

The electronic structure of Ca@C_{60}

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Received 15 December 1992; in final form 22 February 1993

The electronic structure of Ca@C_{60} in the gas phase was probed by ultraviolet photoelectron spectroscopy (UPS) of Ca@C_{60} . The electron affinity of Ca@C_{60} was found to be 3.0 eV. The spectrum suggests that Ca donates its two 4s electrons to the $\text{C}_{60} t_{1u}$ LUMO. Ab initio self-consistent field Hartree-Fock calculations were performed on Ca@C_{60} at four different symmetries, I_h , D_{3d} , D_{5d} , and C_{5v} . We found that the C_{5v} symmetry has the lowest energy with the central Ca^{2+} ion 0.7 Å away from the center of C_{60} and that Ca@C_{60} has a 3A_2 triplet electronic ground state in C_{5v} symmetry.

1. Introduction

Fullerenes have a unique type of inner empty space with their unusual cage-like structures. A wide variety of atoms may reside in this space with little perturbation to the fullerene cage structure. Thus, a whole new series of materials may be created with tailored physical and chemical properties by changing the inside atom. Macroscopic quantities of fullerenes with a metal atom inside were first produced for lanthanum by laser vaporization of a La_2O_3 /graphite composite rod in a high-temperature tube furnace [1]. In the sublimed film, La@C_{60} , La@C_{70} , La@C_{74} , and La@C_{82} were all present, while La@C_{82} was found to be abundant and uniquely soluble in toluene. This finding has since been confirmed by EPR [2] (electron paramagnetic resonance) and XPS [3] (X-ray photoelectron spectroscopy) probes. In fact, many rare earth elements have been found to be readily trapped inside fullerenes with one or more atoms both by the laser vaporization/high-temperature furnace technique [4] and by the carbon arc technique [5].

In this Letter, we report the first study on the electronic structure of a metal- C_{60} fullerene (Ca@C_{60}) in the gas phase with ultraviolet photoelectron spectroscopy (UPS). We found that Ca donates its two

4s electrons to the $\text{C}_{60} t_{1u}$ LUMO (lowest unoccupied molecular orbital). Our theoretical calculations predict that Ca@C_{60} has a C_{5v} Jahn-Teller distorted symmetry and a 3A_2 electronic ground state with the two 4s electrons of Ca on the C_{60} cage, consistent with our UPS experiments.

2. Experimental

Using a CaO/graphite composite rod, we have successfully produced calcium-containing fullerenes with the laser vaporization/high-temperature furnace technique, which has been described in detail earlier [1]. The CaO/graphite rod was made by mixing graphite powder (Poco Graphite Inc.) and a graphite cement (Dylon Industries Inc.), which was then compressed into a 12 mm rod and baked in an Ar atmosphere at 800 K for about 10 h. The CaO concentration in the starting composite graphite rod was very crucial to the yield. A Ca/C ratio of about 0.3% by atom was found to be optimum for making Ca@C_{60} . In particular, Ca@C_{60} was observed to be the dominant metal-containing fullerene and soluble in CS_2 and pyridine. Fig. 1 shows a mass spectrum of a dried CS_2 solution on a Cu substrate probed by a laser-desorption (6 mJ/cm², 532 nm) FT-ICR

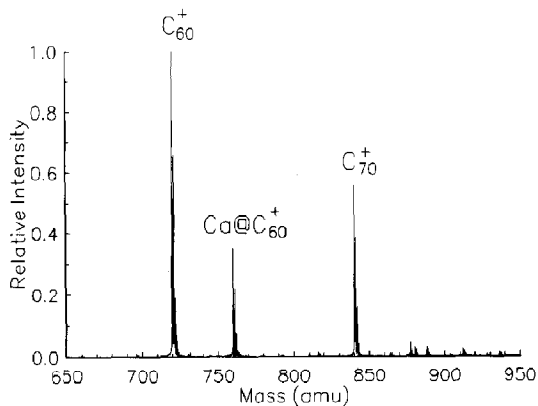


Fig. 1. Mass spectrum from laser desorption of a dried CS_2 solution containing Ca-endothedral fullerenes produced by laser vaporization of a CaO/graphite composite rod.

(Fourier Transform Ion Cyclotron Resonance) mass spectrometer with ArF excimer laser ionization. Note that besides the C_{60}^+ and C_{70}^+ signals, there is a prominent peak at the mass of CaC_{60}^+ . Small amounts of CaC_{70}^+ and CaC_{84}^+ are present, but there is little CaC_{82}^+ . XeCl excimer laser photofragmentation showed that this CaC_{60}^+ ion dissociates by successive C_2 losses, just as C_{60}^+ does. The abundances of the Ca-endothedral fullerenes appear to be quite different from those of the previously discovered rare earth endothedral fullerenes. At the optimum Ca/C ratio in the starting composite rod, the Ca-fullerene abundances are similar to those of the empty fullerenes and there appear to be few multi-Ca fullerenes.

The photoelectron spectrometer used in this experiment was described in detail before [6]. Briefly, it consists of a laser vaporization cluster source with a large waiting room nozzle [7], a time-of-flight mass spectrometer (TOFMS), and a magnetic bottle-type TOF electron energy analyzer. 1 mJ output from a Q-switched Nd:YAG laser (532 nm) was focused to a 1 mm diameter spot on a thin film of Ca@C_n /fullerenes on a Cu substrate, sublimed from soot produced as described above. The laser-desorbed materials were entrained by a He carrier gas and then expanded through a 1.5 mm diameter nozzle. After a skimmer of 6 mm diameter, the negative ions were extracted perpendicularly into the TOFMS. An ArF excimer laser (Questek 2600 series) was used as the detachment laser (1 mJ/cm^2) which was fired at 20 Hz while the PES spectrum was taken at 10 Hz with

alternating shots for background subtraction. Two spectra of Ca@C_{60}^- were taken with 30000 laser shots each and then added together to improve the statistics. The known PES spectrum of C_{60}^- was also taken in the same experimental run for calibration. The spectra were smoothed with a Savitsky-Golay smoothing routine in AXUM #1.

The resulting PES spectrum of Ca@C_{60}^- is shown in fig. 2 along with that of C_{60}^- for comparison. The background noise starts at about 3.5 eV binding energy and increases at higher binding energy. The features at 3.9 and 4.3 eV, as well as the sharp features at higher binding energies, are not real, resulting from the imperfect background subtraction. This is usu-

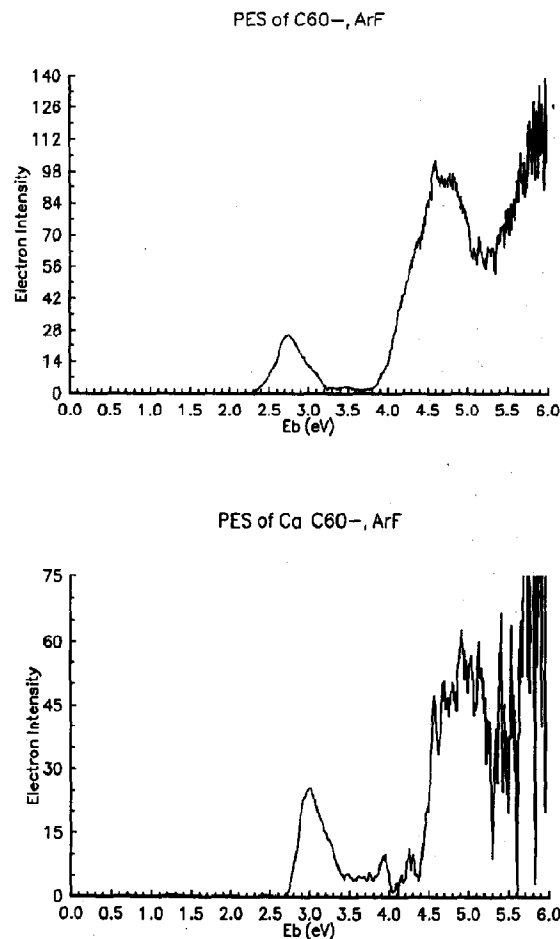


Fig. 2. Photoelectron spectrum of Ca@C_{60}^- compared with that of C_{60}^- .

ally not a serious problem when the signal-to-noise ratio is favorable, as in the case of C_{60}^- .

3. Discussion and theoretical predictions

3.1. The PES spectrum

At first glance, the spectrum of $Ca@C_{60}^-$ is very similar to that of C_{60}^- : an initial small peak followed by a large gap (≈ 1.7 eV). However, there are two important differences: (1) $Ca@C_{60}$ has an electron affinity of 3.0 eV, which is higher than that of C_{60} (2.65 eV) [7]; (2) the intensity ratio of the first peak to the second peak is larger in the spectrum of $Ca@C_{60}^-$. This ratio is about 1:10 in the spectrum of C_{60}^- , corresponding to the occupancies of the LUMO and HOMO (highest occupied molecular orbital) in C_{60}^- which has a ground state configuration of $h_u^{10}t_{1u}^1$. This ratio is about 3:10 in the spectrum of $Ca@C_{60}^-$.

It is known [8] that the outside complex KC_{60} has a lower EA than that of C_{60} , and the EAs of K_xC_{60} decrease linearly with the number of potassium atoms, largely due to electrostatic effects. It is reasonable to expect the same trend for the CaC_{60} outside complex. The electronic structure of bulk Ca_xC_{60} fullerides has been studied [9] and was found to be similar with that of the K_xC_{60} fullerides. The higher EA value in the current experiment provides indirect evidence that the CaC_{60} complex is endohedral. Interestingly, Wastberg and Rosen [10] have calculated the EA of KC_{60} both with the K atom inside and outside the C_{60} cage. They found that the KC_{60} outside complex has a lower EA value than that of C_{60} while the KC_{60} endohedral complex has a higher EA than that of C_{60} , in excellent agreement with the experimental results.

PES probes the occupied molecular orbitals of a molecule. The similarity between the spectra of $Ca@C_{60}^-$ and C_{60}^- indicates that the molecular orbitals of C_{60} are very slightly perturbed in $Ca@C_{60}$. That the intensity ratio of the first to second PES peaks increases to 3:10 in $Ca@C_{60}^-$ suggests there are three electrons in the first occupied MO in $Ca@C_{60}^-$, implying that Ca has donated both of its 4s electrons to the t_{1u} orbital of C_{60} and the interaction between Ca and C_{60} is rather ionic. As will be discussed below,

this is born out from our theoretical calculations.

3.2. Theoretical predictions

There have been several theoretical investigations about C_{60} interacting with a central atom [10–13]. Most notably, Rosen and Wastberg [10,11] have studied $M@C_{60}$, where M includes La atom and all alkaline metal atoms. In all cases, they found that the valence electrons of the central metal atom have been transferred to the C_{60} LUMO, which is stabilized in $M@C_{60}$ with respect to C_{60} , leading to higher EAs for the endohedral complexes. This is in agreement with our PES result for $Ca@C_{60}$. Very recently, Saito and Oshiyama [14] have done a local density approximation calculation on $Ca@C_{60}$ in I_h symmetry and also found a ground state electronic configuration with both Ca 4s electrons donated to the C_{60} shell. However, Chang, Ermler, and Pitzer [12] have done restricted Hartree–Fock ab initio calculations on $Ca@C_{60}$, and found that the ground state of $Ca@C_{60}$ is $^3T_{1u}$ ($a_g^1t_{1u}^1$, where the a_g orbital is from the Ca 4s orbital and the t_{1u} is from the C_{60} LUMO) while the $^3T_{1g}$ state (t_{1u}^2) is some 0.85 eV higher. This is inconsistent with our experimental evidence since a $a_g^1t_{1u}^1$ ground state configuration would give rise to two separate peaks in the UPS spectrum unless the a_g and t_{1u} orbitals are nearly degenerate.

In light of this disagreement, we have further investigated $Ca@C_{60}$ theoretically and found that indeed the two Ca 4s electrons are donated to the C_{60} shell. We also studied the effects of Jahn–Teller distortions in D_{3d} , D_{5d} , and C_{5v} symmetries.

All calculations were carried out using the direct self-consistent field (SCF) Hartree–Fock (HF) method as implemented in the TURBOMOLE package [15] with double-zeta quality basis sets. For the carbon atoms, the 7s3p primitive set of van Duijneveldt was contracted to 4s2p, which is identical to the one used for C_{60} in a previous calculation [16]. The calcium basis set originates in a (12s6p/8s4p) contraction [17]. In a few cases, diffuse p and polarization d functions were added to the Ca basis set. All geometries were individually optimized employing analytic energy gradient techniques. Our theoretical results are presented in tables 1 and 2.

In $Ca@C_{60}$ the Ca 4s orbital is energetically close to the t_{1u} LUMO of C_{60} . Thus, three classes of elec-

Table 1
Theoretical predictions for Ca@C₆₀ electronic states ^{a)}

Symmetry	Configuration ^{b)}	Electronic state	Energy (h)	ΔE (eV)
I _h	t _{1u} ² (2)	³ T _{1g}	-2945.57518	0.00
I _h	t _{1u} ² (2)	¹ H _g	-2945.56659	0.23
I _h	t _{1u} ² (2)	¹ A _g	-2945.55378	0.58
I _h	a _g t _{1u} (1)	S=1	-2945.52701	1.31
I _h	a _g ² (0)	¹ A _g	-2945.50359	1.95
D _{3d}	a _{2u} ² (2)	¹ A _{1g}	-2945.58271	0.00
D _{3d}	e _u ² (2)	³ A _{2g}	-2945.58062	0.06
D _{3d}	a _{1g} a _{2u} (1)	³ A _{2u}	-2945.57314	0.26
D _{5d}	a _{2u} ² (2)	¹ A _{1g}	-2945.58367	0.00
D _{5d}	e _{1u} ² (2)	³ A _{2g}	-2945.58028	0.09
D _{5d}	a _{1g} a _{2u} (1)	³ A _{2u}	-2945.57342	0.28
C _{5v}	e _f ² (2)	³ A ₂	-2945.59326	0.00
C _{5v}	a _f ² (2)	¹ A ₁	-2945.58898	0.12 ^{c)}
C _{5v}	a ₁ a ₁ (1)	³ A ₁	-2945.57301	0.55

^{a)} All calculations used a double zeta basis set at the SCF level of theory. All geometries were individually optimized.

^{b)} The number of Ca 4s electrons in the C₆₀ shell is given in parentheses.

^{c)} When Ca polarization functions are added the triplet-singlet energy difference increases to 0.24 eV (SCF) and 0.38 eV (BLYP) [18].

Table 2
Equilibrium bond-lengths (Å) of the ³A₂(e_f²) ground state of Ca@C₆₀ as predicted at the dz/SCF level of theory

Bond type ^{a)}	Ca@C ₆₀	Δ(Ca@C ₆₀ -C ₆₀)
1	1.445	-0.001
2	1.406	+0.023
3	1.439	-0.007
4	1.396	+0.013
5	1.446	+0.000
6	1.455	+0.009
7	1.375	-0.008
8	1.459	+0.013
9	1.441	-0.005
10	1.450	+0.004
11	1.382	-0.001
12	1.374	-0.009
13	1.450	+0.004
Ca-C	2.789	-0.733

^{a)} See fig. 3 for the bond-type definitions.

tronic states are possible with 0, 1, and 2 of the Ca 4s electrons in the C₆₀ shell. In I_h symmetry the Ca 4s orbitals transform as a_g. The electronic configurations considered are t_{1u}², a_gt_{1u}, and a_g². These configurations contain 2, 1 and 0 of the Ca 4s electrons in the C₆₀ shell, respectively. The t_{1u}² configuration results in three electronic states: ³T_{1g}, ¹H_g, and ¹A_g;

the a_gt_{1u} configuration gives rise to two electronic states: ³T_{1u} and ¹T_{1u}; and the a_g² configuration yields only one state: ¹A_g. According to Hund's rules, the ³T_{1g} and ³T_{1u} states should be the lowest in energy. For the a_gt_{1u} configuration, a mixture of triplet states (indicated as S=1 in table 1) had to be considered in our calculation due to limitations in the computational programs.

Our calculations predict that the ³T_{1g}(t_{1u}²) state, where both Ca 4s electrons are donated to the carbon cage, is the ground state in I_h symmetry. The predicted energy separations between the t_{1u}² states (³T_{1g}, ¹H_g, and ¹A_g) are identical to those obtained by Chang et al. [12], except that they found the ³T_{1u}(a_gt_{1u}) electronic state to be the ground state of Ca@C₆₀.

The I_h electronic states in table 1 with a partially occupied t_{1u} orbital are subject to Jahn-Teller distortion. Two possible components corresponding to D_{5d} and D_{3d} symmetries were analyzed. The t_{1u} LUMO of C₆₀ splits into a_{2u}+e_u and a_{2u}+e_{1u} in D_{3d} and D_{5d} symmetries, respectively. As shown in table 1, the resulting states with two electrons in the C₆₀ cage (¹A_{1g} and ³A_{2g}) are predicted to be very close in energy in both symmetries, while the ³A_{2u} state corresponding to one Ca electron donated to C₆₀ is

found to be higher in energy by 0.26–0.28 eV. The D_{3d} distortion gives slightly lower energies than D_{3d} . The ${}^1A_{1g}(D_{5d})$ state is 0.22 eV lower in energy than the ${}^3T_{1g}(I_h)$ state.

The effect of adding polarization and diffuse functions in the Ca basis set was studied for some states. Calculations with an extended 8s6p2d basis set for Ca were carried out at the double zeta D_{3d} optimized geometries. The exponents for the additional p and d functions are identical to those used by Chang et al. [12]. The calculated energy separations between electronic states are increased from 0.06 to 0.10 eV, and from 0.26 to 0.39 eV (see table 1). However, the ordering of the electronic states is not affected.

We further investigated the possibility that Ca may not remain at the center of the carbon cage. In order to let Ca move away from the center, the molecular symmetry was further reduced from D_{5d} to C_{5v} . Both the a_{2u} and a_{1g} orbitals in D_{5d} transform as a_1 in C_{5v} , whereas e_{1u} transforms as e_u . Thus, three electronic states are obtained in C_{5v} symmetry corresponding to the three states considered in D_{5d} symmetry (see table 1).

In all the C_{5v} states we find that Ca moves away from the center. The effect is more pronounced for the 3A_2 and 1A_1 states (the two Ca 4s electrons are in the C_{60} shell in these two) where the distance from Ca to the nearest C atom is predicted to be 2.79 and 2.93 Å, respectively. In the 3A_1 state, where only one Ca 4s electron is on the C_{60} shell, this distance is 3.23 Å. These results may be rationalized in terms of a favorable $Ca^{2+}-C_{60}^{2-}$ electrostatic interaction for the former cases. We also found that while the potential energy surface is very flat in the region where Ca is at the center of the C_{60} cage, it becomes very repulsive for Ca– C_{60} distances shorter than the optimum. The optimized geometry of the 3A_2 state is presented in fig. 3 with the 13 symmetry-distinct C–C bonds labelled. The equilibrium bond-lengths predicted at the double-zeta SCF level of theory are presented in table 2 and compared with previous calculations on C_{60} at the same level of theory [16]. The average deviation between the $Ca@C_{60}$ and C_{60} bond-lengths is very small, a mere 0.007 Å. We note that while the geometry distortion due to the Jahn–Teller effect ($I_h \rightarrow C_{5v}$) is very small the predicted energy lowering (0.49 eV) is substantial.

In order to test the importance of correlation ef-

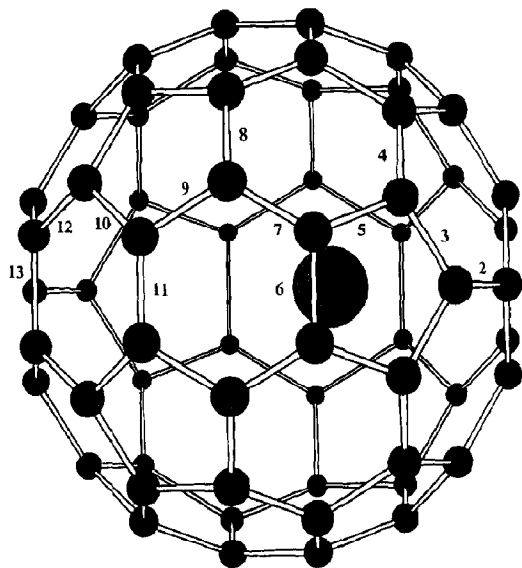


Fig. 3. Equilibrium structure of the 3A_2 ground state of $Ca@C_{60}$ as predicted at the dz/SCF level of theory.

fects we also calculated the ${}^3A_2-{}^1A_1$ energy separation in C_{5v} symmetry employing recently developed density functional methods [18]. These results which we included as footnote c in table 1 indicate that the triplet state is favored by 0.38 eV.

Thus, our theoretical studies predict that $Ca@C_{60}$ has a triplet ground state with Ca moving out of the center of the C_{60} cage. The SCF energy stabilization due to Jahn–Teller distortion from I_h to C_{5v} symmetry is 0.49 eV. Our calculations strongly indicate that the electronic states with two Ca 4s electrons in the C_{60} shell are more favorable than those where only one electron is donated, in agreement with our PES result. Evidently, still better calculations will ultimately determine the quantitative accuracy of the present predictions. We cannot rule out the possibility that $Ca@C_{60}$ may have a lower than C_{5v} ground state symmetry.

Our theoretical studies suggest that $Ca@C_{60}$ has a triplet ground state, and therefore should be detectable in an EPR experiment. We have been unable to conclusively detect this EPR signal from a CS_2 solution of the sample. This may be due to several reasons. First, we dealt with a mixed sample containing empty fullerenes and higher Ca-containing fullerenes. $Ca@C_{60}$ may form complexes with the empty fullerenes and become EPR silent. Second, it is pos-

sible that there is O₂ contamination. In our laser-desorption mass spectrum, we have seen Ca@C₆₀ oxide when using a F₂ laser for the ionization. Indeed, if Ca@C₆₀ has a triplet ground state, it is likely to be oxidized very easily by ground state O₂. It appears that a definitive confirmation will have to await a pure Ca@C₆₀ sample.

4. Conclusions

The electronic structure of Ca@C₆₀ has been investigated by photoelectron spectroscopy. The interaction between the central Ca atom and the C₆₀ cage is largely ionic, and Ca@C₆₀ is more appropriately expressed as Ca²⁺@C₆₀²⁻. Ab initio SCF calculations predict that Ca@C₆₀ has a ³A₂ C_{5v} ground state with both Ca 4s electrons transferred to the C₆₀ shell, in excellent agreement with the UPS study. Confirmation of the triplet ground state of Ca@C₆₀ will make it the first neutral open-shell fullerene with an even number of electrons. A pure crystal of Ca@C₆₀ may have novel physical and chemical properties and should be most interesting to study.

Acknowledgement

We would like to thank Professor Russel M. Pitzer and Professor Arne Rosen for helpful discussions regarding the calculations. This work was supported by the US Department of Energy, Division of Chemical Sciences, and the Robert A. Welch Foundation. GES acknowledges the National Science Foundation (Grant No. CHE-9017706).

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