# Dissociative Adsorption of Nitric Oxide on Fullerene Functionalized with a Scandium Metal Atom: A Quantum Chemical Study

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ABSTRACT: Density-functional theory was used to explore the binding of nitric oxide (NO) with a single and double scandium (Sc)-doped fullerene (C_{60}). The NO molecule physisorbs on a pure C_{60} with a binding energy of about −0.006 eV. The properties of the NO molecule adsorbed on Sc doped on C_{60} at the hexagonal (D and H) sites are investigated. The average binding energy per NO molecule rises to about −2.489 and −3.289 eV for H and D sites, respectively, when the NO molecule binds to a C_{60}−Sc. The

increase in binding is due to the charge transfer from Sc to the fullerene. These observations suggest that the arrangement of Sc atoms on fullerene seems more favorable for the dissociative adsorption of the NO molecule. The final optimizing structure of $C_{60}/(Sc−NO)_2$ at the D site shows that the dissociative adsorption of NO molecules occurred, and the final configuration was very symmetric.
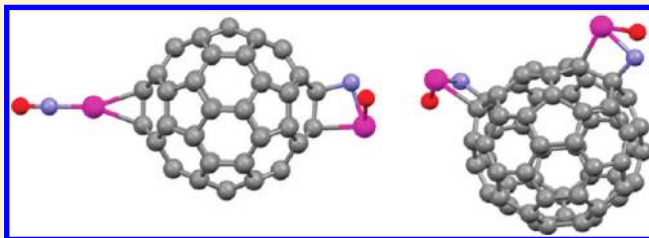
1. INTRODUCTION

Fullerene, an allotropic form of carbon made up of spherical molecules formed from pentagonal and hexagonal rings, was first discovered in 1985. With a highly delocalized, three-dimensional π-system, fullerene is suitable for efficient electron transfer (ET) because the uptake or release of electrons results in minimal structural and solvation changes upon ET.[1] The advent of fullerene chemistry, and the discovery of C_{60} by Smalley and co-workers,[2] has opened new research in the field of molecular chemistry and material and condensed-matter physics. In this respect, the metal−C_{60} interaction is of interest both from a fundamental point of view and for the applications of C_{60} fullerenes as bulk interaction compounds with unique properties,[3] including suitability for hydrogen storage and super-conductivity in the case of alkali metals. The doping of fullerenes and nanotubes by scandium, titanium, or nickel has been first suggested as a possible route[4,5] because the doping of metal atoms on carbon nanostructures greatly enhances the adsorption of H_2 molecules.[6] Fullerene-functionalized transition metal forms a novel class of hybrid carbon materials, which possesses many advantageous properties as compared with pristine fullerene. Much work has been carried out on metallofullerenes with $Sc^{7−9}$ and on Y and La[10] atoms encapsulated inside C_{82} and C_{84} cages. Among these, scandium metallofullerenes are of special interest because of the high variety of fullerene sizes, as well as their relatively high yields.[11−14] Recently, many studies have been performed on metal-doped carbon fullerenes,[15−22] which can bind hydrogen in molecular forms with a binding energy of the order of 0.5 eV/H_2 molecule.[16]

Despite the large amount of research devoted to hydrogen storage by metal coated on the carbon fullerenes, there is no report on the adsorption of the NO molecule by fullerene-functionalized transition metals. Nitrogen oxides (NO_x) have been widely known as typical atmospheric pollutants. They are mostly generated as products of high-temperature combustion of fossil fuels.[23] The interaction of NO with metal and metal oxide surfaces has been the topic of numerous surface science studies. Because NO has an unpaired electron in the $2\pi^*$ orbital, chemisorptions of NO on metal surfaces can be rather complicated compared with that of CO.[24] The adsorption reactions of NO_x with various carbonaceous materials have been studied extensively because they are recognized to be very important for NO emission rates. Unfortunately, the widely varying degree of defects in commercially available graphite makes direct comparisons between experiments and theory very difficult. Karto[25] studied adsorption of NO on graphite, and Fastow et al.[26] studied adsorption of CO and NO on C_{60} using the technique of IR spectroscopy. Smith et al.[27,28] measured isotherms at 119 K and physically measured adsorption at 90 K for NO on partially graphitized carbon blacks, whereas Baierle[29] and Yates et al.[30] studied adsorption of NO on single-walled carbon nanotubes. López,[31] Irle,[32] and Brown et al.[33] measured adsorption of NO on activated carbon at low temperatures. The extensive studies of the interaction of NO with metal surfaces have been reviewed.[34,35] Many studies of various types of reductants for the selective catalytic reduction of NO have been carried out. Recently, $SnO_2−In_2O_3$ nanostructures have been shown to be useful as NO_x sensors.[36] Yokota et al.[37] reported that Pt/mordenite is active for NO reduction with H_2 in the presence of O_2 at around 423 K. They also found that Mo and Na additives widen the temperature window for the reaction.

Several researchers have investigated the selective reduction of NO with H_2 over Pt- and Pd-based catalysts.[38−41] Ogura et al.[42] have reported that NO can be reduced to N_2 with CO over supported iridium catalysts such as Ir/silicalite and that the catalytic activity is not influenced by coexisting SO_2. Wang et al.[43] investigated Pt, Pd, Rh, and Ir catalysts and reported that an Ir/ZSM-5 catalyst exhibited high activity for NO reduction by CO in the presence of excess O_2. To our knowledge, there have been only a few theoretical research studies related to that problem. In our previous research work, we found that an NO molecule can be physisorbed on the surface of CNTs endothermically.[44] Kang et al., using a theoretical method based on first principles, found chemisorptions of NO and NNO molecules on SiCNTs, CNTs, and BNNT.[45] They have also shown that NO and NNO can be adsorbed on silicon carbide nanotubes (SiCNTs) with an appreciable binding energy. No previous theoretical studies regarding NO adsorption on fullerene-functionalized surfaces are presently known to us. This suggests that a closer investigation of the relationship between fullerene-functionalized transition metal and NO reduction is warranted.

In this research work, we have chosen a C_{60} molecule with 7.12 Å diameter as shown in Figure 1. The two distinct bond lengths of fullerene, 1.452 Å for C−C bonds and 1.389 Å for C=C bonds, are compared to the experimental values of 1.43 and 1.39 Å,[46] respectively. The goal of the present study is to characterize, by accurate calculations, the functionalized structure of fullerene by scandium (Sc) metal as an adsorbent of NO. We investigate both C_{60} and $C_{60}-Sc_n$ ($n \leq 2$) structures using density functional theory. We show that the transition metal atom, Sc, can bind externally to fullerene on two different sites. As will be seen below, using Sc as a coating element makes important differences with respect to pristine fullerene to the NO molecule.

2. COMPUTATIONAL METHOD

The DFT calculations were carried out using the G03[47] program package. The modified Perdew−Wang91 exchange[48] plus the Perdew−Wang91 correlation[49,50] functional (MPW1PW91) was used. We have employed a mixed basis set formed by the LANL2DZ[48] for Sc in conjunction with the conventional 6-31G basis set for carbon atoms. Harmonic vibrational frequencies were computed for all structures. This allowed us to estimate the zero-point vibrational energy (ZPVE) correction for each structure, as well as to assess the nature of the stationary points and therefore to characterize whether they are true minima on the respective potential surfaces. We first determined the site that a Sc atom would occupy on C_{60}. There are four possible adsorption sites for Sc on C_{60} that can be considered, as shown in Figure 1: (a) the center of a pentagonal ring, (b) the center of the hexagonal ring (H site), (c) the edge between hexagonal and pentagonal rings, and (d) the edge between two hexagonal rings (D site).[6,7,20] Our calculations prove that the most stable sites for Sc adsorption are the hexagonal sites instead of the pentagonal sites, which agrees with the results of Yildrim et al.[6] and Shin et al.[7]

Conceptual density functional theory provides quite an elegant way to describe chemical processes. Using successive derivatives of the energy with respect to either the number of electrons or the external potential, both local and global descriptors have been defined. Those descriptors are able to measure the whole response of an electronic system to a chemical perturbation.[51] On the one hand, global indexes such
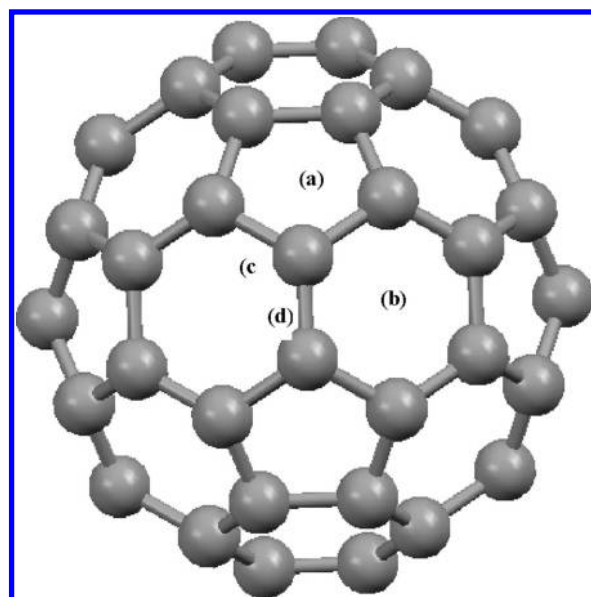

Figure 1. Four possible sites for Sc dispersion at: (a) the center of the pentagonal ring, (b) the center of the hexagonal ring (H site), (c) the edge between pentagonal and hexagonal rings, and (d) the edge between double hexagonal rings of the optimized C_{60} (D site).

as chemical potential[52] and absolute hardness[53] characterize the chemical reactivity. On the other hand, through a set of local descriptors, such as the electronic density, the Fukui function,[54] or the dual descriptor,[54] the regio- and stereoselectivity can be rationalized. Within the conceptual DFT paradigm, some principles have been easily demonstrated. For instance, the idea of hardness was given by Pearson in the context of the hard−soft−acid−base (HSAB)[55] principle, which states that "hard likes hard and soft likes soft". New principles, such as the maximum hardness principle (MHP),[56] have been proposed more recently to account for the favored direction of a chemical reaction. One of these principles, the minimum electrophilicity principle (MEP), has been the main subject of a Chattaraj et al. paper.[57] This principle states that molecules tend to decrease their electrophilicity power during a chemical process, becoming in this way less reactive.

For an N-electron system with a total energy (E) and external potential $v(r)$, electronegativity (χ)[58] and hardness(η)[59] are defined as the following first-order[52] and second-order[53] derivatives, respectively

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_{v(r), T} = -\mu \tag{1}$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r), T} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r), T} \tag{2}$$

where μ is the electronic chemical potential that is defined as the negative of the electronegativity.

Parr and his co-workers[60] have recently introduced an electrophilicity index (w) as

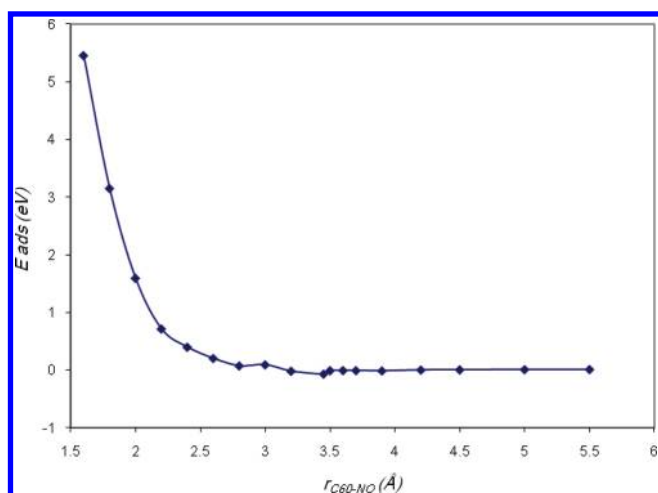$$w = \left(\frac{\mu^2}{2\eta}\right) \tag{3}$$

Figure 2. Potential energy surfaces of the adsorption of NO molecule on C_{60} using the DFT-based MPW1PW91/6-31G method.

which was proposed as a measure of the electrophilic power of a molecule.

3. RESULTS AND DISCUSSION

3.1. Adsorption of a NO Molecule on C_{60}. The geometries were fully optimized in the framework of density functional theory by use of the MPW1PW91 functional. To examine the adsorption properties of the NO molecule adsorbed on fullerene, the adsorption energy curves (Figure 2) of the C_{60}–NO, as well as the pristine C_{60} and NO molecules, were calculated. The adsorption energy, E_{ads}, was calculated using the expression

$$E_{ads} = E_{(C_{60} - NO)} - (E_{C_{60}} + E_{NO}) \qquad (4)$$

where $E_{(C60-NO)}$ is the total energy of C_{60} with an adsorbed NO molecule; E_{C60} is the total energy of pure C_{60}; and E_{NO} is the total energy of the isolated nitric oxide molecule. Hence, a negative binding energy indicates that the system is stable.

We have explored the NO adsorption on bare fullerene. In the case of C_{60}, the NO molecule interacts with the surface of the carbon framework with a bond length of 3.56 Å. The adsorption energy of a single NO molecule to the outer wall of C_{60} is −0.006 eV, which means that the NO molecule is adsorbed on C_{60} through the van der Waals interaction and that the interaction is observed to be extremely weak. As a result, pure C_{60} is not a good candidate for adsorption of the NO molecule. Also, the obtained thermodynamic parameters of the NO molecule adsorption on the C_{60} molecule (see Table 1) are in agreement with the results of adsorption energy and with our previous research work.[44]

3.2. Adsorption and Decomposition of the NO Molecule on Sc Metal Doped on C_{60}. The above results show that the interaction between the C_{60} and NO molecule is very weak and that the NO molecule cannot strongly adsorb or decompose on pristine C_{60}. So, the influence of doping Sc metal on the C_{60} on the adsorption of NO molecule was considered. Although Sc metal atoms can occupy different sites of C_{60} (Figure 3), our calculations prove that the most stable sites for Sc adsorption are hexagonal sites (H and D sites) instead of the pentagonal sites. These results are in agreement with the results of Yildrim et al.[6]

Table 1. Thermodynamic Parameters for the Fullerene–Scandium Metal Atom System, $C_{60}Sc_n$–NO_n (n Indicates the Number of Sc Atoms and NO Molecules) Calculated by the DFT-Based MPW1PW91/6-31G Method[a]

compound	E_{bind} (eV)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol K)
C_{60}–NO	−0.006	−0.0289	26.945	−90.472
C_{60}–Sc (H)	−1.359	−129.752	−99.884	−100.177
C_{60}–Sc (D)	−1.784	−172.637	−139.157	−112.293
C_{60}–Sc_2 (H)	−2.426	−233.882	−162.621	−239.011
C_{60}–Sc_2 (D)	−3.988	−386.142	−314.973	−238.703
$C_{60}Sc$–NO (H)	−2.489	−243.573	−196.970	−156.306
$C_{60}Sc$–NO (D)	−3.289	−322.0173	−266.446	−186.387
$C_{60}Sc_2$–NO_2 (H)	−5.961	−582.503	−488.151	−316.460
$C_{60}Sc_2$–NO_2 (D)	−6.056	−546.736	−440.698	−355.655

[a] E_{bind} is the binding energy of the process. ΔH is the enthalpy change of the process. ΔG is the Gibbs free energy change of the process. $\Delta S = (\Delta H - \Delta G)/T$ is the entropy change of the process.

First, each Sc atom is kept individually above the hexagonal sites, and then the NO molecule is allowed to interact with the Sc atom, as shown in Figure 4a and b. The binding energy (E_{bind}) in this case was computed as below[19]

$$E_{bind} = E_{(C_{60} - Sc_n)} - (E_{(C_{60})} + nE_{Sc}) \qquad (5)$$

As can be seen in Table 1, the interaction between the fullerene molecule and the Sc metal atom is quite strong: the binding energies of the Sc metal atom for D and H sites are −1.784 and −1.359 eV, respectively. Also, the structure where the Sc atom is doped on C_{60} fullerene on the D site is 0.425 eV lower than when it is doped on the H site, which means that the D site structure is more stable than that of the H site (see Figure 3a and b). As reported in Table 2, the shortest distances between carbon atoms of the hexagonal ring and the Sc atom are 2.132 and 2.267 Å for the D and H sites, respectively.

Second, a similar procedure has been followed for a higher number of Sc atoms doped on the C_{60} framework. It is very important to note that if the second Sc atom bonded to the fullerene molecule it would like to prefer D or H sites. We found that if two Sc atoms are supported on a C_{60} fullerene molecule they would like to remain isolated instead of form a cluster (Figure 3c and d). Also, the structure where Sc atoms are supported on D sites (Figure 3c) is more stable than Sc atoms supported on H sites (Figure 3d). The average binding energy (calculated by eq 5) of the D site is 1.562 eV lower than that of the H site, which means that the D site is more stable than the H site. The electron population analysis reveals that considerable electron transfer from the Sc atom to the fullerene molecule has occurred. In the case of the C_{60}–Sc system, the Mulliken charges on Sc atoms derived from the NBO calculation are 0.854 and 1.141 esu for the D and H sites, respectively. In addition, when more than one Sc atom is bonded to fullerene, the charge on each Sc atom almost remains unchanged. In two cases (the D and H sites), the partial charges on C atoms of fullerene bonded to Sc atoms were negative, which induces a strong electrostatic force between the C atoms and the Sc atoms. The Mulliken atomic charges are tabulated in Table 2.

Electronic chemical potential (μ) was calculated as half of the energy of the Fermi level (E_{HOMO}) plus the first eigenvalue of the

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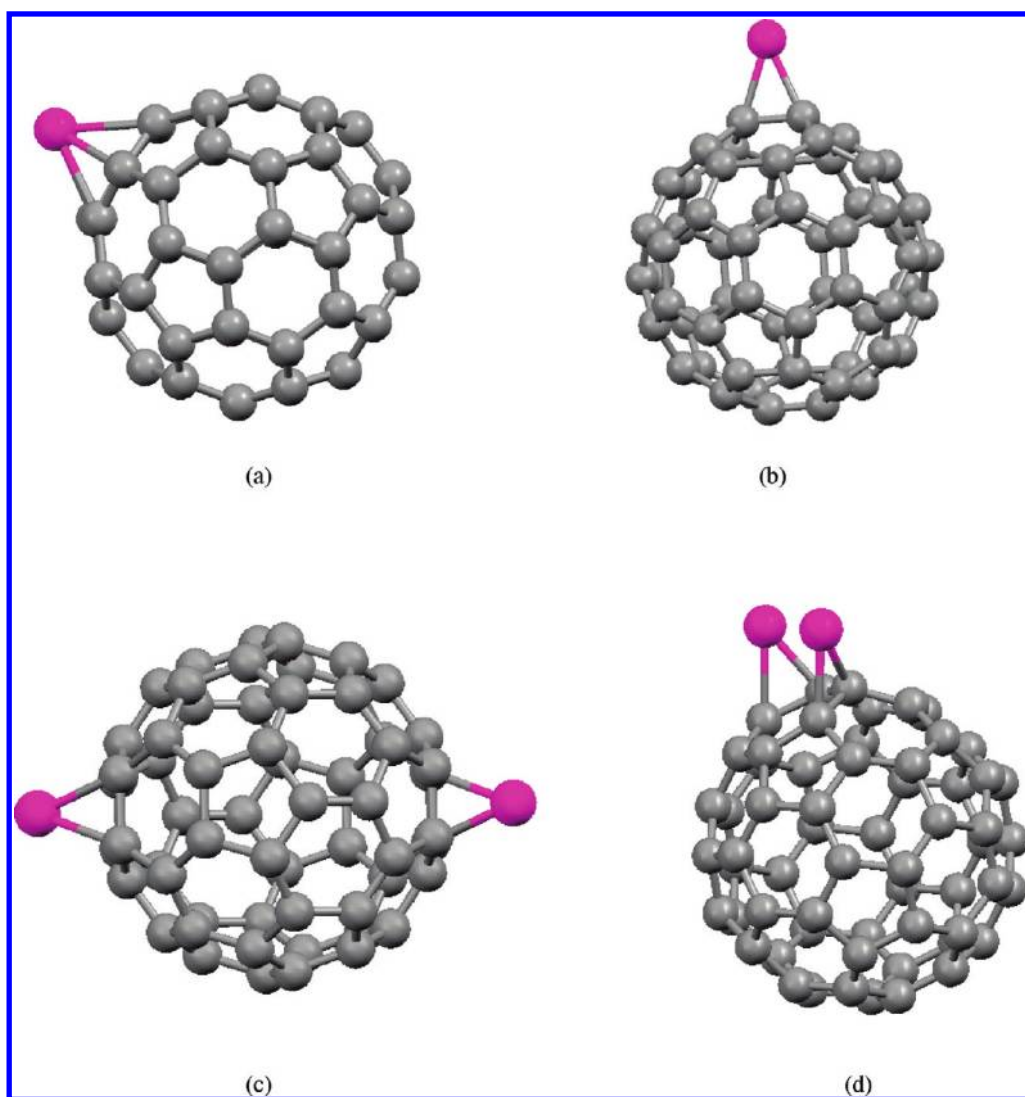dx.doi.org/10.1021/jp201416w |*J. Phys. Chem. C* 2011, 115, 12054–12063

Figure 3. Optimized structures of Sc atoms doped on the C_{60}: (a) and (c) D site; (b) and (d) H site.

valence band (E_{LUMO}), as follows

$$\mu = \frac{(E_{HOMO} + E_{LUMO})}{2} \qquad (6)$$

This definition was driven from eq 1. The operational definition of hardness (η) was obtained by using a finite difference approximation to the second derivative in eq 2, as[61]

$$\eta = \frac{(I - A)}{2} \qquad (7)$$

where I and A are the ionization potential and electron affinity of the system, respectively. Equation 8 could be further approximated as follows, using the Koopmans theorem[62]

$$\eta = \frac{(E_{LUMO} - E_{HOMO})}{2} \qquad (8)$$

Hard molecules thus have a large HOMO—LUMO gap, and soft molecules have a small one.[61]

By considering the global indices reactivity (presented in Table 3) of the C_{60}, C_{60}—Sc, and C_{60}—Sc_2 systems, it is found that when the Sc atom bonded to fullerene the maximum hardness and the minimum electrophilicity were obtained, which indicated that the stability of the system was increased. These results are consistent with the results of binding energy. A comparison between the HOMO—LUMO gap for the D and H sites indicates that the energy gap for the D site is higher than that for the H site. According to the difference between the frontier orbitals energies, when the energy gap is higher, the system behaves like a very stable molecule.

To investigate the thermodynamics of the binding of Sc atoms on C_{60} molecules, the statistical thermodynamic calculations were carried out at 1 atm and 298.15 K using MPW1PW191/6-31G. The thermodynamic parameters such as the Gibbs free energy changes (ΔG), the enthalpy changes (ΔH), and the entropy change of the process (ΔS) were calculated. The results, summarized in Table 1, show the more negative Gibbs free energy changes (ΔG) for all structures, which imply that they occur spontaneously at room temperature. Also, all adsorption processes are exothermic at the D and H sites. On the other hand, the Gibbs free energy and enthalpy changes for the supporting Sc atoms at the D site are more negative than at the H site if the second Sc atom is supported on C_{60}. In conclusion, the stronger
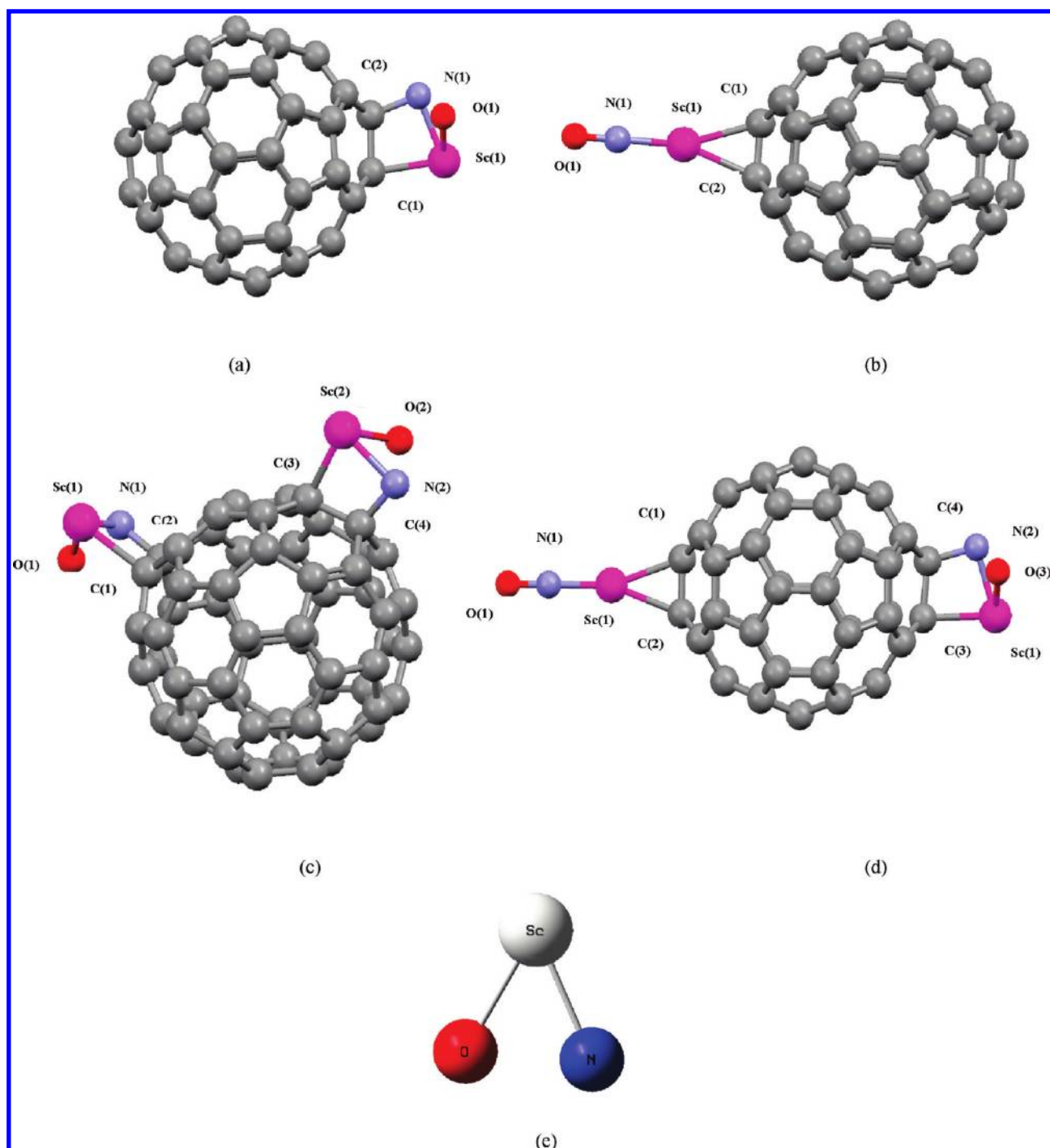
Figure 4. Final optimized geometry of NO molecules on Sc atoms doped C_{60}: (a) and (b) $C_{60}/(Sc-NO)$ at D and H sites; (c) and (d) $C_{60}/(Sc-NO)_2$ at D and H sites; and (e) NO molecule to Sc atom calculated by the MPW1PW91/6-31G method.

binding energy of $C_{60}-Sc_n$ as well as the results obtained from the global indices reactivity, the thermodynamic properties, and the NBO calculations show that the structures formed are of higher stability than pristine C_{60}.

We now turn to a discussion of the dissociative adsorption of NO molecules on the Sc atoms doped on the C_{60} molecule. It is important to emphasize that when the NO (the N−O distance is 1.15 Å) molecule reacts with a single Sc atom it dissociates with an N−O distance of 1.627 Å, and the binding energy of Sc−NO

is −2.86 eV. The molecular adsorption of NO on $C_{60}-Sc$ is due to the same procedure as that on the Sc atom (Figure 4e).

Next, we discuss the adsorption properties of an NO molecule adsorbed on the Sc atom doped on C_{60} at the D and H sites (which means that the NO molecule inserted into the $C_{60}-Sc$ systems). In these cases, we inserted an NO molecule to 3a and b structures ($C_{60}-Sc$ systems). When the first NO molecule is inserted at the D site, the NO molecule dissociates, unlike in the case of the H site (Figure 4a and b). It should be noted that the

12058

dx.doi.org/10.1021/jp201416w |*J. Phys. Chem. C* 2011, 115, 12054–12063

Table 2. Selected Bond Lengths Optimized (Å) and Partial Charges (esu) from NBO Calculation for $C_{60}-Sc_n$, Calculated by the MPW1PW91/6-31G Method

compound	$C_{60}-Sc$		$C_{60}-Sc_2$	
bond	H site	D site	H site	D site
C(1)−C(2)	1.488	1.557	1.501	1.525
Sc(1)−C(1)	2.267	2.132	2.175	2.046
Sc(1)−C(2)	2.230	2.132	2.175	2.211
C(3)−C(4)	-	-	1.508	1.544
Sc(2)−C(3)	-	-	2.175	2.116
Sc(2)−C(4)	-	-	2.174	2.190
charge				
C(1)	−0.137812	−0.320	−0.1705	−0.347
C(2)	−0.119239	−0.320	−0.171	−0.227
C(3)	-	-	−0.177	−0.354
C(4)	-	-	−0.175	−0.262
SC(1)	1.141084	0.855	1.153	0.822
SC(2)	-	-	1.159	0.674

Table 4. Selected Bond Lengths (Å) Optimized for $C_{60}/(Sc-NO)_n$, Calculated by the MPW1PW91/6-31G Method (n Is the Number of Sc Atoms and NO Molecules)

compound	$C_{60}/Sc-NO$		$C_{60}/(Sc-NO)_2$	
bond	H site	D site	H site	D site
C(1)−C(2)	1.505	1.576	1.505	1.576
N(1)−O(1)	1.227	1.557	1.229	1.561
C(2)−N(1)	-	1.532	-	1.533
Sc(1)−C(1)	2.248	2.204	2.252	2.199
Sc(1)−C(2)	2.250	2.535	2.249	2.535
Sc(1)−N(1)	1.898	1.955	1.894	1.955
Sc(1)−O(1)	-	1.850	-	1.849
C(3)−C(4)	-	-	1.578	1.576
N(2)−O(2)	-	-	1.563	1.560
C(4)−N(2)	-	-	1.530	1.534
Sc(2)−C(3)	-	-	2.201	2.198
Sc(2)−N(2)	-	-	1.965	1.953
Sc(2)−O(2)	-	-	1.852	1.850

Table 3. Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Orbital (LUMO), Gap (Δ) Energy, Electronic Chemical Potential (μ), Hardness (η), and Electrophilicity (ω) of $Sc_nC_{60}NO_n$ Systems Calculated by the MPW1PW91/6-31G Method (n Is the Number of Sc Atoms and NO Molecules)

compound	HOMO (eV)	LUMO (eV)	Δ (eV)	μ (eV)	η (eV)	ω (eV)
$C_{60}-NO$	−6.630	−3.475	3.155	−5.053	1.578	8.091
$C_{60}-Sc$ (H)	−4.496	−3.086	1.410	−3.791	0.705	10.190
$C_{60}-Sc$ (D)	−5.422	−3.035	2.388	−4.229	1.194	7.490
$C_{60}-Sc_2$ (H)	−3.874	−2.674	1.201	−3.274	0.600	8.926
$C_{60}-Sc_2$ (D)	−4.984	−2.781	2.203	−3.882	1.101	6.842
$C_{60}Sc-NO$ (H)	−5.5697	−3.713	1.856	−4.641	0.928	11.604
$C_{60}-Sc-NO$ (D)	−5.785	−3.134	2.651	−4.459	1.325	7.502
$C_{60}Sc_2-NO_2$(H)	−5.213	−3.289	1.924	−4.251	0.962	9.391
$C_{60}Sc_2-NO_2$(D)	−5.427	−2.814	2.613	−4.121	1.307	6.497

Table 5. Selected Partial Charges (esu) from NBO Calculation of $C_{60}/(Sc-NO)_n$ Systems Calculated by the MPW1PW91/6-31G Method

compound	$C_{60}/Sc-NO$		$C_{60}/(Sc-NO)_2$	
	H site	D site	H site	D site
C(1)	−0.285	−0.273	−0.283	−0.275
C(2)	−0.286	−0.236	−0.281	−0.235
N(1)	−0.192	−0.248	−0.201	−0.251
O(1)	−0.307	−0.445	−0.340	−0.446
SC(1)	1.203	1.140	1.187	1.108
C(3)	-	-	−0.168	−0.274
C(4)	-	-	−0.277	−0.240
N(2)	-	-	−0.252	−0.247
O(2)	-	-	−0.463	−0.446
Sc(2)	-	-	1.100	1.111

oxygen atom, which is more electronegative than the nitrogen atom in the NO molecule, is directly bonded to the Sc atom, which is more electropositive than the C atom. Likewise, the nitrogen atom is located directly to the carbon atom (C_2) and to the Sc atom. The magnitudes of distance between the Sc atom with N and O atoms are 1.955 and 1.849 Å, respectively (Table 4). Therefore, there can be O−Sc, N−C_2, N−Sc, and C_1−Sc bonds. It is important to note that when the NO molecule bonded to the Sc atom supported on the C_{60} molecule at the D site it dissociated with N−O = 1.557 Å (Figure 4a). The N−C_2 bond length is 1.531 Å, the same as the length of a single covalent bond.[63] In addition, the O−Sc bond is stronger than a single bond, as indicated by its bond length (1.849 Å), which is smaller than that of an O−Sc bond (2.02 Å) in the same structures.[64,65] As a result, the N−O bond is appreciably weakened. In fact, comparison between the length of the N−O bond in the adsorbed molecule (1.557 Å) and single and double N−O bonds (1.15 Å) indicates that the bond order changes from 2.5 to 1. On

the other hand, at the H site, the nitrogen atom directly bonded to the Sc atom, so there can be N−Sc, N−O, C_1−Sc, and C_2−Sc (see Table 4 and Figure 4b). This is probably related to the fact that the hybridization of the Sc atom in the scandium nitride complexes is approximately sd^2 and in the heavier homologues approximately sd. Also, according to the Pearson HSAB principle,[55] the N atom of the NO molecule tends to have a bond with the Sc atom.

As reported in Table 1, the binding energy of the NO molecule adsorbed on D and H sites is more negative as defined by eq 9,[19] which means that the NO molecule strongly adsorbs on Sc-doped C_{60}. In addition, it can be seen that the binding energy of the D site is more negative than that of the H site. The binding energies are about −2.489 and −3.289 eV for the H and D sites, respectively.

$$E_{bind} = E_{(C_{60}/(Sc-NO)_n)} - (E_{(C_{60}Sc_n)} + nE_{NO}) \qquad (9)$$

where $E_{(C_{60}/(Sc-NO)_n)}$ is the total energy of C_{60} with Sc atoms and adsorbed NO molecules; $(E_{(C_{60}Sc_n)}$ is the total energy of the C_{60}
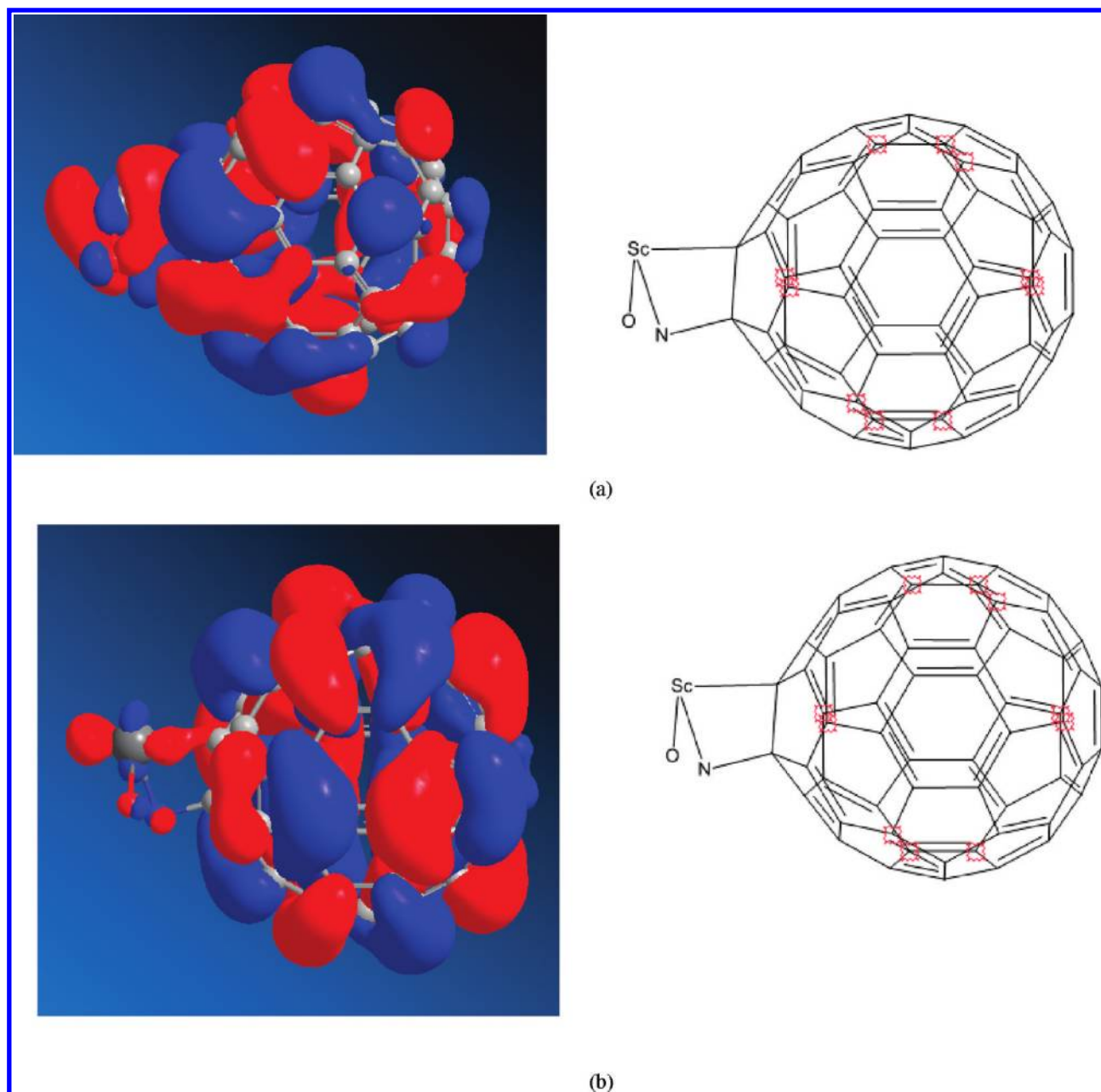
Figure 5. Typical counter plot of (a) HOMO and (b) LUMU of $C_{60}/Sc-NO$ (D site).

doped with Sc atoms; E_{NO} is the total energy of the isolated nitric oxide molecule; and n is the number of NO and Sc atoms.

Second, a similar procedure has been followed for a higher number of Sc atoms doped on the C_{60} framework interacting with NO molecules. The structures in Figure 4c and d show some interesting features. If the second NO molecule is inserted into the structures of 4a ($C_{60}-Sc-NO$ system) at the D site, the final configuration is very symmetric, and the two NO molecules go through dissociative adsorption on the Sc atoms, as was mentioned in the previous paragraph. Figure 4c shows the final optimized structure of $C_{60}-Sc_2$ with dissociative adsorption of two NO molecules on the framework at the D site. As can be seen in Table 4, the Sc—N and Sc—O bond lengths are the same as the $C_{60}-Sc-NO$ structure at the D site. In short, when two NO molecules are adsorbed at the D site, the dissociative

adsorption occurs. The average binding adsorption energy per NO molecule was calculated as defined by eq 9. As reported in Table 1, the adsorption energies of the first and second NO molecules for the D site are −3.289 and −6.055 eV, respectively.

Next, if the second NO molecule is inserted into the structure of 4b ($C_{60}-Sc-NO$ system) at the H site, the interaction of NO is different from the first one at the H site. As was mentioned in the previous section, when the first NO molecule is adsorbed to the H site, the dissociative adsorption of NO does not occur (Figure 4b), while adding a second NO molecule into the structure of 4b shows the dissociative adsorption (Figure 4d). In other words, when the second NO molecule is inserted in Figure 4b, the N atom of the second NO molecule tends to link directly to the Sc and C atoms to form a stable, four-membered ring. Likewise, the O atom of the NO molecule directly bonded
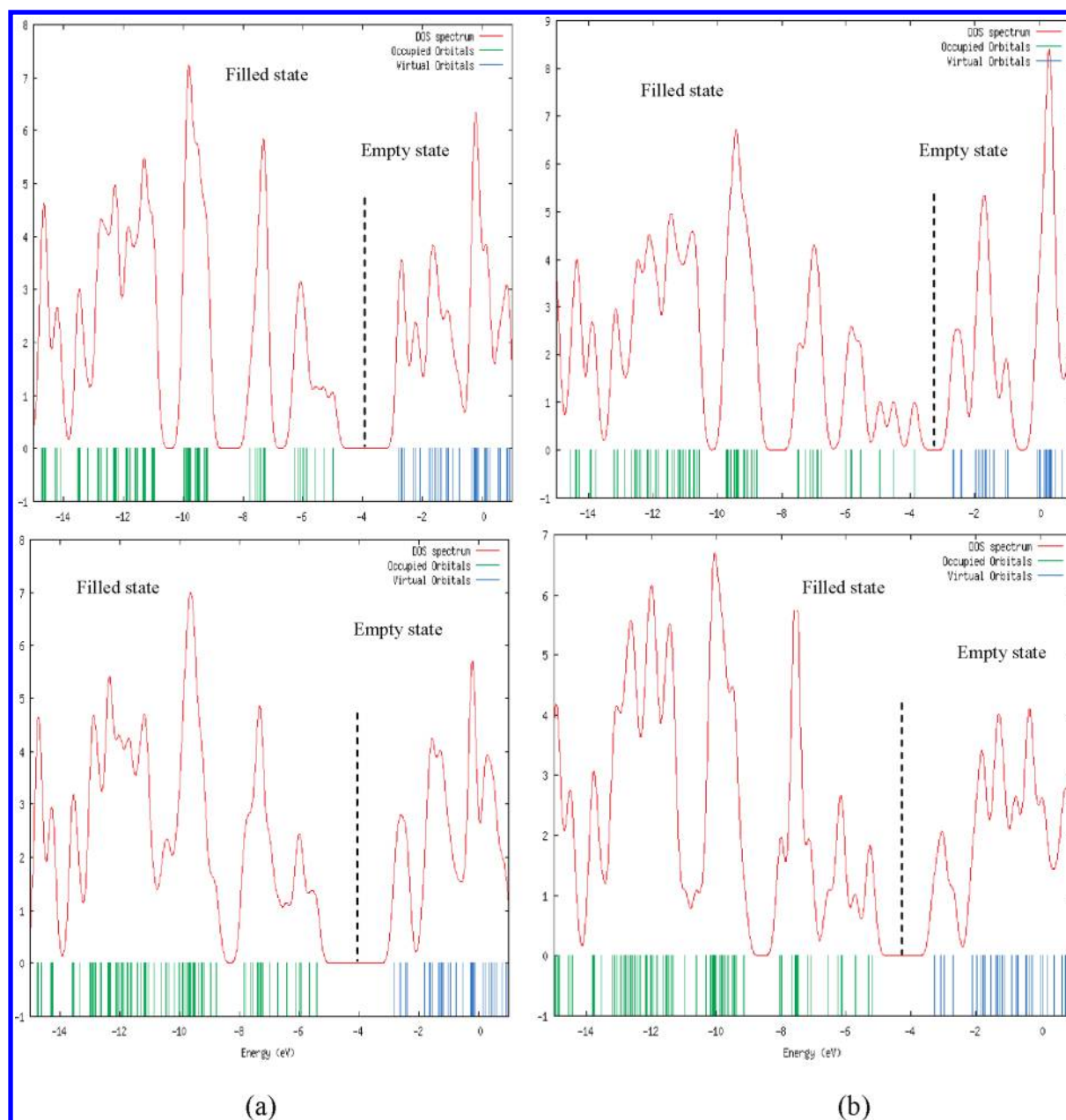
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dx.doi.org/10.1021/jp201416w |*J. Phys. Chem. C* 2011, 115, 12054–12063

Figure 6. Comparison of the electronic density of states (DOS) for $C_{60}/(Sc-NO)_2$ complexes: without NO (top) and with NO (bottom) at D (a) and H (b) sites. Blue lines represent virtual orbitals, green lines represent occupied orbitals, and the red line represents DOS spectra.

to the Sc atom. This may be due to the equatorial direction of the NO molecule parallel to the C—C bond of C_{60}. The results for the adsorption NO molecules at the H sites are summarized in Tables 1 and 4 and in Figures 4b and d. The average binding energy per NO molecule defined by eq 9 was calculated. The binding energy for dissociative adsorption of the second NO molecule is about −5.961 eV, significantly lower than that when the first NO molecule adsorbed at the H site (−2.489 eV).

Up to this point, we have discussed the interaction of NO molecules with a single and double Sc atom bonded to C_{60} at the D and H sites. In comparison, the calculated binding energy is about −5.96 eV for adsorption of two NO molecules with a double Sc atom, which is significantly lower than that when the single NO molecule is adsorbed with a single Sc atom on C_{60} (see Table 1). A possible reason for this is that the C_{60} distorts

more in the second Sc coverage case than in the single Sc coverage. In fact, this effect was observed at the D and H sites, while the D site is the slightly more stable one.

A separate MPW1PW91/6-31G calculation to obtain thermodynamic parameters was performed. The more negative Gibbs free energy changes for all the structures imply that they occur spontaneously at room temperature and that all reactions are exothermic for the D and H sites. The more negative, lowest enthalpy structure is found for the dissociative adsorption of two NO molecules at the D site, corresponding to the most stable state.

To better understand the dissociative adsorption process, the electronic properties of the NO adsorption on C_{60} at the D and H sites were discussed. The charge transfer from the Sc atom to C_{60} makes the Sc atom positively charged. When the Sc atom(s) are

bonded to the C_{60} molecule, substantial charge transfer from the Sc atoms to the fullerene can take place. The values of partial Mulliken charges on Sc, N, O, and C atoms are listed in Tables 4 and 5. In all cases, the charge transfer is about one electron from the Sc atom to the C_{60} molecule. Upon the NO adsorption, the results show that the negative charge on N and O atoms is obtained, and there is a charge transfer from Sc to the NO molecule. For example, in the C_{60}—Sc at the D site, upon the NO adsorption, there is a net charge transfer of 0.78 e from the Sc atom to the NO molecule.

Also, we consider the HOMO—LUMO gap since it is known to be the index of both kinetic stability (reactivity) and electrical conductivity.[66] A comparison between the D and H sites for the HOMO—LUMO gap indicates that the energy gap for the D sites is higher than that for the H sites. In addition, the stronger binding of the NO molecule to C_{60}—Sc and the relatively larger HOMO—LUMO gap of C_{60}/Sc—NO imply that this structure is of high stability. Figure 5 shows the HOMO and LUMO of C_{60}/Sc—NO for the D site. The hard and soft acid and bases (HSAB) theory, with the finite difference approximation, is taken into account to determine the electronic chemical potential (μ), hardness (η), and electrophilicity (ω). HOMO, LUMO, the HOMO—LUMO gap energy, electronic chemical potential, hardness, and electrophilicity indexes for all structures are summarized in Table 3. In $(C_{60}/Sc-NO)_n$ (n = 1 and 2) systems, the results of hardness and electrophilicity indicate the validity of MHP and MEP. These results are in agreement with the results of the binding energy.

The total density of states (DOS) was also calculated from the eigenvalues generated by the MPW1PW91/6-31G level of theory (Figures 6a and 6b). The DOS of a system describes the number of states at each energy level that are available to be occupied. A high DOS at a specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level.[67] Figures 6a and 6b show a DOS spectrum, in which the sharp peaks originating were clearly observed. We defined the gap between the first peaks of the empty and filled states as the energy gap (E_g). The Fermi level (E_f) was located at the center of E_g, indicating that the charge transfer had occurred. Furthermore, there is no significant change in the overall feature of the DOS of the C_{60}—Sc_2 when NO molecules go through dissociative adsorption on C_{60}—Sc_2 structures. A comparison of the DOS of C_{60}—Sc_2 with $C_{60}/(Sc-NO)_2$ shows that there is a significant change in Fermi level and position of the sharp peaks. One may note that the band gap was changed upon adsorption. This observation is consistent with the changes in HOMO and LUMO levels.

4. CONCLUSION

We have investigated systematically how supporting Sc atoms on fullerene can affect their capability for dissociative adsorption of nitric oxide using DFT calculation. The Sc-coated fullerene molecule is demonstrated to be a good candidate for dissociative adsorption of NO molecules. To the author's knowledge, this is the first theoretical work examining in detail the possibility of dissociative adsorption of NO molecules on the functionalized fullerene with Sc atoms. Data on binding energy, thermodynamic properties, electronic structures, and global indices reactivity were obtained, which gives some useful results for NO adsorption. We found that the binding strengths of the NO molecule on

Sc-coated fullerene at two different H and D sites are more negative, which means that the systems are more stable. All NO molecule adsorption on the Sc atoms at the D sites is in dissociative form different from H sites on the C_{60}. Our calculation shows that when two NO molecules are adsorbed on C_{60}—Sc_2 the binding of the second NO is cooperative.

The presence of the Sc atoms on the C_{60} surface considerably enhances the capacity of C_{60} to accept electrons. The population analysis reveals that a charge transfer from the Sc atom to C_{60} has occurred. Also, it was found that the adsorption of the NO molecule on C_{60}—Sc_n is accompanied with a charge transfer from Sc to the NO molecule. Furthermore, NBO calculations essentially show significant change in the C_{60}—Sc_n band gap when NO molecules adsorbed to the Sc atoms coated C_{60}. Finally, these predictions are expected to motivate active research efforts to search for a potential new high capacity for dissociative adsorption of nitric oxide molecules.

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