

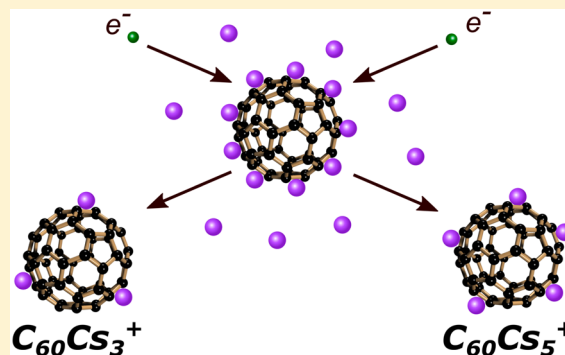
# Positively and Negatively Charged Cesium and $(C_{60})_mCs_n$ Cluster Ions

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**ABSTRACT:** We report on the formation and ionization of cesium and  $C_{60}Cs$  clusters in superfluid helium nanodroplets. Size distributions of positively and negatively charged  $(C_{60})_mCs_n^\pm$  ions have been measured for  $m \leq 7$ ,  $n \leq 12$ . Reproducible intensity anomalies are observed in high-resolution mass spectra. For both charge states,  $(C_{60})_mCs_3^\pm$  and  $(C_{60})_mCs_5^\pm$  are particularly abundant, with little dependence on the value of  $m$ . Distributions of bare cesium cluster ions also indicate enhanced stability of  $Cs_3^\pm$  and  $Cs_5^\pm$ , in agreement with theoretical predictions. These findings contrast with earlier reports on highly Cs-doped cationic fullerene aggregates which showed enhanced stability of  $C_{60}Cs_6$  building blocks attributed to charge transfer. The dependence of the  $(C_{60})_mCs_3^-$  anion yield on electron energy shows a resonance that, surprisingly, oscillates in strength as  $m$  increases from 1 to 6.



## 1. INTRODUCTION

Since the successful development of methods to synthesize fullerenes in macroscopic quantities, the properties of metal-doped fullerene solids and their potential applications have been studied. Early experiments on fullerides doped with alkali (A) metals revealed metal–insulator transitions<sup>1</sup> and the appearance of superconductivity in potassium-doped fullerides below  $T_c = 18$  K.<sup>2</sup> Various crystal structures form depending on the dopant concentration which may be as large as 12:1 in  $Li_{12}C_{60}$ .<sup>3,4</sup> Superconductivity, however, is restricted to the  $A_3C_{60}$  fulleride salts in which the alkalis transfer their valence electrons to the lowest unoccupied triply degenerate molecular orbital of  $t_{1u}$  symmetry, resulting in a half-filled conduction band of  $C_{60}$ . The superconducting transition temperature in binary  $A_1B_2C_{60}$  fulleride salts (A, B = alkali metal) was found to correlate with the lattice parameter.<sup>4</sup> Indeed, the highest transition temperature of any alkali-doped fulleride has been reported for  $Cs_3C_{60}$  which is an insulator at ambient pressure but becomes superconducting below  $T_c = 38$  K at elevated pressure without changing its body-centered cubic structure.<sup>5–7</sup>

In a recent report we presented ion abundances of  $(C_{60})_mCs_n^+$  cations prepared in the gas phase by electron ionization of helium nanodroplets doped with  $C_{60}$  and Cs.<sup>8</sup> A key finding was that  $(C_{60})_mCs_n^+$  ions ( $m \leq 6$ ) are particularly abundant if they contain  $n = 6m + 1$  cesium atoms;  $(C_{60})_mCs_n^{2+}$  dications were abundant (with the exception of  $(C_{60})_4Cs_n^{2+}$ ) if  $n = 6m + 2$ . By and large these results were consistent with earlier photoionization experiments by Martin and co-workers involving potassium and rubidium which indicated that up to six alkali metal atoms per  $C_{60}$  transfer their valence electrons into the  $t_{1u}$  orbital, resulting in particularly stable  $C_{60}A_6$  building blocks.<sup>9,10</sup> One or two additional alkali ions are

needed to provide the net charge of the mono- and dications, respectively.

$C_{60}$  powder is, in fact, known to react rapidly with liquid alkalis to form the body-centered cubic  $C_{60}A_6$  phase.<sup>11</sup> Evidence for  $C_{60}A_6$  building blocks also appeared in abundance distributions of  $(C_{60})_mNa_n^+$  ( $m \leq 10$ ) and  $(C_{60})_mNa_n^{2+}$  ( $m \leq 5$ ),<sup>8</sup> consistent with reports by Martin and co-workers for  $m \leq 3$ <sup>9,10</sup> and photodissociation data reported by Pellarin et al. for  $m \leq 2$ .<sup>12</sup>

Interestingly, the photodissociation experiments by Pellarin et al. revealed another pattern, namely, enhanced abundance of  $C_{60}Na_3^+$  and  $(C_{60})_2Na_5^+$ .<sup>12</sup> The authors noticed that these species marked the onset of cluster ion distributions in spectra reported by Martin and co-workers<sup>9</sup> and proposed the existence of stable  $C_{60}Na_2$  units in which the fullerenes are covalently bonded through a  $[2 + 2]$  cycloaddition. Similar onsets at  $C_{60}A_3^+$  and  $(C_{60})_2A_5^+$  with  $A = K$  or  $Rb$  were noticed in photodissociation experiments by Kappes and co-workers.<sup>13</sup> For  $C_{60}$  trimers, however, Kappes and co-workers reported that  $(C_{60})_3A_8^+$  ( $A = K, Rb$ ) formed the onset<sup>13</sup> whereas Martin et al. identified  $(C_{60})_3Na_7^+$  as onset.<sup>9</sup>

A different experimental approach was pursued by Kern and co-workers who heated neutral  $C_{60}$ -potassium clusters in helium gas.<sup>14,15</sup> The preferred composition of clusters containing four or fewer  $C_{60}$  that survived at 900 K for about 1 ms was  $(C_{60}K_2)_m$ .

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In the present work we have doped helium nanodroplets with much smaller amounts of cesium than in our previous experiments, resulting in ions containing as many as 10  $C_{60}$  and between 1 and about 12 Cs atoms. Furthermore, we investigate cations as well as anions. A surprising finding is a pronounced maximum in the abundance of  $(C_{60})_mCs_3^\pm$  cations and anions for all values of  $m$  except for  $C_{60}Cs_n^-$  whose abundance declines very rapidly with increasing  $n$ . Another, weaker anomaly appears at  $(C_{60})_mCs_5^\pm$ . The fact that these anomalies are independent of  $m$  and the charge state might suggest that they are due to particularly stable cesium cluster ions that are favored irrespective of the number of fullerenes. We observe, indeed, corresponding anomalies at  $n = 3$  and 5 in abundance distributions of neat  $Cs_n^+$  and  $Cs_n^-$ , consistent with theoretical predictions that these ions are particularly stable.<sup>16,17</sup> However, in the literature we find no support for the proposed presence of stable alkali trimer and pentamer units in neutral or charged  $(C_{60})_mA_n$ . We also report the dependence of the abundance of  $(C_{60})_mCs_3^-$  anions on the electron energy which shows an intriguing alternating pattern as  $m$  increases.

## 2. EXPERIMENT AND DATA ANALYSIS

For the  $C_{60}Cs$  experiment neutral helium nanodroplets were produced by expanding helium (Messer, purity 99.9999%) at a stagnation pressure of 20 bar through a 5  $\mu\text{m}$  nozzle, cooled by a closed-cycle refrigerator to 9.3 K, into a vacuum chamber (base pressure about  $2 \times 10^{-6}$  Pa). For the measurements of neat cesium anions the cryostat temperature was lowered to 8.8 K. At these temperatures helium nanodroplets contain an average number of  $4 \times 10^5$  and  $1.2 \times 10^6$  helium atoms, respectively.<sup>18</sup> The resulting supersonic beam was skimmed by a 0.8 mm conical skimmer and traversed a 20 cm long pickup region consisting of two differentially pumped pickup chambers.  $C_{60}$  (MER, purity 99.9%) was vaporized in a resistively heated oven in the first chamber; metallic cesium (Sigma-Aldrich, purity 99.95%) was vaporized in the second chamber. The temperatures of the ovens were varied in order to obtain the optimal experimental conditions for formation of complexes containing several  $C_{60}$  molecules and up to  $\sim 10$  cesium atoms.

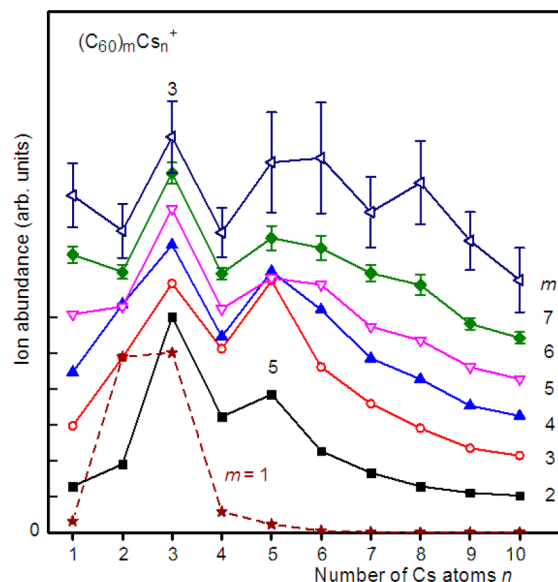
The beam emerging from the dual pickup cell was collimated and crossed by an electron beam in a Nier-type ion source. For cations the energy was 89 eV; for anions the energy was varied between 0 and 35 eV in increments of 0.05 eV. However, distributions shown in this work use increments of 0.35 eV in order to reduce statistical scatter. The ions were accelerated into the extraction region of a reflectron time-of-flight mass spectrometer (Tofwerk AG, model HTOF) with a mass resolution  $\Delta m/m = 1/5000$  ( $\Delta m =$  full-width at half-maximum). The base pressure in the mass spectrometer was  $10^{-5}$  Pa. Ions were extracted at  $90^\circ$  into the field-free region of the spectrometer by a pulsed voltage. At the end of the field-free region they entered a two-stage reflectron which reflected them toward a microchannel plate detector operated in single ion counting mode. Additional experimental details have been provided elsewhere.<sup>19</sup>

Mass spectra were evaluated by means of a custom-designed software.<sup>20</sup> The routine includes automatic fitting of a custom peak shape to the mass peaks and subtraction of background by fitting a spline to the background level of the raw data. It explicitly considers the presence of  $He_n^+$ , a variety of impurity ions (e.g.,  $OHC_{60}^+$ ), and isotopic patterns. The abundance of

ions with a specific composition (specific values of  $m$  and  $n$ ) is derived by a matrix method.

## 3. EXPERIMENTAL RESULTS

Abundance distributions of  $(C_{60})_mCs_n^+$  cations containing up to seven  $C_{60}$  are displayed in Figure 1. The staggered



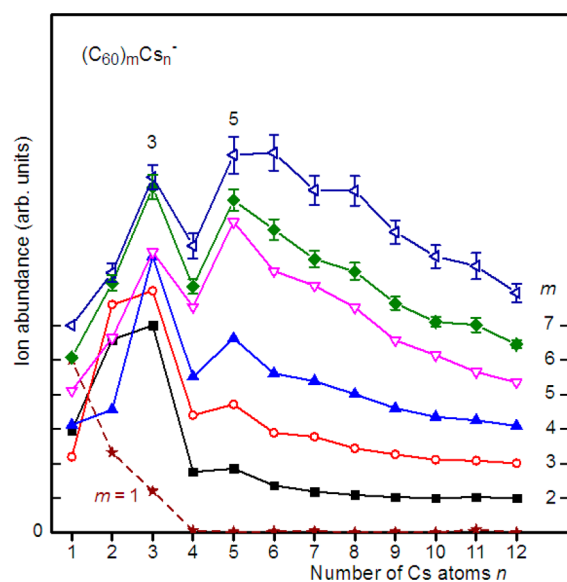
**Figure 1.** Abundance distributions of  $(C_{60})_mCs_n^+$ ,  $m \leq 7$ . The distributions are individually normalized for each value of  $m$  and vertically offset (staggered); baselines are indicated on the ordinate. Error bars are not shown when they are smaller than the symbol size. Maxima or abrupt drops occur at  $n = 3$  and 5 for all but the largest  $m$  values.

distributions have been individually normalized; their baselines and corresponding  $m$  values are indicated along the ordinate on the right. Error bars are plotted if they exceed the size of the symbols. For  $m = 1$  we observe a steep drop in the abundance after  $n = 3$ ; for larger  $m$  values  $n = 3$  forms a local maximum. This maximum persists up to  $m = 10$  (not shown), the largest value for which statistically significant data exist. A weaker local maximum is observed at  $n = 5$ , especially for  $m = 2, 3$ , and 4.

We did not notice these features in our previous report on heavily coated  $C_{60}$  cluster cations, but close inspection of Figure 1 in that report reveals a steep rise in the ion abundance of  $(C_{60})_mCs_n^+$  from  $n = 4$  to 5 followed by a plateau, for  $m = 2, 3$ , and 4.<sup>8</sup> The abundance of ions with  $n \leq 4$  was simply too small to discern any anomalies.

Figure 2 presents staggered abundance distributions of  $(C_{60})_mCs_n^-$  anions formed by electron attachment at 13 eV, for  $m \leq 7$ . They are surprisingly similar to those of cations, with  $(C_{60})_mCs_3^-$  forming local maxima or, for  $m = 2$  and 3, featuring abrupt drops. Secondary maxima appear at  $n = 5$  for  $2 \leq m \leq 6$ . The abundance of  $C_{60}Cs_n^-$  decreases very rapidly with  $n$ ; the presence or absence of anomalies at  $n = 3$  and 5 cannot be assessed.

Distributions of neat cesium cluster ions  $Cs_n^\pm$  are presented in Figure 3a. Data were extracted from mass spectra recorded without  $C_{60}$  doping. For  $Cs_n^+$ , similar distributions were deduced from droplets co-doped with  $C_{60}$  but the yield of  $Cs_n^-$  was very weak in the presence of  $C_{60}$ . We cannot offer a compelling explanation for this difference. A logarithmic scale was chosen for the ordinate because the abundance of cations



**Figure 2.** Staggered, normalized abundance distributions of  $(C_{60})_mCs_n^-$  for  $m \leq 7$ , recorded with an electron energy of 13 eV. Error bars are omitted if they are smaller than the symbol size. Maxima or abrupt drops occur at  $n = 3$  and  $5$  for  $2 \leq m \leq 6$ .

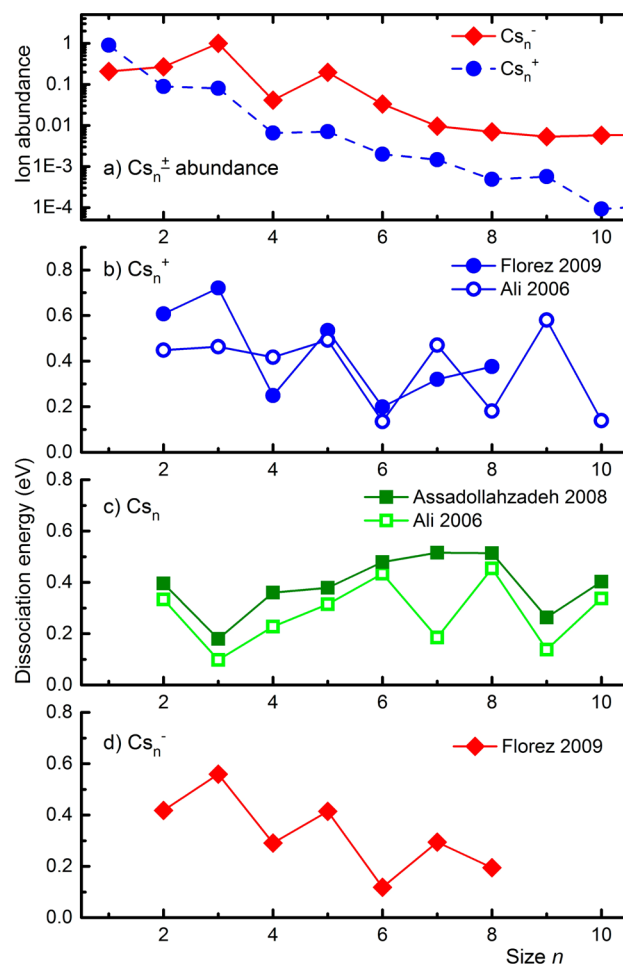
and anions decreases rapidly with  $n$ . Anions display strong maxima at  $n = 3$  and  $5$ .  $Cs_3^-$  is nearly 4 times more abundant than  $Cs_2^-$ ;  $Cs_5^-$  is 5 times more abundant than  $Cs_4^-$ . The most pronounced anomaly in the distribution of cations occurs at  $Cs_9^+$ ; less pronounced drops appear at  $Cs_3^+$  and  $Cs_5^+$ . It is worth mentioning that abundance distributions of  $Cs_n^+$  extracted from a liquid-metal ion source show the same anomalies but the contrast is much larger, roughly 1:10 for the abundance ratio of  $Cs_{n+1}^+$  versus  $Cs_n^+$ , for  $n = 3, 5, 9$ .<sup>21</sup> The contrast ratio depends on instrumental factors such as the time window during which hot cluster ions are allowed to evaporate and whether or not ions produced by unimolecular dissociation after acceleration are detected or rejected.

The dependence of the  $(C_{60})_mCs_3^-$  ion abundance on the electron energy is displayed in Figure 4a for  $1 \leq m \leq 7$ . We selected this ion series (with  $n = 3$ ) because of its prominent appearance in Figure 2. The staggered distributions are normalized; baselines and values of  $m$  are indicated along the ordinate. Surprisingly, the patterns alternate with increasing  $m$ . Ions with odd values of  $m$  feature a broad maximum that gradually shifts from 10 eV for  $m = 1$  to 15 eV for  $m = 5$ ; ions with even  $m$  feature an even broader maximum around 23 eV. For  $m = 7$  and larger (not shown), the distributions become rather similar, exhibiting a maximum between 15 and 20 eV.

The energy dependences of  $Cs_3^-$  and  $Cs_5^-$  are shown (staggered and normalized) in Figure 4b. They feature an abrupt onset at  $18.5 \pm 0.5$  eV. They are virtually identical but in marked contrast to those of  $(C_{60})_mCs_3^-$ . Note that the  $Cs_n^-$  data were recorded in experiments that did not involve co-doping with  $C_{60}$ .

#### 4. DISCUSSION

In a recent report we had measured abundance distributions of  $(C_{60})_mCs_n^+$  cations containing up to six  $C_{60}$  and several dozen Cs.<sup>8</sup> Local maxima in the ion abundance suggested that ions with  $n = 6m + 1$  are particularly stable.<sup>22</sup> The findings were consistent with earlier research by Martin and co-workers on potassium- and rubidium-doped fullerene aggregates; the



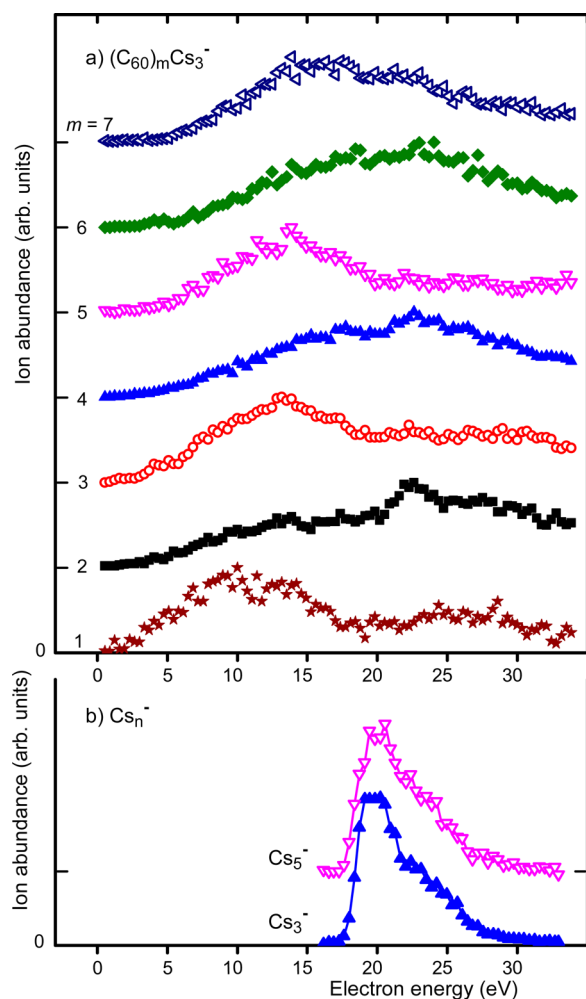
**Figure 3.** (a) Semilogarithmic abundance distributions of  $Cs_n^-$  and  $Cs_n^+$ . Error bars are smaller than the symbol size. Data were obtained from droplets doped with Cs but not  $C_{60}$ . (b–d) Theoretical dissociation energies of cesium cluster cations, neutrals, and anions, deduced from published total binding energies.<sup>16,17,25</sup>

authors suggested the presence of  $C_{60}A_6$  building blocks in which the alkali metal atoms transfer their valence electrons to the 3-fold degenerate lowest unoccupied orbital ( $t_{1u}$ ) of the fullerene, forming essentially ionic bonds.<sup>9,10</sup> Subsequent theoretical studies of sodium and potassium adsorbed on  $C_{60}$  have supported this interpretation.<sup>13,15,23,24</sup> Further support for the model comes from a shift of the anomalies to  $n = 6m + 2$  for  $(C_{60})_mCs_n^{2+}$  dications and to  $n = 6m + 3$  for  $X(C_{60})_mCs_n^+$  where  $X = H_2O$  or  $CO_2$ .<sup>8</sup>

The results in the present study pertain to much weaker doping, i.e., smaller values of  $n$ ; they cannot possibly reveal the existence of  $C_{60}A_6$  building blocks. Instead, from observation of particularly abundant  $(C_{60})_mCs_3^\pm$  and, to a lesser degree,  $(C_{60})_mCs_5^\pm$  ions, either positively or negatively charged, one might conclude that  $Cs_3^\pm$  and  $Cs_5^\pm$  ions are particularly stable entities that form irrespective of the environment. Note that the prominence of  $Cs_3^\pm$  and  $Cs_5^\pm$  could also be augmented by particularly weak binding in  $Cs_4^\pm$  and  $Cs_6^\pm$ .

This interpretation is apparently supported by the enhanced ion abundances of bare  $Cs_3^\pm$  and  $Cs_5^\pm$  cluster ions; see Figure 3a, as well as theoretical studies of these species. Ali et al. have used density functional theory (DFT) to determine the structure and electronic properties (including ionization energies and electron affinities) of  $Cs_n^+$  and  $Cs_n^-$ ,  $n \leq 10$ .





**Figure 4.** Dependence of the anion abundance on electron energy, for  $(C_{60})_mCs_3^-$  with  $m \leq 7$  (a) and  $Cs_3^-$  and  $Cs_5^-$  (b). Data are normalized and staggered; individual baselines are indicated along the ordinate. Statistical uncertainties may be inferred from the scatter. Data in panel b were measured in the absence of  $C_{60}$ -doping.

Dissociation energies  $D_n$ , deduced from plots showing computed total energies in Ali's work<sup>16</sup> are plotted in Figure 3b and Figure 3c for cationic and neutral clusters, respectively.

Florez et al. also applied DFT to compute total energies of  $Cs_n^+$ ,  $Cs_n$ , and  $Cs_n^-$ ,  $n \leq 8$ .<sup>17</sup> Dissociation energies derived from their graphs are displayed in Figure 3b, Figure 3c, and Figure 3d, respectively. Also included in Figure 3c are dissociation energies computed for neutral  $Cs_n$ ,  $n \leq 20$ , by Assadollahzadeh et al.<sup>25</sup> Several other theoretical studies of neutral  $Cs_n$  have focused on much larger clusters;<sup>26,27</sup> those results are not included in Figure 3.

Dissociation energies derived from Florez's work<sup>17</sup> reveal that  $Cs_3^\pm$  and  $Cs_5^\pm$  enjoy enhanced stability. The enhanced stability of  $Cs_3^+$  does not appear in Ali's work<sup>16</sup> which has been criticized by Florez et al. for using an extremely small basis set and neglecting relativistic effects.<sup>17</sup> Within the spherical jellium approximation  $Cs_3^+$  has enhanced stability because it features a closed  $s$  shell.<sup>28</sup> The computed high stability of  $Cs_3^-$  is supported by photoelectron spectra which show that its vertical detachment energy is nearly twice that of  $Cs_2^-$ .<sup>29</sup>

We note in passing that the anomaly in the abundance and computed stability of  $Cs_9^+$  (Figure 3a and Figure 3b) is expected within the spherical jellium model because this ion

would have a closed  $1s^21p^6$  configuration.<sup>28</sup> However, a corresponding anomaly for anions, at  $Cs_7^-$ , is not reflected in the ion abundance (Figure 3a) and only weakly in the computed stability (Figure 3d).

However, the hypothesis of intact  $Cs_3$  and  $Cs_5$  entities in  $C_{60}$  aggregates of either charge state finds little support from other investigations of neutral or charged  $C_{60}$ -alkali complexes. One should emphasize though that previous work mostly pertains to the lighter alkalis ( $A = Li, Na, K$ ) and that their properties are still debated.<sup>30</sup>

One topic of interest has been the nature of bonding which is dominantly ionic.<sup>31</sup> Rayane et al. have computed the susceptibility and electric dipole moment of  $C_{60}$  complexed with one alkali atom.<sup>32</sup> For Cs, Rb, and K the Mulliken charge on the alkali is very close to  $+1.00e$  but it decreases to about  $0.90e$  for Na and  $0.70e$  for Li. Qualitatively the same decreasing trend has been reported by other researchers for Li, Na, K.<sup>23,24,31,33</sup>

For  $C_{60}$  doped with multiple alkalis, however, charge transfer decreases with increasing  $n$ , thus decreasing the Coulombic repulsion between the ions.<sup>13,15,23,34,35</sup> Furthermore, the above-mentioned trend reverses and charge transfer gradually increases from K to Li.<sup>36,37</sup>

Another topic of interest has been the energetically preferred adsorption site of a single alkali. Density functional theory studies find that Na and K alkali atoms preferentially adsorb at a hexagonal site<sup>33,38,39</sup> (note that some studies mentioned here refer to charged complexes). For  $C_{60}Li$ , however, the hexagonal and pentagonal sites are nearly isoenergetic.<sup>23,40,41</sup>  $C_{60}$ -lithium complexes have received the greatest attention because of their potential application as a lightweight medium for hydrogen storage,<sup>42,43</sup> but their properties do not seem to be characteristic of  $C_{60}$  complexed with heavier alkalis; they will not be considered any further in this discussion.

The topic of greatest relevance to the present work is the structure and stability of  $C_{60}$  dressed with several alkali atoms. Theoretical studies reveal a delicate balance between Coulomb repulsion between atomic ions favoring uniform (homogeneous) coverage and metallic bonding favoring island formation, i.e., segregation.<sup>44</sup> Conflicting results have been found for  $C_{60}Na_n$ . On the basis of mass spectra and photoelectron spectra of  $C_{60}Na_n^-$ ,  $n \leq 12$ , Palpant et al. have concluded that sodium forms stable trimers on the fullerene surface.<sup>35,45</sup> Their conclusion is supported by a DFT study of  $C_{60}Na_n^-$  by Wang et al.,<sup>30</sup> although these authors find another preferred motif, a tetrahedral  $Na_4$ . For  $n = 4, 6, 7, 9$  the ground state structure consists of a single three-dimensional sodium cluster, while for  $n = 5$  and  $8$  two isolated clusters form on opposite sides of the fullerene.<sup>30</sup>

Researchers at the University of Lyon have measured the electric susceptibility of neutral  $C_{60}Na_n$  in a molecular beam deflection experiment.<sup>32,46,47</sup> Strong deflection was attributed to complete segregation, i.e., formation of a single sodium droplet for all values of  $n$ . In later work though, supported by DFT studies, it was concluded that the first 8 sodium atoms spread uniformly over the  $C_{60}$  surface.<sup>38,48,49</sup> In a subsequent DFT study Rabilloud concluded that up to 12 sodium atoms prefer to form distinct tetrahedral islands.<sup>33</sup>

The relevance of results pertaining to  $C_{60}$ -sodium complexes for the interpretation of our  $C_{60}$ -cesium data may be questioned, but work on heavier alkalis is scarce. In a DFT study of  $C_{60}K_{12}$  Rabilloud finds the same preference for distinct tetrahedral clusters as for  $C_{60}Na_{12}$ .<sup>37</sup>

The appearance of electronic shell structure in abundance distributions of  $C_{60}^+$  heavily coated with cesium<sup>10,50</sup> has stimulated a few theoretical studies of this core–shell system,<sup>51,52</sup> but they are of little relevance to the present discussion.

Our group has recently investigated adsorption of hydrogen on neutral and cationic  $C_{60}Cs$ .<sup>53</sup> DFT calculations including empirical dispersion correction and harmonic vibrational zero-point corrections resulted in dissociation energies of 0.793 eV for  $C_{60}Cs^+$ . In another DFT study we have concluded that the lowest energy configuration of neutral  $C_{60}Cs_2$  consists of two Cs atoms located on opposite sites of  $C_{60}$ .<sup>54</sup>

The various studies summarized above provide no support for the hypothesis of stable  $Cs_3^\pm$  and  $Cs_5^\pm$  entities; we therefore seek an alternative explanation. As mentioned in the Introduction, Pellarin et al. reported evidence for particularly stable  $C_{60}Na_3^+$  and  $(C_{60})_2Na_5^+$  based on mass spectrometric experiments in which  $C_{60}$ -sodium complexes were deliberately heated by the ionizing laser.<sup>12</sup> The authors pointed out that related features appeared in mass spectra reported by Martin's group in form of abrupt onsets at  $C_{60}Na_3^+$ ,  $(C_{60})_2Na_5^+$ , and  $(C_{60})_3Na_7^+$ .<sup>9,10</sup> Those experiments also involved deliberately heating and fragmenting the cations.

Pellarin et al. conjectured that  $(C_{60})_2Na_5^+$  and  $(C_{60})_3Na_7^+$  might dissociate by losing a  $C_{60}Na_2$  unit. Although this reaction could not be experimentally observed, the hypothesis of stable  $C_{60}A_2$  units has been beautifully confirmed by Kern and co-workers for A = potassium.<sup>14,15</sup> The researchers thermalized neutral  $C_{60}$ -potassium clusters for about 1 ms in hot helium gas; the clusters were then softly ionized by one-photon ionization. At temperatures of 900 K they observed abundance distributions that sharply peaked at  $(C_{60}K_2)_m$  for  $m \leq 4$ . Their DFT calculations of  $C_{60}K_n$  and  $(C_{60})_2K_n$  at finite temperatures revealed that  $(C_{60})_2K_4$  is, indeed, thermodynamically most stable among all  $(C_{60})_2K_n$  species for  $n \leq 6$ . The authors emphasized that  $(C_{60}K_2)_m$  owe their superior stability to their high entropy rather than to closure of any electronic or geometric shells.<sup>14</sup>

The computed ground state structure of  $C_{60}K_2$  features two alkali atoms at opposite hexagonal sites, whereas that of  $(C_{60})_2K_4$  consists of a  $C_{60}$  dimer with the four alkali atoms wrapped around its waiste. This configuration is also favored when atoms or molecules are physisorbed on  $(C_{60})_2$ ,<sup>55</sup> but Coulomb repulsion between adsorbed alkali cations tends to destabilize it. In fact, the most stable geometries computed for  $(C_{60})_2K_5$  and  $(C_{60})_2K_6$  have two K atoms at opposite sites of the  $(C_{60})_2$  dumbbell axis.<sup>15</sup>

The computational results for  $C_{60}K_2$  and  $(C_{60}K_2)_2$  provide little guidance as to the structures of  $(C_{60}K_2)_3$  and  $(C_{60}K_2)_4$  and the reason for their superior thermodynamic stability. Where are the cesium atoms located in clusters containing more than two  $C_{60}$ ? Do the three cesium atoms in the magic  $(C_{60})_mCs_3^+$  ( $m \geq 2$ ) prefer sites that are separated as far as possible, as computed for  $C_{60}K_2$ ,<sup>15</sup> or do they cluster in groove sites as computed for  $(C_{60}K_2)_2$ ?

And why do not we observe an anomaly at the presumably magic  $(C_{60})_3Cs_7^+$ ? Perhaps, one may argue that the low cesium concentration in our experiments renders the observation of this ion impossible and the prominence of  $(C_{60})_mCs_3^\pm$  and  $(C_{60})_mCs_5^\pm$  is owed to the well-known odd–even effect in the stability of alkali clusters.<sup>15,28,56</sup> A look at Figure 1 makes this explanation unconvincing; the falloff in the ion abundance beyond the magic  $(C_{60})_3Cs_5^+$  is gradual and smooth.

We can think of two factors that might cause the differences between our data and previous reports: (i) differences between cesium and its lighter and smaller cousins and (ii) differences in the way by which aggregates are synthesized and ionized. In previous studies, aggregates were formed in gas-phase collisions between  $C_{60}$  and alkali atoms (sometimes brought into the gas phase by laser ablation) and subsequently ionized by photons.<sup>9,10,12–15,34,35,45</sup> In the present study as well as our earlier work<sup>8</sup> aggregates were synthesized in helium droplets and ionized by electrons. In many cases mass spectra resulting from these different approaches are very similar.<sup>57,58</sup> Cesium, however, is exceptional because it is extremely heliophobic. Superfluid helium does not wet bulk cesium;<sup>59</sup> even large neutral cesium clusters will not be solvated by helium nanodroplets but rather remain on the surface.<sup>60</sup>

The situation changes, though, in the presence of other solutes that are highly polarizable. Recently we could show that neutral  $C_{60}$  or  $C_{60}$  aggregates embedded in a droplet will pull neutral cesium clusters into the droplet by a harpooning mechanism, the only exception being atomic cesium. Although not discussed in that work, it seems likely that atomic cesium will be pulled into the droplet once a  $C_{60}A_n$  aggregate has formed because the electric polarizability of  $C_{60}A_n$  is an order of magnitude larger than that of  $C_{60}$ .<sup>47,48</sup> If a Cs dimer but not a Cs atom would be pulled into a droplet containing a  $C_{60}Cs_n$  aggregate, an interesting odd–even effect would appear where  $C_{60}$ -doped helium droplets containing  $n$  Cs atoms would consist of solvated  $(C_{60})_mCs_n$  if  $n$  is even but solvated  $(C_{60})_mCs_{n-1}$  plus a Cs atom on the surface if  $n$  is odd.

Perhaps the most intriguing and hardest to explain feature in our data is the peculiar pattern in the energy dependence of  $(C_{60})_mCs_3^-$  anions which alternates with increasing  $m$ ; see Figure 4. The spectrum of  $C_{60}Cs_3^-$  with its main maximum around 10 eV is not unlike those of  $C_{60}^-$  and  $(C_{60})_2^-$  obtained from  $C_{60}$ -doped helium nanodroplets which feature a broad maximum around 5–10 eV plus a weaker one at about 25 eV.<sup>61</sup> The spectra of  $(C_{60})_2Cs_3^-$  and  $(C_{60})_4Cs_3^-$ , however, are missing the 10 eV resonance. If the  $(C_{60})_m$  aggregates were van der Waals bound, this odd–even effect would be difficult to explain. But are they? Pellarin et al. have proposed that the fullerenes are covalently bonded through a  $[2 + 2]$  cycloaddition.<sup>12</sup> They did not explain how that reaction would be initiated but dimerization of fullerenes in  $(C_{60})_m$  may provide a clue toward the observed odd–even effect.

## 5. CONCLUSION

Electron ionization of helium droplets doped with  $C_{60}$  and cesium results in mass spectra that consistently feature maxima in the abundance of positively and negatively charged  $(C_{60})_mCs_3^\pm$  and  $(C_{60})_mCs_5^\pm$  for a range of  $m$  values. This also holds true for  $m = 0$ , i.e., for bare cesium ions. The most straightforward explanation, the presence of highly stable  $Cs_3^\pm$  and  $Cs_5^\pm$  clusters, is not supported by previous work involving complexes of  $C_{60}$  with lighter alkalis. The features are reminiscent of features in cationic spectra of  $C_{60}$  complexed with lighter alkalis (A) which point to particularly stable  $C_{60}A_2$  building blocks,<sup>9,10,12–15</sup> but we do not observe a corresponding enhancement of the abundance for  $(C_{60})_3Cs_7^\pm$  or  $(C_{60})_4Cs_9^\pm$ . Also, it is not clear why anions should show the same “magic numbers” as cations. Perhaps the most puzzling finding is a pattern in the energy dependence of  $(C_{60})_mCs_3^-$  that alternates with increasing  $m$ . Odd–even effects are well-known for monovalent metal clusters but not for presumably

van der Waals bound C<sub>60</sub> aggregates. Further experiments are needed, preferably involving lighter alkalis that are more amenable to high-level theoretical investigations.

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### Notes

The authors declare no competing financial interest.

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