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ELECTRONIC STRUCTURES AND CONDUCTIVITIES OF HALOGEN-CONTAINING CARBON-SIXTY $C_{60}X$

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Recently it has been reported that solids K_xC_{60} and Rb_xC_{60} ($x=1$—5) can be transformed to conductors[1,2]. If $x=0$ and 6, they are insulators and if $x=3$, they have the largest conductivities. When the temperature goes down to 18K for solid K_xC_{60} and to 28K for solid Rb_xC_{60}, they are transformed to superconductors. These results are very interesting to scientists. Solids K_xC_{60} and Rb_xC_{60} are very unstable in air, so that for practical purposes it is better to synthesize the atom-containing carbon-sixty MC_{60} or $C_{60}X$, in which the metal atom M or non-metal atom X is at the center of C_{60} cage. It has been known experimentally for some years that the atoms other than carbon atom C can enter into C_{60} cage to form atom-containing MC_{60} or $C_{60}X$[3,4].

The electronic structure of carbon-sixty C_{60} has been calculated by some quantum-chemical methods in recent years[5-11], but up to now, the electronic structures for the atom-containing carbon-sixty MC_{60} or $C_{60}X$ have not been calculated. In our another paper[12], C_{60} and MC_{60} (Li, Na, K, Rb, Cs) are computed with EHMO method, and the conductivities of the solid carbon-sixty C_{60} and the solid metal-containing carbon-sixty MC_{60} are discussed. Furthermore, the halogen-containing carbon-sixty $C_{60}X$ (F, Cl, Br, I) are calculated by EHMO method in this paper, then the conductivities of them and $C_{60}X_y$ ($y=0$—10) are discussed in terms of the electronic structures.

1 COMPUTATIONAL METHOD AND MODEL

The EHMO method is used in computation. The orbital exponents ζ's and the

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valence state ionization potentials H_{ii}'s used are as shown in Table 1.

Table 1 The orbital exponents and the valence state ionization potentials (eV)

	C	F	Cl	Br	I
ξ	1.6250	2.6000	2.0330	2.3000	1.9750
H_{ii}(s)	-21.4000	-40.1000	-25.3000	-24.5000	-20.7600
(p)	-11.4000	-18.6000	-13.7000	-12.6000	-11.1500

The computational model for $C_{60}X$ is that the long C-C bond length in 12 regular pentagons is 1.465Å and the short C-C bond length in 20 hexagons is 1.376Å [6] and the halogen atoms X (F, Cl, Br, I) are put at the center of the carbon-sixty C_{60}. The distances between X and each C are 3.551Å. The coordinates of X and each carbon atoms are fixed according to the bond lengths mentioned above and the symmetry of $C_{60}X$.

Using EHMO method to calculate the electronic energy and ASED method to calculate repulsion energy of atom-pairs, the obtained geometrical parameters of the carbon-sixty C_{60} is in agreement with the experimental values [13]. That is to say that the EHMO method is basically feasible for C_{60} systems.

2 RESULTS OF CALCULATION AND DISCUSSION

In Table 2, it is interesting to see that the halogen-containing carbon-sixty $C_{60}X$ (F, Cl, Br, I), in which the halogen atoms X's are put at the center of carbon-sixty C_{60}, are more stable than C_{60} for $C_{60}F$, slightly stable than C_{60} for $C_{60}Cl$ and $C_{60}Br$, and less stable than C_{60} for $C_{60}I$.

Table 2 Energies and stabilities of C_{60} and MC_{60} (eV)

	$E_{C_{60}X}$	E_X	$\Delta E_{C_{60}X}$*
C_{60}	-4206.98		
$C_{60}F$	-4387.24	-173.20	-7.06
$C_{60}Cl$	-4327.58	-119.10	-1.50
$C_{60}Br$	-4319.08	-112.00	-0.10
$C_{60}I$	-4297.06	-97.27	7.19

* $\Delta E_{C_{60}X} = E_{C_{60}X} - (E_X + E_{C_{60}})$

Some important energy levels of C_{60} are shown in Table 3. It has been shown that all the energy levels of C_{60} are of 3-degeneracy, 4-degeneracy and 5-degeneracy except four energy levels having non-degeneracy, in which three of them, HO-31,

HO-17 and HO-16, have symmetry character a_g.

Table 3 Distribution and degeneracy of the energy levels of C_{60} MO (eV)

	HO-31	HO-30	HO-23	HO-17	HO-16	HO-15	HO-14	HO-3	HO-2	HO-1	HOMO
L	-31.82	-31.25	-20.56	-15.63	-15.24	-15.03	-14.62	-12.31	-12.11	-12.07	-11.49
D	$1(a_g)$	$3(t_u)$	$3(t_u)$	$1(a_u)$	$1(a_g)$	$3(t_u)$	$3(t_u)$	$4(g_g)$	$5(h_g)$	$5(h_g)$	$5(h_u)$
	LUMO	LU+1	LU+2	LU+3	LU+4	LU+9	LU+17	LU+24	LU+29	LU+30	LU+31
L	-9.78	-9.00	-7.84	-7.72	-6.60	2.08	15.88	38.27	61.10	70.47	71.57
D	$3(t_u)$	$3(t_g)$	$5(h_g)$	$3(t_u)$	$5(h_u)$	$3(t_u)$	$1(a_u)$	$3(t_u)$	$4(g_g)$	$4(g_u)$	$3(t_g)$

* L—Level, D—Degeneracy, HO-31—Begining level, LU+31—Ending level

C_{60}	$C_{60}F$	F	$C_{60}Cl$	Cl	$C_{60}Br$	Br	$C_{60}I$	I
$38.27t_u$	$38.27t_u$		$38.27t_u$		$38.27t_u$		$38.27t_u$	
$2.08t_u$	$2.08t_u$		$2.08t_u$		$2.08t_u$		$2.12t_u$	
$-9.78t_u$*	$-9.78t_u$*		$-9.78t_u$*		$-9.78t_u$*		$-9.78t_u$*	
$-11.49h_u$**	$-11.49h_u$**		$-11.49h_u$**		$-11.49h_u$**		$-10.17t_u$**	
								$-11.15t_u$
					$-12.45t_u$	$-12.60t_u$		
			$-13.54t_u$	$-13.70t_u$			$-13.88a_g$	
$-14.61t_u$	$-14.62t_u$		$-14.62t_u$		$-14.62t_u$		$-14.62t_u$	
$-15.03t_u$	$-15.02t_u$		$-15.11t_u$		$-15.07a_g$			
$-15.24a_g$	$-15.24a_g$		$-15.12a_g$		$-15.08t_u$		$-15.15t_u$	
$-15.63a_g$	$-15.63a_g$		$-15.63a_g$		$-15.63a_g$		$-15.63a_g$	
	$-18.60t_u$	$-18.60t_u$						
							$-20.51a_g$	
$-20.56t_u$	$-20.56t_u$		$-20.56t_u$		$-20.56t_u$		$-20.56t_u$	
								$-20.76a_g$
					$-24.44a_g$	$-24.50a_g$		
			$-25.25a_g$	$-25.30a_g$				
$-31.25t_u$	$-31.25t_u$		$-31.25t_u$		$-31.25t_u$		$-31.26t_u$	
$-31.82a_g$	$-31.81a_g$		$-31.84a_g$		$-31.84a_g$		$-31.89a_g$	
	$-40.10a_g$	$-40.10a_g$						

*LUMO **HOMO

Fig.1 The situation of linear combination about the abomic orbitals s and p of X with the a_g and t_u molecular orbitals of C_{60}

Since the orbitals s and p of X (F, Cl, Br, I) are of symmetry a_g and t_u respectively, according to the principle of symmetry match, the orbitals s and p of X are only linearly combined with 3 non-degenerate(a_g) and 7 3-degenerate (t_u) molecular orbitals of the carbon-sixty C_{60} respectively, leaving the other molecular orbitals of C_{60} unchanged. The situation of linear combination is shown in Fig.1. From Fig.1 it can be seen that the energy levels of $C_{60}X$ (F, Cl, Br) are simply the addition of those of C_{60} and X, i.e. the energy levels of C_{60} are mixed only slightly

with those of X, but the energy levels of C_{60} are mixed with those of I some more, where the HOMO of $C_{60}I$ is a little different from that of C_{60}, i.e. the former (-10.17 eV) is higher that the latter (-11.49eV). That is to say that putting iodine into the center of C_{60} can increase the HOMO energy from C_{60} to $C_{60}I$ by 1.32eV. The data of electronic structures given above would be very useful for the discussions of their physical and chemical properties. We would like to discuss the conductivities of the solids C_{60}, $C_{60}X$ and $C_{60}X_y$ in the next paragraph using these data.

For molecular crystal, there is a rule about band-position and band-width [14,15]. The solids C_{60}, $C_{60}X$ and $C_{60}X_y$ are molecular crystals, in which at the lattice point is molecule. The distances between the atoms in different molecules are longer than chemical bond, so that the band-positions are around the corresponding energy levels of molecules C_{60}, $C_{60}X$ and $C_{60}X_y$ respectively and the band-widths are much narrow. According to the results and the principle mentioned above, the conductivities of the C_{60}, $C_{60}X$ and $C_{60}X_y$ ($y=0$—10) can be discussed as follows.

The energy gap, i.e. the difference between LUMO and HOMO, of C_{60} is 1.71 eV, which is too large to be conquered by thermal motion, and then the energy band corresponding to LUMO and HOMO are empty and full respectively, so C_{60} is an insulator. This is in agreement with the experimental results.

To put halogen atoms X(F,Cl,Br,I) into the carbon-sixty C_{60} cage only weakly affects its components and the distributions of the energy levels, so only weakly affects the energy-band structure of the solid C_{60}. Therefore, the entering of X (F,Cl, Br, I) into carbon-sixty C_{60} only offers carriers as an electron acceptor. At this situation, the energy-bands corresponding to the HOMO of molecules $C_{60}X$ are unoccupied ones with hole carrier, so that the solid halogen-containing carbon-sixty $C_{60}X$ (F, Cl, Br, I) are good conductors.

For the solids $C_{60}X_y$ ($y=0$—10), although X(F, Cl, Br, I) are not at the center but are located in the gaps between molecules C_{60}, because of longer distance between C and X than a C—X chemical bond, the energy-band distribution of C_{60} will be slightly affected similar to the situation of the solid halogen-containing carbon-sixty $C_{60}X$. Since the HOMO of C_{60} is of 5-degeneracy, so that for the solids $C_{60}X_y$ ($y=0$—10), if not considering the constraint of the gap space in solid, the concentration of carriers in the energy-bands gradually increase when $y=0\rightarrow1\rightarrow2\rightarrow3\rightarrow4\rightarrow5$ and so do conductivities of them; furthermore, the concentration of carriers in the energy-bands gradually decreases when $y=6\rightarrow7\rightarrow8\rightarrow9\rightarrow10$ and so do the conductivities of them. The HOMO becomes empty when $y=10$ and then the solids $C_{60}X_y$ are transformed to insulator.

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含卤原子碳六十 $C_{60}X$ 的电子结构及导电性

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关键词：碳六十 福勒烯 伯克明斯脱福勒烯 $C_{60}X$

摘要 用量子化学 EHMO 方法对碳六十 C_{60} 及含卤原子碳六十 $C_{60}X$ (F, Cl, Br, I) 的电子结构进行了计算。据此，对 C_{60}、$C_{60}X$ 及 $C_{60}X_y$ (y = 1—10)的导电性进行了讨论。