

# Cramping a Molecular Rollerball. Investigation of the Effect of Pressure on the Mössbauer Spectra of Three Cyclopentadienyl(arene)iron(II) Salts

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Received April 10, 1997<sup>Ⓢ</sup>

The effect of pressure on the Mössbauer spectra of salts of  $[\text{CpFePhH}]^+$ ,  $[\text{CpFePhF}]^+$ , and  $[\text{CpFePhMe}]^+$  has been examined over the range of  $10^{-4}$  GPa to about 4 GPa. Dynamic reorientation of salts of the first two cations may be arrested on the Mössbauer time scale by the application of pressure (0.85 and 1.36 GPa). For these two cations, extrapolated quadrupole splitting values were obtained at  $10^{-4}$  GPa at room temperature that help to verify and extend previous models of motion. A simplified theoretical model of the reorientation of the  $[\text{CpFePhH}]^+$  cation is presented. It is also shown that at pressures above those which arrest motion, the compounds manifest a gradual decrease of quadrupole splitting with increasing pressure. An explanation is discussed.

## Introduction

Dynamic reorientation of molecular species and plasticity in crystalline solids are of interest in many areas of science.<sup>1–4</sup> Since the naturally occurring dynamic properties of compounds may be altered by changes in physical conditions, they are potentially of use in the fields of molecular electronics and nanotechnology.<sup>1,4</sup> The use of Mössbauer spectroscopy to study dynamic effects, particularly of iron compounds, is well established.<sup>1,4–8</sup> Until our recent work,<sup>1</sup> the study of dynamic reorientation had been limited to the effect of changes in temperature,<sup>4–8</sup> and the known effect of pressure on iron sandwiches was limited to ferrocene.<sup>9,10</sup>

It has recently become possible to record good quality Mössbauer spectra at high pressures, in a diamond anvil cell (DAC),<sup>1,11</sup> of compounds containing less than 20% natural iron. We have reported that rapid dynamic reorientation in cyclopentadienyl(benzene)iron(II) hexafluorophosphate,  $[(\eta^6\text{-PhH})(\eta^5\text{-Cp})\text{Fe}][\text{PF}_6]$  may be halted on the Mössbauer time scale,<sup>12</sup> (approximately  $1.4 \times 10^{-7}$  s for iron) by the application of pressures above 1.79 GPa at room temperature.<sup>1</sup>

Variable temperature Mössbauer spectroscopic studies,<sup>4</sup> aided by differential scanning calorimetry (DSC) and some X-ray

diffraction,<sup>4</sup> have shown that the cyclopentadienyl(fluorobenzene)iron(II) cations of the salts  $[(\eta^6\text{-PhF})(\eta^5\text{-Cp})\text{Fe}][\text{AF}_6]$ , where A = P, As, Sb, are in a state of rapid isotropic reorientation at room temperature which is halted at lower temperatures. The <sup>57</sup>Fe Mössbauer spectra show sharp singlets at room temperature which broaden and separate into quadrupole doublets on cooling. The appearance of the doublets is accompanied by a phase change from cubic to an unknown structure at 225 K. This system may be considered to be a “molecular rollerball”.

The  $[\text{PF}_6]^-$  and  $[\text{AsF}_6]^-$  salts of the cyclopentadienyl benzene iron(II) cation,  $[(\eta^6\text{-PhH})(\eta^5\text{-Cp})\text{Fe}]^+$ , show more complicated behavior.<sup>5–7</sup> There are two phase changes: at high temperature, the systems are known to be cubic and the Mössbauer spectra show singlets;<sup>5,6</sup> in the intermediate phase stable at room temperature for both compounds (the  $[\text{AsF}_6]^-$  salt is monoclinic,<sup>6</sup> the structure of the  $[\text{PF}_6]^-$  salt has not been established), two quadrupole doublets are seen, the “inner” one having slightly less than half the splitting of the “outer”.<sup>5,6</sup> The low-temperature phases show only a quadrupole doublet.<sup>5,6</sup> The low- and high-temperature phases were interpreted in the same way as the  $[(\eta^6\text{-PhF})(\eta^5\text{-Cp})\text{Fe}]^+$  salts. For the intermediate room temperature phase the doublets of  $[(\eta^6\text{-PhH})(\eta^5\text{-Cp})\text{Fe}][\text{AsF}_6]$  were related to the crystal structure which shows a partly ordered and a disordered iron site; the “inner” doublet was assigned to the disordered site and the small quadrupole splitting (q.s.) attributed to “anisotropic reorientation”, a motion in which the cations reorient about an axis perpendicular to the principal axis of the electric field gradient (EFG); the “outer” doublet was assigned to the partially ordered site and treated as static.<sup>6</sup> Fitting of the data was not entirely satisfactory and did not explain why the “outer” doublet has a q.s. of less than the 78 K value, or why the “inner” doublet should have a q.s. of less than half of the q.s. of outer doublet.

In this paper we present new variable pressure Mössbauer spectroscopic studies of  $[(\eta^6\text{-PhF})(\eta^5\text{-Cp})\text{Fe}][\text{PF}_6]$  (**1**) and include extended data for  $[(\eta^6\text{-PhH})(\eta^5\text{-Cp})\text{Fe}][\text{PF}_6]$  (**2a**).  $[(\eta^6\text{-PhMe})(\eta^5\text{-Cp})\text{Fe}][\text{PF}_6]$  (**3**) has also been studied as a nondynamic system for the purpose of comparison. The results generally confirm the interpretation of the variable temperature studies; however, by extrapolating the q.s. data to  $1 \times 10^{-4}$

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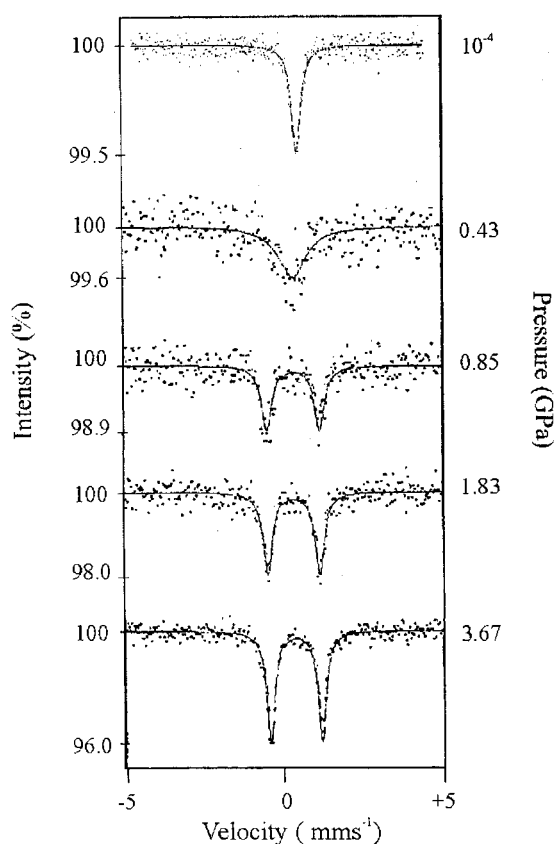
<sup>Ⓢ</sup> Abstract published in *Advance ACS Abstracts*, August 1, 1997.

- (1) Silver, J.; Roberts, R. M. G.; Davies, D. A.; McCammon, C. A. *J. Chem. Soc., Chem. Commun.* **1996**, 11.
- (2) Sherwood, J. *The plastically crystalline solid*. Wiley, Chichester, 1979; p 1.
- (3) Braga, D. *Chem. Rev.* **1992**, 92, 633.
- (4) Fitzsimmons, B. W.; Sayer, I. *J. Chem. Soc., Dalton Trans.* **1991**, 2907.
- (5) Fitzsimmons, B. W.; Hume, A. R. *J. Chem. Soc., Dalton Trans.* **1980**, 180.
- (6) Fitzsimmons, B. W.; Marshall, W. G. *J. Chem. Soc., Dalton Trans.* **1992**, 73.
- (7) Fitzsimmons, B. W. *J. Phys. C1* **1980**, 41, 33.
- (8) Gibb, T. C. *J. Phys. C* **1979**, 9, 2627.
- (9) Vaughan, R. W.; Drickamer, H. G. *J. Chem. Phys.* **1967**, 47, 468.
- (10) Zahner, J. C.; Drickamer, H. G. *J. Chem. Phys.* **1961**, 35, 375.
- (11) Pasternak, M.; Taylor, R. D. *Hyperfine Int.* **1989**, 47, 415.
- (12) Within this paper the terms fast and slow will refer to the time scale of the Mössbauer experiment.

**Table 1.** Variation of Mössbauer Parameters with Pressure for **1–3**

compd	pressure/ GPa <sup>a</sup>	i.s./ mm s <sup>-1</sup>	q.s./ mm s <sup>-1</sup>	Γ/ mm s <sup>-1</sup> <sup>c</sup>	ref
<b>1</b>	1 × 10 <sup>-4</sup>	0.466(8)	0.00	0.15(1)	<i>b</i>
<b>1</b>	0.43(5)	0.431(55)	0.000(28)	0.6(3)	<i>b</i>
<b>1</b>	0.85(5)	0.433(14)	1.663(23)	0.20(2)	<i>b</i>
<b>1</b>	1.83(5)	0.425(7)	1.625(14)	0.18(1)	<i>b</i>
<b>1</b>	3.67(10)	0.417(3)	1.615(6)	0.16(1)	<i>b</i>
<b>2a</b>	1 × 10 <sup>-4</sup>	0.423(3)	1.556(3)	0.13(1)	1
		0.440(3)	0.747(4)	0.13(1)	
<b>2a</b>	1.36(5)	0.438(10)	1.643(20)	0.13(2)	<i>b</i>
<b>2a</b>	1.79(8)	0.395(7)	1.591(18)	0.21(3)	1
<b>2a</b>	3.37(6)	0.380(4)	1.495(13)	0.20(2)	1
<b>3</b>	1 × 10 <sup>-4</sup>	0.468(9)	1.676(17)	0.12(1)	<i>b</i>
<b>3</b>	1.12(5)	0.433(27)	1.651(53)	0.15(4)	<i>b</i>
<b>3</b>	2.06(7)	0.404(17)	1.559(33)	0.12(3)	<i>b</i>
<b>3</b>	2.43(4)	0.393(8)	1.553(16)	0.14(1)	<i>b</i>
<b>3</b>	2.97(5)	0.380(11)	1.512(22)	0.16(2)	<i>b</i>
<b>3</b>	3.90(5)	0.372(12)	1.490(24)	0.18(4)	<i>b</i>

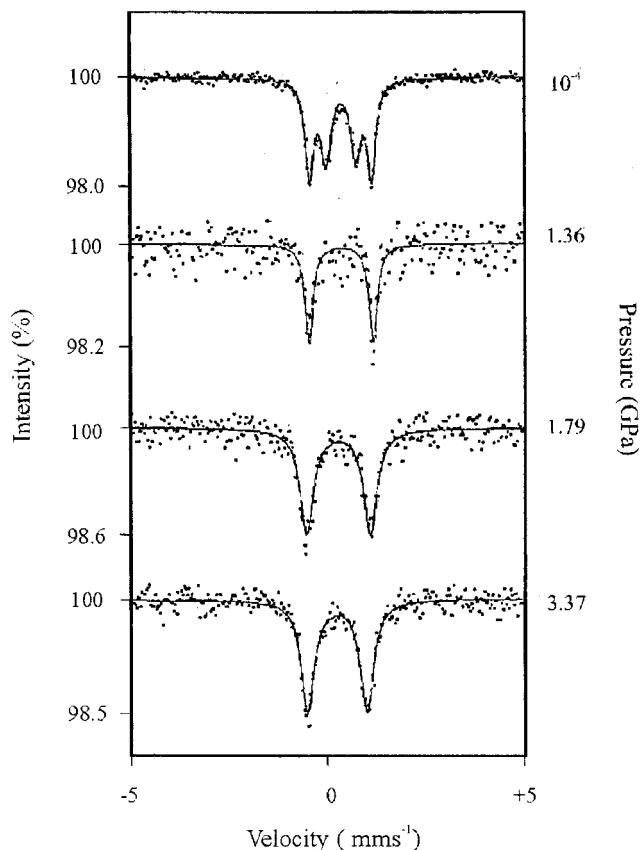
<sup>a</sup> 1 GPa = 10 kbar = 10 000 atm. <sup>b</sup> This work. <sup>c</sup> Γ = half-width at half-height.

**Figure 1.** Mössbauer spectra of **1** at 298 K and varying pressure.

GPa it is possible to derive room temperature values of the q.s., thereby extending the data available, and modify the models of motion. Variations of isomer shift (i.s.) and electric field gradient (EFG) with pressure are discussed briefly in terms of bonding models. We also report that the intermediate phase of **2a** is isomorphous with the monoclinic phase of  $[(\eta^6\text{-PhH})(\eta^5\text{-Cp})\text{Fe}][\text{AsF}_6]$  (**2b**).

## Results and Discussion

The results obtained for the variable pressure Mössbauer spectroscopic studies of **1**, **2a**, and **3** are shown in Table 1 and the spectra obtained during the course of this work are shown in Figures 1–3, respectively. Due to the similarity of the Mössbauer spectra of **2a** and **2b** it has been ascertained that

**Figure 2.** Mössbauer spectra of **2a** at 298 K and varying pressure.

they are structurally similar in the intermediate phase.<sup>5,6</sup> X-ray powder patterns of both salts were recorded at ambient temperature to explore this suggestion. Figure 4 presents these patterns, clearly showing that the unit cells of these salts are very similar in structure though not isomorphous. The unit cell of **2b** is known to be monoclinic at ambient temperature;<sup>6</sup> the fact that the unit cell of **2a** is more complicated suggests that its structure is at best monoclinic, but a detailed analysis of the powder patterns is beyond the scope of this work. However, the obvious similarities in the structures of these two salts permit us to utilize the model previously used to describe the dynamic behavior of **2b** for **2a**.<sup>6</sup>

**Isomer Shifts and *f*-Factors.** The variation of i.s. with pressure for **1**, **2a**, and **3** is shown in Figure 5. The lines connecting the data points are for clarity only. Within experimental error the i.s. decreases with increasing pressure, which is consistent with previous reports<sup>13</sup> and is ascribed mainly to increasing electron density at the iron nucleus. Pressure-induced second-order Doppler shifts (SOD) are small for lattices of low Debye temperature,<sup>14a</sup> and a possible relativistic contribution is also neglected.<sup>14a</sup> As pressure would be expected to reduce volume and hence cause a general increase in electron density, it would be surprising if the i.s. did not decrease with pressure.

*f*-Factors (the probability of zero-phonon absorption)<sup>14b</sup> increase with pressure as would be expected from increasing restriction of the mean nuclear vibration amplitude; this has not been quantified as in a DAC the absorber cross section and thickness change with applied pressure.<sup>15</sup>

(13) Armthauer, G. *High Pressure Research in Geosciences*; Schweizbart'sche, Verlagsbuchhandlung: Stuttgart, 1982, p 269.

(14) Greenwood, N. N.; Gibb, T. C. *Mössbauer Spectroscopy*. Chapman and Hall Ltd: London, 1971; (a) pp 46–54, (b) p 9.

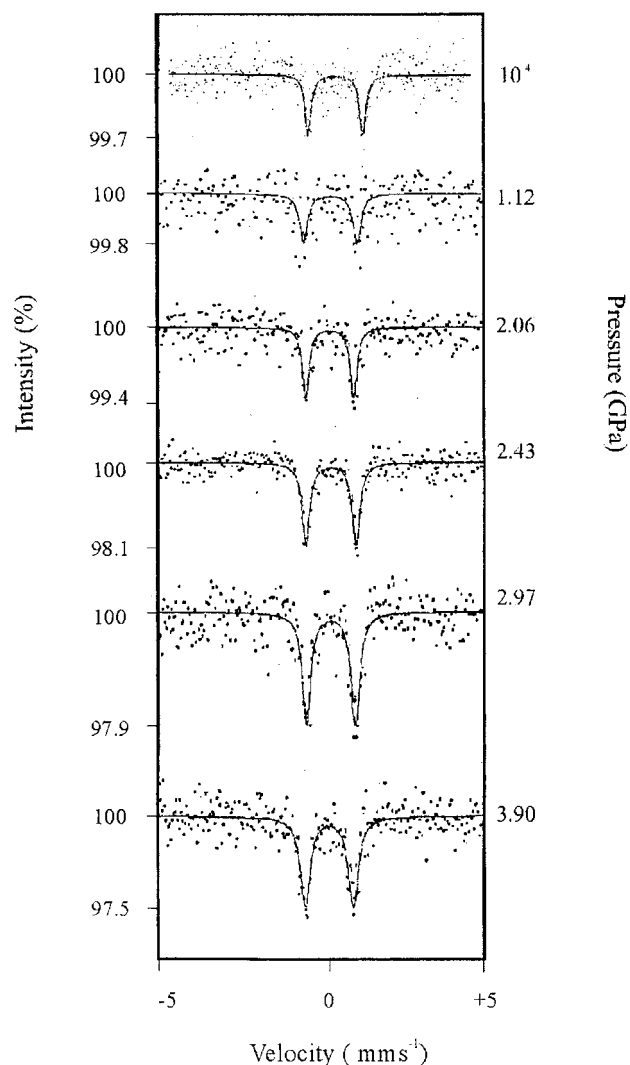


Figure 3. Mössbauer spectra of **3** at 298 K and varying pressure.

**Quadrupole Splitting and Line Shapes.** Figure 6 shows how the q.s. of **1**, **2a**, and **3** vary with pressure; the lines drawn between the points are for clarity only.

**(a) Arrested Motion.** Figure 3 shows that the Mössbauer spectra of **3** do not change their shape under pressure; there is no detectable relaxation of the EFG in this compound. Figures 2 and 3 show how the spectra of **1** and **2a** change quite dramatically in a manner which is similar to that caused by lowering the temperature,<sup>4,5</sup> and interpretations for **1** and **2a** have been approached in similar ways. At atmospheric pressure **1** shows a fairly sharp singlet which broadens at 0.43 GPa before transforming to a sharp doublet at pressures of 0.85 GPa and higher. Figure 7 shows a simulation of the spectra based on spherical (isotropic) reorientation of the EFG at various rates, using the equations given by Tjon and Blume.<sup>16</sup> The simulated spectrum with the relaxation time  $7.19 \times 10^6 \text{ s}^{-1}$  most closely resembles the observed spectrum at 0.43 GPa. At none of the pressures used was there any indication of a doublet with an intermediate q.s. that might suggest anisotropic relaxation.<sup>8</sup> We therefore interpret the behavior of these spectra in a way analogous to the interpretation of the variable temperature studies,<sup>4</sup> *i.e.*, we conclude that the isotropic relaxation of the EFG is slowed by pressures in the range  $10^{-4}$  to 0.85 GPa and effectively halted at pressures above 0.85 GPa. At this pressure

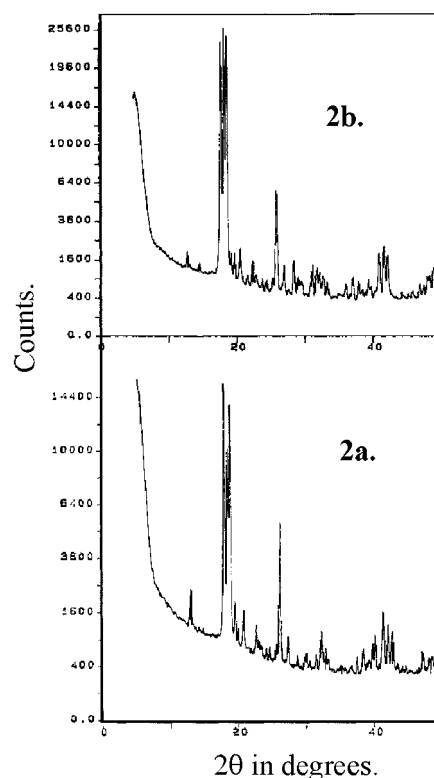


Figure 4. X-ray powder diffraction patterns of **2a** and **2b** at 298 K.

there is no direct evidence of a phase change such as that which occurs at 225 K and atmospheric pressure;<sup>4</sup> however, the system has not yet been studied under pressure using XRD methods.

Compound **2a** shows rather different behavior. Further to our preliminary report,<sup>1</sup> the Mössbauer spectra have now been measured at pressures below 1.79 GPa in an attempt to follow the disappearance of the “inner” doublet. In Figure 6 it has already disappeared by 1.36 GPa and is therefore not plotted on this figure. At 0.5 GPa no spectrum could be detected, which we ascribe to a combination of low *f*-factor and the relaxation rate having come close to the critical value for maximum broadening of the spectrum. The splitting at 1.36 GPa is significantly larger than the value of the “outer” q.s. at  $10^{-4}$  GPa; this is discussed below in sections b and c, but the fact that even at this pressure there is only one sharp doublet indicates that motion has halted.

**(b) Variation of q.s. with Pressure.** Figure 8 shows graphs of observed q.s. against pressure for **1**, **2a**, and **3**. The low-pressure spectra of **1** and **2a** are affected by relaxation of the EFG, as shown above, and are omitted from this figure. It is assumed that the points relate directly to the principal value of the (axially symmetric) EFG. With this proviso the q.s. values of the three salts decrease with increasing pressure; the lines shown were obtained by the linear regression of pressure on the q.s. (correlation coefficients  $-0.88$ ,  $-0.91$ , and  $-0.97$  for **1**, **2a**, and **3**). It is unlikely that a linear equation truly represents the pressure/q.s. relationship, but over this pressure range it is a reasonable approximation and allows extrapolations to  $10^{-4}$  GPa for **1** and **2a**. These extrapolated values ( $1.67(2)$  and  $1.73(5) \text{ mm s}^{-1}$  for **1** and **2a**, respectively) are quite close to the atmospheric pressure q.s. for **3**, to the q.s. at 78 K for **1** and **2a**, and to the q.s. at 4 K of  $1.64 \text{ mm s}^{-1}$  for **2a**.

These results confirm the explanations of the dynamic behavior in the literature.<sup>4,7</sup> The fact that the extrapolated q.s. value of **2a** (range  $1.67\text{--}1.78 \text{ mm s}^{-1}$ ) is higher than the q.s. value of the outer doublet at  $10^{-4}$  GPa ( $1.556(4) \text{ mm s}^{-1}$ ) is especially pleasing since it points to the fact that the so-called

(15) Gibb, T. C. *Principles of Mössbauer Spectroscopy*. Chapman and Hall Ltd, London, 1976; pp 30–36.

(16) Tjon, J. A.; Blume, M. A. *Phys. Rev.* **1968**, *165*, 456.

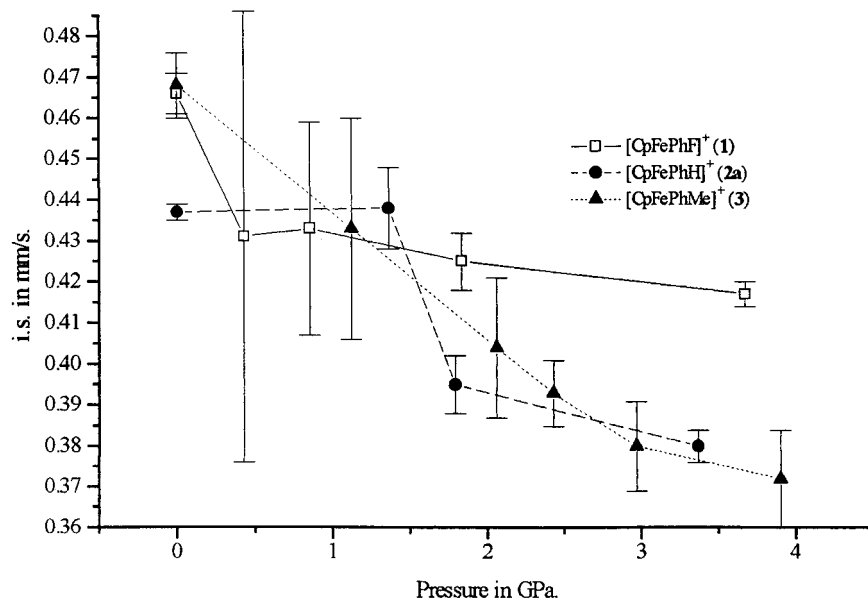


Figure 5. Plot of i.s. against pressure for **1**, **2a**, and **3**.

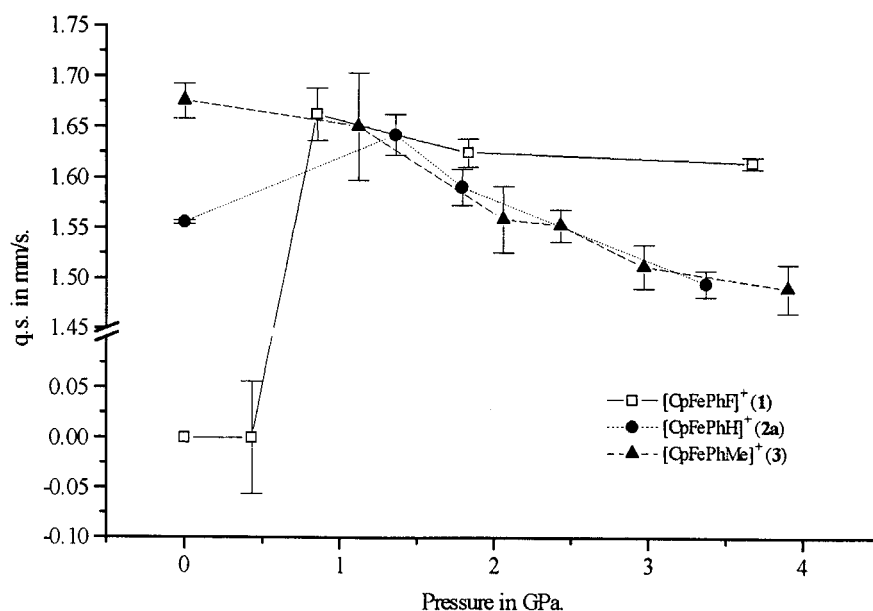


Figure 6. Plot of q.s. against pressure for **1**, **2a**, and **3**.

“static site”<sup>6</sup> is actually undergoing reorientation, and this is the first evidence for this observation.

The relative decrease of the stationary sites with increasing pressure is more pronounced in **2a** than that observed for **1**. In fact the decrease of q.s. with pressure for **2a** above 1.36 GPa is almost identical to that of **3**.

Pressure may be expected to reduce anion–cation distances and reduce the individual sizes of the anions and cations. Changes in the anion size would not directly affect the <sup>57</sup>Fe Mössbauer spectra; changes in anion–cation distance would be equivalent to changes in the “lattice contribution”<sup>14a</sup> to the EFG, which has been considered a minor effect in coordination complexes.<sup>15</sup> Thus the decreasing q.s. is assigned largely to the “valence contribution”,<sup>14a</sup> which arises from variations in the iron 3d-orbital populations controlled by the ligand environment. This has been thoroughly discussed for iron sandwich compounds,<sup>17</sup> and it has been shown that, from a particular starting point, increased ligand to metal bonding in the e<sub>1</sub> orbital

system and increased metal to ligand back-bonding in the e<sub>2</sub> orbital system both cause a decrease in q.s. We therefore suggest that the decrease in q.s. caused by pressure is related to the reduction of cation size, *i.e.*, the ring ligands are forced nearer to the iron giving enhanced overlaps in both e<sub>1</sub> and e<sub>2</sub> orbital systems. Reduction of the ring size is not considered important as C–C bonds are inherently stiffer than the Fe–ring bonds.<sup>18</sup> In further support, it is noted that pressure affects the optical spectra of ferrocene in a way that suggests significant reduction of the Fe–ring distance.<sup>10</sup>

Figure 9 shows plots of q.s. against i.s. (for the same data set as Figure 8) of **1**, **2a**, and **3**. Clearly for **2a** and **3** the range of the pressure-induced changes in both these parameters is greater than those of **1**. From this we conclude that the decrease in i.s. with pressure for **1** is significant and is due to an increase in electron density at the nucleus. Thus as mean ring to metal distances decrease there is more s electron density at the nucleus. We suggest that this effect is more noticeable in **3** because this

(17) Houlton, A.; Miller, J. R.; Roberts, R. M. G.; Silver, J. *J. Chem. Soc., Dalton Trans.* **1990**, 2181.

(18) Adams, D. M.; Williams, D. *J. Phys. Chem. Solids* **1980**, *41*, 1073.

**Table 2.** Calculated Site Populations for **1**<sup>a</sup>

	$q/\text{mm s}^{-1}$	$p_z$	$\theta/\text{deg}$
“outer” doublet	1.556	0.933	15
“inner” doublet	0.747	0.621	38
	-0.747	0.045	77.5

<sup>a</sup>  $Q_0 = 1.73 \text{ mm s}^{-1}$ .

lattice is tighter as evidenced by the fact that the iron “sandwich” is stationary on the Mössbauer time scale at ambient temperature and pressure. Thus the rings that are therefore in closer proximity to the lattice are more immediately affected by applied pressure.

Finally the cation **1** is less sensitive than the other two cations to changes in pressure for both i.s. and q.s. suggesting that the cation of **1** has inherently more “rigid” bonding, *i.e.*, the rings are in a deeper potential well *vis-à-vis* the Fe–ring distance.

**(c) A Reassessment of the Dynamic Model (for 2a).** It is noted above that the “inner” q.s. of **2a** in the room temperature phase is less than half of the “outer” q.s.<sup>5</sup> It is also the case that the “outer” q.s. ( $1.556(3) \text{ mm s}^{-1}$ )<sup>1</sup> is less than the 78 K value ( $1.67(1) \text{ mm s}^{-1}$ ), less than the 4 K value ( $1.64 \text{ mm s}^{-1}$ ),<sup>9</sup> and less than the extrapolated value ( $1.73(5) \text{ mm s}^{-1}$ ) described in section b. The peaks of both of the quadrupole doublets are sharp and do not show the broadening expected of a dynamic process with a rate of the order  $10^7$ – $10^8 \text{ s}^{-1}$ . It is here suggested that both of the doublets at room temperature and pressure are subject to fast dynamic processes, causing reduction of the q.s. In particular the sharpness of the “outer” doublet is due to fast motion, not to the site being stationary.

Following Fitzsimmons and Marshall,<sup>6</sup> the system under ambient conditions is considered as two cation sites, which are crystallographically distinguishable. In both sites the principal axis of the EFG is considered to move at random between three orthogonal directions termed Z, X, Y. (These do not have to correspond to any particular crystal axis.) Each direction has a population  $p_z, p_x, p_y$ . If the jumping rate is much faster than the static q.s. expressed in  $\text{s}^{-1}$  (energy/h), then the observed Mössbauer spectrum is the population-weighted mean of the EFG tensors corresponding to these directions. Use is made of the well-known result that an EFG of value  $Q_0$  relaxing rapidly between two perpendicular directions (X and Y) gives a mean EFG of  $-Q_0/2$  with the principal axis in the Z direction. For the particular case of  $p_x = p_y$ , we then have

$$q_{\text{mean}} = (p_z - 1/2 p_x - 1/2 p_y) Q_0 = (p_z - p_x) Q_0 = (3p_z - 1) Q_0/2$$

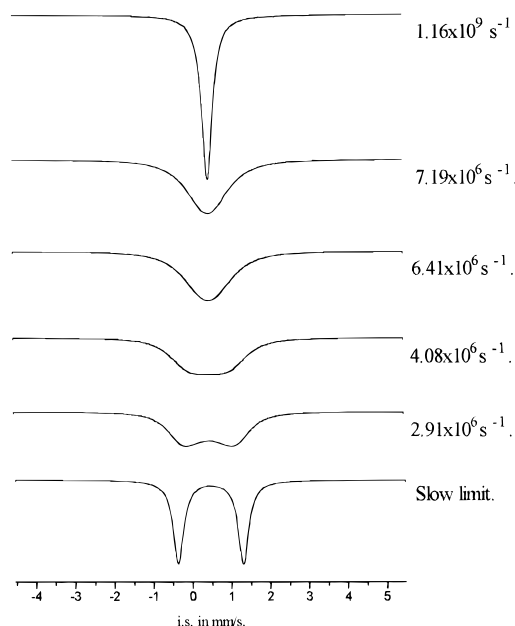
since

$$1 = p_x + p_y + p_z$$

Thus, if  $Q_0$  and  $q$  are known,  $p_z$  may be calculated. The sign of  $Q_0/2$  is generally unknown, but values of  $p_z$  are restricted to  $0 \leq p_z \leq 1$ .

When this simple equation is applied to the “outer” doublet, using the extrapolated value at  $10^{-4}$  GPa as  $Q_0$  and the observed q.s. as  $q$ ,  $q/Q_0$  must be positive to give a positive value for  $p_z$ . When the value of the “inner” q.s. ( $0.747 \text{ mm s}^{-1}$ ) is used, two solutions are obtained depending on the sign of  $q/Q_0$ . The results are collected in Table 2. It can be seen that the narrowing of the “outer” q.s. from the static values corresponds to a small population of X and Y and a large one for Z. Thus what was originally interpreted as a “static site”<sup>6</sup> is in fact in motion.

The value of the “inner” q.s.,  $q/Q_0$  when negative, almost corresponds to the original model of X–Y movement, but with



**Figure 7.** Theoretical Mössbauer spectra for isotropic reorientation. The relaxation rates are given in  $\text{s}^{-1}$ .

the addition of a small Z population. However, when  $q/Q_0$  is positive, there are a relatively large Z and smaller X and Y populations. The sign of  $q/Q_0$  can not be determined from the present data; application of a magnetic field would be necessary. ( $Q_0$  is known to be positive.<sup>5</sup>)

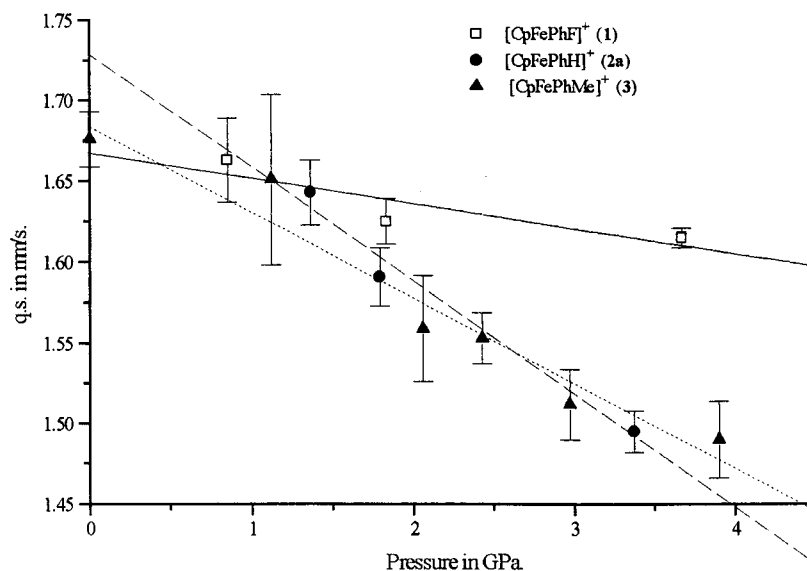
The movements described above are mathematically equivalent to precession, or rotation of the principal axis of the EFG about a fixed direction, with an angle  $\theta$ , between the two axes. By an averaging process of the EFG components over such a movement, it can be seen that

$$q = (3 \cos^2 \theta - 1) Q_0/2$$

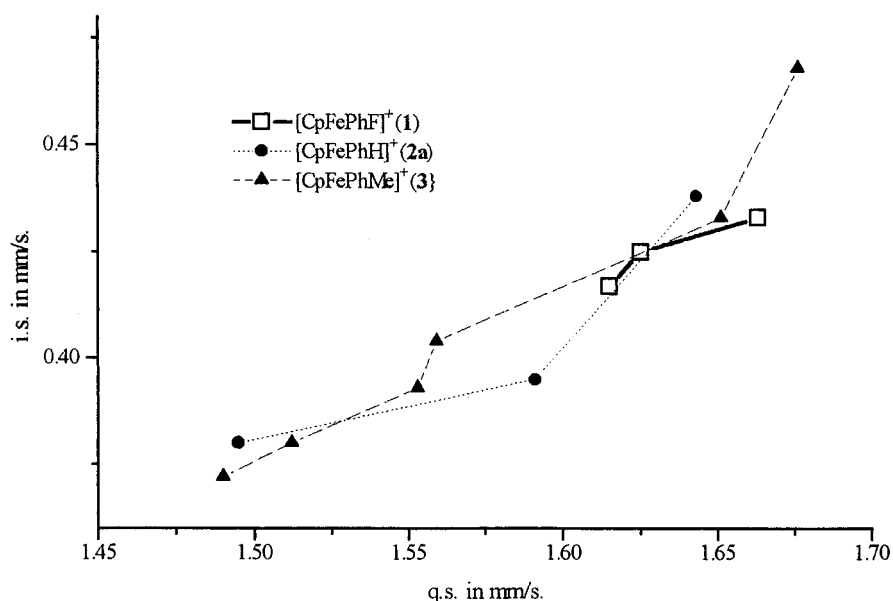
There is thus an equivalence between  $p_z$  and  $\cos^2 \theta$  in the two models. Table 2 also shows the  $\theta$  angles derived. Chemically the precessional movement of the EFG in **2a** is achieved by movement of the ligands. In the case of the outer doublet these rings would wobble slightly so that the axis of the cations moved away from and around its “rest direction”. As a tilt of only  $15^\circ$  is suggested, the rings would be discernible by X-ray diffraction, but individual atoms would not be resolvable.

In the case of the inner doublet the ligand movement is much greater. For the case in which  $q/Q_0$  is negative, the entire cation must rotate, with a slight wobble, about an axis perpendicular to the to the main axis, *i.e.*, it must turn “head over heels”. For positive  $q/Q_0$  the movement is similar to that of the outer doublet, but with a much greater amount of wobble. In either case the rings would not be resolvable by X-ray diffraction, as observed.<sup>10</sup> It is simple to imagine movement of this type being easily arrested by the application of pressure as the amplitudes are quite large. It should be noted that when the motion is arrested, there is no implication that all the cations come to rest with their principal axes in the same direction; it is sufficient that the motion slows to a mean rate  $< 10^6 \text{ s}^{-1}$ , *i.e.*, well below the Mössbauer measurement time scale.

A special case of the precessional model is mentioned here; *viz.*, when  $\theta$  reaches the “magic angle”  $\{\cos^{-1}(1/\sqrt{3})\}$ ,  $q$  becomes zero and the corresponding value of  $p_z$  is  $1/3$ . This is the isotropic reorientation used for the high-temperature phases of **1** and **2a**, but the two models although mathematically equivalent are physically different. The Z, X, Y, population



**Figure 8.** Extrapolated plot of q.s. against pressure for the "stationary" sites of **1**, **2a**, and **3**.



**Figure 9.** Plot of i.s. against q.s. for **1** ( $\square$ ), **2** ( $\bullet$ ) and **3** ( $\blacktriangle$ ). In each series the lowest point is that observed at the highest pressure (3–4 GPa), whereas the highest point is that at the lowest pressure where the cation is considered to be stationary.

model implies random reorientation over all directions with equal probability; the precessional model implies a fixed axis for the precession. The fact that the high-temperature phases have cubic lattices tends to favor the complete spherical rotation description.

## Conclusions

This high-pressure Mössbauer spectroscopy study has been used to (1) arrest motion of a molecular rollerball (**1**) and a molecular rotator (**2a**) on the Mössbauer time scale; (2) allow the extrapolation of experimental q.s. data to give stationary q.s. values at 298 K and  $10^{-4}$  GPa which are consistent with the previous low-temperature data; (3) indicate that the extrapolated q.s. value for **2a** is larger than the experimental "outer" q.s. at ambient temperature showing that the latter site is also dynamic at room temperature and  $10^{-4}$  GPa; and (4) allow explanations of the observed decrease in q.s. of the "stationary" sites with applied pressure to be discussed which suggest that the ring plane to metal distances are reduced by increasing applied pressure.

A simple versatile model has been presented that accounts for all the changes observed in the Mössbauer spectra as functions of both temperature and pressure.

## Experimental Section

**1–3** were prepared using a conventional household microwave oven by the literature method<sup>19,20</sup> and purified on an alumina column using acetone as the eluant. <sup>1</sup>H NMR, <sup>13</sup>C NMR,<sup>4,5</sup> and 78 K Mössbauer<sup>5,21</sup> spectra (at ambient pressure) obtained for all compounds in this work were in agreement with the literature values.

Ambient and high-pressure Mössbauer spectra were recorded in the previously reported apparatus,<sup>22,23</sup> with a starting absorber diameter of 0.5 mm. Hydrostatic pressure was maintained in the DAC using 4:1

- (19) Dabirmanesh, Q.; Roberts, R. M. G. *J. Organomet. Chem.* **1993**, 460, C28.
- (20) Dabirmanesh, Q.; Fernandez, S. I. S.; Roberts, R. M. G. *J. Chem. Soc., Perkin Trans. 1.* **1993**, 743.
- (21) Brown, R. A.; Houlton, A. H.; Howe, S. D.; Roberts, R. M. G.; Silver, J. J. *J. Chem. Soc., Dalton Trans.* **1993**, 3329.
- (22) Hamed, Y.; Hider, R. C.; Silver, J. *Inorg. Chim. Acta* **1982**, 66, 13.
- (23) McCammon, C. A. *Recent trends in high pressure research*; Oxford and IBH: New Delhi, 1982; 824.

ethanol/methanol. The pressure in the DAC was measured using the ruby fluorescence method.<sup>24</sup> Spectra were fitted to Lorentzian line shapes with component areas and widths of quadrupole doublets constrained to be equal. All data are reported referenced to a 25  $\mu\text{m}$  natural iron foil.

Powder X-ray diffraction patterns were recorded using a Phillips PWI 80 X-ray powder diffractometer linked to a PC (Wavelengths  $\alpha_1$  1.540 60  $\text{\AA}$  and  $\alpha_2$  1.544 39  $\text{\AA}$ ). Mössbauer spectral data recorded in this work for **1** to **3** at 78 K for the  $\text{PF}_6$  salts are as follows:

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(24) Barnett, J. D.; Block, S.; Piermarinni, G. J. *Rev. Sci. Instrum.* **1973**, *44*, 1.

**1**, i.s., 0.52(1)  $\text{mm s}^{-1}$ , q.s., 1.68(1)  $\text{mm s}^{-1}$ ,  $\Gamma$ , 0.16(1)  $\text{mm s}^{-1}$ ; **2**, i.s., 0.54(1)  $\text{mm s}^{-1}$ , q.s., 1.77(1)  $\text{mm s}^{-1}$ ,  $\Gamma$ , 0.14(1)  $\text{mm s}^{-1}$ ; **3**, i.s., 0.53(1)  $\text{mm s}^{-1}$ , q.s., 1.72(1)  $\text{mm s}^{-1}$ ,  $\Gamma$ , 0.13(1)  $\text{mm s}^{-1}$ .

**Acknowledgment.** Diamond anvil cell experiments were carried out at the Bayerisches Geoinstitut under the EC "Human capital and mobility—Access to large scale facilities" program (Contract No. ERBCHGECT940053 to D. C. Rubie). The authors wish to thank Dr. Brian Fitzsimmons for his helpful discussion during preparation of this paper.

IC970419Z