Stability of M@C\textsubscript{60} endohedral complexes

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M@C\textsubscript{60} endohedral complexes, which are based on the C\textsubscript{60} molecule and contain encapsulated atoms M, would provide a unique opportunity to tailor specific properties of the C\textsubscript{60} system on a molecular level. The stability of these complexes is calculated using a Born-Haber cycle that was originally applied to determine the formation enthalpy of solid C\textsubscript{60} intercalation compounds. We find that the formation energy of M@C\textsubscript{60} depends crucially on the interaction potential and electron affinity of the endohedral atom and the C\textsubscript{60} molecule. A significant contribution to the formation energy comes from the polarization energy of the cage if the enclosed atom is not at the cage center; this finding is in agreement with available ab initio results. We discuss the potential of these systems to become a new class of superconducting materials.

Following the successful synthesis of bulk amounts of the C\textsubscript{60} molecule [1] with a hollow fullerene structure [2], an extensive research effort has been made to chemically modify this unusual system. Doping solid C\textsubscript{60} in the bulk by metal atoms led to the discovery of a new class of superconducting materials [3,4] with a critical temperature as high as 42 K in Rb\textsubscript{3}CaC\textsubscript{60} [5]. The doped C\textsubscript{60} solid contains the dopant atoms in lattice interstitial sites. A separate goal has been insertion of the dopant atoms inside the C\textsubscript{60} cage itself. Endohedral complexes M@C\textsubscript{60} which could contain encapsulated atoms or molecules M, would provide a unique possibility to tailor specific properties of this system on a molecular level. A permanent electric dipole moment in the endohedral molecule, and ferroelectricity in the bulk compound would be expected in the case of an enclosed polar molecule [6], a molecule with an enclosed ion off-center in the cage. Modifications expected in the electronic and phonon spectra when M@C\textsubscript{60} is substituted for C\textsubscript{60} in the solid could produce a superconducting material, as was the case for the extrinsic intercalation of the C\textsubscript{60} crystal. In both cases, superconductivity should arise from electron-phonon coupling due to stiff on-ball modes [7], but it could provide significantly different values of the critical temperature for superconductivity T\textsubscript{c} in the two systems.

Another advantage of solids based on endohedral fullerenes would be their potential stability against decomposition, even if the corresponding exohedral intercalation compounds prove to be unstable. Of course, metastable endohedrals with a low probability of decomposition could still be generated in collision reactions [8], because of the high activation barrier (> 6 eV) for the passage of atoms or ions through the cage. However, for a successful bulk synthesis, thermodinamic stability of the endohedral complexes is an important issue.

Following the first successful enclosure of a La atom inside the C\textsubscript{60} cage [9], a number of endo-

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b) The Born–Haber cycle for acceptor complexes consists of very similar steps and is shown in fig. 1b. The formation energy $\Delta E_F$ of $M@C_{60}^{-}$ is

$$\Delta E_F(M^{-@C_{60}}) = \Delta E_{\text{int}}(C_{60}^-) - \Delta E_{\text{int}}(C_{60}) - E_{\text{Fermi}}(M^{-@C_{60}}) + E_{\text{Fermi}}(M@C_{60}).$$

Precise experimental data exist for the ionization potentials $I(M^{-})$ and electron affinities $A(M^{-})$ across the periodic table [16]. The electron affinity of the neutral $C_{60}$ molecule is $A(C_{60})=2.74$ eV [17], and its ionization potential is $I(C_{60})=7.54$ eV [18]. Electron affinities and ionization potentials of charged $C_{60}$ molecules have been estimated by Wang et al. [14]. Note that the values of the electron affinity and ionization potential of $C_{60}$ make it both a good electron acceptor and a good electron donor. As mentioned above, the formation of endohedral complexes is driven by a large gain in electrostatic energy $E_C$. We calculate this energy to be $E_C = -e^2/R$, where $e$ is the charge of the ion. Here, we tacitly assume that the $C_{60}$ molecule behaves like a charged sphere of radius $R$. In donor systems, we consider a transfer of all $n$ valence electrons from the enclosed M atom to the $C_{60}$ cage. The electrostatic polarization energy $E_{\text{pol}}$ can be then obtained using the image charge method, which yields

$$E_{\text{pol}} = -n e^2/2R(2R^2 - d^2).$$

Here, $R$ is the radius of the $C_{60}$ molecule and $d$ is the.

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For the above reasons, we adopt a very different approach to determine the stability of molecular endohedral complexes.

We subdivide the process of formation of $M@C_{60}$ from free atoms and molecules into well-defined steps and determine the associated formation energy using a Born–Haber cycle. This procedure, which is in principle exact, has previously been successfully applied to determine the stability of bulk $C_{60}$ intercalation compounds [14] and has recently been experimentally verified for the $A@C_{60}$ compounds ($A=$Na, K, Rh, Cs) [15]. The accuracy of our results depends crucially on the energetics associated with the individual steps. The fact that many steps only involve well-known atomic properties, such as the ionization potential and electron affinity of isolated atoms, allows for simple trend predictions across the periodic table.

The formation energy $\Delta E_F$ at $T=0$ K of $M@C_{60}$ is defined by

$$\Delta E_F = E(M@C_{60}) - E(M) - E(C_{60}).$$

If $\Delta E_F$ is negative, the compound $M@C_{60}$ is stable against decomposition into the pure components, namely $M$ in its atomic form, $M(\text{atom})$, and $C_{60}$, $C_{60}(\text{cluster})$. As mentioned above, we determine $\Delta E_F$ using a Born–Haber cycle consisting of several well-defined steps, many of them involving physically observable quantities. The cycle for the formation of $M@C_{60}$ for both donor and acceptor complexes is illustrated in fig. 1.

We first discuss the energetics associated with the enclosure of donor atoms, shown in fig. 1a.
No dipole and hence no gain in $E_{\text{pol}}$ results for $d=0$. Only as the cation moves off-center does the system gain polarization energy. Recent Hartree-Fock calculations [13] show that enclosed Li$^+$ ion moves off-center by $d=1.297$ Å, while the off-center distance of the larger Na$^+$ is only $d=0.574$ Å. The corresponding energy gain $E_{\text{pol}}$ has determined to be 0.31 eV for Li@C$_60$ and only 0.02 eV for Na@C$_60$ [13]. These values are in good agreement with our results for the polarization energy determined using the above geometries and assuming complete charge transfer between the alkali atom and C$_60$ in eq. (4), namely, $E_{\text{pol}}=0.32$ eV for Li@C$_60$ and 0.03 eV for Na@C$_60$.

Our geometry optimization, based on the minimization of $E_{\text{pol}}$, indicates that for most of the elements considered here the gain in $E_{\text{pol}}$ is strongly reduced by the repulsive M-C$_60$ interaction $E_{\text{rep}}$. Only in selected cases, such as B and Al, is $E_{\text{pol}}$ not strong enough to compensate for the polarization gain $E_{\text{pol}}$, which is maximal (and theoretically infinite) at the radius $R$ of the spherical metal shell representing C$_60$.

Our results for the formation energy $E_F$ and the equilibrium geometry of donor compounds M@C$_60$ are presented in table 1 and those for acceptor compounds in table 2. Among the donors, we find that all the alkalies and heavy alkaline earthy elements form stable endohedral complexes. None of the group IIA and IIIB elements treated, with the exception of Y, form stable compounds. Only the early lanthanide-based M@C$_60$ are endohedral complexes. Among the trivalent lanthanides, La forms the most stable endohedral compound. This agrees with the experimental finding that La can be trapped relatively easily in the larger fullerene [23]. Sm, Eu and Yb have also been observed in the divalent state, and the corresponding ionic radii are available [24]. For this reason, we have also included results for the 2$^+$ state of these elements in table 1. Our results indicate that Sm$^{2+}$, Eu$^{2+}$ and Yb-based complexes are likely to contain these atoms in their divalent rather than trivalent state. The preferential valency is, of course, reflected in a larger stability of the complex. We feel that definitive predictions of the stable valency are premature due to energy uncertainties for some steps in the Born–Haber cycle, and therefore list results for very stable M@C$_60$ complexes, in agreement with the observation of facile production of such metallofullerenes as U@C$_{60}$ [25].

Table 1 displays many trends that have been observed in mass spectrometric studies. For example, Ross and co-workers showed from analysis of both positive and negative ion spectra that La@C$_{60}$ and La@C$_{70}$ are formed preferentially over Y@C$_{60}$ and Y@C$_{70}$ and that Y@C$_{60}$ are formed preferentially over the analogous Sc@C$_{60}$ species [26]. They point out that the concentration of M@C$_{60}$ shows the same trend as the first ionization potential of M=Sc, Y, La with having the lowest and the highest first ionization potential [26]. Recent work with the surface analysis by laser ionization (SALI) mass spectrometric method agrees with this trend assignment for Sc, Y, and La metallofullerenes [27]. Further, temperature-programmed desorption and laser desorption data obtained for primary metallofullerenes produced under identical conditions show significantly different spectral patterns of M@C$_{60}$ for Sm, Eu, and Yb as compared to the other elements studied (La, Ce, Pr, Nd, Gd, Tb, Ho, Er, Lu, Y, Sc) [27]. In fact, mass-spectral patterns for Sm, Eu, and Yb metallofullerenes matched best those from primary metallofullerenes of Ca and Sr. Alkaline earth elements that always exhibit the +2 oxidation state [27]. We would also like to point out that although it is true that the first ionization potentials of Sc, Y, and La show a trend which matches the trend observed for metallofullerenes concentrations, the same trend also exists for the sum of the first three ionization potentials, and Sc, Y, and La are only seen in nature (with the exception of some very unstable compounds) in the +3 oxidation state [24]. It seems likely [26,27] that charge-transfer complexes of type M$^{3+}$C$_{60}$ are the precursors of these metallofullerenes.

Table 2, which contains corresponding results for acceptor atoms, indicates that none of the group VIA and VIA elements are likely to form stable ionic endohedral M@C$_{60}$ complexes. In order to get the second electron affinity (A(M$^+$)) of group VIA elements, which are unstable as isolated doubly charged ions, we proceed as follows. We noted that the total energy of isolated M$^{2+}$ ions, as determined by spin-polarized local density functional (LDA) calculations [28], shows a quadratic dependency on the charge $-x$ across a very large range of charge states from singly ionized to single negatively charged ions. An extrapolation of these results to the M$^{2+}$ state has been used to get the affinities A(M$^+$) from the corresponding total energy differences. The A$^+$ values, listed in table 2, are probably a high estimate for the formation energies of group VIA and VIA elements. For these systems, we expect a substantial amount of covalent bonding between M and the C$_{60}$ cage, which was neglected in our calculations of E$_{f}$=E(M@C$_{60}$).

For atoms such as oxygen, typical covalent bond strengths with carbon-based systems exceed by far the positive value of A$^+$ and hence would make the corresponding endohedral complex stable. Of course, covalent bonding is not restricted to positions inside or outside the C$_{60}$ cage but could occur inside the shell. The stability of such complexes is well beyond the scope of this Letter.

The great stability of alkali endohedrals, and the instability of corresponding group VIA complexes, can be most easily understood by considering the first step in the Born–Haber cycle shown in fig. 1. The energy investment for this step is only about 2 eV for alkali atoms, but typically 4 eV for the halide elements. This energy difference dominates differences in A$^+$ values, since the gain in Coulomb energy upon formation of the endohedral complex from free ions is the same in both cases. While the ionization potentials of the alkalies lie only $\approx 2$ eV above the electron affinities of the halides, the ionization potential of C$_{60}$ lies almost 5 eV above its electron affinity value, i.e. A(M$^+$)$=2.74$ eV [12].

This makes an electron transfer from the C$_{60}$ to an enclosed acceptor atom more difficult than the charge transfer from a donor atom to the C$_{60}$ cage. The general validity of this rule is reflected in our numerical results presented in tables 1 and 2.
Another advantage of the Born–Haber cycle is its straightforward applicability to other carbon fuller- enes. The main modifications in the numerical values used in eqs. (2) and (3) are the electron affinity (or the ionization potential) and the radius of the fullerene. A fullerene radius larger than that of the C$_{60}$ molecule will likely reduce the repulsive interaction between the enclosed ion and the cage while increasing the polarization energy $E_{pol}$. These effects, however, are minor when compared to those on the ionization step and to the gain in Coulomb energy upon formation of the endohedral complex M@C$_{60}$.

The polarization energy of the C$_{60}$, which is discussed above, not only stabilizes the off-center position of the enclosed ion inside the cage but also plays an important role in the formation of the endohedral complexes. In the limiting case of a metallic shell representing the C$_{60}$ cage, the potential energy gain associated with the cage polarization would be infinite whenever an ion approaches the shell surface. The corresponding gain in kinetic energy could assist the ion in the penetration of the cage from outside and hence the formation of the M@C$_{60}$ complex.

We do not expect that the transfer of typically less than three electronic charge, from the enclosed ion and the cage would significantly modify the dielectric properties of the C$_{60}$ cage, which contains 240 valence electrons [1,7]. Specifically, we do not expect the static polarization and the dielectric frequency to differ much between C$_{60}$ and M@C$_{60}$. The static dielectric moment of the M@C$_{60}$ system will depend sensitively not only on the off-center displacement of the ion and the M@C$_{60}$ charge transfer but also on the screening capacity of the cage. A metallic shell, such as a Faraday cage and completely screen the field of the enclosed ion outside the cage. In a realistic description, the C$_{60}$ cage does not provide perfect screening of the enclosed field, so a non-zero electric dipole moment of the M@C$_{60}$ complex results. Another important effect is the breaking of the icosahedral symmetry of the C$_{60}$ molecule, which will modify the selection rules and lead to the observation of previously dipole-forbidden transitions $^6$.

$^6$ This symmetry breaking due to an off-center position of the trapped ion can be either a static or a dynamic effect; the latter is associated with the "rattling" mode of the M@C$_{60}$ system.

Perhaps the most significant effect of the trapped ion is the change in the occupation numbers of the highest occupied and lowest unoccupied orbitals of C$_{60}$ and in the corresponding bands in a solid complex of M@C$_{60}$. In the latter system, we expect an electronic structure which is very similar to that of solid M@C$_{60}$, i.e. electrostatic interactions that show superconducting properties. In M@C$_{60}$, superconductivity has been explained by a dynamical Jahn-Teller effect on individual C$_{60}$ molecules $^{[7,30]}$, which provides a channel for electron-phonon coupling. The superconducting properties of the potential M@C$_{60}$ solid, where a static Jahn-Teller effect splits the level degeneracy near the Fermi level, are not as clear. The strong coupling between vibrational and electronic modes of the charged M@C$_{60}$ molecule $^{[7,30]}$ is likely to lead to an additional mechanism to fragment electronic excitations such as the collective plasmon mode in the spirit of a Franck–Condon effect.

The relative flat potential of the ion enclosed inside the C$_{60}$ cage, reflected in only moderate values of the relaxation energy $E_{relax}$ upon off-center motion of the ion, will give rise to a new low-frequency "rattling" mode, which should be observable by infrared and Raman spectroscopy. This symmetry lowering due to the off-center position of the enclosed ion can lead to a significant distortion of the inertia tensor and a symmetry lowering of the rotational spectrum.

In summary, we used a Born–Haber cycle to determine the stability of C$_{60}$ and M@C$_{60}$ complexes. We determine the stability of C$_{60}$ complexes. We have shown that the systematics of the stability trends across the periodic table can be understood in terms of the ionization potentials and electron affinities of the endohedral atoms and the C$_{60}$ molecule. In cases where the enclosed atom is not at the cage center, the polarization energy of the cage makes an important contribution to the formation energy. Our results are in agreement with available experimental data and ab initio calculations.