



Cite this: *Phys. Chem. Chem. Phys.*,
2016, 18, 10623

Fission of multiply charged alkali clusters in helium droplets – approaching the Rayleigh limit†

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Electron ionization of helium droplets doped with sodium, potassium or cesium results in doubly and, for cesium, triply charged cluster ions. The smallest observable doubly charged clusters are Na₉²⁺, K₁₁²⁺, and Cs₉²⁺; they are a factor two to three smaller than reported previously. The size of sodium and potassium dications approaches the Rayleigh limit n_{Ray} for which the fission barrier is calculated to vanish, *i.e.* their fissilities are close to 1. Cesium dications are even smaller than n_{Ray} , implying that their fissilities have been significantly overestimated. Triply charged cesium clusters as small as Cs₁₉³⁺ are observed; they are a factor 2.6 smaller than previously reported. Mechanisms that may be responsible for enhanced formation of clusters with high fissilities are discussed.

Received 2nd February 2016,
Accepted 16th March 2016

DOI: 10.1039/c6cp00764c

www.rsc.org/pccp

1. Introduction

The instability of highly charged droplets is a phenomenon of broad relevance that occurs on a wide range of length scales. Lord Rayleigh applied a continuum model to determine the maximum charge of macroscopic water droplets beyond which spherical droplets become unstable with respect to spontaneous deformation. This so-called Rayleigh limit occurs when the Coulomb energy exceeds twice the surface energy.¹ Charge-separation of droplets near the Rayleigh-limit is of practical relevance to electrospray sources and inkjet printing^{2,3} and it may prove to be useful to separate carbon nanotubes.⁴ The disintegration of micron-sized liquid glycol droplets at the Rayleigh limit has been imaged by Leisner and coworkers.^{5,6} Imaging by Mason *et al.* revealed that the explosive behavior of millimeter-sized alkali droplets injected into water is due to the Rayleigh instability.⁷

At the other end of the length scale one encounters fission of atomic nuclei.⁸ In between, on the mesoscopic scale, charge-driven instabilities manifest themselves in the absence of multiply charged atomic clusters A_{*n*}^{*z*+} in mass spectra below an experimental appearance size n_{exp} ,⁹ first documented by Sattler *et al.*¹⁰ Numerous reports have explored the energetics and dynamics of

cluster ions in the vicinity of n_{exp} (for reviews, see ref. 11–13). Early work was directed at determining values of n_{exp} , fission barriers, and size distributions of fission fragments with a focus on van der Waals systems.^{14–21} Later work was focused on metal clusters and the role of the electronic shell structure.^{22–26}

Initially it was assumed that clusters of size n_{exp} were near the Rayleigh limit n_{Ray} at which the fission barrier vanishes. In other words, it was believed that their fissility was near $X = 1$ where X is the ratio between the Coulomb energy and twice the surface energy.¹ A more useful relation, when dealing with atomic or molecular clusters of size n , is $X = n_{\text{Ray}}/n$.^{12,27} However, the observation of metastable fission, on the timescale of microseconds, revealed that fission near n_{exp} is thermally activated and competes with evaporation of monomers.^{15,18,21,28–30} In most experiments cluster ions are “boiling hot;” their vibrational temperatures are set by the heat of evaporation and are difficult to vary.³¹ Thus, in spite of the expected temperature dependence, experimental values of n_{exp} have been highly reproducible.³²

Given the competition between fission and evaporation, a meaningful definition of a theoretical appearance size⁹ n_a is the size at which the rate of thermally activated fission equals the rate of monomer evaporation.^{27,28} For multiply charged alkali clusters computed n_a values agree, indeed, closely with experimental appearance sizes n_{exp} ^{24,25,34} but they are much larger than values computed for the Rayleigh limit n_{Ray} . The fissility of the smallest multiply charged alkali cluster ions produced by photoionization ranges from $n_{\text{Ray}}/n_{\text{exp}} = 0.28$ to 0.38.^{12,35} Huber and coworkers demonstrated that colder cluster ions can be produced in collisions with highly charged atomic ions.⁴⁰ They attained fissilities as large as $X = 0.87$ for ten-fold charged sodium clusters but for low charge states the increase in

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† PACS numbers: 36.40.Qv, 79.77.+g, 36.40.Wa, 36.40.Qv, 34.50.Gb.



fissility over photoionization experiments was rather modest. The authors conjectured that fissilities reached in their experiment were limited by the initial cluster temperature.

Here we show that alkali clusters with fissilities approaching 1 can be identified in mass spectra if the neutral precursors are embedded in superfluid helium nanodroplets. The smallest detected doubly charged sodium clusters contain 9 atoms, a factor three less than in previous experiments;⁴¹ and for cesium dications n_{exp} is even lower than values computed for n_{Ray} .^{24,34} Furthermore, we observe triply charged cesium ions that are a factor 2.6 smaller than those reported previously by Martin and coworkers.⁴²

2. Experimental

Helium nanodroplets were produced by expanding helium (Messer, purity 99.9999%) at a stagnation pressure of 20 bar through a 5 μm nozzle, cooled to 9.5 K (sodium and potassium) or 9.1 ± 0.1 K (cesium) in a vacuum. Droplets that form in the expansion contain an average number of 10^5 to 10^6 atoms; at a temperature of 0.37 K they are superfluid.⁴³ The resulting supersonic beam traversed a pick-up cell into which sodium, potassium or cesium (Sigma Aldrich, purity 99.95% based on a trace metal analysis) was vaporized. The doped helium droplets were ionized by electrons at or below 70 eV; cations were accelerated and extracted by a pulsed voltage into a high-resolution reflectron-type time-of-flight mass spectrometer. The mass resolution (measured at full-width-at-half maximum) was 2900. Additional experimental details have been provided elsewhere.⁴⁴

Mass spectra were evaluated by means of custom-designed software.⁴⁵ The routine includes automatic fitting of mass peaks and subtraction of background; it explicitly considers isotopic patterns of all ions. The abundance of specific ions (specific value of n) is derived by a matrix method. Critical regions were also inspected visually and fitted manually in order to ensure that impurity peaks and background were properly taken into account.

3. Results

Fig. 1 displays sections of mass spectra recorded for sodium- and cesium-doped helium droplets. The abscissa has been labeled in terms of the size-to-charge ratio n/z of A_n^{z+} ($A = \text{Na}, \text{Cs}$) or, in other words, the mass/charge ratio m/z divided by the atomic mass of sodium or cesium, respectively (these elements are monoisotopic).

Fig. 1a shows sections of a spectrum of sodium-doped droplets in the vicinity of n/z values that are half-integer, *i.e.* sections where doubly charged ions containing an odd number of atoms would appear (even-numbered Na_n^{2+} cannot be identified because they coincide with singly charged cluster ions half as large). Each section covers a range of $\Delta n/z = \pm 0.01$, equivalent to $\Delta m/z = \pm 0.23$ u. The spectrum clearly establishes the occurrence of odd-numbered Na_n^{2+} for $n \geq 9$. The abundance of

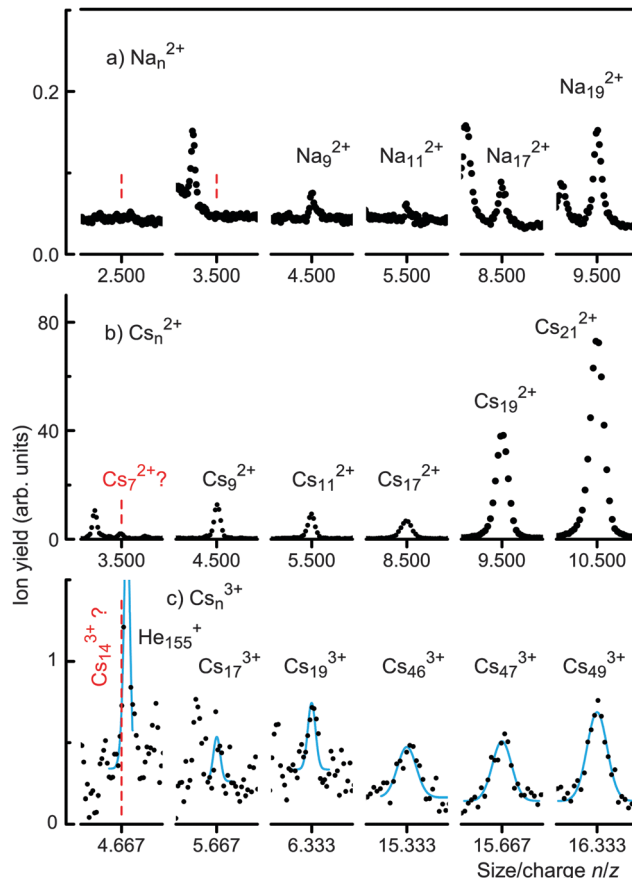


Fig. 1 Sections of mass spectra showing the appearance of Na_n^{2+} , Cs_n^{2+} , and Cs_n^{3+} (panels a–c, respectively). Each section covers a range of ± 0.01 around the expected position of multiply charged ions. The smallest cluster ions that are deemed significant are Na_9^{2+} , Cs_9^{2+} , and Cs_{19}^{3+} ; the expected positions of some smaller ions are marked by dashed lines.

Na_5^{2+} and Na_7^{2+} (marked by vertical dashed lines) is an order of magnitude weaker than that of Na_9^{2+} , and statistically not significant. The smallest dication observed by Martin and coworkers in a multi-step photoionization study using an F_2 laser (photon energy 7.9 eV) was Na_{27}^{2+} .^{41,42}

Fig. 1b shows sections of a spectrum that reveal the appearance of Cs_n^{2+} for $n \geq 9$. Each section covers a range of $\Delta n/z = \pm 0.01$, equivalent to $\Delta m/z = \pm 1.3$ u. The ion yield at the position of Cs_7^{2+} (marked by a vertical dashed line) is not statistically significant. The smallest dication observed by Martin and coworkers was Cs_{19}^{2+} .⁴²

Fig. 1c shows sections where Cs_n^{3+} ions would appear ($3n/z = \text{integer}$). Solid lines represent gaussians fitted to the data. Their positions were fixed at integer values of $3n/z$ and their fixed widths were computed from the mass resolution of the instrument. The right-most trace shows Cs_{49}^{3+} , the smallest trication identified by Martin and coworkers.⁴² Our spectra reveal trications as small as Cs_{19}^{3+} . However, their abundance is two orders of magnitude less than that of small Cs_n^{2+} shown in Fig. 1b. Establishing the existence or absence of even smaller trications is challenging though. Cs_{17}^{3+} appears as a small peak whose statistical significance is doubtful. Cs_{16}^{3+} is masked by a



strong impurity peak. Cs_{14}^{3+} would occur at $\Delta m/z = 0.178$ u to the left of He_{155}^+ as indicated by a vertical dashed line in Fig. 1c. A fit of two gaussians in this region (solid line) shows no significant contribution from Cs_{14}^{3+} .⁴⁶

We now turn to potassium which has two isotopes of significant abundance, ^{39}K (mass 38.964 u, natural abundance 93.26%) and ^{41}K (40.962 u, 6.73%). Combined with the presence of ions that result from water impurities this leads to congested spectra. Fig. 2 shows sections of a mass spectrum that reveal the presence of odd-numbered K_n^{2+} for $n \geq 11$. Each panel covers the four most abundant isotopologues containing zero to three ^{41}K ; the expected positions of these isotopologues are marked by symbols.

In Fig. 2d all four K_{19}^{2+} isotopologues are resolved. A set of four gaussians with individually chosen backgrounds was fitted to the four peaks. Positions and relative peak heights were fixed

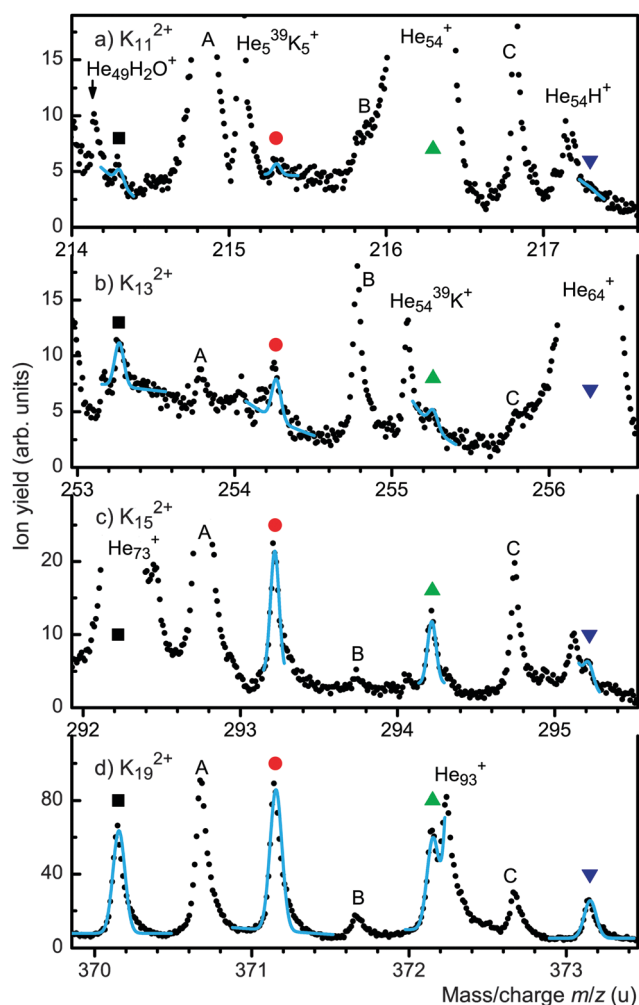


Fig. 2 Sections of mass spectra showing the presence of K_n^{2+} for $n = 11, 13, 15, 19$ (panels a to d). The expected positions of the first four isotopologues (containing $p =$ zero to three ^{41}K isotopes) are marked by full symbols. Solid lines represent the results of fitting sets of three or four gaussians; positions and relative amplitudes were fixed at the expected values. Mass peaks labeled A, B or C correspond to $\text{H}_2\text{O}^{39}\text{K}_{n-1}^{41}\text{K}^+$, $\text{OH}^{39}\text{K}_n^+$, and $\text{H}_2\text{O}^{39}\text{K}_{n-2}^{41}\text{K}_2^+$, respectively.

at the theoretical values; a common value was chosen for the width. The fit (solid cyan line) matches the experimental data very well. All other significant mass peaks in Fig. 2d are identified in the figure or its caption. Spectra covering smaller odd-numbered K_n^{2+} were analyzed similarly. Isotopologues overwhelmed by other peaks (He_m^+ , He_mK^+ or reaction products of H_2O with K_n^+) were excluded from the fit. For K_{13}^{2+} and K_{15}^{2+} three isotopologues are clearly seen in Fig. 2. The yield of K_{11}^{2+} is weak but the amplitudes of the first two isotopologues, containing zero or one ^{41}K , are non-zero with a statistical significance greater than 4σ . K_9^{2+} and K_7^{2+} could not be identified.

Even-numbered doubly charged potassium clusters can be identified for $n \geq 20$ thanks to the presence of isotopologues. Other doubly charged cluster ions that could be identified are $\text{H}_2\text{OK}_n^{2+}$ ($n \geq 16$), OHK_n^{2+} and HK_n^{2+} .

Fig. 3 summarizes our results for doubly charged cluster ions. Solid dots represent their abundances, deduced from mass spectra after correction for background, other interfering mass peaks, and, for potassium, the presence of isotopologues. Odd-numbered Na_n^{2+} and Cs_n^{2+} are observed with high statistical

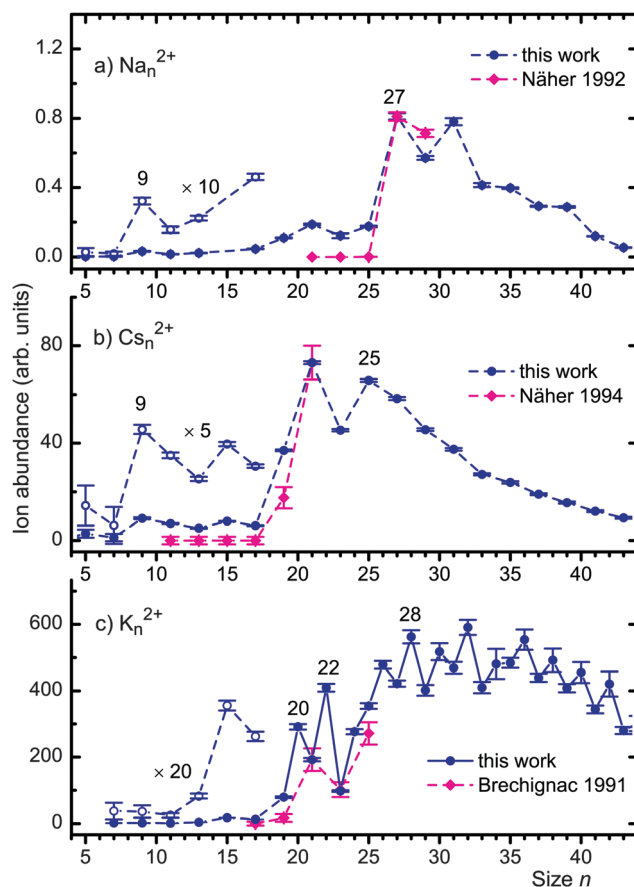


Fig. 3 Full dots: ion abundance of doubly charged Na_n^{2+} , Cs_n^{2+} and K_n^{2+} versus size n . Weak signals for small n are re-plotted with enhanced amplitude. Solid lines connect data available for even and odd n ; dashed lines connect data available for odd n only. Diamonds represent the results of photoionization studies by Näher *et al.*^{41,42} and Brechignac *et al.*²³ Their values were deduced from published mass spectra and scaled to match our values at $n = 27$ (Na) or 21 (Cs, K).



significance for $n \geq 9$; the yields of Na_5^{2+} , Na_7^{2+} and Cs_7^{2+} are zero within the error bars. Diamonds represent the results of previous experiments by Martin and coworkers who identified Na_n^{2+} for $n \geq 27$ and Cs_n^{2+} for $n \geq 19$.^{41,42} Their data and error bars were estimated from published mass spectra and scaled to match our values at $n = 27$ (Na) and 21 (Cs).

The results for potassium-doped helium droplets are summarized in Fig. 3c. Odd-numbered K_n^{2+} ions appear for $n \geq 11$, and even-numbered dications can be identified for $n \geq 20$. The smallest potassium dication reported previously, in a multiphoton ionization study by Brechignac and coworkers using a nitrogen laser (photon energy 3.67 eV), was K_{19}^{2+} .²³ Their data (estimated from a mass spectrum) are shown as diamonds. Their mass resolution was not sufficient for the identification of even-numbered K_n^{2+} .

Our results for Cs_n^{3+} are compiled in Fig. 4. The experimental appearance size is $n_{\text{exp}} = 19$ or, perhaps, 17. The abundances of the next smaller trications (C_{14}^{3+} , C_{13}^{3+} , and C_{11}^{3+}) that do not strongly interfere with other ions are all zero within the statistical error. Cs_{20}^{3+} forms a remarkably strong peak. All larger trications with non-integer values of $n/3$ are statistically significant except perhaps Cs_{26}^{3+} . Diamonds represent the results of previous experiments by Martin and coworkers who identified trications for $n \geq 49$.⁴² Their data were estimated from a mass spectrum and scaled. The difference in the size dependence of the two datasets beyond $n \approx 55$ is likely caused by differences in the size distributions of neutral precursors and the way ions are formed; the difference is not relevant for the present discussion.

Mass spectra of helium droplets doped with sodium and other alkalis produce copious amounts of alkali cations (monomers as well as dimers) complexed with helium.^{47–49} These ions are often referred to as snowballs because electrostrictive forces solidify the helium matrix that surrounds the ion. One may wonder if $\text{He}_m\text{A}_n^{2+}$ (A = sodium, potassium, cesium) dications can be detected for $n > 1$. The answer is no, but that is hardly surprising. Consider, for example, sodium. The most abundant dication is Na_{27}^{2+} . Among all possible $\text{He}_m\text{Na}_{27}^{2+}$ ions the detection threshold would be best for $\text{He}_2\text{Na}_{27}^{2+}$; the ion could be identified if its abundance were at least 5% that of Na_{27}^{2+} . To put this in perspective: the abundance of Na_n^+ with one or two helium attached is about 10% for Na^+ , 4% for Na_2^+ , but only 0.5% for Na_3^+ (relative to the corresponding bare alkali ions).

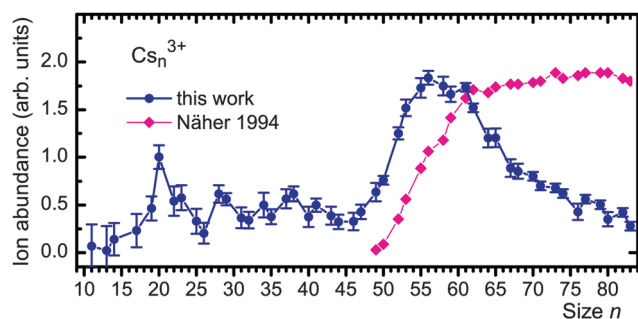


Fig. 4 Full dots: ion abundance of Cs_n^{3+} versus size n . Diamonds represent the results of photoionization studies by Näher *et al.*⁴²

We cannot safely identify any singly charged He_mNa_n^+ ions containing more than 3 sodium atoms. Furthermore, although we observe atomic Na^{2+} its abundance is low; no $\text{He}_m\text{Na}^{2+}$ ions are detected. However, the abundance of Cs^{2+} is much higher and $\text{He}_m\text{Cs}^{2+}$ ions appear at the one-percent level. The only other complexes of dications with helium reported so far (by the Meiwes-Broer group using femtosecond laser pulses^{50,51}) are Mg^{2+} , Ag^{2+} and Pb^{2+} .

4. Discussion

The main results of our experiments are

(1) Detection of Na_n^{2+} , K_n^{2+} , Cs_n^{2+} , and Cs_n^{3+} that are much smaller (by a factor 3 for Na_n^{2+}) than previously observed,

(2) Close agreement of the experimental appearance size n_{exp} , the size of the smallest observed multiply charged clusters, with the Rayleigh limit n_{Ray} , the size for which the calculated fission barrier vanishes (*i.e.* cluster ions with fissility $X = 1$).

We emphasize that observation (1) is not merely the result of enhanced detection efficiency or resolution. These factors may lower n_{exp} but hardly by more than a few percent.³² Instead, in the present work the dramatic decrease of n_{exp} results from enhanced production of small multiply charged ions. This is apparent from the distributions displayed in Fig. 3 and 4. For example, in our work the abundance ratio of $\text{Cs}_{19}^{2+}:\text{Cs}_{21}^{2+}$ is 2.4 times larger than that reported by Martin and coworkers.⁴² For $\text{K}_{19}^{2+}:\text{K}_{21}^{2+}$ our value is five times larger than the value reported by Brechignac *et al.*²³ For $\text{Na}_{25}^{2+}:\text{Na}_{27}^{2+}$ we obtain about 1:5; Martin and coworkers⁵² could not observe Na_{25}^{2+} even though the mass resolution of their instrument (20 000) was seven times better than that of our instrument. From their spectrum⁴¹ we estimate that their ratio was below 1:500.

Before discussing possible mechanisms for the enhanced production of small multiply charged cluster ions we turn to observation (2). Values of n_{Ray} and appearance sizes n_a calculated for doubly charged sodium, potassium and cesium clusters and for Cs trications are listed in Table 1 together with experimental appearance sizes n_{exp} observed in past experiments and in the present work. One notes that (i) previously reported n_{exp} values are close to n_a (about 20% lower for K and Cs, 10% higher for Na), (ii) our current n_{exp} values are close to n_{Ray} . In other words, the fissility of the smallest observed multiply charged clusters is close to 1.

Table 1 Lower size limits of multiply charged alkali clusters. n_{Ray} denotes calculated Rayleigh limits where the fission barrier vanishes (fissility $X = 1$); n_a are theoretical appearance sizes for which thermally activated fission rates equal evaporation rates. n_{exp} specifies the smallest size observed in past experiments (publ) and the present work

	n_{Ray} (theory)	n_a (theory)	n_{exp} (publ)	n_{exp} (this work)
Na_n^{2+}	$6^{a,b}, 7^c, 11^d, 12^e$	$24^e, 27^{c,d}$	$27^{f,g}$	9
K_n^{2+}	$7^{c,h}, 11^e, 12^d$	$22^c, 24^e$	19^i	11
Cs_n^{2+}	$11^e, 12^d$	$23^{d,e}$	19^g	9
Cs_n^{3+}	$19^d, 27^e$	$51^d, 57^e$	49^g	19 (or 17)

^a Ref. 53. ^b Ref. 54. ^c Ref. 25. ^d Ref. 24. ^e Ref. 34. ^f Ref. 55. ^g Ref. 42.

^h Ref. 36. ⁱ Ref. 23.



As n_{Ray} marks the size where the fission barrier vanishes one should always find $n_{\text{Ray}} < n_{\text{exp}}$. The values $n_{\text{Ray}} = 6$ or 7 calculated for Na_n^{2+} by Barnett *et al.*,⁵³ Blaise *et al.*⁵⁴ and Vieira *et al.*²⁵ are consistent with this inequality, but the values 11 or 12 computed by Li *et al.*²⁴ and Garcias *et al.*³⁴ are not. Similarly, n_{Ray} values calculated for K_n^{2+} by Brechignac *et al.*³⁶ and Vieira *et al.*²⁵ are compatible with our experimental value for n_{exp} while other calculated values are too high. In general, n_{Ray} values obtained by *ab initio* molecular dynamics simulations of K_n^{2+36} and $\text{Na}_n^{2+53,54}$ tend to be smaller, more compatible with our experimental results. For Cs_n^{2+} all calculated n_{Ray} values exceed our value $n_{\text{exp}} = 9$. For Cs_n^{3+} we observe $n_{\text{exp}} = 19$ (or perhaps 17) which is in reasonable agreement with the Rayleigh limit $n_{\text{Ray}} = 19$ deduced using a many-body potential based on local density calculations.²⁴ Another value, $n_{\text{Ray}} = 27$ calculated by applying a semi-empirical model to compute fission barriers,³⁴ is clearly too large.

Why is our experimental approach so efficient in the production of long-lived multiply charged ions near $X = 1$? There are two major differences between the present and previous studies, (i) the mechanism by which ions are formed, and (ii) the presence of the helium droplet that cools the neutral precursor to 0.37 K and may help to cool and/or cage the cluster after ionization.⁵⁶

Electron ionization of doped helium droplets involves one or more intermediate steps. If the energy of the incident electrons exceeds the ionization threshold of helium (24.59 eV), ionization proceeds primarily *via* formation of He^+ which will hop, on the timescale of femtoseconds, by resonant charge transfer.⁵⁷ He^+ may ionize the dopant, or localize by forming a vibrationally excited He_2^+ . We have measured the yield of Cs_n^{z+} ($z = 1, 2$) versus electron energy and found a stepwise onset near 21 eV. This implies that ionization proceeds by Penning ionization, involving metastable, electronically excited He^* , He_2^* , or anions.^{58,59} Moreover, neutral cesium clusters will reside on the surface of the droplet.⁶⁰ Neutral sodium and potassium clusters will reside on the surface if they contain fewer than ≈ 20 or ≈ 80 atoms, respectively.^{44,60,61} Location on the surface favors Penning ionization over ionization by He^+ .⁶¹

According to Huber and coworkers, the ability to form multiply charged clusters near $X = 1$ is mainly limited by the initial cluster temperature.⁴⁰ Our experiments involve ultracold (0.37 K) precursors but it is questionable if this is sufficient to suppress fission of nascent multiply charged clusters given that our mass spectra indicate strong fragmentation: in Fig. 3c K_{22}^{2+} stands out particularly strong. According to the spherical jellium model this ion, containing 20 valence electrons (in the configuration $1s^2 1p^6 1d^{10} 2s^2$), is particularly stable.⁶² As growth of neutral clusters in helium droplets is a statistical process, the enhanced K_{22}^{2+} abundance must be a result of ionization induced fragmentation.⁶³

Thus, we face a conundrum: evidence for fragmentation (appearance of magic numbers) and, at the same time, evidence for suppression of fission (X approaching 1). We will sketch two factors that may be relevant but more work is needed to pin down the exact mechanism. First, it is conceivable that multiply

charged cluster ions form by successive ionization, involving two or more incident electrons as observed in some of our past work.^{59,64} Penning ionization at the surface will result in an alkali cluster ion A_n^+ which will dive into the droplet and be cooled to 0.37 K. At some later time (within microseconds) another incident electron will form He^* or He^{*-} which will form A_m^{2+} ($m \leq n$) by Penning ionization. Although successive ionization of bare clusters by photons does not result in multiply charged clusters of high fissility,⁴² effective cooling and caging of singly charged cluster ions submersed in helium may be sufficient to suppress fission. Unfortunately the low ion yield of the newly observed small multiply charged cluster ions makes a systematic study of the dependence of their yield on the electron emission current all but impossible.

Second, fission proceeds on a slower timescale than monomer evaporation because the frequency of collective modes is relatively low; viscosity will further slow down the reaction.^{14,27,65} The extension of the timescale may be particularly strong for solid precursors.¹² Möller and coworkers have reported a dramatic difference in the fission pattern of solid xenon clusters as compared to liquid neon clusters for fissilities near $X = 1$.³⁷ The slower the rate of fission the larger the chance that the helium matrix can remove the excess energy and quench the reaction, provided the fissility is below 1 .

The search for long-lived multiply charged clusters with high fissilities is motivated by the expectation of new physics.^{12,37,40,55} For metal clusters one expects that fission will change from highly asymmetric (emission of trimer ions) to symmetric as X approaches 1 .^{12,26,66} Moreover, the strong effects of the electronic shell structure that govern fission of warm, liquid clusters with X well below 1 may be greatly reduced or even absent.¹² Fission of doubly charged alkali clusters is often likened to alpha decay of radioactive nuclei because of the preference for emission of trimer ions which are favored by electronic shell effects.²⁷ However, with increasing fissility and decreasing temperature the balance shifts toward more symmetric fission;^{26,66} this shift will also contribute to a slowing of the fission reaction.

5. Conclusions

Electron ionization of alkali clusters embedded in helium droplets results in doubly and triply charged clusters that are much smaller than observed previously; their fissility is approaching $X = 1$. We have discussed some factors that might enhance the yield of these small multiply charged cluster ions by suppressing rapid fission. Preparing clusters of high fissility is a first step; future experiments will have to characterize their fission reactions, for example by gentle heating with low-energy photons. Molecular dynamics simulations of multiply charged clusters embedded in helium would be helpful to unravel details.

Acknowledgements

This work was supported by the Austrian Science Fund, Wien (FWF Projects I978 and P26635).



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