^{57}Fe Mössbauer Spectroscopic Study on the Dynamics of Ferrocene Enclathrated in Deoxycholic Acid

Satoru Nakashima,* Mitsuyori Nakashita,† and Hiroshi Sakai††
Radioisotope Center, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739
†*Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739*
††*Department of Chemistry, Faculty of Science, Konan University, Higashi-Nada, Kobe 658*

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The molecular motion of ferrocene molecules enclathrated in deoxycholic acid was investigated by means of ^{57}Fe Mössbauer spectroscopy, and it was newly suggested that an anisotropic vibration of the ferrocene molecule is coupled with the rotation above 280 K.

There is considerable current interest in the dynamics of organometallics in the host lattice.[1] Miki et al. first reported an X-ray diffraction study of the deoxycholic acid (DCA)-ferrocene (2:1) inclusion compound: the ferrocene was fixed in the DCA channel.[2] Imashiro et al. reported the existence of a precession of ferrocene in the DCA inclusion compound by using NMR method.[3] ^{57}Fe Mössbauer spectroscopy is a useful technique to know the molecular motion of ferrocene in the inclusion compound.[4-6] In the present study we investigated the dynamics of the ferrocene molecule in the DCA inclusion compound from the temperature dependence of the ^{57}Fe Mössbauer spectra.

The needle-like crystals of the ferrocene-DCA (1:2) inclusion compound were obtained by the reported procedure.[2] The compound was confirmed by X-ray diffraction powder pattern and elemental analysis.[7] ^{57}Fe Mössbauer spectra of the powdered sample were measured at the temperature range from 80 to 343 K. Typical spectra are shown in Figure 1. The values of the isomer shift (I. S.) and the quadrupole splitting (Q. S.) of the 80 K spectrum are found to be 0.53 mm s^{-1} relative to iron foil and 2.38 mm s^{-1}, respectively. These values are in good agreement with those of polycrystalline ferrocene (I. S.= 0.520 mm s^{-1}, Q. S.= 2.381 mm s^{-1}).[4] It can easily be seen that the asymmetry of the quadrupole doublet increases and the Q. S. values decrease with increasing temperatures.

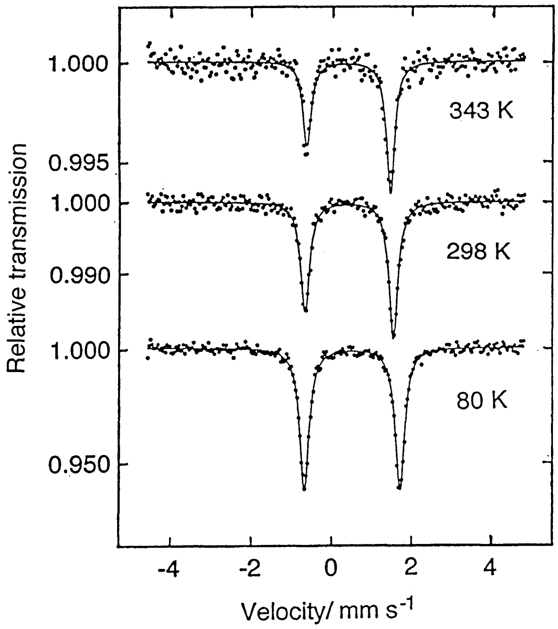

Figure 1. Typical ^{57}Fe Mössbauer spectra for the ferrocene-DCA inclusion compound.

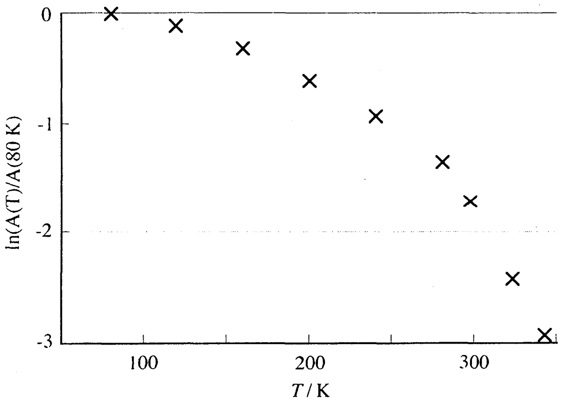

Figure 2. Temperature dependence of area intensity relative to that at 80 K for the ferrocene-DCA inclusion compound.

Figure 2 shows the temperature dependence of the area intensity relative to that at 80 K for the ferrocene-DCA inclusion compound. According to the Debye approximation at high temperatures, the logarithmic value of the recoil-free fraction of the ^{57}Fe Mössbauer spectrum is expected to decrease linearly with increasing temperature.[8, 9] It can be seen from Figure 2 that the slope of the logarithmic value of the relative area intensity is altered at ~280 K. This fact indicates that there is a change in the state of lattice vibration around this temperature.

The temperature dependences of the area intensity ratio of the high energy peak to low energy peak and the Q. S. values are shown in Figures 3 and 4, respectively. Symmetric doublet was observed in the range of 80 to 280 K, while above 280 K the doublet became asymmetric. The asymmetry was increased with an increase in the temperature. It is known that the asymmetry of the doublet is due to a preferred orientation and/or an anisotropy of lattice vibration (Gol'danskii-Karyagin effect).[8] It is thought that the asymmetry is due to the Gol'danskii-Karyagin effect, because the sample was powder and the asymmetry showed the temperature dependence. The changing temperature of the asymmetry corresponds to that of the change of area intensity. The electric field gradient (V_{zz}) of ferrocene is positive.[10] In this case ($V_{zz}>0$) it is concluded from the asymmetry of the doublet that the vibration to a direction perpendicular to the molecular axis becomes more intense than that to a direction parallel to the axis over 280 K ($<u_z^2> < <u_{x,y}^2>$).

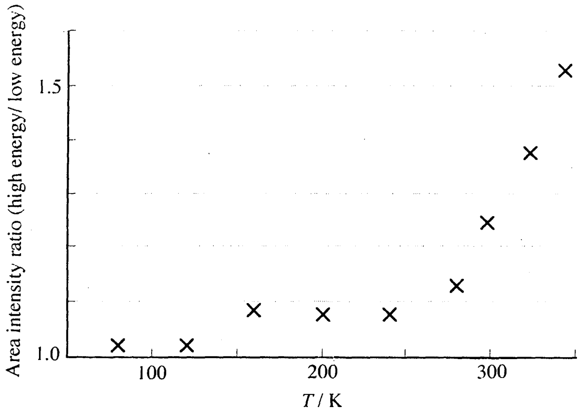

Figure 3. Temperature dependence of the area intensity ratio of high energy peak to low energy peak in the doublet of Mössbauer spectra for the ferrocene - DCA inclusion compound.

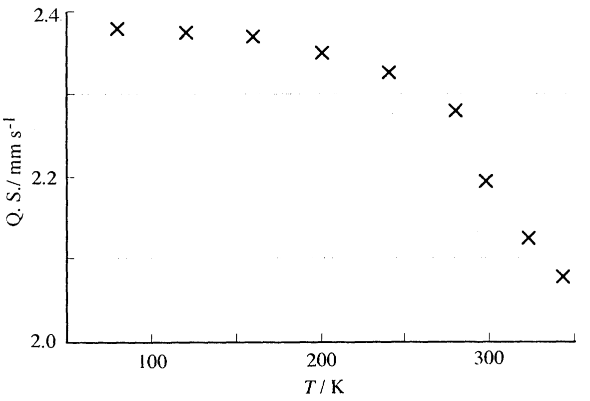

Figure 4. Temperature dependence of the quadrupole splitting (Q. S.) value of Mössbauer spectra for the ferrocene -DCA inclusion compound.

It can be seen from Figure 4 that Q. S. values decrease from 80 to 280 K gradually and above 280 K the decrease becomes abrupt. It is interesting that the temperature is similar to that of the change of asymmetry of the doublet. Imashiro et al. reported the rotation of five-fold axis on a cone with a half-angle of 18° at ambient temperature.[3] By considering the rotation of the ferrocene molecule about 14% of decrease in Q. S. value is expected.[11] In the present study about 14% of decrease was observed at 343 K. It is thought from an agreement of the changing temperature between Figures 3 and 4 that the anisotropic lattice vibration is coupled with the precession of ferrocene molecule.

References and Notes

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7 Found : C, 71.38 ; H, 9.25 %. Calcd for $C_{24}H_{40}O_4 \cdot 1/2(C_{10}H_{10}Fe)$: C, 71.73; H, 9.34%.

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11 It is thought that the Q. S. value becomes $(3\cos^2 18°-1) / (3\cos^2 0°-1)$ times of the initial value by the rotation of the five-fold axis on a cone with a half-angle of 18°.