

Atomic and Molecular Motion in Iron Organometallics

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Temperature-dependent ^{57}Fe Mössbauer effect studies have been carried out on orange needle-shaped crystals of acetyl ferrocene over the range $90 \leq T \leq 350$ K in an effort to elucidate the motional behavior of the metal atom up to temperatures near the melting point (359K). The spectra consist of one well resolved doublet at all temperatures, with an isomer shift of 0.554 ± 0.002 and 0.438 ± 0.001 mm s $^{-1}$ at 90 and 298 K, respectively. The temperature dependence of the isomer shift corresponds to an effective vibrating mass of 74 ± 2 daltons, and, in conjunction with the temperature dependence of the recoil-free fraction, to a Mössbauer lattice temperature of 134 K. There is a small but significant vibrational anisotropy of the metal atom motion evident in the spectroscopic data above ~ 200 K.

Introduction

Gamma ray resonance scattering (the Mössbauer effect) has proven itself to be an excellent tool for the study of atomic motion in solids, especially those involving iron and tin. In a number of recent studies¹⁻³ it has been shown that the motion of the iron atom in organometallics can serve as a sensitive diagnostic tool for the elucidation of the relationship between the molecular level architecture involving the metal atom and the macroscopic properties of these diamagnetic solids. Until fairly recently, these studies have usually involved low-temperature investigations, since the recoil-free fraction drops off sharply with increasing temperature, and thus the anisotropy of the metal atom motion, which can become pronounced at higher temperatures, has not been extensively documented in the literature.

Because of its centrality in the development of modern organometallic chemistry, ferrocene [$\text{Fe}(\eta_5\text{-C}_5\text{H}_5)_2$] [102-54-5] has been the subject of numerous Mössbauer effect studies⁴, and a recent detailed examination of this compound with reference to the iron atom dynamics at temperatures ranging from 90 to 370 K, has been reported.³ Because of the complexity of the molecular and crystal structure of this compound, which involves several phase transitions between liquid nitrogen and room temperature, a large number of X-ray crystallographic investigations have been undertaken,⁵⁻⁸ and the thermal factors ($U_{i,j}$ values) derived from such studies have permitted a validation of the Mössbauer data in terms of these parameters at several different temperatures.⁹

In addition to the temperature dependence of the recoil-free fraction (derived from the area under the resonance curve for an optically "thin" absorber), such Mössbauer studies have also permitted an elucidation of the anisotropy of the metal atom motion (derived from the intensity asymmetry of the two components of the quadrupole-split spectrum), commonly referred to as the Gol'danskii-Karyagin effect (GKE).¹⁰ Until recently, it has been assumed that the GKE in iron organometallics is small or negligible, but a number of recent studies of such compounds in the high temperature regime have shown that this effect is much more ubiquitous than had previously been suspected. This motional anisotropy is of particular interest in connection with the ferrocenoid solids,

since the onset of ring rotation and libration has a pronounced effect on this parameter.

In this connection, the study of acetyl ferrocene [$\text{Fe}[(\eta_5\text{-C}_5\text{H}_5)(\eta_5\text{-C}_5\text{H}_4\text{COCH}_3)]$] [1271-55-2] [**1**] has proven to be of particular interest, and a detailed study of this solid over the temperature range 90 to 348 K is summarized in the present communication. The reported melting point of this solid is 359 K. It should be noted that an earlier detailed Mössbauer investigation of **1**, as well of its crystal structure by X-ray diffraction, has been reported by Sano et al.¹¹⁻¹³ and others,¹⁴ and the present study should be considered as an extension (and re-examination) of the earlier work reported by the Japanese group.

Experimental

High purity (>99%) crystals of **1** were obtained commercially (Merck) and showed only a single doublet resonance spectrum at all temperatures. These crystals were ground with BN, transferred to a plastic sample holder, and examined in transmission geometry, as detailed earlier,¹⁻⁴ using a ^{57}Co in Rh source at room temperature. It should be noted that the plastic sample holders used in this study were thoroughly sealed with hard-setting plastic cement for two reasons. First, it is well known that iron organometallics of the type examined in this study readily sublime, especially at temperatures near T_{mp} . Since sample loss by sublimation on increasing the temperature would mimic an anomalous reduction in the recoil-free fraction, it is important to guard against sample loss by this process. (Moreover, as will be noted below, it is equally important in this connection to acquire Mössbauer data in both heating and cooling regimes and to monitor the gamma-ray transmission rate as a function of time). Second, since small, unavoidable temperature gradients in the sample holder may result in sublimation, and hence in deposition of crystals preferentially oriented with respect to the gamma ray axis, and since this would drastically effect any evidence for a GKE in these samples, it is important to minimize such changes in the texture effect. A rigorously sealed sample container which develops its own vapor pressure is assumed to minimize this problem. Spectrometer calibration was effected using a room temperature 18.81 mgm cm $^{-2}$ $\alpha\text{-Fe}$ absorber, and all isomer shifts are reported with respect to the centroid of this spectrum.

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Results and Discussion

The temperature dependence of the isomer shift (IS) is summarized in Figure 1 and evidences a departure from linearity at low temperature as has been noted previously. At high temperatures (above ~ 273 K), the data are well fit by a linear regression with a correlation coefficient of 0.999 for 18 data points. The IS calculated from the high temperature data is 0.554 ± 0.002 mm s⁻¹ at 90 K and 0.438 ± 0.001 at 298 K. This latter value is in good agreement with that of 0.40 – 0.42 mm s⁻¹ quoted in the earlier study¹² (although the temperatures for these values are not explicitly stated). The effective recoiling mass, M_{eff} , calculated from the high temperature $d \text{ IS} / d T$ data is 74 ± 2 daltons, a value which is significantly smaller than that previously reported¹⁵ for other ferrocenoid solids. The slope of the $d \text{ IS} / d T$ curve does not evidence any significant departure from linearity between room temperature and the melting point, and there is no evidence from these data of an experimentally significant change in the electron density around the metal atom in this temperature regime.

The temperature dependence of the quadrupole splitting (QS) is summarized graphically in Figure 2 and shows the expected decrease with increasing temperature in the temperature range 175–275 K, due to the thermal expansion of the covalent solid. The QS observed at 297 K is 2.275 ± 0.001 mm s⁻¹ in modest agreement with the value reported earlier.¹² At temperatures above 300 K, there appears to be no definite variation of QS with temperature, and the relatively large

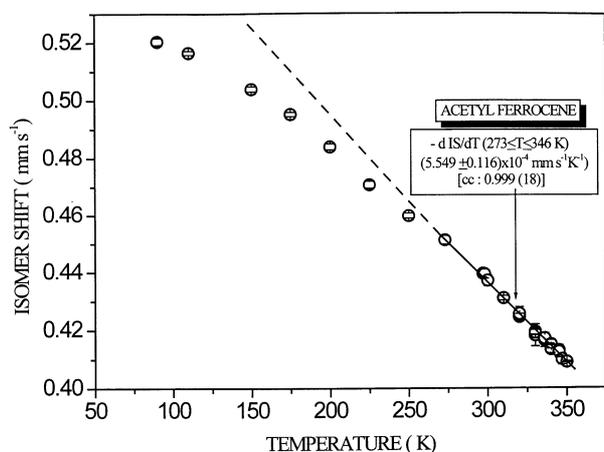


Figure 1. Temperature dependence of the isomer shift of acetyl ferrocene. The isomer shift is with respect to the centroid of a room temperature spectrum of α -Fe. The slope data at high temperatures are used to calculate M_{eff} as discussed in the text.

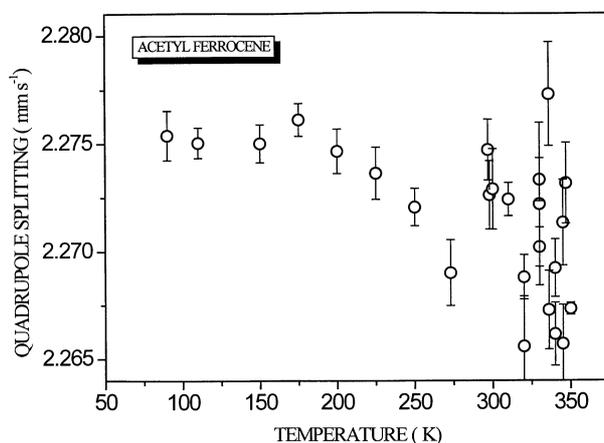


Figure 2. Temperature dependence of the quadrupole splitting parameter for acetyl ferrocene. The error bars reflect the precision of the individual measurements.

errors (on the total QS scale) preclude further interpretation of these data.

The temperature dependence of the recoil-free fraction (given by the temperature dependence of the area under the resonance curve for an optically “thin” absorber), normalized to its 90 K value, is shown in Figure 3. The data in the interval $90 \leq T \leq 320$ K are well fit by a linear regression with a correlation coefficient of 0.992 for 11 data points. The calculated value of $-d \langle x^2 \rangle / d T$ is $(5.79 \pm 0.10) \times 10^{-3}$ K⁻¹, in quite reasonable agreement with the value of 5.08×10^{-3} K⁻¹ extracted from Figure 1 of the 1987 data of Iwai et al.¹³ This temperature dependence, together with the $d \text{ IS} / d T$ value given above, leads to a calculated Mössbauer lattice temperature, Θ_M , of 134 K, which is significantly higher than lattice temperatures reported for ferrocene itself, mono-substituted ferrocenes, and fully ring substituted ferrocenes. At temperatures above ~ 330 K, there is a marked decrease in the recoil-free fraction with increasing temperature, indicating an *increase* in the mean square amplitude of vibration (msav) of the metal atom as the melting point is approached. In this context, it has not been possible in this study to reproduce the earlier data reported in the literature, which suggest a *decrease* in the msav at temperatures above ~ 320 K. This point will be discussed further below.

In a further attempt to elucidate the metal atom dynamics in the high temperature regime, a detailed examination of the line width of the resonance has been carried out, and these data are summarized graphically in Figure 4. At low temperatures, the

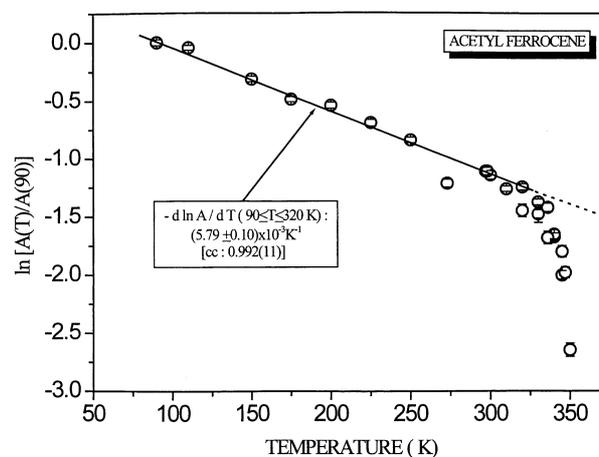


Figure 3. Temperature dependence of the recoil-free fraction for the Fe atom in acetyl ferrocene extracted from spectral area measurements. The slope data at low temperatures are in good agreement with those reported in the literature, and are used to evaluate a Mössbauer lattice temperature of 134 K, as discussed in the text.

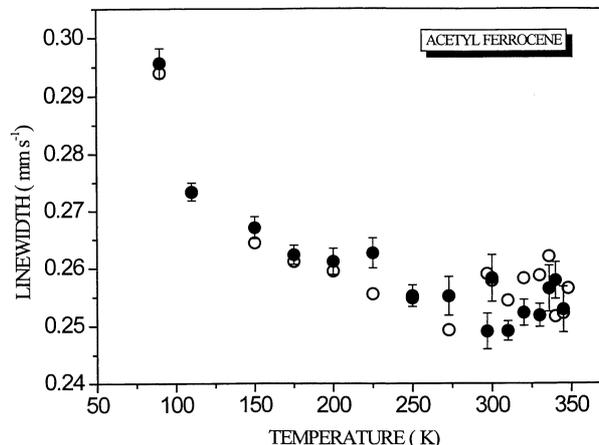


Figure 4. Temperature dependence of the line widths observed in the Mössbauer spectra of acetyl ferrocene. The open and closed circles reflect the A(+) and A(-) values, respectively.

line width shows the expected increase with decreasing temperature due to saturation effects (i.e.: the absorber can no longer be considered optically "thin"). Above ~ 200 K the line width reaches a constant limiting value, and above 300 K, this parameter has a mean value of $\sim 0.255 \pm 0.004$ mm s⁻¹ (15 data points). The excess of this value above twice the natural line width of the 14.4 keV ⁵⁷Fe gamma ray, 0.194 mm s⁻¹, is primarily due to radiation damage effects¹⁶ and ⁵⁷Fe accumulation in the 1.5 year old source matrix (originally 100 mCi). The data reported in the earlier study¹² evidences an increase of ~ 0.12 mm s⁻¹ in Γ between 273 and 355 K. Since this is more than 40 times the average line width error observed in the present data set, this broadening should have been readily detected in the data. However, it has not been possible to reproduce those earlier results in the present study, and the reported increase in line width with increasing temperature has not been observed in the present data.

One additional parameter, related to the intensity asymmetry of the resonance doublet, can be extracted from the present data set. These data, reported in terms of the intensity ratio $R = A(+)/A(-)$ [where $A(+)$ and $A(-)$ are the intensities of the resonance line at more positive and more negative values than the spectrum centroid, respectively] are shown in Figure 5 which summarizes only the *temperature-dependent part* of R . From this figure it is inferred that there is a small but definite increase in R with increasing temperature, and that this effect becomes more pronounced at $T > \sim 300$ K. The origin of this effect is presumed to arise from a motional anisotropy of the metal atom with respect to the *pseudo* symmetry axis running normal to the two Cp ring planes and through the iron atom position. This motional anisotropy is also readily evident in the detailed X-ray structure reported by Sano et al.¹² in which the ellipsoid of motion (at the 50 % probability level) shows a clear departure from spherical symmetry. However, additional study, using ⁵⁷Fe enriched absorbers (*vide infra*) are clearly needed to show conclusively whether this motional anisotropy is reversible over the whole temperature range after the sample has been warmed to a few degrees of T_{mp} .

On the basis of the foregoing data, it is now possible to understand the apparent differences between the results reported in the earlier Mössbauer study and those observed in this work. It is well known that many organic and organometallic solids can be formed in a number of polymorphic crystal structures, and that the rate of interconversion of one polymorphic form to a more stable one can occur over large time and temperature ranges.¹⁷ Frequently, the energy differences between polymorphs of covalent crystals are quite small, on the order of a few kilocalories per mole.¹⁸ Using ¹H

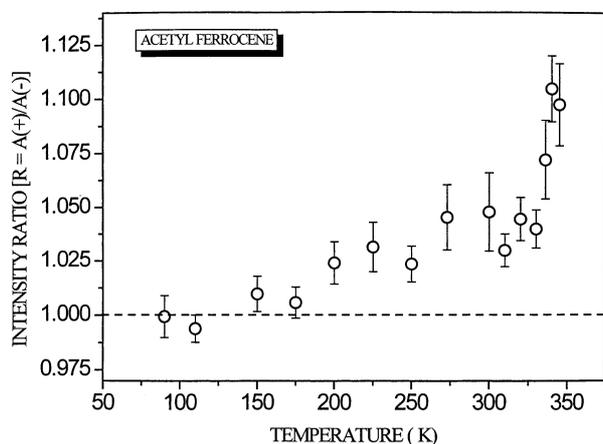


Figure 5. Temperature dependence of the intensity ratio $[R = A(+)/A(-)]$ for acetyl ferrocene. A temperature-independent contribution from preferential crystallite orientation ("texture effect") extracted from low temperature data has been corrected for in these results.

spin-lattice relaxation NMR experiments at 20 MHz on solid acetyl ferrocene, over the temperature range 80–359 K, Kubo et al.¹⁹ have reported the activation energy for C_5 reorientation as amounting to 5.02 and 5.74 kcal mol⁻¹ in the close packed crystal structure. There was no evidence for a phase transition below T_{mp} . In the case of acetyl ferrocene, three different morphological species have been reported,²⁰ depending on the solvent of recrystallization and the details of the purification process.²¹ In particular, wine-red needles, wine-red leaflets and light orange needle shaped crystals can be isolated from pentane and pentane-benzene solutions. Microscopic examination of the samples used in the present study show the marked predominance of orange needle shaped crystals which most probably belong to a hexagonal or trigonal crystal system, although no detailed X-ray study has been attempted in this work.

On this basis it is plausible that the sample(s) of brown needle shaped crystals of acetyl ferrocene examined by Sano et al.¹² were in fact of a different morphology than those here reported, and that both the apparent *decrease* in ΔE of the iron atom with increasing temperature, as well as the apparent increase in line width, can be accounted for by a change in the crystal structure from a meta-stable to a more stable configuration. This interpretation is not at variance with the crystal structure reported in the earlier study, since these diffraction data were acquired on a single crystal of dimension $0.30 \times 0.25 \times 0.35$ mm, whereas the Mössbauer data, of necessity, involved a macroscopic ensemble of crystals.

It is clearly desirable to resolve the apparent differences between the results of the present and earlier study, and such a resolution may best be effected by examination of well-crystallized ⁵⁷Fe enriched samples at temperatures between 300 K and the melting point, where the recoil-free fraction drops off sharply with increasing temperature. Using enriched samples and strong gamma ray sources is expected to reduce the relatively large statistical errors encountered in Mössbauer studies of organometallics near their melting point. It is hoped that such a detailed examination can be effected in the near future.

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