

Structure and Dynamics of Solid C_{60}

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Results of *ab initio* molecular-dynamics simulations of the properties of solid C_{60} are reported. The soccer-ball structure of molecular C_{60} is well preserved in the solid. The $T=0$ structure consists of alternating single and double bonds, but this distinction becomes blurred at relatively low temperatures. The intermolecular interactions are so weak that the individual C_{60} can rotate at relatively low temperatures. At high temperatures vibrations cause large distortions, but the cage structure is still preserved. The present results are in excellent agreement with photoemission and NMR data.

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The recent discovery of a new method of preparing¹ the C_{60} molecule opened a new, very active research area. The C_{60} molecules, which assume the structures of soccer balls with the C atoms situated at each vertex (see Fig. 1), form a close-packed molecular solid with a nearest-neighbor distance of 10.04 Å. This solid, which can be made in quantity using a simple graphite arc source,¹ constitutes a new form of solid carbon. X-ray crystallography^{1,2} has indeed confirmed the earlier conjecture³ that the unusually large abundance and low reactivity of the C_{60} cluster was due to it assuming the fullerene structure. However, the positions of the carbon atoms have not yet been determined and indirect measurements indicate that the fullerenes rotate even at low temperatures.

There are now several indications that fullerene structures form readily and in a variety of sizes. For example, one can obtain a 70-atom elongated "rugby-ball" structure by inserting atoms in a band of hexagons around the middle of the C_{60} fullerene. Indeed, C_{70} clusters have a substantially larger abundance and lower reactivity than clusters of similar size. Very recently, a C_{70} component has been isolated in a pure form,^{2,4} although its full

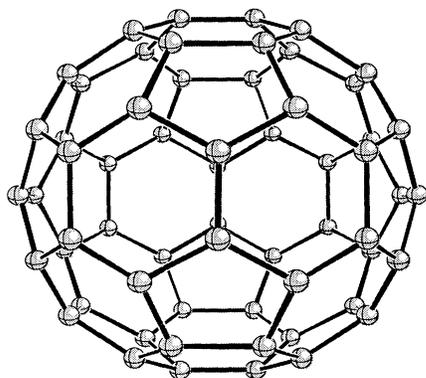


FIG. 1. The structure of the C_{60} buckminsterfullerene. Note the alternating fivefold and sixfold rings.

characterization has not yet been completed. Furthermore, cluster-fragmentation data show trends reminiscent of the C_{60} patterns for clusters containing several hundred carbon atoms. Cage and spiral structures based on twelve pentagonal faces and a large number of hexagonal faces have been predicted from purely geometric considerations.⁵ These new forms of molecular and solid carbon open an entirely new area for experimental and theoretical investigations. They may also provide a rich variety of cage structures for applications in tribology, catalysis, and biology.

The present Letter describes the results of symmetry-unconstrained structure optimization and finite-temperature *ab initio* molecular-dynamics simulations of solid C_{60} . The results show that the intermolecular interactions are weak and do not substantially affect the structure of the individual fullerenes. The calculated photoemission spectra are in excellent agreement with experimental data. The effects of temperature on the structure and stability of C_{60} and on the rotational-vibrational motion in the solid are examined by constant-temperature simulations. The simulations show that the C_{60} molecules indeed rotate at relatively low temperatures, in good agreement with NMR data.

The structure optimization and the simulations were carried out using the local-density theory and the Car-Parrinello method.⁶ The carbon atoms were represented by a soft-core pseudopotential⁷ which reproduces well the structural properties of both diamond and graphite, as well as the results of a previous calculation for C_4 .⁸ The fullerenes were placed in a close-packed fcc structure at the experimentally observed nearest-neighbor distance of 10.04 Å.⁹ Plane waves with kinetic energies of up to 35 Ry were included in a symmetry-unconstrained structure optimization. Since a structure optimization using a 26-Ry cutoff resulted in errors of only 0.01 Å in the bond lengths and minimal changes in the bond angles, we used this cutoff in the simulations.

The optimization of the structure proceeded using a dynamical relaxation algorithm in which the electrons and ions followed Car-Parrinello equations containing an

extra friction term. In addition, whenever the velocity of any atom was antiparallel to the force acting on it, the velocity was reduced by a constant factor. The friction force and the quenching of the velocity thus provided the dissipative forces for an approach to equilibrium. Our tests on this and other systems have shown that procedures of this type result in much faster structure optimizations than either the steepest-descent or the conjugate-gradient algorithm. In the finite-temperature simulations the ions followed Nosé dynamics¹⁰ adapted to Car-Parrinello simulations,¹¹ while the electrons were kept on the Born-Oppenheimer surface. The time step in the simulations was 1.2×10^{-16} s and up to 2000 steps were taken after equilibration.¹²

The structure optimization led to an almost ideal fullerene with an average diameter of 7.1 Å. Similar to what has been predicted for the free molecules,¹³⁻¹⁶ two carbon-carbon bond distances were found, corresponding to nominally single and double carbon-carbon bonds. The average lengths in the optimized structure for the double and single bonds are 1.40 and 1.45 Å, respectively. As expected, these values straddle the nearest-neighbor bond length in graphite which is 1.42 Å. The presence of the two bonds is due to the inequivalence of the pentagonal and hexagonal rings. In hexagonal rings the single and double bonds alternate, while only single bonds are present in pentagonal rings. The bond alternation can most clearly be seen in a charge-density plot in the plane of the hexagonal ring (see Fig. 2). For the purpose of examining intermolecular interactions, Fig. 2 also shows parts of the charge density associated with adjacent fullerenes. It is clear from the figure that the overlap of charge densities of nearest-neighbor fullerenes is very small in solid C₆₀.

The geometry-optimization calculations in this work were symmetry unconstrained and were carried out for solid C₆₀. Previous calculations¹³⁻¹⁶ were symmetry re-

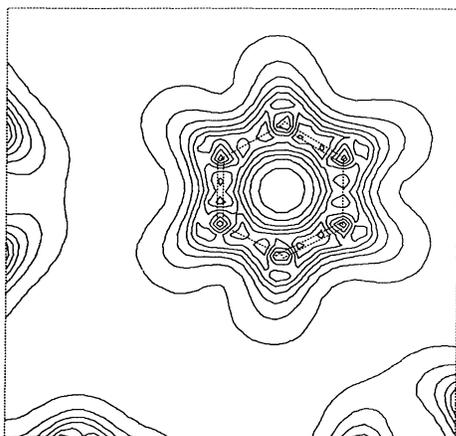


FIG. 2. Charge density in the plane of the hexagonal ring. Note the alternating single and double bonds.

stricted and were carried out for the isolated molecule. However, due to the closed-shell nature of C₆₀ and the large intermolecular distance, the differences between the optimized C₆₀ structure in the solid and the symmetry-constrained isolated C₆₀ are not substantial. The previous calculations predicted somewhat shorter bond lengths and, except for Ref. 16 which also used local-density theory, larger variations between single-bond and double-bond distances. These discrepancies are most likely due to the differences in computational methods rather than structural changes upon the formation of the solid. The intermolecular interactions in the solid do introduce small variations in bond lengths, however, not exceeding 0.01 Å at $T=0$ K. Similarly, deviations in the bond angles from the ideal pentagon and hexagon values do not exceed 1°.

Very recently, and after these calculations had been completed, photoemission spectra of solid C₆₀ were obtained.¹⁷ In Fig. 3 we show a comparison of broadened eigenvalue spectra to the experimental data. Two broadenings have been used: a constant Gaussian broadening with a width $w=0.25$ eV, and a variable width $w=0.25+0.04(E-E_{\text{HOMO}})$ eV (where HOMO denotes highest occupied molecular orbital). The variable-width broadening accounts for the shorter lifetimes of the deeper holes. The agreement between the calculated and the measured spectra is excellent. It provides a further confirmation of the structure of C₆₀ and

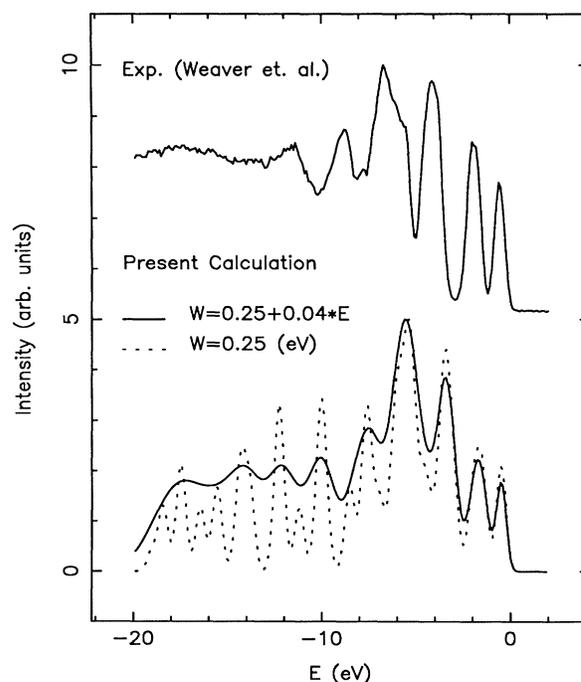


FIG. 3. Comparison between the measured and calculated photoemission spectra for solid C₆₀. The data are from Ref. 17. See text.

of the reliability of our procedures for calculating its electronic and structural properties. However, since the eigenvalues, and therefore the calculated and measured spectra, are not very sensitive to small changes in the atomic positions, the confirmation of the precise atomic positions will require a more structure-sensitive measurement. Since there is a clear one-to-one correspondence between most of the peaks in the electron-distribution spectrum and the eigenvalue spectrum, matrix-element effects appear to be small at this photon energy (65 eV). Much stronger matrix-element effects occur at other energies¹⁷ and a full analysis of the photoemission spectra is discussed by Weaver *et al.*¹⁷

Constant-temperature simulations were carried out for a number of representative temperatures. They utilized the quantum molecular-dynamics version¹¹ of Nosé dynamics¹⁰ and started from the optimized atomic positions. Since Nosé dynamics does not conserve angular momentum, the fullerenes can both rotate and vibrate subject to the constraint of constant average temperature. Since the simulation times possible on today's computers correspond to very short real times, the equilibrium between the rotational and vibrational motion could not be obtained. Our starting conditions have nevertheless always led to a mixture of rotational and vibrational modes and it was particularly easy to induce rotations. For example, heating the system to $T_{\text{Nosé}} = 300$ K already led to rotational motion. The presence of rotations at this low temperature proves that the intermolecular bonding is very weak and is consistent with the lack of significant bonding interactions between the fullerenes (cf. Fig. 2). Since the van der Waals interactions are not well described in local-density theory, we did not attempt to determine the onset temperature for the rotation, whose angular velocity varied between 1.5×10^{12} and 2.8×10^{12} /s depending on the Nosé temperature and the details of the simulations. Experimentally, the NMR spectrum consists of a single narrow line at temperatures above 70 K, while lower-temperature spectra broaden substantially and show structure.^{18,19} The single NMR line at temperatures above 70 K provides strong evidence for rotation and our simulations are consistent with this interpretation.

We turn now to the analysis of bond-length and bond-angle distributions at various temperatures (Fig. 4). At $T = 0$ K one can clearly distinguish between single and double bonds. Since each carbon atom forms two single and one double bond, the single-bond peak at 1.45 Å is twice as strong as the double-bond peak at 1.41 Å [Fig. 4(a)]. However, at vibrational temperatures as low as 375 K the vibrational amplitudes are sufficiently strong to wash out the small difference between the single- and double-bond lengths and only a single broad peak is present. This is consistent with the results of Cox *et al.*²⁰ who report a single bond length of 1.42 Å extracted from room-temperature extended x-ray-absorption fine-structure

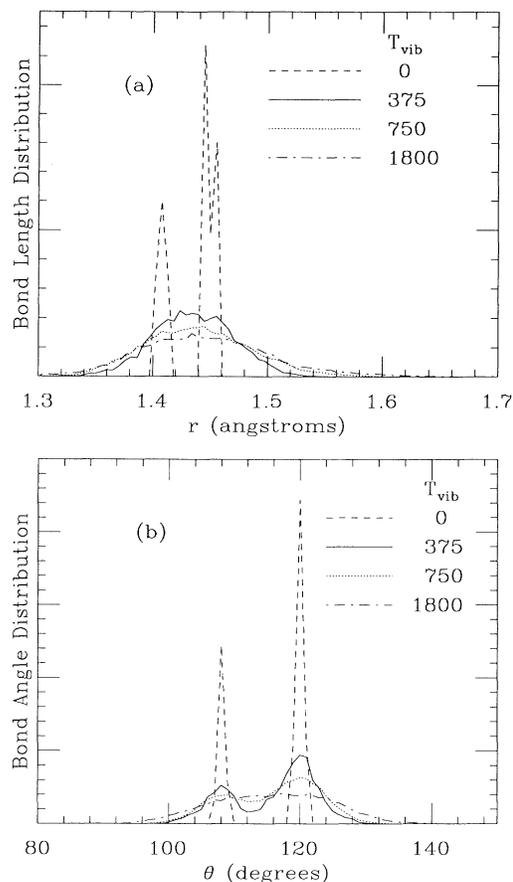


FIG. 4. Bond-length and bond-angle distributions in solid C₆₀ at various temperatures. A 26-Ry cutoff was used in these simulations. See text.

ture data of C₆₀ deposited on a gold surface. At higher temperatures further broadening and bond softening is observed, but the fullerene structure remains intact.

Similar trends are observed in the bond-angle distribution [Fig. 4(b)]. At $T = 0$ K two peaks are present, centered around the ideal bond angles for the hexagon (120°) and the pentagon (108°). Since each atom participates in two hexagonal and one pentagonal ring, the 120° peak has twice the strength of the 108° peak. At $T_{\text{vib}} = 375$ K vibrations broaden the two peaks, but the amplitudes of bond-bending vibrations are relatively small and the peaks are still clearly distinguishable. Only at the highest temperature we tried, $T_{\text{vib}} = 1800$ K with fluctuations of up to 750 K, did the two peaks merge into one. However, the fivefold and sixfold rings are well defined even at that temperature, although the distortions from the ideal spheroidal structure are large. A more quantitative measure of the distortions from the ideal structure is provided by the ratio of the maximum distance to the corresponding minimum distance of any of the carbon atoms from the center of mass of the C₆₀.

At $T=0$ this ratio is 1.01. The slight deviation from unity is caused by the weak crystal field. At $T=375$, 750, and 1800 K, this ratio, averaged over the duration of the simulations, increases to 1.08, 1.09, and 1.22, respectively. However, the average diameter of the C_{60} remains almost constant, increasing by only 0.02 Å upon heating from $T=0$ to 1800 K.

In summary, we have investigated solid C_{60} by the *ab initio* molecular-dynamics method. The celebrated buckminsterfullerene structure is very well preserved in the solid. The intermolecular interactions are weak and lead only to minor changes in bond lengths and bond angles upon solidification. The calculated eigenvalue spectrum is in excellent agreement with photoemission data, while the details of the geometry-optimized structure still await experimental confirmation. The alternating single and double bonds are preserved in the solid, but this distinction becomes blurred at moderate temperatures. In constant-temperature *ab initio* simulations the C_{60} molecule starts to rotate at relatively low temperatures, which is in very good agreement with NMR data. The ease with which this rotation can be initiated constitutes a further confirmation of the weakness of the intermolecular interactions. At high temperatures the vibrational amplitudes are substantial but the cage structure is preserved, indicating excellent high-temperature stability. The last result is consistent with the ease of formation of the C_{60} structure in the high-temperature laser ablation and graphite arc sources, since it may be one of the very few nonreactive molecules which are still stable at the operating temperatures of these sources.

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