

## Formation and Stability of High-Spin Alkali Clusters

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Helium nanodroplet isolation has been applied to agglomerate alkali clusters at temperatures of 380 mK. The very weak binding to the surface of the droplets allows a selection of only weakly bound, high-spin states. Here we show that larger clusters of alkali atoms in high-spin states can be formed. The lack of strong bonds from pairing electrons makes these systems nonmetallic, van der Waals-like complexes of metal atoms. We find that sodium and potassium readily form such clusters containing up to 25 atoms. In contrast, this process is suppressed for rubidium and cesium. Apparently, for these heavy alkalis, larger high-spin aggregates are not stable and depolarize spontaneously upon cluster formation.

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The binding properties of nanostructured materials play a key role both for understanding the electronic nature of size-limited systems and for designing novel devices having specific electronic characteristics [1]. Clusters of metals have been established as excellent objects for studying the transition from molecular electronic properties towards metallic bulk material [2,3]. Still an important issue is the understanding of the size dependence of metallic properties from microscopic or atomic interaction mechanisms. So far, to our knowledge only for two elements (Mg, Hg) cluster sizes  $n$  have been associated with a metal transition: By following the band gap closure with increasing size, photoelectron spectroscopic studies revealed  $n \approx 18, 400$  for Mg [4], Hg [5], respectively. On the other hand, clusters of alkalis are ideal candidates for this type of study as far as electronic conductance is concerned with the high degree of delocalization of the valence electrons even for clusters containing only a few atoms [6]. Hence, giant resonances of collective excitations (plasmons) appear, allowing one to characterize electronic structures. Although there has been an ongoing controversy about the interpretation of the collective excitations in these size-limited aggregates, experimental studies at lower temperatures (down to 35 K) have pointed out the importance of thermal excitations and in this way partially resolved contradicting viewpoints [7]. Finally, alkalis are, in particular, interesting, since there have been many theoretical studies on their structural as well as electronic properties of clusters [8,9].

During the last decade helium nanodroplet isolation (HENDI) has been established as a new tool for preparation and study of molecules, clusters, and weakly bound complexes in a very gentle environment at temperatures of 380 mK [10,11]. The droplets are an ideal laboratory for studying the electronic properties of aggregates of metal atoms. The formation and study of small alkali clusters in this temperature range can clearly eliminate

temperature-related effects and provide new insight into the nature and, e.g., lifetimes of collective resonances.

In our experiments, helium droplets condense in a supersonic expansion of high-pressure helium ( $P_0 = 50$  bars) from a cold ( $T = 20$  K) nozzle into vacuum, forming a beam of droplets, each containing about 5000 He atoms on average. We exploit HENDI to consecutively collect alkali atoms from atomic alkali vapor. When forcing an alkali atom into liquid helium, the repulsive interaction of helium with the wide distribution of the alkali valence electron results in the formation of a bubble (low density helium environment) [12,13]. As a consequence, alkali atoms do not submerge in helium droplets and instead reside, very weakly bound, at the surface [14,15]. Since the pair interaction between an alkali and a helium atom is among the weakest in nature (potential well depth  $< 1$  cm<sup>-1</sup>), the resulting binding energy to the surface of a helium droplet only adds up to  $\approx 15$  cm<sup>-1</sup> ( $= 1.9$  meV) [15]. This very weak binding to the surface is the key to a special selection mechanism when forming molecules and clusters using this method: A helium droplet is an excellent heat bath at 380 mK. A large input of energy, e.g., the chemical binding energy set free upon molecule or cluster formation appears as local heat to be dissipated by massive evaporation of helium atoms, also boiling off the attached complex. In this way, only weakly bound complexes survive in the beam.

Alkalis can form weakly bound, van der Waals-like molecules and clusters in which all the spins of the binding valence electrons are in the same spin state. The much more stable chemically bound complexes which one usually observes, however, gain their large binding energy from pairing electrons in the same orbital state with different spin orientations (see Table I). We already learned from spectroscopic identification that dimers in the spin-polarized triplet state formed on helium droplets outnumber the singlets by up to a factor of 10 000 because of their lower binding energy [22]. Moreover, in several

TABLE I. Comparison of the binding energies given in wave numbers ( $\text{cm}^{-1}$ ) of alkali dimers and larger sodium clusters in different spin states.

	Unpolarized	Completely polarized	Reference
$\text{Li}_2$	8523	317	[16]
$\text{Na}_2$	5892	174	[17]
$\text{K}_2$	4289	254	[18]
$\text{Rb}_2$	3875	250	[19]
$\text{Cs}_2$	3629	267	[19]
$\text{Na}_3$	8200	850	[20]
$\text{Na}_4$	14 259	2903	[21], [9]
$\text{Na}_5$	19 033	3428	[21], [9]
$\text{Na}_6$	26 566	4233	[21], [9]

studies probing alkali trimers, only the high-spin van der Waals molecules have been found so far. This already demonstrates that the selection mechanism for the formation of alkali clusters on the surface of helium droplets is very efficient. Apparently the existence of only one electron pair reduces the abundance of finding such a molecule in the beam by several orders of magnitudes. As a consequence, only species having all the valence electrons in the same spin state are expected to survive with sufficient probability. Furthermore, the heat capacity of the droplet must be sufficient to dissipate both the translational energy and the binding energy upon cluster formation: The total energy a droplet of mean size can dissipate is about 3 eV. This means that the formation of a  $\text{K}_6$  cluster bound by unpolarized electrons already completely evaporates such a droplet [23]. Vongehr *et al.* probed the formation of sodium-doped helium droplets by electron impact ionization [25] and developed a statistical model to look at the formation probabilities [26]. This model predicts that the growth of high-spin states could be probed by measuring abundances of specific cluster sizes varying the vapor pressure in the pickup cell. Experiments selecting clusters by spectroscopic means seem to confirm such a behavior [27].

In the experiments reported here, femtosecond photoionization of alkali-doped helium droplets is used to study cluster formation by sequential pickup. Pulses (100 fs FWHM) from a titanium:sapphire laser, intersecting perpendicularly, ionize the dopants, which are extracted and analyzed in a quadrupole mass filter. Depending on preparation conditions, cluster sizes containing up to 25 atoms have been observed for sodium and potassium (see Fig. 1). One finds an alternating intensity distribution with pronounced maxima at certain cluster sizes which does not show the abundance upon formation but already reflects the fragmentation upon the laser ionization discussed below. Upon formation the number of picked-up alkali atoms per helium droplet is expected to have a smooth distribution. After laser ionization we observe an alternating ion intensity (Fig. 1) with pronounced maxima at, e.g.,  $\text{K}_5^+$  and  $\text{K}_9^+$ , reflecting the stability of *ionized* alkali clusters resulting from

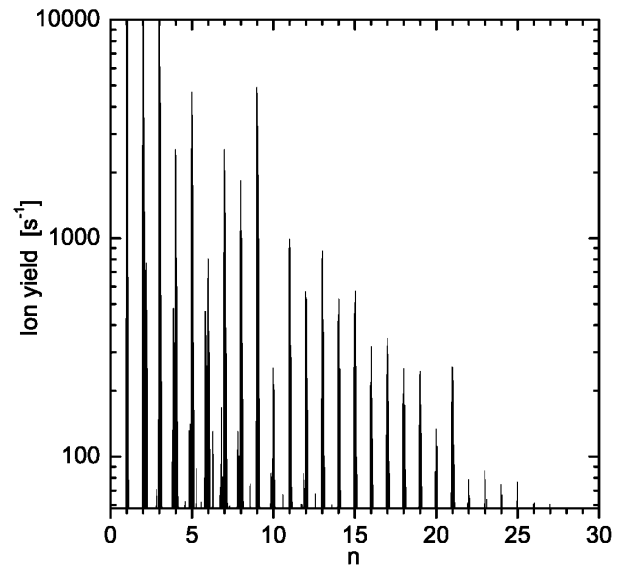


FIG. 1. Mass spectrum of potassium doped helium nano-droplets upon femtosecond photoionization and mass selection in a quadrupole analyzer. The alternating ion intensity, with pronounced maxima at  $\text{K}_5^+$ ,  $\text{K}_9^+$ , and  $\text{K}_{21}^+$ , reflects the stability of ionized potassium clusters. Upon photoionization of the high-spin state the cluster collapses and about 0.5 eV binding energy per potassium atom is released resulting in massive fragmentation of the ionized cluster.

electronic shell closures [6]. This means fragmentation occurs upon photoionization. In general, the required fragmentation energy during the ionization process can stem from the injected excess energy (e.g., electron impact ionization or photoionization employing either high-power or high-photon-energy lasers). In our experiment the thermal energy at 380 mK as well as heating by successive absorption of laser photons, known from nanosecond laser excitation, does not contribute significantly. Furthermore, having rather low laser power density ( $2.6 \text{ MW/cm}^2$ ) and a well-defined fs-3-photon ionization process, fragmentation does not occur when ionizing metallic alkali clusters because of the missing thermal activation in our experiments [28]. A further mechanism supplying energy arises from the enhanced binding of helium atoms to the charged dopants. The helium environment around alkali monomer ions has been calculated to form a quite dense and partially well ordered shell [29]. Estimating the amount of extra binding energy of a  $\text{K}^+$  by assuming that all helium atoms in the first shell contribute the  $\text{K}^+\text{He}$  pair binding energy gives only about 0.25 eV. In contrast, upon photoionization of high-spin clusters, spin flips are induced and chemically bound clusters are formed. The released binding energy ( $\approx 0.5$  eV of energy per spin flip) can heat the alkali clusters which eventually fragment (cf. the model in [26]). Following the high-spin growth model [26], one expects the distribution of cluster sizes  $n$  to fall off approximately like  $(n+1)/2^n$  instead of having Poissonian size distributions, the maximum of which would be determined by

the mean number of collisions. The measured mass spectrum (Fig. 1) does not follow the exponential decrease of the model but levels off substantially slower. This might be seen as an argument against a high-spin scenario. On the other hand, although using elevated pickup intensities, the distribution does not evolve a maximum. Of course, fragmentation and the available cluster sizes might suppress the larger sizes. However, for a rigorous comparison a better knowledge of the fragmentation rates is necessary.

We extended our studies by probing cluster formation of the heavier alkalis. Figure 2 gives the mass distributions comparing Na, K, Rb, and Cs. Since sodium and potassium clusters are readily observed in sizes up to  $n = 25$ , there appears to be an upper limit of cluster size for the heavier alkalis ( $n = 5$ ,  $n = 3$  for Rb, Cs, respectively). This is another surprising result because for these alkalis one might expect even larger clusters to be formed: On one hand, the binding energies of polarized species do not significantly alter due to the mass; hence there is no difference in the selection of spin-polarized clusters [30]. On the other hand, the binding of atoms and molecules towards the surface of a helium droplet slightly increases from 13.2 to 15.6  $\text{cm}^{-1}$  going from sodium to cesium [15]. Taking into account the substantial increase in the mass of the bound atoms and momentum conservation arguments, desorption during the cluster formation process should be substantially reduced; consequently, Rb and Cs clusters should be more abundant. Furthermore, from the reduced ionization potentials of heavier alkali clusters, photoionization might even be much more efficient because the ionic state can be reached with two photons only [31].

The reason for the lack of larger Rb and Cs clusters apparently lies in the nonexistence of stable high-spin states. In other words, the time for spontaneous depolarization is short compared to the time scale of the experiment (on the order of 100  $\mu\text{s}$  [32]). There are two ways for spin flips to occur: (a) When extra metal atoms attach during cluster growth, interaction increases for all the constituents as well as the density of available states. On that account, from a certain size on, coupling to orbital angular momentum allows transitions into states with different spin orientation. The resulting enhanced interaction and reduced spatial equilibrium positions contract the geometric structure, thus releasing much potential energy. Eventually a hot unpolarized cluster emerges. (b) With increasing cluster size the valence electron wave functions start to overlap sufficiently for electrons to migrate more or less freely from one atom to another and for that reason spin flips occur. The formally localized, spin-polarized electrons change into a delocalized, collective state. This collective property of small alkali clusters having electrons moving freely among the whole cluster can be interpreted as metallic behavior [6,33]. In this sense the collapse could be seen as a Mott transition [34,35], corresponding to the band gap closure mentioned

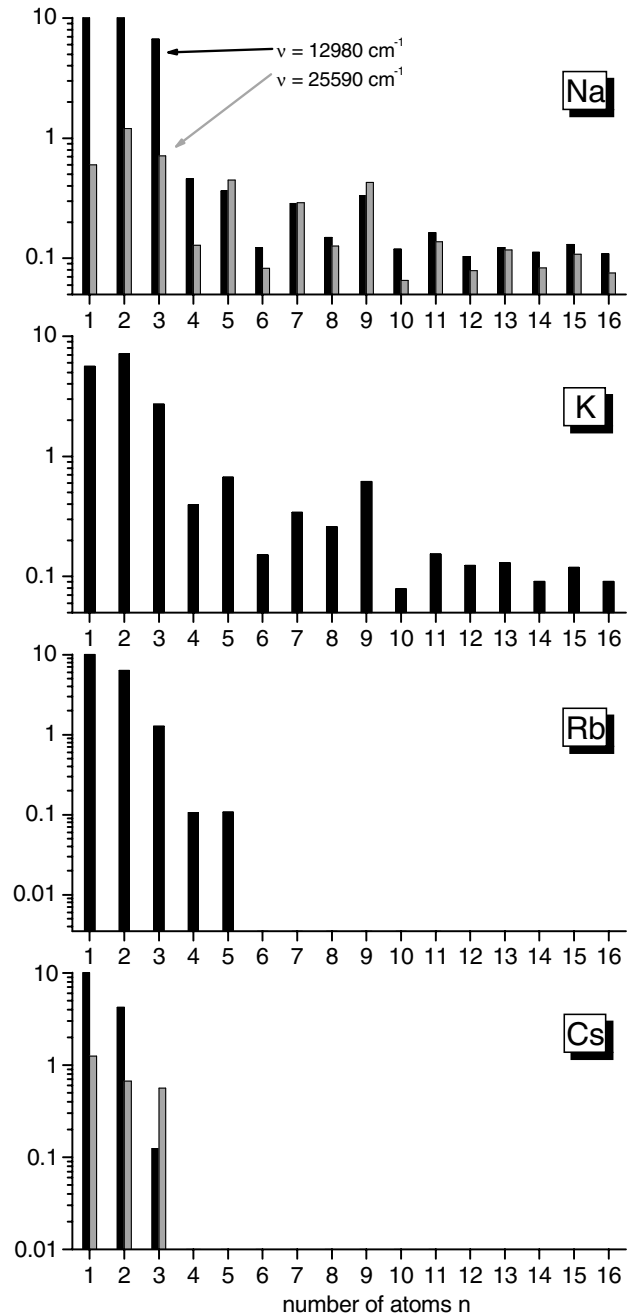


FIG. 2. Comparison of the cluster formation probing different alkalis. The upper limit for rubidium clusters is  $n = 5$  and for cesium clusters  $n = 3$ . The lack of larger Rb and Cs clusters indicates spontaneous depolarization of high-spin states. Different colors (black, gray) indicate different photon energies (12980  $\text{cm}^{-1}$ , 25590  $\text{cm}^{-1}$ , respectively).

above. A transition of that type for the alkalis at very small cluster sizes will offer new insight in comparison with state-of-the-art theoretical tools.

So far, the formation of lithium clusters has not been discussed. In our experiments we find only monomers and dimers even upon high lithium densities within the pickup oven. We did not include Li in the discussion given above because lithium behaves differently compared to the rest of the alkalis for several reasons: Although the

predicted binding energy towards the surface of helium is comparable to the heavier alkalis, the results on the spectroscopy of Li-doped helium droplets exhibited much less number densities. We think that lithium atoms evaporate considerably more upon dissipation of energy because its mass is less when compared to the mass of the shell of helium atoms that directly interact with the dopant. This means that vibrational energy from doping and recombination processes is efficiently transferred into translational energy of the light metal atom or dimer. Furthermore, the absorption spectrum of lithium atoms attached to helium droplets is in contrast to all other alkalis redshifted to the gas-phase absorption [14], indicating different interaction properties with the surface. Finally, high-spin states of Li clusters appear to have significantly higher binding energies and cannot be considered as van der Waals clusters [9]. Hence, even high-spin states might not be carried by the droplets. If already on that account Li clusters are not agglomerated on helium droplets or, if the enhanced interaction shifts the maximum cluster size for stable high-spin aggregates down to  $\text{Li}_2$ , cannot be answered at present.

After a long-standing discussion, the metallic behavior of alkali clusters down to small cluster sizes seemed to be well established; on the other hand, clusters with spin-polarized valence electrons, which are selected on helium droplets, form nonmetallic species. These are, in turn, right at the limit of being stable and tend to spontaneously depolarize as observed for very small Rb- and Cs-cluster sizes. In future experiments, spin polarization of these clusters will be probed by applying external magnetic fields. In this way, both the huge magnetic moments can be verified and tentative perturbations in the spin polarization by external fields can be studied. Furthermore, spectroscopic information is desired to determine geometric and electronic structures.

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