

Ionicity of the M–C₆₀ bond in M@C₆₀ endohedral complexes

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Abstract

The character of the bond between encapsulated atoms and the enclosing C₆₀ shell in M@C₆₀ endohedral complexes is revisited using the density functional formalism. Mulliken population analysis indicates that this bond is strongly ionic in the case of K@C₆₀, predominantly covalent in the case of O@C₆₀, and has a mixed ionic and covalent character for Li@C₆₀. In all these cases, van der Waals forces play only an insignificant role in the M–C₆₀ interaction. The significant polarizability of the C₆₀ shell lies at the origin of the energy gain upon an off-center displacement of the encapsulated alkali ions.

One of the most interesting questions related to the intriguing M@C₆₀ endohedral complexes [1] is whether the encapsulation of atoms in the C₆₀ cage is of purely kinetic nature, or alternatively whether the M–C₆₀ bond in a given system has a predominantly ionic, covalent, or van der Waals character. In the case of not purely kinetic entrapment, one would further like to know what determines the equilibrium position of the enclosed atoms in the C₆₀ cage, and how important a role the polarization of the cage plays in the stability of the endohedral complexes.

The closed-shell nature of the C₆₀ molecule [2], with a large gap between the highest occupied and lowest unoccupied molecular orbitals, would suggest that the attractive force between the cage and the encapsulated atoms may be dominated by dispersion forces, as suggested recently [3]. Independent calculations and experiments, on the other hand, suggest the polarizability of the C₆₀ molecule to be large and comparable to that of a classical metal sphere of the

same size¹. This would suggest that encapsulated ions, when in an off-center position, may polarize the cage significantly, thus modifying the total energy of the system.

The delicate question addressing the significance of polarization effects in the total energy can be most reliably addressed in an ab initio study of the system. To answer this question, we revisited the results of our recent ab initio density functional calculation [5]. This calculation focused predominantly on an accurate determination of the M–C₆₀ interaction potential along many high-symmetry directions inside C₆₀ and gave results in good agreement with those of comparable studies [6–14]. In particular, our results for the equilibrium geometry, summarized in Table 1, show that encapsulated Li, K, and O atoms are

¹ Early theoretical and experimental results can be found in Ref. [4].

Table 1

Equilibrium properties of Li@C_{60} , K@C_{60} and O@C_{60} : off-center distance r_{eq} , Mulliken charge Q_{eq} , dipole moment p_{eq} , and binding energy (with respect to free C_{60} and encapsulant atom) E_b

	r_{eq} (Å)	Q_{eq} (e)	p_{eq} (D)	E_b (eV)
Li@C_{60}	1.5	+0.6	1.18 ^a	-1.89
K@C_{60}	0.3	+1.0	0.22 ^a	-2.25
O@C_{60}	2.0	-0.4	2.22 ^a	-0.06

^a The unit of the dipole moment, 1 D, corresponds to the dipole moment of an e^+e^- pair separated by 0.208 Å. The direction of the calculated dipole moments of Li@C_{60} , K@C_{60} , and O@C_{60} is from the cage center to the encapsulated ion.

most stable in an off-center position. An analysis of these results showed that the off-center displacement is often associated with a gain in Coulomb energy of the system containing encapsulated ions, which causes a polarization of the C_{60} cage.

To investigate the polarization of the endohedral systems quantitatively, we performed a Mulliken population analysis for all our geometries. Our results are presented in Fig. 1 as a function of the off-center distance, and the molecular properties at the equilibrium geometry are summarized in Table 1. These data indicate a positive charge of about 1 e or less on encapsulated Li and K atoms, and a negative charge of less than 0.5 e on oxygen. This alone

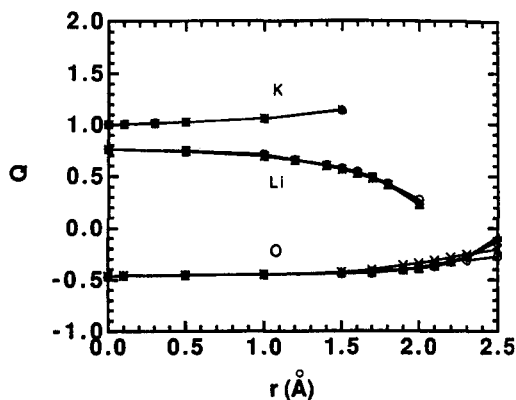


Fig. 1. Net Mulliken charge Q on encapsulated Li, K, and O atoms in C_{60} , as a function of the distance r of the enclosed atom from the center of the cage. The high-symmetry displacement directions connect the center of C_{60} and the C atoms of the cage (Δ), the centers of the C–C single bonds ($*$) and double bonds (\diamond), the centers of the hexagons (\circ), and the centers of the pentagons (\times).

would suggest that the M– C_{60} bond may be purely ionic in the case of encapsulated K, and partly ionic in the case of Li and O. This conclusion is confirmed by the investigation of the character of the bonding states in the complexes. The transition from purely ionic to increasingly covalent bonding, which we find in the order $M = \text{K}, \text{Li}, \text{O}$, is also reflected in the M– C_{60} interaction potential which is nearly isotropic for encapsulated K, less isotropic for Li, and extremely anisotropic for encapsulated O [5].

We find the O@C_{60} complex to be stable only if the oxygen atom bridges the shorter C–C ‘double’ bond, establishing an ‘inside epoxy’ bond. (In this simplified notation, we call C–C bonds shared by a pentagon and a hexagon ‘single’ bonds, and all other bonds ‘double’ bonds.) For O@C_{60} , we find the off-center position of the encapsulated atom to be dictated by the optimum way to establish a covalent bond. In the cases involving alkali ions, the Coulomb energy gain upon their off-center displacement suggests the cage polarization (and *not* the dispersion interaction [3]) is a dominant cause of this geometry change. The different judgement of this effect in Ref. [3] has been partly caused by a mistake of the authors in the image charge calculation.

The computed dipole moments of the endohedral complexes are summarized in Table 1. In the covalently bonded O@C_{60} complex, the dipole moment is entirely generated by the charge redistribution in the local vicinity of the oxygen atom. The negative Mulliken charge on the oxygen $Q_{\text{eq}}(\text{O}) \approx -0.4 e$ is compensated by a positive Mulliken charge $Q_{\text{eq}}(\text{C}) \approx +0.12 e$ on the two neighboring carbon atoms and a positive charge $Q_{\text{eq}}(\text{C}) \approx +0.03 e$ on the four next nearest neighbor carbon sites. Carbon atoms which are further away all carry a charge not exceeding 0.01 e .

The net dipole moment of O@C_{60} results from the localized charge redistribution near the encapsulated oxygen anion. The dipole moment vector points from the oxygen to the positively charged neighboring carbon cage atoms, corresponding to a dipole direction from the cage center to the encapsulated ion.

In the case of the Li@C_{60} and K@C_{60} complexes, our Mulliken population analysis indicates a partly ‘metallic’ behavior of the C_{60} cage. The off-center displacement of the enclosed alkali cations

polarizes the (negatively charged) cage by attracting electrons to their vicinity, hence in the direction of their displacement. This negative charge is found to be centered between the cage center and the encapsulated cation, resulting in a nonvanishing, but small dipole moment. (A truly metallic shell would, of course, completely screen the field of the encapsulated ions and hence carry zero dipole moment.) The direction of the net dipole moment is the same as in the case of $O@C_{60}$, namely from the cage center to the encapsulated ion. In contrast to $O@C_{60}$, the induced charge on the C_{60} cage is extensively delocalized and does not exceed the value of $0.02 e$ at any site of the cage.

We found it interesting that the ab initio potential energy data for alkali intercalants could be well represented by a simple potential [5]. The first part of this potential is reminiscent of the polarization energy gain in a hollow metallic shell enclosing an ion with the proper Mulliken charge. The second part parametrizes the rest of the energy by pairwise M–C interactions, and contains the effect of covalency as well as the van der Waals interactions in the $M@C_{60}$ complexes.

In conclusion, we found the characterization of the M– C_{60} bond as ionic most appropriate for encapsulated K atoms which transfer their full valence charge to the C_{60} shell. The Li– C_{60} bond is partly covalent, judging from the Mulliken population analysis which finds less than one protonic charge on the encapsulated Li ion. Finally, the O– C_{60} bond is predominantly covalent, judging from the small negative charge on the oxygen site, the extreme anisotropy of the O– C_{60} interaction potential, and the strong preference of oxygen for the formation of an ‘inside epoxy bond’ bridging a C–C ‘double’ bond. The off-center geometry of encapsulated oxygen is caused by the rigid C–O–C covalent bond. The off-center displacement of encapsulated alkali ions is associated with a gain in Coulomb (or polarization) energy. In none of the cases addressed above could we find dispersion interactions to play the dominating role in the off-center displacement of the encapsulated ions.

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