Formation and Stability of High-Spin Alkali Clusters

C.P. Schulz
Max-Born-Institut, Max-Born-Str. 2a, D-12489 Berlin, Germany

P. Claas, D. Schumacher, and F. Stienkemeier
Fakultät für Physik, Universität Bielefeld, D-33615 Bielefeld, Germany
(Dated: Received 11 August 2003; accepted 11 November 2003)

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 non-metallic, 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.

PACS numbers: 36.40.Cg, 71.30.+h

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 \( n \approx 18, 400 \) 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 830 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 \((P_0 = 50 \text{ bar})\) from a cold \((T = 20 \text{ K})\) 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 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 \(< 1 \text{ cm}^{-1}\)), the resulting binding energy to the surface of a helium droplet only adds up to \(\approx 15 \text{ cm}^{-1} (\approx 1.9 \text{ meV})\) [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 [16]. Moreover, in several 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 K_6 cluster bound by unpolarized electrons already completely evaporates such a droplet [32]. Vongehr et al. probed the formation of sodium-doped helium droplets by electron impact ionization [17] and developed a statistical model to look at the formation probabilities [18]. 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 pick-up cell. Experiments selecting clusters by spectroscopic means seem to confirm such a behavior [19].

In the experiments reported here, femtosecond photoionization of alkali-doped helium droplets is used to study cluster formation by sequential pick-up. 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. K_5^+ and K_9^+, reflecting 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.

![Image](https://via.placeholder.com/150)

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

<table>
<thead>
<tr>
<th></th>
<th>Unpolarized</th>
<th>Completely Polarized</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li_2</td>
<td>8523</td>
<td>317</td>
<td>[27]</td>
</tr>
<tr>
<td>Na_2</td>
<td>5892</td>
<td>174</td>
<td>[28]</td>
</tr>
<tr>
<td>K_2</td>
<td>4289</td>
<td>254</td>
<td>[29]</td>
</tr>
<tr>
<td>Rb_2</td>
<td>3875</td>
<td>250</td>
<td>[30]</td>
</tr>
<tr>
<td>Cs_2</td>
<td>3629</td>
<td>267</td>
<td>[30]</td>
</tr>
<tr>
<td>Na_3</td>
<td>8200</td>
<td>850</td>
<td>[31]</td>
</tr>
<tr>
<td>Na_4</td>
<td>14259</td>
<td>2903</td>
<td>[25], [9]</td>
</tr>
<tr>
<td>Na_5</td>
<td>19033</td>
<td>3428</td>
<td>[25], [9]</td>
</tr>
<tr>
<td>Na_6</td>
<td>26566</td>
<td>4233</td>
<td>[25], [9]</td>
</tr>
</tbody>
</table>

![Graph](https://via.placeholder.com/150)

**FIG. 1:** Mass spectrum of potassium doped helium nanodroplets upon femtosecond photoionization and mass selection in a quadrupole analyzer. The alternating ion intensity, with pronounced maxima at K_5^+ and K_9^+, 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.
There appears to be an upper limit of cluster size for the 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 [33]. On the other hand, the binding of atoms and molecules towards the surface of a helium droplet slightly increases from 13.2 cm\(^{-1}\) to 15.6 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 2 photons only [34].

The reason for the lack of larger Rb and Cs clusters apparently lies in the non-existence of stable high-spin states. In other words, the time for spontaneous depolarization is shorter compared to the time scale of the experiment (on the order of 100 \(\mu s\) [35]). 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, 22]. In this sense the collapse could be seen as a Mott transition [23, 24], corresponding to the HOMO-LUMO gap closure mentioned above. A transition of that type for the alkali 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 only find monomers and dimers even upon high lithium densities within the pick-up oven. We did not include Li in the discussion given above because lithium behaves different 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 dopant interactions and recombination processes is efficiently transferred into translational energy of the light metal atom or dimer.

![Comparison of the cluster formation probing different alkalis](image.png)

**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 cm\(^{-1}\), 25590 cm\(^{-1}\), respectively).
Furthermore, the absorption spectrum of lithium atoms attached to helium droplets is in contrast to all other alkalis red-shifted 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 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 non-metallic 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.

Stimulating discussions on the manuscript with G. Scoles, W. Meyer and V. Kresin are gratefully acknowledged. This work is financially supported by the DFG.

[32] The amount of energy to be dissipated amounts to 2.7 eV, binding energy plus 0.3 eV collision energy from picking up 6 atoms at \(T = 450 K\). The capacity of the droplet is determined by a mean cluster size of 5000 and a binding energy of one helium atom to a helium droplet of 0.6 meV \[26\].
[33] The formation of larger “unpolarized” clusters is also favored for Rb and Cs because of their reduced internal binding energies (c.f. Tab. I); accordingly, the fact that no large clusters are observed validates again the detection of exclusively high-spin states.
[34] Apart from the well-known electronic transitions of monomers, dimers and trimers, no resonant enhanced ionization has been observed in the wavelength range studied.
[35] Unfortunately this time cannot be varied substantially to study decay times.