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Raman study of vibrational properties in solid C_{60}

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Raman scattering has been performed on pure polycrystalline C_{60} powder over a frequency range of 20–2500 cm^{-1}. The phonon Raman lines appearing only between 250 and 1600 cm^{-1} can be assigned to all the Raman-active vibrational modes $(2A_g+8H_g)$ predicted for the isolated C_{60} molecules, which suggests only minor effects of intermolecular coupling on the properties of molecular vibrations. A comparison of the spectra taken at room temperature and low temperature (150 K) shows no significant change of the vibrational Raman modes after an orientational ordering transition.

The proposed molecular architecture (truncated-icosahedron structure) for the C_{60} cluster[1] has attracted great theoretical interest. The recent success in synthesis of macroscopic quantities of solid C_{60} (Ref. 2) activated intense experimental efforts. Since the confirmed fullerene structure of C_{60} can cage other atoms or molecules, a variety of physical properties is expected. Indeed, fairly high conductivities have been achieved in alkali-metal-doped C_{60},[3] and even superconductivity with T_c as high as 18 and 28 K were discovered in K_xC_{60} (Ref. 4) and Rb_xC_{60},[5,6] respectively. Raman scattering[7] served, along with ir absorption[2] and photoemission,[8] as essential spectroscopic methods for the confirmation of the structure of C_{60}. Recently, an *in situ* comparison between the behavior of a certain Raman mode of a pristine C_{60} film and of the same film after potassium doping showed a large frequency softening upon doping,[3] which may suggest a strong electron-phonon coupling. The very interesting issue of the role of phonons in this type of superconductivity should be pursued.

In this paper, we present a Raman study of pure C_{60} powder over a large frequency range, to investigate the molecular vibrational modes and possible external lattice modes. A comparison of the present results with the existing theoretical calculations for single C_{60} molecules may reveal the possible influence of intermolecular coupling on the molecular vibrations upon solidification. Furthermore, we can investigate the effects of orientational ordering on the vibrational properties through measurements at temperatures both above (293 K) and below (150 K) the phase transition temperature, 249 K.

Our sample of C_{60} powder was prepared by resistively vaporizing graphite rods under a helium atmosphere as previously described[9,10] and purified by high-performance liquid chromatography (HPLC) to $>99\%$.[11] Raman spectra were taken by focusing an Ar^+ laser beam (500 μW at 5145 Å) to 150 μm in diameter directly on the sample powder, which was pressed into an open end of a capillary and held in a cryostat in a helium atmosphere. Despite the roughness of the illuminated area a combination of a double spectrometer (Spex 1401) with a homemade third monochromator still enabled us to record spectra down to 20 cm^{-1}.

Figure 1 shows a typical Raman spectrum of the powder at 150 K, which is similar to the room-temperature spectrum (not shown here) except for some change in intensities of the Raman lines. Two strong lines at 498 and 1468 cm^{-1} and eight weak lines at 272, 430, 710, 770, 1080, 1255, 1430, and 1576 cm^{-1} can be clearly observed. Two more weak lines at 855 and 1515 cm^{-1} can hardly be resolved above the noise level. No Raman features in the spectral ranges 20–250 and 1600–2500 cm^{-1} can be seen here. In an early Raman experiment on films in mixed phases of C_{60} and C_{70}, Bethune *et al.*[7] already identified the lines at 273, 497, and 1469 cm^{-1} in their spectra with Raman modes of C_{60} and, in addition, the five lines at 260, 1062, 1185, 1230, and 1568 cm^{-1} with those of C_{70} by comparing intensities of various Raman peaks of two films with different C_{60}-C_{70} ratios, but the other scattering features including the lines at 435, 711, 773, and 1430 cm^{-1}, which are also observed in our spectrum for pure C_{60}, remain unidentified due to their small intensities. Since our spectrum was taken on a purified sample with C_{70} content less than 1%, all the Raman lines recorded here should be intrinsic for C_{60}, except that the strongest line of C_{70} at 1568 cm^{-1} appears as a shoulder near the 1576-cm^{-1} line due to the tiny amount of C_{70} impurity.

The vibrational properties of the single C_{60} molecule have been calculated by several authors.[12–15] The icosahedral structure I_h of the isolated molecule gives rise to 46 normal modes:

$$\Gamma = 2A_g+3T_{1g}+4T_{3g}+6G_g+8H_g$$
$$+A_u+4T_{1u}+5T_{3u}+6G_u+7H_u\,,$$

among which only the two nondegenerate A_g modes (selection rule $\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$) and eight fivefold-degenerate H_g modes [selection rule $\alpha_{xx}+\alpha_{yy}-2\alpha_{zz}$, $\sqrt{3}(\alpha_{xx}-\alpha_{yy})$, α_{xy}, α_{yz}, α_{xz}] are Raman active, and the four T_{1u} modes are infrared active. There would be three major changes in vibrational properties after forming free molecules into crystals. First, the molecular modes may change their symmetries as the site symmetries of molecules in a unit cell are always equal to or lower than those of free molecules and, therefore, the intermolecular interactions may lift degeneracies of some free-molecular modes as well as shift vibrational frequencies. Second, the

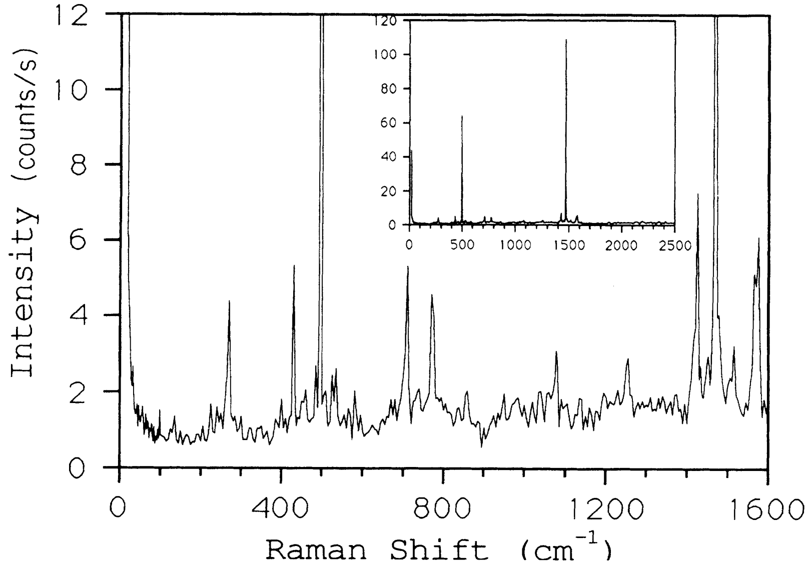

FIG. 1. Raman spectrum of polycrystalline C_{60} powder at 150 K over the frequency ranges 20–1600 and 20–2500 cm^{-1} (inset).

intermolecular motions will introduce translational and librational vibrations, known as "external" modes. Finally, the translational invariance of a lattice allows descriptions of the vibrations of a huge number of molecules in a crystal in the Brillouin zone. Since, for soft molecular crystals, molecules are bonded by weak van der Waals forces and the individual molecular structure is still well defined, weak effects on the molecular vibrational properties are expected. In the case of C_{60}, the molecules of 7.1 Å in diameter are in a fcc lattice separated from each other by a distance of 2.9 Å, which is twice as large as the intramolecular carbon bond length.[16,17] Therefore, we should expect the high-frequency intermolecular modes to resemble the free-molecular case.

The two strong lines at 1468 and 498 cm^{-1} can be attributed to the two molecular A_g modes due to, as reported by Bethune *et al.*,[7] their strong intensities as well as low depolarization ratios. The former corresponds mainly to the stretching vibration of C=C double bonds while the pentagons constructed by C—C single bonds pinch; the latter mainly corresponds to the pentagon breathing mode.[12] In both cases the bond lengths change so as to retain the same vortex angles and thus the total symmetry. The eight weak lines at 272, 430, 710, 770, 1080, 1255, 1430, and 1576 cm^{-1} could be related to all the H_g modes of the molecule. A progressive evolution of the distortion character from radial (bond-bending) to tangential (bond-stretching) motion increases the frequency of these modes. In extreme cases, the 272-cm^{-1} line could be assigned to the lowest-frequency H_g mode, corresponding to an almost radial distortion while the highest-frequency H_g mode (at 1576 cm^{-1}) corresponds to an almost tangential distortion of the icosahedral molecule into an ellipsoid.[12] The origin of the remaining weaker Raman features is unclear at present. They might be introduced by some trace impurities or by activating certain Raman-forbidden modes. A comparison with theoretical calculated frequencies is listed in Table I. Calculated frequencies both higher and lower than the experimental ones have been obtained by various force field methods,[12-15] and for the high-frequency modes theoretical values are usually too large. The same trend also appears in comparing the calculated T_{1u} frequencies with the lines in an infrared spectrum.[2] Although this quantitative discrepancy demands further theoretical efforts, the qualitative agreement of theories with both Raman and ir results provides another confirmation of the structure of C_{60} and indicates the weak effect of the intermolecular coupling on the molecular vibrations. Considering the graphitene isomer of C_{60}, which has D_{6h} symmetry, 39 modes are expected, including 10 A_{1g} Raman modes and 25 ir modes,[15] which are unacceptably different from the experimental findings. On the other hand, if the interaction between the molecules in the lattice strongly affect the free-molecular vibrations, lifting of degeneracies of certain molecular modes and optical activation of certain silent modes are

TABLE I. Experimental Raman frequencies, their assignments and comparison with those from two theoretical calculations.

Frequency (cm^{-1})	Symmetry	Theory (Ref. 12) (cm^{-1})	Theory (Ref. 15) (cm^{-1})
498	A_g	510	388
1468	A_g	1830	1409
272	H_g	274	218
430	H_g	413	435
710	H_g	526	645
770	H_g	828	743
1080	H_g	1292	1004
1255	H_g	1575	1221
1430	H_g	1910	1468
1576	H_g	2085	1601

expected.

No Raman lines can be resolved between the lower experimental limit (~ 20 cm^{-1}) and the lowest H_g frequency (272 cm^{-1}), a range in which some lattice modes might occur. We can roughly estimate the frequencies of the translational modes by $\omega \sim \sqrt{4k/m}$, where m is the mass of a C_{60} molecule, and the force constant k can be evaluated approximately by its relation to the bulk compressibility $9a_0/4k = -(1/V)(dV/dp)$. Using the experimental value $-(1/V)(dV/dp) = 6.9 \times 10^{-12}$ cm^2/dy for the compressibility and the lattice constant of the fcc cell $a_0 = 14$ Å,[17] a typical value of 60 cm^{-1} can be obtained, which is within our spectral range. However, the rotational (librational) modes with frequencies < 20 cm^{-1}, as predicted by a theoretical calculation,[18] could not be probed in our experiment. Several x-ray-diffraction measurements[16,17] identified that the C_{60} molecules are located on sites of a fcc lattice with point group O_h, but with a high degree of rotational disorder in forming crystals to remove the symmetry-forbidden occupation of the O_h sites, by icosahderal (I_h) molecules. This fcc structure provides no optical lattice vibrations. A recent experimental structural study[19] revealed a first-order phase transition from the fcc to simple-cubic structure induced by an orientation ordering transition at 249 K. This phase transition will break the equivalence of the four sites per fcc cell and results in optical lattice modes. Sachidanandam and Harris[20] have pointed out that the space group of the low-temperature structure should be T_h^6 ($Pa3$) instead of T_h^2 ($Pn3$) as suggested by Heiney *et al.*[19] All four inequivalent molecules are centered at S_6 sites and yield 12 translational modes $A_u + E_u + 3T_u$ (including three acoustic modes) as well as 12 librational modes $A_g + E_g + 3T_g$. The fact that no lattice mode was detected here at temperatures both above (293 K) and below (150 K) the structural phase transition can be well explained; the translational optical modes with frequencies calculated in the range of 20–50 cm^{-1} (Ref. 18) are not Raman active, while the Raman-active librational modes have frequencies, calculated between 6–17 cm^{-1},[18] that are too low to be observed in our experiment.

In summary, all ten Raman-active modes in free C_{60} molecules have been observed and assigned. Our work not only confirms the observation and assignment of three Raman lines at 273, 497, and 1469 cm^{-1} in an earlier Raman work by Bethune *et al.*[7] on films in a mixed phase of C_{60} and C_{70}, but also identifies all the remaining Raman modes of the isolated C_{60} molecule. The experimental Raman frequencies can be reasonably compared to the existing theoretical values, but further improvement in theoretical calculations is desired to provide quantitative agreement with experiments. Neither any lattice mode nor any obvious deviation from the intramolecular modes expected for free-molecular C_{60} have been found in solid C_{60} either above or below the orientational ordering transition temperature. These results indicate minor influences of the intermolecular coupling upon solidification of C_{60} on the vibrations of free molecules and agree well with recent theoretical predictions for the low-temperature structure after the orientational ordering transition.

Note added. During this study we learned that Cappelletti *et al.*[21] have performed neutron measurements of intermolecular vibrational modes in solid C_{60}. Excellent agreement can be found between their vibrational spectra and the frequencies of our Raman lines.

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