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Polarizability and intermolecular potential of C_{60}

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An intermolecular potential model of C_{60} that includes repulsive, dispersive, and Coulombic terms is proposed. The repulsive and dispersive terms are represented by one simple Lennard-Jones interaction site, which accounts for the almost spherical form of this molecule. The deviations of its spherical form are fully given by the Coulombic interactions. A model of distributed polarizable dipoles that reproduce the *ab initio* electrostatic multipolar moments [Yildirim *et al.*, Phys. Rev. B **48**, 1888 (1993)] and polarizability of the C_{60} molecule is proposed. The configurational energy, main molecular orientation, and several barriers to reorientational motion of low-temperature C_{60} crystals are well reproduced. [S0163-1829(98)10603-3]

I. INTRODUCTION

There is strong experimental evidence that the Coulombic interactions[1–4] stabilize the observed cubic structure and molecular orientation of C_{60} in its low-temperature T_h^6 ($Pa3$) phase,[1] with the characteristic feature that a short bond (electron excess) of one molecule faces an electron-poor pentagonal face of a neighbor. This relative molecular orientation can be obtained in the cubic T_h^6 structure by a 98° counterclockwise rotation around the corresponding [1,1,1] crystallographic axes of the $Z=4$ primitive unit cell; the starting configuration corresponds to the O_h^3 ($Fm\overline{3}$) structure, with three of the molecular symmetry C_2 axes aligned along the [1,0,0] crystallographic directions.[1,2]

In spite of all experimental evidence, *ab initio* calculations[5] of the electrostatic interactions fail to reproduce the measured molecular orientation in the ordered phase. In Ref. 5, the quantum-mechanical charge distribution was used to calculate the electrostatic molecular multipolar moments $Q_{l,m}$ of C_{60} up to $l=18$. Due to the I_h molecular symmetry, only moments with $l=6,10,12,16,18,\ldots$ are different from zero. The electrostatic lattice sums are slowly convergent in C_{60} crystals and the contribution given by these high-order terms is not negligible at the nearest-neighbor intermolecular distance.[5] Several sets of discrete charges were afterward fitted to reproduce the *ab initio* $Q_{l,m}$ values.[5] Finally, using these sets of charges, the electrostatic intermolecular interactions were calculated and it is with these last models that the observed $Pa3$ structure is not reproduced.[5]

In this work the configurational energy U of the $Pa3$ low-temperature C_{60} crystals, as given by several intermolecular potential models, is calculated as a function of the above-mentioned reorientational angle φ, $0° \leq \varphi \leq 120°$, and hereafter it will be referred to as $U(\varphi)$. Figure 1 shows $U(\varphi)$ calculated with the model of 153 effective charges of Ref. 5: 60 charges at C atoms (of $0.675\,e$), two charges in the 30 short bonds ($-0.277\,e$), 12 charges at the center of the pentagonal faces ($0.688\,e$), 20 charges at the center of the hexagonal faces ($3.218\,e$), and a charge at the molecular center to attain neutrality ($-96.496\,e$). The absolute minimum is calculated at $\varphi=27°$ instead of 98°, the experimental data.

In fact, the result of Ref. 5 shows the same kind of problem of other semiempirical models.[3,4,6,7] The atom-atom term of these models (60 C sites) gives the main contribution to the crystal packing and dynamics of C_{60}, but this term alone fails to reproduce the observed C_{60} orientation in the low-temperature structure. A potential model consisting of only 60 Lennard-Jones (LJ) interaction sites at C atoms gives for $U(\varphi)$ a minimum at 38°, with a secondary minimum at 98°. Moreover, molecular-dynamics simulations found that the unit cell distorts to an orthorhombic unit cell.[6] A simplified model of 12 LJ interaction sites maintains the cubic unit cell in all ranges of temperatures, but the pattern for $U(\varphi)$ is equal to that of the 60 C model and the temperature of the order-disorder phase transition is found to be too low.[7]

Correct orientation and cubic unit cell are obtained by two semiempirical models. Sprik *et al.*[3] proposed a set of 90 interaction sites (LJ centers plus charges), located at the 60 C atoms and at the 30 sites in the middle of the short bonds, to simulate the extra charge in these sites. The model proposed by Lu *et al.*[4] consisted of 60 LJ sites at the C atoms, plus 90 charges: 30 in the middle of the short bonds and 60 in the middle of the large bonds. Both models give a cubic unit cell, with a $U(\varphi)$ minimum at 98°, but the *ab initio* calcula-

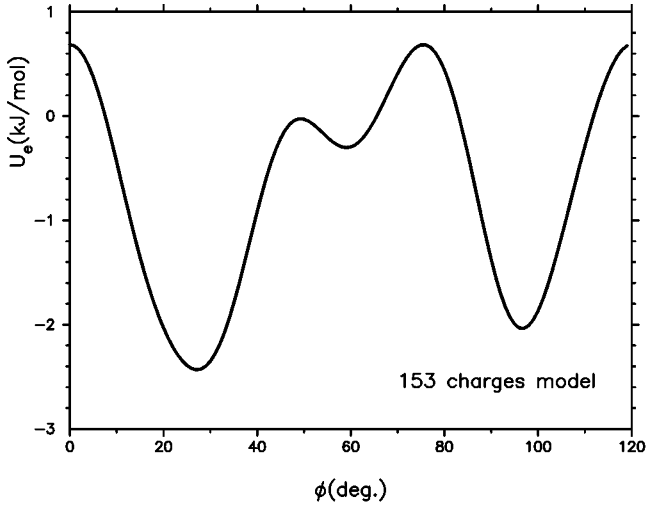

FIG. 1. Electrostatic potential energy calculated with the 153-charge model of Ref. 5; $a=14.00$ Å.

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TABLE I. Molecular multipolar moments $Q_{l,m}$ in units of $|e|r^{l}_{\mathrm{mol}}, r_{\mathrm{mol}}=3.5485$ Å.

$Q_{l,m}$	*Ab initio*	$12Sq$	$12Sd$	$20Sq$	$20Sd$
$Q_{6,0}$	0.295	−1.65	−9.9	1.52778	9.16664
$Q_{10,0}$	3.550	−1.54375	−15.43750	−3.97055	−39.70555
$Q_{12,0}$	−0.751	2.91178	34.94137	−0.16642	−1.99693
$Q_{16,0}$	−2.614	−0.53378	−8.54050	0.91526	14.64441
$Q_{18,0}$	22.895	−1.21595	−21.88722	−0.88803	−15.98466

tions of Ref. 5 showed that the value of their charges (in fact, of their corresponding $Q_{l,m}$ moments) are several times larger than those given by the quantum electronic distribution.

There are additional experimental data on the C_{60} intermolecular potential: Early neutron scattering data[1] and thermal conductivity measurements[8] determined that the two most probable orientations (at 27° and 98°) are nearly degenerate and differ by ~12 meV (1.15 kJ/mol), with an energy barrier between them of ~280 meV (26.9 kJ/mol). Recent NMR measurements[9] show that the molecular reorientations involve uniaxial rotations about [1,1,1] axes with barriers of ~64 meV (6.14 kJ/mol) and flipping of the uniaxial axis with barriers of ~250 meV (~24 kJ/mol). In the ordered phase [stable up to 90 K (Ref. 1)] the thermal energy is less than 8 meV.

Taking into account the recent experimental results,[9] here we estimate the effect of the molecular polarizability on the intermolecular interactions of C_{60} crystals. The Coulombic intermolecular interactions are simulated with a set of distributed polarizable dipole moments that reproduce the *ab initio* electrostatic $Q_{l,m}$ moments[5] and the available data on C_{60} multipolar polarizabilities. The distributed polarizable dipole model was developed and found useful to study configurational energies and the intensity of vibrational lattice modes of azabenzene and acetylene molecular crystals.[10]

II. CALCULATIONS AND INTERMOLECULAR POTENTIAL MODEL

The convergence of the electrostatic multipolar lattice sums is very slow in C_{60} crystals.[5] Instead of using the total molecular multipolar moments, these interactions can be equivalently calculated using sets of distributed charges or dipoles, with values and locations adjusted so as to reproduce all the needed molecular electrostatic multipolar moments.[11] This form is accurate and simple to implement in numerical simulations because higher multipolar moments are included by default.

The electrostatic molecular multipolar moments, due to a set of discrete charges q_i located at $\mathbf{r}_i$, are defined as

$$Q_{l,m}=\sum_i P_l^m(\mathbf{r}_i)q_i ,$$

where P_l^m are the Legendre polynomials. Similarly, for discrete distributed dipoles $\mathbf{p}_i$ located at $\mathbf{r}_i$, they can be calculated as

$$Q_{l,m}=\sum_i \sum_k \frac{\partial P_l^m(\mathbf{r}_i)}{\partial x_k}\delta x_k q_i=\sum_i \sum_k \frac{\partial P_l^m(\mathbf{r}_i)}{\partial x_k}\,\mathbf{p}_i ,$$

where k sums over Cartesian components. In the same way, distributed dipolar polarizabilities can be used to simulate the molecular multipolar polarizabilities.[11]

The contribution to the crystalline configurational energy U_C given by these polarizables dipole moments is calculated as

$$U_c=-\frac{1}{2}\sum_{\mu,i}\sum_{\nu,j}\sum_{k,l} p_k^{\mu i} S2^{\nu j}_{\mu i}(k,l) p_l^{\nu j} ,$$

where μ,ν denote molecules in the primitive unit cell, i,j sites in the molecules, and k,l Cartesian components. $\mathbf{p}$ denotes the total dipoles: the permanent plus the induced contribution. The tensor $S2$ is defined as

$$S2^{\nu j}_{\mu i}(k,l)=\sum_{\beta}{}' \frac{\partial}{\partial r_k}\frac{\partial}{\partial r_l}\frac{1}{r},$$

where $\mathbf{r}=\mathbf{r}_{\mu,i}-\mathbf{r}_{\nu,j}$ is the distance between the site j in molecule ν of the primitive unit cell β and the site i in molecule μ in the reference cell; Σ' implies that $\beta\neq 1$ when $\mu=\nu$. The lattice sum is performed using Ewald's method, taking into account the self-interaction terms between sites within the same molecule.

Thinking in terms of future applications to numerical simulations, here we search for a simple and accurate model of the intermolecular potential. If we take into account that C_{60} is very nearly a spherical molecule, it can be seen that the rough behavior of the centers of mass, i.e., its fcc packing, configurational energy, and unit cell parameters as a function of pressure and temperature, is roughly described by a spherical molecule of mass $m=720$ a.u., interacting through a LJ potential with constants $\epsilon=21$ kJ/mol and $\sigma=9.14$ Å.[7]

In addition to the LJ term, we considered that the anisotropy of the reorientational potential is just given by the Coulombic interactions. Table I quote the *ab initio* molecular multipole $Q_{l,m}$ moments up to $l=18$, in spherical coordinates, for $l=6$, 10, 12, 16, and 18.[5] Table I also gives the calculated $Q_{l,m}$ values for some very simple models, of distributed charges or distributed dipoles, with I_h symmetry. Models $12Sq$ and $12Sd$ consists of 12 charges and 12 dipoles, respectively, located in the center of the pentagonal faces. Models $20S$ are for charges and dipoles located at the center of the 20 hexagonal faces. All values given in Table I are calculated for charges of 1 e, dipoles of 1 e Å, and distances of 1 Å to the molecular center of mass. A linear combination of these simple models can be used to fit the *ab initio* values.

Using a few charges, the *ab initio* values can only be fitted by locating some of them very far from the molecular origin, implying a superposition of charge distributions between nearest neighbors in the crystal. Using distributed dipoles, the fit is simple and the final model used in our calculations consists of two sets of 12Sd and two sets of 20Sd, oriented along the C_5 and C_2 molecular axes, respectively. Their final values and positions are jointly adjusted with our proposed model of distributed dipolar polarizabilities that simulate the molecular multipole polarizabilities. The final values are 12 dipoles at 3.479 Å of 1.928 e Å, 12 dipoles at 4.082 Å of $-0.359\,e$ Å, 20 dipoles at 3.479 Å of $-3.344\,e$ Å, and 20 dipoles at 3.059 Å of 8.917 e Å. In Ref. 12 it is shown that the electronic cloud, although centered at the molecular radius, extends well inside and outside the molecule. The calculated distribution shows two maximum at 3 and 4 Å,[12] in close agreement with our proposed model.

Ab initio calculations of the C_{60} dipolar polarizability give a value $\alpha_{mol}=85.8$ Å^3,[13] very close to that obtained from indirect measurements $\alpha_{mol}=88.9$ Å^3.[14] On the other hand, Guha *et al.*[15] and Snoke *et al.*[16] fitted the values of dipolar polarizabilities located at short and long bonds of C_{60} molecule in order to reproduce Raman intensities of the intramolecular vibrational modes. Assuming that the anisotropy of the 60 single long bonds is $\alpha^l_\parallel-\alpha^l_\perp=1.28$ Å^3, as in organic molecules,[15] the anisotropy of the 30 double short bonds is $\alpha^s_\parallel-\alpha^s_\perp=0.32(9)$ Å^3, $\alpha^l_{av}=0.672$ Å^3, and $\alpha^s_{av}=1.630$ Å^3. These values are very similar to those obtained in Ref. 16. Considering that the distributed dipolar polarizabilities can be geometrically added, several moments of this distribution can be calculated. As there are no other available data on the multipolar polarizabilities of C_{60}, these estimated values are the ones used to fit our proposed simplified model.

The estimated multipole polarizabilities are simulated with a simplified model of 32 polarizable dipoles located at 3.479 Å from the molecular center. Twelve dipolar polarizabilities are along the C_5 molecular axes, with components $\alpha^{12S}_\parallel=0.889$ Å^3 and $\alpha^{12S}_\perp=3.165$ Å^3; 20 dipolar polarizabilities are along the C_3 molecular axes, with components $\alpha^{20S}_\parallel=2.490$ Å^3 and $\alpha^{20S}_\perp=3.280$ Å^3. This model is not unique, although the calculated location is always very close to 3.48 Å.

The final Coulombic model consists of 64 distributed dipole moments, half of them polarizables. They reproduce the *ab initio* electrostatic multipolar moments of C_{60} (Ref. 5) and an estimation of its multipole polarizabilities.

III. RESULTS

Figure 2 shows the Coulombic contribution $U_C(\varphi)$ calculated for our model of distributed polarizables dipoles, which contains all the anisotropy of the intermolecular potential. The unit cell parameter is $a=14.00$ Å, which gives the unit cell of minimum configurational energy; the atom-atom term contributes with $U_{aa}=-180.93$ kJ/mol. The main minimum is at $\varphi=100^\circ$, with $U_C=-7.38$ kJ/mol. The secondary minima is at $\varphi=24^\circ$, with $U_C=-5.06$ kJ/mol. The difference between both minima is 2.32 kJ/mol and the barrier for molecular reorientation around [1,1,1], within the $Pa3$ crystalline group, is 8.51 kJ/mol.

The experimental evidence[9] shows that there is a flipping of the [1,1,1] reorientational axis to nonequivalent orientations within the $Pa3$ structure; the flipping is between the different main diagonals of the cubic unit cell. The measured barrier is about 250 meV (~24 kJ/mol), although several barriers of this order of magnitude are not disregarded.

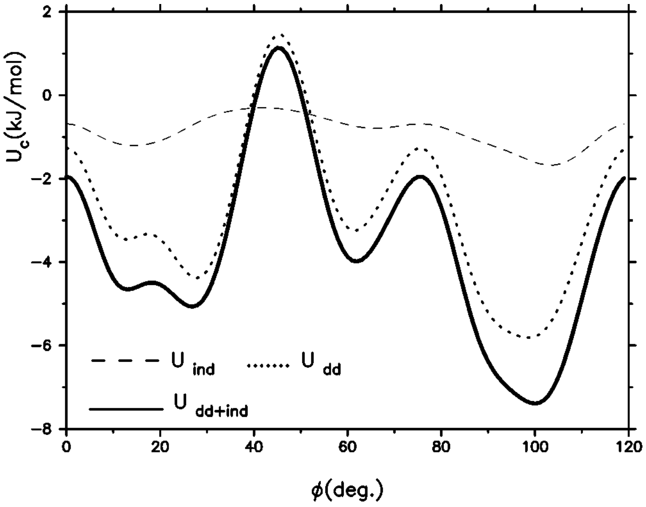

FIG. 2. Contribution of the anisotropic terms of our model, due to permanent and induced moments, for molecular reorientations allowed by the $Pa3$ unit cell symmetry, $a=14.00$ Å.

Within the $Pa3$ structure, that is, with the allowed symmetry relationships between the four molecules in the unit cell, the calculated barrier is that of Fig. 2. Nevertheless, several reorientations can be considered by relaxing the $Pa3$ symmetry constraints, as suggested by the experimental data.[9] Figure 3 shows just one of these possibilities: in this case the potential barrier for molecules reorientating around the same C_2 unit cell axis. The initial orientation for the molecule at the origin is that of the experimental $Pa3$ structure; the other three are generated with the identity. This shows that if the reorientation is not restricted to the $Pa3$ symmetry, which implies some degree of disorder, then the barrier can be approximately of the measured value. The maximum value of $U_C(\varphi)$ in Fig. 3 is 10.74 kJ/mol, the minimum of Fig. 2 is -7.38 kJ/mol, and the anisotropy between both possibles configurations is about 18.12 kJ/mol.

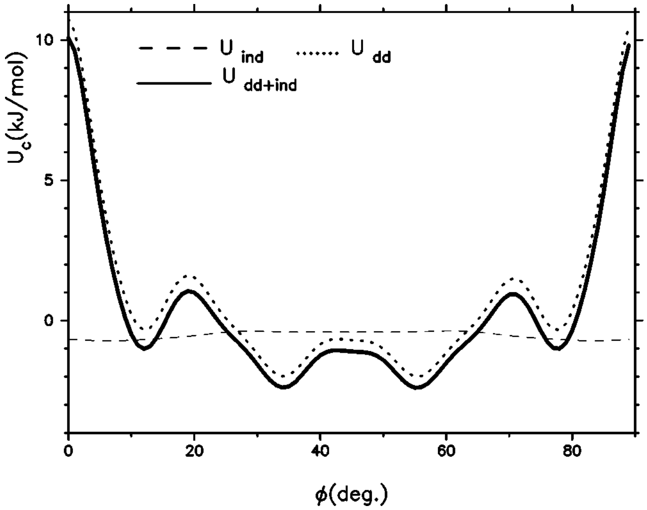

FIG. 3. Same as in Fig. 2, but for molecular reorientations not restricted to the $Pa3$ structure. See the text for details.

In Ref. 17, the absolute minimum has been measured as slightly shifting to higher values when decreasing temperature. Our calculations do not include temperature, but using lattice sums we calculated the unit cell of minimum configurational energy as a function of pressure, obtaining cubic unit cells. The calculation was performed by relaxing the unit cell parameters, with the four molecules in the unit cell generated by the C_2^x, C_2^y, and C_2^z axes of the cubic structure. Due to this result, we calculated $U(\varphi)$, as in Fig. 2, for several cubic cells with parameters between $a=14.00$ and 13.50 Å (which roughly corresponds to a pressure of 6 kbar). The minimum is always found around 100°, slightly shifting to 102° at $a=13.50$ Å, following the same trend as the experimental data.

IV. CONCLUSIONS

In the preceding section we showed that all of our calculated values compare well with experimental data. Energy values, main molecular orientation, and several barriers to reorientational motion in low-temperature C_{60} crystals are well reproduced.

The distributed polarizable model gives a good account of the Coulombic intermolecular interactions due to permanent plus induced multipolar moments. The repulsive and dispersive terms of the intermolecular C_{60} interactions are represented with a simple atom-atom model, consisting of one LJ interaction site. This proposed molecular potential model is of an almost spherical form, with the anisotropy given only by the short-range Coulombic interactions. The effect of the polarizability is to enhance the electrostatic contribution.

Due to the high molecular symmetry I_h, this is a case in which a simple model of distributed polarizable dipole moments can simply and accurately reproduce the high-order interactions in the crystalline phases. Thinking in terms of numerical simulations, the model is simpler to implement than high-order multipole molecular interactions. As suggested in Ref. 5, their failure to reproduce the intermolecular interactions can be due to the slow convergence of the electrostatic series in C_{60} crystals. Probably a series based on distributed dipoles is of faster convergence than one using distributed charges or one based on centered molecular multipoles.

Our main result is that Coulombic interactions can account for the intermolecular interactions in C_{60} crystal, as suggested by all experimental data. The discouraging results of the calculations in Ref. 5 could be due to the slow convergence of the model used to simulate their *ab initio* results. An *ab initio* calculation of the molecular multipolar polarizabilities is also needed to test our proposed values and location of dipolar polarizabilities.

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