

Ab Initio Intermolecular Potential of Solid C₆₀ in the Low-Temperature Phase

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We present *ab initio* calculations for the intermolecular potential of C₆₀ in the low-temperature $Pa\bar{3}$ structure as function of both the rotation angle and the lattice constant. These investigations are based on density-functional total-energy studies in the framework of the local-density approximation (LDA). The zero pressure ground-state phase, selected Raman frequencies, and the equation of state are determined in agreement with experimental data. These results show that despite their well-known deficiencies, LDA calculations are able to properly describe the angular and distance dependence of the intermolecular potential for C₆₀ thus emphasizing the importance of short-range chemical bonding in the $Pa\bar{3}$ phase.

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The discovery of fullerenes [1] has stimulated a great deal of experimental and theoretical work. Especially fullerene solids have gained a lot of attention. This is based on the fact that they represent a new class of carbon crystals besides graphite and diamond, offer new options in materials development due to their large cagelike structures, and show superconductivity in compounds with alkali metals [2]. The transition temperatures are among the highest which have been observed in organic superconductors.

Fullerene solids show usually very strong intramolecular C-C bonds as well as very weak intermolecular interactions thus belonging to the class of molecular crystals. Among all of the fullerene crystals C₆₀ plays a prominent role due to its high molecular symmetry. It is being formed by 12 pentagons and 20 hexagons with the carbon atoms at the corners of these pentagons and hexagons. We have two kinds of bonds: those between atoms located at the hexagons only ("short") and those between hexagons and pentagons ("long"). The phase diagram has been studied in great detail. At high temperatures above 260 K, the system shows an fcc structure due to orientational disorder while below this temperature a simple cubic structure has been observed with four molecules per unit cell [3]. The centers of the molecules are still located on an fcc lattice but with different orientations. The structure shows $Pa\bar{3}$ symmetry. Experiments revealed that the orientational order is not complete, but two kinds of optimal orientations coexist; those with short bonds of one molecule facing the pentagon centers of neighboring molecules (pentagon orientation) and those where the short bonds face the center of hexagons on neighboring C₆₀ molecules (hexagon orientation). These two configurations are almost equal in energy which results in dynamical reorientations between these two optimal structures. At about 90 K the orientations are frozen in and a glasslike transition occurs [4]. At ambient pressure, the pentagon orientation is energetically favored, while the hexagon phase is stabilized by applying pressure [5–7].

Total-energy calculations based on the density-functional theory in the local-density approximation (LDA) have been very successful in describing various properties of the intramolecular bonds: the calculated bond distances [8] as well as the calculated molecular eigenfrequencies are in excellent agreement with experiment [9–11]. The latter statement is of particular importance in view of the fact that also the predicted displacement patterns of the vibrational modes were confirmed by experiment [12]. On the other hand, our understanding of the weak intermolecular forces is much less advanced. Because full LDA calculations for the $Pa\bar{3}$ structure have not been possible so far, most studies in the past have been based on model potentials [13–15], with the semiempirical model of Savin *et al.* as the most refined one [16]. Density functional based studies have been restricted to idealized geometries or tight-binding descriptions [17–22], which were not able to address the question of the stable low-temperature phase. The most sophisticated LDA calculation for the $Pa\bar{3}$ structure was carried out so far only with the approximate Gordon-Kim approach, but failed to give the proper ground state [23,24]. This situation clearly demonstrates the need for a full scale LDA calculation for the low-temperature $Pa\bar{3}$ structure of C₆₀.

In this Letter, we present a total-energy study of the low-temperature $Pa\bar{3}$ structure which is based on density-functional theory in the local-density approximation. We calculate from first principles the intermolecular potential both as function of orientation angle and lattice constant. This allows us to determine the bulk modulus, the equation of state, the pressure dependence of the ground-state orientation, and librational frequencies. All results are at least in qualitative, in some cases even in quantitative, agreement with experimental observations.

In dealing with the low-temperature $Pa\bar{3}$ structure the major difficulties one is facing are the large number of atoms in the unit cell (240 atoms) and at the same time the high accuracy needed for total-energy differences. We

were able to deal with both by using a mixed basis pseudopotential formulation which has been used successfully in the past for the calculation of intramolecular phonon frequencies [11]. However, compared to these calculations we had to increase the size of the basis set substantially. Besides localized $2s$ and $2p$ functions we had to use plane waves up to an energy of 17 Ry while for the intramolecular phonon calculations an energy cutoff of 12 Ry was sufficient. The increase of the basis set mainly affected the quantitative aspects of the potential curve discussed below (e.g., barrier heights), while calculations with a cutoff of 12 Ry already reproduced the correct ground state. Details of the method as well as the pseudopotential used can be found in Ref. [11]. For the exchange and correlation part the Hedin-Lundqvist approximation has been used [25]. Because of the large size of the unit cell the calculated results were very insensitive to the sampling of the Brillouin zone as long as the size of the unit cell was kept constant. Thus for calculations of the total energy as function of the molecular orientation 1 k -point [$2\pi/a(1/4, 1/4, 1/4)$] was enough to obtain energy differences converged to 5 meV/molecule. An error of the same size is also introduced by limiting the plane-wave part of the basis set to 17 Ry, as inferred by checks with 20 Ry.

In Fig. 1 we show the orientation dependence of the energy for two different lattice constants. The lines are cubic spline fits to the calculated results. The molecular geometry was taken from our previous study [11], and possible small relaxations of the atomic positions were neglected. Figure 1a shows the results for the experimental lattice constant $a = 14.04 \text{ \AA}$. We find two minima at rotation angles of 24.2° and 88.4° corresponding to the pentagon orientation and hexagon orientation, re-

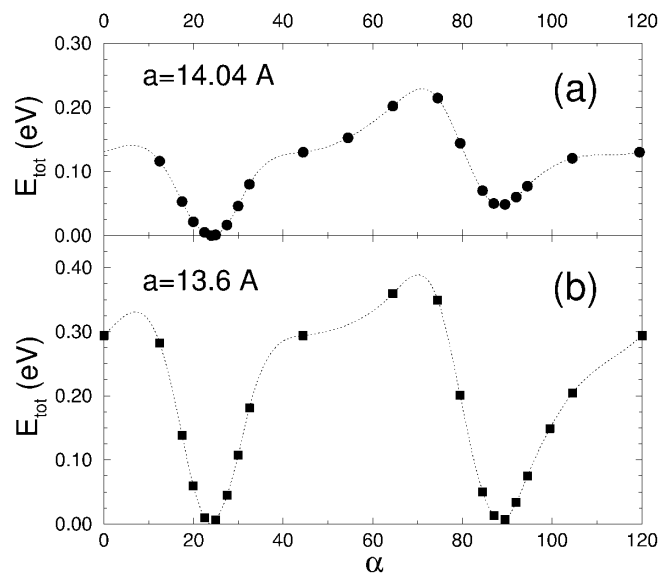


FIG. 1. Total energy per molecule as function of the rotation angle α of the $Pa\bar{3}$ structure for two different lattice constants.

spectively. The pentagon angle agrees well with experimental results ranging from 22.5° [4] to 26.5° [26], while the theoretical angle for the fully ordered hexagon phase is slightly larger than the experimental values of 82.5° [4] and 86.5° [26], which are deduced from disordered pentagon phases. The pentagon orientation is energetically favored by 40 meV/molecule over the hexagon situation. The energy barrier between the two minima is 130 meV/molecule. The curvature in the minima determines the frequency of a totally symmetric libration (A_g symmetry). The value of 2.7 meV for the pentagon minimum is in perfect agreement with the experimental value [27,28]. For the hexagon minimum the value 2.5 meV is slightly lower. We note that our energy barriers cannot be compared directly with experimental information, because the energy barrier deduced from experiments refers to single molecule jumps between the hexagon and the pentagon orientation and not to a collective reorientation of the molecules. Calculation of the reorientational barrier for a single molecule requires supercells containing at least 32 molecules, which is beyond the present day computation capabilities.

The shape of the potential curve in Fig. 1a differs significantly from those derived from phenomenological models. For example, the semiempirical model of Savin *et al.* [16] predicts a very flat hexagon minimum and barrier energies twice as large as in the *ab initio* calculation. These differences come despite the fact that the experimental libron frequency has been used in the construction of the model resulting in a curvature at the pentagon minimum which is very similar to the one in Fig. 1.

To gain insight into the stability of the orientational phases under pressure, we have performed similar calculations for a lattice constant $a = 13.6 \text{ \AA}$, which corresponds to a pressure of 1.5 GPa. The results are shown in Fig. 1b. In this case, the hexagon and the pentagon orientation are degenerate (within the accuracy limits of 5 meV). Results with higher accuracy favor slightly the hexagon situation. This behavior is in agreement with pressure data which also indicate a favoring of the hexagon orientation over the pentagon one with increasing pressure [5,7]. The positions of the minima are hardly affected but the libration frequencies are now shifted to 3.6 and 3.4 meV for the pentagon phase and the hexagon phase, respectively. This shift is consistent with Raman measurements, which find a frequency of 3.7 meV at a pressure of 1.5 GPa in the pentagon phase [28]. The main results are summarized in Table I.

So far we have concentrated on the orientational dependence of the intermolecular interaction. We have also probed the radial part by performing total-energy calculations as function of the lattice constant, while keeping the orientation and the radius of the molecules unchanged. These results were, however, very much more difficult to obtain than those for the orientational dependence. Because of the change in lattice constant a 1 k -point

TABLE I. Angles of local minima of the intermolecular potential $E(\alpha)$ and librational frequencies calculated from the second derivative of $E(\alpha)$ for two different lattice constants.

a (Å)	α_{\min} (P/H)	ω (meV)
14.04	24.2/88.4	2.7/2.5
13.6	23.9/88.7	3.6/3.4

sampling was no longer enough to obtain energy differences which are converged to 5 meV/molecule. We had to use up to 11 k -points in the irreducible part of the Brillouin zone which increased the computational effort substantially. To estimate the influence of a possible compression of the C_{60} molecule under pressure, we have also determined the total energy for several molecular radii in the case of the smallest lattice constant considered below ($a = 13.2$ Å). For a reduction of the radius by 0.5%, we already find an energy increase indicating a very small compression with negligible influence on the total energy. In Fig. 2 we show the results for the pentagon and hexagon orientation. We clearly see that the pentagon orientation is the absolute minimum; however, the theoretical lattice constant is slightly smaller than the experimental value. With decreasing lattice constant the hexagon orientation finally wins. The calculated values were fitted with a Murnaghan equation of state. Table II summarizes results for lattice constant, bulk modulus, and pressure derivative of the bulk modulus in comparison to experimental results. The agreement is very satisfactory. Figure 3 shows the equation of state obtained from the Murnaghan fit in comparison with experimental data. At small pressures up to 0.5 GPa the agreement with single crystal neutron diffraction data of Pintschovius *et al.* [29] (taken for a hexagon rich phase at 70 K) is excellent. The inset of Fig. 3 shows a larger pressure range together with three results of x-ray diffraction studies. Our theo-

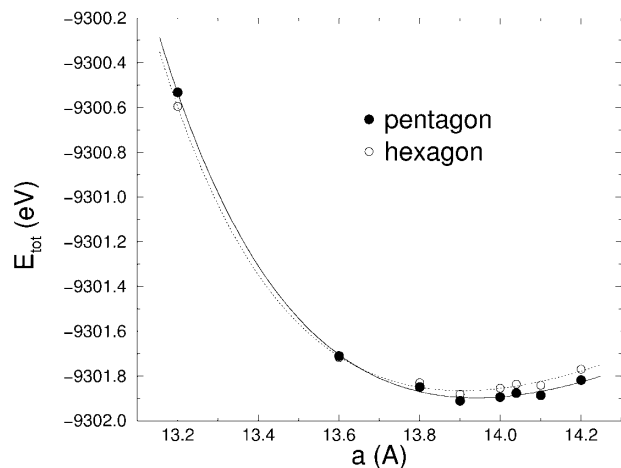


FIG. 2. Total energy per molecule as function of the lattice constant for fixed orientations corresponding to the two minima of Fig. 1.

TABLE II. Theoretical lattice constant, bulk modulus, and its pressure derivative for pentagon and hexagon phases. Experimental values from Ref. [29] correspond to partly disordered phases at 70 K with predominantly pentagon (P) and hexagon (H) orientations, respectively.

	Orientation	a_{\min} (Å)	B (GPa)	dB/dp
Theory	P	13.94	12.9	11.7
	H	13.90	12.9	12.6
Experiment	83% P		14.5	
	90% H		13.2	10

retical curve lies well within the range of experimental data, which exhibit larger scattering at larger pressures. It should be noted that the measurements of Duclos *et al.* [30] (triangles) and Haines and Léger [31] (squares) have been performed at room temperature and include a volume jump of $\approx 1\%$ due to the transition from the pentagon to the hexagon phase at ≈ 0.3 GPa. However, correcting the data for this volume jump improves agreement with our theory only slightly.

Comparing now all of our results to experimental data we see that LDA calculations certainly describe the low-temperature phase of C_{60} in the $Pa\bar{3}$ structure qualitatively correct. This is already a large progress compared to all semiempirical methods which depend sensitively on model fitting. A simultaneous description of the orientational as well as the radial part of the potential is very difficult to achieve in these methods. The LDA calculations even give certain properties in quantitative agreement with experiment as the A_g libration

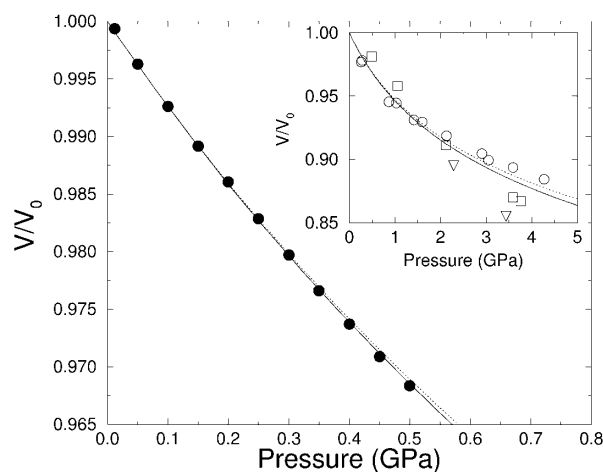


FIG. 3. Pressure dependence of the relative volume. Solid and dashed lines are the theoretical results for the pentagon phase and the hexagon phase, respectively, as derived from the Murnaghan equation of state with parameters taken from Table II. Filled dots denote neutron diffraction results for the hexagon rich phase from Pintschovius *et al.* [29]. The inset shows an extended pressure range together with x-ray diffraction data from Duclos *et al.* [30] (squares), Haines and Léger [31] (triangles), and Ludwig *et al.* [32] (circles).

frequency, the bulk modulus, and the equation of state at low pressures.

Currently, all experiments probing the intermolecular interaction in the low- T phase are influenced by the intrinsic orientational disorder. Our results for the angle dependence of the intermolecular potential for orientationally well-ordered phases thus provide additional information not accessible experimentally which can be useful to improve existing phenomenological models. This can also lead to a better understanding of the high- T rotator phase, where experimental [33] and theoretical [34] investigations indicate short-range orientational order reminiscent to those observed in the low- T phase, but which cannot be studied directly by first-principles methods due to prohibitively large numerical costs.

It is well-known that LDA fails to correctly describe the van der Waals (vdW) interaction at large distances. The success of the present calculation demonstrates that in the present case corresponding errors are of minor relevance suggesting that the asymptotic (long-range) regime of the vdW interaction is not probed in a significant way. The failure of phenomenological models, which employed only vdW-type contributions, to even qualitatively describe the angle dependence of the potential further emphasizes the importance of the short-range chemical bonding in the low- T phase. Within the present approach, however, a clear separation of chemical bonding and vdW-type interactions is not possible.

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