Nondestructive evaluation of C\textsubscript{60} fullerene by FTIR spectroscopy

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We report a well-resolved infrared spectrum of C\textsubscript{60} fullerene samples recorded nondestructively. The spectral analysis has been done in the light of morphological variations.

The discovery of fullerenes\textsuperscript{1-3} with their unique molecular symmetry and intriguing properties has attracted widespread attention. Various methods including infrared spectroscopy have been used to understand the chemistry and physics of these materials. Kratschmer \textit{et al.}\textsuperscript{4} were the first to report IR spectral features of C\textsubscript{60} deposited on silicon substrate (~2 \textmu m thick). This report was then followed by a few others\textsuperscript{5-7} including that of Haufler \textit{et al.}\textsuperscript{6} who also observed the four bands characteristic of C\textsubscript{60} material thus supporting the observations of Kratschmer \textit{et al.}\textsuperscript{4}. Graja \textit{et al.}\textsuperscript{8} recently reported IR spectra in KBr pellets in the range 80-340 K and observed that most intense C\textsubscript{60} bands change in the phase transition temperature region and this variation has been ascribed to the rotational vibrational coupling. Theoretical studies\textsuperscript{9-13} on C\textsubscript{60} have also been reported.

In the present study we report our work on IR measurements on fullerene samples of different morphologies. Possibly for the first time we report here well-resolved IR spectra of fullerene samples as such (without any dilution or substrate) using our improved DRIFT set-up.

\textbf{Experimental}

IR spectrum of fullerene sample as KBr disc was recorded in vacuum using Bruker IFS 113V FTIR spectrometer in transmission mode at a resolution of 2 cm\textsuperscript{-1}. However, for recording IR spectra of fullerene samples of different morphologies (powder and crystalline samples) as such without any dilution (or substrate), improved diffuse reflectance infrared Fourier transform (DRIFT) technique was used. After proper alignment, the parameters were optimised to get the highest intensity. The spectral accumulation was done under vacuum at a resolution of 2 cm\textsuperscript{-1} for 256 scans keeping low mirror velocity (2 cm/sec) with zero filling factor of 2 and 4P apodization.

\textbf{Results and discussion}

IR spectrum (Fig. 1) of one of our samples recorded as KBr disc shows all the four bands which are comparable to those reported by others\textsuperscript{4,6-8} (Table 1). The spectra recorded by us without any dilution are shown in Fig. 2. Two samples reported here have different morphologies and represent two different sources. First sample (powder) is known to contain a small quantity of residual organic solvent (0.89%) which is clearly revealed in the vCH stretching region (<2800-3000 cm\textsuperscript{-1}) in its spectrum (Fig 2A). This is also seen even in the spectrum recorded as KBr disc.

The IR spectrum of the second sample of C\textsubscript{60} which was a black crystalline material shows a very close resemblance with that of sample 1 (Fig. 2) incorporating almost all the bands especially in the region (2500-4000 cm\textsuperscript{-1}). The variation in the spectral characteristics beyond 2500 cm\textsuperscript{-1} could be attributed to the difference in method of preparation, e.g., nature of residual organic solvents.

Weeks \textit{et al.}\textsuperscript{9-11} have reported a detailed theoretical calculation assuming icosahedral symmetry of C\textsubscript{60} using subgroups chain defined projection operators on the basis of a classical spring mass model of bucky...
Table 1 - Comparison of main peaks observed in IR spectrum of $C_{60}$ samples.

<table>
<thead>
<tr>
<th></th>
<th>KBr Disc</th>
<th>Low Temp.</th>
<th>Present Work</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Haufler</td>
<td>Grazia</td>
<td>Wilson</td>
</tr>
<tr>
<td>et al</td>
<td>et al</td>
<td>et al</td>
<td>et al</td>
</tr>
<tr>
<td>527.4</td>
<td>527</td>
<td>528</td>
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<td>577</td>
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</tr>
<tr>
<td>675*</td>
<td>-</td>
<td>675</td>
<td>-</td>
</tr>
<tr>
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<td>1183</td>
<td>1182</td>
</tr>
<tr>
<td>1400*</td>
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<td>2190</td>
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</tr>
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<td>1429</td>
<td>1428</td>
</tr>
<tr>
<td>1450*</td>
<td>-</td>
<td>2190</td>
<td>-</td>
</tr>
<tr>
<td>1620*</td>
<td>-</td>
<td>2330</td>
<td>-</td>
</tr>
<tr>
<td>2855*</td>
<td>-</td>
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<td>2848</td>
</tr>
<tr>
<td>2925*</td>
<td>-</td>
<td>2922</td>
<td>2922</td>
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</table>

* In case of reduced material

(ii) In addition, there exist three bands exactly at the same positions in both the samples, viz, 725, 960 and 2334 cm$^{-1}$. Kratschmer et al. have also reported a vibrational mode at 675 cm$^{-1}$ and attributed this to be of solid state rather than molecular origin. By analogy we may also consider 725 cm$^{-1}$ band to be of similar category. The band at 2334 cm$^{-1}$ (and also 2190 cm$^{-1}$) found in both the samples, may imply the attachment of CO$_2$ or CO to a small fraction of the total number of $C_{60}$ molecules as also suggested by Kratschmer et al. This is further supported by the fact that intensities of both these bands are low in case of sample 2 (crystalline) compared to that of 1 (powder) implying higher absorption (of CO$_2$/CO) capacity of the latter due to larger surface area. The low band intensity ratio (i.e. $I_{225}$ / $I_{390}$) in case of sample 2 could be due to dominant crystalline phase.

(iii) Another observation worth mentioning here is that a large number of bands show a systematic shift by 4 cm$^{-1}$ from crystalline to powder phase.

(iv) Apart from the above there are distinct bands which are shifted by 31-62 cm$^{-1}$ (Table 2). These are at higher positions in case of the powder sample. These may be attributed to morphological variations though it is difficult to establish this. A noticeable
Table 2 - Spectral characteristics of C\textsubscript{60} samples (powder & crystalline)

<table>
<thead>
<tr>
<th>Powder (cm\textsuperscript{-1})</th>
<th>Crystalline (cm\textsuperscript{-1})</th>
<th>Difference (cm\textsuperscript{-1})</th>
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<tr>
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<tr>
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<td>31</td>
</tr>
<tr>
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<tr>
<td>3765</td>
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<td>8</td>
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</table>

A feature is shift by 31 cm\textsuperscript{-1} in the case of 1026 cm\textsuperscript{-1} band and by 62 cm\textsuperscript{-1} in the case of 1674 cm\textsuperscript{-1} band.

(v) It may be mentioned here that the majority of the bands observed in the present study vis-a-vis those predicted theoretically based on the icosahedral symmetry and benzene spring mass constant show a fairly close similarity. The shift between observed and predicted values could be due to the factors like (a) absorption by C\textsubscript{70} molecules which may be present as impurity and (b) breaking of highest icosahedral symmetry to lower in the final product due to higher isotopes of carbon or mutual interaction of C\textsubscript{60} molecules in the solids. The possibility of method of preparation and/or morphology affecting such a high symmetry, however, cannot be ruled out.

Acknowledgement

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References: