How to stop a molecular rotator. Mössbauer spectroscopic studies on (η-benzene)(η-cyclopentadienyl)iron(II) hexafluorophosphate in the presence and absence of high pressure

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Application of a pressure of 1.79 GPa, at room temperature on (η-benzene)(η-cyclopentadienyl)iron(II) hexafluorophosphate is shown to arrest the dynamic reorientation of the cations; the effect of pressure is studied using Mössbauer spectroscopy.

Mössbauer spectroscopy has proved to be a suitable technique to study molecular motion in iron containing compounds such as clathrates of ferrocene[1] and in some iron sandwich compounds.[2–4] These compounds are useful models for molecular rotators/motors. For (η-benzene)(η-cyclopentadienyl)iron(II) hexafluorophosphate **1a**, or hexafluoroarsenate **1b**, and (η-fluorobenzene)(η-cyclopentadienyl)iron(II) hexafluorophosphate **2** it proved possible to study such motion for cases where the electric field gradient (e.f.g.) fluctuates slowly compared to the lifetime of the excited nuclear state (97.81 ns).[2] The theoretical effect of such a slow fluctuation of the e.f.g. has been documented by Tjon and Blume.[5]

The motion of arene cyclopentadienyliron(II) cations may be either isotropic,[3] as in the case of compound **2**, or anisotropic,[2,4] as in the cases of compounds **1a** and **1b**, depending on the nature of the lattice. The temperature at which the movement starts is dependent on the anion.[4]

The isotropic motion of compound **2** starts at about 228 K. (Movement of this kind is distributed evenly through all planes.) This is observed in the Mössbauer spectra as a collapse of the quadrupole splitting (q.s.) into a single line.[3] The motion observed in compounds **1a** and **1b** can be fitted to an anisotropic model.[2,4] In these compounds certain molecules have lower energy barriers to motion in one plane, and thus reorientation occurs preferentially in this plane. The activation energy for these processes can be thought of as containing the energy needed to expand the lattice to allow room for the motion to take place. This type of motion is manifest in the Mössbauer spectrum by the appearance of a second q.s. within the first.[2,4] The crystal structure of compound **1b** showed that the unit cell contains two sets of anions and cations in different sites.[4] One of these is ordered and the other is disordered. The energy barriers to rotation of these sites differ. As the temperature is increased the ions having the lower energy barrier begin to rock and eventually move. This motion changes the direction and magnitude of the e.f.g. and causes the inner q.s. to develop.[4] To date such motion has only been stopped by cooling to a temperature lower than that where the motion starts.

Since increase in temperature causes lattice expansion, we decided to study the effect of pressure on such a compound at a temperature where the motion occurred freely. Compound **1a** was prepared,[6] and pressure was exerted using a diamond anvil cell (DAC).[7]‡ Mössbauer spectra were recorded at room temperature and at atmospheric pressure, then at 0.47, 1.79 and 3.37 GPa.§ The q.s. value at 1.79 GPa is the same as that found in the 77 K (1 × 10^{-4} GPa) spectrum where no motion occurs. At 0.47 GPa the Mössbauer spectrum was poor, which is possibly due to a decrease in the f fraction caused by motion.[1] The Mössbauer data are presented in Table 1, and some representative spectra are shown in Fig. 1.

It can be seen that the isomer shift (i.s.) decreases with pressure, showing an increase in s-electron density at the nucleus with pressure.[8] For the two highest pressure experiments the f factors were high, resulting in a large signal to noise

Table 1 Variation of Mössbauer parameters with pressure for (η-benzene)(η-cyclopentadienyl)iron(II) hexafluorophosphate

P/GPa	i.s./mm s^{-1}	q.s./mm s^{-1}	Γ^{a}/mm s^{-1}
1 × 10^{-4b}			
Site 1	0.43(1)	1.56(1)	0.13(1)
Site 2	0.43(1)	0.75(1)	0.13(1)
1.79 ± 0.08	0.39(1)	1.69(2)	0.22(3)
3.37 ± 0.06	0.38(1)	1.49(1)	0.20(2)

[a] Half width at half height. [b] At 1 × 10^{-4} GPa two iron sites are observed in the spectrum (see text).

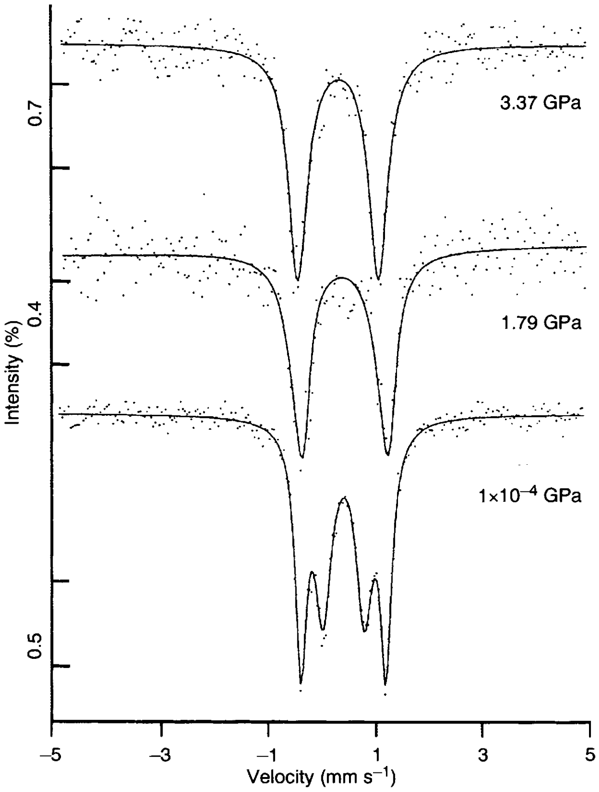

Fig. 1 Mössbauer spectra for (η-benzene)(η-cyclopentadienyl)iron(II) hexafluorophosphate at a range of pressures and 298 K

ratio. We interpret this as evidence that squeezing the lattice limits vibrations and thus has the same effect as lowering the temperature *viz.* 'f' fraction increases. Several other interesting points arise.

(*i*) Only one q.s. with a large splitting is observed. Thus motion has been switched off, on the Mössbauer spectroscopy timescale ($\leqslant$97.81 ns).

(*ii*) At 1.79 GPa the q.s. was 1.69(2) mm s^{-1} which is very close to that observed at 77 K and atmospheric pressure. We interpret this as evidence of pressure-induced lattice contraction, and as others have shown, by low-temperature differential scanning calorimetry, that there is no motion at 77 K we therefore assume that we have in fact stopped the motion completely at 1.79 GPa.[2–4]

(*iii*) At 3.37 GPa the q.s. is seen to decrease to 1.49(1) mm s^{-1}. This decrease may be due to squeezing the aromatic rings closer to the iron atom causing greater back bonding,[9] and/or a deformation of the lattice towards cubic symmetry. Earlier work carried out on ferrocene where there is no dynamic reorientation process at room temperature, showed a reduction in q.s. with increasing pressure,[10] similar to that seen by increasing the applied pressure from 1.79 GPa to 3.37 GPa in this work. However in this work both the q.s. values for the two iron sites in the room temperature spectra at 1×10^{-4} GPa are lower than the initial high pressure (1.79 GPa) q.s. value. Thus even the q.s. value of the non-moving iron site is less than that of the initial high pressure (1.79 GPa) value.

It has proved possible to turn off a naturally occurring molecular motion by the application of pressure. There is no reason why nanotechnology needs to be confined to a single pressure regime. This work demonstrates that pressure may be used to counteract an effect of temperature. Thus a molecular rotator/motor could be controlled by a switched on/off system based on lattice relaxation and restrain (expansion and contraction). To the best of our knowledge, we believe this is the first report of pressure being used to switch off a molecular rotator.[11,12]

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Footnotes

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‡ (η-Benzene)(η-cyclopentadienyl)iron(II) hexafluorophosphate was prepared by a literature method[6] and purified by chromatography on an aluminium oxide column using acetone as the eluent. ^{1}H NMR {[$^{2}H_6$]-acetone, $SiMe_4$}: δ 5.23 (5 H, C_5H_5), 6.47 (6 H, C_6H_6); ^{13}C NMR {[$^{2}H_6$]acetone, $SiMe_4$}, δ 67.06 (C_5H_5), 78.81 (C_6H_6). Mössbauer spectroscopic data (77 K), i.s. = 0.52(1) mm s^{-1}, q.s. = 1.68(1) mm s^{-1}, Γ = 0.16(1) mm s^{-1}. Ambient[13] and high-pressure[14] Mössbauer spectra were recorded by a previously reported method. A 4 : 1 methanol–ethanol mixture was used to maintain hydrostatic pressure. The pressure in the cell was measured using the ruby fluorescence method.[15] Spectra were fitted to Lorentzian line shapes with component areas and widths constrained to be equal. All spectra are referenced to a 25 μm natural iron foil.

§ 1 GPa = 10 kbar = 10 000 atm.

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