

Dopant-induced solvation of alkalis in liquid helium nanodroplets

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Abstract

Alkali metal atoms and small alkali clusters are classic heliophobes and when in contact with liquid helium they reside in a dimple on the surface. Here we show that alkalis can be induced to submerge into liquid helium when a highly polarizable co-solute, C_{60} , is added to a helium nanodroplet. Evidence is presented that shows that all sodium clusters, and **probably** single Na atoms, enter the helium droplet in the presence of C_{60} . Even clusters of cesium, an extreme heliophobe, dissolve in liquid helium when C_{60} is added. The sole exception is atomic Cs, which remains at the surface.

Helium droplets provide a unique, low temperature liquid environment in which to explore a variety of physical and chemical phenomena at the nanoscale.^{1,2} Dopants such as atoms and molecules can be added to these droplets and most submerge into the liquid helium because of the favorable potential energy delivered by an interior location, even though helium is a very poor solvent. However, alkali atoms and small alkali clusters are notorious exceptions.³⁻⁹ These dopants reside in a dimple on the surface of the droplet because their diffuse valence electron density is prohibitive to submersion, since more energy is required to displace helium atoms to create room for the dopant than is gained by the additional (exceptionally weak) attractive interactions with the surrounding helium atoms.

As the size of the alkali cluster increases, the energetics become more favorable for an interior location and so the possibility exists for submersion into liquid helium beyond a critical cluster size. This threshold cluster size was first predicted by Stark and Kresin using a phenomenological model which combined a classical treatment of the van der Waals attractive and repulsive energies between the metal and the helium with incorporation of surface tension effects for liquid helium.¹⁰ When sufficiently large the alkali cluster possesses a polarizability that can create a favorable net attractive interaction with the liquid helium, thus causing the cluster to sink into the liquid rather than stay at the surface. The threshold cluster sizes predicted for sodium and potassium have recently received experimental support using data extracted from electron ionization mass spectrometry.^{11,12} These experiments were able to demonstrate that sufficiently large Na_n and K_n clusters do indeed submerge and approximate threshold cluster sizes of $n > 20$ and $n > \sim 80$ were determined, which are remarkably close to the theoretical predictions.¹⁰

Intuitively, one might expect the energetic balance between surface and interior locations for small alkali clusters to be altered by the addition of a second dopant located

inside the helium droplet. This follows from the modification of the van der Waals interactions caused by the presence of a second dopant and could, if sufficiently attractive, induce the alkali to submerge. The only previous experimental evidence for such behavior was obtained in a study by Lugovoj *et al.* of the chemiluminescence reaction between a Ba atom and N₂O.¹³ Ba atoms are known to reside on the surface of a helium droplet for reasons similar to those of the alkalis. When N₂O was added it reacted with Ba to form BaO and the resulting chemiluminescence spectrum from this molecule was characteristic of a hot BaO molecule ejected into the gas phase. However, when a sufficient number of Xe atoms were added to make a Xe_n cluster *prior* to the addition of Ba and N₂O, the chemiluminescence spectrum became characteristic of a vibrationally cold BaO molecule, suggesting that reaction had now taken place *inside* the helium droplet. In other words, the Ba atom was assumed to be ‘dragged’ inside the droplet through interaction with a highly polarizable Xe_n cluster (estimated to contain ~15 Xe atoms on average) and subsequent reaction with N₂O was followed by rapid vibrational quenching of the electronically excited BaO by the surrounding liquid helium. In a different study the effect of Xe on the location of an alkali atom, Rb, was explored using density functional theory.¹⁴ For a droplet containing 500 helium atoms there was insufficient attraction between the Xe atom and a Rb atom to induce submersion of the latter, demonstrating that Rb is strongly heliophobic.

In this study we show for the first time that the location of alkali atoms and alkali clusters in a helium nanodroplet can be altered by the addition of a strongly polarizable molecule. The molecule chosen here is C₆₀ and two alkalis were investigated, Na and Cs. The apparatus employed for these experiments has been described in detail previously.¹¹ A beam of helium droplets with a mean size in the region of 5×10^5 atoms was passed through two pick-up cells in series, the first containing C₆₀ vapor and the second holding vapor of the chosen alkali. It is known that C₆₀ readily enters helium droplets. However, since alkali

clusters may be inside the droplet or on the surface, we need a method to distinguish between these locations. The method adopted is electron ionization mass spectrometry. In particular we exploit the fact that species at the surface of a helium droplet tend to be ionized via a Penning process involving electronically excited helium atoms. These excited helium atoms are generated by electron impact and are preferentially located near the surface of helium droplets. Ionization by this route has a threshold energy near 20 eV in the gas phase. On the other hand, dopants that are deep inside helium droplets are more likely to be ionized by He^+ and will therefore have an energy threshold close to 25 eV. Full details of this means of assigning a dopant location can be found elsewhere.¹¹ Note also that the journey from the final pick-up zone to the ionization region is $\sim 500 \mu\text{s}$, so the doped droplets have plenty of time to re-equilibrate after dopant pick-up before being subject to electron bombardment.

We have collected data for a variety of $(\text{C}_{60})_N$ cluster sizes and for illustration, Figure 1 shows the findings obtained by detecting ions with $N = 2$. However, it is important to note that the key findings are unaffected by the value of N .¹⁵ The lower panel in Figure 1 shows data obtained when sodium was added to the helium droplets after C_{60} was added. Yields for several ions are presented as a function of electron kinetic energy and there is a striking difference between the ion yield curves with and without C_{60} . The ion yield curve for HeNa^+ is essentially identical to those for other Na-containing ions (not shown), such as bare Na_2^+ and larger cluster ions up to $n \approx 20$.¹² We choose to present the findings for the complex between Na^+ and He in Figure 1 rather than bare Na^+ in order to eliminate any background contributions from Na vapor that might drift into the mass spectrometer: the HeNa^+ ions can only come from Na atoms in contact with a helium droplet. The threshold for production of Na^+ is close to 21 eV and is characteristic of Penning ionization, thus showing that Na atoms and small Na_n clusters reside at the surface of a helium droplet, as demonstrated in earlier

work.¹¹ The onset is close to 21 eV rather than 20 eV because additional energy is needed to inject an electron into liquid helium.¹⁶

On the other hand, complexes between Na_n and C_{60} show a small onset in ion production near to 22 eV but at energies above 25 eV the cross section undergoes a steady rise with incident electron energy, showing that dopant ionization in this case is dominated by charge transfer from He^+ inside the helium droplets. It is conceivable that such complexes could be formed by a multi-step process, starting with $(\text{C}_{60})_N$ inside the droplet and with Na_n on the surface. Initial ionization of C_{60} may then lead to Na_n being pulled into the droplet through an ion-induced dipole interaction. This route seems most unlikely for several reasons but the most obvious objection is that no comparable process is seen for Cs (see below), even though it is known that Cs^+ is stable inside helium droplets.¹⁷ Thus small Na_n clusters, and most probably even individual Na atoms, are drawn into the helium droplets by the presence of the highly polarizable C_{60} molecule. The mass spectra do not allow us to be certain about the actual threshold cluster size because fragmentation is possible on ionization.

The findings for Cs show some similarities, but also some important differences, when compared with Na. As with Na the ion signals from droplets containing only Cs and small Cs_n clusters (no added C_{60}) show an ionization threshold characteristic of Penning ionization, with no evidence of any secondary threshold arising from ionization by He^+ near 25 eV. This demonstrates the surface location of Cs atoms and small Cs_n clusters and is entirely consistent with theoretical predictions,^{10,18,19} spectroscopic studies of doped helium nanodroplets,^{17,20-22} and experimental measurements of the non-wetting of metallic Cs by superfluid helium.²³⁻²⁶ However, the signal for a single Cs^+ ion in combination with one or more C_{60} molecules now shows an ion yield curve which is indicative of Penning ionization, in marked contrast to the Na case. The most likely explanation is that ionization first occurs by production of Cs^+ at the surface by Penning ionization. Once the ion is formed it can, as explained in the preceding

paragraph, enter the droplet. This creates the opportunity for Cs^+ and a $(\text{C}_{60})_N$ cluster to collide, generating $(\text{C}_{60})_N\text{Cs}^+$, before being released into the gas phase.

The behavior seen for Cs_n^+ cluster ions for $n \geq 2$ is dramatically different. The ion yield curves for Cs_2^+ and larger cluster ions in the presence of C_{60} show a response characteristic of interior ionization by He^+ . The interpretation of these observations is that all clusters of Cs, beginning with the simplest, Cs_2 , submerge into the helium when one or more C_{60} molecules is already present. This is a remarkable observation given that superfluid helium does not wet pure Cs. The mass spectral data imply (assuming ion fragmentation is negligible) that only a single Cs atom is able to resist this dopant-induced wetting process.

There are two plausible mechanisms that could account for our findings. The first is that the entrance of the alkalis into helium is dictated by a simple balance of forces. Such arguments have been used previously to account for the submersion of large alkali clusters into liquid helium.¹⁰⁻¹² For this model the van der Waals attraction between the alkali and C_{60} is assumed to be sufficient to overcome the energy barrier required to insert the heliophobic alkalis into liquid helium, with the exception of atomic Cs. The two dopants first need to approach close enough for a significant attractive force to occur. Molecular dynamics simulations show that dopants can undergo widely ranging excursions within helium droplets after pick-up,²⁷ which is a consequence of the relatively flat confining potential for molecules in helium droplets away from the surface.²⁸ The strong dispersion interaction between alkalis such as Na and Cs with C_{60} is known to deliver a low energy scattering cross section which is more than an order of magnitude larger than the hard sphere cross section in the case of Na.²⁹ It is therefore possible that C_{60} could be guided towards the alkali atom or cluster by the resulting long-rang potential energy gradient until close enough to induce submersion. However, while this is an appealing picture, it has its difficulties. In particular we might expect the balance of forces to alter with the number of C_{60} molecules added to the helium

droplet. A cluster containing multiple C_{60} molecules is a more polarizable entity than a single C_{60} molecule and so the attractive forces should increase substantially in the former case. However, we see no detectable change in submersion behavior whether there is one C_{60} molecule or even as many as five C_{60} molecules in the droplet. For this reason we think the simple submersion model is unlikely to apply here.

An alternative model involves what amounts to a chemical reaction between the alkali and the C_{60} . In particular we propose that a long-range electron transfer (harpoon reaction) can occur between the alkali at the surface and a C_{60} molecule (or cluster), which leads to the formation of a salt, such as $Na^+C_{60}^-$. This could be preceded by the aforementioned long-range dispersion interaction between the alkali and the C_{60} , which draws the two dopants close enough to allow harpooning to occur. To try and explain why Cs_2 can submerge in this model but Cs cannot, we have used density functional theory to predict the potential energy curves for the interaction of these dopants with C_{60} . Details of these calculations can be found in the Supplemental Material.¹⁵ For Cs_2 there are two possible spin states, singlet and triplet, resulting from a combination of two Cs atoms. The expectation is that the triplet state will dominate in our experiments because the energy release when the stronger bond forms in the singlet state tends to cause evaporation of the dimers from the helium droplet surface.^{30,31} Nevertheless, calculations have been performed for both spin states of Cs_2 along with the ground (2S) state of atomic Cs and Figure 2 shows the resulting potential energy curves. These curves document a very strong intermolecular interaction which has its origin in charge transfer from the alkali to C_{60} . The ionic character of $M^+C_{60}^-$ molecules in the gas phase has been confirmed through measurements of the electric dipole moments for $M = Li - Cs$.³²

For Cs_2 the binding energy with C_{60} is substantially deeper in both spin states when compared with the interaction of atomic Cs. Furthermore, in the triplet state, the minimum occurs at a much shorter distance than for atomic Cs. Preliminary calculations performed at

different Cs_2 bond lengths show a strong dependence of the $\text{Cs}_2\text{-C}_{60}$ binding energy on the dimer geometry, while the actual spin state of Cs_2 has a negligible effect on the energy. The increased binding energy for Cs_2 with C_{60} when compared to atomic Cs is therefore a consequence of the higher polarizability and lower ionization energy of Cs_2 , i.e. it is more electropositive than Cs. This makes submersion into helium an energetically more favorable event for Cs_2 and helps to explain why this cluster dissolves in helium in the presence of C_{60} whereas Cs does not. However, a detailed DFT benchmark study on He-C_{60} predicts a relatively strong binding energy of about 52 cm^{-1} .³³ Consequently, we anticipate that a firm layer of helium atoms will form around the C_{60} molecule which will impede direct contact with the alkali.

Providing the two species come within a critical distance, which is defined by the crossing point of the neutral van der Waals and ionic potential energy curves, long range electron transfer can occur from the alkali to the C_{60} and the harpoon mechanism³⁴ will draw the two species together. This process will occur at longer range for Cs_2 than for Cs and therefore the lack of solvation of atomic Cs can be explained by assuming that the critical distance for $\text{Cs} + \text{C}_{60}$ lies inside the tightly bound helium layer around the C_{60} .

The anticipated mechanism is illustrated in cartoon form in Figure 3. In the upper part of the figure we start with a single Cs atom on the helium droplet surface and a single C_{60} molecule inside the droplet. Penning ionization of the Cs atom at the surface of the droplet leads to Cs^+ formation and subsequent combination of this ion with C_{60} , either via submersion of the Cs^+ or through combination with the C_{60} when the latter approaches the droplet surface.

For Cs_2 the scenario is different, as illustrated in the lower images in Figure 3. Here long range electron transfer occurs when C_{60} moves close to the alkali near the droplet surface. The resulting strongly attractive force between the ions then leads to displacement of the helium and allows the Cs_2^+ and C_{60}^- to make contact. This ion-pair can then dissolve in the

liquid helium and will subsequently be ionized for mass spectrometric detection by charge transfer from He^+ after electron ionization of the droplet.

To conclude, the addition of a strongly polarizable and electrophilic dopant, C_{60} , has been shown to induce small alkali clusters, and in the case of sodium even single atoms, to dissolve in liquid helium. However, a single Cs atom is resistant to this submersion process. Given these observations it would be interesting to explore this unusual effect in more detail by choosing a wider range of co-dopants with different polarizabilities and different electron affinities to combine with the alkalis. Furthermore, simulations that can provide more mechanistic detail about how the dissolution process proceeds would be particularly welcome.

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Figure captions

1. Yields of various cations as a function of the kinetic energy of added electrons. The lower plot shows data obtained for Na vapor added to helium droplets. The blue line derives from Na atoms (and potentially Na_n clusters) in the absence of C_{60} and corresponds to the signal derived from detection of HeNa^+ ions. The other curves in the lower plot were obtained when C_{60} was added prior to the sodium. In the upper plot ion yield curves are shown for experiments where Cs vapor was used instead of Na.
2. Calculated potential energy curves for the Cs-C_{60} and $\text{Cs}_2\text{-C}_{60}$ systems. The distance shown on the horizontal axis is the separation between the centers of mass of the two interacting partners. The structures of Cs_2 and C_{60} were held constant in these calculations. Two spin states for Cs_2 can be distinguished. In the case of the singlet state, the Cs-Cs distance was fixed at the equilibrium value for the free singlet dimer. For the triplet state, the Cs-Cs equilibrium distance is longer than the singlet case and to generate the potential energy curve this was also fixed. Note that the triplet dimer shows a much stronger binding to C_{60} than singlet Cs_2 .
3. Illustration of the mechanism for ionization of droplets doped with a Cs/C_{60} mixture. The upper series of images illustrate the sequence of events when only one Cs atom is present whereas the lower series shows the different ionization mechanism posited for Cs_2 . Note that dissociation of the Cs_2 following charge transfer is proposed on the basis of calculations described in the Supplemental Material.¹⁵

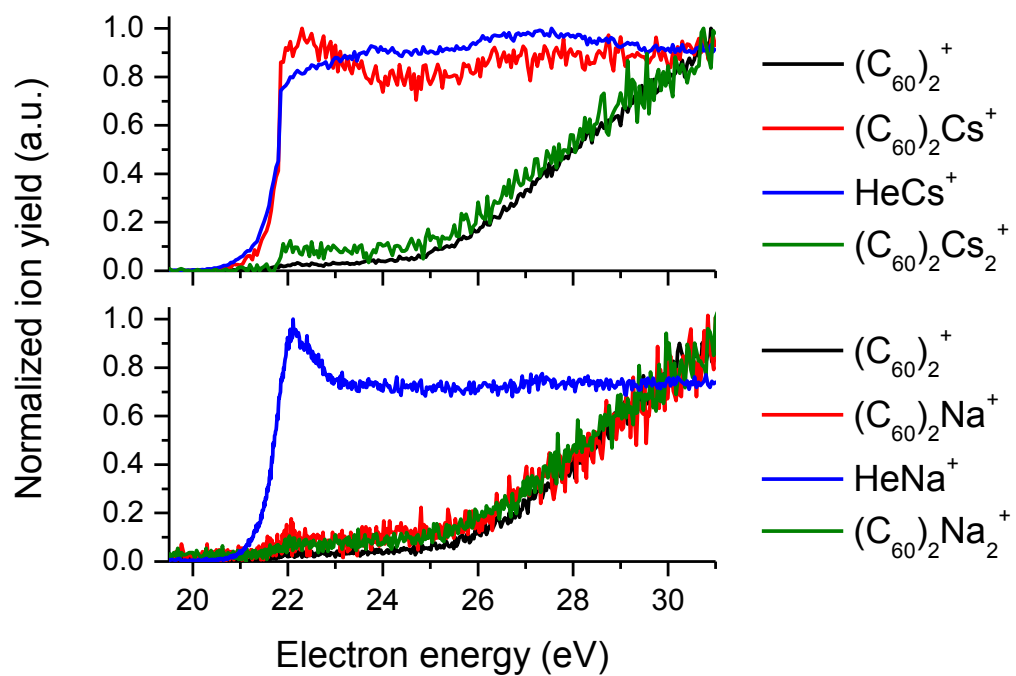


Figure 1

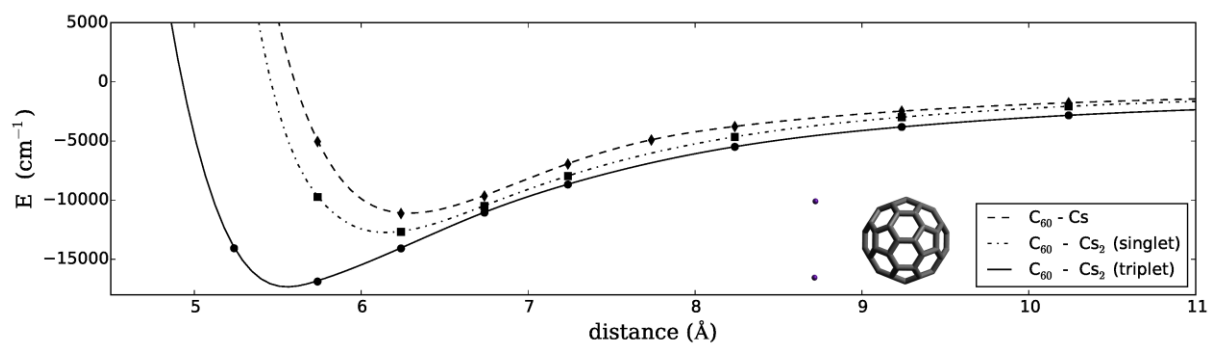


Figure 2

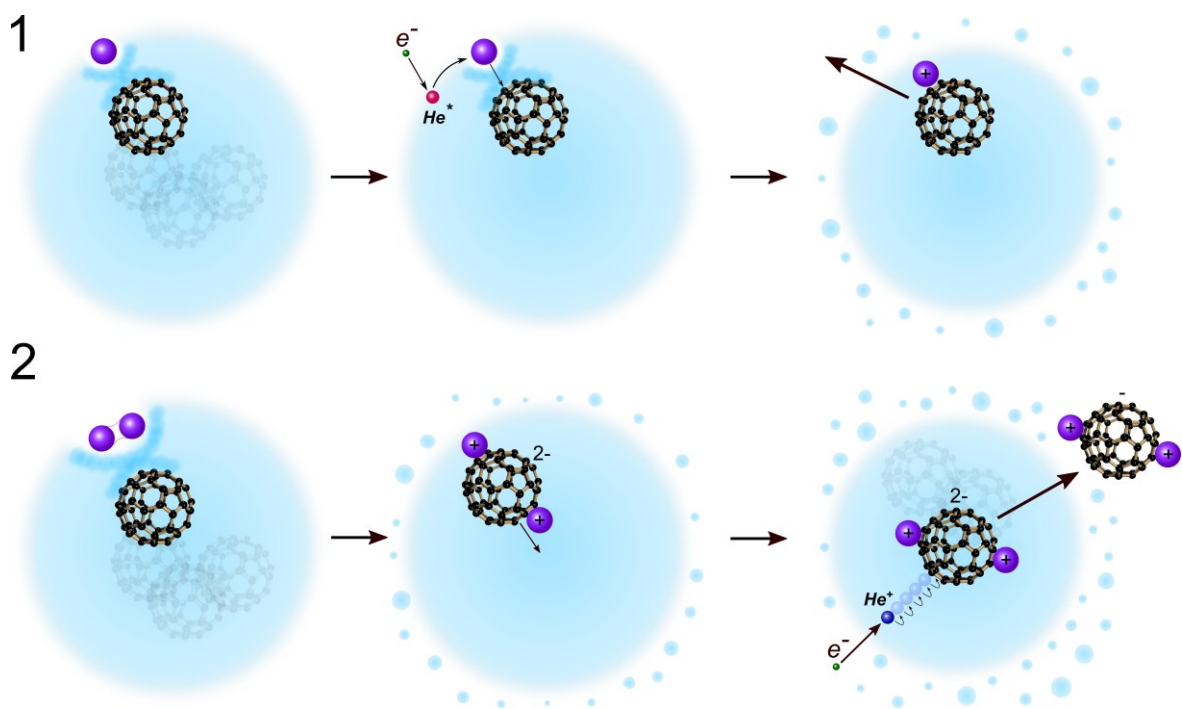


Figure 3