liquid-drop model [17], and a molecular dynamics simulation of Xe_n^{2+} [19], yield nearly the same values for the critical sizes of doubly charged van der Waals clusters. The model also ignores the dynamics and thermally activated processes. The initial vibrational excitation may be quite large as a result of dimer ion formation, but most of this excess energy will be released by monomer ejection which proceeds significantly faster than fission [19,23]. Furthermore, thermally activated fission does not significantly change the critical size because the fission barrier increases rapidly with cluster size [17]. Another shortcoming of the model is the neglect of coupling of the recoiling fragments with internal (vibrational) modes. Such a coupling was reported for collision-induced fission of $(CO_2)_n^{2+}$ but it is much smaller for fissioning of Ar_n^{2+} which has fewer internal degrees of freedom (see Ref. [18] in [4]). The molecular dynamics study of Xe_{51}^{2+} [19] also indicates very inefficient coupling with intracluster modes in elemental clusters.

As pointed out by an anonymous referee, our observed critical sizes are strikingly close to those predicted by the classic Rayleigh model [3]. Using the Lennard-Jones parameters listed in Ref. [7] and ignoring the $n^{1/3}$ correction in the Tolman expression for the surface energy (a reasonable approximation for these rather large clusters), we compute critical sizes n_2 and n_3 that are less than 10% below the experiment. The agreement is surprising because a major shortcoming of the Rayleigh model for clusters that are neither metallic nor highly charged is its assumption of a continuous charge distribution. The success of the Rayleigh model for neon is, perhaps, fortuitous (the model is much less successful for the heavier rare gases), but given the failure of the seemingly more realistic liquid-drop model that incorporates discrete charges [7], outright dismissal of the Rayleigh model might be premature.

In conclusion, the critical sizes of doubly and triply charged neon cluster ions are much smaller than predicted by a liquid-drop model [7]. Furthermore, the small size and low kinetic energy of fission fragments are at variance with the model. Although the model is crude and ignores the dynamics, it has successfully explained previous experiments on atomic clusters of heavier inert gases and many molecular clusters. Furthermore, its predictions were found to agree with more refined models applied to xenon and carbon dioxide clusters [17,19]. Possible factors in the failure of the model for neon are quantum effects, and the effect of the solvation shell which will reduce the separation between the holes over the simplified estimate that places the holes on the surface of the cluster. The discrepancy for a system as "simple" as neon demonstrates the lack of a detailed understanding of the fission dynamics. Future experiments on hydrogen and helium clusters and the application of molecular dynamics simulations will be required to develop a thorough understanding of fission in the most weakly bound atomic clusters.

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