Lattice Phonon Modes in Solid C_{60} Studied by Far-Infrared Spectroscopy

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The far-infrared transmission spectrum of solid C_{60} is presented in the 7.5–420-cm^{-1} range at 2 K. It is found that the cubic environment of C_{60} molecules in the solid results in the activation and splitting of silent molecular modes. The two infrared-active translational modes propagating in the C_{60} solid are observed below 60 cm^{-1}. Their energies are found to be significantly higher than predicted by molecular-dynamics simulations. This suggests a harder intermolecular potential for solid C_{60} than presently used in these simulations.

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Stimulated by the discovery of an efficient method for producing macroscopic quantities of C_{60} [1], a tremendous activity is currently directed at understanding the basic physical properties of C_{60} and related fullerenes. Various phenomena ranging from the unique dynamics of this highly spherical molecule [1–3] to high-temperature superconductivity in alkali-doped solid C_{60} [4] have been observed. A good knowledge of lattice modes in solid C_{60}, combined with information on its band structure and of that of doped fullerenes [5–7], would be helpful in elucidating the electron-phonon coupling [8] in this new class of molecular solids which exhibit either superconductivity (e.g., K_3C_{60}) [4,6] or semiconductor behavior (e.g., K_6C_{60}) [6,7]. In this paper, we report on a study of the translational modes of C_{60} by means of far-infrared (FIR) spectroscopy. The comparison of their energies with the predictions of molecular-dynamics calculations (MD) [9,10] will provide a stringent test for the parameters used in such calculations. In this respect, the present paper suggests a harder intermolecular potential in solid C_{60} than presently used.

In view of the abundant converging literature devoted to it [1–3,11,12], the dynamics of C_{60} molecules may be considered as rather well understood. In particular, MD simulations succeed in reproducing its main features [13]. The 174 degrees of freedom result in only 46 distinct frequencies due to the I_h symmetry. Among them, the four infrared-active ($4F_{1u}$) and the ten Raman-active ($2A_g + 8H_g$) modes are well documented [1,2]. Dynamical properties of the molecular solid that forms due to van der Waals forces between C_{60} molecules proves extremely rich. The famous cage structure is preserved in the solid [14]. At room temperature, the crystal structure is face-centered cubic (fcc) [15] and the C_{60} molecules rotate freely [16]. There is an orientationally induced phase transition to a simple cubic (sc) structure at 260 K [3,17,18]. Rotational disorder of C_{60} molecules persists in the solid at much lower temperature [16,18], possibly down to 90 K [19]. As compared to the free molecules, new features appear in the phonon spectrum of a molecular solid such as C_{60}. First, the reduced symmetry results in mode splittings and/or activation of silent molecular modes [20]. This has been observed recently for some even modes of C_{60} by means of Raman scattering [21]. Second, at much lower energy than molecular vibrations, collective rotational (librational) modes and translational modes are expected to propagate in the solid. Low-temperature neutron-scattering measurements have been recently reported on librational modes around 20 cm^{-1} [22]. To the best of our knowledge, none of the experimental studies published so far has reported on the energies of translational modes in solid C_{60} to compare with existing calculations.

The full FIR-spectroscopy analysis (frequencies and mode assignments) usually requires the use of large-area single crystals (typically 4 mm×4 mm×0.5 mm shaped platelets). Since the growth of such large C_{60} single crystals remains a challenge, we have prepared samples suitable for our measurements which, we believe, reveal interesting new aspects of solid C_{60} dynamics. Three different sets of C_{60} powder were produced using standard methods [23]: The only solvents used for Soxhlet extraction and chromatography are cyclohexane and toluene. From these powders, we have compressed ($P \lesssim 0.5$ kbar) three pellets. The results presented here were obtained with a 4-mm-diam, 0.73-mm-thick pellet. Several characterizations have been made to check the quality of this sample or of the initial powder. Scanning electron microscopy shows the existence of large grains (10 μm) both at the surface and in bulk of the sample. Room-temperature x-ray characterization of the powder confirms the fcc structure with a 14.166(6)-Å lattice pa-

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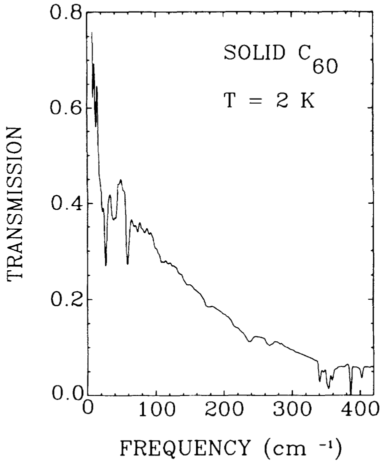

FIG. 1. Far-infrared transmission spectrum of solid C_{60} ($T=2$ K) over the entire frequency range accessible with our system. This spectrum makes the link between the individual vibrational modes of C_{60} seen as transmission dips at high frequency ($E > 340$ cm^{-1}) and the collective phonon modes at low frequency ($E < 60$ cm^{-1}). The dip around 386 cm^{-1} is a spurious feature due to the sapphire window placed in front of the detector.

rameter, in excellent agreement with Fleming's data [15]. Mass spectroscopy reveals no detectable trace of C_{70}. Since C_{60} usually suffers from a non-negligible contamination with the solvents used during the purification, we have performed a chemical microanalysis which reveals the presence of 0.052 ± 0.004 H atom per C atom. FIR transmission has been measured between 7.5 and 420 cm^{-1} at low temperature ($T=2$ K) using a fast-scan Fourier-transform spectrometer (Bruker IFS 113 v) and a high-sensitivity Ge bolometer sealed by a sapphire window. The resolution was taken at 2 cm^{-1}. Several beam splitters were used to cover a wide energy range.

In Fig. 1, we show the transmission spectrum over the entire frequency range. This spectrum consists essentially of two rich structures at high frequency ($E > 340$ cm^{-1}) and low frequency ($E < 60$ cm^{-1}), superimposed on a decreasing background due to elastic scattering in our granular material.

Details of the high-frequency part of the spectrum are shown in Fig. 2. This structure is due to the lowest odd vibrational modes of individual C_{60} molecules, as evidenced by the agreement with neutron-inelastic-scattering (NIS) data [12] and confirmed by calculations [11]. The observation of these modes in our FIR measurements is an illustrative manifestation of the solid environment on vibrational modes of C_{60} molecules. Indeed, these modes are not infrared active in the symmetry group I_h (the lowest active F_{1u} mode is at 526 cm^{-1} [1,2]). However, they are turned on in the sc phase whose space group is T_h^6 in which the four inequivalent C_{60} molecules occupy sites with $\bar{3}$ symmetry [24]. This produces activation and splitting of all odd modes since their decompositions into irreducible representations of the T_h group all include its infrared-active mode T_u (e.g., $F_{2u} \rightarrow A_u + E_u + 3T_u$ [20,25]). Such a behavior is indeed seen in Fig. 2, in contrast to the NIS data which were not able to resolve these splittings [12]. The mode at 340.5 cm^{-1} is split into (at least) two components and that at 353.7 cm^{-1} into three partly resolved components, while the mode at 402.2 cm^{-1} apparently remains unsplit. Note that the sharp dip at 386 cm^{-1} due to the sapphire optical window of the detector might mask some splittings. Recently, van Loosdrecht, van Bentom, and Meijer [21] have reported that all even modes are similarly Raman activated in the solid, and they observed splitting for some of them.

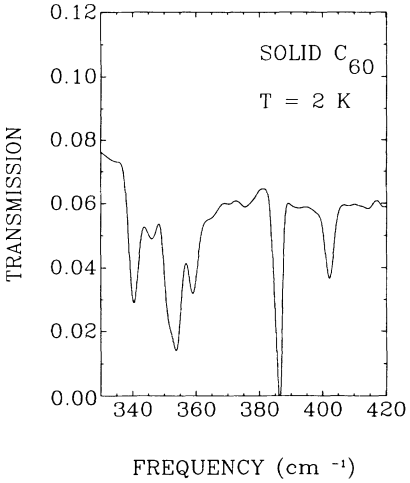

FIG. 2. Details of the high-frequency part of the spectrum showing activation and splitting in the solid of infrared-inactive modes of C_{60} molecules. As in Fig. 1, the dip at 386 cm^{-1} is due to the optical window of the bolometer.

Apart from the above effects on the molecular modes, the low-temperature solid phase manifests itself in the existence of 24 low-frequency phonon modes. These phonons originate from the six translational (F_{1u}) and rotational (F_{1g}) center-of-mass degrees of freedom of the four molecules that constitute the unit cell. Factor-group analysis shows that twelve translational modes $A_u + E_u + 3T_u$ [20,25] (with respective dimensions 1, 2, and 3) and twelve librational modes $A_g + E_g + 3T_g$ are expected. Among them, the overall translation T_u and overall rotation T_g of the crystal must be taken out. Therefore, one is left with four zone-center translational modes, two of them being infrared active ($2T_u$), and four zone-center librations which are all Raman active. The low-frequency part of the transmission spectrum is shown in Fig. 3. Its low-energy location suggests that it is due to phonons propagating in the solid. By comparison with other samples with higher H contamination, up to 0.106 H atom per C atom (see Fig. 3), we find that the two salient peaks at 26.6 and 58.5 cm^{-1} clearly dominate the FIR spectrum of all of the samples. Therefore, we assign

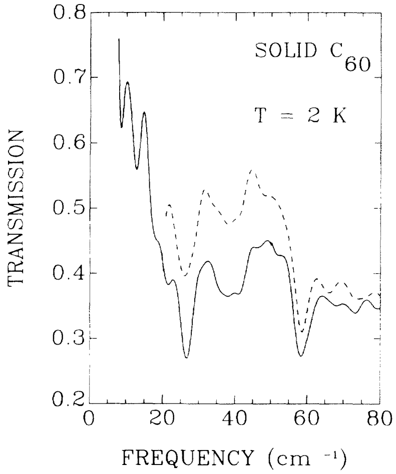

FIG. 3. The low-frequency part of the spectrum showing lattice phonon modes in solid C_{60}. The thin vertical lines point out where the beam splitter was changed during the experiment. The dashed curve shows the spectrum of a C_{60} pellet with a higher contamination from the solvents (0.106 H atom per C atom).

them to the two infrared-active T_u modes of solid C_{60}.

There exist recent calculations of solid C_{60}. Here, we refer to a MD simulation [9] in which pairs of C atoms of different molecules, arranged in a small (32 or 108 molecules) fcc lattice, interact via a (12-6) Lennard-Jones potential obtained from graphite. A potential depending on the relative orientation of the molecules is also included. This simulation succeeds in reproducing the zero-pressure lattice parameter and the compressibility coefficient of fcc C_{60}. However, the calculated low-temperature phase is tetragonal rather than the cubic phase found experimentally. The phonon density of states (DOS) is obtained from the Fourier transform of the velocity autocorrelation function. At 100 K, sharp peaks in the translational DOS are obtained at roughly 23, 28, 35, and 41 cm^{-1} [9]. Another calculation predicts the translational modes to have energies below 45 cm^{-1} [26].

It is clear that the intense peak observed at 58.5 cm^{-1} has significantly higher energy than calculated. It seems unlikely that the discrepancy with the MD calculation is due to the much lower temperature in the experiment. A more plausible explanation for the above discrepancy is that the potential used in the MD simulation is too soft. This potential has been recently refined [10], mainly to account for the essential finding that in the sc phase, electron-rich bonds face electron-poor regions of adjacent molecules [19]. This improvement succeeds in stabilizing the T_h^6 phase. With this improved potential, the librational DOS is pushed substantially higher in energy, bringing it into closer agreement with experiment [22]. It is likely that a similar effect occurs for the translational DOS.

There are several additional points arising from our measurements. First, the broad band seen in Fig. 3 at approximately 39 cm^{-1}, which comprises two partly resolved peaks at 37 and 41 cm^{-1}, is also reproducible from sample to sample. A possible explanation for these peaks is that they are due to the silent A_u and E_u modes. Second, at very low frequency, additional peaks are seen at 8.5, 12.8, 17.7, and 21.6 cm^{-1}. Although our data are limited to only one sample at $\nu < 12\ \mathrm{cm}^{-1}$, the three other peaks are present in all samples. Their low-energy positions suggest that they may be due to librational modes [10,22] which are not, however, infrared active in the T_h group. A possible reason for infrared activation of silent odd modes and of Raman-active even modes is a small symmetry lowering below cubic symmetry (see, e.g., Ref. [20]). Further indication for such a symmetry lowering comes from the observation in all samples of a mode at 266.7 cm^{-1} (see Fig. 1) which coincides rather well with the Raman-active H_g molecular mode at 273 cm^{-1} [1,2]. The latter splits into several components at lower energy in the solid [21]. It is also worth noting that recent Raman measurements (which probe only even modes in a crystal with inversion symmetry) on a C_{60} single crystal at 150 K [21] were reported on a lattice mode at 56 cm^{-1} which is very close to the T_u infrared-active mode reported here at 58.5 cm^{-1}. This is also consistent with a symmetry lowering. Returning to Fig. 1, we can observe several peaks between 60 and 340 cm^{-1}. Among them, the only feature which is well resolved in all of the samples is that at 266.7 cm^{-1}, as already mentioned.

To summarize, we have reported a FIR optical study of solid C_{60} which makes the connection between the high-frequency individual and low-frequency collective vibrational modes in this material. Our data are the first compelling ones to be compared with computations of the dynamical properties of solid C_{60}. The results presented here will help to refine the parameters included in the calculations, thus providing the possibility of calculating various physical properties of solid C_{60} which are directly connected to dynamical processes such as specific heat [27] and sound velocity [18].

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