

Observation of Highly Charged Sodium Clusters

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Multistep ionization of mass-selected Na_n^+ is found to yield Na_n^{z+} clusters with $2 \leq z \leq 14$. The energy required for each stage of ionization is observed to vary with cluster size in a manner well described by a classical electrostatic model.

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Photoionization in combination with time-of-flight mass spectroscopy is an efficient technique for examining the properties of clusters in the gas phase. By careful variation of the intensity and wavelength of the ionizing laser, electronic shell structure can be revealed in the mass spectrum. Thermal and optical properties and in some cases even the geometric structure of the clusters can be determined. Normally, the clusters in such experiments are only singly ionized by the laser. More highly charged clusters, if present, are usually seen as an unpleasant background for the following reason. Since a mass spectrometer does not measure the mass of a cluster, but rather the ratio of mass to charge, spectra containing multiply charged clusters will be complex. Mass peaks corresponding to multiply charged clusters will progressively fill in the interval between Na_n^+ peaks. If the

mass resolution is not sufficient to separate all this structure, a broad "fragmentation" background will form. Nevertheless, deliberate multiple ionization can be a useful tool for providing information about the stability and electronic properties of clusters. Doubly and triply ionized molecular [1-3] and metal [4-6] clusters and four-fold ionized Ge clusters [7-9] have been observed previously. These investigations were concerned mainly with the fragmentation or fission of unstable clusters [10-13]. The clusters considered in this Letter are all stable against spontaneous fission. Below we describe an experimental setup that enables us to multiply ionize clusters of selected size, analyze their charge, and determine the energy required for each stage of ionization.

The apparatus used is shown in Fig. 1. The cluster source is a low-pressure condensation cell [14]. Sodium

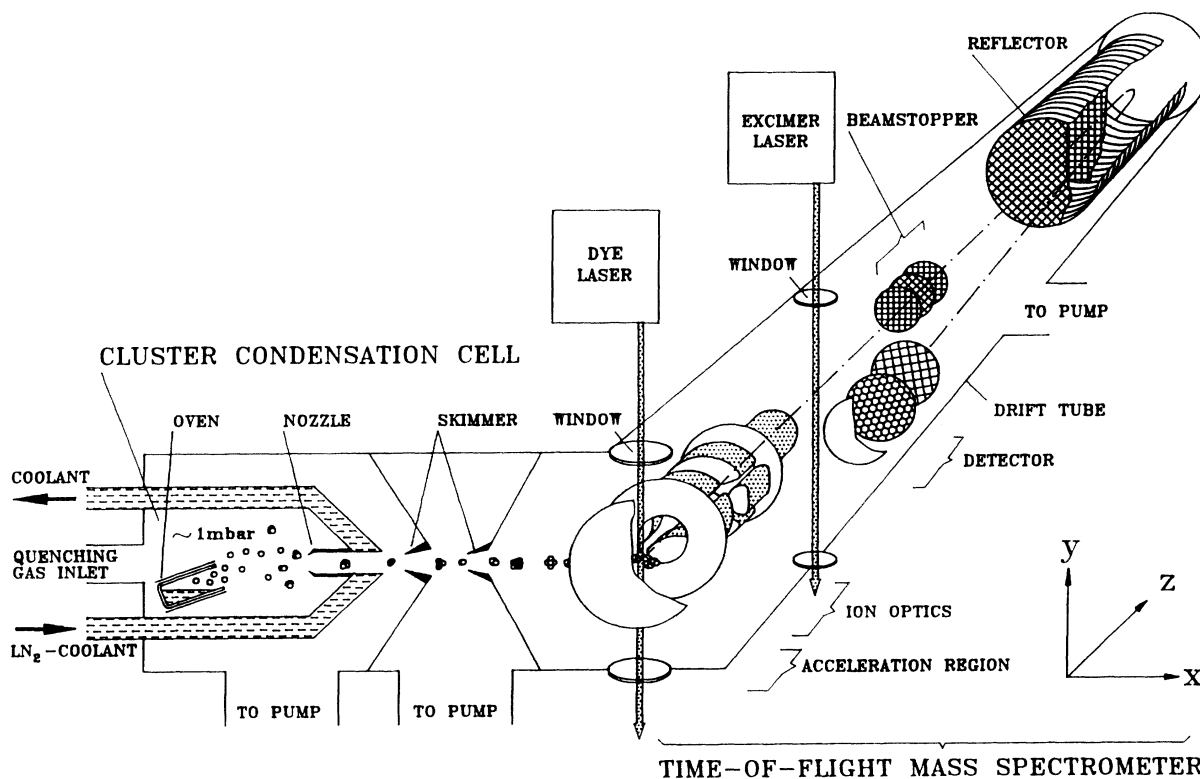


FIG. 1. Experimental setup. The neutral clusters move horizontally from the oven chamber to the ionization region where they intersect the dye laser beam at right angles. The ionized clusters are accelerated into the drift tube which is perpendicular to the neutral cluster beam. A second excimer laser beam intersects the cluster ion beam in the middle of the drift tube.

vapor is quenched in cold helium gas having a pressure of about 1 mbar. Na clusters condense out of the quenched vapor and are transported by the gas stream through two chambers of intermediate pressure into a high vacuum chamber where they are photoionized with a $50\text{-}\mu\text{J}/\text{cm}^2$, $1\times 0.5\text{-mm}^2$, 15-ns dye laser pulse at a wavelength of 400 nm. As a result of the low laser power and the low photon energy near the ionization threshold of Na clusters [15], the clusters are only singly charged by this laser. The cluster source was trimmed to produce large clusters in the range of 400 to 20000 Na atoms. For mass selection we used a high-resolution time-of-flight mass spectrometer [16]. It has a mass resolution of better than 20000 and a mass range of over 600000 amu. The ionized clusters are accelerated by a constant electric field. After being focused by quadrupole ion optics they pass into a long drift tube (~ 2 m) to a two-stage reflector. The reflected clusters are detected by a multichannel plate detector.

In the current experiment an additional excimer laser operating at various photon energies [4.0 eV (XeCl), 5.0 eV (KrF), or 6.4 eV (ArF)] is used to multiply ionize the already singly charged clusters shortly after they have entered the drift tube (Fig. 1). The beam of this laser is perpendicular to the cluster beam. Its width is about 1 mm. The photon fluence per pulse is about $100\ \mu\text{J}/\text{mm}^2$. Clusters having different masses pass the window in the drift tube at different times. Therefore, the pulse of the excimer laser hits only clusters in a narrow mass range ($\Delta m/m \sim 1/100$). This mass range can be shifted by changing the delay time between the pulses of the two lasers.

Figure 2(a) shows the time dependence of the cluster signal in the interval of $t = 1200$ to $2400\ \mu\text{s}$. The distinct depletion at $t = 2070\ \mu\text{s}$ ($n = 4600$) has been caused by the excimer laser pulse (KrF). Clusters of this size are multiply ionized. These multiply charged clusters appear in the spectrum at the peaks between $t = 1400$ and $1700\ \mu\text{s}$.

A cluster which is multiply ionized in the drift tube will arrive at the detector earlier than the corresponding singly charged cluster because of a shorter time of flight in the reflector part of the mass spectrometer. More highly charged clusters are reflected more quickly. In the drift tube the multiply charged clusters maintain their initial velocity. A detailed calculation with the specific parameters of our mass spectrometer allows the transformation of the time-dependent spectrum of Fig. 2(a) into a charge-dependent representation [Fig. 2(b)]. This definitely identifies the peaks in Fig. 2(a) as multiply charged clusters with the same mass as those missing at $t = 2070\ \mu\text{s}$. Except for the structured peak of the sixfold-charged clusters there is no sign of fragmentation or evaporation of the clusters due to heating by the laser pulse.

Notice that it appears in Fig. 2(a) that more multiply

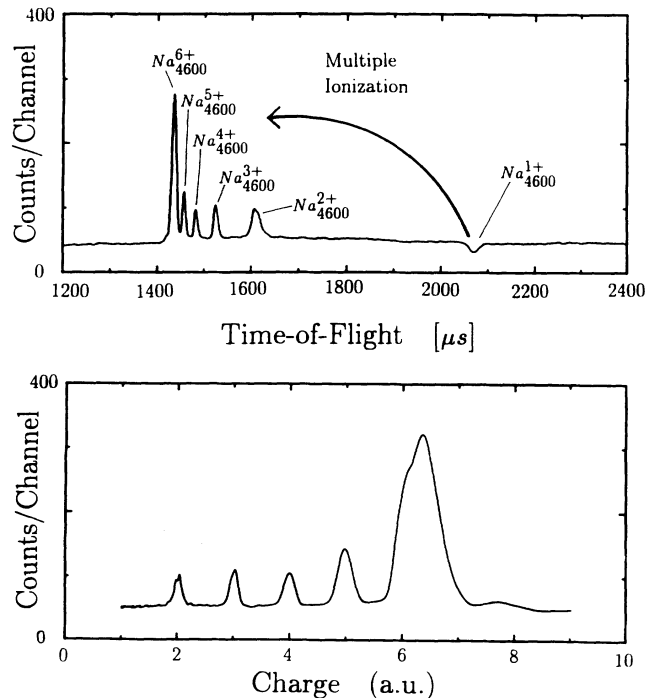


FIG. 2. Averaged mass spectrum of sodium clusters. Singly charged Na_{4600} clusters are multiply ionized by the excimer laser pulse (5.0 eV). Because of a shorter time of flight in the reflector the highly charged clusters arrive earlier at the detector. The lower picture shows the same spectrum plotted as a function of charge.

charged clusters are detected than singly charged clusters are missing at $t = 2070\ \mu\text{s}$. There is a simple explanation for this effect: Shortly before the clusters arrive at the detector, they are postaccelerated by an electric field. Here, multiply charged clusters will gain higher velocity. The higher impact energy at the detector increases their detection probability.

An additional test for the charge of the clusters can be carried out by reducing the reflector voltage U_R . The time of flight in the reflector is proportional to $(U_R q)^{1/2}$, q being the charge of the clusters. When the reflector voltage is reduced, for example by a factor of 5, a fivefold-charged peak will be shifted on the time scale to the time of flight of a singly charged cluster at the initial reflector voltage. By this method the factors by which U_R must be reduced to shift the peaks to the time of flight of singly charged clusters of the same mass ($t = 2070\ \mu\text{s}$) can be evaluated. This results in the same charges as presented in Fig. 2(b).

Figure 3 shows an ionization spectrum of sodium clusters containing about 7600 atoms. A KrF laser was used, the pulse energy varied from $10\ \mu\text{J}/\text{mm}^2$ to $200\ \mu\text{J}/\text{mm}^2$. Compared to Fig. 2 the clusters in Fig. 3 are much larger. This was achieved by increasing the time interval between the two laser pulses. The variation of the degree of ionization with increasing laser flux can be clearly seen. If

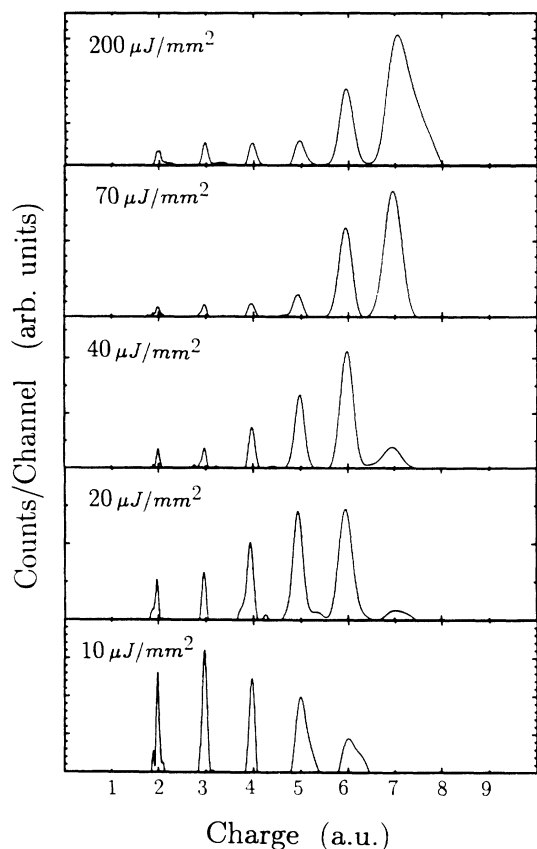


FIG. 3. Dependence of the degree of ionization on laser fluence. Na_{7600} clusters were ionized with a KrF excimer laser (5.0 eV).

we assume that the ionization cross section is the same for each ionization step, the average degree of ionization should increase linearly with the laser power. However, this appears to hold only for low laser flux. For higher laser power the degree of ionization seems to saturate at the value 7. The saturation effect can be understood in the following way. The energy required to remove an electron from a cluster increases with each successive stage of ionization. Eventually a degree of ionization is reached for which the photons used do not have enough energy to remove one more electron. Increasing the photon fluence but not the photon energy merely forces all clusters into this limiting charged state. For the cluster size and laser wavelength considered in Fig. 3 that final state is +7.

Notice in Fig. 3 that for high laser fluence the peak corresponding to the last stage of ionization broadens. We believe this is an indication that the cluster is beginning to heat up and to evaporate atoms. Apparently, the cross sections for lower degrees of ionization are much larger than that for absorption. Only in the last stage of ionization does the ionization cross section drop sharply allowing the absorption channel to dominate. A similar behavior can be seen in Fig. 2. The broadening of the

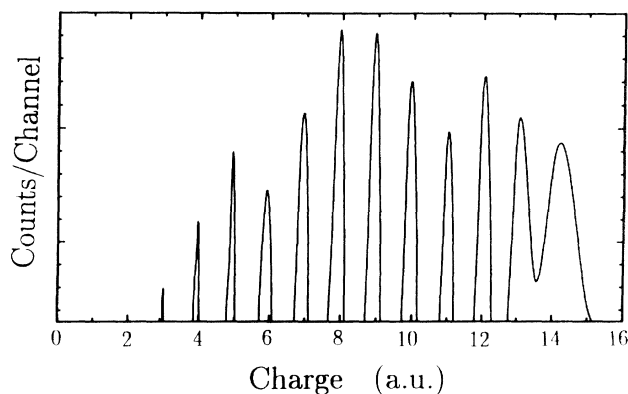


FIG. 4. Multiply charged Na_{16000} clusters were produced with an ArF excimer laser (6.4 eV).

peak that corresponds to the highest degree of ionization is a clear indication that the threshold energy for further ionization has passed beyond the laser photon energy. That is, the next ionization step would require photon energies of more than 5 eV. Nevertheless, the maximum degree of ionization for Na_{7600} (Fig. 3) is higher than that for Na_{4600} (Fig. 2). This is an indication that the threshold for multiple ionization is a function of cluster size. Figure 4 shows the multiple ionization of very large clusters ($n=16000$). Up to fourteenfold positively charged clusters can be observed. An ArF excimer laser was used to obtain this spectrum. We measured the maximum degree of ionization z_{max} as a function of cluster size for different photon energies (4.0, 5.0, and 6.4 eV). Figure 5 shows the results. z_{max} is plotted versus the number of atoms on a $\sqrt[3]{n}$ scale. The maximum charge obviously increases with cluster size. Higher photon energies shift the threshold to more highly charged clusters. The dashed lines in Fig. 5 correspond to a simple electrostatic model which is discussed in the following paragraph.

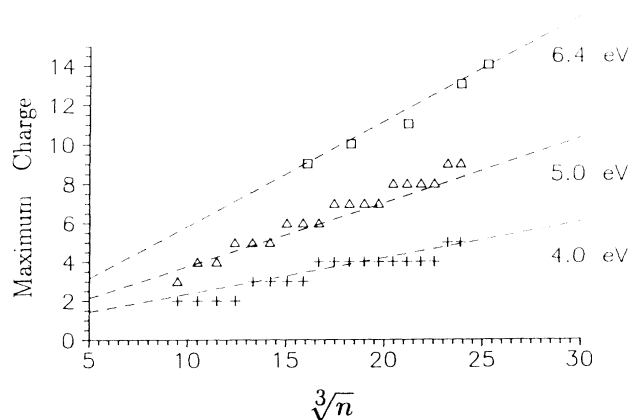


FIG. 5. Maximum charge as a function of cluster size for different photon energies. The dashed lines correspond to a classical electrostatic model for the ionization threshold.

In this model we assume that the energy necessary for the multiple-ionization process $\text{Na}_n^{+z} \rightarrow \text{Na}_n^{+(z+1)}$ can be split into the bulk work function of sodium W_B and an electrostatic term which considers the limited size of the cluster [17,18]. The bulk work function of polycrystalline sodium is 2.75 eV [19]. The electrostatic term can be well approximated by means of the self-energy of a charged conducting sphere, $q^2/2R$ [20]. Accordingly, in the classical limit the first ionization energy of a sodium cluster can be written [21]

$$I_1 = W_B + e^2/2R, \quad R = r_s n^{1/3}, \quad (1)$$

where r_s is the Wigner-Seitz radius. For the subsequent ionization steps the difference of the self-energies before and after the ionization step must be regarded. This yields

$$I_z = W_B + \frac{z^2 e^2}{2R} - \frac{(z-1)^2 e^2}{2R} = W_B + \frac{(2z-1)e^2}{2R}. \quad (2)$$

With $r_s = 2.08 \text{ \AA}$ for sodium [22] and $I_{z \max} \approx h\nu_{\text{laser}}$ it follows that

$$z_{\max} = \frac{1}{2} + \frac{h\nu[\text{eV}] - 2.75}{6.92} n^{1/3}. \quad (3)$$

The approximation $I_{z \max} \approx h\nu_{\text{laser}}$ corresponds to the assumption that the multiple-ionization process is limited by the photon energy of the laser. Figure 5 shows that this relation for $h\nu = 4.0, 5.0,$ and 6.4 eV is in good agreement with our experimental results. It is worth emphasizing that this purely classical model contains no fitting parameters.

We expect that future investigations using this newly expanded degree of freedom, the total charge, will lead to a better understanding of the electronic properties and spontaneous fission in metal clusters.

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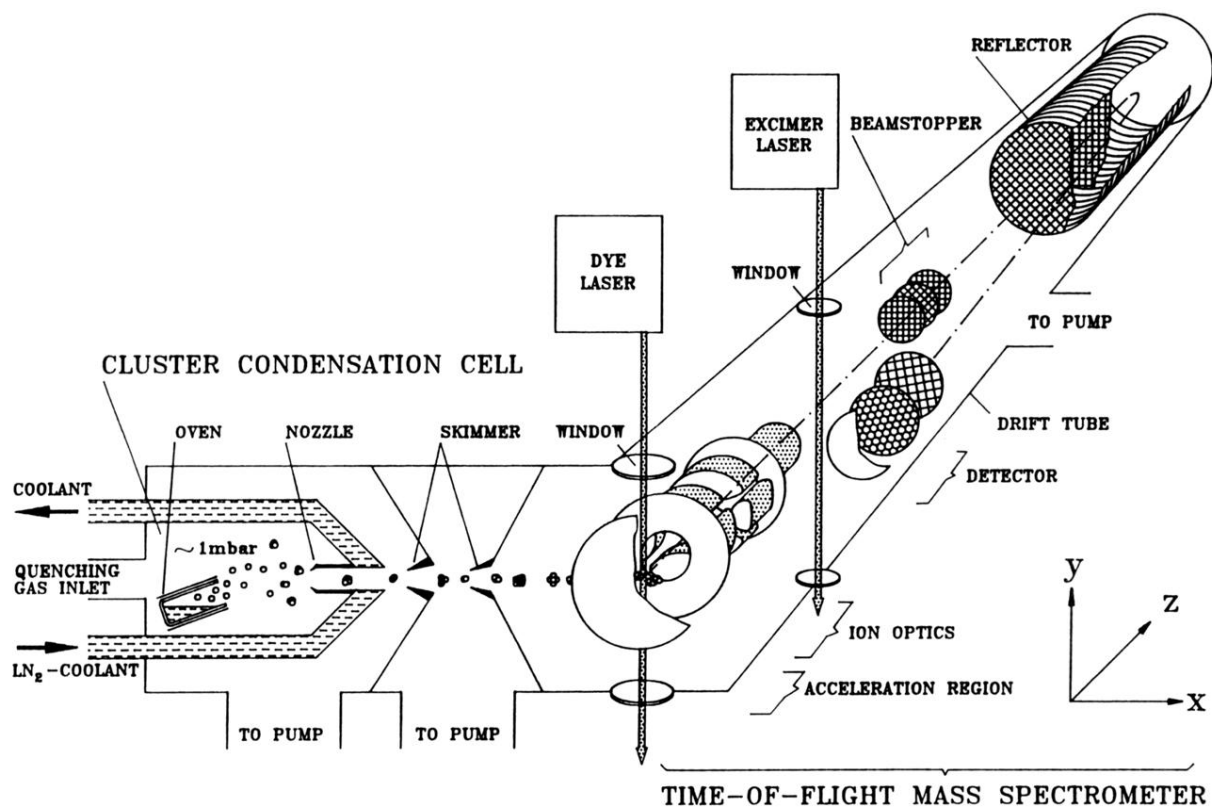


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