

The IR Spectra of Fullerene-60 and -70

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The IR spectra of fullerene-60 and fullerene-70 have been measured and assigned on the basis of available vibrational calculations.

Since the discovery of a C_{60} cluster and the association of geodesic factors inherent in a closed cage with its apparent stability,¹ it is clear that IR spectroscopy might contribute substantially to elucidation of the structure. Theoretical calculations²⁻⁹ indicate that fullerene-60 should exhibit a very simple spectrum consisting of only four allowed vibrations due to high symmetry. Kraetschmer *et al.*^{10,11} observed four weak, but distinct features in the IR spectrum of arc-processed carbon, the frequencies matching theoretical predictions within the acceptable tolerance. The subsequent successful solvent extraction of fullerenes by Kraetschmer *et al.*¹² and Taylor *et al.*¹³ provided structural confirmation through X-ray and electron diffraction analyses,¹² and ^{13}C NMR spectroscopy.¹³

Benzene solutions of chromatographically separated¹⁴ fullerene-60 and -70 were deposited on KBr discs, and the solvent removed under reduced pressure. [Both fullerene-60 and -70 retain tenaciously, solvents such as benzene and chloroform, but these can be removed by heating at 170 °C under vacuum (7 mmHg) for 2 h.] The IR of the resulting thin solid films were recorded on a Perkin-Elmer FTIR model 1720 instrument at 1 cm^{-1} resolution.

The characteristic four-band spectrum of fullerene-60 is shown in Fig. 1, and the measured vibrational assignments, together with the theoretical calculations of Bakowies and Thiel,⁹ are listed in Table 1. The more complicated observed and calculated spectrum of fullerene-70 (the ^{13}C NMR spectrum of which confirms the D_{5h} symmetry¹³) is shown in Fig. 2, and the associated frequencies are given in Table 2. It is well known that MNDO-based calculations invariably overestimate frequencies by 10–30% and intensities may vary significantly in error. The calculated frequencies [Fig. 2(a)] have been scaled by 0.85 uniformly across the range. The intensities have also been scaled so that all relative intensities of the medium and weak bands, illustrated by Bakowies and Thiel,⁹ are enhanced by a factor of three relative to the unique

and very strong band calculated to lie at 1592 cm^{-1} . The very weak band positions, listed but not illustrated, are indicated by negative lead lines [Fig. 2(a)]. The comparison between observation and theory for fullerene-60, summarised in Table 1, serves as a preliminary gauge of the degree of reliability that might be expected for the fullerene-70 analysis. The fullerene-

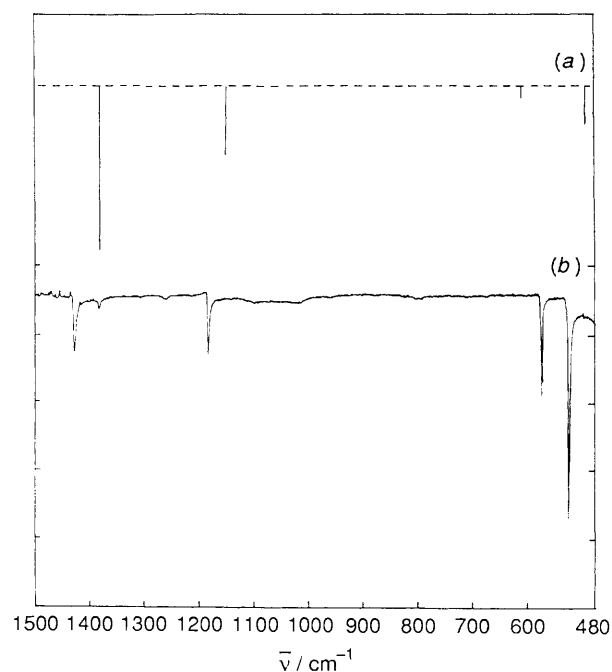


Fig. 1 IR spectrum of fullerene-60 (a) theoretical spectrum scaled by a factor of 0.85; (b) spectrum of a chromatographed sample of fullerene fullerene-60

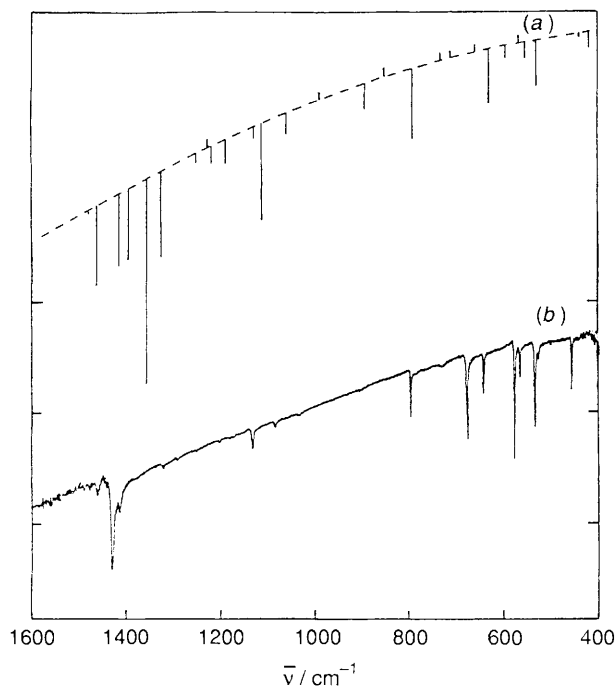


Fig. 2 IR spectrum of fullerene-70 (a) theoretical spectrum scaled by a factor of 0.85; (b) spectrum of a chromatographed sample of fullerene-70. The band assignment shown is discussed in the text. The calculated frequencies have been scaled by 0.85 across the range. The intensities are scaled so that relative intensities of the medium and weak bands are three times relative to the strong band calculated at 1592 cm^{-1} . The positions of the very weak bands are listed but not illustrated. The films invariably yielded spectra on a rising scattering background which has been approximated in the presentation of the calculated spectrum. The very weak feature on the low frequency side of the 535 cm^{-1} band is the strongest feature of fullerene-60 (528 cm^{-1}), present in the sample to the extent of 2.5%.

Table 1 Vibrational data for fullerene-60

Observed ^a frequency	Calculated ^b frequency (scaled $\times 0.85$)	Scale ^c factor	Assignment
527 s	578 (491) m	0.91	t_{1u}
576.5 m	718 (610) m	0.80	t_{1u}
1182.5 m	1352 (1149) w	0.88	t_{1u}
1429 m	1628 (1384) s	0.88	t_{1u}

^a Frequencies given in ref. 12 are 528, 577, 1183 and 1429 cm^{-1} .

^b From ref. 9. ^c (obsd. freq.)/(calcd. freq.).

60 comparison, given in Table 1, indicates that the ratio of the observed to the calculated frequencies varies from 0.91 to 0.80 for the two low frequency bands observed at 528 and 577 cm^{-1} respectively and that the relative intensities are in rather good agreement. The scale factor is *ca.* 0.88 for the high frequency bands but there is rather poor agreement for the intensity estimates relative to the low frequency bands.

For fullerene-70 there is clearly good agreement between the very strong band observed at 1430.7 cm^{-1} and the band calculated to lie at 1592 cm^{-1} . However, other assignments are subject to uncertainty although the overall comparison between the observed and calculated band patterns is quite good. On the basis of the semiquantitative comparison (Fig. 2) the preliminary assignment indicated in this diagram and listed in Table 2 has been made. It is of course subject to the provisos discussed above.

At this early stage in fullerene vibrational theory it is clear that although the calculations are only in reasonable semi-

Table 2 Vibrational data for fullerene-70

Observed frequency	Calculated ^a frequency (scaled $\times 0.85$)	Scale ^b factor	Assignment
458.2 m	492(418)w	0.93	a_2''
535.5 ms	627(533)w	0.85	e_1'
565.7 m	650(553)w	0.87	e_1'
578.0 s	740(630)w	0.78	e_1'
642.4 ms	701(596)w	0.92	$a_2''?$
674.2 ms	929(790)m	0.73	e_1'
795.1 s	1051(893)w	0.76	e_1'
1087 w	1248(1061)w	0.87	e_1'
1133.2 mw	1314(1117)m	0.86	a_2''
	1328(1129)w ^c		e_1'
	1397(1187)w ^c		e_1'
	1429(1215)w ^c		e_1'
	1470(1250)w ^c		e_1'
1414	1555(1322)m	0.91	e_1'
1430.7 vs	1592(1353)vs	0.90	e_1'
1461 m	1637(1391)m	0.89	a_2''
	1659(1410)m ^c		e_1'
	1721(1463)m ^c		e_1'
	1742(1481)w ^c		a_2''

^a From ref. 9. ^b (obsd. freq.)/(calcd. freq.). ^c Several very weak features are observable for fullerene-70 at 1183, (1203), (1249), 1257, (1291), (1321), and 1377 cm^{-1} ; those in parentheses are each 0.90 times the four predicted bands between 1328 and 1470 cm^{-1} .

quantitative agreement with observation, discrepancies preclude some assignments. This is interesting as these discrepancies should contain the information through which refinements in the force field can be derived. As the only previous polycyclic networks are mainly flat carbon systems with hydrogen atoms at the edges, one might expect inconsistencies. Further experimental and theoretical analysis of these novel species promises to yield a most interesting picture of the global vibrational dynamics of such novel cages. The present work is to be considered as the first step to the elucidation of accurate force fields for the fullerene skeleton.

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