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Adsorption of C_{60} molecules

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A self-consistent real-space scheme for calculating the van der Waals interaction energy between a fullerene molecule and substrate with atomic surface corrugation is presented. The interaction of a single fullerene molecule with various substrates is then considered, to determine the optimum binding energy, plus the rotational and translational diffusion barriers. The van der Waals energy is calculated using linear response theory to evaluate the dipole-dipole interactions between the molecule and the substrate. The method is extended beyond the treatment of the substrate as a continuous dielectric medium to a discrete stratified substrate including the atomic nature of the surface. For C_{60} on graphite the fullerene is always preferentially oriented so as to present a six-membered ring to the surface. The optimum binding energy is found to be 0.96 eV, with the molecule positioned so as to continue the natural stacking of the hexagonal planes. For C_{60} on NaCl(001) the most stable position is found to be above a sodium cation with a five-membered ring oriented towards the surface, and a binding energy of 0.42 eV. Unlike the situation for graphite, though, the orientation of the molecule changes with adsorption site. The energy barrier for rotation of an isolated C_{60} molecule is of the order of 0.03 eV on both surfaces. Lüthi *et al.* [Science **266**, 1979 (1994)] recently reported that islands of C_{60} deposited on NaCl(001) could be moved by the action of the tip of a scanning force microscope, whereas for C_{60} on graphite, collective motion of the islands could not be achieved, instead the islands were disrupted by the tip. These results can be explained in terms of the relative strengths of the C_{60}-C_{60}, C_{60}-graphite, and C_{60}-NaCl interactions and the reduction of the rotational barriers of the interface molecules due to collective effects.

I. INTRODUCTION

Recent experimental studies of the growth of thin films of C_{60} on a wide range of substrates have shown that it is generally possible, under suitable conditions, to produce structures consisting of close-packed (111) monolayers stacked parallel to the surface, with the same density as in bulk fullerite.[1] The all important factor determining the quality of the subsequent film growth is the structure of the first layer. Lattice matching is critical, but there must also be a strong enough interaction within the film and between the film and the substrate for ordering to occur. Furthermore, the impinging molecules must be sufficiently mobile to obtain equilibrium. Growth should then proceed in a layer-by-layer manner. In situations where these criteria are not satisfied the initial growth proceeds by the formation of islands on the surface.[2,3]

The interactions between the C_{60} molecules are relatively well understood to be of the van der Waals type, whereas the interaction between the C_{60} molecules and the substrate is still very much unexplored. This interaction, although being highly substrate specific, is expected to be significantly van der Waals–like in character even on strongly bonding substrates, due to the molecular nature of the adsorption.[4] Charge redistribution or transfer may then give rise to additional covalent or ionic bonding between the fullerene and the substrate.

In this paper we address this problem for the interaction of a C_{60} molecule with graphite, and NaCl(001). These surfaces were chosen for their simplicity, and also for their current experimental interest.[2,3] On neither substrate is there any lattice matching resulting in island growth. It was recently shown by Lüthi *et al.*[3] that islands of C_{60} deposited on NaCl(001) could be moved by the action of the tip in a scanning force microscope, but for C_{60} on graphite collective motion of the islands could not be achieved; instead, the islands were disrupted by the tip. It was proposed that the differences were due to the differences in the bonding between the fullerenes and the substrate and the possible rotational freezing of the fullerenes by such interactions.

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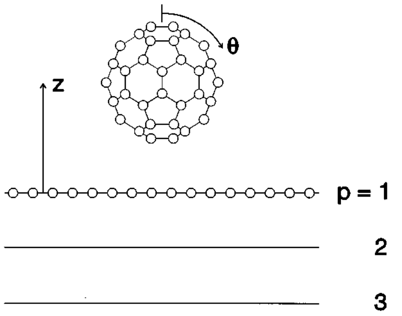

FIG. 1. Schematic of the model surface showing the discrete stratified substrate and the atomic nature of the surface. The distance z is the height of the center of the C_{60} molecule above the surface, and the angle θ defines the orientation of molecule.

For each system, the preferred adsorption sites and orientation of the fullerene molecule are determined, as well as the translational and rotational diffusion barriers. These results may then provide some insight into the aforementioned experimental results, and also act as a guide to general trends applicable to more complex systems. Preliminary results for the adsorption of C_{60} on $C_{60}(111)$, calculated using the Girifalco potential,[5] are presented for further comparison.

Within the model the fullerene molecule is treated as rigid cluster of N dynamic dipoles located at the position of the carbon atoms. The attractive van der Waals interaction of a fullerene molecule with a substrate is calculated, using linear response theory, from the change in normal modes of the adsorbed molecule. Previous theoretical studies have treated the substrate as a continuous dielectric medium.[4] This is now extended to a stratified substrate with a discrete atomic surface, thus including corrugation, see Fig. 1. This discretization of the surface removes any ambiguity in the definition of the position of the continuum edge. All that is required for the description of the fullerene molecule and the substrate are the dynamic electronic polarizabilities of the fullerene carbon atoms and the surface atoms, plus the atomic positions of the carbon atoms and the lattice vectors of the substrate.

An important result from the previous theoretical studies[4,6] was that the interaction energy between two fullerene molecules exhibited a minimum of ~280 meV at a spacing of ~10 Å (both values are in good agreement with those of bulk fullerite), which was rigidly shifted down in energy by the presence of a substrate. That is, the C_{60}-C_{60} and C_{60}-substrate interactions are simply additive.

The paper is arranged as follows. In Sec. II, the real-space method for the calculation of the van der Waals interaction between a C_{60} molecule and a stratified substrate with a discrete atomic surface is described. In Sec. III, the results for the adsorption of a C_{60} molecule on graphite and NaCl(001) are presented, and discussed further in Sec. IV.

II. METHOD

The van der Waals interaction energy, U_T, of a C_{60} molecule with a solid surface is given by

$$U_T=U_D+U_I+U_R. \tag{1}$$

The three terms on the right-hand-side are: The long-range many-body dispersion energy, U_D, arising from the lowering of the quantum zero-point energy of the system due to correlated fluctuations of the adsorbate and substrate atomic dipoles as a result of their electromagnetic interactions; the induction energy, U_I, arising from the polarization of the adsorbate by the static surface electric field (for ionic substrates only); and the short-range atomic repulsion energy, U_R, arising from the overlap of the electronic clouds of the adsorbate and the substrate at very short distances.

A. The dispersion energy

We begin by considering the electromagnetic response of a fullerene molecule in the presence of a solid surface. The fullerene molecule is treated as a rigid cluster of N discrete dipoles of local isotropic polarizability $\alpha_i(\omega)$ at the atomic equilibrium positions $\vec{r}_i$. For some external electric field, $\vec{E}_0(\vec{r},\omega)$, of arbitrary spatial dependence, the resulting effective electric field, $\vec{E}(\vec{r},\omega)$, at each atomic site in the fullerene molecule is given by[4]

$$\vec{E}(\vec{r}_i,\omega)=\vec{E}_0(\vec{r}_i,\omega)+\sum_{j=1}^{N}\mathbf{S}(\vec{r}_i,\vec{r}_j,\omega)\alpha_j(\omega)\cdot\vec{E}(\vec{r}_j,\omega)$$
$$+\sum_{j\neq i}\mathbf{T}(\vec{r}_i-\vec{r}_j)\alpha_j(\omega)\cdot\vec{E}(\vec{r}_j,\omega), \tag{2}$$

where we have assumed a linear response for the induced dipoles. The tensor $\mathbf{S}(\vec{r}_i,\vec{r}_j,\omega)$ is the dipolar field susceptibility (or propagator) of the solid surface. This is the fundamental quantity for calculating the dispersion energy between an adsorbate and a surface,[7] describing how a dipolar source field is modified in the immediate proximity of the solid surface. The tensor $\mathbf{T}(\vec{r}_i-\vec{r}_j)$ is the usual nonretarded dipolar propagator in vacuum.

The solution of the $(3N\times 3N)$ scattering matrix, defined by Eq. (2), gives the self-consistent field at each atomic site on the fullerene molecule. Formal solution is facilated by introducing two supervectors defined by

$$\underline{\mathbf{F}}_0(\omega)=[\vec{E}_0(\vec{r}_1,\omega),\vec{E}_0(\vec{r}_2,\omega),\ldots,\vec{E}_0(\vec{r}_N,\omega)],$$

$$\underline{\mathbf{F}}(\omega)=[\vec{E}(\vec{r}_1,\omega),\vec{E}(\vec{r}_2,\omega),\ldots,\vec{E}(\vec{r}_N,\omega)]. \tag{3}$$

Equation (2) then becomes

$$\underline{\mathbf{F}}(\omega)=\underline{\mathbf{F}}_0(\omega)+\underline{\mathbf{B}}(\omega)\cdot\underline{\mathbf{F}}(\omega), \tag{4}$$

where $\underline{\mathbf{B}}(\omega)$ represents a $(3N\times 3N)$ matrix given by

$$\underline{\mathbf{B}}(\omega)=\begin{pmatrix} \alpha_1\cdot\mathbf{S}_{1,1} & \alpha_2\cdot(\mathbf{S}_{1,2}+\mathbf{T}_{1,2}) & \dots & \alpha_N\cdot(\mathbf{S}_{1,N}+\mathbf{T}_{1,N}) \\ \alpha_1\cdot(\mathbf{S}_{2,1}+\mathbf{T}_{2,1}) & \alpha_2\cdot\mathbf{S}_{2,2} & \dots & \alpha_N\cdot(\mathbf{S}_{2,N}+\mathbf{T}_{2,N}) \\ \dots & \dots & \dots & \dots \\ \alpha_1\cdot(\mathbf{S}_{N,1}+\mathbf{T}_{N,1}) & \alpha_2\cdot(\mathbf{S}_{N,2}+\mathbf{T}_{N,2}) & \dots & \alpha_N\cdot\mathbf{S}_{N,N} \end{pmatrix} \tag{5}$$

with $\alpha_i = \alpha_i(\omega)$, $\mathbf{S}_{i,j} = \mathbf{S}(\vec{r}_i,\vec{r}_j,\omega)$, and $\mathbf{T}_{i,j} = \mathbf{T}(\vec{r}_i-\vec{r}_j)$. The matrix $\underline{\mathbf{B}}(\omega)$ contains all the dynamical and structural information about the fullerene-surface system. The diagonal elements describe the direct coupling between each carbon atom and the substrate, while the off-diagonal elements describe the direct and substrate mediated many-body interactions between the different carbon atoms in the fullerene molecule.

The solution of Eq. (2) can now be written in a very compact form,

$$\underline{\mathbf{F}}(\omega)=[\underline{\mathbf{I}}-\underline{\mathbf{B}}(\omega)]^{-1}\cdot\underline{\mathbf{F}}_0(\omega). \tag{6}$$

If the source field $\underline{\mathbf{F}}_0(\omega)$ vanishes, then we are left with a simple eigenvalue problem

$$\underline{\mathbf{F}}(\omega)=\underline{\mathbf{B}}(\omega)\cdot\underline{\mathbf{F}}(\omega). \tag{7}$$

The allowed coupled modes of the fullerene-surface system are then the solutions of the standard dispersion equation,

$$D(\omega)=\det[\underline{\mathbf{I}}-\underline{\mathbf{B}}(\omega)]=0. \tag{8}$$

Knowledge of the dispersion equation is sufficient to determine the dispersion energy of the fullerene-surface system, the zeros of $D(\omega)$ giving the coupled modes of the system [provided $D(\omega)$ has no poles]. From the theory of analytic functions, the dispersion energy of the fullerene-surface system is given by[8]

$$U_D^{\text{total}}=\frac{\hbar}{2\pi}\int_0^\infty \ln[D(i\xi)]d\xi, \tag{9}$$

where the integral is over imaginary frequencies, $i\xi$. However, U_D^{total} includes two contributions. The first is the van der Waals cohesive energy of the isolated C_{60} molecule, U_D^{self}. This can be extracted, without any formal difficulty, by solving the dispersion equation, Eq. (8), in the absence of coupling with the surface, i.e., for the molecule at infinite distance from the surface,

$$U_D^{\text{self}}=\frac{\hbar}{2\pi}\int_0^\infty \ln[D_0(i\xi)]d\xi. \tag{10}$$

The second contribution to U_D^{total} is the physical relevant quantity, namely, the van der Waals interaction between the C_{60} molecule and the substrate, U_D. This is simply the difference between U_D^{total} and U_D^{self}

$$U_D=\frac{\hbar}{2\pi}\int_0^\infty \ln[D(i\xi)/D_0(i\xi)]d\xi. \tag{11}$$

This technique allows us to compute the answer with a great numerical stability as it is not necessary to directly calculate the small difference, U_D, between two large numbers, U_D^{total} and U_D^{self}.

1. The dipolar field susceptibility of the surface

The dipolar field susceptibility of the surface, $\mathbf{S}(\vec{r},\vec{r}\,',\omega)$, is defined in terms of the potential susceptibility of the surface, $\mathbf{K}(\vec{r},\vec{r}\,',\omega)$, by[9]

$$\mathbf{S}(\vec{r},\vec{r}\,',\omega)=\vec{\nabla}_{\vec{r}}\vec{\nabla}_{\vec{r}\,'}\mathbf{K}(\vec{r},\vec{r}\,',\omega). \tag{12}$$

The functional form of the tensor $\mathbf{K}(\vec{r},\vec{r}\,',\omega)$ is given by[9]

$$\begin{aligned}\mathbf{K}(\vec{r},\vec{r}\,',\omega)=&\sum_s \frac{\alpha_s(\omega)}{A_S}\sum_p \sum_{\vec{g}} e^{-i\vec{g}\cdot(\vec{\tau}_s+\vec{\tau}_p)}\\ &\times\int dk\,\frac{\vec{K}\cdot\vec{K}_g^*}{k|\vec{k}+\vec{g}|}e^{-i[\vec{k}\cdot\vec{\ell}-(\vec{k}+\vec{g})\cdot\vec{\ell}\,']}\\ &\times e^{-k(z-z_p)-|\vec{k}+\vec{g}|(z'-z_p)},\end{aligned} \tag{13}$$

where $\vec{K}=(i\vec{k},k)$, $\vec{K}_g=[i(\vec{k}+\vec{g}),|\vec{k}+\vec{g}|]$, and $\vec{K}\cdot\vec{K}_g^* =\vec{k}\cdot(\vec{k}+\vec{g})+k|\vec{k}+\vec{g}|$. Also, $\vec{r}=(\vec{\ell},z)$, $\vec{r}\,'=(\vec{\ell}\,',z')$, the $\vec{g}$ are the surface reciprocal lattice vectors, A_S is the area of the surface unit cell, $\alpha_s(\omega)$ is the isotropic polarizability of atom s, $\vec{\tau}_s$ defines the position of atom s in the surface unit cell, and $\vec{\tau}_p$ defines the position of an equivalent atom in the plane located at z_p, and the summations s, p are over all atoms in the surface unit cell.

If we consider only the $\vec{g}=0$ term in Eq. (13), giving rise to the continuum component, $\overline{\mathbf{K}}(\vec{r},\vec{r}\,',\omega)$, of the potential susceptibility, then

$$\begin{aligned}\overline{\mathbf{K}}(\vec{r},\vec{r}\,',\omega)=&\frac{2}{A_S}\sum_s \alpha_s(\omega)\\ &\times\sum_p \int dk e^{-i\vec{k}\cdot(\vec{\ell}-\vec{\ell}\,')}e^{-k(z+z'-2z_p)}.\end{aligned} \tag{14}$$

On evaluating the integral, we have

$$\overline{\mathbf{K}}(\vec{r},\vec{r}\,',\omega)=\frac{4\pi}{A_S}\sum_s \boldsymbol{\alpha}_s(\omega)\sum_p \frac{Z+Z'}{[X^2+Y^2+(Z+Z')^2]^{3/2}}, \tag{15}$$

where $X=x-x'$, $Y=y-y'$, $Z=z-z_p$, and $Z'=z'-z_p$.

From Eq. (12), after some differentiation, we obtain for the continuum component, $\overline{\mathbf{S}}(\vec{r},\vec{r}\,',\omega)$, of the dipolar field susceptibility,[10]

$$\overline{\mathbf{S}}(\vec{r},\vec{r}\,',\omega)=\frac{12\pi}{A_S}\sum_s \alpha_s(\omega)\sum_p \mathbf{M}(\vec{r},\vec{r}\,'), \tag{16}$$

where

$$\mathbf{M}(\vec{r},\vec{r}\,')=\begin{pmatrix} (Z+Z')/D^5(1-5X^2/D^2) & -\,5XY(Z+Z')/D^7 & (X/D^5)[5(Z+Z')^2/D^2-1] \\ -\,5XY(Z+Z')/D^7 & (Z+Z')/D^5(1-5Y^2/D^2) & (Y/D^5)[5(Z+Z')^2/D^2-1] \\ -(X/D^5)[5(Z+Z')^2/D^2-1] & -(Y/D^5)[5(Z+Z')^2/D^2-1] & (Z+Z')/D^5[5(Z+Z')^2/D^2-3] \end{pmatrix} \tag{17}$$

with $D^2=X^2+Y^2+(Z+Z')^2$.

For the corrugation component to the field susceptibility, $\tilde{\mathbf{S}}(\vec{r},\vec{r}\,',\omega)$, assuming that only the atoms in the first surface layer [$p=1$, which must then be excluded from the summation in Eq. (16)] make a non-negligible contribution, see Fig. 1, we can adapt a method of summation by pairs:

$$\tilde{\mathbf{S}}(\vec{r},\vec{r}\,',\omega)=\sum_s \alpha_s(\omega)\sum_n \mathbf{T}(\vec{r}-\vec{r}_{sn})\mathbf{T}(\vec{r}_{sn}-\vec{r}\,'), \tag{18}$$

where $\vec{r}_{sn}=n_1\vec{a}_1+n_2\vec{a}_2+\vec{\tau}_s+z_s\vec{z}$. The dipolar field susceptibility of the surface is then

$$\mathbf{S}(\vec{r},\vec{r}\,',\omega)=\frac{12\pi}{A_S}\sum_s \alpha_s(\omega)\sum_{p\geqslant 2} \mathbf{M}(\vec{r},\vec{r}\,') + \sum_s \alpha_s(\omega)\sum_{n,p=1} \mathbf{T}(\vec{r}-\vec{r}_{sn})\mathbf{T}(\vec{r}_{sn}-\vec{r}\,'). \tag{19}$$

Notice that in Eqs. (16) and (18), by assuming that the surface atoms are isotropically polarizable, the frequency and spatial dependence of the field susceptibility have been separated.

2. *The atomic polarizability*

Now we need to specify the dynamic polarizabilities, already assumed to be isotropic, for the fullerene carbon atoms and the surface atoms. Throughout we shall use a simple Lorentzian model,

$$\alpha_i(\omega)=\frac{\alpha_i(0)}{1-\omega^2/\omega_i^2}, \tag{20}$$

where $\alpha_i(0)$ and ω_i are the static polarizability and characteristic frequency of atom i, respectively, see Table I.

TABLE I. The static polarizability, $\alpha_i(0)$, characteristic frequency, ω_i, for an atom of species i, Eq. (20), and the parameters A_{ij}, λ_{ij}, Eq. (23), for the short-range repulsion energy between a carbon atom j and an atom of species i.

i	$\alpha_i(0)$ (Å^3)	$\hbar\omega_i$ (eV)	A_{i-C} (eV)	λ_{i-C} (Å)
C	1.100[a]	18.15[a]	3224.9[c]	0.2778[c]
Na$^+$	0.145[b]	57.36[b]	740.5[d]	0.2271[d]
Cl$^-$	3.135[b]	12.92[b]	1285.3[d]	0.3336[d]

[a] Reference 18.
[b] Reference 19.
[c] Reference 20.
[d] Reference 21.

B. The induction energy

For an ionic substrate, the static surface electric field, i.e., the external field, $\vec{E}_0(\vec{r})$ at $\vec{r}=\vec{\ell}+z\vec{z}$, is calculated by a Ewald summation technique,[11,12]

$$\vec{E}_0(\vec{r})=-\vec{\nabla}_{\vec{r}}\sum_s \frac{2\pi q_s}{A_S}\sum_{\vec{g}\neq 0} \frac{e^{i\vec{g}\cdot(\vec{\ell}-\vec{\ell}_s)}}{|\vec{g}|}\,\frac{e^{-|\vec{g}|(z-z_s)}}{1-e^{-|\vec{g}|d}}. \tag{21}$$

where the summation s is over all ions, with positions $(\vec{\ell}_s,z_s)$ and charges q_s in the unit cell, and the $\vec{g}$ are the reciprocal lattice vectors in the plane of the surface.

The resulting static effective field at each carbon site, $\vec{E}(\vec{r}_i)$, follows from Eq. (6). The induction energy of the fullerene is then

$$U_I=\frac{1}{2}\sum_{i=1}^{N} \alpha_i(0)\vec{E}(\vec{r}_i)\cdot\vec{E}(\vec{r}_i). \tag{22}$$

This contribution is expected to be small, of the order of a few percent of the dispersion energy, for dielectric substrates such as NaCl.

C. The repulsion energy

The short-range repulsive energy, between the carbon atoms of the fullerene molecule and the surface atoms, arising from the overlap of electronic clouds, is described by a pairwise summation of Born-Mayer potentials,

$$U_R=\sum_{i=1}^{N}\sum_s\sum_p\sum_n A_{is}e^{-|\vec{r}_i-\vec{r}_{spn}|/\lambda_{is}}, \tag{23}$$

where $\vec{r}_{spn}=n_1\vec{a}_1+n_2\vec{a}_2+\vec{\tau}_s+\vec{\tau}_p+(z_s+z_p)\vec{z}$. The parameters A_{is} and λ_{is} are generally available in the literature for many atomic species, see Table I.

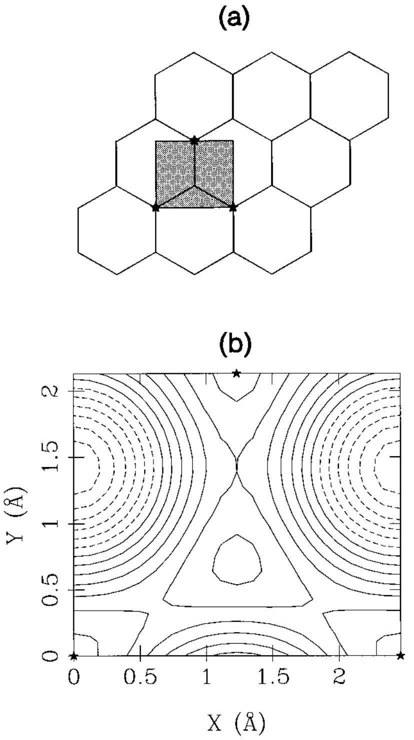

FIG. 2. Minimum energy contours (b) for a C_{60} molecule adsorbed on a graphite surface (a). The optimum position of the molecule (star symbols) is for a six-membered ring parallel to the surface, with the carbon atoms of the molecule directly above those in the second graphite layer, thus continuing the natural stacking order of the hexagonal lattice. The adsorption energy of the molecule is then 968 meV; contour spacing 1 meV. The highest energy levels are represented by dashed curves.

III. RESULTS

A. C_{60}/graphite

For a C_{60} molecule on a graphite surface, the most stable orientation of the molecule, irrespective of position within the surface unit cell, is found to be with a six-membered ring parallel to the surface. The optimum position of the molecule is with these six carbon atoms of the ring directly above those in the second layer, thus continuing the natural stacking order of the hexagonal lattice, whereas the least stable position corresponds to the six carbon atoms directly above the atoms in the first layer, breaking the natural stacking order. The adsorption energy and the height of the center of the molecule above the surface are then 968 meV, 6.55 Å, and 955 meV, 6.56 Å, respectively; see Fig. 2. Thus the fullerenes are strongly bound to a rather flat surface, with a corrugation of only 13 meV, and at room temperature isolated C_{60} molecules are expected to be mobile on the graphite surface. The potential energy surface for a fullerene molecule as a function of height above the surface, and the orientation of the molecule, defined by the angle θ in Fig. 1, is shown in Fig. 3(b). The corresponding projection of the fullerene as a function of θ is given in Fig. 3(a). The energy barrier for rotations of the fullerene resulting in a change of the number of carbon atoms in contact with the surface is of the order of 28 meV. The height of the fullerene above the surface as a result of such a rotation is now ~6.6 Å. The energy barrier for rotation about the axis perpendicular to the surface, i.e., spinning of the six-membered ring, is very small, of the order of a few meV.

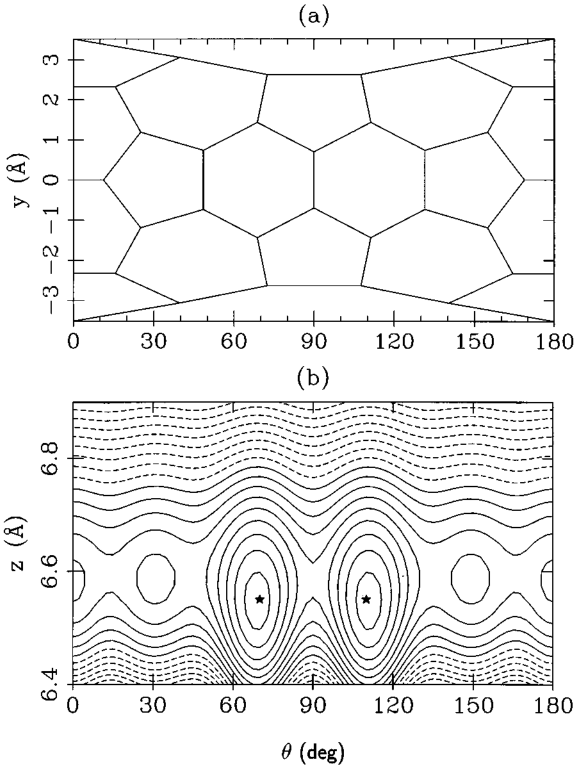

FIG. 3. (a) Projection of the fullerene carbon network on the surface plane as defined by the angle θ, Fig. 1. (b) The potential energy surface for a C_{60} molecule as a function of height above a graphite surface, and orientation θ. The highest energy levels are represented by dashed curves. The most stable orientation (star symbols) corresponds to a six-membered ring parallel to the surface. The rotational energy barrier is 28 meV; contour spacing 6 meV.

The rotational energy barrier in bulk fullerite is of the order of 20 meV. Since the C_{60}-graphite interaction is so much stronger than the C_{60}-C_{60} interaction, the collective effects in an ensemble of fullerenes is not expected to be sufficient to lift the rotational energy barrier at the surface, so that at room temperature, those molecules at the interface are expected to be freely spinning, but rotationally hindered.

B. C_{60}/C_{60}(111)

To estimate the properties of C_{60} adsorbed on C_{60}(111) we have used the Girifalco potential[5] with an optimized C_6 parameter ($C_6 = 15.2$ eV Å^6, $C_{12} = 12\,000$ eV Å^{12})[4]. Due to the spherical averaging of the Lennard-Jones potential, it is not possible to determine the rotational barrier of the adsorbed molecule. The resulting "average" adsorption energy of C_{60}/C_{60}(111) is estimated to be 813 meV (approximately three times C_{60}-C_{60} interaction[13]), showing no preference for fcc or hcp sites, and the diffusion barrier of 168 meV between adjacent sites. By comparison, the C_{60}-substrate interaction is 20% stronger for graphite than for C_{60}(111), but the corrugation is an order of magnitude smaller.

C. C_{60}/NaCl(001)

For C_{60}/NaCl(001), things are a little more complicated. The orientation of the molecule now depends on the position of the center of the molecule within the surface unit cell. For the center of the fullerene above a Na cation, site 1 (see Fig. 4), the favored orientation is with a five-membered ring facing the surface, not quite parallel to the surface, but such that three of the five carbon atoms are in the closest possible proximity to the ion, Fig. 5. The same effect was found for C_{60} on other ionic substrates, MgO, and LiF.[14] A similar effect, called cation trapping, has previously been observed for atoms, and small molecules on ionic substrates.[15,16] Above a Cl anion, site 2, the favored orientation was with a six-membered ring parallel to the surface (Fig. 6), maximizing the distance between the ion and any carbon atom of the fullerene. On the bridge site between two ions, site 3, the favored orientation was found to be for a double bond parallel to the line between two Na ions, Fig. 7. For the three sites the binding energy and the height of the center of the fullerene molecule above the surface are as follows: site 1, 416 meV, 6.44 Å; site 2, 372 meV, 6.63 Å; and site 3, 405 meV, 6.49 Å. The maximum corrugation of the surface is therefore ~45 meV. The energy barriers for rotation of the fullerene molecule, from Figs. 5–7, are of the order of 20–30 meV, slightly less than the surface corrugation. Thus as a fullerene molecule diffuses on the NaCl(001) surface, it will also rotate.

In an ensemble of fullerene molecules, because the C_{60}-NaCl interaction is rather week, compared to the C_{60}-C_{60} interaction, the collective effect of other C_{60} molecules will act to lift the interface molecules, effectively reducing the surface corrugation, and rotational barriers, such that the interface fullerenes are freely rotating at room temperature as in bulk fullerite.

D. Discussion

A first aim of this discussion is to assess the importance of the many-body interactions relative to the two-body contribution. The latter is the dispersion term proportional to both the C polarizability and the substrate propagator **S** in the development of ln det$[\underline{\mathbf{I}}-\underline{\mathbf{B}}(\omega)]$ [Eqs. (8)–(11)]. It is written as

$$U_D^{(2)}=-\frac{\hbar}{2\pi}\int_0^\infty \mathrm{Tr}\left(\sum_{j=1}^{N}\alpha_j(i\xi)\mathbf{S}(r_j,r_j,i\xi)\right)d\xi. \qquad (24)$$

Higher-order terms in the development can be identified as three-body, four-body, etc., interactions. The data given in Table II indicate that the two-body term accounts for 87% of the total attraction energy at the equilibrium position of the fullerene molecule, on both graphite and NaCl(001). The many-body terms all together contribute the remaining 13% attraction. This latter contribution is of the same magnitude as the one found with the dielectric-continuum approximation,[4] except that the many-body contribution is found negative here.

TABLE II. Various contributions to the adsorption energy of C_{60} on graphite and NaCl(001). All data are for the most stable position of the molecule and are expressed in meV. U_T, U_R, and U_D are the total, repulsive [Eq. (23)] and attractive [Eq. (11)] energies, respectively. $U_D^{(n)}$ denotes the n-body contribution to the attractive energy, with $n=2$ [Eq. (24)], 3, and 4, and $\Delta U_D^{(3)}$ [Eq. (25)] is the surface correction to the three-body term (see text).

Substrate	U_T	U_R	U_D	$U_D^{(2)}$	$U_D^{(3)}$	$\Delta U_D^{(3)}$	$U_D^{(4)}$
Graphite	−968	379	−1347	−1169	163	233	−423
NaCl(001)	−416[a]	238	−641	−564	88	17	−217

[a] Including the induction energy [Eq. (22)].

It is important to realize that the surface layer is described by a pairwise model [see Eq. (18)]. For that reason, the triple-dipole interaction discussed by Kim and Cole,[17] which couples a dipole on the molecule to two dipoles on the substrate, is missing. This three-body contribution has been evaluated separately by

$$\Delta U_D^{(3)}=-\frac{\hbar}{4\pi}\int_0^\infty \mathrm{Tr}\Bigg(\sum_{j=1}^{N}\sum_{s,n}\sum_{s',n'}\alpha_j(i\xi)\mathbf{T}(\vec{r}_j-\vec{r}_{sn})\times\alpha_s(i\xi)\mathbf{T}(\vec{r}_{sn}-\vec{r}_{s'n'})\alpha_{s'}(i\xi)\mathbf{T}(\vec{r}_{s'n'}-\vec{r}_j)\Bigg)d\xi, \qquad (25)$$

where, as in Eq. (18), the index n (n') runs over all the sites of the two-dimensional lattice generated by the surface atom s (s'). The contribution of Eq. (25) was found positive (see Table II). It is a small correction in the case of C_{60} on NaCl(001) (3% of $|U_D^{(2)}|$) and it is weakly corrugated (2-meV variation between site 1 and site 2). The three-body correction is much larger with graphite, because the atomic density of the surface layer is increased by a factor of ~3. $\Delta U_D^{(3)}$ represents 20% of the two-body attraction of C_{60} on graphite and is therefore not negligible.[17] It was found to be of the same magnitude as the other three-body interactions, which are properly taken into account in the present formalism (see Table II). It is worth mentioning that the corrugation of $\Delta U_D^{(3)}$ for the case of C_{60} on graphite represents 2 meV only and, therefore, should not affect too much the shape of the energy map illustrated in Fig. 2. There is even no guarantee that an improvement would be gained by adding $\Delta U_D^{(3)}$ to the adsorption energy of the molecule because the terms generalizing Eq. (25) to higher orders might partly compensate the three-body surface correction (compare $U_D^{(3)}$ and $U_D^{(4)}$ in Table II).

The other point now being discussed concerns the influence of intrinsic anisotropic properties of both graphite and C_{60} on the magnitude of the van der Waals energy. This effect, specific to sp^2 carbon networks, has been disregarded in the numerical applications presented in the previous sections. It could be included in the numerical scheme by introducing in Eqs. (2) and (13) relevant anisotropic polarizabilities to describe the dynamic response of *in situ* carbon atoms.[12,17] A rough qualitative estimation of such an effect leads to a small increase of the C_{60}-graphite binding energy around the predicted equilibrium position.

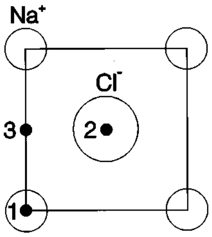

FIG. 4. The surface unit cell of NaCl(001), showing the three different adsorption sites: site 1, above the cation; site 2, above the anion; and site 3, on the bridge between equivalent ions.

IV. CONCLUSIONS

We have presented a simple method for calculating the van der Waals interaction between a fullerene molecule and a substrate with atomic surface corrugation. This method has then been applied to the adsorption of fullerenes on graphite and NaCl(001).

The optimum adsorption energies are 968 and 416 meV for a C_{60} molecule on graphite and NaCl(001), respectively. These should be compared with 813 meV, which is the adsorption energy of a C_{60} molecule on C_{60}(111). For C_{60}/graphite, the preferred orientation of the molecule is always with a six-membered ring parallel to the surface, while for C_{60}/NaCl(001), the orientation of the molecule depends on position. The surface corrugations are also very different, with graphite being almost flat, showing variations of 13 meV, while for NaCl(001), the maximum corrugation is ~40 meV. For isolated molecules, both surfaces show large energy barriers to rotations, which results in a change in the number of carbon atoms in contact with the surface, ~30 meV. These values are larger than the rotational barrier in bulk fullerite, ~20 meV, deduced from the rotational ordering transition temperature.

For an island of C_{60} molecules grown on NaCl(001), the C_{60}-C_{60} interactions, being stronger than the C_{60}-substrate interactions, are expected to lift the interface molecules reducing the rotational energy barrier so that these molecules are then freely rotating. For C_{60}/graphite, the strong C_{60}-graphite interaction will preclude this effect, so that interface molecules will remain rotationally hindered. Thus, as in the experiment of Lüthi *et al.*,[3] when an island of C_{60} molecules is pushed on NaCl(001), the interface molecules will be able to roll, whereas for graphite the interface molecules will be static, increasing the interface friction. Experimentally, this friction would appear to be so strong that the C_{60} island deforms before sliding occurs.

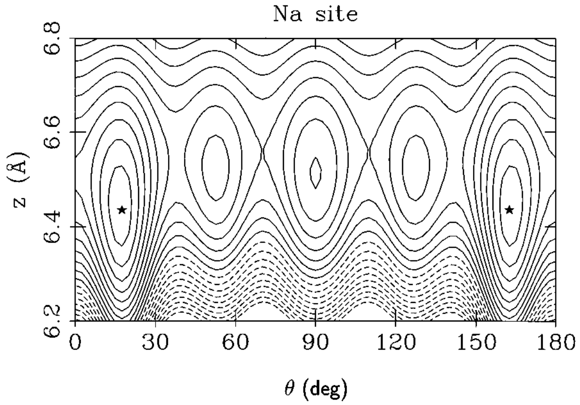

FIG. 5. The potential energy surface for a C_{60} molecule in site 1, see Fig. 4, as a function of height z above the surface and orientation θ; see Fig. 3(a). The highest energy levels are represented by dashed curves. The most stable orientation (star symbols) corresponds to a five-membered ring oriented towards the surface. The adsorption energy of the molecule is then 416 meV; contour spacing 4 meV.

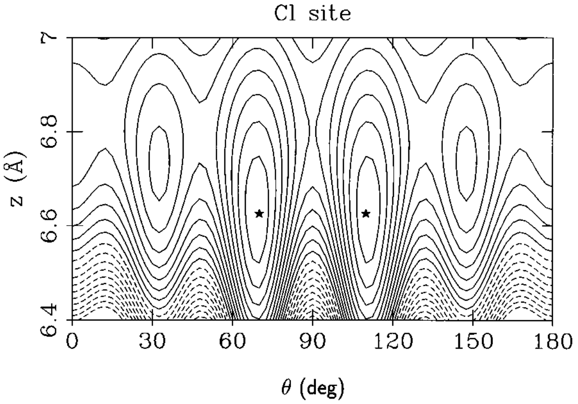

FIG. 6. Same as in Fig. 5 for a C_{60} molecule in site 2; see Fig. 4. The most stable orientation (star symbols) corresponds to a six-membered ring oriented towards the surface. The adsorption energy of the molecule is then 372 meV; contour spacing 6 meV.

In an earlier paper by several of the present authors,[12] it was proposed, based purely upon the interpretation of the experimental and calculated surface dipoles for C_{60}/GeS(001) that the C_{60} molecules sit above the rows of positive Ge ions, oriented such that a five-membered ring was facing the surface. In the light of the new results presented for NaCl(001), this interpretation would appear to be reinforced.

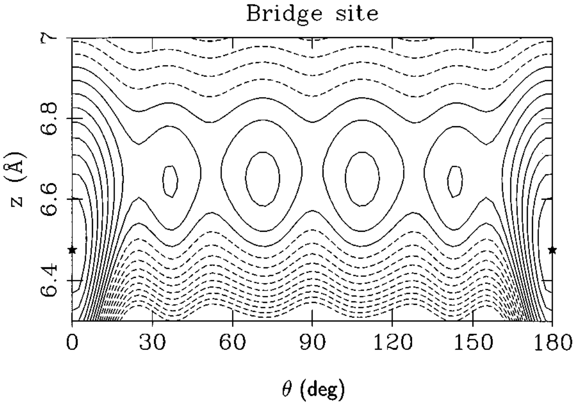

FIG. 7. Same as in Fig. 5 for a C_{60} molecule in site 3; see Fig. 4. The most stable orientation (star symbols) corresponds to a double bond parallel to the bridge between two Na ions. The adsorption energy of the molecule is then 405 meV; contour spacing 5 meV.

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