

Growing ultracold sodium clusters by using helium nanodroplets

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Abstract

The aggressive doping of helium droplets ($\sim 10^5$ atoms) with sodium vapor results in the growth of sodium clusters having up to at least 13 atoms, as determined by a Penning ionization technique. Signatures of electronic shell effects are observed in Na_k^+ cluster ions, including an odd–even intensity oscillation and an enhanced Na_7^+ peak, which is a magic number effect. The size distributions are consistent with cluster ion fragmentation rather than simply sequential pickup statistics. The dependence of ion yield on mean ionizing electron energy suggests that neutral alkali clusters are located preferentially on the droplet surfaces. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Alkali clusters have served as prototypes in a number of experimental and theoretical studies whose common goal has been a deep understanding of confined quantum systems. Much effort has been devoted to understanding the electronic structure of these clusters, including single-particle and collective states, their interactions, and their correlation with the ionic structure [1–4]. Pursuant to this, spectroscopic studies of electronic transitions have been carried out at low temperatures [5], where it is reasonable to expect that the physics is not obscured by averaging over

thermal ensembles. Unfortunately, however, spectra of medium-sized Na clusters are still broadened by thermal effects, even at the lowest reported temperatures, i.e., Na_k ($k \leq 15$) at 35 K [6]. Though yet lower temperatures can be achieved by deposition on cold substrates, the spectra of such matrix-deposited clusters are shifted and broadened inhomogeneously, thus compromising their utility.

Spectroscopic studies can now be carried out by using ultracold (0.4 K) superfluid ^4He droplets (hereafter referred to as He_n) whose average number of atoms, $\langle n \rangle$, can be varied from several hundred to several million [7]. These serve as inert, individual matrices for carrying out detailed studies. The use of high He_n fluxes, together with the pickup method for capturing gaseous molecules (according to a Poisson distribution), enables

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good experimental sensitivity to be achieved with well-characterized samples, while avoiding the condensation that occurs in bulk liquid helium.

The He_n pickup technique has been used to examine a number of metal clusters embedded in He_n , e.g., Ag_{1-150} [8,9], In_{1-10} [8], and Mg_{1-80} [10]. With alkalis, however, it has been shown that helium does not wet bulk surfaces of the heavy alkalis because of Pauli repulsion between its *s* electrons and those of the metal [11,12]. Likewise, alkali atoms are known to bind weakly to He_n surfaces in dimple-like sites with binding energies of 1.6–1.9 meV [13].

In a series of thorough spectroscopic studies, Na, Na_2 , and Na_3 residing on He_n surfaces have been examined [14–19]. It has been discovered that high-spin states (i.e., Na_2 triplets and Na_3 quartets) are produced efficiently by using the pickup process, with these states remaining intact on He_n surfaces for long times. The efficient preparation of high-spin states of Na_2 and Na_3 on He_n is consistent with their modest binding energies relative to free atoms, i.e., 20 and 100 meV, respectively [18]. Namely, such amounts of energy can be dissipated readily by the evaporation of only 12 and 60 He atoms, respectively. It is noteworthy that the Na_2 and Na_3 ground states are significantly less populated than the high-spin states (e.g., by up to three orders of magnitude in the case of Na_2) [18]. This is consistent with facile sodium desorption from the cluster due to the energy that is released upon forming the Na_2 and Na_3 ground electronic states. For larger clusters, it is unrealistic to expect a comparable degree of

stability for high-spin states [20], in which case the syntheses of such clusters will require dissipation of the ground state binding energy, i.e., 0.7–1 eV per atom [21,22].

Until now, the only alkalis that have been identified on He_n are Li_{1-2} [23], Na_{1-3} [14–19], and K_{1-6} [24]. This Letter reports the first observations of medium-sized Na clusters (i.e., up to 13 atoms) grown by using the He_n pickup technique.

2. Experiment

Molecular beams containing He_n are prepared by using low-temperature expansion into vacuum [7,25], as indicated in Fig. 1. Briefly, ultra-high-purity helium at 20–40 bar passes through a $5 \pm 1 \mu\text{m}$ diameter orifice whose temperature is controlled in the range 10–16 K by using a closed-cycle refrigerator. This enables droplets containing up to $\sim 5 \times 10^5$ atoms (corresponding to geometrical cross-sections up to $\sim 10^{-11} \text{cm}^2$) to be produced in supercritical expansions [26].

The molecular beam is formed by using a 0.4 mm diameter skimmer. It enters the pickup chamber (background pressure $\sim 10^{-7}$ mbar) where it is chopped, and passes through a resistively-heated copper pickup cell containing sodium. Temperatures up to 500 K yield sodium vapor densities up to 10^{13}cm^{-3} . The effective scattering length through the pickup cell is $3.8 \pm 0.2 \text{cm}$; the uncertainty is due to the vapor flow conditions at the entrance and exit apertures.

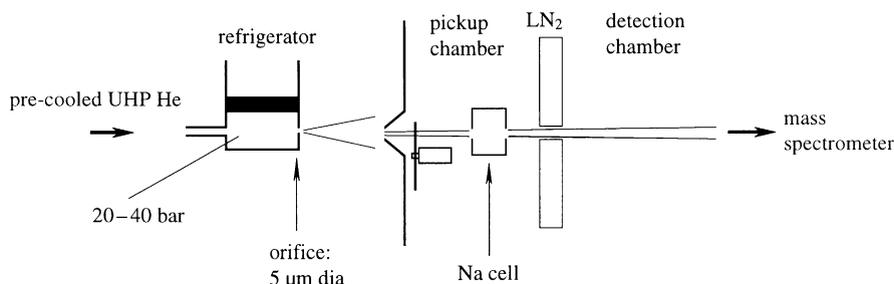
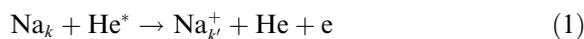


Fig. 1. Schematic of the experimental arrangement. A supersonic nanodroplet beam is formed by expanding helium gas from a nozzle. The central part of the expansion enters the pickup chamber where it is chopped, and passed through a heated cell containing sodium vapor. In the detection chamber, cluster ions are prepared by using electron impact and mass selected by using a quadrupole.

After traversing the pickup cell, the beam passes through a 5 mm aperture in an LN₂ trap and enters the detection chamber (background pressure $\sim 6 \times 10^{-8}$ mbar), which contains a quadrupole mass spectrometer (UTI 100C) equipped with an electron impact ionizer and a conversion dynode electron multiplier detector. The distance between the pickup cell and the mass analyzer is 60 cm (corresponding to a flight time of approximately 2 ms), which enables sodium that is desorbed from the droplet to leave the beam path. The mass spectrometer output is sent to a lock-in amplifier synchronized with the beam chopper. The mass spectrometer is set to high throughput and correspondingly reduced resolution. Its 300 amu range limits sodium cluster ions to those containing ≤ 13 atoms; doubly charged species were not detected.

With alkalis, even at high pickup cell temperatures, the metal cluster ion signals are typically much smaller than the He_{*n*} fragment ion peaks. It is therefore desirable to introduce a scheme that minimizes the helium ion signals while maintaining efficient ionization of the sodium. Thus, use has been made of Penning ionization. For He_{*n*} mass spectrometry, this method has been pioneered in [27], and it has been applied to the detection of small lithium complexes [23]. The mean electron energy is set between the He ionization threshold (24.6 eV) and the energy of the 2³S state (He*) at 19.8 eV. As a result, the helium ion background is reduced drastically and the relatively low ionization potential (IP) dopants that are ionized by He* dominate the mass spectrum. For example, the IPs of sodium clusters are 4–5 eV, and the large energy release upon ionization results in the (essentially) complete loss of helium from the sodium cluster ions. Though the overall ionization efficiency in the Penning regime is lower than near the peak of the electron impact ionization curve (~ 60 eV), the signal to noise ratio (*S/N*) is larger.

As the mean electron energy is increased, there is competition between Penning ionization



and charge exchange



where it is understood that all $k' \leq k$ and $k'' \leq k$ must be taken into consideration. Eqs. (1) and (2) are highly schematic, i.e., fragmentation pathways can be complicated, and He* and He⁺ refer to the condensed phase counterparts of the excited and ionized atomic states, respectively. As discussed below, the variation of the ion yield with mean electron energy provides evidence concerning the location of the dopant at the time of ionization, i.e., on the surface versus inside. For dopant mass spectra, it was convenient to use 25–30 eV, where the alkali signals were intense.

3. Results

Fig. 2 shows cluster mass spectra obtained by using Penning ionization and pickup cell temperatures of 438 and 478 K, corresponding to metal vapor densities of 4×10^{11} and 4×10^{12} cm⁻³, respectively. For a density of 4×10^{12} cm⁻³, a droplet containing 10^5 helium atoms encounters

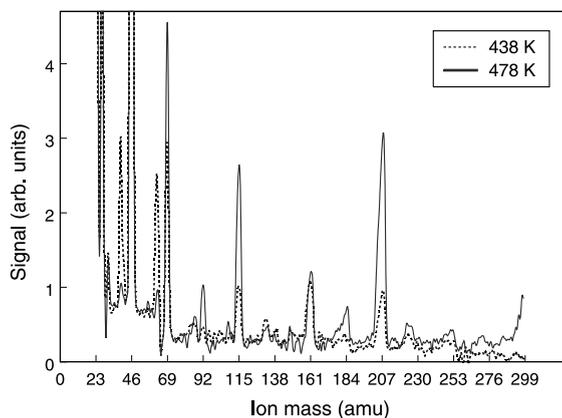


Fig. 2. Mass spectrum acquired near the ionization maximum for alkali species (mean electron ionization energy of 28.1 eV) for two different pickup cell temperatures. The spectrum shows prominent Na_{*k*}⁺ peaks (sodium mass is 23 amu; slight shifts at the high end of the mass spectrum are due to calibration imperfections of the quadrupole). The spectrum shows and odd-even oscillation rather than sequential pick-up statistics. The nozzle temperature was approximately 11 K and the gas pressure 40 bar. The sodium atom and dimer peaks are off-scale (their intensities exceed that of the trimer by factors of 13 and 9, respectively, at 478 K and by twice these amounts at 438 K). The peaks at 39 and 62 amu are NaO⁺ and Na₂O⁺.

on average up to ~ 200 sodium atoms in traversing the pickup cell. This estimate takes into account the shrinkage of the He_n droplet caused by dissipation of the incident translational energies of the picked up sodium atoms, as well as the sodium-cluster binding energies. A similar situation has been reported for small CsI clusters inside medium-sized argon clusters [28]. Such conditions will be referred to hereafter as *aggressive doping*.

It is likely that impinging sodium atoms penetrate the clusters upon impact. Therefore, it is interesting to consider the extent to which embedded atoms assemble into clusters while within the He_n . Such a growth mechanism would circumvent a size limitation in which clusters growing on the surface are expelled by the energy released in forming ground state clusters.

Fig. 3 shows an odd–even oscillation in the intensities of the metal ion peaks. Such oscillations are well known in mass spectra of metal clusters. They reflect the higher stabilities of even-electron systems, as explained, for example, by the electronic shell model [1,29]. In this regard, note the peak at Na_9^+ , which is higher than the peaks adjacent to it

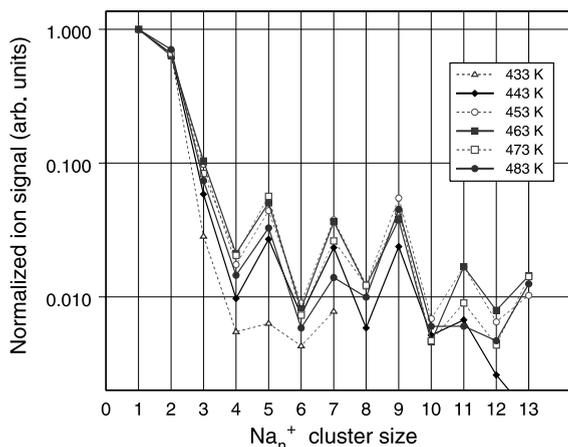


Fig. 3. The odd–even oscillation, plotted here as ratios of sodium cluster ion peak intensities, remains stable over a wide range of cell vapor pressures. The atom and dimer ions are the most abundant, and their intensity ratio does not vary with the cell temperature. This implies that Na^+ and Na_2^+ derive primarily from ionization-induced fragmentation of larger clusters. At a cell temperature of 448 K the Na_{13}^+ cluster starts to appear.

due to the strong binding of the closed-shell eight electron system. A similar odd–even pattern has been seen in silver clusters in He_n [8,9], and has been cited as evidence for considerable fragmentation accompanying ionization by 70 eV electrons. The data presented in Fig. 3 suggest that Penning ionization also causes significant fragmentation. Namely, at high sodium vapor concentrations, the monomer and dimer ion peaks dominate and maintain a monomer-to-dimer ratio of 0.67. This is consistent with Na^+ and Na_2^+ deriving from ionization-induced fragmentation, because it is known that sodium cluster ions fragment primarily by expelling monomers and dimers [21,30,31].

The odd–even oscillation cannot be attributed solely to the pickup process, which yields a Poisson distribution [32]

$$P(k, T) = \frac{(\sigma N L F)^k}{k!} e^{-\sigma N L F}, \quad (3)$$

where k is the number of picked up atoms, σ is the capture cross-section, N is the sodium atom vapor density, L is the path length, and F accounts for the thermal velocity of the sodium atoms. Values of F are usually in the range 1–2; they are tabulated in [33]. Eq. (3) predicts a smooth variation with k , which differs qualitatively from the observed oscillation.

In addition to this difference, ratios of $P(k, T)$ values for either even or odd k values given by Eq. (3) are inconsistent with the data. For example, for the neutral trimer and pentamer, Eq. (3) predicts

$$\frac{P(3, T)}{P(5, T)} = \frac{20}{[\sigma N(T) L F]^2}. \quad (4)$$

Because $N(T)$ depends exponentially on temperature, the ratio given by Eq. (4) has an exponential temperature dependence. The experimental value, however, is 2.1 ± 0.5 for all temperatures above 438 K. The fact that the presence of the tetramer ion has not been reported previously might be due, at least in part, to its mass being close to that of He_{23}^+ and its intensity suppressed by the odd–even effect.

The fact that the Na_{13}^+ signal is larger than the Na_{11}^+ signal at cell temperatures of 473 and 483 K (Fig. 3) suggests the likely presence of cluster ions larger than Na_{13}^+ . The mass spectra also reveal

Na_kHe_n^+ , $\text{Na}_k\text{H}_2\text{O}^+$, Na_kOH^+ , and Na_kO^+ . The last three derive from background water vapor. Though sodium is hydrophilic, these peaks are weak, indicating that water molecules are not serving as condensation centers that stabilize the sodium clusters.

As discussed in [23], the variation of ionization yield with mean electron energy provides a diagnostic for the location of the dopant in/on the He_n . As shown in Fig. 4, both thresholds and shapes (including maxima at ~ 30 eV) of the yield curves of pure sodium species reflect a strong contribution from Penning ionization. Note that since Na^+ and Na_2^+ signals primarily derive from larger particles (see above), their ionization behavior reflects that of all the sodium clusters investigated here. For instance, Fig. 4 also includes the examples of Na_5^+ and Na_7^+ , which are seen to behave similarly. On the other hand, the thresholds and shapes (monotonically increasing) of the yield curves of He_2^+ , He_6^+ , and NaI^+ (studied in a separate experiment) are quite different and are consistent with the charge exchange mechanism.

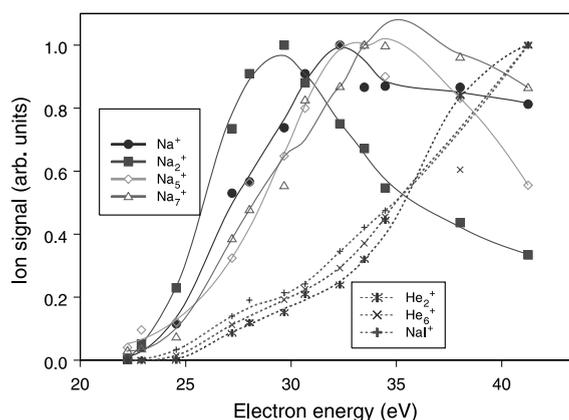


Fig. 4. Ion yield curves of dopant ions and He_2^+ and He_6^+ fragments as a function of mean electron energy. The instrument scale of the electron ionizer has been corrected for calibration shifts by setting the helium dimer threshold close to that of the free atom, 24.6 eV. The line shapes and appearance thresholds for pure alkali species are markedly different from those of the embedded NaI molecule and of helium fragments. This shows that Penning ionization contributes significantly to the production of sodium cluster ions, and implies that they are located at the droplet surfaces.

A He^+ hole migrates quickly ($\sim 10^{-10}$ s) to the center of the droplet [27,34], whereas He^* is surrounded by a bubble and prefers the surface. Therefore the Penning channel might be more effective for dopants that reside on the surface. Based on the ionization behavior of the alkali clusters observed here, we conclude that they are located at the droplet surface.

Finally, we note that because bulk sodium surfaces are wetted by liquid helium [12], there should be a critical cluster size for which the attraction between the helium and the highly polarizable metal cluster overcomes their Pauli repulsion and ‘sinks’ the cluster [35].

4. Conclusions

The efficient production of alkali clusters having at least 13 atoms, and probably more, has been demonstrated by using the He_n pickup technique. The cluster ion abundances in the measured mass spectra display an odd–even oscillation, an electronic shell closing edge, and evidence of fragmentation. Detection is facilitated by using a Penning ionization method that is sensitive to low-IP dopants. Though more gentle than charge exchange, Penning ionization nonetheless results in significant fragmentation of the sodium cluster ions. Ionization yield curves suggest that the alkali clusters are probably located on the He_n surfaces. Obvious experimental extensions include increasing the mass spectrometer range, alternate ionization methods, other alkalis, spectroscopic studies, and the use of ‘seed’ dopants to promote metal cluster growth.

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