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Raman depolarization ratio of vibrational modes in solid C₆₀

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Abstract

We studied the dependence of the Raman depolarization ratio in a C₆₀/C₇₀ film within the temperature interval 20–300 K. The experimentally determined RDR is compared with that expected from the corresponding Raman tensors for the low- (s.c.) and high- (f.c.c.) temperature phase of solid C₆₀. We demonstrate that RDR can be successfully used for detection of subtle C₆₀-mode-splitting in insufficiently resolved spectra. © 1999 Published by Elsevier Science Ltd. All rights reserved.

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Pristine C₆₀ undergoes a first-order transition from a face-centered (f.c.c.-space group Fm3m) to a simple cubic (s.c.-space group Pa3) lattice at ≈256 K [1]. In the high-temperature f.c.c. phase, C₆₀ molecules execute quasifree rotations and exhibit an almost complete orientational disorder [2,3]. The low-temperature s.c. phase is characterized by reducing the rotation to “ratchet-like” orientational motions (librational modes) about the four specific (111) directions [4,5]. These modes freeze out upon cooling and a merohedrally disordered phase is established below 90 K [6].

Detailed structural investigations have evidenced that electrostatic interaction between adjacent buckyballs essentially contributes to the intermolecular potential below the f.c.c.–s.c. transition [5,7]. Along with a slowing down of the C₆₀ rotation, these interactions enhance the influence of the crystal field on the vibrational properties of fullerite as revealed by a number of Raman studies [8–11]. Consequently the Raman lines should split and give rise to a fine structure. This splitting, however, is expected to be small because of the weak van-der-Waals interaction between C₆₀ molecules in fullerenes, and therefore it is difficult to detect it experimentally.

In this communication, we demonstrate how the experimentally determined Raman depolarization ratio (RDR) can be used for an investigation of unresolved Raman line

splitting in C₆₀ fullerite. We also present the temperature dependence of the RDR for C₆₀ modes in a mixed C₆₀/C₇₀ film (≈10:1). The RDR of the C₇₀-modes serves as a convenient reference because the crystal field effects should be minimal on C₇₀ molecules dissolved in a C₆₀ fullerite.

The mixed C₆₀ and C₇₀ film (≈10:1) of thickness 2 μm was prepared by evaporating onto a suprasil substrate in vacuum, as described in Ref. [12]. The film was first cooled down from room temperature to 12 K and then measured in back-scattering geometry with a Dilor multichannel spectrometer at various temperatures in the interval 300–12 K. The Raman spectra were recorded at each temperature for both parallel and crossed polarization of incoming and scattered light, the spectrometer slits being set to 3.5 cm⁻¹ spectral width. The Ar⁺-line at 5145 Å (2.41 eV) was used as an excitation source. The laser beam was focused to a spot of ≈30 μm diameter on the film surface. The laser power was kept below 100 μW. We used an oxygen-exposed sample to prevent photo-transformation of the film and to exclude the influence of the photoexcited triplet state of C₆₀ [13].

The high-temperature C₆₀ f.c.c. crystal structure is compatible with T_h site symmetry of the molecule in the crystal lattice [14]. This leads to a partial lifting of the mode degeneracy and the H_g modes split into E_g and T_g whereas the A_g modes remain unchanged. In the f.c.c. phase, however, the crystal–field effects are largely smeared out due to the rapid rotation of C₆₀. A possible splitting may also be hidden by roto-vibrational broadening of the C₆₀ lines in the f.c.c. phase.

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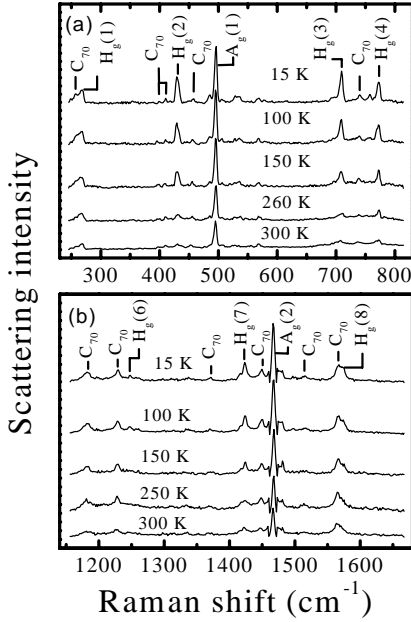


Fig. 1. The Raman spectra of a C_{60}/C_{70} film in parallel polarization geometry, given for five elevated temperatures: (a) low frequency region (200 cm^{-1} – 800 cm^{-1}); (b) high frequency region (1200 cm^{-1} – 1600 cm^{-1}).

In the s.c. phase there are four inequivalent molecules per primitive cell and the molecular rotation is hindered. Thus one should expect a number of static (Bethe) and dynamic (Davidov) splittings of the A_g and H_g modes according to the scheme [14]:

$$A_g \rightarrow A_g + T_g \quad \text{and} \quad H_g \rightarrow A_g + 2E_g + 5T_g. \quad (1)$$

Indeed, a fine structure of the Raman-active modes was observed in a number of experiments [8–10], the splitting being attributed to crystal field [8] as well as to isotope effects [10]. In the spectra of the mixed fullerene film shown in Fig. 1, however, there is no evident line-splitting except for a shoulder on the left side of the $H_g(7)$ line. The lineshape of the $H_g(3)$ and $H_g(4)$ modes suggests an unresolved splitting, but it seems to be small due to the weak interaction between neighboring molecules in fullerite. We suggest here that in such a situation it is instructive to study the temperature dependence of the depolarization ratios. The experimental RDR $\rho = I_{\perp}/I_{\parallel}$ is determined from the integrated line intensity as measured for crossed (I_{\perp}) and parallel (I_{\parallel}) polarization of incoming and scattered light. Fig. 2(a) and (b) displays the temperature dependence of RDR, $\rho(T)$, for some of the Raman-active modes. For randomly oriented scatterers, as in the C_{60}/C_{70} polycrystalline film, the RDR is given by [15]:

$$I_{\perp} \propto \frac{1}{15} [\alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2 - (\alpha_{xx}\alpha_{yy} + \alpha_{yy}\alpha_{zz} + \alpha_{zz}\alpha_{xx}) + 3(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2)], \quad (2)$$

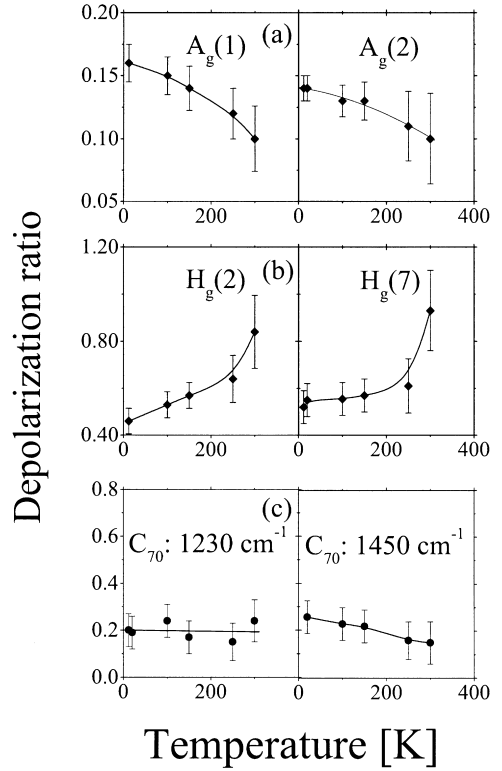


Fig. 2. Temperature dependence of the depolarization ratios (see Eqs. (6) and (7) in the text): (a) of the $A_g(1)$ -line at 494 cm^{-1} and the $A_g(2)$ -line at 1469 cm^{-1} ; (b) of the $H_g(2)$ -line at 428 cm^{-1} and the $H_g(7)$ -line at 1423 cm^{-1} ; (c) of two C_{70} modes with E -symmetry: at 1230 cm^{-1} and at 1450 cm^{-1} . Solid curves are only guides to the eye.

$$I_{\parallel} \propto \frac{1}{15} [3(\alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2) + 2(\alpha_{xx}\alpha_{yy} + \alpha_{yy}\alpha_{zz} + \alpha_{zz}\alpha_{xx}) + 4(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2)], \quad (3)$$

where α_{ij} refer to the corresponding entries in the Raman tensor. The Raman tensors for the I_h group are [16]:

$$A_g^{I_h} : \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix},$$

$$H_g : \begin{pmatrix} c & 0 & 0 \\ 0 & c & 0 \\ 0 & 0 & -2c \end{pmatrix}, \quad \begin{pmatrix} 0 & 0 & \sqrt{3}c \\ 0 & 0 & 0 \\ \sqrt{3}c & 0 & 0 \end{pmatrix},$$

$$\begin{pmatrix} 0 & -\sqrt{3}c & 0 \\ -\sqrt{3}c & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \begin{pmatrix} -\sqrt{3}c & 0 & 0 \\ 0 & \sqrt{3}c & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

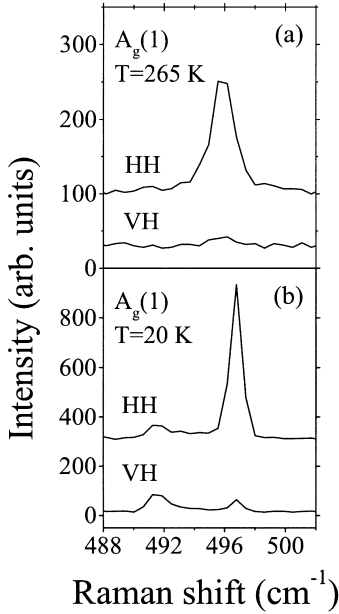


Fig. 3. Polarized Raman spectra of the $A_g(1)$ of a C_{60} single crystal, given for: (a) 265 K and (b) 20 K. Upper curves refer to parallel (HH) and lower curves—to perpendicular (VH) polarization of the scattered light with respect to the incident laser light.

$$\text{and } \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\sqrt{3}c \\ 0 & -\sqrt{3}c & 0 \end{pmatrix}. \quad (4)$$

From Eqs. (2) and (3), and the I_h tensors it follows that $\rho(A_g) = 0$ and $\rho(H_g) = 0.75$ for the f.c.c. phase, provided we neglect the splitting. These results are in good agreement with the experimental values for 300 K given in Fig. 2. In the s.c. phase, the H_g -components have the following Raman tensors (point group T_h):

$$\begin{aligned} A_g^{T_h} &: \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}, \\ E_g &: \begin{pmatrix} b & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & -2b \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} -\sqrt{3}b & 0 & 0 \\ 0 & \sqrt{3}b & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (5) \\ T_g &: \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix}, \\ & \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned}$$

In the split phase (s.c.), the corresponding tensor elements must be combined according to Eq. (1) to obtain the observed ρ values (i.e. averaged over a split but unresolved Raman modes):

$$\rho(A_g) = \frac{3d^2}{5a^2 + 4d^2}, \quad (6)$$

$$\rho(H_g) = \frac{12b^2 + 12c^2 + 15d^2}{5a^2 + 16b^2 + 16c^2 + 20d^2}. \quad (7)$$

The Raman intensity of the C_{60} vibrations increases upon cooling in the s.c. phase which has been related to an enhancement of the a, b, c and d Raman tensor components [11]. However, the A_g lines intensity in the spectra in Fig. 1 remains about an order of magnitude larger than that of the H_g lines for the whole temperature range 300–12 K. Thus a in Eqs. (6) and (7) is several times larger than b, c and d . This is not surprising because it is well known that totally symmetric (A_g) modes modulate more efficiently the molecular polarizability than the non-totally symmetric (H_g) ones [17]. In addition, we note that the Raman scattering from solid C_{60} is at resonance when excited with the 5145 Å laser line [18]. According to the Albrecht’s treatment of Raman intensity [19], two terms mainly contribute to the non-resonant scattering tensor: the **A**- (Frank–Condon) term is responsible for the elastic scattering and the **B**- (Herzberg–Teller) term normally describes the one-phonon Raman scattering. However near a resonance the **A**-term can also contribute to the Raman scattering from the totally symmetric modes.

Although the values of a, b, c and d may vary for different modes, the relation $a \gg b, c$ and d should hold for all ten Raman-active modes in C_{60} . Therefore, from Eqs. (6) and (7) one expects $\rho(A_g)$ to increase slightly and $\rho(H_g)$ to decrease significantly upon cooling below the phase transition. Such a behaviour is indeed seen in Fig. 2(a) and (b), where the $H_g(2)$ and the $H_g(7)$ modes were selected because they do not overlap with C_{70} lines. The graduality of this behaviour could be explained with the presence of librational modes that affect the orientational ordering but slow down upon cooling to 90 K [6]. For comparison the RDR of two C_{70} modes with E -symmetry are plotted in Fig. 2(c). C_{70} molecules in the mixed C_{60}/C_{70} film may be well considered isolated at all temperatures, and their RDR indeed exhibits no systematic change between 20 K and 300 K. For these modes RDR values in the range 0.15–0.40 were obtained so far at room temperature [20,21] which is in reasonable agreement with our values of ≈ 0.20 .

We further check the above results by measuring the polarized Raman spectra of the $A_g(1)$ mode in a C_{60} single crystal at higher resolution: 2.5 cm^{-1} spectral linewidth and 0.6 cm^{-1} absolute accuracy. These spectra are presented in Fig. 3. The A_g -linewidth in Fig. 3 is only $1.5\text{--}2 \text{ cm}^{-1}$ which allows the observation of a double-peak structure at 20 K. The Raman-scattering intensity of modes in a single crystal

is given by:

$$I \propto |\mathbf{e}_s \cdot \hat{\alpha} \cdot \mathbf{e}_i|^2 \quad (8)$$

where \mathbf{e}_s and \mathbf{e}_i are unit vectors along the polarization direction of the scattered and incident light, respectively, and $\hat{\alpha}$ stands for the Raman tensor. In this case the A_g and T_g modes should be observable only for parallel and crossed polarizations, respectively. It is evident from Fig. 3 that the main peak at $\approx 496 \text{ cm}^{-1}$ fulfills this selection rule and thus has A_g symmetry whereas the additional peak at $\approx 491 \text{ cm}^{-1}$ behaves as a T_g mode in agreement with the prediction from Eq. (1). A double-peak structure for the $A_g(1)$ mode with this polarization behavior has also been observed by Matus and Kuzmany [22] at low temperatures.

Raman depolarization ratios are particularly useful for the identification of symmetry-split modes with a flat dispersion in the solid phase as that of the $A_g(2)$ mode in C_{60} . A recent theoretical study [23] predicts a dispersion bandwidth of $\approx 9 \text{ cm}^{-1}$ for the $A_g(1)$ mode and less than 3 cm^{-1} for the $A_g(2)$ mode in solid C_{60} . This is in reasonable agreement with the observed splitting of 5 cm^{-1} for the $A_g(1)$ mode and no splitting for the $A_g(2)$ mode, considering that the Davydov splitting should be within the dispersion width of the phonon branch. It is worth noting that even if the Davydov splitting is resolvable, sometimes it is difficult to distinguish from other small splitting effects as for instance the isotope effects [10]. In such cases as well as for powder and film samples with broad linewidths, RDR provides useful information for possible splitting.

In summary, we have examined the influence of the molecular orientational ordering on the symmetry of the Raman active modes in solid C_{60} . We have demonstrated that RDR is sensitive to symmetry and dynamic splitting of the vibrational modes in going from the f.c.c. to s.c. phase of C_{60} fullerite.

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