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

Huant *et al.* [1] have measured the far-infrared spectrum of solid C_{60} at 2 K. They report a series of peaks below 60 cm^{-1} which are attributed to external crystal vibrations in the ordered $Pa\overline{3}$ phase, where the crystal has four molecules per unit cell. At the Brillouin zone center Γ, molecular translational motions give rise to two infrared active F_u (or T_u) modes, and to one A_u and one E_u silent mode, which are uncoupled by symmetry from the molecular librations. These produce three F_g (or T_g), one E_g and one A_g Raman active modes.

The reported spectrum contains two salient peaks at 26.6 and 58.5 cm^{-1}, assigned by the authors to the two F_u modes on the sole basis of their intensity. The remaining features are interpreted in terms of vibrations activated by impurities or crystal imperfections: a broad band comprising two peaks at 37 and 41 cm^{-1} is tentatively attributed to the silent E_u and A_u modes, whereas additional peaks at 8.5, 12.8, 17.7, and 21.6 cm^{-1} are assigned to librational motions.

Very recently, we have calculated a series of static, dynamical, and thermodynamical properties of solid C_{60} in both known crystalline phases [2], using an interaction potential consisting of C-C Buckingham 6-exp interactions with parameters fitted by Pertsin and Kitaigorodsky [3] to hydrocarbon molecules, and electrostatic interactions represented by charges $q = 0.25e$ and $(-5/2)0.25e$ located at the double bond and pentagon centers, respectively. We found good overall agreement with a wide variety of experiments, and predicted Γ frequencies at $57.6(F_u)$, $42.6(E_u)$, $41.6(F_u)$, $39.5(A_u)$, $26.1(F_g)$, $18.9(F_g)$, $16.2(A_g)$, $14.3(E_g)$, and $14.1(F_g)$ cm^{-1} for the ordered phase at 0 K. Furthermore, we obtained a large band centered at about 17 cm^{-1} in the phonon density of states, due to librational motions, which is in the vicinity of the 21–23 cm^{-1} observed by neutron scattering [4].

The intermolecular potential may be expanded in terms of spherical harmonic symmetry functions [5]. The isotropic monopole-monopole term is obtained by averaging the interaction energy over all relative molecular orientations. The librational motions are driven by the anisotropic intermolecular interactions, whereas the translational modes are determined mainly by the isotropic part of the potential. Taking into account only the molecule-centered monopolar potential, the $Pa\overline{3}$ becomes an fcc structure. We have used this potential to compute the translational vibrations, obtaining one triply degenerate mode at 55.4 cm^{-1} and a sixfold degenerate one at 39.1 cm^{-1}. This is easily understood by noting that the longitudinal and transverse modes at point X in the fcc Brillouin zone fold into Γ in the simple cubic structure; the longitudinal modes produce F_u vibrations and the transverse ones an $F_u + E_u + A_u$ manifold. The molecular anisotropy slightly shifts the longitudinal modes (from 55.4 to 57.6 cm^{-1}) and splits the transverse modes into components which are less than 3 cm^{-1} apart; the eigenvectors of the F_u modes are practically unchanged. The ratio between the frequencies of the two F_u modes of $Pa\overline{3}$ obtained with other intermolecular potentials [6] is also nearly $\sqrt{2}$, the same relation found theoretically and experimentally between longitudinal and transverse modes at X for fcc rare gas crystals [7]. It is almost impossible to find a physically sound potential which will make this ratio 2.2, as proposed in Ref. [1].

Absorption bands corresponding to F_u modes in $Pa\overline{3}$ C_{60} are expected to be very weak, since they are activated by nonspherical interactions which only slightly perturb the translational motions: possibly other, symmetry forbidden, modes will achieve comparable intensities when activated by impurities or crystal imperfections. In view of the discussion above, we reinterpret the observed spectrum in the following way: the band at 58.5 cm^{-1} is the F_u mode corresponding to the fcc longitudinal motion; the broad band centered at 39 cm^{-1} is due to F_u, E_u, and A_u modes related to the fcc transverse motions; and the lower frequency features are due to librational motions.

After submission of the present manuscript it has been called to our attention that FitzGerald and Sievers [8] repeated the experiment of Ref. [1], finding that after degassing the sample only two bands, at 54.7 and 40.9 cm^{-1}, remain in the FIR spectrum at 1.5 K. This result is completely consistent with our theoretical predictions.

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