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Infrared spectroscopy through the orientational phase transition in fullerene films

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Infrared-absorption studies of thin fullerene films as a function of temperature reveal a splitting of an absorption line at 245±3 K. Another absorption line narrows and its frequency shifts without splitting. These observations support earlier neutron- and x-ray-diffraction findings of an orientational phase transformation at 250 K in bulk samples. We provide an explanation based on an accepted crystal structure of C_{60}.

The recent discovery of the efficient synthesis of C_{60} (Ref. 1) has resulted in a flurry of experimental and theoretical investigations of this highly symmetric cage structure. In addition, observations of photoconductivity[2] and superconductivity[3,4] in doped C_{60} have focused our attention on the electronic structure and temperature dependence of structural properties of this unusual material. In this paper we report temperature-dependent infrared (IR) spectra of thin films of C_{60} from room temperature to 10 K. We have studied two of the four IR-active modes. One of the IR absorptions at 1183 cm^{-1} narrows and shifts slightly toward higher energies while the other mode at 1429 cm^{-1} splits at approximately 245 K, and becomes better resolved as the temperature is further lowered to 10 K. We offer an explanation based on a model of the vibrational modes of C_{60} (Ref. 5) and proposed crystal structures.[6–10] These observations are consistent with the recently reported orientational ordering in bulk C_{60} studied using ^{13}C NMR (Ref. 11 and 12) and x-ray and neutron diffraction.[6–10]

C_{60} was prepared in an arc and purified chromatographically to remove impurities including C_{70}. Thin films of C_{60} were prepared by sublimation[13] onto a silicon substrate. Films of about 5500-Å thickness were deposited following outgassing of the starting material at 200 °C and subsequent sublimation at 300 °C. The silicon substrates were mounted on a copper block for insertion into a continuous-flow cryostat. The sample temperature was measured using a silicon diode mounted directly on the sample. The temperature was measured and controlled to ±0.5 K. Prior to cooldown, the sample chamber was evacuated to below 10^{-6} Torr. Infrared-absorption spectra of the C_{60} films were recorded between 800 and 5000 cm^{-1} at apodized resolutions of 2, 0.4, and 0.075 cm^{-1} using a Bomem Fourier-transform spectrometer. Spectra were recorded at 19 temperatures between 295 and 8 K. Each of the spectra was referenced to a spectrum of a blank silicon substrate at the same temperature.

Four infrared active modes have been predicted and observed for this icosahedrally symmetric molecule.[1,14] We focus our attention on the 1183- and 1429-cm^{-1} modes which are within the capabilities of the present experiment. Weak extra features at 1530 and 2150 cm^{-1} are seen and are most likely due to oxygen and residual carbon monoxide which readily incorporate into the C_{60} films even after a brief exposure to air.[15]

Figures 1 and 2 show the temperature dependence of the observed IR-absorption features of the C_{60} films at 0.4-cm^{-1} resolution from 270 to 8 K. Both the 1183- and 1429-cm^{-1} features have the same symmetry, T_{1u}. The 1183-cm^{-1} modes narrows somewhat continuously and shifts slightly from a center frequency of 1183.1 to 1183.4 cm^{-1} around 240 K. The 1429-cm^{-1} mode has a weak shoulder around 1424 cm^{-1} and begins to show further structure at approximately 245 K. This is very close to the temperature of 250 K at which Heiney *et al.*[6] have reported a transition from fcc to a simple cubic structure in bulk C_{60}. The 1424-cm^{-1} shoulder becomes well defined below 245 K and an additional peak appears at 1428 cm^{-1}. At 8 K, the cluster consists of peaks centered at 1424.5, 1427.9, and 1431.2 cm^{-1} with widths of 1.5, 1.2, and 3.1 cm^{-1}, respectively. The middle line shifts to 1429 cm^{-1} at 250 K and the 1431.2-cm^{-1} peak shifts more gradually down to 1430 cm^{-1} in the region of 230 K. Another absorption feature at 1215 cm^{-1} appears but is left unassigned for the present. Peak positions and widths were determined by a linear least-square-fitting algorithm. As the film temperature is lowered below 240 K, the 1429-cm^{-1} mode splits into three distinct features. Since the low-temperature bulk C_{60} has been shown to be rotationally locked,[8–12] the observed splitting of the 1429-cm^{-1} mode could arise from the reduction of symmetry which lifts the degeneracy associated with the state. The 1183-cm^{-1} mode is best fit to a single Lorentzian and the 1429-cm^{-1} cluster is best fit to a superposition of three Lorentzians. No additional features can be discerned in spectra obtained with higher resolution (0.075 cm^{-1}). The insets to Figs. 1 and 2 show the changes in the linewidths as a function of temperature. For the 1429-cm^{-1} cluster, the width of the 1424-cm^{-1} line is roughly constant and not plotted. The widths of the 1428- and 1431-cm^{-1} lines are shown. The sharpening of the central feature of the 1429-cm^{-1} cluster is seen below 250 K and a separate line is distinguishable at 240 K. We assign the transition temperature as 245 K ±3 K based on the midpoint of the linewidth change as a function of temperature.

As the sample temperature is lowered, a large, diffuse absorption peak appears in the 3200-cm^{-1} region. This is similar to the features observed by Nuzzo *et al.*[16] in a re-

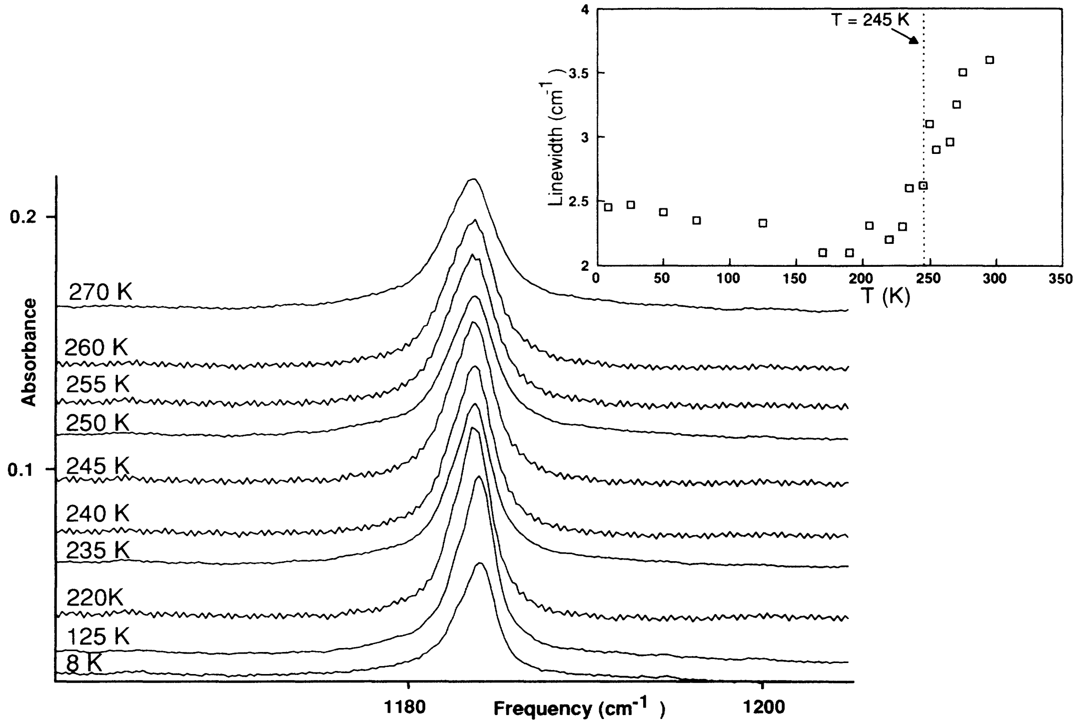

FIG. 1. Temperature dependence of the 1183-cm^{-1} mode at 0.4-cm^{-1} resolution. Traces are offset for clarity, and the inset shows linewidth as a function of temperature.

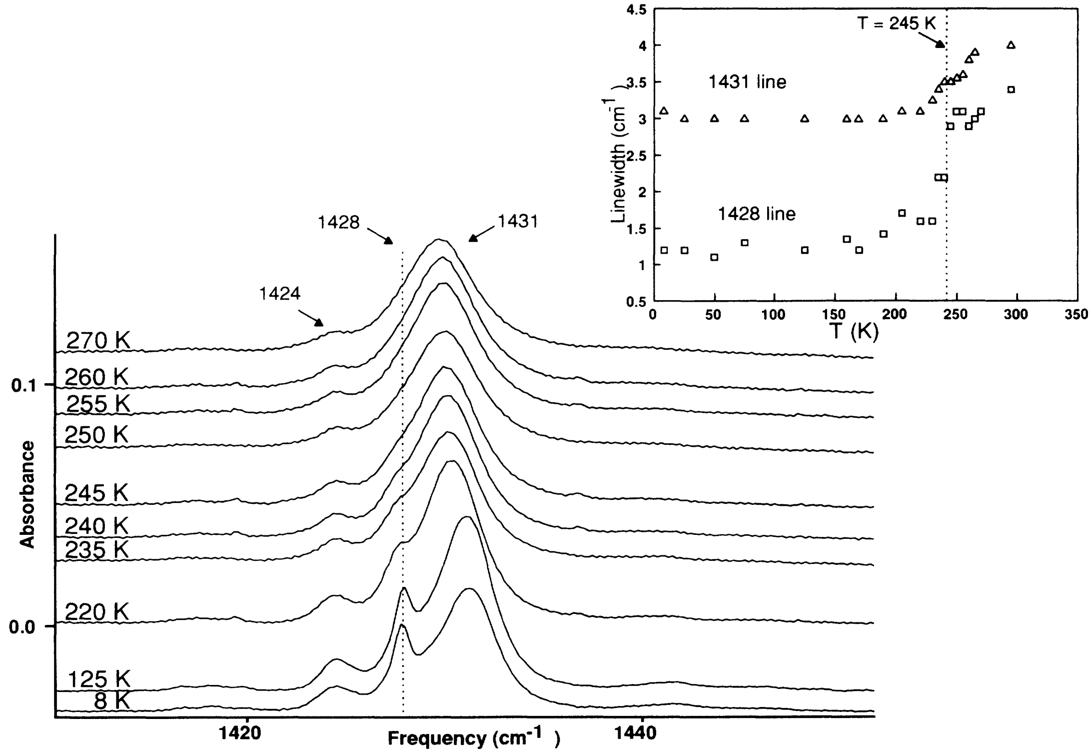

FIG. 2. Temperature dependence of the 1429-cm^{-1} mode at 0.4-cm^{-1} resolution. At approximately 245 K, a weak shoulder becomes apparent and below this temperature, a separate line is clearly visible. Traces are offset for clarity and the inset shows the linewidth as a function of temperature for the lines centered at 1428 and 1431 cm^{-1}.

cent study of amorphous and crystalline water layers adsorbed on organic films. The feature at 3200 cm^{-1} in the present study is ascribed to the residual water vapor in the cryostat forming a $\mathrm{H_2O}$ layer on the C_{60} film.

The observed line splitting of only one of the two modes is interesting because both the modes have the same symmetry. One would expect the lifting of degeneracy of both the modes on lowering of symmetry. In addition, splittings are not expected *a priori* because unsplit T_{1u} modes are supported in both space groups ($Fm\bar{3}$ and $Pa\bar{3}$). The observed splitting pattern must, therefore, be related to changes in local crystal field (i.e., differences in interball couplings) which affect the two modes differently. David *et al.*[9] have shown that in the low-temperature crystal structure deduced by Harris and Sachidanandam,[7] the electron-rich bond between two hexagons (6-6 bond) points into an electron-deficient pentagonal ring on an adjacent molecule. This weak bond explains the change from a fcc to a simple cubic structure with only a very small change in lattice parameters.[10] Furthermore, David *et al.*[9] propose that electron repulsion causes a change in electron density away from the $\langle 110\rangle$ direction towards the $\langle 100\rangle$ direction. This results in a *molecular* symmetry change from I_h to S_6 which is sufficient to split a T_{1u} line into $A_{1u}+E_u$ lines. We propose that the lifting of degeneracy in only one of the modes can be explained by examining the normal modes of the C_{60} molecule.

Several groups have calculated the vibrational frequencies and normal modes of C_{60}.[5,17–19] We use the coordinates and displacements obtained by Raghavachari and Rohlfing[5] to examine the behavior of the 6-6 bond and the pentagonal motions.

Figure 3 shows a stereoscopic view of the cubic phase ($Pa\bar{3}$), generated from the data in Ref. 9. The six C_{60} molecules are nearest neighbors, four in a plane, one in front, and one in back. The pentagon to 6-6 bond correlation is readily seen. Figures 4(a) and 4(b) show a portion of two neighboring molecules with an emphasis on a 6-6 bond and an adjoining pentagon. The arrows indicate the direction of motion of the respective molecules. There are three distinct motions per mode corresponding to the triple degeneracy. One motion per mode is shown. The highest energy vibration shows significant compression and distention along the 6-6 bond. The pentagon facing this bond is, itself, attached to 6-6 bonds at each carbon vertex. It therefore undergoes expansions and contraction when a 6-6 bond length changes. This should result in a significant change in overlap between a 6-6 bond and the pentagon on the C_{60} molecule adjacent to it. The 1183-cm^{-1} mode, by contrast, shows no such drastic change in the 6-6 bond length. Rather, the bond appears to move tangential to the surface of the ball while maintaining its length. The separation between the 6-6 bond and the pentagons also appears to be roughly constant in this case. The small frequency shift and line narrowing of this mode are characteristic of anharmonic coupling to modes of the solid. We propose that, in the solid, the differences in the overlap seen in the higher energy mode are sufficient to make the splitting observable under high resolution (i.e., a splitting due to a crystal field.) We note further that above 245 K, the C_{60} molecules are free to rotate so that the question of overlap is moot. The narrow width of the high-temperature line, however, indicates that it is not merely a superposition of an inhomogeneous distribution of low-temperature configurations. The data indicate that some motional narrowing seems to be taking place. This issue will be addressed in future work. The weak shoulder at 1424 cm^{-1} suggests that rotation in one of the triply degenerate modes may be slightly hindered even above 245 K, perhaps due to oxygen or other impurities, or that the polycrystalline nature of the films causes some residual site inhomogeneity even at high temperatures.

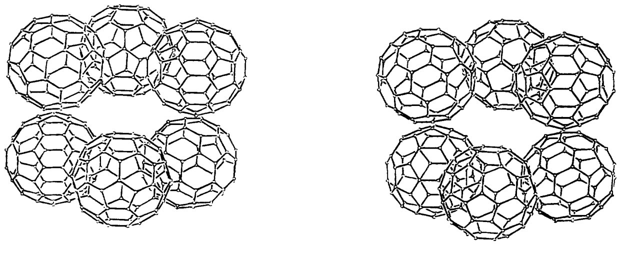

FIG. 3. Stereographic projection of six nearest-neighbor C_{60} molecules in the low-temperature simple cubic structure. The relationship between the electron-deficient pentagonal rings and the electron-rich 6-6 bonds as described in Ref. 9 is apparent. This figure is best viewed with commonly available stereoscopic viewers.

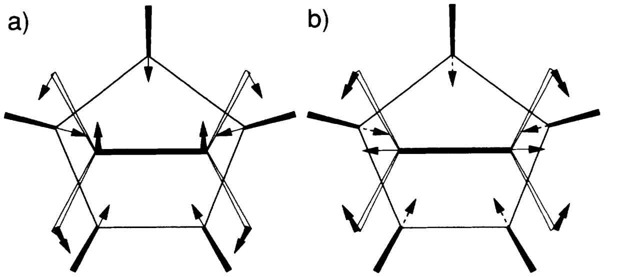

FIG. 4. Projection along an interball axis. The 6-6 bonds (heavy lines) attached to each pentagonal vertex project out of the plane of the paper. The pentagon faces a 6-6 bond from a molecule facing it. The four bonds attached to this 6-6 bond project behind the plane of the paper. (a) Atomic motions characteristic of the unsplit mode at 1183 cm^{-1}. The 6-6 bond moves tangentially while maintaining its length. Heavy arrows indicate out-of-plane motions. (b) Atomic motions characteristic of the split mode at 1429 cm^{-1}. The 6-6 bond undergoes compression and elongation. The facing pentagon is, itself, attached to 6-6 bonds at each vertex and undergoes a breathing motion. This change in overlap is proposed as the crystal field which lifts the triple degeneracy. Heavy and dashed arrows indicate out-of-plane motions.

In conclusion, we have reported the temperature dependence of two of the IR-active modes of undoped C_{60} thin films studied at high resolution. The observed differences in the behavior of the two modes are ascribed to differences in the local crystal field which arise when the solid C_{60} goes into a rotationally locked phase below 250 K. This shows the utility of IR spectroscopy as a probe of important structural dynamics in the condensed phase. Similar studies of IR-active modes in doped C_{60} films which show superconductivity at 20–40 K are underway. The behavior of vibrational modes upon injection of charges should provide additional valuable insights into the science of this molecular solid.

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