Infrared Study of Vibrational Property and Polymerization of C\textsubscript{60} and C\textsubscript{70} under Pressure

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Infrared spectra were measured for solid C\textsubscript{60} and C\textsubscript{70} to 7 GPa under hydrostatic or quasi-hydrostatic pressure at room temperature. Some vibrational modes showed negative or insensitive dependence of frequency on pressure, suggesting destabilization of C\textsubscript{60} and C\textsubscript{70} molecules by compression. In solid C\textsubscript{60} new absorption bands gradually grew with increasing pressure in association with an intensity decrease of the original bands. These spectral changes were interpreted in terms of polymerization of C\textsubscript{60} molecules. Polymerized molecules recovered at ambient pressure were converted back to the monomer by thermal annealing at 473 K.

Introduction

The structural stability and reaction activity of C\textsubscript{60} (solid) have been intensively studied. High-pressure experiments are capable of tuning intermolecular distances and provide an effective method for study of the molecular structure and bonding nature of C\textsubscript{60}. It has been shown from X-ray diffraction measurement that the spherical C\textsubscript{60} molecule is stable to at least 20 GPa under hydrostatic pressure, whereas uniaxial stress deforms the molecular shape or crystal structure even below 10 GPa.\textsuperscript{1} Conversion to diamond was reported for a recovered specimen which blew out during pressure release from 20 GPa.\textsuperscript{2} Transformation to amorphous carbon was also indicated by Raman measurement above 14 GPa.\textsuperscript{3}

The vibrational modes of C\textsubscript{60} have been studied under pressure by infrared absorption\textsuperscript{4-6} and Raman spectroscopy.\textsuperscript{3} An interesting result was the “softening” in some of the intramolecular modes. One of the four IR active modes, which is characterized as a radial vibrational motion, showed a negative dependence of the frequency on pressure.\textsuperscript{4} Recent Raman measurements also showed that several bands shifted to lower frequency with pressure.\textsuperscript{3} This softening probably reflects a change in the chemical bonding within, and between, C\textsubscript{60} molecules under pressure.

We have measured the infrared spectra of C\textsubscript{60} under hydrostatic or quasi-hydrostatic condition. The purpose was to investigate the high-pressure behavior of the molecular vibrations and to explore the possibility of pressure-induced chemical reaction in the solid state. The spectra of C\textsubscript{70} were also measured. The high-pressure data on C\textsubscript{70} are of great help for understanding the characteristic bonding nature of the fullerenes molecules.

Experimental Section

High-pressure infrared spectra were measured with a gasketed diamond anvil cell.\textsuperscript{7} The sample chamber was a small hole 0.3 mm in diameter drilled in a metal gasket of Inconel X-750 approximately 0.1 mm thick. Infrared transmission spectra were recorded on a Microscope FT-IR instrument (HORIBA FT-330) with a wide-band MCT (mercury–cadmium–tellurium) detector sensitive down to 450 cm\textsuperscript{-1}. Four hundred repeated measurements were accumulated to obtain a spectrum of good quality with a spectral resolution of 0.5 cm\textsuperscript{-1} for a masked measuring area of 100 × 100 μm\textsuperscript{2}. Powders of pure C\textsubscript{60}, and of pure C\textsubscript{70}, were prepared by standard techniques previously reported in the literature.\textsuperscript{8} All measurements were made at room temperature, and the pressure was determined by using the ruby fluorescence method.\textsuperscript{9}

Two kinds of infrared measurement were undertaken. First, infrared frequencies were measured for solid C\textsubscript{60} and C\textsubscript{70} so as to investigate vibrational properties of these fullerenes under high pressure. A flake approximately 20 μm thick was made by compressing one grain of the fullerite, and its small fragment was packed into the gasket hole. Subsequently, a pressure medium (Xe or Kr) was charged in the hole. Both media are capable of generating a quasi-hydrostatic environment in the relatively low pressure region. In addition to the measurements on solid C\textsubscript{60} and C\textsubscript{70}, infrared spectra of a Cs\textsubscript{2} solution of C\textsubscript{60} (about 3 × 10\textsuperscript{-3} mol/dm\textsuperscript{3}) were measured. A thicker gasket (≈0.3 mm) was used in order to obtain sufficient absorption intensity for the solubilized C\textsubscript{60}.

Second, the dependence of infrared absorption intensity on applied pressure was measured for solid C\textsubscript{60}. Before compression, a reference spectrum was taken for the solid C\textsubscript{60} placed in the gasket hole of the opened diamond cell. The specimen was then packed with a methanol–ethanol (4:1) mixture and compressed in the closed cell to the desired pressure. After holding the pressure for 1 day, the cell pressure was reduced to ambient. The opened cell was heated in a vacuum oven at 340 K in order to evaporate the pressure medium. An infrared spectrum was again measured for the recovered specimen and compared with the reference spectrum.

Results and Discussion

Frequency Shift in Solid C\textsubscript{60} and C\textsubscript{70}. The pressure dependence of the infrared frequencies was obtained for the four infrared active modes of C\textsubscript{60} (1\textsubscript{E}g, 2\textsubscript{F}g, 3\textsubscript{F}u, and 4\textsubscript{F}u\textsuperscript{6}) in a quasi-hydrostatic condition up to 6 GPa. The present results agree with the previous infrared data measured to 19.5 GPa by direct compression of powdered C\textsubscript{60}.\textsuperscript{6} All absorption bands broadened and weakened substantially as the pressure was increased, so that further measurement beyond 6 GPa was prevented. No indication of a phase transition was observed. New bands, however, appeared in the frequency region from 600 to 800 cm\textsuperscript{-1}, suggesting molecular deformation or chemical reaction. This remarkable spectral change will be described in detail in the following sections.

In the Cs\textsubscript{2} solution of C\textsubscript{60}, three of the four bands were observed up to 1 GPa. The 4\textsubscript{F}u\textsuperscript{5} band expected to appear around 1500 cm\textsuperscript{-1} overlapped with the strong band of the stretching mode of Cs\textsubscript{2}. The 2\textsubscript{F}g and 3\textsubscript{F}u bands shifted to higher frequency, giving
derived pressure coefficients, $d\omega/dp = 3.9$ and $3.7 \text{ cm}^{-1}/\text{GPa}$, respectively, whereas the $1\text{F}_{1u}$ band shifted to lower frequency with a pressure coefficient of $-1.0 \text{ cm}^{-1}/\text{GPa}$. Although the frequencies of $1\text{F}_{1u}$ and $2\text{F}_{1u}$ modes in solution state were about $2 \text{ cm}^{-1}$ higher than those in solid state in the pressure range measured, no significant difference was observed in the pressure dependence. The $3\text{F}_{1u}$ mode showed the same peak position and pressure dependence as those of the solid state. It was observed by visual inspection with a microscope that $C_{60}$ crystals separated out from $C_{60}$ solution at 1 GPa. This prevented us from proceeding with further measurement. In the measured pressure region, solidification was not observed in $C_{60}$ which is known to crystallize at 1.3 GPa and room temperature.

For solid $C_{60}$, only 11 bands of the 31 modes ($10A_{2u} + 21E'$) predicted as infrared active were observed. The observed band frequencies of $C_{60}$ are plotted as a function of pressure in Figure 1. The frequencies, whose ambient-pressure values agree well with those reported previously, change linearly with pressure. It is notable that three bands originally located at 578, 673, and 795 $\text{cm}^{-1}$ (filled circles in Figure 1) shift to lower frequency, as was the case for the lowest frequency $1\text{F}_{1u}$ mode of $C_{60}$. In solid $C_{60}$ however, the lowest frequency band at 458 $\text{cm}^{-1}$ shifts to slightly higher frequency. Besides the shift of the band positions, no significant change was observed in the spectra. This was in contrast to $C_{60}$, which showed appearance of the new absorptions growing with increasing pressure. An order–disorder transition associated with the molecular reorientation has been observed in solid $C_{60}$ below 1.2 GPa by powder X-ray diffraction experiment. In our infrared measurement no discontinuous change in frequency was found at the corresponding pressure region. Pressure coefficients $d\omega/dp$ obtained by fitting the $\omega-p$ relation with a linear equation and mode Grünisen parameters $\gamma_\omega = K_0 d \ln d \ln d \ln \omega$ calculated by using the bulk modulus $K_0 = 18.1 \text{ GPa}$ of solid $C_{60}$ are summarized in Table 1.

Table 1: Infrared Frequencies ($\omega_\omega$) at Ambient Pressure, Pressure Coefficients ($d\omega/dp$), and Grünisen Mode Parameters ($\gamma_\omega$) for Solid $C_{60}$

<table>
<thead>
<tr>
<th>$\omega_\omega$ (cm$^{-1}$)</th>
<th>$d\omega/dp$ (cm$^{-1}$/GPa)</th>
<th>Huang et al.$^a$</th>
<th>$\gamma_\omega$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>458</td>
<td>0.54</td>
<td>2.8</td>
<td>0.020</td>
</tr>
<tr>
<td>534</td>
<td>2.50</td>
<td>2.7</td>
<td>0.085</td>
</tr>
<tr>
<td>566</td>
<td>3.80</td>
<td>3.4</td>
<td>0.121</td>
</tr>
<tr>
<td>578</td>
<td>-0.20</td>
<td>-0.4</td>
<td>-0.006</td>
</tr>
<tr>
<td>642</td>
<td>0.28</td>
<td>0.3</td>
<td>0.006</td>
</tr>
<tr>
<td>673</td>
<td>-0.39</td>
<td>-0.5</td>
<td>-0.010</td>
</tr>
<tr>
<td>795</td>
<td>-0.44</td>
<td>-0.6</td>
<td>-0.010</td>
</tr>
<tr>
<td>1133</td>
<td>3.10</td>
<td>0.7</td>
<td>0.050</td>
</tr>
<tr>
<td>1414</td>
<td>5.44</td>
<td>-7.6</td>
<td>0.070</td>
</tr>
<tr>
<td>1430</td>
<td>5.38</td>
<td>1.3</td>
<td>0.068</td>
</tr>
<tr>
<td>1493</td>
<td>3.01</td>
<td></td>
<td>0.036</td>
</tr>
</tbody>
</table>

$^a$Reference 5. $^b$For $C_{60}$ were evaluated by using a bulk modulus of $K_0 = 18.1 \text{ GPa}$ in solid $C_{60}$ (ref 1).

Figure 2. $\gamma_\omega-\omega_\omega$ relation in solid $C_{60}$ and $C_{60}$ (O, IR for $C_{60};$; Raman for $C_{60}$; $*$, IR for $C_{60};$ Raman for $C_{60}$). The $\gamma_\omega$ for Ramn bands were evaluated by using the previous Raman data.$^3$

The mechanism of the softening of the radial mode in $C_{60}$ remains unclear. Evidently the interaction of the $C_{60}$ molecule with its nearest neighbors change as a function of pressure in such a way that the radial normal mode frequency is lowered. However this is not an interaction which is specific to a $C_{60}-C_{60}$ nearest neighbor force field, because the frequency of the purely tangential $1\text{F}_{1u}$ mode also decreases in the dilute $C_{60}$ solution. The observed pressure coefficients $d\omega/dp$ of $C_{60}$ in $C_{60}$ corresponded well with those for the pure $C_{60}$ solid. The $C_{60}$ molecules in the dilute $C_{60}$ solution should be surrounded almost entirely by $C_{60}$ solvent molecules, on average. Apparently the influence of nearest neighbor molecules on $C_{60}$ vibrational frequency shift is quite similar whether the nearest neighbor molecules are $C_{60}$ or $C_{60}$. This presents, we feel, a clue for future theoretical treatments, which are needed for a deeper understanding of the experimental data.

We speculate that the stress tensor which are individual $C_{60}$ molecule experiences as a function of pressure must be quite similar for $C_{60}$ in $C_{60}$, and for $C_{60}$ solid, in the pressure range studied. The face-centered cubic (fcc) $C_{60}$ is an isotropic solid, and the stress tensor for hydrostatic loading is also isotropic. At very low applied pressure the $C_{60}$ solution remains a liquid, and...
between the compressed and phototransformed specimens is fairly
good, as shown in Table II. A mass spectrum of the phototrans-
formed C₆₀ showed formation of a series of cross-linked fullerenes
(C₆₀ₓ). A similar polymerization likely occurs in compressed
solid C₆₀, where the adjacent molecules get sufficiently close to
form cross-linking bonds. Our observations of recovery of C₆₀,
band intensities and removal of the new bands by thermal
annealing at 473 K are indicative of destruction of cross-linking
bonds and reproduction of the C₆₀ monomer. The measured large
reduction in intensity of the characteristic C₆₀ monomer bands
shows that the polymerization is significantly accelerated at high
pressures. Further study in the degree of polymerization and its
pressure dependence is needed to clarify the reaction mechanism.

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