Stability of two-component alkali clusters formed on helium nanodroplets

G. Droppelmann, M. Mudrich, C.P. Schulz, and F. Stienkemeier

1 Fakultät für Physik, Universität Bielefeld, 33615 Bielefeld, Germany
2 Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany
3 Max-Born-Institut, Berlin, Germany

Received: date / Revised version: date

Abstract. The stability of two-component clusters consisting of light (Na or K) and heavy (Rb or Cs) alkali atoms formed on helium nanodroplets is studied by femtosecond laser ionization in combination with mass spectrometry. Characteristic stability patterns reflecting electron shell-closures are observed in dependence of the total number of atoms contained in the mixed clusters. Faster decay of the stability of mixed clusters compared to the pure light ones as a function of size indicates a destabilizing effect of heavy alkali atoms on light alkali clusters, presumably due to second order spin-orbit interaction.

PACS. PACS-key describing text of that key – PACS-key describing text of that key

1 Introduction

Metal clusters have proven to be particularly well suited test objects for studying the transition from molecular quantum dynamics to solid state physics [1,2,3,4]. Clusters formed of monovalent alkali metals have been studied in great detail both experimentally as well as theoretically [1,2,3,5,6,7]. In these simple metal clusters the electronic structure is dominated by the number of valence electrons whereas the ionic cores are of secondary importance. The electrons are delocalized, and the electronic system exhibits a shell structure that is closely related to the well-known nuclear shell structure. The simple model of the free-electron gas inside a spherical potential well of the dimension of the cluster (Jellium model) applies particularly well to alkali clusters [2,3,6,7].

Important information on the electronic structure of metal clusters has been gained from simple cluster abundance spectra, reflecting the stability with respect to fragmentation: Clusters in which the number of valence electrons matches the spherical shell-closing numbers are produced more abundantly. In addition, odd-even alternations reflect the enhanced stability of paired electron configurations [8,2]. These shell effects have also been observed with metal clusters formed in helium nanodroplets [9].

Besides the strongly bound clusters (covalent or metallic) which are usually observed in experiments, alkalis can form van der Waals-type molecules and clusters in which all electrons are spin-oriented and strongly localized [5,10]. Although bonding in these high-spin clusters was predicted to be quite strong for lithium clusters (‘ferromagnetic bonding’), sodium clusters were theoretically found to be much more loosely bound than their metallic counterparts [5], and the same behavior may be expected for the heavier alkali species.

While most atomic species reside inside the helium droplets due to the attractive interaction with the helium surroundings, alkali atoms and molecules are weakly bound to the droplet surface in bubble states. This weak binding energy of the order of 10 K leads to the fact that out of all clusters formed on the droplet surface preferentially the weakly bound ones remain attached to the droplets [11]. This leads to an enrichment of weakly bound high-spin diatomic and triatomic molecules of up to a factor $10^4$ [12,13].

The formation of high-spin alkali clusters using the helium nanodroplet technique has been reported by our group [10]. In this previous experiment we observed characteristic differences in the abundance spectra of light and heavy alkali clusters. While alkali clusters of sizes up to 25 atoms were seen in the case of sodium (Na) and potassium (K), cluster sizes exceeding 5 and 3 atoms are strongly suppressed in the case of rubidium (Rb) and cesium (Cs), respectively. This behavior has been interpreted in terms of the reduced stability of high-spin states of Rb and Cs clusters with respect to depolarization, leaving behind hot, unpolarized clusters that may fragment and escape out of the detection volume. Depolarization may be induced by the strong second-order spin-orbit interaction present in the heavy alkali atoms, causing spontaneous spin flipping into the unpolarized state. Alternatively, the localized, spin-oriented electrons may evolve into a delocalized collective state as the cluster size grows larger, which eventually gives rise to spin flipping [10].
Based on these findings the question arises how stable mixed clusters of light and heavy alkali atoms in high-spin states are. In other words, how does the binding of one or several heavy alkali atoms (Rb or Cs) to a cluster consisting of light alkalis (Na or K) affect the stability of the compound cluster? In order to shed some light on this issue we report on a series of measurements of abundance spectra of mixed alkali clusters formed in high-spin states on the surface of helium nanodroplets using femtosecond (fs) photo ionization (PI) in combination with mass-selective ion detection.

2 Experimental

Besides numerous techniques for producing beams of metal clusters [11], the aggregation of metal atoms inside helium nanodroplets has been established as an alternative route to forming metal clusters of well defined composition [11]. Using this technique, the metal clusters are formed in the ultracold environment of the helium droplets at temperatures in the millikelvin range. Moreover, helium nanodroplets can be efficiently loaded with a variety of different atomic or molecular species.

In the experiment reported here, a beam of helium nanodroplets is consecutively doped with two different species of alkali atoms in two separate pickup cells to form two-component clusters on the droplets. The growth statistics for alkali clusters is found to deviate from the form two-component clusters on the droplets. The growth species of alkali atoms in two separate pickup cells to nanodroplets is consecutively doped with two different atomic or molecular species.

The mass spectrum of mixed K \( N \) \( = \) 0 \( - \) 3 clusters for \( M = 0 \) to \( M = 3 \) plotted in Fig. 1 as green and red bars, respectively, display a strikingly similar abundance pattern compared to the one of pure K \( N \) clusters. The excess energy due to the nonresonant nature of the ionization process leads to desorption and fragmentation of the ionized clusters. Thus, the abundance spectra reflect the stability pattern with respect to fragmentation rather than the abundance upon formation on the helium droplets. Prominent steps at masses 3, 5 and 9 clearly reflect the electronic shell closures of the ionized clusters. Besides, the mass spectra display a pronounced odd-even alternation with odd-numbered clusters being more abundant. Thus, the stability of two-component K \( N \) \( - M \) \( C _ { S } M \) clusters with respect to the electronic structure appears to be determined by the total number of constituents and not by the number of atoms of one species. Since under the given experimental conditions fragmentation of strongly bound metallic clusters would not be expected, we conclude that mixed as well as
pure alkali clusters formed on helium nanodroplets are in high-spin states [10].

Interestingly, mixed clusters containing one or two Cs atoms tend to fall off slightly faster with increasing number of K atoms than pure K$_N$ clusters. This trend is even more pronounced as the number of Cs atoms grows larger. This points at the fact that mixed K-Cs clusters tend to be destabilized by the presence of Cs atoms, in particular when more than one Cs atom is involved. Mixed clusters containing one Cs atom, K$_{N-1}$Cs$_1$, are detected up to $N = 13$, those containing two Cs atoms, K$_{N-2}$Cs$_2$, are observed up to $N = 9$, and K$_{N-3}$Cs$_3$ clusters are detected with high uncertainty up to $N = 5$.

The peak intensities of pure Cs$_N$ clusters are significantly lower than the ones of pure K$_N$ clusters. Since no substantial difference in the doping efficiencies is expected, this discrepancy is attributed to a more efficient PI process in the case of K$_N$ clusters. In contrast, two-component clusters, K$_{N-M}$Cs$_M$, are expected to have PI cross sections comparable to those of pure K$_N$ clusters. The fact that mixed clusters K$_{N-1}$Cs$_1$ and K$_{N-2}$Cs$_2$ are significantly less abundant than pure K$_N$ clusters therefore implies that these mixed clusters actually are less stable.

Besides the mentioned stability pattern as a function of the number of K atoms, the more pronounced limitation to maximum cluster size appears to be imposed by the number of Cs atoms attached to a mixed clusters of a given size. E.g., mixed clusters containing three Cs atoms, K$_{N-3}$Cs$_3$, are less abundant by about one order of magnitude compared to mixed clusters with one Cs, K$_{N-1}$Cs$_1$, which roughly matches the reduced abundance of the pure Cs$_3$ cluster as compared to the Cs monomer (hatched bars in Fig. 1). However, this behavior is a consequence of co-doping the helium droplets with K atoms. When loading the droplets only with Cs atoms at the same pickup cell temperature, the detected Cs$_N$ abundance spectrum is peaked at Cs$_2$ with roughly equal signal intensities at the masses of Cs and Cs$_3$.

In order to study this effect a series of measurements at variable K pickup conditions is depicted in Fig. 3. Shown are count rates of a representative selection of different mass peaks as a function of the approximate mean number of picked up K atoms. These values are computed from the vapor pressure curve of K using the calibration $10^{-4}$ mbar $\approx 1$ atom per droplet. This calibration has been checked by means of laser-induced fluorescence spectroscopy in earlier experiments.

The data shown in Fig. 3 indicate the following general trend. Both pure Cs$_1$ and Cs$_2$ clusters as well as combined clusters K$_2$Cs$_1$ and K$_3$Cs$_2$ are suppressed in the mass spectrum upon multiple doping with K atoms. In particular, abundances of clusters containing two Cs atoms, Cs$_2$ and K$_2$Cs$_2$, fall off more rapidly than the ones containing only one Cs atom. When adding up all signals from clusters containing one, respectively two Cs atoms, (not shown in the graph) the same trend holds. Thus, the rapid disappearance of mixed clusters of a given size containing more than one Cs atom is a combined effect of the low stability of large pure Cs$_N$ clusters and the reduction of stability of mixed clusters with an increasing number of K atoms.

Fig. 2 displays mass spectra of two-component clusters containing Na and Cs atoms. The pure Na$_N$ cluster abundances are dominated by the Na$_2$ dimer mass peak due to a resonance in the PI cross section of Na$_2$ at the chosen laser wave length [17]. Mixed clusters composed of Na and Cs atoms are less abundant than pure Na$_N$ clusters by about one order of magnitude. This is mainly due to a lower level of doping with Cs atoms compared to the experiment with mixed clusters made of K and Cs, discussed above. Thus, combinations involving 2 Cs atoms, Na$_{N-2}$Cs$_2$, are only visible at selected cluster sizes and Na$_{N-3}$Cs$_3$ is not present in the spectrum. Neverthe-
less, a faster dropping off of the mixed cluster intensities of Na$_{N-1}$Cs$_1$ with respect to the pure Na$_N$ mass peaks is again clearly visible, indicating that Na$_N$ clusters tend to be destabilized by the presence of Cs atoms as it is seen in the spectra of mixed clusters with K atoms.

In addition to the mixed alkali clusters discussed so far, clusters made up of Rb and either Na or K have been studied. In comparison with the K$_{N-M}$Cs$_M$ cluster spectrum, larger quantities of mixed clusters K$_{N-M}$Rb$_M$ are observed. Clusters containing up to $M = 5$ Rb atoms are clearly detected. The abundance pattern both of pure an mixed clusters as a function of total number of atoms, $N$, is modulated by the effect of shell closures and odd-even alterations, as in the K-Cs case. Also, mixed cluster abundances fall off faster as $N$ grows larger compared to pure K$_N$ clusters, indicating the destabilizing effect of additional heavy alkali atoms. The abundance of mixed clusters of a fixed size is also reduced the more Rb atoms are present in the clusters. However, the latter effects are not as pronounced as in the K-Cs combination. Two-component clusters containing only one Rb atom, K$_{N-1}$Rb$_1$, appear systematically less abundant than those containing more Rb atoms. Furthermore, the influence of the order of doping of first K atoms in a first pickup cell and then Rb atoms in a second one, and vice versa, was also compared. However, no significant difference in the cluster abundance spectra was observed.

The mass spectrum of mixed Na$_{N-M}$Rb$_M$ clusters is similar to the one of K$_{N-M}$Rb$_M$ except for the fact that pure Na$_N$ clusters have much lower abundances compared to pure Rb$_N$ clusters and even compared to mixed clusters, which is due to the small ionization cross section of Na$_N$ for $N > 2$. As in the K$_{N-M}$Rb$_M$ mass spectra, clusters containing only one Rb atom, Na$_{N-1}$Rb$_1$, are systematically less abundant than those containing a larger number of Rb atoms. This type of mixed clusters apparently has minimum stability as compared to all other cluster compositions. Cluster sizes as large as Na$_2$Rb$_9$ are observed in the mass spectrum.

4 Conclusion

Two-component high-spin alkali clusters composed of light (Na, K) and heavy (Rb, Cs) atoms can be formed on helium nanodroplets with rather large abundance. The stability pattern of the mixed clusters with respect to photo fragmentation follows the one of pure clusters, with the total number of atoms in the clusters being the determining parameter. Characteristic features such as electron-shell closures and odd-even alternations are clearly visible in the mass spectra. No sudden breakdown of cluster abundance upon addition of one or a specific number of heavy alkali atoms to the cluster is observed. However, the abundance of mixed clusters of a given size is systematically lower than the one of the pure lighter alkali clusters Na$_N$ and K$_N$ of the same size, roughly following the dropping abundance distributions of pure heavy alkali clusters Rb$_N$ and Cs$_N$. Furthermore, for a fixed number of Rb or Cs atoms attached to Na$_N$ of K$_N$ clusters, the abundance of the mixed clusters falls off faster as the number of Na or K atoms increases than for the pure Na$_N$ of K$_N$ clusters. Thus, admixing heavy Rb or Cs atoms to light Na$_N$ of K$_N$ clusters tends to destabilize the resulting two-component clusters.

The fact that the number of heavy alkali constituents imposes the dominant limitation to the maximum size of stable two-component clusters rather than the total number of atoms points at second-order spin-orbit interaction being the dominant effect that leads to depolarization and fragmentation. Delocalization of the electron wave functions which would cause spontaneous depolarization as the high-spin clusters grow larger can therefore be ruled out. The largest two-component clusters are observed in the combination of Na and Rb yielding mixed clusters of sizes up to Na$_{10}$Rb$_6$ and Na$_2$Rb$_8$. No significant influence of the doping order on the mass spectra of mixed clusters, as studied with K-Rb clusters, is observed.

However, the helium droplet source conditions are found to crucially influence the abundance of pure and mixed clusters. Larger droplets have higher cooling capacity and therefore sustain the aggregation of larger spin-polarized clusters and possibly of metallic clusters as well. Therefore studying abundance spectra of pure and mixed alkali clusters at variable helium droplet beam conditions may provide valuable information on the formation and stability of high-spin clusters. Besides, time-resolved measurements of the fragmentation process, e.g. using the pump-probe technique, will add to the understanding of the laser-induced dynamics of many-body systems isolated in helium nanodroplets.

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

1. Walt A. de Heer. Rev. Mod. Phys., 65:611, 1993.
2. H. Haberland. Clusters of Atoms and Molecules I and II. Springer Series in Chemical Physics, Vol. 52 and 56, Springer, Berlin, 1994.
3. W. Ekkardt. Metal Clusters. Wiley, New York, 1999.
4. Josef Tigggesbäumker and Frank Stienkemeier. Phys. Chem. Chem. Phys., 9:4725, 2007.
5. S. P. de Visser, D. Danovich, and S. Shaik. Phys. Chem. Chem. Phys., 5:158–164, 2003.
6. M. Brack. Rev. Mod. Phys., 65:777–732, 1993.
7. B. von Issendorff and O. Cheshnovsky. Ann. Rev. Phys. Chem., 56:549–580, 2005.
8. W. D. Knight et al. Phys. Rev. Lett., 52:2141–2143, 1984.
9. Th. Diederich et al. Phys. Rev. A, 72:023203, 2005.
10. C. P. Schulz et al. Phys. Rev. Lett., 92:013401, 2004.
11. F. Stienkemeier, W. E. Ernst, J. Higgins, and G. Scolles. J. Chem. Phys., 102:615–617, 1995.
12. J. Higgins et al. J. Phys. Chem. A, 102:4952–4965, 1998.
13. Johann Nagl et al. Phys. Rev. Lett., 100:063001, 2008.
14. S. Vongehr and V. K. Kresin. J. Chem. Phys., 119:11241–11229, 2003.
15. G. Droppelmann. PhD thesis. Bielefeld University, 2005.
16. P. Claus et al. J. Phys. B, 39:S1151, 2006.
17. P. Claus et al. J. Phys. Chem. A, 111:7537, 2007.