Orientational phase transitions in C_{70}: A Raman spectroscopic investigation

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Raman investigations of C_{70} films in the 14–370-K range show significant changes across the orientational phase transitions around 270 and 330 K. Seven of the Raman modes of C_{70} soften smoothly across the transitions, the magnitude of the decrease in frequencies being in the range of 2–5 cm^{-1}. Linewidths of the bands increase in the transition region over and above the anharmonic contributions.

The fullerene C_{60} exhibits many fascinating properties, the specially noteworthy ones being superconductivity in the alkali-metal fullerides and ferromagnetism in C_{60}·*tetrakis* dimethylaminoethylene.[1,2] In addition, pristine C_{60} solid, being composed of nearly spherical molecules, undergoes a phase transition involving orientational ordering. In the ordered state, electron-rich double bonds between two hexagons (6-6 double bonds) are adjacent to the electron-deficient pentagonal faces on nearest-neighbor molecules. X-ray diffraction and calorimetric experiments[3] show that solid C_{60} undergoes a first-order phase transition from the high-temperature free-rotor fcc phase ($Fm\bar{3}$) to the orientationally ordered simple cubic phase ($P2_1/a3$) around 250 K. Spectroscopic investigations of the orientational-ordering transition in C_{60} include Raman[4-6] and infrared[7] studies. In going from the orientationally disordered to the orientationally ordered phase, frequencies of the Raman modes increase abruptly, accompanied by a steplike decrease in the linewidths. The abrupt hardening of the modes, first attributed to the decrease in unit-cell volume ($\sim 2.5\%$) near the transition, was later ascribed to be partly due to laser-induced electronic excitations into the metastable triplet state.[8] Raman experiments of Matus, Kuzmany, and Kratschmer[4] do not, however, reveal discontinuities in the peak position and linewidth of the strongest C_{60} mode at 1468 cm^{-1} at the transition temperature. Hadjiev and Thomson[9] have observed that the abrupt changes in frequencies could be due to possible contamination of C_{60} by a small amount of C_{70}.

C_{70}, being nearly spherical, would also be expected to undergo phase transitions involving orientational ordering and such transitions have been identified by x-ray and calorimetric measurements by Vaughan et al.[10] at 337 and 276 K. These workers have shown that the high-temperature phase is essentially fcc, but could not unambiguously decide on the structures formed on cooling. Verheijen et al.,[11] based on single-crystal x-ray studies, have obtained the structure of the minority hcp phase since the fcc crystals are twinned. Constant-pressure molecular-dynamics simulation[12] predicts that cooling the high-temperature free-rotor phase I gives rise to a partially ordered trigonal phase II where the free rotation

only occurs around the fivefold axis. On cooling II, a fully ordered monoclinic phase (phase III) is predicted. A recent infrared spectroscopic study[13] of the phase transitions of C_{70} has shown changes in the absorbance and linewidths of the 674-, 643-, and 577-cm^{-1} modes across the phase transitions. There was no clear evidence for the variation in the frequency of these modes. Verheijen et al.[11] have mentioned that one of the phase transitions has been observed using Raman spectroscopy by van Loosdrecht. We have carried out a detailed Raman study of C_{70} to investigate changes in the Raman band positions, linewidths, and intensities across the phase transitions and present the essential results in this paper.

Films of C_{70} were deposited on single crystals of Si(100) by the vapor-phase temperature gradient method.[13] In order to ensure elimination of toluene, the films were annealed in vacuum at 600 K for about 2 h. C_{70} films deposited in the same manner on KBr single crystals did not show absorbance at 527 and 1183 cm^{-1}, signifying absence of C_{60} contamination.[7,13] Based on the intensities of the 377- and 328-nm bands in the UV spectrum, the purity of C_{70} is estimated to be $\sim 98\%$. Furthermore, the 1467-cm^{-1} line of C_{60} had negligible intensity. Raman spectra were recorded ($\lambda_{exci} = 5145$ Å, 0.2 mW) in backscattering geometry on the films mounted in the He closed-cycle cryostat in the temperature range of 14–370 K (temperature stabilization better than 0.2 K). Spectra were recorded using a DILOR X-Y spectrometer equipped with with a liquid-nitrogen-cooled charge-coupled device detector. Laser power densities in the range 5–80 W/cm^2 had no observable effect on the spectra and the spectra were therefore recorded with a power density of ~ 20 W/cm^2. Spectra at 296 and 14.3 K were recorded with the incident and the scattered field parallel (VV configuration) and perpendicular (HV configuration) to each other. Here V (H) specifies vertical (horizontal) polarization. At other temperatures, unpolarized spectra were recorded.

In Fig. 1 we show the Raman spectra of C_{70} at 296 and 14.3 K in VV ($\parallel$) configuration. The peak position and intensities obtained from fitting the Lorentzian line shapes to the data for the two polarizations at these temperatures are listed in Table I. The intensities are normalized
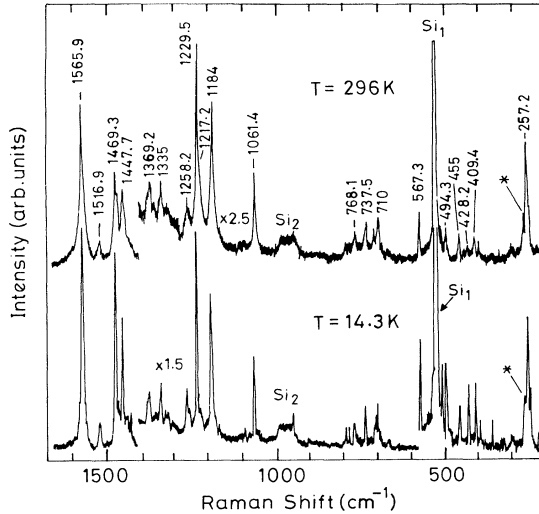
FIG. 1. Raman spectra of a C_{70} film in parallel configuration at 296 K (upper curve) and 14.3 K (lower curve). The peaks marked as Si_1 and Si_2 are first- and second-order Raman spectra of the Si substrate. Asterisks designate plasma lines.

observe more modes at the lower temperature consistent with the lower symmetry (monoclinic phase). The depolarization ratios at 296 K differ from those of Bethune *et al.*[15] for the C_{70} film on suprasil. Our purpose in measuring the depolarization ratio ρ was to examine whether it changes with temperature. The results in Table I show that significant changes occur in the depolarization ratio at low temperatures which is expected since the low-temperature phase is monoclinic.

In Figs. 2–4 we demonstrate the temperature dependence of the peak position, full width at half maximum (FWHM), and intensity (normalized with respect to the corresponding intensities of the strongest line at 1566 cm^{-1}) for seven bands with satisfactory signal-to-noise ratios. The dotted vertical lines in the figures mark the two transition temperatures reported in the literature (270 and 330 K). Solid lines are drawn to guide the eye. The line-shape parameters were obtained by fitting the data to a sum of the appropriate number of Lorentzian functions with a baseline. The error bars obtained from the fit are less than 0.2 cm^{-1} for the peak position and 0.5 m^{-1} for the FWHM.

From Fig. 2 we see that frequencies corresponding to the band maxima of the seven modes examined do not vary significantly up to ~270 K. Around this temperature, however, there is a noticeable decrease in the frequencies. The slopes $d\omega/dT$ become marked above 270 K and show changes at both transition temperatures.

by taking $I_\parallel$ (1566 cm^{-1}) to be 100. Out of the 53 Raman-allowed modes corresponding to symmetry species $12A_1' + 22E_2' + 19E_1''$ of the point group D_{5h} for the C_{70} molecule,[14] we observe bands due to 26 distinct modes similar to those reported by Bethune *et al.*[15] We

TABLE I. Phonon frequencies, normalized intensities $I_\parallel$ and $I_\perp$ for parallel (UV) and perpendicular (HV) polarizations, and depolarization ratios $(\rho = I_\perp/I_\parallel)$ for C_{70} at 296 and 14.3 K.

|	$T = 296.0$ K				$T = 14.3$ K		
ν (cm^{-1})	$I_\parallel$	$I_\perp$	$\rho = I_\perp/I_\parallel$	ν (cm^{-1})	$I_\parallel$	$I_\perp$	$\rho = I_\perp/I_\parallel$
1565.9	100.00	61.38	0.61	1567.0	100.00	38.59	0.39
1516.9	9.15	9.82	1.07	1516.7	13.07	7.68	0.59
1469.3	74.11	23.88	0.32	1470.0	92.53	16.80	0.18
1459.5	14.73	9.38	0.64	1460.0	9.34	2.70	0.29
1447.7	43.75	17.86	0.41	1449.1	54.77	11.62	0.21
1437.5	12.72	10.49	0.82	1436.3	8.09	3.53	0.44
1369.2	12.05	12.95	1.07	1370.6	11.20	4.98	0.44
1335.0	6.03	0.00	0.00	1336.6	9.13	11.00	1.20
1258.2	8.26	7.37	0.89	1259.3	12.03	11.62	0.97
				1252.8	7.68	5.39	0.70
1229.5	78.35	27.23	0.35	1230.2	56.22	29.46	0.52
1217.2	19.87	4.91	0.25	1218.8	6.02	0.00	0.00
1184.0	71.88	21.43	0.30	1186.1	39.42	24.07	0.61
				1162.6	2.49	5.81	2.33
1061.4	42.63	10.71	0.25	1062.1	23.44	12.86	0.55
				797.2	7.05	4.77	0.68
768.1	6.92	7.81	1.13	769.6	6.64	5.19	0.78
737.5	11.16	6.03	0.54	739.9	8.71	9.75	1.12
710.0	5.36	0.00	0.00	708.9	9.54	7.88	0.83
701.6	16.29	9.82	0.60	701.9	11.83	5.39	0.46
567.3	9.60	4.69	0.49	569.0	12.14	3.22	0.26
505.6	7.48	6.03	0.81	505.8	10.79	4.77	0.44
494.3	Intensity very low			494.1	9.02	2.70	0.30
455.0	5.13	3.13	0.61	455.6	5.19	2.18	0.42
428.2	6.03	5.13	0.85	430.3	6.43	3.42	0.53
409.4	6.36	4.35	0.68	409.9	7.26	0.00	0.00
257.2	26.34	10.16	0.39	258.3	12.97	3.84	0.30
250.1	10.27	5.02	0.49	250.4	6.22	3.01	0.48
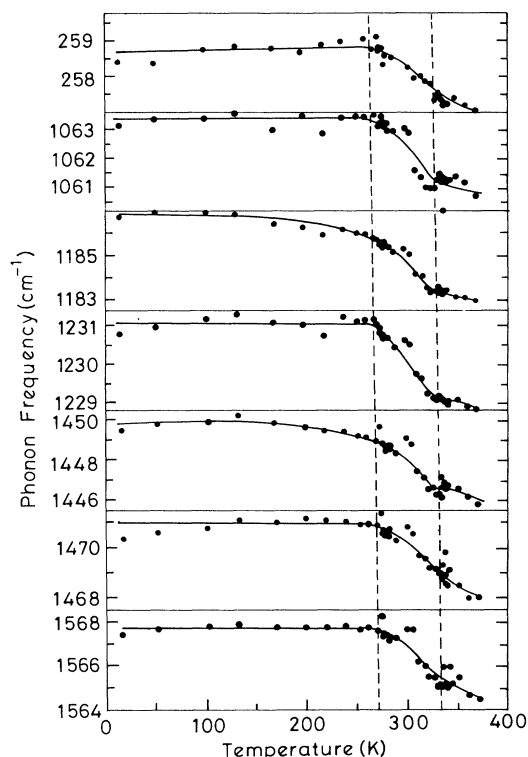
FIG. 2. Temperature dependence of the peak position for seven Raman modes.
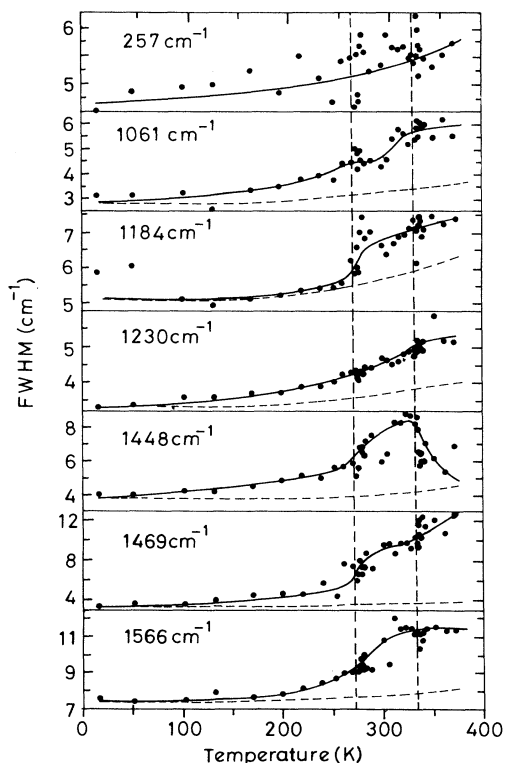

FIG. 3. Temperature dependence of the FWHM of seven Raman modes. The dashed lines represent the cubic anharmonic contribution.
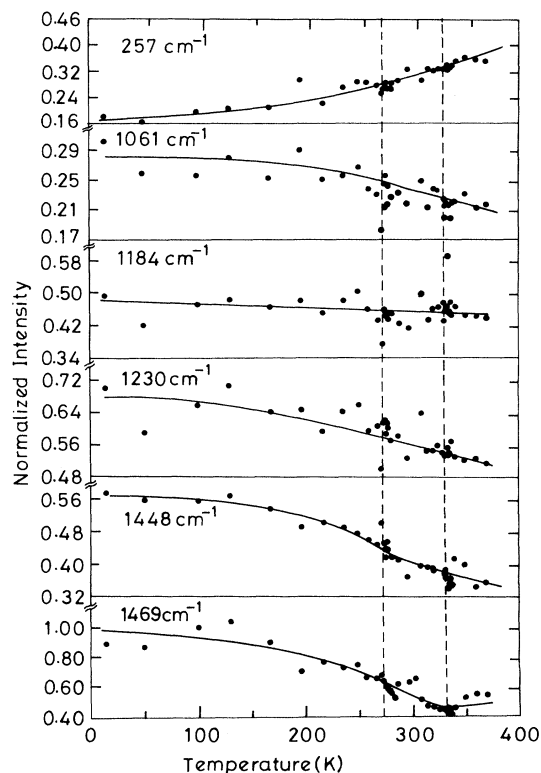

FIG. 4. Temperature dependence of the intensity of the modes with respect to the intensity of the strongest peak at ~ 1566 cm^{-1}.

There are no discontinuous changes in the peak positions. Comparing with C_{60}, this behavior is in contrast to the results of van Loosdrecht, van Bentum, and Meijer[5] but is similar to that found by Matus, Kuzmany, and Kratschmer.[4] It can be noted from Fig. 2 that in the temperature range 270–330 K, $d\omega/dT$ is larger for 1566-, 1469-, 1448-, and 1184-cm^{-1} modes than those for the 1230-, 1061-, and 257-cm^{-1} modes. Beyond 330 K, the temperature coefficient $d\omega/dT$ decreases for all the modes compared to the values in the 330–270-K range. The hardening of the modes in partially and fully orientationally ordered phases II and III can arise either due to decrease in volume at low temperatures or due to increased intermolecular interactions. The latter seems to be probable as these are also manifested in the increased hindrance of rotational motion of the molecules in the low-temperature phases.

The FWHM's of all seven bands show changes at the transition temperature (Fig. 3). Even though there is considerable scatter, the variation of the linewidth for the 1449-cm^{-1} mode appears anomalous. The increase in linewidth is not entirely due to the anharmonic processes, which gives $\Gamma(T)=\Gamma(0)\{1+2[\exp(\hbar\omega_0/2k_BT)-1]^{-1}\}$ for the decay process of the phonon in the two lower modes of equal energy. The dashed lines show this anharmonic contribution for the six modes other than the lowest-frequency 257-cm^{-1} mode, because the latter does not have available phonon states at half of its frequency. The $\Gamma(0)$ values used are 7.4, 3.4, 3.8, 3.3, 5.2, and 2.7 for

the 1566-, 1469-, 1448-, 1230-, 1184-, and 1061-cm^{-1} modes, respectively. The increased linewidths over and above the anharmonic contributions arise from coupling of the phonons with the rotational motion of the molecules in phases II and III which decreases the lifetime of the phonons. The hindrance of the molecular rotation decreases the density of available rotational states resulting in the decrease of the linewidth arising from vibrational-rotational coupling in the low-temperature ordered phases.[5] Below ~ 150 K or so, the rotational motion is expected to be completely frozen out and the linewidths do not, therefore, show any further decrease as seen in Fig. 3.

Figure 4 shows that as the temperature is decreased, the intensities of the modes at 1469, 1448, 1230, 1184, and 1061 cm^{-1} with respect to that of the corresponding 1566-cm^{-1} mode increase whereas the intensities of the 257-cm^{-1} model decrease. Although the reason for this behavior is not clear, we feel that this may be related to the different nature of the displacements associated with the modes. The modes at 1566, 1469, 1448, 1184, and 1061 cm^{-1} have predominantly tangential displacements whereas the 257-cm^{-1} mode has radial displacements. What is also to be noted is that the 1469- and 1448-cm^{-1} bands which show a marked decrease in frequency also show a significant decrease in intensity, but this feature is not universal. All the Raman modes discussed hitherto are due to intramolecular vibrations. We could not unambiguously observe external modes expected to lie below 100 cm^{-1}. The calculated librational modes lie below 20 cm^{-1}.[16]

In summary, we have shown that Raman line positions and widths show smooth changes in their temperature coefficients across the phase transitions of C_{70} near 270 and 330 K. The depolarization ratios also show significant changes with temperature suggesting that a systematic study in high-quality single crystals of C_{70} would be desirable. The absence of discontinuous changes is understandable since the measurements refer to intramolecular modes rather than the libration modes.

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[1] Acc. Chem. Res. **25**, 97 (1992); Indian J. Chem. **31A/31B**, F1 (1991).

[2] J. Phys. Chem. Solids **53**, 1321 (1992).

[3] P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. W. Denenstein, J. P. McCauley, Jr., A. B. Smith III, and D. E. Cox, Phys. Rev. Lett. **66**, 2911 (1991).

[4] M. Matus, H. Kuzmany, and W. Kratschmer, Solid State Commun. **80**, 839 (1991).

[5] P. H. M. van Loosdrecht, P. J. M. van Bentum, and G. Meijer, Phys. Rev. Lett. **68**, 1176 (1992).

[6] N. Chandrabhas, M. N. Shashikala, D. V. S. Muthu, A. K. Sood, and C. N. R. Rao, Chem. Phys. Lett. **197**, 319 (1992).

[7] B. Chase, N. Herron, and E. Holler, J. Phys. Chem. **96**, 4262 (1992); V. S. Babu and M. S. Seehra, Chem. Phys. Lett. **196**, 569 (1992); L. R. Narasimhan, D. N. Stoneback, A. F. Hebbard, R. C. Haddon, and C. K. N. Patel, Phys. Rev. B **46**, 2591 (1992).

[8] P. H. van Loosdrecht, P. J. M. van Bentum, and G. Meijer,

Phys. Rev. Lett. **69**, 1147 (1992).

[9] V. G. Hadjiev and C. Thomsen, Phys. Rev. Lett. **69**, 1146 (1992).

[10] G. B. M. Vaughan, P. A. Heiney, J. E. Fischer, D. E. Luzzi, D. A. Ricketts-Foot, A. R. McGhie, W. J. Romanow, B. H. Allen, N. Coustel, J. P. McCauley, Jr., and A. B. Smith III, Science **254**, 1350 (1991).

[11] M. A. Verheijen, H. Meekes, G. Meijer, P. Bennema, J. L. de Boer, S. van Smaalen, G. van Tendeloo, S. Amelinckx, S. Muto, and J. van Landuyt, Chem. Phys. **165**, 287 (1992).

[12] M. Sprik, A. Cheng, and M. L. Klein, Phys. Rev. Lett. **69**, 1660 (1992).

[13] V. Varma, R. Seshadri, A. Govindaraj, A. K. Sood, and C. N. R. Rao, Chem. Phys. Lett. **203**, 545 (1993).

[14] Z. Slanina, J. M. Rudzinski, M. Togasi, and E. Osawa, J. Molecular Structure (Theochem.) **202**, 169 (1989).

[15] D. S. Bethune, G. Meijer, W. C. Tang, H. J. Rosen, W. G. Golden, H. Seki, C. A. Brown, and M. S. de Vries, Chem. Phys. Lett. **179**, 181 (1991).

[16] A. Cheng and M. L. Klein, Phys. Rev. B **46**, 4958 (1992).