Articles

A Theoretical Study of Electronic Structure and Properties of the Neutral and Multiply Charged C_{60}

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The electronic structures and properties of the neutral and multiply charged C_{60}^{n} ions ($n=2+$ to $6-$) with spin states have been investigated by semi-empirical MNDO calculations. In the ground state, C_{60}^{1-} has the lowest total energy and the highest binding energy. The neutral C_{60} ion is supposed to have a high ionization potential and a high electron affinity. The HOMO and LUMO positions are lower in the cationic C_{60} than in the anionic C_{60}. The LUMO energy becomes increasingly positive from C_{60}^{1-} to C_{60}^{6-} and the HOMO energy becomes increasingly negative from C_{60}^{2+} to C_{60}. The HOMO-LUMO gap of the neutral C_{60} ion is higher than that of the multiply charged C_{60} ions. From the HOMO-LUMO gap, it seems reasonable to expect that electrons of the multiply charged C_{60} ions will be more polarizable than those of the neutral C_{60} ion. The HOMO and LUMO energies increase as the negative charge increases.

Introduction

The recent discovery[1] and synthesis[2] of C_{60}, the so-called fullerene or Buckminsterfullerene, have provoked a widespread investigation into the properties of this molecule. The applications of C_{60} and its derivatives show promise as an optical limiters[3] and as an enhancement of photoconducting properties for some polymers.[4] C_{60} solid with a doping alkali metal, called fulleride, has superconductor properties.[5~8] The alkali-fulleride superconductor, X_nC_{60}, represents transition temperatures; 19, 28 and 30 K for X=K, Rb, and Cs, respectively. In order to obtain and understand new C_{60} derivatives, Boheme and co-workers[9~10] synthesized many C_{60} derivatives with small or organic molecules using the multiply charged C60. They showed that these multiply charged C_{60} ions have specific characteristics in chemical reactions.

Until now, many theoretical works[11~15] have for the most parts investigated the structural, electronic, and spectroscopic properties of the neutral C_{60} ion by many theoretical methods. The multiply charged C_{60} ions are very important to the fullerene materials and its chemical reactivities, because these ions have the variety of multiplicity and different electronic characteristics than the neutral C_{60} ion. In this paper, we have considered of the neutral and multiply charged C_{60}^{n} ions ($n=2+$ to $6-$) with spin states. In order to understand the electronic structures and properties of these ions, we have used semi-empirical restricted Hartree-Fock (RHF) MNDO[16] calculations. The total energies, relative energies, and binding energies of the neutral and multiply charged C_{60} ions on the ground states have also been discussed.

Computational Methods

The generation of the starting geometry for C_{60} was done by Stanton[17] by stereographic projection and a dual graph method. In this work, the initial structure of C_{60} was created by molecular modeling, HyperChem,[18] and the geometry of the neutral C_{60} ion was completely optimized by MNDO calculations on the basis of the Polak-Ribiere[19] optimizer with symmetry-unrestricted geometry. The optimization conditions are convergence limit of 0.01, iteration limit of 150, and iteration of root-mean square gradient of 0.1 kcal/Åmol.

In order to study the electronic structures of the neutral and multiply charged C_{60} ions, one must consider spin states on the ground states. For closed- and open-shell system, the C_{60} ions have four spin states according to odd and even numbers of electrons, respectively. These spin states are singlet, doublet, triplet, and quartet. Also, spin multiplicity, which is related to the total spin angular momentum, is 1 for a singlet state, 2 for a doublet 3 for a triplet, and 4 for a quartet.

All the calculations of the multiply charged C_{60} ions have been performed with the quantum mechanics of semi-empirical restricted Hartree-Fock MNDO. With RHF MNDO method, pseudo-RHF calculations can also be performed for open-shell systems in the C_{60} ions. This method is well-known as the RHF half-electron technique.[20] The calculation produces a set of molecular orbitals appropriate for this pseudo-wave function, assigns the unpaired electron its proper spin, and substitutes this electron in the orbital formerly occupied by the half electrons.

The binding energies (E_b) of the neutral and multiply charged C_{60} ions with spin state were obtained from the difference between total energies of the neutral or multiply charged C_{60} ion and the summation of the ground state elect-

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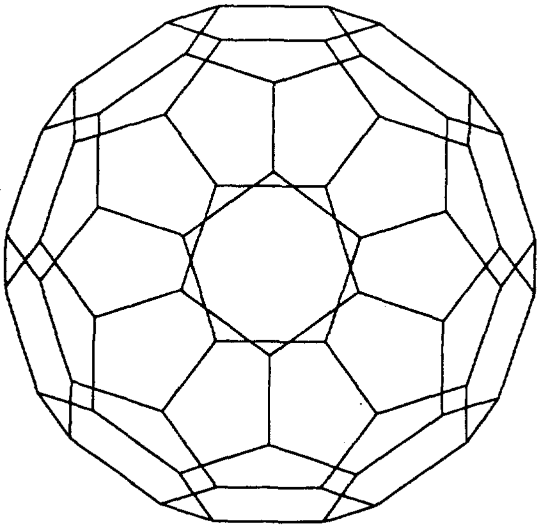

Figure 1. Completely optimized geometry of the C_{60} ion.

Table 1. C-C bond lengths and diameter of the neutral C_{60} ion

C-C bond length (Å)		Diameter (Å)	
Calc.	Expt.	Calc.	Expt.
1.40, 1.47	1.40, 1.45[a]	7.173	7.113[b]
1.40, 1.474[c]	1.401, 1.458[b]		7.000[d]

[a]Ref. 25. [b]Ref. 12. [c]Ref. 26. [d]Ref. 21.

ronic energy of the isolated C atom, that is,

$$E_b=[E_{tot}(C_{60}{}^n)-\sum E(\text{C Atom})]/60$$

where E_{tot} is the total energy of $C_{60}{}^n$ and E is the energy of the carbon atom. And, n is 2+ to 6− charge of the neutral or multiply charged C_{60} ion.

Results and Discussion

Optimized geometry of the neutral C_{60}. For the neutral C_{60} ion, the optimized geometry is shown in Figure 1. The results of the optimization calculations are listed in Table 1. The diameter of the neutral C_{60} ion is about 7.173 Å. The diameter of C_{60} is in good agreement with experimental values.[21~22] Interestingly, this diameter is nearly the same value, 7.40 Å, of a 12-ring of zeolite-Y molecular sieve.[23] The diameter of C_{60} has been considered as a possible host for various guest atoms and molecules. Due to the lobes of p orbitals, the inner and outer surfaces are covered with electrons. It has been known that the p orbitals at each vertex of C_{60} appear to have sphericalaromaticity[24] which can make various inside or outside metal-fullerene complexes. Very recently, Smalley and co-workers[25] synthesized inside and outside metal-fullerene complex as (M@C_{60}) and M(@C_{60}), respectively, where M is a metal. Also, the carbon atom at each vertex of C_{60} has sp^2 hybridization from two single bonds and one double bond. From these calculations, the single and double bond lengths for the neutral C_{60} ion are 1.47 Å and 1.40 Å, respectively. These values are in good agreement with experimental[22,26] and other theoretical values.[27] The double bonds with sharing hexagonal rings are shorter by 0.07 Å than the single bonds fused hexagonal and pentagonal rings.

Table 2. Total energies (E_{tot}), relative energies (E_{rel}), and binding energies (E_b) with spin states of the neutral and multiply charged $C_{60}{}^n$ ions (n=2+ to 6−)

n	Spin state	E_{tot}	E_{rel}	E_b
2+	s	−279.890873	21.18	−6.45
	t	−279.894172	21.08	−6.45
1+	d	−280.340137	8.94	−6.66
	q	−280.237053	11.75	−6.61
0	s	−280.669140	0.00	−6.81
1−	d	−280.767723	−2.68	−6.85
2−	s	−280.749412	−2.18	−6.84
	t	−280.752905	−2.28	−6.84
3−	d	−280.618383	1.38	−6.78
	q	−280.624194	1.22	−6.79
4−	s	−280.370728	8.12	−6.67
	t	−280.373231	8.05	−6.67
5−	d	−280.008911	17.97	−6.51
	q	−280.028664	17.43	−6.52
6−	s	−279.530762	30.98	−6.29
	t	−279.549081	30.48	−6.30

[a]The notation s, d, t, and q refers to singlet, doublet, triplet and quartet states, respectively. [b]Total energies in a.u.. [c]Relative energies in eV. [d]Binding energies in eV/atom unit.

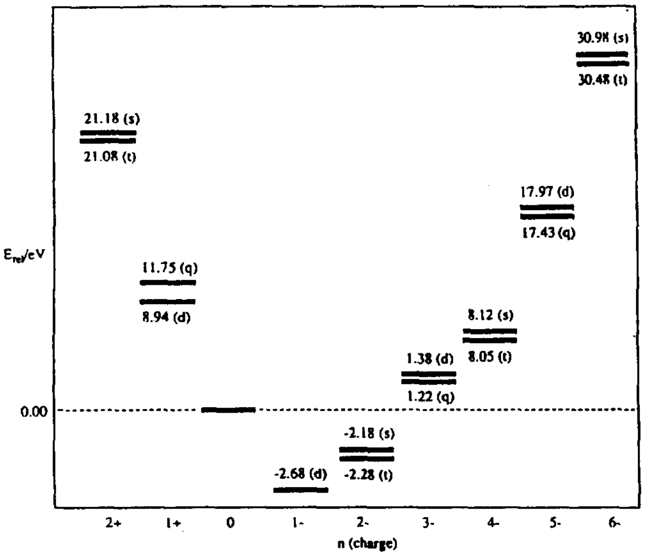

Figure 2. Relative energies of the neutral and multiply charged $C_{60}{}^n$ ions (n=2+ to 6−) with low and high spin states. The notation s, d, t, and q refers to singlet, doublet, triplet and quartet states, respectively.

Relative stability. The total energies, relative energies and binding energies of the neutral and multiply charged C_{60} ions with low and high spin states in the ground states are listed in Table 2. And, the scale of relative energies for their C_{60} ions is shown in Figure 2. The total energies

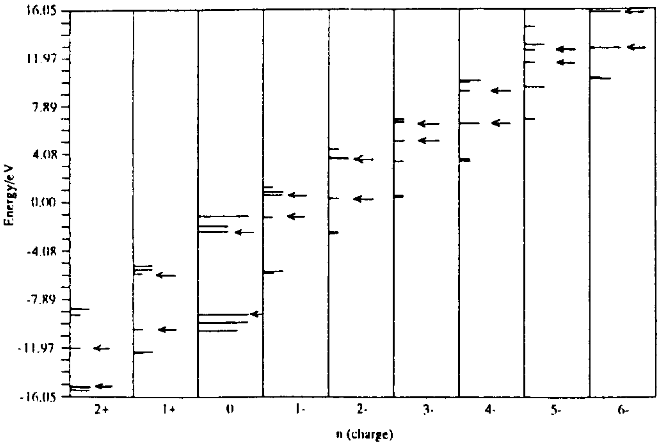

Figure 3. Molecular energy levels and degenerates of the neutral and multiply charged C_{60}^{n} ions ($n=2+$ to $6-$) with low spin states from the LUMO+2 to the HOMO−2 energy levels. Arrow are the position of the HOMO and LUMO energy levels, respectively.

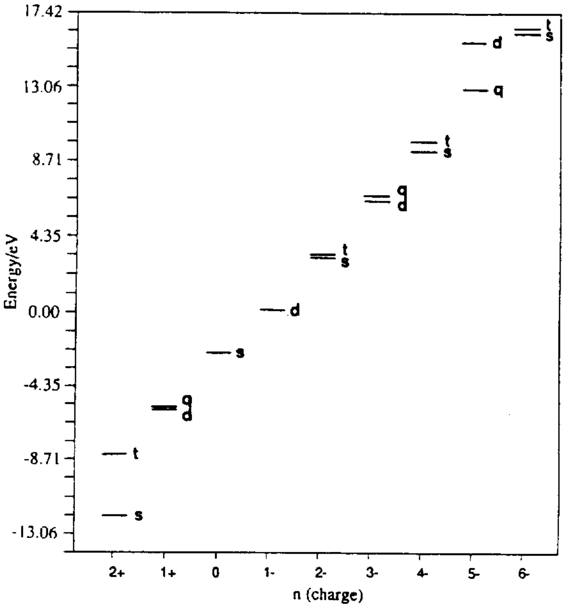

Figure 4. The HOMO energy levels of the neutral and multiply charged C_{60}^{n} ions ($n=2+$ to $6-$) with low and high spin states, respectively.

of the multiply charged C_{60} ions are in the order C_{60}^{1-}(d)<C_{60}^{2-}(s)<C_{60}(s)<C_{60}^{3-}(d)<C_{60}^{4-}(s)<C_{60}^{1+}(d)<C_{60}^{5-}(d)<C_{60}^{2+}(s)<C_{60}^{6-}(s) with low spin states and C_{60}^{2+}(t)<C_{60}^{2-}(t)<C_{60}^{3-}(q)<C_{60}^{4-}(t)<C_{60}^{1+}(q)<C_{60}^{5-}(q)<C_{60}^{6-}(t) with high spin states. It has been estimated that the lowest total energy of the neutral and multiply charged C_{60} ions in the ground state are the C_{60}^{1-}(d) and C_{60}^{2-}(t) ion with low and high spin state, respectively. In addition to relative energies of the multiply charged C_{60} ions with low spin states, C_{60}^{2+}(s) and C_{60}^{6-}(s) are less stable than C_{60}(s) by 21.18 eV and 30.98 eV, respectively. However, C_{60}^{1-}(d) and C_{60}^{2-}(s) are more stable than the C_{60}(s) by −2.68 eV and −2.18 eV, respectively. It appears that the neutral C_{60} ion has electron accepting properties. In the anionic C_{60}, the total energies of C_{60}^{1-} and C_{60}^{2-} are increase in the order C_{60}^{1-}(d)<C_{60}^{2-}(t)<C_{60}^{2-}(s). Our MNDO calculations are the same as ab initio calculations using [(9,5,1)/(4,2,1)] basis set.[28] Clementi and co-workers[28] have suggested that the total energy, E(SCF+B), obtained by adding the correlation energy correction with the Becke algorithms of ground state for C_{60}^{1+}(d), C_{60}(s), C_{60}^{1-}(d), C_{60}^{2-}(s), and C_{60}^{2-}(t) are in the order C_{60}^{1-}(d)<C_{60}^{2-}(t)<C_{60}^{2-}(s)<C_{60}(s)<C_{60}^{1+}(d). For C_{60}^{2-}, both singlet and triplet states were calculated to have C_1 symmetry, resulting in a triplet state lower in energy by 0.10 eV than a singlet state. This is in agreement with Hund's rules for atoms; that is, as multiplicity increases, so does stability.

Binding energies. The binding energies per carbon atom of the neutral and multiply charged C_{60} ions are also reported in Table 2. The computed value of the neutral C_{60} ion, −6.81 eV/atom, which is different from theoretical values[29] of −7.23 eV/atom by the generalized gradient approximation method and −8.49 eV/atom by the local density approximation method, is in agreement with the evaluated value from experimental formation energy[29] of −6.94 to −6.99 eV/atom. The difference in binding energy calculated with the experimental structure and the completely optimized structure may be small. The reason is that the bond lengths calculated with the completely optimized structure are in excellent agreement with experimental values. Also, the highest binding energy of the neutral and multiply charged C_{60} ions in the ground state is the C_{60}^{1-}(d) ion. The binding energy of C_{60}^{1-} is lower than that of infinite graphite[29] of −7.37 eV/atom. It may be explained that the difference of binding energy of C_{60} and infinite graphite is due to the strain energy of the five-membered rings.

HOMO and LUMO energies. Figure 3 presents molecular energy levels and degenerates of the neutral and multiply charged C_{60} ions with low spin states from the HOMO-2 to the LUMO+2. The length of each parallel bar is degenerate with energy levels and arrows present the HOMO and LUMO positions. The HOMO and LUMO states of the neutral C_{60} ion are 5- and 3-fold degenerate, respectively. If electrons of the neutral C_{60} ion are added or removed, it is known that the breaking of degenerates arises from the neutral C_{60} ion to the multiply charged C_{60} ions. It is true that the unequal electron populations of the LUMO for the charged C60 ions lead to distortion of the orbitals because of the Jahn-Teller effect. The HOMO and LUMO positions are lower in the cationic C_{60} than in the anionic C_{60}. The HOMO-LUMO gap of the neutral C_{60} ion is higher than that of the multiply charged C_{60} ions. The large HOMO-LUMO gap found for C_{60} is typical of molecules with a well defined closed-shell ground state. From the HOMO-LUMO gap, it seems reasonable to expect that electrons of the multiply charged C_{60} ions will be more polarizable than those of the neutral C_{60} ion.

The neutral and multiply charged C_{60} ions with low and high spin states of the HOMO and LUMO energies are shown in Figures. 4 and 5, as a function of charge. From the function of charge with the HOMO and LUMO energies, the HOMO and LUMO energies increase as negative charge increases. From Koopmans' theorem, ionization potential (IP) and electron affinity (EA) are related to the HOMO and LUMO energy, $-\varepsilon_{HOMO}=IP$ and $-\varepsilon_{LUMO}=EA$. In addition

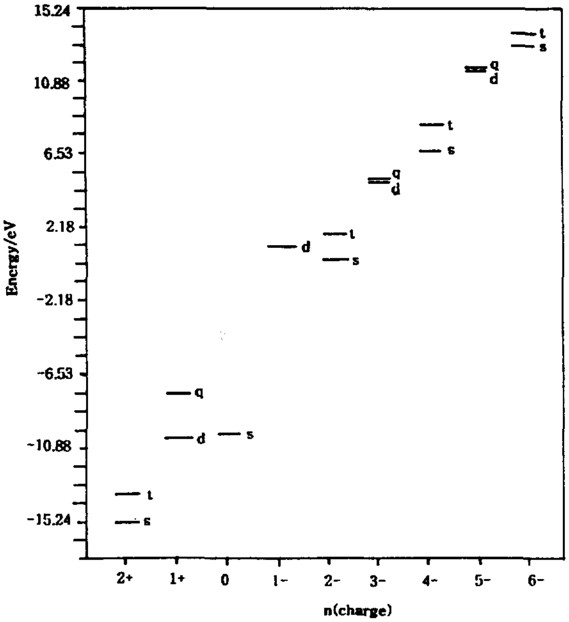

Figure 5. The LUMO energy levels of the neutral and multiply charged C_{60}^{n} ions (n=2+ to 6−) with low and high spin states, respectively.

to IP and EA, it is known that the neutral C_{60} ion has a high IP and a high EA. The LUMO energy becomes increasingly positive from C_{60}^{1-} to C_{60}^{6-}. This indicates that the electron accepting properties of C_{60}^{1-} decreases, and reductive reactions should become exceedingly difficult for $n=$ 1-~6-. On the other hand, the HOMO energy becomes increasingly negative from C_{60}^{2+} to C_{60}. In particular, the LUMO energy for the neutral C_{60} ion is negative. However, it is very interesting to note that the negative LUMOs are not common for closed-shell molecules in the RHF method. The HOMO and LUMO state of the neutral and multiply charged C_{60} ions becomes more stable with increasing positive charge. The HOMO energies are lower singlet and doublet states than triplet and quartet states for $C_{60}^{2+,1+,2-\sim6-}$. Also, the LUMO energies are lower in the singlet and doublet state than in the triplet and quartet state for $C_{60}^{2+,1+,2-\sim6-}$. Hence, the HOMO and LUMO energies of the neutral and multiply charged C_{60} ions are generally lower on low spin states than on high spin states.

The sign of the HOMO and LUMO energies is very important to chemical reactivity. The cationic C_{60} reacts to form derivatives, $C_{60}M$ (M is a small molecule such as NO, NH_3, O_2, etc.), due to its high IP and the negative HOMO energy. Recently, the charge-transfer reaction[30] of C_{60}^{2+} with NH_3 having low ionization potentials has been published. The properties of accepting electrons by C_{60}^{2+} are enhanced by a charge-transfer reaction. We will further study the chemical reaction for the neutral and multiply charged C_{60} ions.

Conclusions

On the basis of semi-empirical MNDO calculations, the electronic structure and properties of the neutral and multiply charged C_{60} ions have been investigated. The neutral C_{60} ion is supposed to have a high ionization potential and a high electron affinity. It has been confirmed that the binding energy is related to bond length geometry. C_{60}^{1-} in the ground state has the lowest total energy and the highest binding energy. The LUMO energy, which is related to electron affinity, becomes increasingly positive from C_{60}^{1-} to C_{60}^{6-} and HOMO energy becomes negative from C_{60}^{2+} to C_{60}. Also, the HOMO and LUMO energies of the neutral and multiply charged C_{60} ions are generally lower on low spin states than on high spin states.

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Improved Photoluminescence from Light-Emitting Silicon Material by Surface Modification

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A light-emitting silicon material was prepared by electrochemical etching of n-Si single crystal wafers in a solution of hydrofluoric acid and ethanol. Visible photoluminescence from the silicon was inhomogeneous and decayed rapidly in the ambient laboratory conditions or with photoirradiation. Substantial improvements in photoluminescence which include little-dependent luminescence peak energy with excitation energy variation and longer-lasting room temperature visible photoluminescence were achieved when the surface of photoluminescent silicon material was derivatized with the surface modifier of octadecylmercaptan. Surface modification of the photoluminescent silicon was evidenced by the measurements of contact angles of static water drops, FT-IR spectra and XPS data, in addition to changed photoluminescence. Similar improvements in photoluminescence were observed with the light-emitting silicon treated with dodecylmercaptan, but not with octadecane. The present results indicate that sulfurs of octadecylmercaptans or dodecylmercaptans appear to coordinate the surface Si atoms of LESi and perturb the surface states to significantly change the luminescent characteristics of LESi.

Introduction

We have been interested in electrochemically producing light-emitting silicon (LESi) materials and controlling their luminescent properties.[1~3] In this work, we describe significantly improved photoluminescent characteristics from thin porous silicon materials derivatized with surface modifiers of octadecylmercaptan and dodecylmercaptan.

Although the origin and mechanism of recent observations of room temperature visible photoluminescence from porous silicon remains unsolved,[4~8] it can be regarded as a good starting point to fabricate optoelectronic devices based on silicon material in the future as far as the phenomenon of strong light emission at the room temperature is reproducible. In the present stage of the development of science in this area, improvement of light-emitting properties of the silicon material should be considered with importance, although electroluminescence has to be eventually shown to the useful. Photoluminescence, which is visible to the naked eye in the dark laboratory conditions, is inhomogeneous and lacks long-term stability,[7~10] which may present a set of problems in fabricating devices, as is recently described by Jung.[11] Improvements in these two aspects of LESi material photoluminescence are the ones we concern in the present work. Previous efforts in this direction were made by heat treatments of porous silicon materials.[12~13]

Experimental

All the chemicals used were of the best quality available commercially. Si single crystal wafers used in the present experiments were n-type (p-doped, 10-20 Ω·cm resistivity) with (100) orientation. The Si surface was anodized in an ethanolic solution of hydrofluoric acid (1 : 1) at 5-7 V versus silver quasi-reference electrode under UV irradiation (Spectronic Co. Model ENF-240C) for 30 min. In our previous work,[1] we have anodized n-type (p-doped, 1.0-2.0 Ω·cm resistivity, (100) orientation) samples in the electrolyte solution of the same composition at 1-3 V versus platinum quasi-reference electrode under the same UV irradiation conditions for 20 min. Our present work used the experimental conditions as was described in the above because of the sample availability and convenience. Surface modifications were made by treating the luminescent silicon dried in the nitrogen atmosphere, in the pure thiol atmosphere for one day at 80 ℃. Surface-derivatized silicon materials thus prepared were washed with ethanol and water to remove unreacted surface modifiers. Because it is known that luminescent properties of LESi strongly depend on the preparation conditions of n- or p-type starting silicon chips, resistivity, current