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# Infrared and Raman Spectra of $C_{60}$ and $C_{70}$ Solid Films at Room Temperature

by

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# Infrared and Raman Spectra of $C_{60}$ and $C_{70}$ Solid Films at Room Temperature

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## Abstract:

Infra-red and high resolution Raman spectroscopic probes of thin films of $C_{60}$ and $C_{70}$ are presented and discussed in terms of previous measurements, semi-empirical calculations and plausible molecular geometries.

The development of simple methods for the gram scale synthesis of air stable hollow core all-carbon clusters (fullerenes)[1] has accessed a new class of solid materials whose properties are expected to hold many useful surprises. For example, preliminary studies on alkali doped $C_{60}$ have shown resulting materials to be molecular superconductors with transition temperatures in the 18-30 K range[2]. Pure fullerenes are presently being studied in applications ranging from lubrication[3] to the nucleation of diamond thin films[4]. An understanding of the molecular level processes accessed in such studies requires structural determination, as well as sensitive and selective quantitative analysis. Both can be achieved via vibrational spectroscopy.

First FT-IR absorption [1,5-7] and Raman measurements[8,9] have established that room temperature solid films of $C_{60}$ and $C_{70}$ manifest characteristic vibrational spectra differing strongly from those of other carbon modifications. The high symmetry of the $C_{60}$ truncated icosahedron (see figure 1) gives rise to only 4 IR and 10 Raman active modes[10-12]. Their tentative assignment in IR and Raman measurements of $C_{60}$ thin films has provided strong evidence for the proposed molecular structure[9]. Interestingly, the associated Raman depolarization ratios suggest effectively random molecular orientation at room temperature - consistent with a plastic r.t. phase inferred from solid state $^{13}$C-NMR[13]. The supposed lower symmetry molecular structure of $C_{70}$ [14] would be expected to lead to much more complicated vibrational spectra [15,16] and in fact 21 Raman and 16 IR features have so far been reported for this cluster[9].

In this letter we present Raman and IR measurements on $C_{60}$ and $C_{70}$ thin films. Raman data were obtained at significantly greater resolution (9x) than in previous studies. Results encompass a confirmation of $C_{60}$ IR and Raman spectral assignment[9] as well as the identification of multiple previously unresolved $C_{70}$ vibrational features, which are compared to computational prediction. Detailed analysis of the underlying vibrational dynamics at various film temperatures is ongoing and will be reported elsewhere. This study is part of an investigation into the vibrational properties of carbon species involved in the nucleation and growth of diamond thin films[4].

$C_{60}$ and $C_{70}$ were obtained from carbon soot, prepared by graphite evaporation in a helium atmosphere [1,17]. Fullerenes were solvent extracted and chromatographically separated [18]. Purity of resulting $C_{60}$ and $C_{70}$ fractions was confirmed by electron impact mass spectroscopy (see below). Thin films were generated by subliming the respective purified solids under high vacuum onto Si(100) or KBr substrates. $C_{60}/C_{70}$ were sublimed at 450/550° C, respectively. At lower evaporator temperatures, the substrate was kept shuttered. Raman spectra of fullerene films on silicon substrates were taken in air at room temperature in a backscattering geometry using either the 514 nm or 488 nm lines of an Ar$^{+}$ laser (20 mW). No significant excitation frequency dependence was observed. Both polarized and unpolarized spectra were obtained. Instrument resolution was 1 $cm^{-1}$ with absolute error ± 1 $cm^{-1}$. IR measurements were performed on KBr substrates using an $N_2$-purged Mattson FTIR at 2 $cm^{-1}$ resolution.

Unpolarized Raman spectra of $C_{60}$ and $C_{70}$ are shown in Figures 1a and 1b, respectively and compared to semi-empirical computation[15]. Tables I and II contain peak positions, intensities and symmetry assignments. Also listed are depolarization ratios for bands having sufficient signal-to-noise to yield meaningful numbers. Figures 2a and 2b show the corresponding IR absorption spectra again compared to calculation. IR spectral features are also listed in Tables I and II.

(i) $C_{60}$. IR and Raman spectra are in good agreement with previous work[9]. Using more recent semi-empirical calculations for $I_h$ $C_{60}$ vibrational fundamentals [12], our data confirm the proposed spectral assignment, including 1100 and 1250 $cm^{-1}$ features which had only been tentatively identified before. All IR active (4) and Raman active (10) modes are now clearly resolved. Among several additional (weaker) IR features, contaminant lines at 805, 1257, 1539 $cm^{-1}$ (IR) are not tabulated [9]. Remaining minor tabulated features reflect combination bands or matrix effects.

(ii) $C_{70}$. The proposed $D_{5h}$ structure (see figure 1) encompasses 31 IR and 53 Raman active modes. IR absorption studies have so far resolved 16 features[9]. We confirm 13 of these. At the higher resolution and sensitvities accessed, 21 previously identified Raman lines give way to a total of 33 features, some with discernible (and likely further separable!) shoulders. While similarities are apparent between experiment and $D_{5h}$ semi-empirical prediction[15] for both IR and Raman spectra, assignment must await: (i) more highly resolved measurements on thin films of $^{13}C_{70}$ and $^{12}C_{70}$ at various temperatures and (ii) calculations of Raman cross sections. In the interim, Table II gives tentative vibrational symmetry assignments for a number of lines based on calculations for the $D_{5h}$ structure[15].

The isolation of $C_{70}O$, $C_{76}/C_{78}$, $C_{84}$ and $C_{92}$ from fullerene preparations has recently been reported[19]. The underlying "statistical synthesis" from graphite likely forms traces of even larger all carbon clusters. Their isolation and mass spectral characterization is ongoing[8]. It is likely that such larger species will share with $C_{60}$ and $C_{70}$ the hollow core structural motif comprising 12 five fold rings (to achieve closure) supplemented by hexagons (20 in the case of $C_{60}$). Given enough carbon atoms, the vibrational spectra of large fullerenes should approach those of (perturbed) microcrystalline graphite[20]. Systematic Raman studies of these systems may be of great interest in unraveling the size dependent transition from molecular vibrational to bulk phonon behaviour.

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## Tables

I. $C_{60}$ IR and Raman line positions[a], relative intensities (unpolarized), Raman depolarization ratios and assignments.

| Assignment | $\nu_{IR}$ | $I_{IR}$ | $\nu_{RAMAN}$ | $I_{RAMAN}$ | $\rho^b$ |
|---|---|---|---|---|---|
| | | | 267(S) | 7 | |
| $H_g$ | | | 273 | 15 | .36 |
| $H_g$ | | | 434 | 3 | .47 |
| | | | 486(S) | 3 | |
| $A_g$ | | | 496 | 13.1 | .07 |
| $F_{1u}$ | 527 | 100 | | | |
| $F_{1u}$ | 577 | 37 | | | |
| $H_g$ | | | 710 | 4 | .40 |
| $H_g$ | | | 774 | 4 | .46 |
| $H_g$ | | | 1100 | 1 | |
| $F_{1u}$ | 1183 | 23 | | | |
| $H_g$ | | | 1250 | 1 | |
| $H_g$ | | | 1426 | 13.1 | .35 |
| $F_{1u}$ | 1428 | 24 | | | |
| | | | 1464(S) | 29.2 | |
| $A_g$ | | | 1470 | 100 | .08 |
| $H_g$ | | | 1576 | 8.1 | .39 |

---

[a] Positions in wavenumbers. All features with signal to noise > 2 are listed (see figs. 1/2 and text). Typical relative intensity variations between measurements were ± 10%. Raman measurements were done on essentially pure $C_{60}$ and $C_{70}$ samples. The $C_{70}$ IR sample was slightly contaminated by $C_{60}$. [b] Depolarization ratios refer to $I_{perpendicular}/I_{parallel}$. Numbers are not tabulated for weak signals or incompletely resolved shoulders (s).

II. $C_{70}$ vibrational line positions, relative intensities, Raman depolarization ratios and tentative assignments[a].

| Assignment (IR/Raman) | $\nu_{IR}$ | $I_{IR}$ | $\nu_{RAMAN}$ | $I_{RAMAN}$ | $\rho$ |
|---|---|---|---|---|---|
| | | | 224(S) | 5 | |
| | | | 229 | 5 | |
| | | | 252(S) | 24 | |
| $a_1'$ | | | 260 | 31 | .24 |
| | | | 400 | 7 | |
| | | | 413 | 17 | |
| | | | 436 | 3 | |
| | | | 457 | 10 | |
| | 458 | 16 | 508 | 4.3 | |
| | | | 521 | 5 | |
| | 535 | 47 | | | |
| $/a_1'$ | 565 | 16 | 572 | 17 | .12 |
| | 578 | 53 | | | |
| | 641 | 16 | | | |
| $e_1'/?$ | 673 | 35 | 704 | 19 | .4 |
| | | | 715 | 12 | |
| $e_2'$ or $e_1''$ | | | 740 | 16 | .75 |
| $e_2'$ or $e_1''$ | | | 771 | 7 | .7 |
| $e_1'$ | 795 | 19 | | | |
| | | | 1053(S) | 7 | |
| $a_1'$ | | | 1063 | 26 | .29 |
| $a_2''/$ | 1133 | 13 | 1167 | 9 | |
| $/a_1'$ | 1181 | 7 | 1187 | 69 | .25 |
| $a_1'$ | | | 1232 | 76 | .2 |
| $e_2'$ or $e_1''$ | | | 1259 | 10 | .62 |
| | | | 1301 | 7 | |
| $e_2'$ or $e_1''$ | | | 1316 | 12 | .5 |
| $/e_2'$ or $e_1''$ | 1320 | 7 | 1335 | 14 | .54 |
| | | | 1371 | 24 | .67 |
| $e_1'$ | 1415 | 26 | | | |
| $e_1'/$ | 1429 | 100 | 1439(S) | 26 | |
| | | | 1443(S) | 33 | |
| $a_1'$ | | | 1449 | 71 | .23 |
| | | | 1461(S) | 26 | |
| | 1460 | 6.9 | 1463(S) | 26 | |
| $a_1'$ | | | 1471 | 52 | .21 |
| $e_2'$ or $e_1''$ | | | 1515 | 22 | .59 |
| $a_1'$ | | | 1569 | 100 | .29 |

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[a] See table I footnotes.

## Figure Captions

Figure 1. Unpolarized Raman spectra of purified films of $C_{60}$ and $C_{70}$ on Si(100) substrate - see text and Tables. Superimposed are the calculated Raman active modes [MNDO frequencies scaled to $C_{60}$ measurement using 0.872x]$^{15}$ for both the $C_{60}$ $I_h$ structure and the postulated $C_{70}$ $D_{5h}$ structure.

Figure 2. FTIR spectra of purified films of $C_{60}$ and $C_{70}$ on KBr substrates. Also shown are the semi-empirical computational predictions of ref. 15 upon which we base the symmetry assignments in Tables I and II.

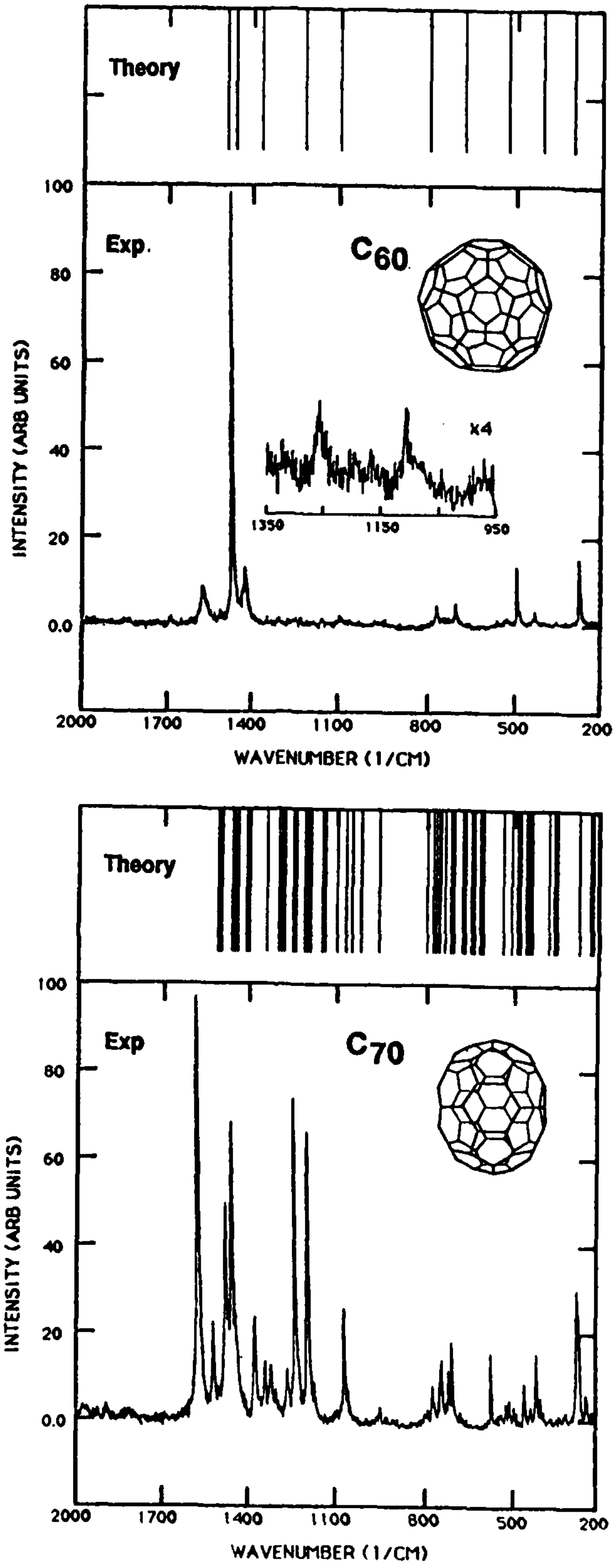
Theory
Exp.
C60
x4
1350
1150
950
INTENSITY (ARB UNITS)
100
80
60
40
20
0.0
2000
1700
1400
1100
800
500
200
WAVENUMBER (1/CM)
Theory
Exp
C70
INTENSITY (ARB UNITS)
100
80
60
40
20
0.0
2000
1700
1400
1100
800
500
200
WAVENUMBER (1/CM)

Figure 1

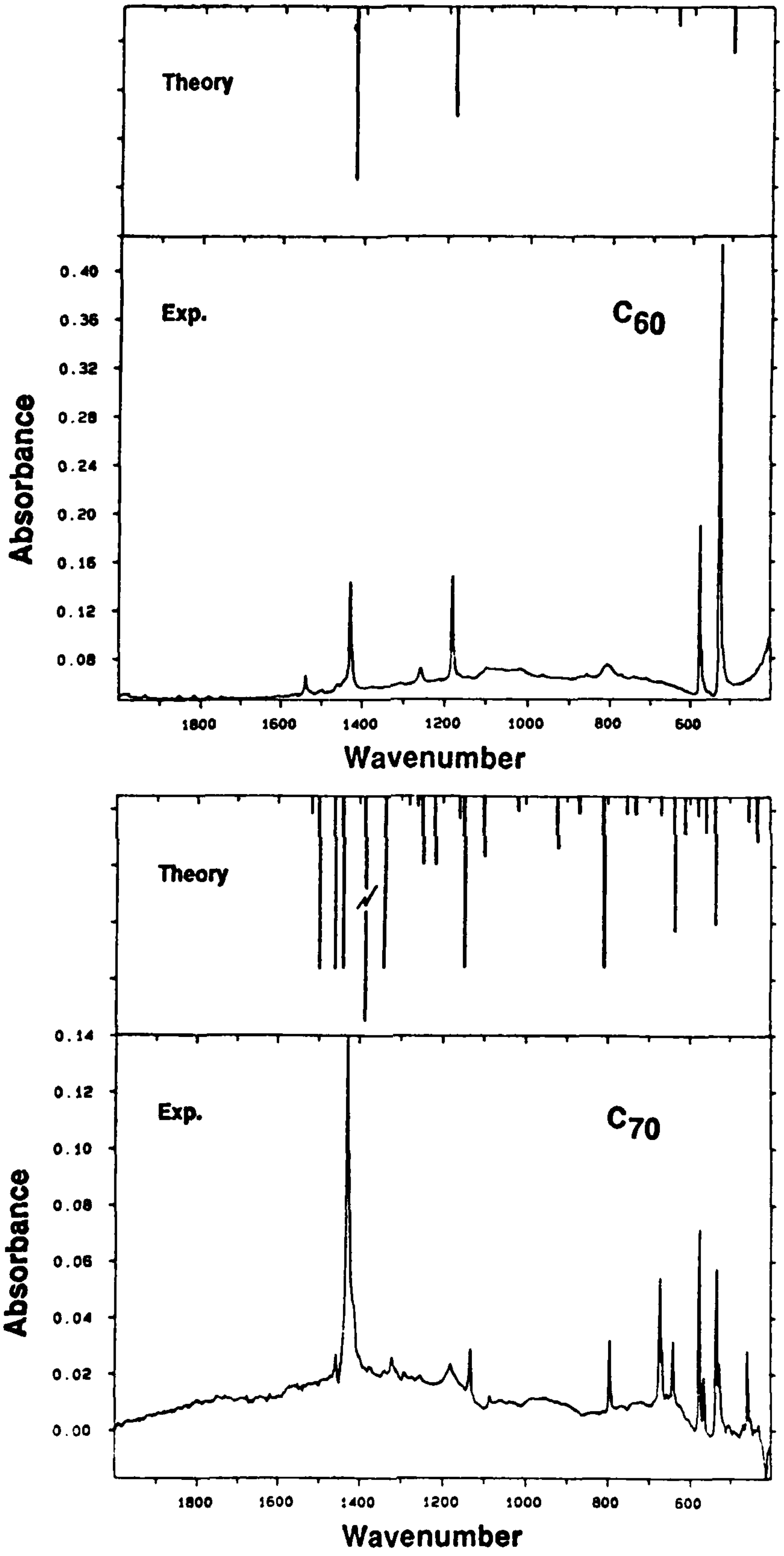
Theory
Exp.
$C_{60}$
Absorbance
0.40
0.36
0.32
0.28
0.24
0.20
0.16
0.12
0.08
1800
1600
1400
1200
1000
800
600
Wavenumber
Theory
Exp.
$C_{70}$
Absorbance
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
1800
1600
1400
1200
1000
800
600
Wavenumber

Figure 2

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