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Endohedral Chemistry: Electronic Structures of Molecules Trapped Inside the C_{60} Cage

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Abstract: Ab initio electronic structure calculations, carried out at the Hartree–Fock level, reveal that the C_{60} carbon cage ("footballene") is capable of encapsulating small molecules to form endohedral ("inside a cage") complexes in which the guest molecules remain positioned close to the center of the cage while being able to tumble freely. In these unusual systems, the cage acts as a polarizable sphere that stabilizes the polar molecules and destabilizes the nonpolar ones. This conclusion is drawn from studies on the $C_{60}{\cdot}H_2$, $C_{60}{\cdot}N_2$, $C_{60}{\cdot}CO$, $C_{60}{\cdot}HF$, $C_{60}{\cdot}LiH$, and $C_{60}{\cdot}LiF$ complexes for which the equilibrium bond lengths of the guests, the frequencies of vibrational and librational motions, the stabilization energies, the GAPT charges, and the dipole moments were calculated. The present study raises the possibility of the existence of endohedral complexes in which the guest molecules are expected to exhibit properties radically different from those in the gas phase.

Introduction

The recently reported[1] preparation of pure samples of the C_{60} cluster[2] is without doubt one of the most exciting discoveries in the last decade of chemistry. During the five years that have passed since the original publication describing the possible presence of the C_{60} clusters in the graphite vapors[3] an abundance of reports[4–19] on both ab initio and semiempirical electronic structure calculations dealing with the stability, ionization potentials, and the IR and UV spectra of this truly unusual molecule appeared in the chemical literature.

The recent prediction of large polarizability of the C_{60} molecule[18] prompted us to investigate the interactions present in the endohedral ("inside a cage") complexes in which atoms and ions are trapped inside the C_{60} cage. The possibility of the existence of such complexes has been already speculated on the basis of the mass spectra of the species formed by a laser vaporization of graphite impregnated with metal salts.[20] Our study on the $C_{60}{\cdot}F^-$, $C_{60}{\cdot}Ne$, $C_{60}{\cdot}Na^+$, $C_{60}{\cdot}Mg^{2+}$, and $C_{60}{\cdot}Al^{3+}$ systems[19] revealed intricate elements of the electronic structure of these complexes that play important roles in determining their properties. In particular, the C_{60} cage was found to act as a polarizable sphere, with the mean distance of the electrons from the center substantially larger than the sphere's radius (as defined by the position of the carbon nuclei). More importantly, the mixing between the orbitals of the cage and those of the guests was found to be negligible. On the basis of these observations, we predicted that sufficiently small neutral molecules should be able to form endohedral complexes in which the guest molecules are positioned near the center of the cage. The radius of the cage should remain almost unchanged from that of the free C_{60} cluster. Moreover, the large polarizability of the sphere should give rise to solvation-like effects such as stabilization of polar guests that would affect their equilibrium bond distances and vibrational frequencies.

Table I. Hartree–Fock Energies of the Molecules under Study

molecule	E_{HF} (au)	molecule	E_{HF} (au)
H_2	−1.129 052	$C_{60}{\cdot}H_2$ (D_{5d})	−2269.646 755
N_2	−108.936 459	$C_{60}{\cdot}H_2$ (D_{3d})	−2269.646 756
CO	−112.728 004	$C_{60}{\cdot}N_2$	−2377.440 808
HF	−99.997 903	$C_{60}{\cdot}CO$	−2381.229 873
LiH	−7.979 043	$C_{60}{\cdot}HF$ (C_{5v})	−2368.520 646
LiF	−106.902 361	$C_{60}{\cdot}HF$ (C_{3v})	−2368.520 684
C_{60}	−2268.519 653	$C_{60}{\cdot}LiH$	−2276.502 500
		$C_{60}{\cdot}LiF$	−2375.445 815

Table II. Calculated Stabilization Energies of Endohedral Complexes

molecule	ΔE (kcal/mol)	molecule	ΔE (kcal/mol)
H_2 (D_{5d})	1.22	HF (C_{5v})	−1.94
H_2 (D_{3d})	1.22	HF (C_{3v})	−1.96
N_2	9.60	LiH	−2.39
CO	11.20	LiF	−14.94

In this paper, we present the results of large-scale ab initio electronic structure calculations on the endohedral complexes formed between the footballene molecule and the H_2, N_2, CO, HF, LiH and LiF molecules (Chart I). These results not only confirm our predictions but also give rise to an exciting possibility of altering the chemical properties of molecules by encapsulating them in cages composed of carbon (or other) atoms.

Details of Calculations

The calculations began with placing the guest molecules under study along the 5-fold symmetry axis that connects the centers of two opposite five-membered rings of the C_{60} cage. The guest molecules were initially positioned in a symmetrical manner with the atomic coordinates determined by the optimized bond lengths of free molecules. The cage was constructed with the distances of 2.7397 au for the single and 2.5892 au for the double bonds. This yielded a cage with the radius of 6.6547 au. The distances, which correspond to the 4-31G-optimized geometry[19] of a free C_{60} cluster, were kept frozen in all calculations.

The atomic coordinates of the guest molecules were determined in an iterative manner. Each iteration consisted of a series of three Hartree–Fock energy, dipole moment, and gradient calculations carried out with the 4-31G basis set on the cage and DZP basis set on the guests. Such a choice of basis sets allows for a reasonably accurate description of the

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(2) Also known as footballene, soccerballerene, buckminsterfullerene, [60]-fullerene, or simply fullerene.

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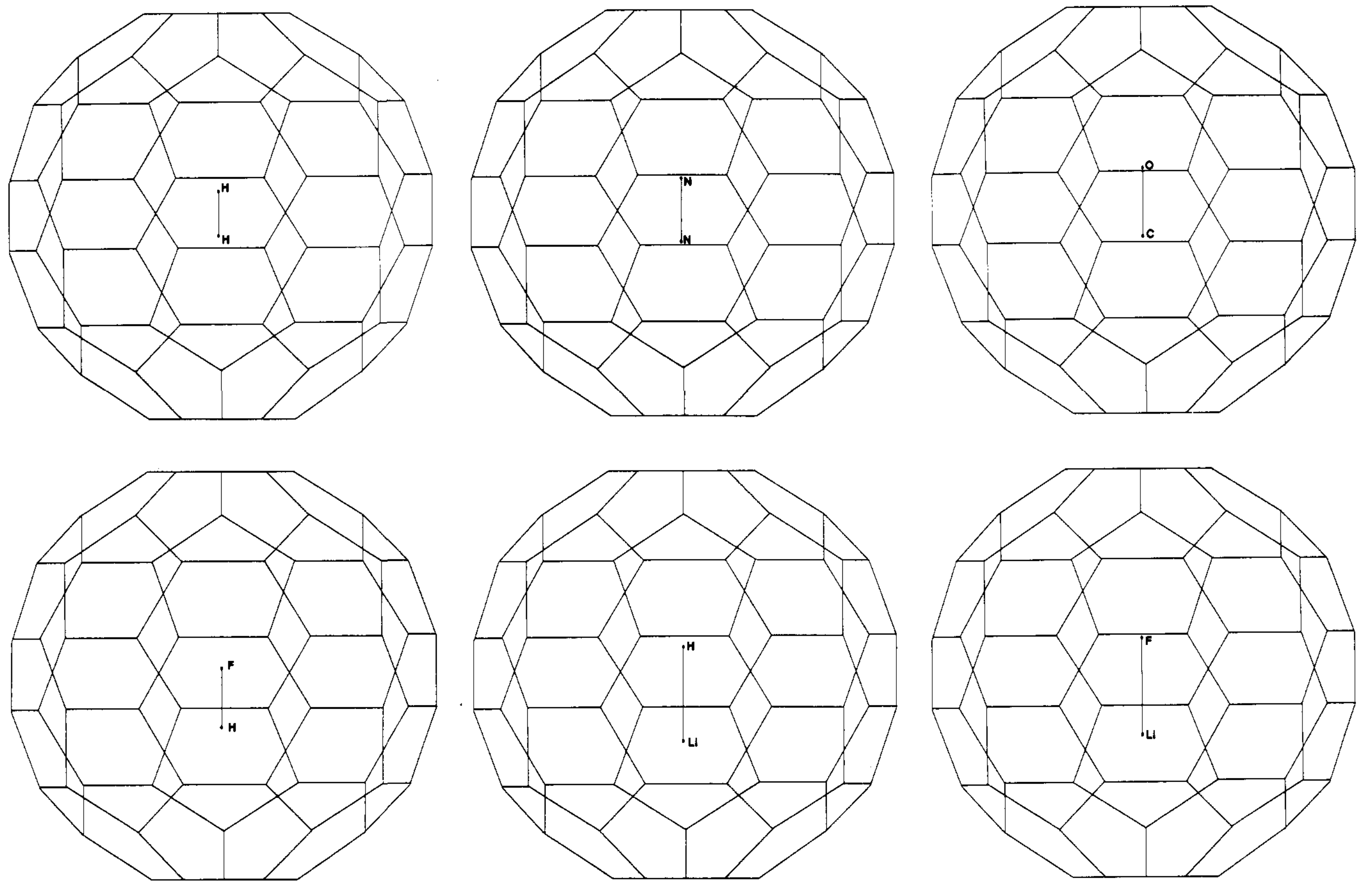
Chart I



guest molecules without requiring an excessive amount of computer time. One should remark that, due to the relatively large separation of the guest and the cage, the basis set superposition error between the two components of the complexes is very small. One calculation was carried out for the input geometry, while in the two others the nuclei of the guest were slightly displaced along the molecular axis. The displacement was equal to 0.01 au in the first iteration and 0.001 au in the subsequent ones. Each iteration produced an estimate of the equilibrium geometry (which was used in the next iteration), together with the force constants and the nuclear derivatives of the dipole moments (both by finite differences). The iterations were carried out until the equilibrium geometries were determined within ca. 0.0001 au. This usually required three iterations.

For the H_2 and HF guests, complexes with C_{3v} (D_{3d} for homonuclear guests) symmetry were studied in addition to the ones with C_{3v} (D_{5d} for homonuclear guests) symmetry. Properties of these complexes were calculated by performing the aforementioned optimization process with the guest molecules positioned along the 3-fold symmetry axis connecting two opposite six-membered rings. This optimization was ca. 6 times more expensive than the one for the C_{5v} geometries.

The GAPT charges[21] for the atoms of the guest molecules were calculated from the computed nuclear derivatives of the dipole moments. All calculations were performed with TURBOMOLE system of programs[22] running concurrently on several DEC 5000 workstations. The entire project required ca. 6000 h of CPU time.

Results

The calculated Hartree–Fock energies of the C_{60} cage, the guests, and the complexes are listed in Table I. The stabilization energies, computed from the respective differences of the Hartree–Fock energies, are given in Table II. It is evident that formation of the endohedral complexes from nonpolar or slightly polar molecules, such as H_2, N_2, and CO, is an endothermic process. On the other hand, polar molecules, such as HF, LiH, and LiF, are stabilized by encapsulation in the C_{60} cage. The encapsulation has a profound effect on the equilibrium bond lengths, vibrational frequencies, and dipole moments of the guest molecules. This is supported by the data presented in Table III. The equilibrium bond lengths of the trapped H_2, N_2, CO, and LiH molecules are slightly smaller than those in the free molecules. The bonds in the HF and LiF molecules lengthen upon encapsulation. In the latter molecule, the bond length increases by more than 0.04 Å!

Table III. Calculated Equilibrium Bond Lengths, Stretching Vibrational Frequencies, and Dipole Moments

	in vacuo			endohedral complex		
molecule	R (au)	ν (cm^{-1})	μ (au)	R (au)	ν (cm^{-1})	μ (au)
H_2 (D_{5d})	1.4108	4591.8	0.000	1.4047	4681.3	0.000
(D_{3d})				1.4047	4687.4	0.000
N_2	2.0262	2776.9	0.000	2.0208	2811.3	0.000
CO	2.0925	2458.2	−0.072	2.0871	2488.3	−0.034
HF (C_{5v})	1.7045	4452.9	−0.761	1.7058	4448.0	−0.168
(C_{3v})				1.7059	4461.4	−0.170
LiH	3.0238	1464.0	−2.303	3.0117	1526.1	−0.568
LiF	2.9240	1007.1	−2.549	3.0037	909.7	−0.611

Similar changes are observed in the vibrational frequencies of bond stretching. The largest positive change (90 cm^{-1}) is observed for the $C_{60}{\cdot}H_2$ complex. The other complexes exhibit much smaller (mostly positive) changes, the C_{60}·LiF system being the only exception. In this complex, the frequency is shifted downward by 97 cm^{-1}. As predicted by our previous calculations,[19] the C_{60} cage screens the dipole moments of the trapped molecules, decreasing them almost uniformly by a factor of 4. The same relative decrease is observed for the GAPT atomic charges in the guest molecules, which are given in Table IV. The effect of the encapsulation on the equilibrium bond distances, the vibrational frequencies, the dipole moments, and the GAPT atomic charges

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Table IV. Calculated Librational Frequencies, Optimized Cartesian Coordinates of Nuclei, and the GAPT Atomic Charges

molecule	ν_{libr} (cm^{-1})	z^a (au)		Q_{GAPT}	$Q_{\text{GAPT}}{}^b$
C_{60}·H_2 (D_{5d})	222.2	H,	−0.7023	−0.001	0.000
		H,	0.7023	−0.001	0.000
(D_{3d})	220.6	H,	−0.7024	−0.001	0.000
		H,	−0.7024	−0.001	0.000
C_{60}·N_2	182.4	N,	−1.0104	−0.013	0.000
		N,	1.0104	−0.013	0.000
C_{60}·CO	194.9	C,	−0.8613	0.129	0.361
		O,	1.2257	−0.154	−0.361
C_{60}·HF (C_{5v})	84.5	H,	−1.6026	0.105	0.416
		F,	0.1032	−0.107	−0.416
(C_{3v})	81.1	H,	−1.6278	0.103	0.416
		F,	0.0780	−0.104	−0.416
C_{60}·LiH	293.2	Li,	2.1709	0.170	0.637
		H,	0.8409	−0.172	−0.637
C_{60}·LiF	154.2	Li,	2.0080	0.206	0.890
		F,	0.9957	−0.219	−0.890

[a] With respect to the center of the carbon cage. [b] In vacuo.

is almost the same in the complexes with the C_{5v} and the C_{3v} symmetries. The same is true of the stabilization energies (Table II).

As in the case of the C_{60}·Ne complex, the equilibrium positions of the guest molecules close to the center of the cage are true minima on the respective potential energy hypersurfaces. This is reflected by the computed librational frequencies. Except for the C_{60}·H_2 and the C_{60}·N_2 molecules, the guest molecules are positioned asymmetrically with respect to the cage center (Table IV). It appears that the C_{60} cage is capable of accommodating all of the molecules under study without much steric hindrance.

A final comment concerning the calculated HOMO and LUMO orbital energies is in place. Although, for obvious reasons, these energies vary considerably among the molecules in vacuo, the HOMO and LUMO orbital energies of the complexes fall within a very narrow range (0.0036 au for ϵ_{HOMO} and 0.0018 au for ϵ_{LUMO}). Inspection of the orbital coefficients reveals that these HOMOs and LUMOs are invariably the MOs of the C_{60} cage. In the complexes with the C_{5v} symmetry, the H_u HOMO of the C_{60} molecule is split into $A_2 \oplus E_1 \oplus E_2$, whereas the T_{1u} LUMO splits into $A_1 \oplus E_1$. Which of these components has the highest or the lowest energy depends on the guest molecule.

Discussion and Conclusions

The properties described above are consistent with the description of the endohedral complexes as composed of polarizable spheres of carbon atoms with freely tumbling guest molecules "suspended" inside. Contrary to the complexes with ions,[19] the neutral guests do not exhibit the tendency to displace considerably from the cage center. The presence of almost free rotation is of a practical importance, since it allows one to carry out electronic structure calculations for highly symmetrical orientations of the guests without the loss of generality.

There is a negligible charge transfer between the cage and the guest. The only role the carbon cages play in these complexes is to provide reaction fields in response to the electric fields generated by the guest molecules and to provide a steric hindrance that allows for confinement of the guests. This results in stabilization of polar molecules and weakening of ionic bonds. These effects are clearly visible in the C_{60}·LiF complex. On the other hand, the steric effects cause the overall destabilization of nonpolar molecules and shortening of covalent bonds. The stabilization or destabilization can be as large as 15 kcal/mol. While the reaction field effects depend on the dipole moment of the guests, the steric hindrance increases with their size.

It is obvious from the above discussion that the endohedral complexes are bound to occupy a unique place in chemistry. They resemble the inclusion complexes, such as clathrates, intercalation compounds of graphite, and complexes of calixarenes or crown ethers. At the same time, the interactions between the carbon cages and the guests are reminiscent of the solvation effects described within the continuum models in which the solute molecules are placed inside hollow spheres or ellipsoids.[23,24] However, unlike in the solvents composed of randomly oriented molecules or in the inclusion complexes with flexible hosts, the geometry of the cage and the positions of the guests with respect to the cage are well-defined. This makes it possible to study the electronic structure of endohedral complexes with rigorous quantum-mechanical methods. Results of such calculations will aid in better understanding of solvation effects.

The data presented in this paper can serve two purposes.

Firstly, should the endohedral complexes be isolated (presumably among the products of laser vaporization of an impregnated graphite or a pristine graphite evaporated in the presence of a gaseous guest), the calculated properties can provide means for an independent confirmation of the experimental results. In particular, the calculated vibrational frequency shifts and the librational frequencies, which according to our estimates are accurate within 10–20%, can aid in interpretation of the experimental IR and Raman spectra.

Secondly, the present calculations clearly demonstrate that the recent isolation of the C_{60} cluster may well signal the arrival of a new kind of chemistry: the endohedral chemistry. By manipulating the size and composition of the cages, one may expect to be capable of altering the properties of trapped molecules. This may allow one to design clusters that would act as molecular-scale reaction tanks in which particular chemical reactions can be favored or suppressed. The experimental possibility of transferring the guest molecules into and out of the C_{60} cage has been speculated upon recently.[25] In fact, similar principles are involved in the zeolitic catalysts that are widely used in the chemical industry. However, the endohedral complexes, unlike the zeolites, are amenable to ab initio electronic structure calculations, which makes them particularly attractive to both the theorists and the experimentalists interested in rational design of new materials and in carrying out novel chemical reactions.

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