PHYSICAL REVIEW A VOLUME 52, NUMBER 1 JULY 1995

Interaction sites of a Na^+ ion and a Na atom with a C_{60} molecule

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(Received 6 March 1995)

The interactions of the Na^+ ion and the Na atom with the C_{60} molecule are investigated within the formalism of unrestricted Hartree-Fock theory. Adsorption energies, structural parameters, and electronic energy levels are discussed for four and five sites inside the cage and outside the case, respectively. Possibilities of significant charge transfer from the adatom to the C_{60} molecule and subsequent decreases in the highest occupied molecular orbital–lowest unoccupied molecular orbital gaps are explored. Detailed comparisons with available experimental and theoretical data in the literature are presented.

PACS number(s): 31.15.Ar, 34.20.Gj

I. INTRODUCTION

The study of the C_{60} molecule, other fullerenes and their derivative molecules, as well as that of bulk fullerenes and fullerides is of increasing interest to many physicists and chemists, both theoreticians and experimentalists [1–10]. This interest has been fueled in part by the discovery of a superconducting phase in alkali-atom-doped C_{60} [11–12] and the potential role of C_{60} in the search for a cure for AIDS [13]. Other possible applications of technological materials based on C_{60} include nanosize wires, polymers, electronic and optical devices, and lubricants [14–16]. We present, in this paper, an *ab initio* theoretical study of the interactions of the Na^+ ion and the Na atom with a single C_{60} molecule. We first discuss some relevant literature.

In a series of papers, Schmidt, Dunlap, and White [17]; Ballaster and Dunlap [18]; and Dunlap, Ballaster, and Schmidt [19], applied the linear combination of Gaussian-type orbital (LCGTO) techniques to study the interactions of Li, Na, and K atoms and ions with the C_{60} molecule, and energy minima for Na^+ along the C_{5v} and C_{3v} axes of C_{60} were found to be displaced from the center of the fullerene by less than 1.0 Å. Near degeneracy in energy of 32 equilibrium positions along the C_{5v} and C_{3v} axes, and the possible tunneling of the ion between these equilibrium positions, were obtained. Chang, Ermler and Pitzer [20] used relativistic core potentials within the restricted Hartree-Fock (RHF) formalism to study the endohedral complexes of C_{60} with the atoms and cations of a series of elements. They found that with the alkali atom at the center of the carbon cage, the adatom donated one electron to the cage. Cioslowski and Fleischmann [21] also investigated the interactions of the C_{60} molecule with a number of ions, atoms, and molecules, within RHF theory. The complexes with the ions at the center of the C_{60} were local maxima of energy, but the position at the center of the cage was an energy minimum for interactions with the neutral Ne atom. Two other important findings were the contraction of the cage in the complexes with negative ions, and expansion with positive ions.

From the experimental point of view, the endohedral complexes of C_{60} have been of interest since the experiments of Heath *et al.* [2] in which a complex of this type was first suspected to have been formed. However, the endohedral nature of the proposed $C_{60}La$ complex was challenged by Cox and co-workers [22] and the formation of endohedral complexes was proved conclusively only after further experimental work [23–24]. Specifically Weiske and co-workers [24] accelerated fullerene monocations electrostatically and caused them to collide with helium atoms. Evidence for the formation of endohedral complexes was provided by the fact that fragmentation of the resulting complexes required activation energies of 100–130 kcal/mole, while the binding energy of the exohedral $C_{60}He$ complex is 1 kcal/mol. Recently, Beyers *et al.* [25] have succeeded in preparing pure crystals of an endohedral fullerene complex with scandium atoms. Also of relevance to the present study, in terms of identification of the favored interaction sites of the alkali atoms, is the experimental research on exohedrally Na-doped C_{60} by Rosseinsky *et al.* [26] and by Tanigaki *et al.* [27]. It is expected that the theoretical study of the interactions of an Na^+ ion with the fullerene molecule will be useful in the interpretation of experiments involving interactions with C_{60} in molecular form and studies of the interactions of the Na atom with a C_{60} molecule should be more significant in interpretation of experiments involving C_{60} in solid form.

II. INTERACTIONS OF THE NA^+ ION WITH C_{60}

The theoretical formalism used in this study is the unrestricted Hartree-Fock (UHF) formalism, and uses the 3-21G basis set to represent all the atoms [28]. The

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GAUSSIAN92 suite of programs [29] was used in all our calculations. It should be noted that the 3-21G optimized values [30] of the two distinct types of bondlengths in C_{60}, namely 1.453 and 1.365 Å, agree to within 2%, with the experimental values of 1.434 and 1.386 Å obtained by Hawkins [31]. Comparison with nuclear magnetic resonance (NMR) results of Yannoni and coworkers [32] gives agreement within 0.00 and 0.03 Å for the two bond lengths.

The first part of our calculations focused on the interactions of the Na^+ ion with the C_{60} molecule. For the Na^+ ion inside the cage, four types of interaction sites were considered: fivefold (C_{5v}), threefold (C_{3v}), midbond site on the long bond ($B1$), and the short midbond site ($B2$). For the first type of approach position, the line of approach of the adsorbate passes through the centers of the cage and one of the cage pentagons. In the threefold site, the line of approach of the adsorbate passes through the centers of the cage and a cage hexagon. The remaining two types of interaction sites are of low symmetry, and are characterized by lines of approach that join the cage center with the midpoints of the two types of bonds that are found to occur in the C_{60} molecule. For the ion outside the molecule, a total of five types of interaction sites are important, which include the four types similar to those mentioned for the ion inside the molecule, and one additional type, namely on top. In the low symmetry on top approach position, the line of approach of the ion joins the cage center to a cage atom. These interaction sites are illustrated by Fig. 1, where $B1$ and $B2$ denote the sites above the long and short bonds, respectively.

For each type of approach, the distance d of the Na^+ ion from the center of the cage was varied to minimize the total UHF energy of the system. The adsorption or interaction energy E_a is then calculated from

$$E_a = E(C_{60}) + E(Na^+) - E(C_{60}Na^+) , \tag{1}$$

where $E(C_{60})$ and $E(Na^+)$ denote the ground state energies of the separated constituents. Different spin multiplicities were, of course, considered to obtain the true ground state.

The results, in terms of equilibrium distances and adsorption energies, for the interaction of the Na^+ ion and with C_{60} are shown in Table I. The heights R of the adsorbate above the appropriate face, atom or bond of the cage, corresponding to the equilibrium distances d, are also displayed for the cases of adsorption of Na^+ outside the cage (see Fig. 2). For the ion inside the cage the adsorption energy is 1.47 eV for all four adsorption sites, which is in general agreement with the results obtained by other researchers [17,21]. However, counting the 20 hexagons, 12 pentagons, and 60 bonds in C_{60}, this gives 92 energetically degenerate minima inside the cage compared to the 32 observed by Schmidt, Dunlop, and White [17]. Our value for adsorption energy is about five times the value of 0.29 eV obtained by Cioslowski and Fleischmann [21], and 16.7% larger than the value of 1.26 eV found by Dunlap, Ballaster, and Schmidt [19]. Examining the lowering of the total energy of the complex in moving from the cage center to the equilibrium position, we obtain a value of 0.029 eV compared to the value of 0.036 eV calculated by Cioslowski and Fleischmann, and the value of 0.12 eV obtained by Ballaster and Dunlap [18]. The large discrepancy with the value of Ballaster and Dunlap [18] is probably due to the use of local density approximation used by them [33]. In terms of the

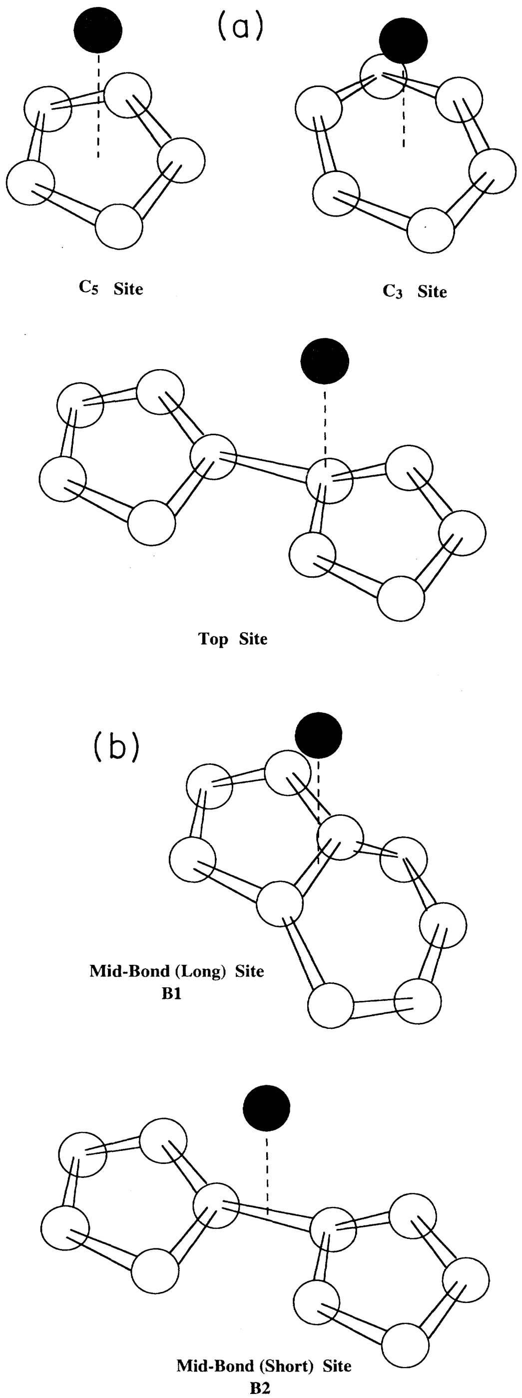

FIG. 1. Lines of approach for the interaction of Na^+ and Na with the C_{60} molecule. The white circles denote fullerene atoms, while the dark circles denote the adsorbate. $B1$ and $B2$ denote the lines passing through the long and short bonds, respectively.

TABLE I. Equilibrium distances and adsorption energies for the interaction of the Na^+ ion with C_{60}. R denotes the height of the adsorbate above the appropriate face or bond of the cage.

Adsorption site	Equilibrium distance d (Å)	Adsorption energy E_a (eV)
	Inside	
Cage center	None	1.44
C_5 axis	0.60	1.47
C_3 axis	0.60	1.47
Midbond $B1$ (Long)	0.55	1.47
Midbond $B2$ (Short)	0.54	1.47
	Outside	
C_5 axis	5.85 ($R=2.55$)	1.06
C_3 axis	5.67 ($R=2.44$)	1.08
Midbond $B1$ (Long)	5.93 ($R=2.48$)	1.01
Midbond $B2$ (Short)	6.06 ($R=2.60$)	0.96
On top	6.06 ($R=2.54$)	0.98

equilibrium distance from the cage center, the Na^+ ion lies at distances of 0.55 and 0.54 Å to the center, for adsorption at sites lying directly below the midpoints of the long and short bonds, respectively, compared to the identical Na^+ distances of 0.60 Å obtained for fivefold and threefold sites. This trend can be attributed to the greater repulsion experienced by the positive ion in the proximity of the two carbons forming a bond, when it absorbs at the midpoint sites, than the repulsion experienced by it due to the proximity of the carbons forming a pentagon or a hexagon, when it absorbs in the more open fivefold or threefold site. This conclusion is in general agreement with the approximate model of a double-layer polarizable C_{60} cage, with an approximately spherical shell of electronic charge lying outside the positively charged cage of carbon monocations, derived by Cioslowski and Fleischman [21] based on their *ab initio* RHF results. Our value of 0.60 Å for the Na^+ equilibrium distance in the fivefold site is close to the corresponding values of 0.660 and 0.7 Å found by Cioslowski and Fleischman [21] and Schmidt, Dunlap, and White [17], respectively; while the equilibrium distance for the adsorption of the ion in the threefold site obtained by Schmidt, Dunlap, and White is in exact agreement with our result.

The results for Na^+ adsorption outside the cage show greater variation in terms of both the adsorption energies and the equilibrium distances d of the ion. The adsorption energies range from a low of 0.96 eV for the midbond site at the short-bond to 1.08 eV at the threefold site. In general, we find that Na^+ interaction at the fullerene faces is favored over the interaction at the bond sites or directly above the carbon atoms. Also of interest are the C-Na^+ distances for the carbons which are closest to the ion. For exohedral complexes, these "bond-lengths" are all shorter for adsorption at midbond and on top sites (between 2.54 and 2.69 Å) than for adsorption at the threefold and fivefold sites (2.82 and 2.84 Å). In contrast, the C-Na^+ distances for the four endohedral complexes are almost identical at 2.98 Å. The trends that emerge from the data presented here for adsorption energies and C-Na^+ distances are important for the experimental identification of the endohedral and exohedral complexes of C_{60} with Na^+ and for experimentally distinguishing between the Na^+ adsorption at different sites, when such experimental data become available. We make three main predictions: first, the endohedral complexes are expected to be more stable than exohedral complexes, which is in agreement with the experimental results on the interaction of He and Fe^+ with C_{60} [30,34], secondly, the C-Na^+ distances in the endohedral complexes will be longer than those in the exohedral complexes; finally, the variations in adsorption energies and the C-Na^+ distances for endohedral complexes will be less than the corresponding variations for exohedral complexes.

The electronic energy levels of the five sets of occupied molecular orbitals with the highest energies and of the five sets of unoccupied molecular orbitals with the lowest energies for the bare C_{60}, and for $C_{60}Na^+$ with Na^+ in the fivefold site with the ion inside the cage, are shown in Fig. 3. Theoretical predictions for the patterns of spectral lines derived from similar calculations for C_{60} and C_{70} have proved to be crucial in inferring their geometrical structure from experimental data. Moreover, band-structure calculations by Erwin and Pickett [35] have shown that these energy levels are important in understanding the origins of conductivity, superconductivity, and insulating behavior in the bulk phases of alkali-atom doped C_{60}. In their LDA study of potassium-doped C_{60}, they found that the role of the K atom was to donate electrons to the conduction band of C_{60}. Our results for the energy levels of the bare C_{60} in terms of the ordering of the various symmetries for the orbitals and the orbital energies, are in general agreement with the previous theoretical work in the literature 1,3,5,36–38]. For the highest occupied molecular orbital (HOMO) and the four occupied energy levels below it, Haddon, Brus, and Raghavarchari [3] found the ordering of the symmetries to be h_u, g_g+h_g, g_u, and t_{2u}. The energy degeneracy observed in their results for the occupied orbitals of g_g and h_g symmetries was seen to be broken in the studies by Haymet [1] and Hale [36], with the g_g orbitals lying above the h_g orbitals. However, our calculations show that the h_g orbitals lie above the g_g orbitals, and this ordering is confirmed by the theoretical results obtained by Laszlo and Udvardi [6] using the Pariser-Parr-Pople method with configuration interaction (PPP CI), by Larsson, Volsov, and Rosen [37] using the complete neglect of differential overlap method with configuration interaction between singly excited states of a singlet configuration (CNDO/S), and by Fowler, Lazzeretti, and Zanasi [38] using the self-consistent field (SCF) method with a series of basis sets ranging from Slater-type orbital with three Gaussians (STO-3G) to 6-31G*. Comparisons of the actual orbital energies obtained in our calculations with those obtained in the literature show agreement to within 3.1% with the Hartree-Fock with triple-ζ polarizations (HF/TZP) results of Scuseria [9], and to within 3.2% with values reported by Fowler *et al.* at the HF/6-31*G* level of theory. In comparison with the experimental value of 7.6±0.2 eV for the ionization potential bare C_{60} found by Lichtenberger *et al.* [39], our theoretical estimate of 8.3 eV differs by 0.7 eV. However, our disagreement with experiment is much less than the corresponding disagreement of 1.7 eV seen in LDA results [10].

Apart from the ordering of the levels, the most prominent effect is a deepening or lowering of the energy levels for both the occupied and unoccupied orbitals. For the occupied orbitals of h_u symmetry, the energy lowering is about 3.48 eV for Na^+ inside the cage and ranges from 2.42 to 2.48 eV for the ion outside. For the energy level of t_{1u} symmetry, the energy lowering is 3.50 eV for the Na^+ inside the cage and 2.52 to 2.71 eV for the ion outside. In the cases of the five highest occupied energy levels of C_{60}, the difference between the two extreme cases of largest and smallest energy lowering is only 0.06 eV

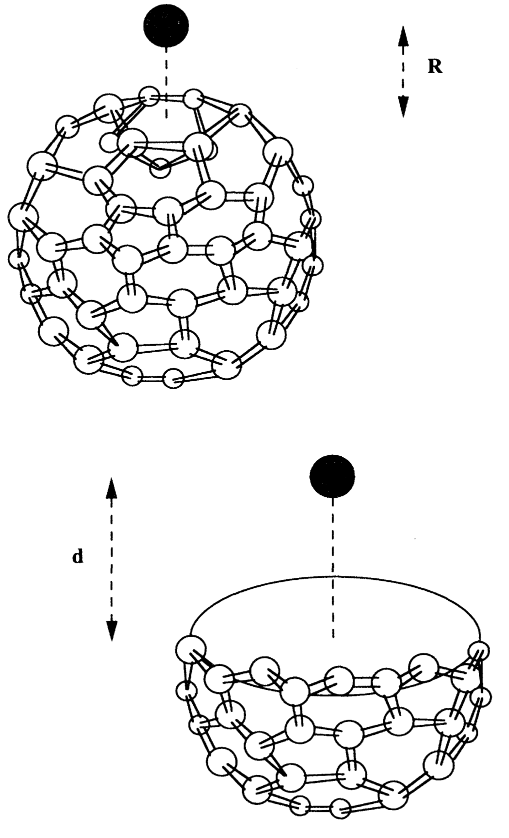

FIG. 2. Illustration of the structural parameters R and d of the C_{60}-guest systems. This figure is for adsorption in the threefold site. The white circles denote the fullerene atoms, while the dark circles denote the adsorbate.

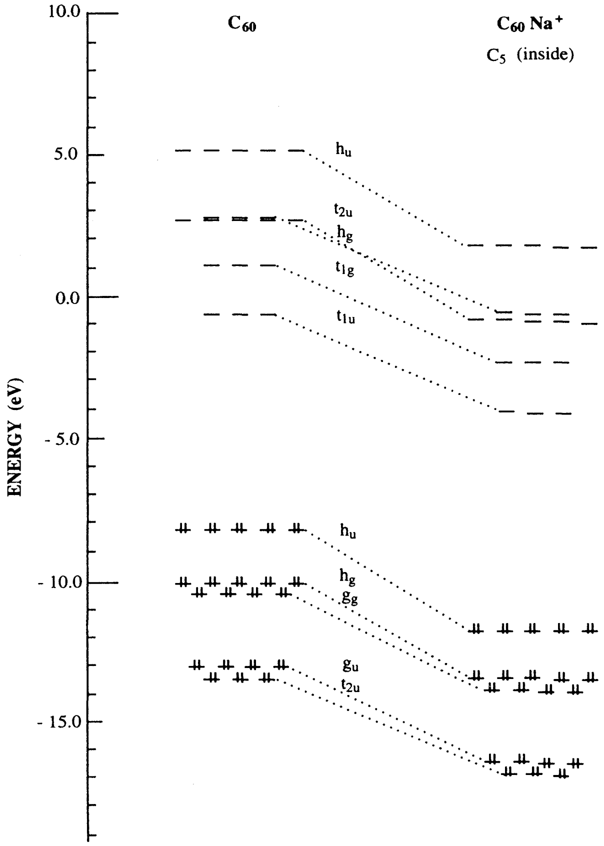

FIG. 3. Effects of the adsorption of the Na^+ ion in the C_5 site on the energy level of the HOMO and the four occupied energy levels below it in the bare C_{60} molecule, and on the energy level of the LUMO and the four unoccupied energy levels above it in C_{60}.

whether the ion is inside or outside the fullerene. On the other hand, in the cases of the five lowest unoccupied energy levels, the corresponding differences are 0.17 eV and 0.78 eV for Na^+ inside and outside the fullerene. There are two important consequences of energy lowering. The first is the increase in the number of bound, but unoccupied, electronic orbitals provided by the C_{60} molecule. On the one hand, the bare fullerene can accept only six extra electrons corresponding to the three spatial orbitals in the lowest unoccupied molecular orbital (LUMO) level, which should be a contributing factor to the stability of metallofullerene compounds such as K_6C_{60} and Na_6C_{60} in the bulk material and films. On the other hand, the number of excess electrons that the C_{60} molecule can accept is predicted to increase to approximately 11, due to the increase in the availability of unoccupied bound orbitals as a result of Na^+ adsorption. Moreover, this adsorption-induced increase in the availability of excess bound orbitals provided by the C_{60} molecule is predicted to be larger for the endohedral complexes than for the corresponding exohedral complexes. The second consequence of the deepening of the electronic energy levels in the fullerene are the shifts that should be observed experimentally in its ultraviolet photoelectron spectra (UPS). Larsson, Volsov, and Rosen [37] predicted that the three of the important symmetry-allowed transitions between the energy levels of C_{60} that would lead to peaks in the experimental spectra are HOMO→LUMO+1, HOMO→LUMO+2, and HOMO-1→LUMO. The first of these optical peaks has been experimentally identified at 3860 Å [7]. Our results show that for the HOMO→LUMO+1 peak, the interaction of the C_{60} molecule with Na^+ outside the cage may shift this peak upwards by as much as 1.59 eV, corresponding to a 191 Å downward shift in terms of wavelength. The predicted shift in this peak for the ion inside the cage is only 0.03 eV upwards, while the predicted shifts for the other two peaks are 0.06 and 0.01 eV, respectively. Also, the HOMO→LUMO+2 and HOMO-1→LUMO peaks for adsorption outside are predicted to be shifted downwards in energy by up to 1.69 and 0.29 eV.

The trends in the energy peaks for the HOMO→LUMO+1 and HOMO→LUMO+2 transitions just mentioned are related to a second feature seen in our results for the electronic energy levels of C_{60} and C_{60} Na^+, namely a change in the ordering of the second and third lowest unoccupied energy levels. Thus, we find that as a result of the interaction with the ion outside the cage, the unoccupied energy level with t_{1g} symmetry now lies above the unoccupied energy level with h_g symmetry instead of lying below the latter, as it did in the bare fullerene. A third important feature of these results is the splitting of many of the orbital energies which are degenerate in the bare fullerene due to the interactions with the ion. Such splittings of energy levels arise from the reduced symmetry of the $C_{60}Na^+$ system compared to the C_{60} molecule, and are analogous to the splittings seen in the theoretical results for the C_{70} and C_{84} molecules [10]. These splittings should contribute to broadening of the experimentally-observed spectra, which will be useful in identifying the experimental formation of the different $C_{60}Na^+$ complexes that are being considered here. Our results reveal that the level splittings are larger for the exohedral complexes than for the endohedral complexes. For the latter type of complexes, with the ion inside the cage, the largest splitting is found to be 0.10 eV and is seen in the case of the unoccupied energy level with h_g symmetry when the ion is in the fivefold site. However, for nine out of the ten energy levels being considered, the splittings are 0.05 eV or less for the endohedral complexes. The splittings are 0.08 eV or more for nine out of the ten energy levels in the cases of exohedral complexes. For the exohedral complexes, the largest splitting is found to be 1.02 eV in the case of the unoccupied energy level with h_u symmetry when the ion is the $B1$ site.

III. INTERACTIONS OF THE Na ATOM WITH C_{60}

The results for the interactions of the Na atom with the C_{60} molecule are shown in Table II. We note first the weaker adsorption of the atom compared to the adsorption of the ion. The second feature, is the stronger adsorption of Na inside the cage compared to the adsorption outside. The third feature consists of two trends for Na adsorption. For example, the adsorption strength for the neutral atom varies by 0.1 eV between the two extreme cases for adsorption inside the cage, but is site-independent for adsorption outside the cage. These are opposite to the trends seen for the Na^+ ion. The fourth feature is that the decrease of the total energy caused by the displacement of the adsorbate from the center of the fullerene to the position with the minimum total energy for Na is 0.092 eV, which is more than three times the corresponding value found for Na^+. Finally, we note that, of the four sites considered for Na adsorption inside the cage, the $B1$ site beneath the midpoint of the long bond is most stable and the site along the fivefold axis is least stable. These results highlight the importance of studying energy minima for atomic and ionic adsorbates at sites other than those lying along the two high-symmetry axes of the cage, as has been customary in the literature.

Examining the data for the equilibrium distances from the cage center for Na sites inside the cage, we find that the values of d obtained for Na interactions, ranging from 0.54 to 0.71 Å, are of the same order as those obtained for Na^+ interactions. However, we do find large differences between the two values of bond lengths at the same adsorption sites for Na inside the outside the cage. These range from 2.06 Å for the $B2$ site to 2.33 Å for the threefold site for Na adsorption, which should be contrasted with the corresponding values for Na^+ adsorption where the maximum difference was found to be 0.40 Å in the case of $B1$ site. While for Na^+ adsorption the C-Na^+ bond lengths are shorter for cases with the adsorbate outside the cage than for cases with the adsorbate inside, the reverse is true for Na adsorption. Thus, the values of R range from 4.50 Å in the on-top site to 5.18 Å in the five-fold site for the Na atom outside the cage.

The most important of the trends in electronic energy levels is the transfer of the valence electron of the sodium

TABLE II. Equilibrium distances and adsorption energies for the interaction of the Na atom with C_{60}. R denotes the height of the adsorbate above the appropriate face or bond of the cage.

Adsorption site	Equilibrium distance d (Å)	Adsorption energy E_a (eV)
	Inside	
Cage center	None	0.91
C_5 axis	0.55	0.93
C_3 axis	0.65	1.00
Midbond $B1$ (Long)	0.71	1.01
Midbond $B2$ (Short)	0.54	0.98
	Outside	
C_5 axis	8.48 ($R=5.18$)	0.10
C_3 axis	8.31 ($R=5.08$)	0.10
Midbond $B1$ (Long)	8.45 ($R=5.00$)	0.10
Midbond $B2$ (Short)	8.46 ($R=5.00$)	0.10
On top	8.02 ($R=4.50$)	0.10

atom from the HOMO of the alkali atom to one of the LUMO orbitals of the fullerene. Thus, our calculations with a single C_{60} molecule are sufficient for at least a qualitative indication of the changes in the electronic structure of the C_{60} which, in bulk material or thin films, should lead to phase transitions in fullerene-based materials induced by the intercalation of alkali-metal atoms. Similar prediction for the donation of valence electrons has been made in an LDA study of potassium-doped bulk C_{60} [35]. In our theoretical results, the donation of the valence electron from Na to the fullerene is caused by the splitting of the threefold LUMO level into two separate levels, one of which lies lower than the 3*s* level of the sodium. The level splittings for the Na atom inside the cage are 0.22 eV or larger for eight out of the ten levels considered for each of the four adsorption sites, and is largest for the LUMO level in the $B2$ site at 3.89 eV. In contrast to the case of the endohedral complexes, the level splittings are found to be 0.24 eV or smaller for nine out of the ten levels for each of the five adsorption sites with Na atom outside the cage. In general, the largest level splittings for the interaction of the Na atom with the C_{60} are expected for the first two LUMO energy levels. Such splittings have possible consequences for the magnetic properties of the C_{60} molecule and bulk material. However, the values of the energy splittings seen in our results are too small for emergence of paramagnetic behavior in the C_{60}Na complexes under study. We also note that the HOMO-LUMO gap observed for the bare fullerene decreases significantly in the C_{60}Na complexes. For Na adsorption in the fivefold site inside the cage, the gap value is 48.4% of the value observed in the bare C_{60}. The gap values for Na adsorption inside the cage are smaller than the gap values for Na adsorption outside the cage for all the cases considered. These reductions of the HOMO-LUMO energy gaps are indicators of possible phase transitions in the C_{60} and are consistent with experimental results from photoemission studies which demonstrate that C_{60} doped with Na or Li atoms is on the verge of a metal-insulator transition [40].

We now summarize our results on the transfer of electronic charge due to the interactions of Na^+ and Na with the C_{60} molecule. For the endohedral complexes of C_{60} with Na^+, the outermost electrons of the ion are delocalized equally for all four adsorption sites. For the exohedral complexes of C_{60} with Na^+, the cation gains in electronic charge density at the expense of a group of fullerene atoms. In addition, the group of fullerene atoms closest to Na^+ also gain in charge density, and the net result of the interaction in the ion is increased polarization of the fullerene. Only 4 to 12 fullerene atoms appear to be almost unaffected in exohedral $C_{60}Na^+$. The polarization of C_{60} induced by the Na^+ ion when it is outside the cage, but not when it is inside, can explain why the adsorption energies are site-dependent for exohedral $C_{60}Na^+$ but not for endohedral $C_{60}Na^+$.

For the Na atom inside the cage, the alkali atom donates its valence electron to the fullerene molecule in agreement with the experimental findings of partial charge transfer from the Raman spectra of Na_xC_{60} and other compounds of C_{60} intercalated with alkali atoms [41]. As was found true for exohedral $C_{60}Na^+$ complexes, polarization contributes to the site dependence of adsorption energies of the endohedral C_{60}Na complexes. But since the C_{60} molecule does not show increased polarization in the present case, it is reasonable to assume that the polarization of the Na is a very significant factor in explaining the interaction of the atom with the fullerene. Finally, we note that the polarization and charge transfer effects in the exohedral $C_{60}Na$ complexes are negligible.

ACKNOWLEDGMENTS

The authors gratefully acknowledge partial support from the Welch Foundation, Houston, Texas (Grant No. Y-1092). Computational support from the University of Texas Center for High Performance Computing and the National Science Foundation Pittsburgh Supercomputing Center (Grant No. PHY930047P) are also acknowledged. One of the authors (A.S.H.) is also grateful to the Office of Naval Research for financial support and to Dr. Charles Hicks and Dr. Roger Boss for stimulating discussions.

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