

Stability of $M@C_{60}$ endohedral complexes

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$M@C_{60}$ endohedral complexes, which are based on the C_{60} molecule and contain encapsulated atoms M , would provide a unique opportunity to tailor specific properties of the C_{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_{60} intercalation compounds. We find that the formation energy of $M@C_{60}$ depends crucially on the ionization potential and electron affinity of the endohedral atom and the C_{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_{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_{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_2CsC_{60} [5]. The doped C_{60} solid contains the dopant atoms in lattice interstitial sites. A separate goal has been insertion of the dopant atoms inside the C_{60} cage itself. Endohedral complexes $M@C_{60}$, 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 ex-

pected in the electronic and phonon spectra when $M@C_{60}$ is substituted for C_{60} in the solid could produce a superconducting material, as was the case for the extrinsic intercalation of the C_{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_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, thermodynamic stability of the endohedral complexes is an important issue.

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

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hedral fullerenes have been synthesized using metal atoms such as Ca. These atoms transfer their valence charge to the lowest unoccupied molecular orbital (LUMO) [10] of the C_{60} molecule [11]. The formation energy of the endohedral molecules is crucial for their stability. Here, we present calculations of the formation energy and equilibrium structure of endohedral molecules for significant parts of the periodic table, focusing on the alkali, alkaline earth, group III, and rare earth metal elements forming donor complexes. We will also consider candidates from the VIA and halide groups; these elements constitute potential acceptor endohedral complexes that have not yet been synthesized.

The most accurate way to determine the stability of endohedral complexes involves use of *ab initio* techniques, such as the Hartree–Fock configurational interaction or local density functional formalisms. The large molecular size of these systems requires a very large basis set, which exceeds presently available computer resources. Quantum chemistry calculations at the less sophisticated Hartree–Fock level have therefore been used to calculate the ground and excited states of the endohedral complexes [12,13]. These results indicate that trapped atoms or molecules do exchange charge with the enclosing C_{60} cage. An off-center displacement of the enclosed ion, causing a polarization of the shell, stabilizes the endohedral complexes. Because of the large radius of the C_{60} molecule ($R=3.5 \text{ \AA}$), the enclosed ion is well separated from the cage. In this case, the validity of the Hartree–Fock technique and the reliability of the corresponding total energies is lim-

ited. 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 bcc A_6C_{60} compounds ($A=Na, K, Rb, Cs$) [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 ΔE_f at $T=0 \text{ K}$ of $M@C_{60}$ is defined by



If ΔE_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} . As mentioned above, we determine ΔE_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.

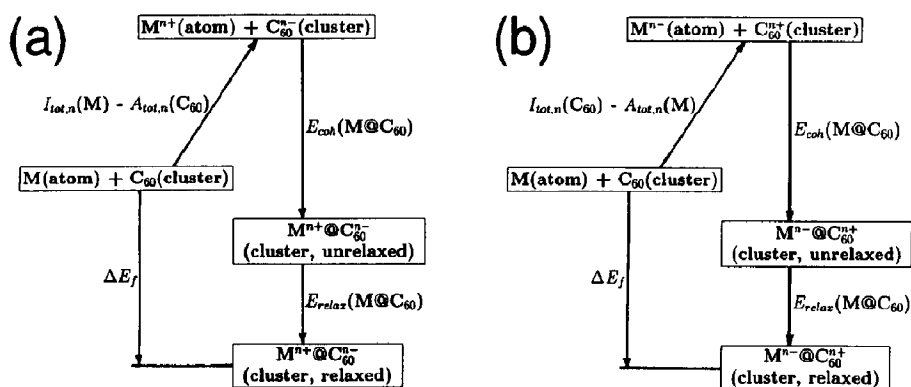


Fig. 1. Born–Haber cycle used to predict the formation energy ΔE_f of (a) donor and (b) acceptor $M@C_{60}$ endohedral complexes.

In the first step, we consider the energy involved in transferring valence electrons from the M atom to the C₆₀ molecule. This step requires the total ionization energy of the M atom, $I_{\text{tot},n}(\text{M}) = I(\text{M}) + \dots + I(\text{M}^{(n-1)+})$, where I is the ionization potential and n the number of electrons transferred. These electrons, when transferred to the C₆₀ molecule, release the energy given by the total electron affinity $A_{\text{tot},n}(\text{C}_{60}) = A(\text{C}_{60}) + A(\text{C}_{60}^-) + \dots + A(\text{C}_{60}^{(n-1)-})$. Here, A denotes the electron affinity of an individual state. In the next step of the cycle, the Mⁿ⁺ ion is brought in from infinity and placed in the center of the C₆₀ⁿ⁻ cage to form M@C₆₀. The energy gain in this step, given by $E_{\text{coh}}(\text{M}^{n+}@\text{C}_{60}^{n-})$, is mainly due to the Coulomb attraction, and is only partly reduced by the repulsive energy between the enclosed atom M and the cage. Finally, allowing the enclosed ion to move off the central site will lead to an energy gain $E_{\text{relax}}(\text{M}^{n+}@\text{C}_{60}^{n-})$. This gain is dominated by the polarization energy of the system and is only partly compensated by the increased repulsion between the enclosed ion at an off-center site and the cage. The Coulomb, the repulsive, and the polarization parts of E_{coh} and E_{relax} will be discussed in more detail below.

Hence, the total energy gain during the formation of Mⁿ⁺@C₆₀ⁿ⁻ is

$$\Delta E_f(\text{M}^{n+}@\text{C}_{60}^{n-}) = I_{\text{tot},n}(\text{M}) - A_{\text{tot},n}(\text{C}_{60}) - E_{\text{coh}}(\text{M}^{n+}@\text{C}_{60}^{n-}) - E_{\text{relax}}(\text{M}^{n+}@\text{C}_{60}^{n-}). \quad (2)$$

The corresponding Born-Haber cycle for acceptor complexes consists of very similar steps and is shown in fig. 1b. The formation energy ΔE_f of Mⁿ⁻@C₆₀ⁿ⁺ is

$$\Delta E_f(\text{M}^{n-}@\text{C}_{60}^{n+}) = I_{\text{tot},n}(\text{C}_{60}) - A_{\text{tot},n}(\text{M}) - E_{\text{coh}}(\text{M}^{n-}@\text{C}_{60}^{n+}) - E_{\text{relax}}(\text{M}^{n-}@\text{C}_{60}^{n+}). \quad (3)$$

Precise experimental data exist for the ionization potentials $I(\text{M}^{n+})$ and electron affinities $A(\text{M}^{n-})$ across the periodic table [16]. The electron affinity of the neutral C₆₀ molecule is $A(\text{C}_{60}) = 2.74$ eV [17], and its ionization potential is $I(\text{C}_{60}) = 7.54 \pm 0.04$ eV [18]. Electron affinities and ionization potentials of charged C₆₀ molecules have been estimated by Wang et al. [14]. Note that the values of the electron affinity and ionization potential of C₆₀ 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 $E_C = -n^2e^2/R$, where ne is the charge of the ion. Here, we tacitly assume that the C₆₀ molecule behaves like a charged shell of radius R . In donor systems, we consider a transfer of all n valence electrons from the enclosed M atom to the C₆₀ cage. Experimental evidence for this charge transfer has been found in complexes such as Ca@C₆₀ [11]. The energy gain given by E_C is somewhat reduced by the repulsive energy E_R between the enclosed atom M and the cage. We describe E_R in the spirit of the embedded atom method [19], as a unique function of the C₆₀ charge density ρ at the site of the trapped atom. The parametrization $E_R(\rho)$ is obtained using our previous results for the repulsive interaction between the C₆₀ cage and exohedral atoms. This repulsive interaction, given by M-C₆₀ Born-Mayer repulsive potentials [20], has been used with success to determine structural and elastic properties of bulk C₆₀ intercalation compounds [14].

The endohedral complex can be further stabilized by the polarization of the C₆₀ cage in cases where the enclosed ion is off-center. The large degree of delocalization of primarily the π system of electrons results in large calculated and measured static and dynamical polarizabilities of the C₆₀ [21], with values approaching those of a metal sphere. An analogous behavior is observed in graphite intercalation compounds with a similar π system of conduction electrons, where the interaction between donor intercalants and the graphite layers is dominated by the interaction of the cation with the induced charge [22]. For off-center sites, the gain in polarization energy is partly compensated by the increased repulsive interaction between the enclosed ion and the cage.

The upper limit for this polarization energy is obtained if we substitute a thin metallic shell for the C₆₀ molecule. The electrostatic polarization energy E_{pol} can then be obtained using the image charge method, which yields

$$E_{\text{pol}} = -n^2e^2 \frac{d^2}{2R(R^2 - d^2)}. \quad (4)$$

Here, R is the radius of the C₆₀ molecule and d is the

distance of the cation from its center.

No dipole and hence no gain in E_{pol} results for $d=0$. Only as the cation moves off the center site does the system gain polarization energy. Recent Hartree-Fock calculations [13] show that enclosed Li^+ ion moves off-center by $d=1.297 \text{ \AA}$, while the off-center distance of the larger Na^+ is only $d=0.574 \text{ \AA}$. The corresponding energy gain E_{relax} has been 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, $E_{\text{pol}}=0.32 \text{ eV}$ for Li@C_{60} and 0.05 eV for Na@C_{60} .

Our geometry optimization, based on the minimization of E_{relax} , indicates that for most of the elements considered here the gain in E_{pol} is strongly reduced by the repulsive $\text{M}-\text{C}_{60}$ interaction E_{R} . Only in selected cases, such as B and Al, is E_{R} not strong enough to compensate for the polarization gain E_{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 ΔE_{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

Table 2

Predicted formation energy ΔE_{f} and the distance d of the enclosed ion from the cage center in M@C_{60} endohedral complexes. Results are presented for acceptor elements M from the VIA and VIIA groups of the periodic table

$\text{M}^{2-}@\text{C}_{60}^{2+}$	$\text{M}^{-}@\text{C}_{60}^{+}$
O $\Delta E_{\text{f}} \leq 12.58\text{eV}$ $d=0.15\text{\AA}$	F $\Delta E_{\text{f}} \leq 0.45\text{eV}$ $d=0.0\text{\AA}$
S $\Delta E_{\text{f}} \leq 7.97\text{eV}$ $d=0.0\text{\AA}$	Cl $\Delta E_{\text{f}} \leq 1.35\text{eV}$ $d=0.0\text{\AA}$
Se $\Delta E_{\text{f}} \leq 7.13\text{eV}$ $d=0.0\text{\AA}$	Br $\Delta E_{\text{f}} \leq 2.38\text{eV}$ $d=0.0\text{\AA}$
Te $\Delta E_{\text{f}} \leq 9.31\text{eV}$ $d=0.0\text{\AA}$	I $\Delta E_{\text{f}} \leq 4.63\text{eV}$ $d=0.0\text{\AA}$

all the alkalis and heavy alkaline earths form stable endohedral complexes. None of the group IIIA and IIIB elements treated, with the exception of Y, form stable compounds. Only the early lanthanide-based M@C_{60} endohedrals are stable. Among the trivalent lanthanides, La forms the most stable endohedral compound. This agrees with the experimental find-

Table 1

Predicted formation energy ΔE_{f} and the distance d of the enclosed ion from the cage center in M@C_{60} endohedral complexes. Results are presented for donor elements M from the IA, IIA, III, lanthanide, and actinide groups of the periodic table

$\text{M}^{+}@\text{C}_{60}^{-}$	$\text{M}^{2+}@\text{C}_{60}^{2-}$	$\text{M}^{3+}@\text{C}_{60}^{3-}$	$\text{M}^{3+}@\text{C}_{60}^{3-}$				$\text{M}^{2+}@\text{C}_{60}^{2-}$
Li $\Delta E_{\text{f}} = -1.36\text{eV}$ $d=0.2\text{\AA}$	Be $\Delta E_{\text{f}} = 5.90\text{eV}$ $d=2.0\text{\AA}$	B $\Delta E_{\text{f}} = 33.27\text{eV}$ $d=R(\text{C}_{60})$	La $\Delta E_{\text{f}} = -2.53\text{eV}$ $d=1.15\text{\AA}$	Sm $\Delta E_{\text{f}} = 1.22\text{eV}$ $d=1.35\text{\AA}$	Ho $\Delta E_{\text{f}} = 1.25\text{eV}$ $d=1.50\text{\AA}$	Ac $\Delta E_{\text{f}} = -4.63\text{eV}$ $d=1.30\text{\AA}$	Sm $\Delta E_{\text{f}} = -2.71\text{eV}$ $d=0.0\text{\AA}$
Na $\Delta E_{\text{f}} = -1.54\text{eV}$ $d=0.00\text{\AA}$	Mg $\Delta E_{\text{f}} = 1.76\text{eV}$ $d=1.70\text{\AA}$	Al $\Delta E_{\text{f}} = 15.14\text{eV}$ $d=R(\text{C}_{60})$	Ce $\Delta E_{\text{f}} = -2.05\text{eV}$ $d=1.25\text{\AA}$	Eu $\Delta E_{\text{f}} = 2.80\text{eV}$ $d=1.40\text{\AA}$	Er $\Delta E_{\text{f}} = 1.20\text{eV}$ $d=1.50\text{\AA}$	Th $\Delta E_{\text{f}} = -2.07\text{eV}$ $d=1.55\text{\AA}$	Eu $\Delta E_{\text{f}} = -2.54\text{eV}$ $d=0.00\text{\AA}$
K $\Delta E_{\text{f}} = -2.02\text{eV}$ $d=0.00\text{\AA}$	Ca $\Delta E_{\text{f}} = -1.88\text{eV}$ $d=1.00\text{\AA}$	Ga $\Delta E_{\text{f}} = 12.69\text{eV}$ $d=2.35\text{\AA}$	Pr $\Delta E_{\text{f}} = -0.98\text{eV}$ $d=1.25\text{\AA}$	Gd $\Delta E_{\text{f}} = -0.22\text{eV}$ $d=1.40\text{\AA}$	Tm $\Delta E_{\text{f}} = 2.33\text{eV}$ $d=1.55\text{\AA}$		Yb $\Delta E_{\text{f}} = -1.27\text{eV}$ $d=0.8\text{\AA}$
Rb $\Delta E_{\text{f}} = -1.91\text{eV}$ $d=0.00\text{\AA}$	Sr $\Delta E_{\text{f}} = -2.88\text{eV}$ $d=0.65\text{\AA}$	In $\Delta E_{\text{f}} = 11.27\text{eV}$ $d=1.90\text{\AA}$	Nd $\Delta E_{\text{f}} = -0.38\text{eV}$ $d=1.25\text{\AA}$	Tb $\Delta E_{\text{f}} = 0.05\text{eV}$ $d=1.45\text{\AA}$	Yb $\Delta E_{\text{f}} = 3.92\text{eV}$ $d=1.55\text{\AA}$	U $\Delta E_{\text{f}} = -6.43\text{eV}$ $d=1.85\text{\AA}$	
Cs $\Delta E_{\text{f}} = -1.04\text{eV}$ $d=0.0\text{\AA}$	Ba $\Delta E_{\text{f}} = -4.08\text{eV}$ $d=0.00\text{\AA}$	Tl $\Delta E_{\text{f}} = 10.39\text{eV}$ $d=1.60\text{\AA}$	Pm $\Delta E_{\text{f}} = -0.07\text{eV}$ $d=1.30\text{\AA}$	Dy $\Delta E_{\text{f}} = 1.10\text{eV}$ $d=1.45\text{\AA}$	Lu $\Delta E_{\text{f}} = 0.52\text{eV}$ $d=1.60\text{\AA}$		
		Sc $\Delta E_{\text{f}} = 3.36\text{eV}$ $d=1.30\text{\AA}$					
		Y $\Delta E_{\text{f}} = -0.31\text{eV}$ $d=1.50\text{\AA}$					

ing that La can be trapped relatively easily in the larger fullerenes [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-, Eu-, 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 $U@C_{2n}$ [25].

Table 1 does pick up several 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 $La@C_{80}$ and $La@C_{82}$ are formed preferentially over $Y@C_{80}$ and $Y@C_{82}$; and that $Y@C_{2n}$ are formed preferentially over the analogous $Sc@C_{2n}$ species [26]. They point out that the concentration of $M@C_{2n}$ shows the same trend as the first ionization potential of $M=Sc, Y, La$, with La having the lowest and Sc 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 metallofullerene soots produced under identical conditions show significantly different spectral patterns of $M@C_{2n}$ 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 metallofullerene soots 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 metallofullerene 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 $M^{3+}C_n^{3-}$ are the precursors of these metallofullerenes.

Table 2, which contains corresponding results for acceptor atoms, indicates that none of the group VIA and VIIA 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 proceeded as follows. We noted that the total energy of isolated M^{x-} 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 ΔE_f values, listed in table 2, are probably a high estimate for the formation energies of group VIA and VIIA 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 $E_{coh}(M@C_{60})$. For atoms such as oxygen, typical covalent bond strengths with carbon-based systems exceed by far the positive value of ΔE_f 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 ΔE_f 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 alkalis lie only 1-2 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. $A(C_{60})=2.74$ eV [17]. 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 fullerenes. 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 $M@C_n$ from the ions.

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 is infinitely large 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 electrons between the enclosed ion and the cage would significantly modify the dielectric properties of the C_{60} cage, which contains 240 valence electrons [12,29]. Specifically, we do not expect the static polarizability and the σ plasmon frequency to differ much between C_{60} and $M@C_{60}$. The size of the static dipole 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 would, of course, act 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 ion 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 C_{60} by the enclosed ion, which will modify the selection rules and lead to the observation of previously dipole-forbidden transitions^{#1}.

^{#1} 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 composed of $M@C_{60}$. In the latter system, we expect an electronic structure which is very similar to that of solid M_xC_{60} exohedral intercalation compounds that show superconducting properties. In M_xC_{60} compounds, 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 C_{60} molecule [7,30] is likely to act as an additional mechanism to fragment electronic excitations such as the collective plasmon mode in the spirit of a Franck–Condon effect.

The relatively 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. The 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} -based endohedral complexes $M@C_{60}$ for elements M across the periodic table. We found that most alkalis and some other donor elements form stable $M@C_{60}$ 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.

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