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^{57}Fe- AND ^{119}Sn-MÖSSBAUER SPECTROSCOPIC STUDIES OF THE MOLECULAR DYNAMICS OF $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$ AND $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$

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The Mössbauer effect of the 14.4 keV ^{57}Fe and 23.8 keV ^{119}Sn transitions has been studied in $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$ and $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$ crystals. From the temperature dependence of the recoil-free fraction in iron and tin experiments, practically the same characteristic temperature (58 K for each Mössbauer resonance) has been found in the $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$, while two slightly different values (42 K for the iron resonance and 47 K for the tin resonance) have been estimated in the $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$.

We have demonstrated that the recoil-free fraction of a Mössbauer spectrum depends upon the intermolecular bonding in a number of compounds.[1-5] The results were interpreted by assuming that the intermolecular bonding restricts the motion of the Mössbauer atoms in the direction of the bonding and the recoil-free fraction increases in this direction.[2,5] This interpretation has later been confirmed for the same compounds as those we studied and several similar compounds by Herber *et al.*[6,7] and was applied to determine the intermolecular association of bis(trialkyltin) sulfate, selenate, and chromate in solid.[8,9] However, there have been few studies in which the detailed temperature dependence of the recoil-free fraction with respect to more than one atom in a given molecule has been examined by Mössbauer spectroscopy. A unique investigation of stannic iodide was carried out by Bukshpan and Herber, giving quite different characteristic temperatures for tin and iodine resonances.[10] Their results were analyzed by Hazony in terms of the inter- and intramolecular vibrations.[11] In the present paper we describe the characteristic temperatures estimated from ^{57}Fe- and ^{119}Sn-Mössbauer spectra for $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$ and $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$ in order to clarify the effect of the site of Mössbauer atom in a molecule on the characteristic temperature.

^{57}Fe- and ^{119}Sn-Mössbauer absorption spectra were obtained by using a 5 mCi ^{57}Co(Pt) source and a 5 mCi Ba^{119m}SnO$_3$ source, respectively, moving at room temperature. Other experimental details pertaining to the temperature control, the spectrometer, the velocity calibrations, and the behavior of the spectral area associated with a resonance line have already been discussed elsewhere.[10,11] A detailed analysis for the evaluation of "absolute" value of the recoil-free fraction, f_a, of ^{119}Sn atoms has also been described in our previous works.[3)]

Based on the Debye approximation, the "relative" recoil-free fraction is given by

$$f_a \simeq \exp\left[-\frac{3E_\gamma^{\,2}}{Mc^2k\theta^2}T\right], \qquad (T \leq \frac{\theta}{2}) \qquad (1)$$

where E_γ is the energy of the Mössbauer transition, θ is the Debye temperature, and M is an effective mass associated with the thermally excited motion of the Mössbauer nuclide. The "relative" values of the recoil-free fraction of ^{57}Fe and ^{119}Sn were estimated from the temperature dependence of the total spectral area, A, over the temperature ranges, 80 to 340 K and 80 to 240 K, respectively, by assuming that the area is practically proportional to the recoil-free fraction for thin absorbers.

$$\frac{d\ln A}{dT} = \frac{d\ln f_a}{dT} = -\frac{3E_\gamma^{\,2}}{Mc^2k\theta^2} \qquad (2)$$

The compounds, $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$ and $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$, were prepared by following the method described in ref. 14. Their purities were checked by elemental analyses and melting points and found to be more than 99.5 % for the both.

Figure 1 shows the ^{57}Fe- and ^{119}Sn-Mössbauer spectra of the compounds measured at liquid nitrogen temperature. The Mössbauer parameters are in good agreement with those previously reported for these compounds.[15), 16)] The temperature dependences of the "relative" recoil-free fraction of ^{57}Fe and ^{119}Sn atoms and of the "absolute" recoil-free fraction of ^{119}Sn atoms for the compounds are shown in Fig. 2, where $\log_{10}f_a$ has been plotted against the temperature T.

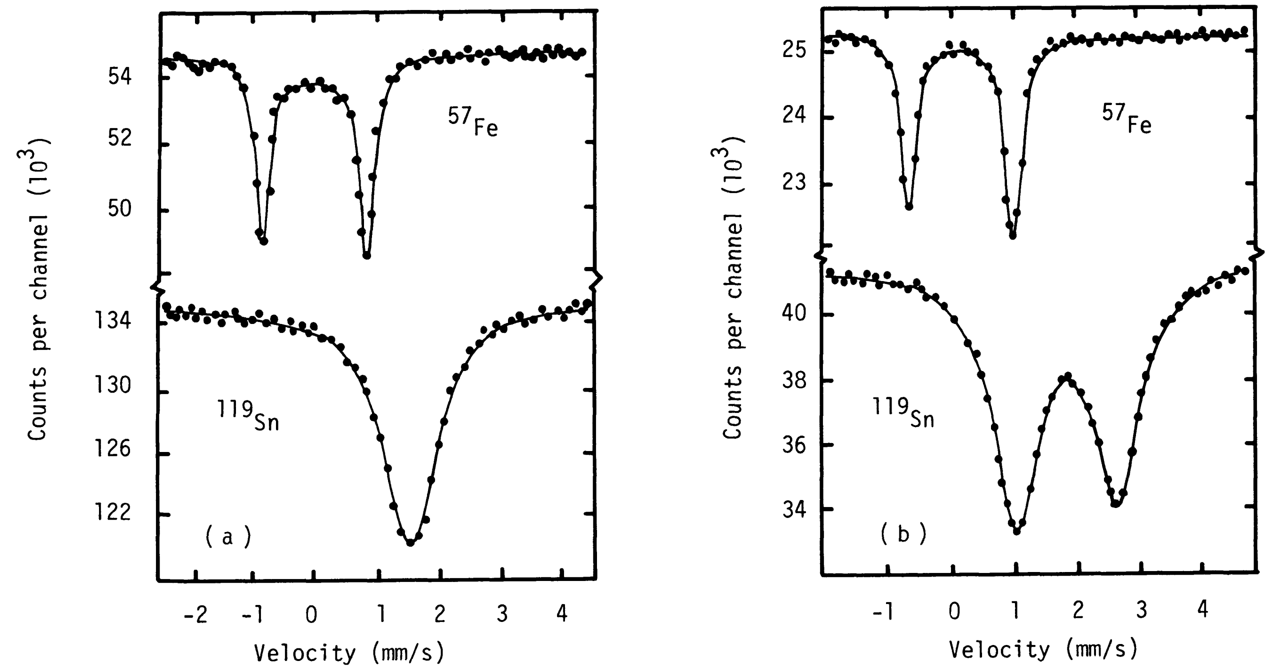

Fig. 1. ^{57}Fe- and ^{119}Sn-Mössbauer spectra of (a) $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$ and (b) $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$ at liquid nitrogen temperature. The velocity scales are normalized with respect to metallic iron and barium stannate, respectively.

The "relative" f_a shows almost the same values as the values of "absolute" f_a for each compound, although the "absolute" f_a does not always extrapolate to unity as T goes to zero, as is found in our previous studies of the "absolute" value of f_a for a number of organotin compounds.[1, 3, 4, 9] The apparent discrepancy between the "relative" and the "absolute" values of f_a suggests that the Debye approximation be not strictly applicable for such compounds especially in the low temperature region. We have applied the Debye approximation only to the slope, $d\ln f_a/dT$, to derive the characteristic temperatures with respect to ^{57}Fe and ^{119}Sn atoms by using Eq. (2), since both the slopes of the "relative" and the "absolute" values of f_a are essentially the same and the difference between both the values at the same temperature is negligibly small.

Letting M equal the molecular mass of the compound, we have calculated θ for ^{57}Fe and ^{119}Sn by using 14.4 and 23.8 keV as E_γ, respectively. The Debye temperatures are tabulated in Table I together with the Mössbauer parameters for the compounds. The Debye temperature is related with the maximum lattice frequency $\nu_{max} = k\theta/h$, giving $\nu_{max} = 40$ and 29 cm^{-1} when $\theta = 58$ and 42 K, respectively. Although an attempt to detect those low frequency peaks in the Laser Raman spectra of the compounds was so far unsuccessful because of the decomposition of those colored compounds, it has been recently demonstrated for colorless monomeric organotin compounds by Herber *et al.* that the ν_{max} estimated by Mössbauer spectroscopy coincides with one of the low-lying Raman frequencies.[17, 18]

Substantially the same characteristic temperatures (*i. e.*, maximum frequencies) obtained for both the ^{57}Fe and ^{119}Sn resonances in $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$ indicate that the intermolecular lattice vibration is predominantly reflected in the temperature dependence of the recoil-free fraction. The difference between the values of θ obtained for $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$ may be ascribed to a little contribution of molecular libration, since the iron atom sits far off the center of gravity of the

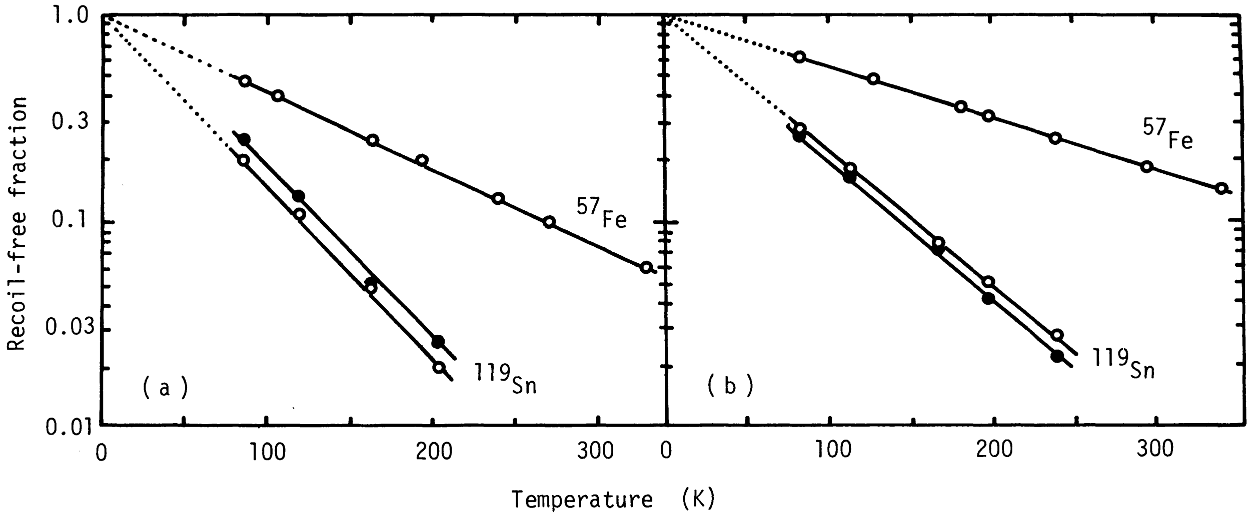

Fig. 2. Temperature dependences of the "relative" values (open circles) and the "absolute" values (filled circles) of recoil-free fraction of ^{57}Fe and ^{119}Sn in (a) $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$ and (b) $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$.

Table I. Debye characteristic temperatures and Mössbauer parameters.

Compound	Mössbauer nuclide	Debye temperature* (K)	Isomer shift** (mm/s)	Quadrupole splitting** (mm/s)
$(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$	^{57}Fe	41.9 ± 0.6	0.36 ± 0.02	1.76 ± 0.02
	^{119}Sn	46.7 ± 0.6	1.48 ± 0.02	0 (unresolved)
$(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$	^{57}Fe	57.7 ± 0.6	0.39 ± 0.02	1.86 ± 0.02
	^{119}Sn	58.6 ± 0.6	1.72 ± 0.02	1.79 ± 0.02

* Based on a least squares fit of the experimental data. The error quoted is a standard deviation.

** The values obtained at liquid nitrogen temperature. Isomer shift data are reported with respect to a room temperature metallic iron and barium stannate, respectively. No change in line position associated with singlets or doublets was observed over the entire pertinent temperature range within the experimental error. In consonance with the continuity of the temperature dependence of f_a, this may rule out the possibility of such phase transition as found in bispyridinmetal dichlorides.[20)]

molecule as seen in the X-ray structure of the compound.[19)] On the other hand, both the sites of iron and tin atoms are so well-balanced with respect to the center of gravity that the effect of libration may be of a similar extent on each characteristic temperature in $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$.[21)]

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