

In Situ High-Resolution FT-IR Study of the Glass Transition in a C₆₀ Film

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The infrared absorption spectra of a water-free C₆₀ film were examined in the range 82–100 K, using in situ high-resolution (0.25 cm⁻¹) Fourier transform infrared (FT-IR) spectroscopy. The changes in the half-widths and integrated absorbances of the four fundamental and five silent modes were observed at 84–88 K, which is in good agreement with previously reported values of 85–90 K for the glass transition. On the other hand, no noticeable change in the peak positions of the four fundamental and silent modes was observed upon the glass transition.

Introduction

Solid C₆₀ has three phases in its crystal. Above $T_c \approx 260$ K, the highest temperature phase (“rotor” phase) with a face-centered-cubic (fcc) structure exists, in which C₆₀ molecules rotate freely.^{1,2} At T_c , the crystal undergoes an orientational phase transition and transfers from the rotor phase to an intermediate temperature phase (“ratchet” phase).³ In this phase, solid C₆₀ assumes a simple-cubic (sc) structure and the C₆₀ molecules freely jump between two energetically closed orientational sites (the energy difference between the two orientations is estimated to be 8.7–12.3 meV^{4–6}) with an energy barrier of 219–288 meV between them.^{5–10} The two molecular orientations were characterized by atomic configurations between adjacent C₆₀ molecules.¹¹ For the energetically lower orientation (“pentagon” orientation), the electron-rich C=C double bond of the molecule faces the electron-deficient pentagonal ring of the adjacent molecule via an electrostatically attractive interaction. On the other hand, for the energetically higher orientation (“hexagon” orientation), the C=C double bond faces the electron-rich hexagonal ring of the adjacent C₆₀ molecule via an electrostatically repulsive interaction. As the substrate temperature decreases, the ratio of the energetically favored “pentagon” orientation to the “hexagon” one increases. At $T_g \approx 90$ K, the rotational jumping between the two orientational sites stops abruptly, because the C₆₀ molecules in the solid cannot pass the energy barrier by thermal activation.¹¹ Below T_g , the molecular rotations freeze completely and the energetically higher “hexagon” orientation remains as 17%¹¹ of the whole orientation in the solid C₆₀ (“locked” phase). The phase transition at T_g is called the glass transition. Anomalies of some physical quantities, such as lattice constant,^{4,10,11} intensities of the X-ray diffraction,^{12,13} heat capacity or specific heat,^{8,14} and thermal conductivity,^{5,6,15} at the glass transition have been observed in the range 85–90 K.

The drastic change in rotational dynamics at the glass transition may affect C₆₀ molecular vibrations. The frequency and intensity of the IR vibrational mode are sensitive to the changes in the intermolecular interaction among C₆₀ molecules; therefore, IR spectroscopy is a useful tool to study the phase transition.

Babu et al. reported the temperature dependence of the four fundamental IR-active modes for the study of the glass

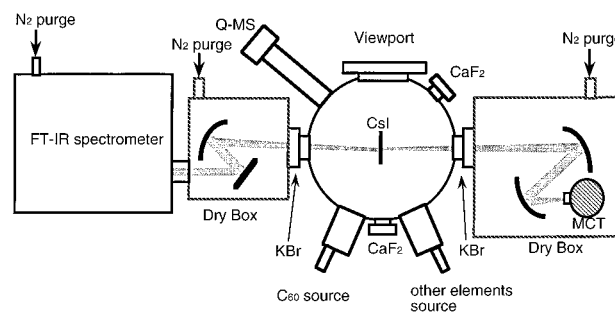


Figure 1. Schematic representation of an in situ high-resolution FT-IR apparatus for the study of the glass transition of C₆₀ film.

transition, using a KBr disk pellet containing C₆₀ powder.¹⁶ They observed small but clear shifts of the peak positions before and after the glass transition. However, the following problems were left unsolved: (1) no measure was taken to prevent contamination by water vapor in air and some residual organic solvents (these contaminants will affect the glass transition of C₆₀); (2) the influence of pressure applied during the formation of the KBr pellet on the C₆₀ bulk structure was not taken into consideration; and (3) because of the low resolution

(1 cm⁻¹) of measurements, variations of less than 1 cm⁻¹ in the peak position and half-width of each IR-active mode could not be detected. Consequently, it is questionable whether the KBr method provides sufficient information for the study of the glass transition.

In a recent paper,¹⁷ we have developed an apparatus for the study of C₆₀ films with in situ high-resolution FT-IR spectroscopy that enables one to prevent the exposure of the film to air and have successfully investigated the orientational phase transition of a C₆₀ film. In the experiment, we observed the drastic changes in the peak positions and half-widths of the four fundamental modes upon the orientational phase transition.

In this paper, we studied the glass transition of a C₆₀ film by examining the temperature dependence of the four fundamental modes and silent modes in the range 82–100 K using the above apparatus.

Experimental Section

Figure 1 shows a schematic representation of the apparatus for the study of the glass transition of a C₆₀ film with in situ high-resolution FT-IR spectroscopy. As shown in Figure 1, the FT-IR spectrometer (Mattson, research series) was connected to a vacuum chamber via an external optical system mounted in a plastic box with N₂ purge. The IR beam that passed through

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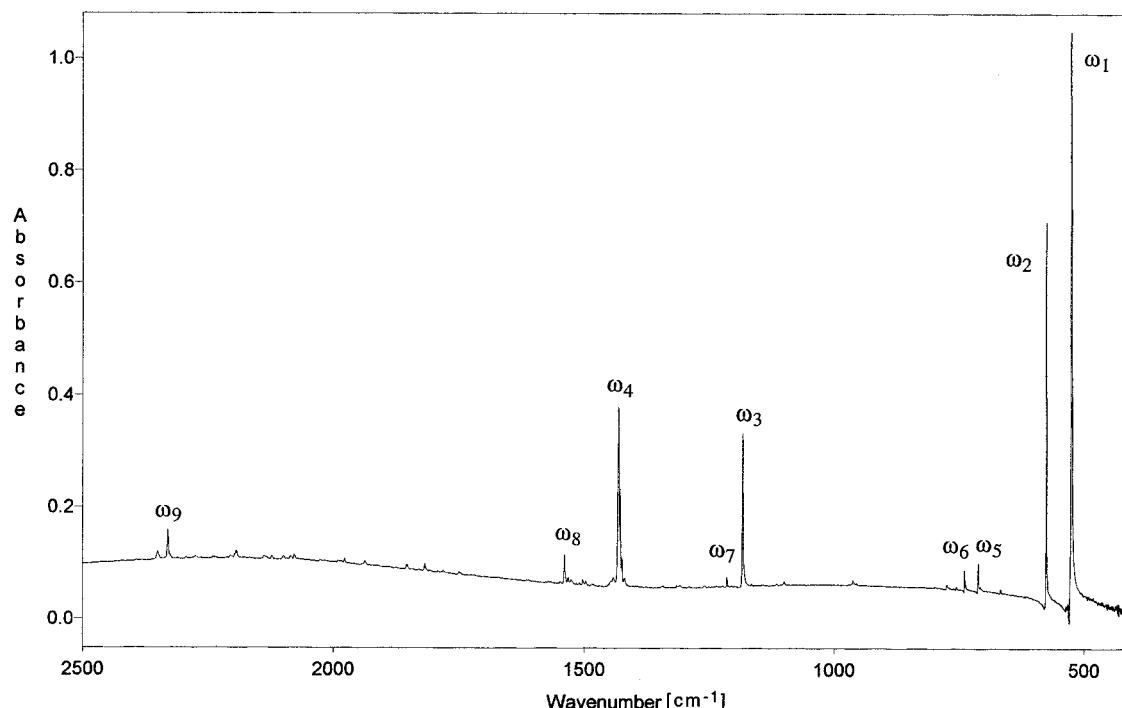


Figure 2. FT-IR spectrum of the C₆₀ film sublimed onto a CsI substrate at 82 K.

the CsI substrate was incident on the MCT detector which was placed in a similar N₂ purge box connected to the opposite side of the chamber. Two KBr single crystals of 50 mm diameter and 12 mm thickness were installed in the vacuum chamber as an IR beam window. Dry N₂ gas coming from a liquid N₂ tank was introduced at a rate of 50 L/min into the FT-IR spectrometer and the two external boxes in order to sufficiently eliminate water vapor from the IR beam optical path. The details of this system were described in ref 17.

About 1000 mg of C₆₀ powder (Matsubo, >99.98% pure) was placed into a quartz crucible (15 mm in diameter and 50 mm long). The crucible was then held at 200 °C in vacuo for more than 10 h in order to remove the residual organic solvents from the C₆₀ powder. Thin films of C₆₀ were formed onto a CsI substrate (Pureoptics, 20 mm diameter and 2 mm thick) by sublimation at 400 °C for 90 min in a vacuum chamber (base pressure 3×10^{-9} Torr) under a pressure of about 10^{-8} Torr. During the deposition of C₆₀, the substrate was heated to and maintained at 100 °C in order to obtain good crystallinity (fcc structure) in the C₆₀ film.¹⁸ The thickness of the C₆₀ film thus formed was estimated to be about 1300 Å, using the Lambert–Beer equation, $A = \kappa d$, where A , κ , and d denote absorbance, absorption coefficient, and thickness, respectively. The value of A for each IR-active mode was obtained experimentally, and the value of κ for individual modes used in the calculations was taken from experiment.¹⁹

After the formation of the C₆₀ film on the CsI substrate, the sample holder was rotated by 90° in order to measure FT-IR absorption spectra of the four fundamental and silent modes of the C₆₀ with a high resolution of 0.25 cm⁻¹. An S/N ratio of more than 200 was obtained for 500 scans at 0.25 cm⁻¹ resolution. For FT-IR measurement, the substrate was cooled to 82 K by a liquid N₂ cryostat, and the FT-IR absorption spectra of the C₆₀ film were then measured by heating the substrate temperature from 82 to 100 K with an increment of 2 K. In every measurement, the accuracy of the temperature was kept within ± 0.1 K. The partial pressure of the residual gases was very low during the FT-IR measurement. Actually, the partial pressures of H₂O, H₂, He, CH₄, CO₂, Ar, and other hydrocarbons

were less than 10^{-10} Torr, and those of N₂, O₂, and CO were on the order of 10^{-10} Torr. Total pressure of the residual gases was about 3×10^{-10} Torr.

Results and Discussion

Figure 2 shows the infrared spectrum of the C₆₀ film measured at 82 K. It was found that no diffuse absorption peak corresponding to water vapor appeared in the 3200 cm⁻¹ region even when the film was measured at this low temperature. Accordingly, it can be said that the effect of the residual water vapor was negligible in the present measurement. The C₆₀ molecule with I_h symmetry has four intensive fundamental IR-active modes, which are denoted as ω_1 , ω_2 , ω_3 , and ω_4 . In Figure 2, the absorption peaks of the three lower frequency modes, ω_1 – ω_3 , were not split and appeared at 525.75, 576.37, and 1183.60 cm⁻¹, respectively. On the other hand, the highest frequency mode, ω_4 , was split into three subpeaks located at 1432.13, 1428.27, and 1424.42 cm⁻¹.

We next examined the temperature dependence of the peak positions, half-widths, and integrated absorbances of these fundamental modes. Figure 3 shows the temperature dependence of the peak positions for the fundamental IR modes. For the ω_4 mode, we plotted the positions of the three split peaks as a function of the substrate temperature. It was found that no change in the peak positions of these modes was observed on heating the C₆₀ film within the temperature range 82–100 K. This indicates that the influence of the glass transition on the frequencies of the four fundamental modes was negligible. The frequency, ν , can be expressed as $\nu = (1/2\pi)\sqrt{\kappa/\mu}$, where κ and μ denote the force constant and reduced mass, respectively; therefore, Figure 2 shows that the force constants of the four fundamental modes remain constant through the glass transition. This suggests that intermolecular interaction between adjacent C₆₀ molecules was independent of the transition. Although Babu et al. observed clear peak shifts of the fundamental modes at the glass transition,¹⁶ it is questionable that these shifts were caused by the glass transition. They may have originated from contamination by water vapor and some residual organic solvents.

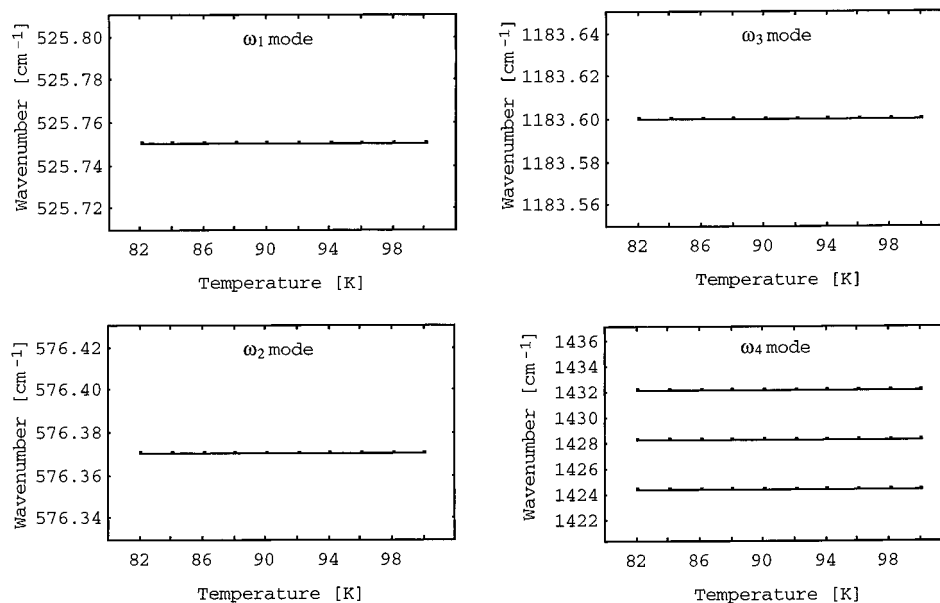


Figure 3. Temperature dependence of the line shift for the four IR-active modes of C₆₀ film. For the ω_4 mode, the line shifts of the three split subpeaks are plotted.

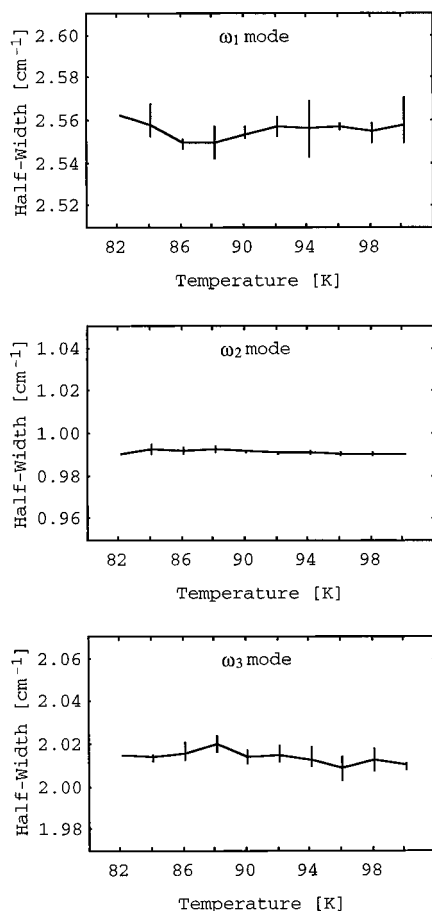


Figure 4. Temperature dependence of the half-width for the ω_1 – ω_3 modes.

Figure 4 shows the plots of the half-widths of the ω_1 , ω_2 , and ω_3 modes as a function of the substrate temperature, where the length of each vertical bar represents reproducibility of the present results. Because the ω_4 mode was split into three subpeaks, its whole half-width was difficult to estimate. The half-width of the ω_1 mode decreased with increasing substrate temperature in the range 82–87 K, although it began to increase slowly above ~ 87 K. On the other hand, the half-width of the

ω_3 mode showed the opposite trend of that of the ω_1 mode. Contrary to the two modes, the half-width of the ω_2 mode did not show any noticeable change in the temperature region 82–100 K. The extrema at 87 and 88 K found in the ω_1 and ω_3 modes, respectively, are in good agreement with previously reported values of 85–90 K.^{4–8,10–15} The half-width is related to the activation energy, E_a , necessary for molecular rotation excitation: the half-width is proportional to $\exp(E_a/k_B T)$, where k_B is the Boltzmann constant.²⁰ Accordingly, those extrema suggest that the mechanism behind the rotation excitation was changed before and after the glass transition.

Figure 5 shows the temperature dependence of the integrated absorbance for the ω_1 – ω_4 modes. The integrated absorbances of the ω_1 and ω_4 modes slightly decrease with increasing substrate temperature. It should be noted that a marked change in the integrated absorbance was found around ~ 87 K in the ω_1 mode and ~ 84 K in the ω_4 mode. These results indicate that the transition dipole moments of these modes were somewhat affected by the glass transition. For the ω_2 mode, it is difficult to specify the temperature range of the glass transition because the integrated absorbance of the mode showed a marked change in the whole temperature range of the experiment. On the contrary, the integrated absorbance of the ω_3 modes was not changed significantly.

The molecular symmetry of C₆₀ in the fcc bulk structure is lower than that in a free molecule; thus some absorption peaks of the silent modes are allowed to appear, as shown in Figure 2. We focused on the five intensive silent modes marked ω_5 (712.33 cm⁻¹), ω_6 (739.81 cm⁻¹), ω_7 (1214.94 cm⁻¹), ω_8 (1539.16 cm⁻¹), and ω_9 (2330.08 cm⁻¹). From the results of the IR and Raman experiments reported by Martin et al.,²¹ the ω_5 – ω_9 modes can be assigned to $F_{2u}(2)$, $G_u(2)$, $F_{2g}(3)$, $G_g(2) \otimes H_u(2)$, and $H_g(8) \otimes G_u(3)$, respectively.

We also examined the temperature dependence of the peak position and the integrated absorbance for these silent modes in a manner similar to the four fundamental modes. Since these modes as well as the ω_4 mode were split, one cannot measure the half-widths of these modes. As with the four fundamental modes, no change was found in the peak positions for the silent modes. Figure 6 shows the plots of the integrated absorbances of the ω_5 – ω_9 modes as a function of the substrate temperature. While the ω_5 – ω_8 modes showed no noticeable change in the

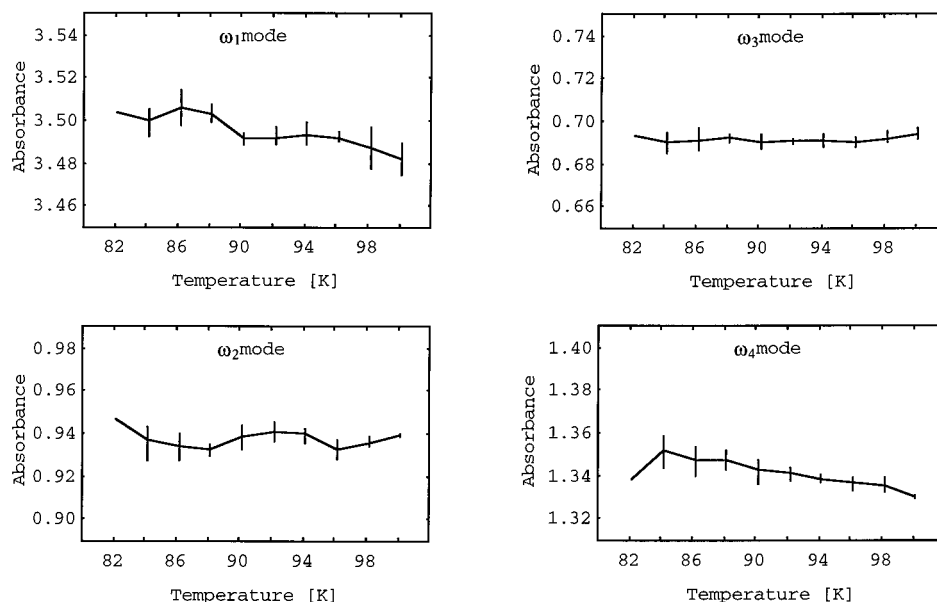


Figure 5. Temperature dependence of the integrated absorbance for the ω_1 – ω_4 modes.

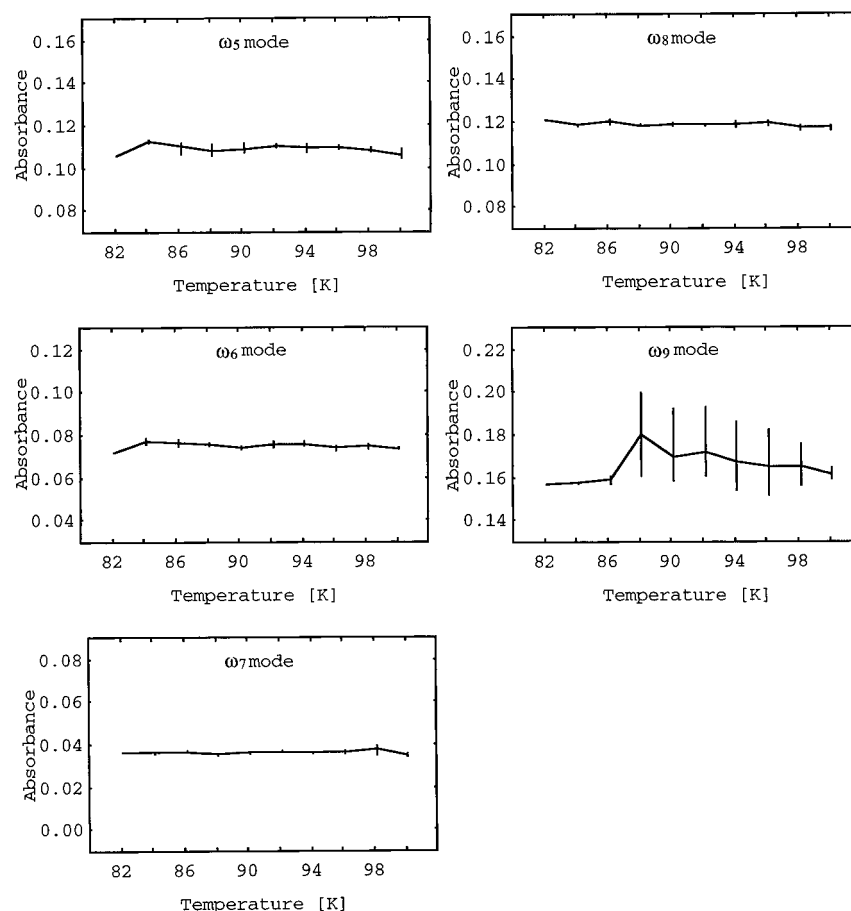


Figure 6. Temperature dependence of the integrated absorbance for the ω_5 – ω_9 modes.

temperature range 82–100 K, the ω_9 mode showed a remarkable change at ~ 87 K. This can be qualitatively explained in terms of an electron–phonon coupling. According to the theoretical investigations for the mechanism of the superconductivity of solid M_xC₆₀,^{22–25} H_g symmetry couples strongly with f_{1u} conduction electrons. In particular, Antropov et al. have reported that the electron–phonon coupling constant λ of the H_g(8) mode is the largest one among H_g modes.²⁵ Actually, using the value of 2.5 eV^{−1} for the density of states, $N(0)$,²⁶ their reported value (0.022 eV) of $\lambda/N(0)$ is 0.055, which is

larger by almost 2 times than the largest value of 0.039 among the electron–phonon coupling constants of the four F_{1u} IR-active vibrations.²⁷ Since the symmetry of the ω_9 mode consists of H_g(8) and G_u(3), the ω_9 mode showed a large change in its integrated absorbance at the glass transition. The other silent modes ω_5 – ω_8 did not contain the H_g symmetry.

Summary

We have performed in situ high-resolution FT-IR measurements for the study of the glass transition in a C₆₀ film under

a water-vapor-free condition by examining the temperature dependence of the four fundamental and five silent modes in the range 82–100 K. The peak positions of both fundamental and silent modes did not show any noticeable changes during the glass transition occurring at 85–90 K. On the other hand, remarkable changes in the half-widths and integrated absorbances of the fundamental modes were observed at 84–88 K, which is in good agreement with previously reported values of 85–90 K. Furthermore, among the five silent modes, it was found that a marked change in the integrated absorbance of the ω_9 mode appeared at ~ 87 K. This may be due to the fact that the ω_9 mode contains the $H_g(8)$ symmetry exhibiting a strong electron–phonon coupling.

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