Vibrational Raman and infrared spectra of chromatographically separated C_{60} and C_{70} fullerene clusters

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We report vibrational Raman and infrared spectra for chemically separated C_{60} and C_{70} fullerenes. Thin film samples were prepared by subliming the chromatographically separated species onto appropriate substrates. The C_{60} Raman spectrum shows eight clear lines and two weaker ones. If C_{60} in fact has the proposed buckminsterfullerene structure (as is strongly indicated by recent experiments), the present Raman measurements together with the four observed IR frequencies give a complete set of Raman and infrared active fundamental frequencies for this molecule. A comparison of this set with the calculated spectrum for buckminsterfullerene shows satisfactory agreement.

1. Introduction

The discovery that macroscopic samples of fullerenes can be produced and accumulated [1–3] has made it possible to carry out various experiments that reveal the microscopic characteristics of these species [1,2,4–8]. In keeping with its reputation as a molecular fingerprint, it was the infrared spectrum of C_{60} – restricted by symmetry to a mere four lines – that led Krätschmer, Fostiropoulos and Huffman to believe that C_{60} clusters were present in soot produced by simply heating graphite in an inert gas [1]. This belief was soon confirmed by those authors and others [2,6,9]. Because C_{60} has icosahedral (I_h) symmetry [5,6], and both 1D [6] and 2D [10] NMR confirm a proposed [11] C_{70} structure with D_{5h} symmetry, the IR and Raman active modes are mutually exclusive for these species. In both cases, therefore, vibrational Raman spectroscopy provides a complementary method to probe the highly characteristic spectrum of molecular vibrations. In a previous study of the Raman spectra of these molecules, thin films of mixtures of C_{60} and C_{70} were produced by directly subliming these species from carbon soot [4]. Vibrational Raman lines of both C_{60} and C_{70} were identified, and the three strongest C_{60} lines were assigned on the basis of earlier theoretical work on the buckminsterfullerene (Bf) structure for C_{60} [12–17]. Five C_{70} lines were identified but not assigned.

In this paper we extend this earlier work, and report the vibrational Raman and infrared spectra of chromatographically separated samples of C_{60} and C_{70}. A comparison of the spectrum of observed vibrational frequencies for C_{60} (both Raman and IR) shows agreement with the vibrational spectrum predicted for Bf to within the level of accuracy expected for the calculations. For C_{60}, therefore, we believe that these measurements provide a complete set of fundamental frequencies for all of its Raman and infrared active modes. For C_{70}, numerous Raman lines have been identified and characterized by depolarization ratio measurements. The C_{70} infrared spectrum is also very rich. The principal features of these distinctive spectra are tabulated.

2. Experimental

C_{60} and C_{70} fullerenes were produced by arc heating of graphite in He, a method used by Krätschmer,

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Sorg and Huffman to produce carbon clusters as early as 1984 [18], well before they realized that peculiar features they sometimes observed in the UV spectrum of the soot deposits were a signature of fullerene production [19]. A recent implementation of this method has been described by Haufler et al. [8]. Briefly, a current of ≈100 A was passed between two 6 mm diameter carbon rods, nearly in contact, in 100–150 Torr of He. C_{60} and C_{70} were extracted from the collected soot with hot toluene. Separation of the C_{60} and C_{70} molecules was achieved by dispersing a 10 mg sample of the extracted material onto 1 g of silica, applying the dispersion to the top of a column of active alumina, and eluting with 500 ml each of hexane, 5% benzene in hexane, and finally 20% benzene in hexane at a flow rate of 1.5 ml/min. The fractions were analyzed by laser desorption/laser ionization mass spectrometry. The separated C_{60} contained $\leqslant 1\%$ C_{70}, while the C_{70} fractions had $\leqslant 5\%$ C_{60}. Solutions of purified C_{60} and C_{70} appeared violet and orange-brown respectively, and when evaporated yielded yellow-brown and black solids. Films were prepared by loading ≈100 μg of the purified material (dissolved in toluene) into a small resistively heated stainless steel tube oven which was placed in a bell jar and evacuated to $\approx 10^{-6}$ Torr. After heating the oven to 150°C for 5 min, a substrate window was placed 2–5 mm above the 1 mm opening in the tube. Heating the tube further (to ≈550°C) then sublimed the molecules onto the window.

Raman spectra of the fullerene samples on suprasil slides were taken in air at room temperature using a micro-Raman spectrometer. The Ar ion laser beam (280 μW at 514 nm) was focused to a 13 μm diameter spot on the sample film. A back-scattering geometry was used, and the instrumental resolution was $\approx 9\ \text{cm}^{-1}$. Transmission FTIR spectra were obtained at $2\ \text{cm}^{-1}$ resolution using a Bomem model DA3 Fourier transform infrared spectrometer, with the optical path evacuated to $\leqslant 0.3$ Torr. A wide band liquid nitrogen cooled mercury cadmium–cadmium telluride (MCT) detector was used in conjunction with a KBr beamsplitter. Spectra obtained with a sample film on KBr (1000 scans) were referenced against the (1000 scan) spectrum of a KBr plate which had undergone the entire preparation process, but with the fullerene material omitted. The spectra were calculated using a Hamming apodization function.

3. C_{60} vibrational frequencies

The vibrational Raman spectra obtained for purified C_{60} are presented in figs. 1a and 1b showing unpolarized and polarized spectra, as indicated. Eight clear lines and several weaker but reproducible ones are found. The sample purity is confirmed by the absence of the intense C_{70} line at $1569\ \text{cm}^{-1}$. The measured line positions, intensities for the polarized spectra, and depolarization ratios are summarized in table 1.

As discussed in ref. [4], the three strongest C_{60} Raman lines can be assigned on the basis of their frequencies and depolarization ratios. The lowest fre-

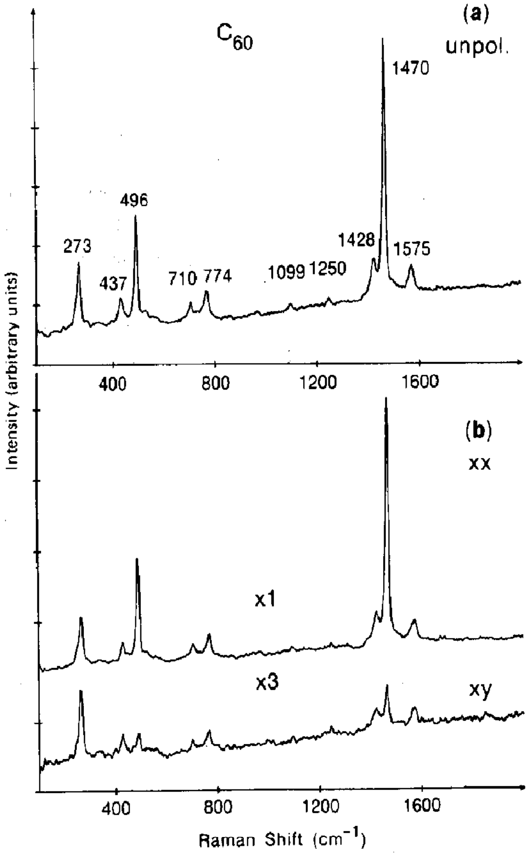

Fig. 1. Raman spectra of a film of purified C_{60} on a suprasil substrate. (a) Unpolarized, and (b) polarized.

Table 1
Observed C_{60} infrared line positions (cm^{-1}), and Raman line positions (± 2 cm^{-1}), intensities (for parallel and perpendicular polarizations, with $I_{\parallel}(1470) \equiv 100$), depolarization ratios ($\rho \equiv I_{\perp}/I_{\parallel}$), and assignments

ν_{IR}	ν_{Raman}	$I_{\parallel}$	$I_{\perp}$	$\rho(\pm 0.02)$	Assignment
	273	20.4	9.7	0.48	H_g squashing
	437	9.1	3.1	0.34	H_g
	496	42.7	3.1	0.07	A_g breathing
527					F_{1u} IR active
577					F_{1u} IR active
	710	6.5	1.6	0.25	H_g
	774	10.2	2.7	0.27	H_g
	1099	2.3			H_g (tentative)
1183					F_{1u} IR active
	1250	2.3			H_g (tentative)
	1428	13.8	3.1	0.22	H_g
1428					F_{1u} IR active
	1470	100	6.1	0.06	A_g pent. pinch
	1575	9.4	2.6	0.28	H_g

quency C_{60} Raman line is at 273 cm^{-1}, in agreement with theoretical predictions for the H_g squashing mode of Bf [12–16]. Fig. 1b shows that this line is strongly depolarized. On the other hand, the two strongest C_{60} lines at 496 and 1470 cm^{-1} are seen to be highly polarized, strongly suggesting that the associated modes are totally symmetric. These lines can thus be assigned to the two totally symmetric A_g modes of Bf. For these radial breathing and tangential stretching (or pentagonal pinch) modes the pentagons and hexagons of the structure expand and contract in and out of phase, respectively. In addition to the three strongest lines, five clear lines appear at 437, 710, 774, 1428, and 1575 cm^{-1}. All have intermediate depolarization ratios, $0.22 \leqslant \rho \leqslant 0.34$. Finally, several weak but reproducible features appear in the spectrum. The most convincing of these are lines at 1099 and 1250 cm^{-1}, and these are tentatively assigned to modes of C_{60}. No additional lines were observed in the ranges 90–200 and 2000–2500 cm^{-1}.

The infrared spectrum measured for C_{60} is shown in fig. 2a. The frequencies measured for the four strong lines (527, 577, 1183 and 1428 cm^{-1}) agree with the values reported by Krätschmer et al. [1,2]. These lines are included in table 1. Weak features at 1259 and 1375 cm^{-1} are common to the C_{60} and C_{70} spectra and may be due to some contaminant. Other weak features at 1452, 1460 and 1540 cm^{-1} are unexplained.

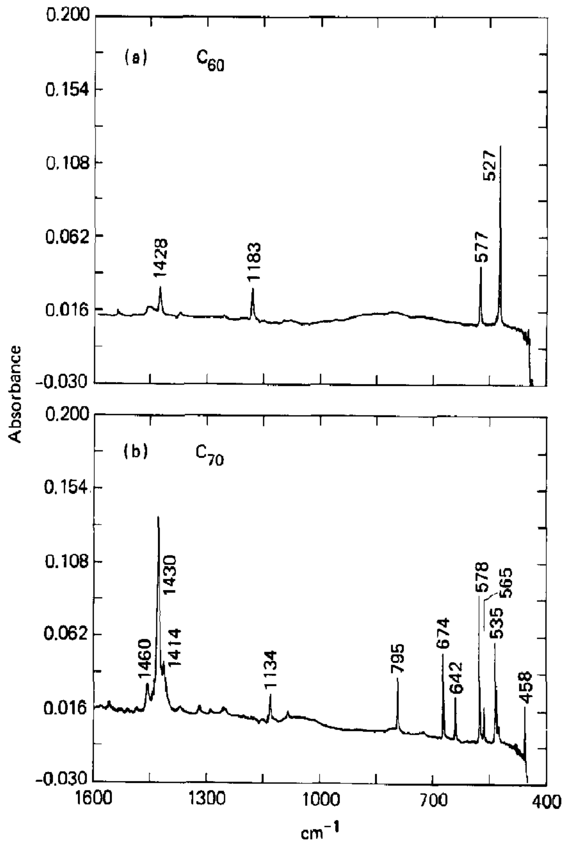

Fig. 2. Absorbance FTIR spectra of films of chromatographically separated (a) C_{60} and (b) C_{70} on KBr substrates. Absorbance values are for samples with undetermined thicknesses.

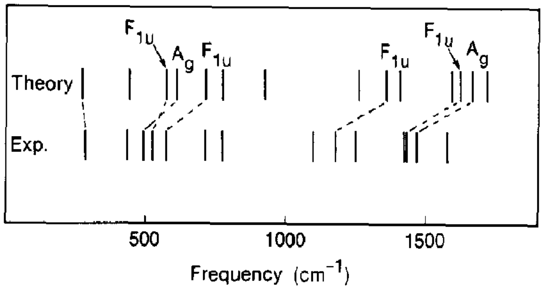

Fig. 3. Comparison of the frequencies of the IR active F_{1u} and Raman active A_g and H_g modes calculated for Bf in ref. [15] with the observed Raman and infrared frequencies for C_{60}. Theoretical lines without labels correspond to H_g modes. The dashed lines indicate assignments for the infrared lines, the strong highly polarized Raman lines, and the depolarized lowest frequency Raman line.

An overview comparison of all of the IR and Raman frequencies attributed to C_{60} with the spectrum calculated by Stanton and Newton [15] for Bf (including *all* Raman and infrared active modes) is shown in fig. 3. The totally symmetric A_g modes and infrared active F_{1u} modes are labelled, and the remaining eight theoretical frequencies are for the H_g modes. The dashed lines indicate the assignments of the three strong Raman lines and the four infrared lines. The overall patterns are in striking qualitative agreement. Because this pattern depends on both the molecular symmetry and the nature and arrangement of the bonds, this agreement is very strong evidence in favor of the Bf model for C_{60}.

4. C_{60} vibrational frequencies

Raman spectra taken of a C_{70} film on suprasil are shown in fig. 4. Eighteen clear peaks are labelled. Table 2 summarizes the line frequencies, the intensities $I_{\parallel}$ and $I_{\perp}$, and the depolarization ratios ρ for this spectrum. For most of the lines ρ is ≈ 0.2, but the lines at 739 and 1517 cm^{-1} have markedly higher values (0.39 and 0.44). These are weaker, overlapped lines however, with larger uncertainties in ρ. Table 2 includes frequencies for three weak shoulders at 400, 1298 and 1317 cm^{-1}.

The infrared spectrum of a purified C_{70} film on a KBr substrate is shown in fig. 2b. The 11 clearest lines are labelled, and their positions are summarized in table 2. A second group of weaker reproducible features, possibly due to C_{70}, are included in table 2 and are designated by question marks. A weak but clear line at 527 cm^{-1} indicates the presence of a few percent of C_{60} in the sample, in agreement with mass spectrometry. Infrared data for purified C_{70} has also been reported by a group at Exxon [20]. While many of their lines coincide with those observed here, there are some differences. In particular, three lines reported in ref. [20] at 692.7, 723.6 and 791.4 cm^{-1} are not present in our spectrum.

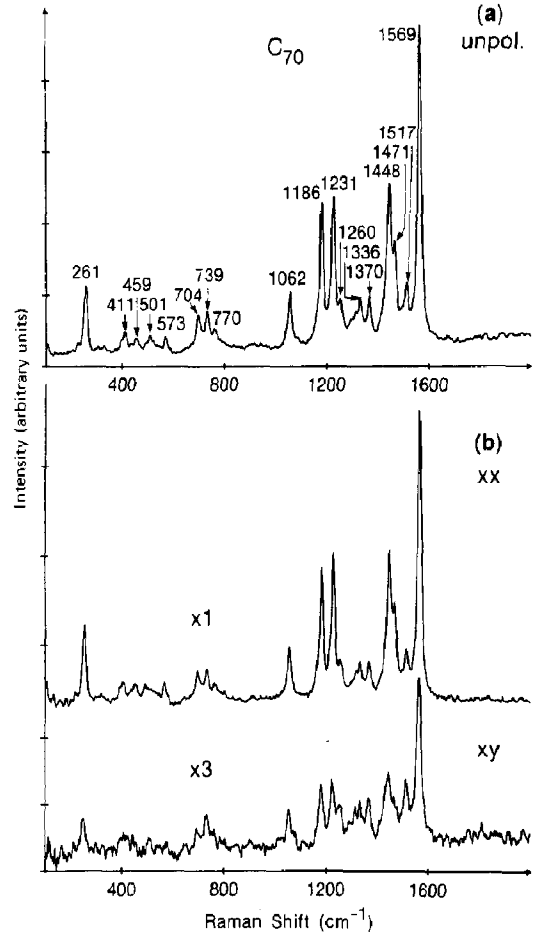

Fig. 4. Raman spectra of a purified film of C_{60} on a suprasil substrate. (a) Unpolarized, and (b) polarized.

Vibrational frequencies for C_{70} have been calculated by Slanina et al., assuming a structure with D_{5h} symmetry [13]. For this symmetry, their analysis showed that C_{70} should have 31 allowed infrared ab-

Table 2

Observed C_{70} infrared line positions, and Raman line positions (± 2 cm^{-1}), intensities (for parallel and perpendicular polarizations, with $I_{\parallel}(1569) \equiv 100$), and depolarization ratios ($\rho \equiv I_{\perp}/I_{\parallel}$)

ν_{IR}	ν_{Raman}	$I_{\parallel}$	$I_{\perp}$	$\rho(\pm 0.02)$
458	261	28.2	4.5	0.16
535	400	(shoulder)		
565	411	6.7		
578	459	6.7		
642	501	6.0		
674	573	6.5		
795	704	11.1	2.1	0.19
1086 (?)	739	11.5	4.5	0.39
1134	770	5.0		
1252 (?)	1062	18.9	4.7	0.25
1292 (?)	1186	46.3	7.5	0.16
1321 (?)	1231	51.1	8.0	0.16
1414	1260	5.2		
1430	1298	(shoulder)		
1460	1317	(shoulder)		
1562 (?)	1336	13.3		
	1370	13.2		
	1448	51.9	8.6	0.17
	1471	25.0		
	1517	17.7	7.7	0.44
	1569	100	19.4	0.19

sorption lines (corresponding to symmetry species $10A_2'' + 21E_1'$) and 53 Raman lines (corresponding to symmetry species $12A_1' + 22E_2' + 19E_1''$). The remaining modes ($9A_2' + 9A_1'' + 20E_2''$) are inactive. Comparison of our Raman data with this more complicated predicted spectrum is difficult because the symmetry species associated with a given calculated frequency was not determined. However, frequencies associated with infrared active modes were indicated in ref. [13]. No obvious correspondence between the patterns of the calculated and observed infrared spectra can be discerned. Intensity predictions would be of great value in making this comparison.

5. Conclusions

Only ten Raman frequencies and four infrared frequencies are expected for the Bf structure. The availability of purified samples of C_{60} has made it possible to identify eight clear Raman lines, and to tentatively identify two additional weaker lines for this species. If C_{60} in fact has the Bf structure (as is strongly indicated by recent experiments), the present Raman measurements together with the four observed IR frequencies give a complete set of Raman and infrared active fundamental frequencies for this molecule. A comparison of this spectrum with that calculated for Bf shows good qualitative agreement of the overall patterns. The calculated frequencies are relatively accurate for the lowest frequency modes, and become increasingly too high for higher frequency modes. This trend is expected from the tendency of the calculational methods to overestimate stretching frequencies by about 10% [15]. The mode vectors for the squashing mode and the two totally symmetric modes are qualitatively clear. Insight into the character of the atomic motions for the higher order H_g modes can be obtained from the work of Stanton and Newton [15] and from very helpful stereographic representations of the vibrations of a ball-and-spring model buckyball given in the paper of Weeks and Harter [14].

The situation for C_{70} is not so complete nor so simple. Roughly 1/2 as many IR frequencies as expected for the C_{70} structure are identified, and 2/5 of the expected number of Raman lines are found. The observed spectral patterns are nevertheless highly distinctive, and their assignment poses a formidable challenge.

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