

Effect of condensation of C_{60} molecules on Raman spectra of solid C_{60} : Study of structural phase transition*

K. Matsuishi, K. Tada, S. Onari and T. Arai

Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305, JAPAN

The Raman spectra of C_{60} films with and without oxygen exposure were measured in the temperature range 18 ~300 K in order to investigate the effect of condensation of C_{60} molecules into the solid forms as well as the oxygen effect on the vibration modes in solid C_{60} . The splitting and the activation of some modes were observed with decreasing temperature below the structural phase transition temperature near 250 K. This indicates the importance of the solidification effect in understanding the vibrational modes of solid C_{60} . We attribute the appearance of enhanced A_g Raman mode in the low temperature phase and the oxygen-diffused high temperature phase to the resonance with the electronic states of the solid forms.

1. INTRODUCTION

Since it was found by Fleming et al. [1] that the truncated icosahedron-shaped C_{60} molecule which has the geometrical structure of a soccer ball with a carbon atom on each of the C_{60} equivalent corners crystallizes into a cubic form, much effort on theoretical and experimental investigations has been devoted for solid C_{60} and their derivatives. It has been shown by X-ray [2,3] and NMR [4] results that the solid C_{60} has a first-order phase transition at a temperature near 250 K. The high temperature phase has a fcc (face-centered cubic) structure with C_{60} molecules executing continuous rotational diffusion, while the low temperature phase exhibits a sc (simple cubic) structure with C_{60} molecules jumping between symmetry-equivalent orientations. Since the interaction between C_{60} molecules in the solid form is considered to be weak due to the van der Waals bonding, Raman and infrared spectra of solid C_{60} have been explained on the basis of the molecular vibrations of C_{60} [5,6]. However, more detailed analyses [7,8] suggest that not only the molecular symmetry but also the crystal symmetry would be important in understanding the vibrational modes in solid C_{60} , as we address in the present paper.

Effects of oxygen on solid C_{60} have drawn much attention, since the dissolution of O_2 into the solid sample would hide essential properties of pure solid C_{60} . The results of NMR measurements have shown that oxygen molecules diffuse readily into the octahedral interstitial sites of the fcc lattices of C_{60} [9]. Oxygen effects on the crystal structure as well as on the structural phase transition still remain unclear. Hence, it should be studied in order to clarify the essential properties of solid C_{60} .

In the present study, we address the importance of solid effect as well as oxygen effect on the vibrational modes in solid C_{60} . The details of Raman modes of solid C_{60} before and after oxygen exposure are investigated in the temperature range 18~300 K. The enhanced Raman mode which is observed in low temperature phase and the oxygen-diffused high temperature phase is discussed in the light of resonance effect with the electronic states.

2. EXPERIMENT

Films were prepared by a sublimation method in a vacuum 5×10^{-6} Torr system. About 15 mg of the well-purified powder of C_{60} (Texas Fullerenes Corp.)

*This work was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, in Japan.

was placed in a tungsten boat in a bell jar. In order to remove residual solvent from the powder the boat was first heated at 200°C for two hours, and then heated to about 500°C to initiate the growth of a C₆₀ film on Si as a substrate at ambient temperature. After the deposition of 4 hours, the as-grown film was immediately placed in a cryostat in vacuum, and subjected to Raman measurements without exposure to oxygen.

Raman scattering spectra were measured with a triple spectrometer system (Jasco TRS-600). Excitation was provided by the 514.5 nm Ar⁺ laser line. A CCD system (Photometrics TK512CB) was used as a detector. All Raman data were taken in a backscattering geometry with the laser spot size of about 200 μ in diameter on a sample. To prevent a damage of sample by laser and/or a change of Raman spectrum during measurements, the laser power was chosen less than 10 mW.

3. RESULTS AND DISCUSSION

3.1. Oxygen effect on the Raman spectrum

In Figures 1 (a) and (b) are shown the polarized Raman spectra of C₆₀ films at room temperature before and after oxygen exposure, respectively, in the frequency range of 190~1620 cm⁻¹. The notations of HH and HV represent the polarization direction of incident light parallel and perpendicular, respectively, to that of scattered light. The Raman spectrum before oxygen exposure exhibits 23 appreciable peaks. After oxygen exposure, significant changes are seen in the Raman spectrum. The Raman spectrum after oxygen exposure consists of 19 appreciable peaks in good agreement with the previous observation [5]. In Figure 2 is shown the time evolution of the Raman spectrum of C₆₀ film under oxygen exposure in the frequency range of 1400~1500 cm⁻¹. It is seen that the 1469 cm⁻¹ mode increases rapidly in intensity with oxygen exposure time. At the same time the 1433 cm⁻¹ mode shifts to the lower frequency (1426 cm⁻¹). We also found that the intensity of 1569 cm⁻¹ mode decreases with oxygen exposure, and the modes at 1480 and 1575 cm⁻¹ appear newly. It should be noticed that the number of modes observed in the Raman spectrum before oxygen exposure is much more than the one which is anticipated in the I_h

symmetry of C₆₀ molecule. This may be attributed to the effect of the condensation of C₆₀ molecules into the fcc lattice at room temperature.

3.2. Effect of condensation on vibrational modes

The importance of the solid effect in understanding the vibrational modes can be realized when the temperature is decreased below the structural phase

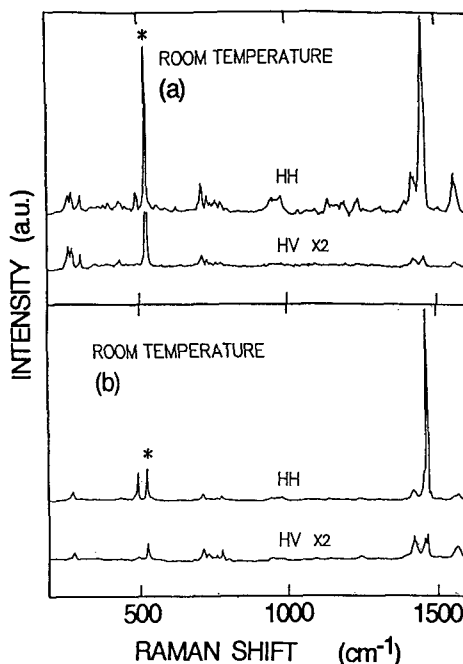


Figure 1. Polarized Raman spectra of C₆₀ films at room temperature. (a) Before and (b) after oxygen exposure. The * represents the Raman line of Si.

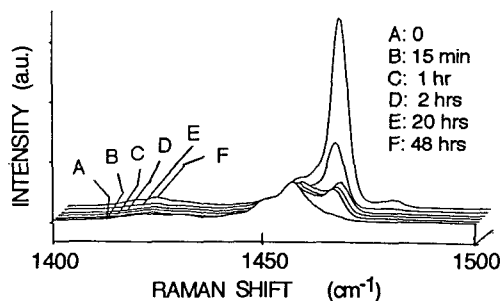


Figure 2. Time evolution of Raman spectrum of C₆₀ film under oxygen exposure in the frequency range 1400~1500 cm⁻¹.

transition temperature near 250 K at which the structure is transformed to a sc lattice from the fcc lattice. Figures 3 (a) and (b) show the polarized Raman spectra of C_{60} films before and after oxygen exposure, respectively, at 80 K. The fact that the oxygen effect on the Raman spectra cannot be seen in the low temperature phase is in contrast with the observation in the high temperature phase. It is found, in comparison with the spectra of the high temperature phase, that the splitting and the appearance of some modes are observed in the low temperature phase, for example, as seen in Figure 4. Especially, the film before oxygen exposure exhibits a drastic change in the Raman spectrum at the phase transition. Figure 5 shows the temperature dependence of Raman spectrum of C_{60} film without oxygen exposure in the frequency range 1400~1500 cm^{-1} . The significant feature seen in Figure 5 is that the 1469 cm^{-1} mode grows rapidly below the structural phase transition.

The 174 vibrational modes of the C_{60} molecule (I_h symmetry) exhibit the following symmetrical structure, $\Gamma_{1h} = 2A_g + A_u + 3T_{1g} + 4T_{2g} + 4T_{1u} + 5T_{2u} + 6G_g$

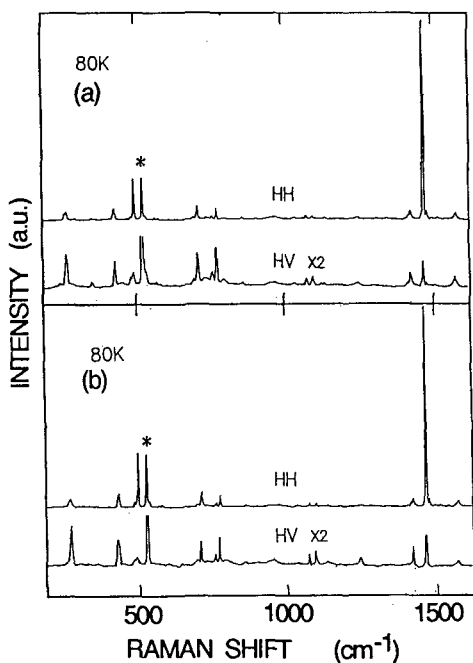


Figure 3. Polarized Raman spectra of C_{60} films at 80 K. (a) Before and (b) after oxygen exposure. The * represents the Raman line of Si.

$+6G_u + 8H_g + 7H_u$. Thus, one-, three-, four- and five-fold degenerate modes are involved. According to the selection rules, the $2A_g + 8H_g$ modes are Raman active, and four T_{1u} modes are infrared active. When C_{60} molecules condense in the solid form, one would expect that peak-splitting and activation of some vibrational modes in a C_{60} molecule occur depending on the crystal symmetry. First, Raman forbidden modes in a C_{60} molecule would appear both in the fcc and sc phases, that is, all of 23 gerade modes of a

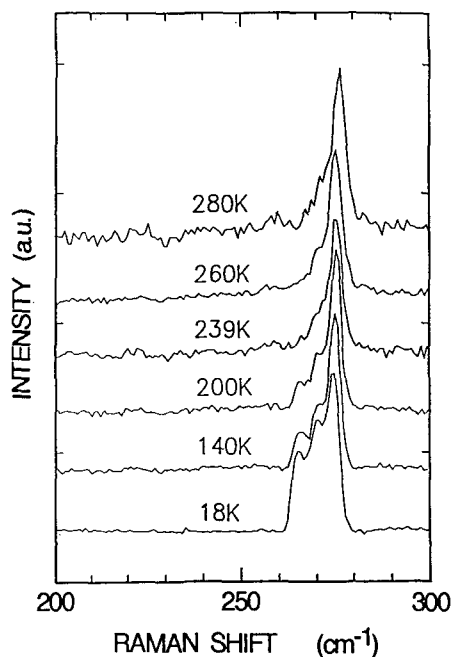


Figure 4. Temperature dependence of Raman spectrum of C_{60} film without oxygen exposure in the frequency range 200~300 cm^{-1} .

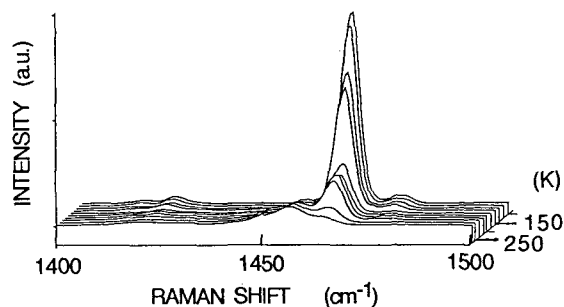


Figure 5. Temperature dependence of Raman spectrum of C_{60} film without oxygen exposure.

C_{60} molecule become Raman active in the solid forms. Second, depending on the crystal symmetry, the vibrational modes of a C_{60} molecule would split into different-symmetrical modes in the solid forms.

For example, the molecular A_g and H_g modes split into A_g+F_g and $A_g+2E_g+5F_g$, respectively, in the sc phase. In the fcc phase, the $H_g \rightarrow E_g+F_g$ splitting is anticipated. The third effect of the condensation of C_{60} molecules is that the local crystal field and the interaction between molecules in the solid forms would induce the lifting of degeneracy of molecular vibrational modes.

3.3. Enhanced Raman modes

The fact that the A_g mode at 1469 cm^{-1} is strongly enhanced with oxygen exposure, as seen in Figure 2, is the most significant in the influence of oxygen on the Raman spectrum of high temperature phase of solid C_{60} . It was found that the intensity of 1469 cm^{-1} mode became nearly 10 times stronger than that of 1461 cm^{-1} mode in a day with oxygen exposure. The appearance of 1469 cm^{-1} mode is also seen without oxygen exposure when the temperature is decreased below the structural phase transition (Figure 5). What are seen in Figure 5 is quite similar to the observations shown in Figure 2. The relative intensity of the A_g mode at 1469 cm^{-1} to the H_g mode at 1425 cm^{-1} is plotted as a function of temperature in Figure 6. Open and solid circles represent the C_{60} films with and without oxygen exposure, respectively. The oxygen diffusion into

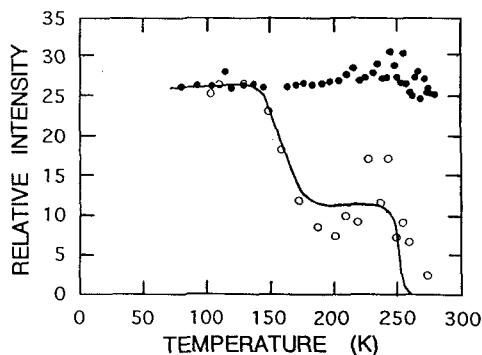


Figure 6. Temperature dependence of relative Raman intensity of the 1469 cm^{-1} A_g mode to the 1425 cm^{-1} H_g mode in C_{60} films with (●) and without (○) oxygen exposure.

the fcc lattice of the high temperature phase could make a change in the electronic state somehow through the slowing of molecular rotation and/or the modification of crystal field due to a symmetry change. The change in the electronic state could occur also through the structural phase transition. We attribute the appearance of the enhanced A_g Raman mode observed in low temperature phase and oxygen-diffused high temperature phase to the resonance with the electronic states of the solid forms.

4. CONCLUSION

The splitting and activation of some modes have been observed with decreasing temperature below the structural phase transition temperature near 250 K . This indicates the importance of the effect of condensation in understanding the vibrational modes of solid C_{60} . While the film without oxygen exposure exhibits a drastic change in the Raman spectrum at the phase transition, the change is much less pronounced for the film with oxygen exposure. The effect of oxygen on the Raman spectra has not been seen in the low temperature phase below 250 K . The resonance Raman scattering involving the electronic transition in the solid forms of C_{60} would be responsible for the appearance of enhanced A_g Raman mode in the low temperature phase and the oxygen-diffused high temperature phase.

REFERENCES

1. R.M. Fleming et al., Mater. Res. Soc. Symp. Proc., 206 (1991) 691.
2. R. Sachidanadam and A.B. Harris, Phys. Rev. Lett., 67 (1991) 1467.
3. P.A. Heiney et al., Phys. Rev. B, 45 (1992) 4544.
4. R. Tycko et al., Phys. Rev. Lett., 67 (1991) 1886.
5. D.S. Bethune et al., Chem. Phys. Lett., 179 (1991) 181.
6. P. Zhou et al., Phys. Rev. B, 46 (1992) 2595.
7. P.H.M. van Loosdrecht et al., Phys. Rev. Lett., 68 (1992) 1176.
8. L.R. Narasimhan et al., Phys. Rev. B, 46 (1992) 2591.
9. R.A. Assink et al., J. Mater. Res., 7 (1992) 2136.