MOLECULAR ROTATION AND LATTICE DYNAMICAL PROPERTIES FOR CYCLODEXTRIN-FERROCENE AND SOME ITS RING—SUBSTITUTED DERIVATIVE CLATHRATES

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ABSTRACT. This paper reports the unusual relaxation effect in the ^{57}Fe Mössbauer spectra of α-cyclodextrin(η-cyclopentadienyl)(η-ethylcyclopentadienyl)iron(II) clathrate. At low temperatures it consists of a simple quadrupole doublet. However, the Mössbauer spectrum collapses to a broad peak at 320 K. This behavior is interpreted in terms of a model that a ferrocene molecule in the cavity of clathrate lattices rotates as temperature is raised. The relaxation reaches a critical rate, a lifetime of the excited nuclear state. The relaxation time for the reorientation of (η-cyclopentadienyl)(η-ethylcyclopentadienyl)iron(II) in a cavity was 1.2×10^{-7} s at 320 K and a barrier to rotation of about 8.8 KJ/mol was estimated.

1. INTRODUCTION

There have recently been some Mössbauer spectra that were interpreted as being produced by a fluctuating electric field gradient(efg) at the nucleus, in which all atomic and electric motions are fully time-averaged because the efg tensor is fluctuating at a rate comparable with the inverse of the lifetime of the excited nuclear states. Such fluctuations of efg have been attributed to Jahn-Teller effects(1,2), jump diffusion of vacancies(3), electric relaxation, or molecular motion(rotation)(4-7).

Molecular rotation in the cavity has been discussed for many compounds using nmr(8,9), esr(10) and Mössbauer spectroscopy(4,5). A complete description of the Mössbauer spectrum for such a case has been given by Gibb(4) for that of the 3:1 clathrate of thiocarbonyl diamide and bis(η-cyclopentadienyl)iron(II). Evidence for conformational isomerism has been presented recently based on the ir spectra of η-cyclopentadienylmetal carbonyl complexes such as $CpFe(CO)_2SiCl_2Me(11)$, π-$MeC_5H_4Mn(CO)_2(P(OMe)_3)(12)$ and others(13), and on the Mössbauer spectra of $CpFe(CO)_2S(CH_2)_4$(tetrahydrothiophene)(14). Cyclodextrin(CyD) forms a number of inclusion compounds both in crystalline states and in an aqueous solution with a variety of molecules. X-ray analysis of the cyclodextrin clathrates with potassium acetate(15), iodine(16), and water(17) has proved that a guest molecule is included in the cavity of cyclodextrin. Molecular rotation of ethylferrocene in the cavity of CyD

and the lattice dynamical properties of the clathrate are examined in this paper.

2. EXPERIMENTAL

Ferrocene clathrate was prepared by mixing α-CyD in water and ferrocene purchased from Tokyo Kasei Inc. in a hot ethanol solution, separating the clathrate precipitated, and then washing with ethanol. (η-cyclopentadienyl)(η-ethylcyclopentadienyl)iron(II) was prepared according to the reference(18). Clathrates were recrystallized from water-alcohol prior to the Mössbauer measurement. Chemical analysis for the microcrystal gave the stoichiometry of 0.65:1 for guest:host. Mössbauer spectrometer used was described elsewhere(19). A cobalt-57 source diffused into a palladium foil was used. The isomer shift(IS) was measured relative to the center of the spectrum of an iron foil enriched with iron-57 at 296 K, which was also used as a standard material for the velocity calibration. The Mössbauer data were corrected for the weak absorption of impurities contained in a sample holder and in the window of a counter and fitted to a Lorentzian line shape using the least square method at the Computer Center, Kyushu University.

3. RESULTS AND DISCUSSION

The complexes included in this study can be classified into two categories according to the possibilities for rotational isomerism. First of all, clathrates of α-CyD: These clathrates can have rotational isomers and show broad peaks above 300 K. The second category consists of β-CyD or γ-CyD clathrates. Unlike the first group, these complexes cannot have rotational isomers. The molecular structure of CyD is toroidal with an inner aperture of about 0.50 nm in diameter, an outer diameter of 1.35 nm and height of 0.85 nm. As the shortest Fe-Fe distance in solid ferrocene is 0.59 nm(20), the molecular size of ferrocene is assumed to be about 0.60 nm. A molecular model for ferrocene may not be in symmetry, but molecular shape is rather globular. Adducts are known to be crystallized in two major forms(21). In the channel-type structure the CyD rings are arranged on top of each other with the apertures forming "endless" channels. In the cage-type structures the CyD rings are arranged crosswise with the apertures of one CyD ring blocked at both ends by continuous CyD molecules. The molecule of ferrocene would be in the cavity of cage-type structure of β-CyD because the size of a ferrocene molecule seems to be as large as that of the intramolecular cavity of β-CyD. On the other hand, α-CyD-ferrocene clathrates may have channel type structure and a ferrocene molecule is enclosed in the intermolecular cavity of α-CyD.

The Mössbauer spectra of powdered samples of the clathrate are shown in Fig. 1. The statistics of the spectra is very poor at high temperature due to a low Debye-Waller factor (the absorption is 0.4 % at 320 K) and a relaxation phenomenon(absorption becomes broad in the region of the relaxation time of 120 ns. The accumulated counts are more than a million counts above 250 K. The low temperature spectra of this clathrate are quite normal: The efg for ferrocene derivatives is known to be essentially of molecular origin and the QS values do not
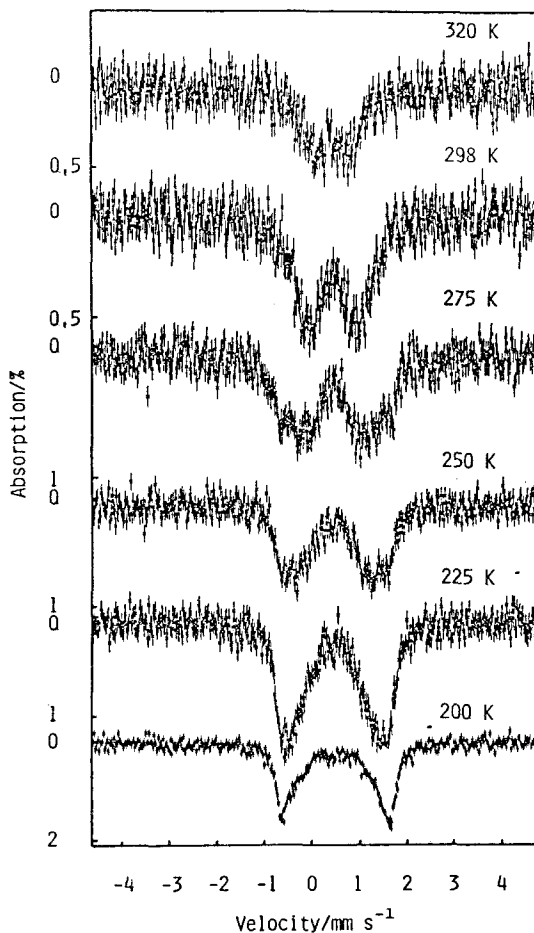
Fig. 1. Variable temperature Mössbauer spectra of
α-CyD-(η-cyclopentadienyl)(η-ethylcyclopentadienyl)iron(II) clathrate.

show temperature dependence. However, in this clathrate the peaks become broad at around 200 K and then collapse gradually inward above 250 K. However, shoulders are observed on the inside of the spectra at 200 K. These shoulders suggest the existence of phase transitions or anisotropic relaxation. The Mössbauer spectra are different from those observed at the low temperature limit at which the molecular motions are effectively frozen. The feature that the Mössbauer spectra for the clathrate collapse to a single peak with raising temperature can be understood by taking a model of isotropic relaxation of efg i.e. ferrocene molecules are free to rotate in the cavity.

It is necessary to present some theoretical spectra to compare them with our data. The theory of relaxation produced by fluctuating efg at a nucleus has been described by Tjon and Blume(22) and they applied it
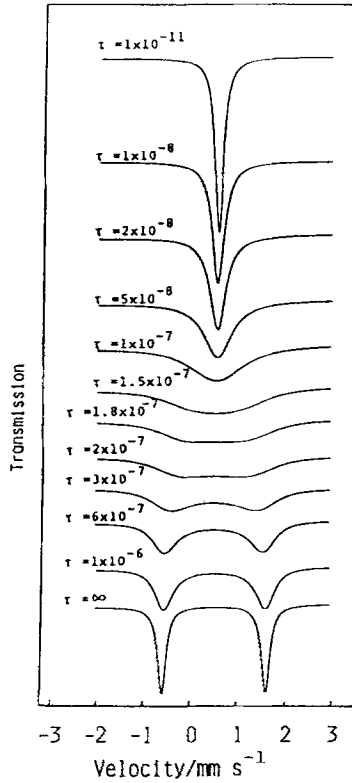
Fig. 2. Theoretical Mössbauer line shape for the isotropic relaxation of the electric field gradient. Here $p_x=p_y=p_z$. Relaxation time τ is shown in the figure.

to thiourea—ferrocene clathrate(4) and the same ionic salts containing organometallic cations(5). The time—dependent quadrupole interaction Hamiltonian for an axially symmetric efg and a nucleus of spin I is

$$H(t)=(QS/6)(1-\frac{3}{2}f^2(t))(3I_z^2-I^2) + (QS/8)f(t)(I_+^2 + I_-^2) \quad (1)$$

where H is the electric field Hamiltonian. $QS=\frac{1}{2}e^2qQ$ is the quadrupole splitting which would arise from the stationary interaction and f(t) is a random function of time with values of 0 and $\pm$ 1. I_+, I_- and I_z are usual quantum mechanical spin operators. The relative probability for absorption at any given frequency is given by

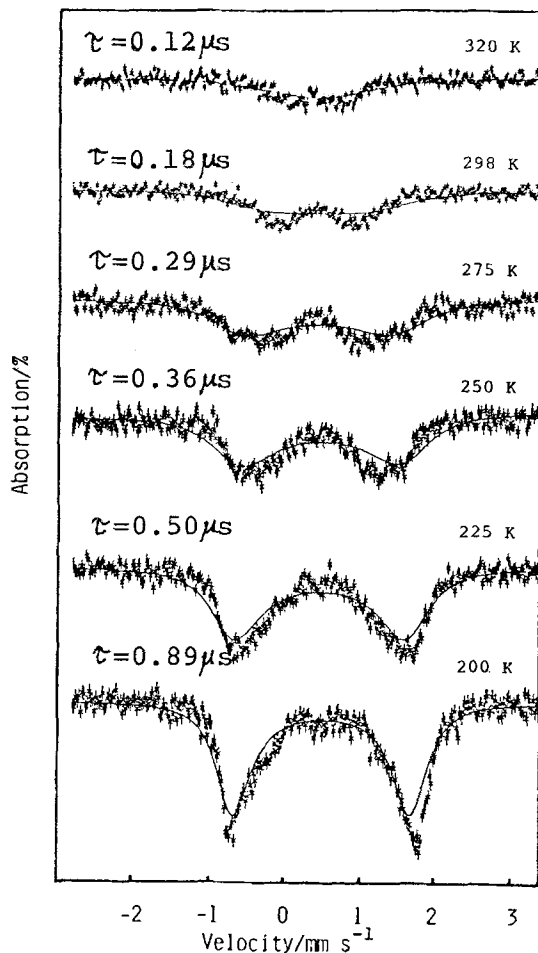$$I(\omega)= 2Re\int_0^\infty dt \; exp(i(\omega-\omega_0)t \; -\frac{1}{2}\Gamma(t)G(t) \quad (2)$$

Fig. 3. A fit between the Mössbauer spectra of the α-CyD-(η-cyclopentadienyl)(η-ethylcyclopentadienyl)iron(II) clathrate and the theoretical curve. Here $p_x = p_y = p_z$ and a single relaxation time τ is taken.

where ω_0 is the centroid of the spectrum, ω is the natural linewidth and $G(t)$ is a correlation function under the assumptions that the samples are random polycrystalline and that all lattice sites are equivalent. If the system is under isotropic relaxation, algebraic evaluation of eq. (2) produces the following results.

$$G(p) = \frac{p + 3W}{p^2 + 3pW + 4\alpha^2} \tag{3}$$

where $\alpha = QS/4$ and $p = -i(\omega - \omega_0) + \frac{1}{2}\Gamma$. The transition probabilities per unit cell, W_{ij} (now, $W_{ij}(i=j)=W$) for changing from value i to j are
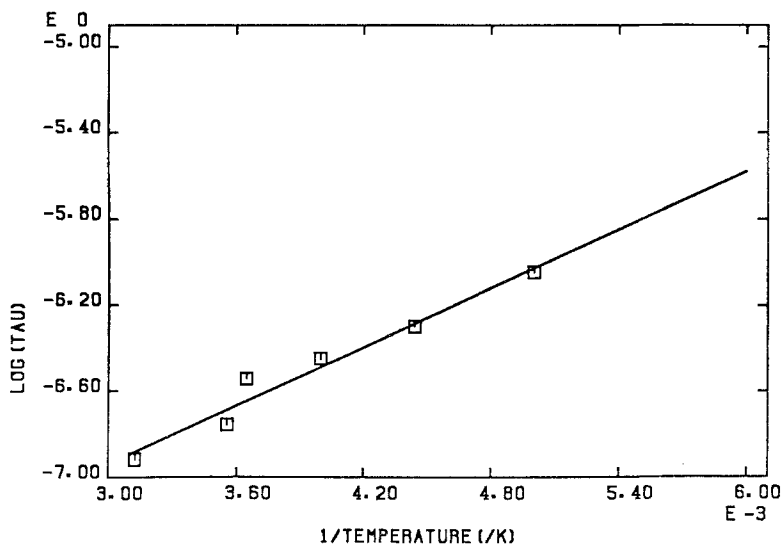
Fig. 4. Arrhenius plot for the reorientation of $(\eta$-cyclopentadienyl$)(\eta$-ethylcyclopentadienyl)iron(II) molecule in the cavity of α-CyD.

identifiable with the transition probabilities for the principal components of the efg, and then the transition probability can be converted to the correlation time by

$$T_{ij} = (0.978 \times 10^{-7}\ s)/W_{ij}$$

     Curves calculated using eq. (3) are shown for different values of τ in Fig. 2. The effect of decreasing relaxation time leads to the inward collapse of the normal doublet Mössbauer spectra. Variable temperature Mössbauer spectra for the clathrates are not in good accordance with the spectra calculated for this isotropic relaxation model. Solid curves in Fig. 3 are calculated under the assumption of isotropic relaxation of efg and relaxation times are calculated using the least squares method for fitting the observed data under constant QS value. The system was specified in terms of one activation energy E_a such that $\tau = \tau_{ij}$ $\exp(E_a/RT)$ and E_a =8.8 KJ/mol is calculated from the inclination of the curve above 200 K(Fig. 4). This value is smaller than 15 KJ/mol for thiocarbonyl diamide-bis$(\eta$-cyclopentadienyl)iron(II) clathrate(4). The rotational motion of the guest molecule can be induced thermally if the size of the cavity is just in accordance with that of the guest molecule, because a progressive inward collapse of the spectrum was not observed in the Mössbauer spectra of the β-CyD-(η-cyclopentadienyl)(η-ethylcyclopentadienyl)iron(II) clathrate whose cavity is larger than that of α-CyD.
     The effective vibrating mass can frequently be estimated from the second-order Doppler shift and is given in the literature(23).

$$M_{eff} = -\frac{3kE_r}{2\,c^2}(d(IS)/d(T))^{-1}$$

$$=-4.1684\times10^{-2}(d(IS)/d(T))^{-1}$$

where E_r is resonance γ-ray energy, k is Boltzmann constant, and c is velocity of light. From the temperature dependence of the value of the IS, M_{eff}=122±15 mass unit is calculated for α-CyD-(η-cyclopentadienyl)(η-ethylcyclopentadienyl)iron(II) between 100 and 300 K.

Lattice temperature for the compounds is calculated, assuming a Debye model for the solid(23).

$$\theta = 11.659\times\left(\frac{-d\ln(A(T)/A(100))}{dT}\right)^{-1/2}$$

where A(T) is the Mössbauer absorption area under the resonance curve. The variations of $d\ln(A(T)/A(100))/dT$ are not linear with respect to temperature, thus the discussion is limited in the temperature range in which the curve is linear. θ for the clathrate is calculated to be 132±3 K between 100 and 275 K. The deviation from a linear curve between 275 K and 320 K for the clathrate suggests the existence of a phase transition. Lattice dynamics of a host is strongly effected in θ because a recoilless fraction is dependent on an acoustic mode in solid. Therefore, a guest molecule would be used as a probe molecule to study lattice dynamics of host materials. However, these values must be considered as an approximation. A more detailed study of the temperature dependence of the line widths of these clathrates is in progress to obtain the lattice dynamical properties of clathrates.

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