

## Theoretical Studies of the $C_{60}$ and Alkali Metal-Containing Complexes $C_{60}M^*$

ZHANG Daren<sup>†</sup>, WU Ji'an<sup>‡</sup>, KONG Jing<sup>\*</sup>, YAN Jimin<sup>\*</sup>

<sup>†</sup>Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing 100085

<sup>‡</sup>Institute of Semiconductors, Academia Sinica, Beijing 100083;

and Laboratory for Quantum Optics, Academia Sinica, Shanghai 201800

<sup>\*</sup>Institute of Chemistry, Academia Sinica, Beijing 100080

(Received 20 July 1992 )

The electronic structures of  $C_{60}$  and  $C_{60}M$  ( $M=Li, Na, K, Rb$  and  $Cs$ ) were calculated by using an atom superposition and electron delocalization molecular orbital method. The results indicate that  $s$  valence electron of the atom of alkali metal was completely transferred to  $5T_{1u}$  orbital of  $C_{60}$ . The stabilization energy of the system results mainly from the electrostatic interaction between polarized  $C_{60}$  and alkali metal atom.

PACS: 36. 90. +f, 31. 20. Pv

Although the football-shaped  $C_{60}$  molecule was already suggested by Japanese chemists in 1970s,<sup>1,2</sup> it stimulates intense interest only after the discovery of the compound in experiments in 1985.<sup>3</sup> Besides  $C_{60}$ , its intracage complexes (endohedral complexes)<sup>4,5</sup> and extracage complexes<sup>6</sup> have also been observed. The endohedral complexes,<sup>7</sup> in which atoms or ions are trapped inside the cage resulting in an encapsulation complex, may construct new materials. They have also strongly attracted the attentions of both chemists and physicists. Therefore, a great number of experimental<sup>6,8-11</sup> and theoretical<sup>7,12-16</sup> investigations on  $C_{60}$  and its complexes were undertaken.

Electronic structure calculations of  $C_{60}$  molecule have been carried out using *ab initio*<sup>12,13</sup> and some semiempirical<sup>14,15</sup> methods, respectively. In this work, atom-superposition and electron-delocalization molecular-orbital (ASED-MO) theory<sup>17,18</sup> was used to optimize the geometries of the  $C_{60}$  and  $C_{60}M$  ( $M=Li, Na, K, Rb$  and  $Cs$ ) and to calculate their electronic structures. The stabilities of these complexes and the interactions between  $C_{60}$  and guest metal atoms are revealed based on our calculated results.

The semiempirical ASED-MO method,<sup>17,18</sup> in which the repulsive energy was taken into account, improved the extended Hückel molecular orbital (EHMO) method. The method is based on partitioning molecular charge density into perfectly-following (on the nuclei) spherical atomic components and non-perfectly-following components, e.g. for a diatomic molecule a-b

$$\rho(\mathbf{r}, \mathbf{R}_b) = \rho_a(\mathbf{r}) + \rho_b(\mathbf{r} - \mathbf{R}_b) + \rho_{\text{npf}}(\mathbf{r}, \mathbf{R}_b), \quad (1)$$

where  $\mathbf{r}$  and  $\mathbf{R}_b$  are electron and nuclear coordinates placing the coordinate origin on nucleus a. The electrostatic force on nucleus b is

$$\mathbf{F}(\mathbf{R}_b) = \mathbf{F}(\mathbf{R}_b, \rho_a, Z_a) + \mathbf{F}(\mathbf{R}_b, \rho_{\text{npf}}), \quad (2)$$

\*Supported in part by the National Natural Science Foundation of China.

where  $Z_a$  is the nuclear charge of atom  $a$ . The interaction energy is the integral of Eq. (2) times  $-1$

$$E(R_b) = E_R(R_b) + E_{\text{npf}}(R_b), \quad (3)$$

where

$$E_R(R_b) = Z_b \left[ \frac{Z_a}{R_b} - \int \frac{\rho_a(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_b|} d\mathbf{r} \right] \quad (4)$$

is the repulsive energy. Though  $E_R$  is easy to be calculated, it is impossible to evaluate  $E_{\text{npf}}$  straightforwardly. Fortunately, the energy obtained from an EHMO calculation is generally a good approximation of  $E_{\text{npf}}$ , and Hamiltonian used in ASED-MO has the form:

$$H_{ii}^{aa} = -(\text{VSIP})_i^a, \quad (5)$$

$$H_{ij}^{ab} = 1.125(H_{ii}^{aa} + H_{jj}^{bb})S_{ij}^{ab}\exp(-0.13R), \quad (6)$$

where VSIP is the valence-state ionization potential,  $R$  is the internuclear distance and  $S_{ij}$  is the overlap integral.

Table 1: Orbital exponents ( $\xi$ ) and ionization potentials (VSIP) used in the calculation.

Atom		C	Li	Na	K	Rb	Cs
$\xi$	$s$	1.8174	0.6396	0.8358	0.8738	0.9969	1.0605
	$p$	1.7717					
VSIP(eV)	$s$	16.59	5.392	5.139	4.341	4.180	3.890
	$p$	11.26					

All the parameters used in the calculations are given in Table 1. The VSIP's are taken from experimental measurements.<sup>19</sup> The orbital exponents are taken from self-consistent-field atomic wave functions.<sup>20,21</sup> But for C atom, a scaling factor of 1.13

Table 2: Calculated and experimental bond lengths ( $\text{\AA}$ ) of  $C_{60}$ .

Method	Single bond	Double bond	Reference
STO-3G	1.465	1.376	12
DZ basis set	1.453	1.369	13
4-31G	1.450	1.370	7
MNDO	1.474	1.400	14
INDO/2	1.451	1.398	15
x-ray	1.432	1.388	23
<sup>13</sup> C NMR	1.450	1.400	24
ASED-MO	1.457	1.389	This work

was introduced, the orbital exponents of C have successfully been used in the calculations of graphite and diamond.<sup>22</sup> The molecules calculated in the study have a truncated icosahedron structure, i.e.  $I_h$  symmetry.  $C_{60}$  molecule consists of 20 six-membered rings and 12 regular five-membered rings. Two different bond lengths, i.e. C-C bond lengths for six-six ring fusions (double) and six-five ring fusions (single), need to be optimized.

In Table 2 the optimized bond lengths are presented along with ones obtained by other calculation methods or experiments reported in the literature. The bond lengths obtained by ASED-MO theory in this calculation are in good agreement with experimental values, and are even better than those obtained by *ab initio* method. Placing alkali atoms Li, Na, K, Rb and Cs at the center of  $C_{60}$  cage, the corresponding bond lengths of molecules were also optimized. The obtained results are given in Table 3. It

is obvious that the introduction of alkali metal atoms into  $C_{60}$  cage was accompanied by only slight changes in geometry. The larger the  $s$ -orbital radius of the metal atom is, the stronger the shrinkage of the  $C_{60}$  cage is, i. e. the stronger the interaction between the  $C_{60}$  cage and central metal atom is.

Table 3: Optimized bond lengths and cage radii of  $C_{60}$  and  $C_{60}M$ .

Central atom	Single bond length (Å)	Double bond length (Å)	Radius (Å)
None	1.4568	1.3887	3.5492
Li	1.4527	1.3901	3.5440
Na	1.4498	1.3897	3.5390
K	1.4463	1.3851	3.5294
Rb	1.4432	1.3822	3.5218
Cs	1.4428	1.3816	3.5207

Some energy levels of  $C_{60}$  and  $C_{60}M$ , including two lowest orbitals and frontier orbitals, are listed in Table 4. We find the  $s$ -orbital electrons of all alkali metal atoms were transferred to the lowest unoccupied molecular orbital (LUMO)  $5T_{1u}$  of  $C_{60}$ . This charge transfer is easy to un-

derstand because the  $s$ -orbital energies of alkali metal atoms are far higher than LUMO orbital energy of the  $C_{60}$ . In  $C_{60}$  molecule  $A_g$  orbitals can interact with  $s$ -orbitals of metal atoms, but only the energy of  $1A_g$  has changed and become lower and lower with the increase of  $s$ -orbital radii of metal atoms (see Table 4).

Table 4: Energies of two lowest orbitals ( $1A_g$  and  $1T_{1u}$ ) and some frontiers of  $C_{60}$  and  $C_{60}M^*$ .

Molecule	$C_{60}$	$C_{60}Li$	$C_{60}Na$	$C_{60}K$	$C_{60}Rb$	$C_{60}Cs$
Orbital symmetry	Energy (eV)					
$1A_g$	-24.0780	-25.5694	-26.0054	-28.9401	-30.9533	-34.1260
$1T_{1u}$	-23.7328	-23.7508	-23.7675	-23.7993	-23.8242	-23.8280
	⋮	⋮	⋮	⋮	⋮	⋮
$4G_g$	-12.4746	-12.4694	-12.4685	-12.4754	-12.7793	-12.4802
$7H_g$	-12.4459	-12.4477	-12.4500	-12.4557	-12.4598	-12.4605
$4H_u$	-11.8064	-11.7978	-11.7935	-11.7938	-11.7924	-11.7925
$5T_{1u}$	-10.2129	-10.2246	-10.2257	-10.2059	-10.1943	-10.1916
$2T_{1g}$	-9.5968	-9.6053	-9.6030	-9.5754	-9.5577	-9.5540
$8H_g$	-8.3930	-8.3659	-8.3439	-8.3092	-8.2803	-8.2761

\*  $4H_u$  and the orbitals lower than it are completely filled. On the frontier  $5T_{1u}$  the occupation number is 0 and 1 for  $C_{60}$  and  $C_{60}M$ , respectively.

The shake-up spectra of the x-ray photoemission of  $C_{60}$  indicated that the lowest electronic transition is 1.9 eV.<sup>16</sup> The highest occupied molecular orbital (HOMO) ( $4H_u$ )  $\rightarrow$  LUMO ( $5T_{1u}$ ) transition is calculated at 1.6 eV. The result can reasonably compare with the experiment, considering the limit of a single electronic configuration applied in this calculation.

The stabilization energy defined by the difference between the total energy of a complex and the sum of energies of its separated components can directly be obtained in our calculations and are listed in Table 5. We found that the complexes become more

stable with the increase of *s*-orbital radii of containing metal atoms. The orbital interactions between C<sub>60</sub> and metal atoms are small as mentioned above, the stabilization energy could be mainly considered as result of the electrostatic interaction of polarized C<sub>60</sub> and metal atom. The energy gaps between LUMO and HOMO are nearly identical for C<sub>60</sub>M and far less than the one of C<sub>60</sub>. All values of energy gaps are also listed in Table 5.

Table 5: Calculated stabilization energies (eV) and energy gaps (eV) between LUMO and HOMO.

Center atom	None	Li	Na	K	Rb	Cs
Stabilization		8.077	9.249	15.820	19.810	26.255
Energy gap	1.5935	0.6192	0.6227	0.6306	0.6366	0.5976

In summary, the calculated results indicate that the *s* valence electron of alkali metal in C<sub>60</sub>M is completely transferred to C<sub>60</sub> cage, hence the alkali metals and C<sub>60</sub>M might be used as donors in C<sub>60</sub> solid. The stabilization not only results from the interaction between orbitals of C<sub>60</sub> and M, but also the electrostatic interaction of polarized C<sub>60</sub> and M, and the later is more important.

## References

- [1] E. Osawa, *Kagaku* 25(1970) 854 (in Japanese).
- [2] Z. Yoshida *et al.*, *Aromaticity* (Kagakudojin, Kyoto, 1971) 174 (in Japanese).
- [3] H. W. Kroto *et al.*, *Nature*, 318 (1985) 162.
- [4] J. R. Heath *et al.*, *J. Am. Chem. Soc.* 107 (1985) 7779.
- [5] F. D. Weiss *et al.*, *J. Am. Chem. Soc.* 110 (1988) 4464.
- [6] J. R. Heath *et al.*, *J. Chem. Phys.* 87 (1987) 4236.
- [7] J. Cioslowski *et al.*, *J. Chem. Phys.* 94 (1991) 3730.
- [8] P. J. Benning *et al.*, *Science*, 252 (1991) 1417.
- [9] M. J. Rosseinsky *et al.*, *Phys. Rev. Lett.* 66 (1991) 2830.
- [10] K. Holczer *et al.*, *Science*, 252 (1991) 1154.
- [11] S. P. Kelty *et al.*, *Nature*, 352 (1991) 223.
- [12] L. D. Raymond *et al.*, *Chem. Phys. Lett.* 125 (1986) 465.
- [13] H. P. Luthi *et al.*, *Chem. Phys. Lett.* 135 (1987) 357.
- [14] M. D. Newton *et al.*, *J. Am. Chem. Soc.* 108 (1986) 2469.
- [15] J. Feng *et al.*, *Int. J. Quantum Chem.* 37 (1990) 5599.
- [16] J. H. Weaver *et al.*, *Phys. Rev. Lett.* 66 (1991) 49.
- [17] A. B. Anderson, *J. Chem. Phys.* 62 (1975) 1187.
- [18] A. B. Anderson *et al.*, *J. Phys. Chem.* 91 (1987) 4245.
- [19] W. Lotz, *J. Opt. Soc. Am.* 60 (1970) 206.
- [20] E. Clementi *et al.*, *J. Chem. Phys.* 38 (1963) 2686.
- [21] E. Clementi *et al.*, *J. Chem. Phys.* 47 (1967) 1300.
- [22] K. Nath *et al.*, *Phys. Rev. B* 41 (1990) 5652.
- [23] J. M. Hawkins *et al.*, *Science*, 252 (1991) 312.
- [24] C. S. Yannoni *et al.*, *J. Am. Chem. Soc.* 113 (1991) 3190.