Rotation-vibrational dynamics of solid C_{60}: A Raman study

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The rotational dynamics of C_{60} fullerites has been examined by measuring the Raman-active intramolecular modes at various temperatures. The linewidth of the H_g modes increases significantly upon heating from slightly below (sc phase) to room temperature (fcc phase), whereas the broadening of the A_g line is much weaker. We analyze these results considering the appearance of rotational satellite bands of the H_g vibrational lines above $T_c = 256$ K. We also discuss small additional contributions that may arise from rotation-vibrational interactions in both the fcc and sc phases of the C_{60} fullerite. [S0163-1829(99)00743-2]

The C_{60} fullerite is an unique molecular crystal in which phenomena typical for the isolated molecules coexist with those responsible for the solid state. It undergoes a first-order transition from a face-centered (fcc-space group Fm3m) to a simple cubic (sc-space group $Pa3$) lattice at $T_c = 256$ K.[1] In the high-temperature fcc phase C_{60} molecules execute quasi-free rotations thus exhibiting an almost complete orientational disorder.[2] In the low-temperature sc phase the C_{60} rotations are reduced to ''ratchetlike'' orientational motions (librational modes) about the [111] directions.[3,4] These modes freeze out upon further cooling and a merohedrally disordered phase is established below 90 K.[5]

The H_g intramolecular vibrations usually have a relatively narrow linewidth in the Raman spectra of sc-solid C_{60} that significantly increases at higher temperatures.[6–8] In contrast, the Raman lines of nondegenerate A_g modes only moderately change their linewidth in going from the sc to the fcc phase. The temperature behavior of the frequency and the linewidth of some intramolecular Raman active modes were investigated in Refs. 6 and 7. Van Loosdrecht et al.[6] suggested that the broadening of H_g lines in the fcc phase is due to a strong rotation-vibrational coupling, without presenting an estimate of these coupling effects. Hricha et al.[7] evaluated the rotational-diffusion contribution to the linewidth of the C_{60} intramolecular modes. The model of Ref. 7 assumes no coupling between rotational motions and the intramolecular vibrations. Then the rotational-diffusion processes that cause the quasielastic peak in inelastic neutron scattering experiments[9] contribute to the line broadening.

In this report, we present results on the broadening of the spectral lines of the Raman-active fundamentals in a C_{60} single crystal with increasing temperature. We analyze the rotation-vibrational coupling effects in the fcc phase of solid C_{60} and their contribution to the line shape of H_g modes.

A C_{60} single crystal embedded in an indium plate was first cooled down from room temperature to 20 K for 2 h and then measured on a Dilor multichannel spectrometer at various temperatures in the interval 20–305 K. The spectrometer slits were set to 3.5 cm^{-1} spectral width and the 5145 Å line of an Ar$^+$ laser was used for excitation. The laser beam was focused to a spot of ≈ 2 μm in diameter on the crystal surface using microscope optics. The laser power was kept below 100 μW, and an oxygen exposed sample was used in order to prevent the phototransformation and the influence of the photoexcited triplet state of C_{60} on the spectra.[10] This was assured by monitoring the position of the ''pentagonal pinch'' A_g mode at 1469 cm^{-1}: no downshift of this mode was observed throughout the measurements.

The Raman spectra of the C_{60} crystal are given in Fig. 1. They manifest a strong temperature dependence of the Raman intensity[11] and linewidth of the C_{60} modes. In Fig. 2, we show the measured linewidths full width at half maximum of the A_g and the six most-intensive H_g vibrations in the spectra. The linewidth of A_g modes is 2–4 cm^{-1} and exhibits a very weak broadening upon heating. At room temperature, the H_g linewidth reaches 16 cm^{-1} while below the phase transition it decreases below 4 cm^{-1} (for the split lines at low temperatures the width of the most intensive component was taken).

In the fcc phase C_{60} molecules rotate almost freely. The rotational correlation time at room temperature is $\tau \approx 9$ ps as obtained from NMR experiments.[12] This value is only three times longer than the characteristic reorientation time for free-gas molecules.[13] Therefore, the plastic fcc phase of the fullerite can be compared to a gas phase as far as rotational features are concerned.

The rotational Raman effect is symmetry forbidden for spherical top molecules with an isotropic ground-state polarizability such as C_{60}. However, in the excited vibrational states it can be activated.[14] When the vibration is Raman allowed, it appears in spectra as a central peak with two rotational bands (O and S branches) on both sides. This is a well-known case for many spherical top molecules, e.g., CH_4.[14–16] The C_{60} polarizability becomes anisotropic when excited in the vibrational states of asymmetric H_g modes.
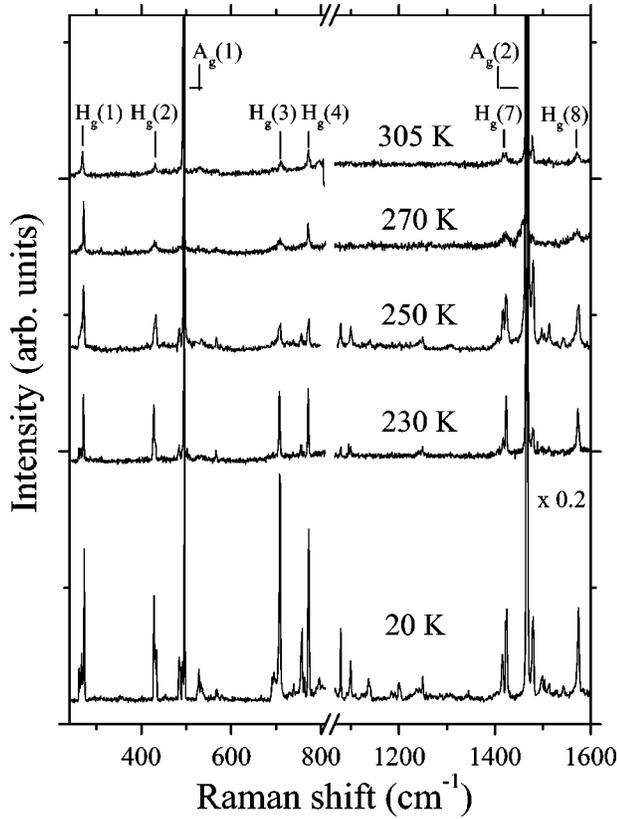
FIG. 1. The Raman spectra of a C_{60} single crystal at five temperatures.

The corresponding vibrational lines should appear in the Raman spectra accompanied by rotational satellites. In contrast, the spectral lines of totally symmetric vibrations exhibit no rotational structure since the molecular polarizability remains isotropic throughout the vibrational motion. This physical picture is in accordance with the sharp and narrow line shapes of the A_g modes observed in our spectra.

Let us now concentrate on the expected rotational fine structure of the H_g lines. At first we estimate the most populated rotational state $J=J_{max}$ of the C_{60} molecule as a function of temperature. The moment of inertia of a C_{60} molecule is $I=1\cdot10^{-43}$ kg m^2 provided one assumes that the molecule is a hollow sphere with a mass distributed over its surface. Because of the large I the rotational energy constant is extremely small: $B=\hbar^2/2I=2.78\cdot10^{-3}$ cm^{-1}. This allows the rotational spectrum to be regarded as quasicontinuous. The rotational energy of C_{60} is given by:

$$E_r^c=\frac{I\bar\omega^2}{2} \quad \text{and} \quad E_r^q(J)=BJ(J+1), \qquad (1)$$

in the classical and the quantum-mechanical limits, respectively. From $E_r^c=E_r^q(J_{max})$ one obtains a direct relation between J_{max} and the reorientational correlation time τ by using the general expression for the mean angular velocity: $\bar\omega=1/\tau$. J_{max} of the C_{60} molecule can thus be expressed as a function of the temperature T

$$J_{max}\approx\frac{I}{\hbar\,\tau(T)}. \qquad (2)$$
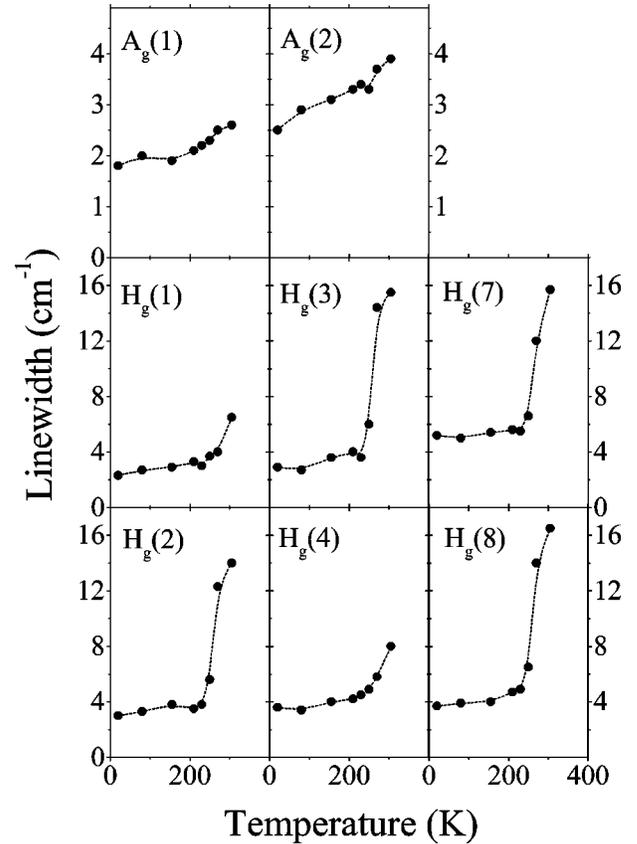
FIG. 2. The Raman linewidths of the A_g modes and the most intensive H_g modes of a C_{60} single crystal as a function of the temperature.

In Table I, we present the J_{max} values from Eq. (2) using the NMR data for the reorientational correlation time τ in C_{60} fullerites at different temperatures.[12]

In order to obtain a quantitative estimate of the parameters describing the C_{60} rotation we now calculate J_{max} for a free rotating molecule. For this purpose, one can use the thermal distribution function for the population of the rotational levels of a spherical top molecule[14,17]

$$N_J=N(2J+1)^2\exp[-BJ(J+1)/k_BT], \qquad (3)$$

where N is a normalization factor and k_B the Boltzmann constant. From $\partial N_J/\partial J=0$ we calculated J_{max} for several temperatures in the fcc phase relevant for the measurements in Ref. 12. The J_{max} values determined from Eq. (3) (see Table I) are about twice as large as those from the experiment [Eq. (2)]. This indicates that the rotational diffusion in the fcc phase still exhibits some effects of intermolecular

TABLE I. Most-populated C_{60} rotational levels J_{max} given for various temperatures as obtained from Eq. (2) and experimental data of Ref. 12, and calculated from Eq. (3).

$T(K)$	J_{max} [Eq. (2) and Ref. 12]	J_{max} [Eq. (3)]
312	128	278
297	114	272
283	104	265
267	86	257
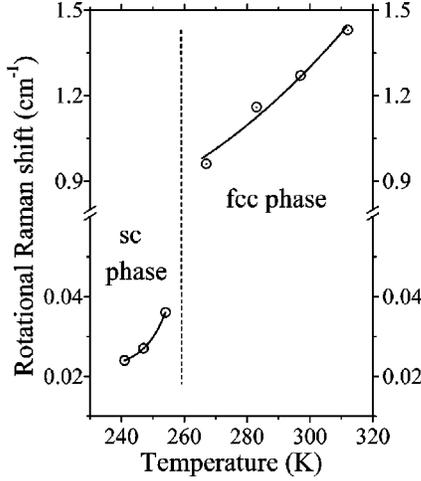
FIG. 3. The rotational Raman shift calculated using the data given in Fig. 4 of Ref. 12.

correlation that influence the population of the levels. However, with increasing temperature the J_{max} values for C_{60} rotation in the solid state approach those for free rotation in the gas phase.

The J_{max} values correspond to the most intensive Stokes and anti-Stokes components of the rotational Raman bands. Given the selection rule $\Delta J = \pm 2$,[14] their position with respect to the vibrational line is

$$\Delta E_r(S - \text{branch}) = 4B(J_{max} + 3/2),$$

$$\Delta E_r(O - \text{branch}) = 4B(J_{max} - 1/2). \quad (4)$$

The temperature dependence of this rotational Raman shift as obtained from Eqs. (2) and (4) is given in Fig. 3. It should increase exponentially with T in accordance with the Arrhenius behavior found for the rotational correlation time τ in Ref. 12. The separation of neighboring rotational lines is small: $4B = 0.011$ cm^{-1}. Therefore, in a standard experiment one should observe a single broad line shape for the satellite. From Eq. (3), we can obtain the full width at half maximum $\Delta\Gamma$ of a rotational satellite band, defined as $(J_{\Delta\Gamma}^{(2)} - J_{\Delta\Gamma}^{(1)})4B$, where $J_{\Delta\Gamma}^{(1)}$ and $J_{\Delta\Gamma}^{(2)}$ are given by the condition $N_{J_{\Delta\Gamma}} = N_{J_{max}}/2$. Using $J_{max} = 278$ at 312 K (Table I), one finds that $J_{\Delta\Gamma}^{(1)} = 133$ and $J_{\Delta\Gamma}^{(2)} = 453$ approximately determine $\Delta\Gamma = 3.5$ cm^{-1}. Therefore, the presence of rotational satellites may lead to an effective broadening of the central vibrational line by ≈ 7 cm^{-1} with a behavior that follows the temperature dependence of J_{max}. From a comparison of this value with the H_g linewidths in Fig. 2, it follows that rotational satellites can contribute significantly to vibrational line shapes.

An effect that is expected from the rotation-vibrational interaction is the Coriolis splitting of rotational levels coupled to the degenerate H_g modes.[14] The splitting can be estimated from expectation values of the first-order Coriolis term $\hat{H}_C = 2B\zeta\hat{J}\cdot\hat{L}$ in the rotation-vibrational Hamiltonian[17–19]

$$\langle\hat{H}_{rot-vib}\rangle = E_{vib} + BJ(J+1) - 2B\zeta\langle\hat{J}\cdot\hat{L}\rangle, \quad (5)$$

where E_{vib} is the energy of a pure vibration, ζ are the Coriolis coupling constants and $\hat{L}$ is the angular momentum of the vibrational mode. The rotational-vibration coupling splits the $2(L=2)+1=5$ orbitally degenerate H_g mode vibrational level into five levels that can combine with the Jth rotational level in the following way:

$$\langle\hat{H}_C\rangle = -6B\zeta - 2B\zeta(2J-1) \quad \text{for } J-L=J-2;$$

$$\langle\hat{H}_C\rangle = -6B\zeta - 2B\zeta(J+1) \quad \text{for } J-L=J-1;$$

$$\langle\hat{H}_C\rangle = -6B\zeta \quad \text{for } J-L=J;$$

$$\langle\hat{H}_C\rangle = -6B\zeta + 2B\zeta(J-1) \quad \text{for } J-L=J+1;$$

$$\langle\hat{H}_C\rangle = -6B\zeta + 2B\zeta(2J+3) \quad \text{for } J-L=J+2.$$

The coupling constants ζ of C_{60} have only been calculated for the T_{1u} modes and found to be negative.[17] However, for the $H_g(i)$ modes one may assume that the average constant is $|\zeta_{H_g(i)}| \approx 0.1$ using the sum rule that $\Sigma_{i=1}^{8}|\zeta_{H_g(i)}|$ must be of order one.[14,19] Thus the overall splitting of the $J_{max} = 278$ level (at 312 K) is $8B|\zeta_{H_g(i)}|J_{max} \approx 0.6$ cm^{-1} and that of the $J_{\Delta\Gamma}^{(2)} = 453$ level is ≈ 1 cm^{-1}. This could cause an additional effective broadening of the whole rotational satellite band of ≈ 1 cm^{-1}.

So far, we have considered the asymmetric Raman modes in the fcc phase (T_h crystal symmetry) to be fivefold degenerate, that is, of H_g symmetry, as is the case for an isolated C_{60} molecule (I_h). This is somewhat in contrast to the fact that the crystal field with T_h symmetry splits the H_g modes according to $H_g \rightarrow E_g + T_g$.[11,20] However, the chaotic rotations of C_{60} in the fcc phase partly smear out the crystal-field effect[11] and make the above analysis to some extent applicable. A recent high-resolution Raman study of Horoyski et al.[21] has revealed a doublet structure of some of the H_g lines above 260 K with line splitting varying from 2 to 6 cm^{-1}. However, at least half of the H_g lines remain nonsplit in the fcc phase in spite of the high resolution of 0.1 cm^{-1} used in Ref. 21. We note that unresolved splitting could mimic a line broadening, and therefore, this case should be analyzed as well. It is interesting that once split by the crystal field, the E_g and T_g vibrations originating from the same H_g mode may couple to each other via Coriolis interaction involving rotations because $E_g \otimes T_g$ contains the T_g rotation.[14] The coupling introduces a mutual repulsion between the Jth components of the E_g and T_g rotation-vibrational energy levels[22]

$$\delta\omega_{E,T}^J = \frac{B^2\zeta_{E,T}^2 J(J+1)}{|\omega_{E_g} - \omega_{T_g}|}, \quad (6)$$

where ω_{E_g} and ω_{T_g} are the vibrational frequencies and $\zeta_{E,T}$ a coupling constant. A crude estimate gives $\delta\omega_{E,T}^{J_{max}} \approx 0.1$ cm^{-1} for the frequency shift at room temperature of the rotational satellite maximum, provided both $\zeta_{E,T} = 1$ and $\omega_{E_g} - \omega_{T_g} = 1$ cm^{-1}. Therefore, the effect is again weak and alone cannot account for the nonuniform splitting observed in Ref. 21.

A small contribution to the H_g linewidths in the fcc phase is also expected to come from the phonon renormalization due to the anharmonic coupling to the vibrational states and, to some extent, from the inhomogeneous broadening.[7]

In the sc phase just below $T_c = 256$ K the H_g lines are still a little broadened as compared to their low-temperature linewidths. In going from the fcc to sc phase the quasicontinuous rotational excitations transform into discrete librational modes.[8] This largely cancels the rotational satellite effects and the rotation-vibrational coupling. The interaction of the phonons with the librational modes then becomes the main process determining the phonon lifetime.

In summary, we have examined by means of Raman scattering the influence of the rotational dynamics on the intramolecular modes in solid C_{60}. The appearance of rotational satellites around the asymmetric vibrational lines along with a nonresolved vibrational splitting are the most likely mechanisms for the H_g line broadening in the fcc phase. Rotation-vibrational coupling effects in C_{60} are generally weak because the rotational energy scale for this molecule is set up by the extremely small constant B. However, these effects may contribute to the vibrational line shape and linewidth in cumulative manner. In addition to these effects, rotational diffusion leads to a line broadening of $1-2$ cm^{-1}.[7]

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