

MANIFESTATION OF THE JAHN-TELLER EFFECT IN THE EPR SPECTRA OF NAPHTHALENECYCLOPENTADIENYLIRON

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Summary

The anisotropic EPR spectrum of $C_{10}H_8FeC_5$ undergoes Jahn-Teller effect induced transition to the isotropic spectrum at 123 K in the solid phase. Iron atom tunnelling between the naphthalene benzene nuclei may serve as a model of motion averaging g -factor anisotropy.

The model is confirmed by studies of the α - $MeC_{10}H_7FeC_5H_5$ and β - $FC_{10}H_7FeC_5H_5$ EPR spectra. The latter two compounds show splitting of the g_{\parallel} signals into two components corresponding to dissimilar isomers at temperatures above 77 K. The isomers differ in the mode of iron bonding with the substituted and unsubstituted naphthalene nuclei.

EPR manifestations of the Jahn-Teller effect in coordination compounds have been summarized in references 1 and 2. The importance of this effect for sandwich compounds has been discussed [3].

We have observed an anomalous temperature behaviour in the EPR spectrum of naphthalenecyclopentadienyliron, $C_{10}H_8FeC_5H_5$ (I): the anisotropic spectrum ($g_{\parallel} = 2.09$, $g_{\perp} = 2.006$) underwent transformation into the isotropic one, $\bar{g} = 1/3 (g_{\parallel} + 2g_{\perp})$, at 153 K. Averaging of the g factor anisotropy with increasing temperature was observed in other arenecyclopentadienyliron complexes obtained by reduction of the corresponding cations with sodium metal in 1,2-dimethoxyethane at temperatures near the solvent melting point, 203 K [4]. We attributed these anomalies to a transition from the static to the dynamic Jahn-Teller effect, although the type of motion involved was not determined. The possibility of a Jahn-Teller effect in iron arenecyclopentadienyl complexes arises from the quasi-degenerate nature of the d^7 iron state, $a_{1g}^2 e_{2g}^4 e_{1g}^1$, in which the e_{1g}^* level of the unpaired d_{xz} , d_{yz} electron is split by low-symmetry interactions with the arene ligand [4].

This paper describes the results of a study on the nature of the motion causing averaging of the g -factor anisotropy.

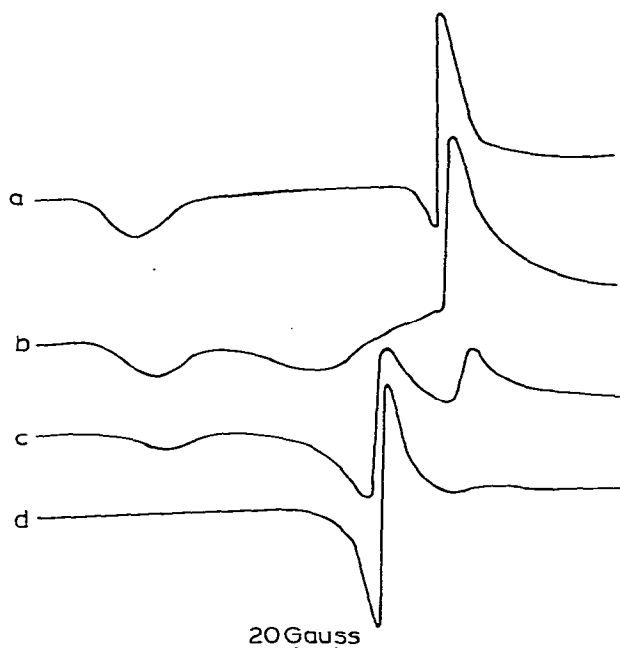


Fig. 1. EPR spectra of $C_{10}H_8FeC_5H_5$ at various temperatures, a, 77 K; b, 113 K; c, 143 K; d, 153 K.

The EPR spectra of I obtained at various temperatures are shown in Fig. 1. The isotropic spectrum is observed in the range 113 to 293 K. The particular feature of the transition in I is the appearance of both isotropic and anisotropic spectra simultaneously, whereas unquenching of rotational degrees of freedom in other complexes upon melting of 1,2-dimethoxyethane leads first to the dis-

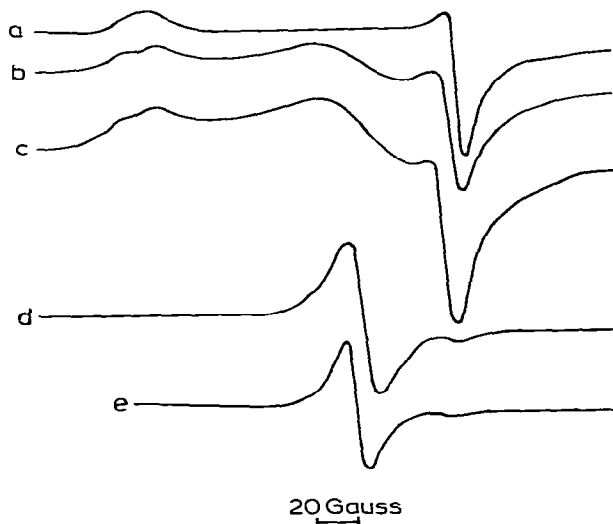


Fig. 2. EPR spectra of $\alpha\text{-Me}C_{10}H_7FeC_5H_5$ at various temperatures, a, 77 K; b, 133 K; c, 143 K; d, 163 K; e, 173 K.

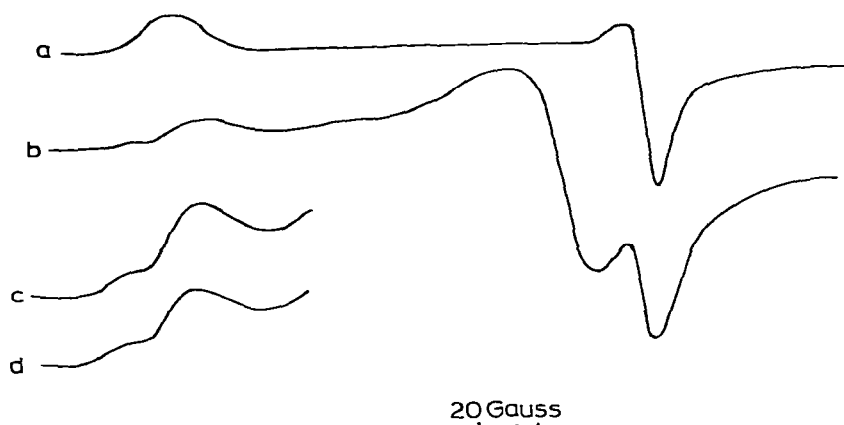
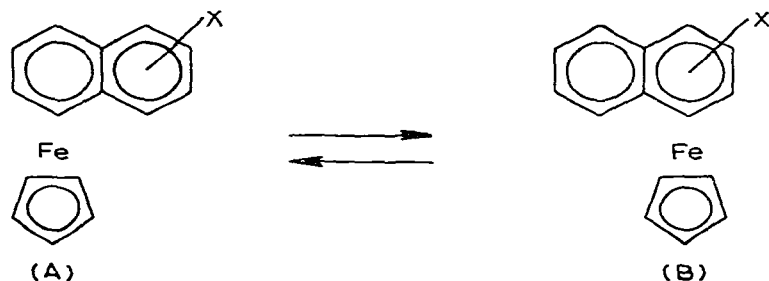


Fig. 3. EPR spectra of $\beta\text{-FC}_{10}\text{H}_7\text{FeC}_5\text{H}_5$ at various temperatures a, 77 K; b, 153 K; c, 153 K; d, 158 K. Solvents: 1,2-dimethoxyethane (1), tetrahydrofuran (2). Cation reduction temperature: 173 K.

appearance of the g_{\parallel} and g_{\perp} signals caused by signal broadening, and then to the appearance of the signal corresponding to \bar{g} . The EPR spectrum of $\text{C}_{10}\text{H}_8\text{-FeC}_5\text{H}_4\text{C}_2\text{H}_5$ did not differ markedly from that of I. Figures 2 and 3 show the EPR spectra of $\alpha\text{-MeC}_{10}\text{H}_7\text{FeC}_5\text{H}_5$ (II) and $\beta\text{-FC}_{10}\text{H}_7\text{FeC}_5\text{H}_5$ (III). These are similar to the spectrum of I at 77 K. Temperature rise leads to splitting of the g_{\parallel} signal for II and III into two components.

We explain the appearance of two signals with different g_{\parallel} values by the occurrence of two isomers, as the g_{\parallel} value is strongly dependent on the nature of the arene ligand [4]. Comparison with the spectrum of I shows that the spectra of II and III observed at 77 K correspond to the isomer A. As is seen



from Figs. 2 and 3, the signal corresponding to the lower g_{\parallel} value is stronger than that corresponding to the higher g_{\parallel} value in both compounds. A lower g_{\parallel} value implies a larger e_{1g}^* level splitting and the corresponding isomer A is thermodynamically more stable than B [4]. The $g_{\parallel}^A - g_{\parallel}^B$ difference gives a ΔE_{AB} value of about 200 cm^{-1} . According to the NMR spectra of $\beta\text{-MeC}_{10}\text{H}_7\text{FeC}_5\text{H}_5$ and $\alpha\text{-FC}_{10}\text{H}_7\text{FeC}_5\text{H}_5$ the A/B ratio is equal to 55/45 for the first compound whereas only isomer A occurs for the second one [5]. The anisotropic to isotropic spectrum transition for II and III occur at a somewhat higher temperature than for I. The splitting of the g_{\parallel} signals into two components is observed at temperatures below the transition point.

In Fig. 4, a plot of the $\text{C}_{10}\text{H}_8\text{FeC}_5\text{H}_5$ potential energy vs. the coordinate

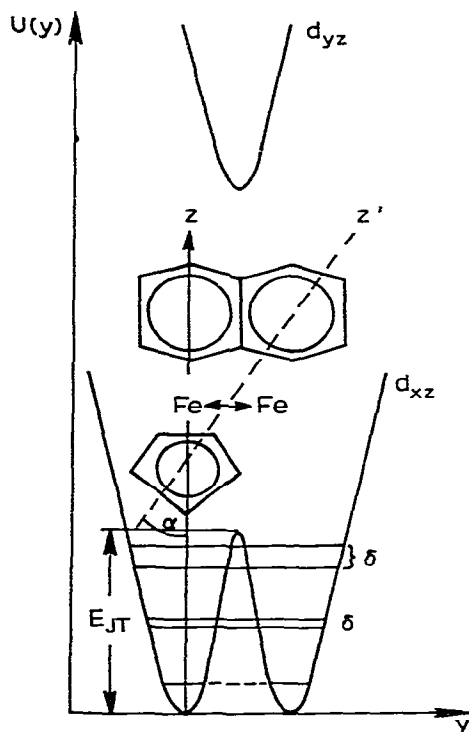


Fig. 4. Potential energy curve for $C_{10}H_8FeC_5H_5$.

describing the displacement of the Fe atom from the position symmetrical with respect to both naphthalene aromatic nuclei is given, and the corresponding Jahn-Teller stabilization energy, ΔE_{JT} , is shown. For simplicity, Fe is drawn opposite the centre of one of the nuclei in Fig. 4, though the actual displacement may be smaller than that. Theoretically [1,2], systems of this type should exhibit tunnel splitting whose magnitude determines the frequency of transitions between the potential surface minima. The splitting is small for the ground vibrational state and increases on going to the excited states.

Shifts of the iron atom between the naphthalene nuclei result in rotation of the molecular z axis about the magnetic field by some angle. Rotations of the z axis rather than its vibrations with respect to the equilibrium position are probably due to additional rotations of the naphthalene ligand about the molecular axis. Simultaneous observation of both the isotropic and anisotropic spectra is interpreted as being indicative of the absence of tunnelling in the ground state (the anisotropic spectra) and fast transitions between the energy minima in vibrationally excited states (isotropic spectra) populated at the higher temperatures [7]. This model requires that the ground state reverse life time, $1/\tau$, be smaller than the $(g_{\parallel} - g_{\perp})H\gamma_e$ value. The validity of the relation $1/\tau \ll (g_{\parallel} - g_{\perp})H\gamma_e$ follows from the observation of closely spaced g_{\parallel} (A) and g_{\parallel} (B) signals over the whole temperature range where the anisotropic spectrum is observed.

To estimate the excitation energy to states characterized by effective tunnel-

ling, we have determined the isotropic signal temperature dependence by graphically integrating the EPR spectra, and also by using the corresponding formula [6]. The logarithmic dependence of the isotropic signal on reverse temperature gave a value of 300 cm^{-1} . This value may be taken to represent the energy of one or several vibrational quanta in one of the potential energy minima. An analysis of the Jahn-Teller effect active vibrations of sandwich molecules has been carried out previously [3].

The isotropic spectrum line width, $(\Delta H_0 + \Delta H)$, varies in the spectrum of $\text{C}_{10}\text{H}_8\text{FeC}_5\text{H}_5$ from 25 Gauss at 130 K to 10 Gauss at 153 K. The intrinsic line width of the anisotropic spectrum ΔH_0 , is equal to 10 Gauss at 77°K. If the broadening, ΔH , in the isotropic spectrum from the intrinsic line width, ΔH_0 , is determined by the tunnel splitting, $\delta = h\omega$, it may roughly be estimated from the relation

$$\Delta H = \gamma_e [(g_{\parallel} - g_{\perp})H]^2 / \omega$$

which gives for δ a value of 1 to 3 cm^{-1} .

Analysis of the experimental data [4] shows that splitting of the e_{1g}^* level depends on the donor-acceptor interactions between the arene ligand and the positively charged iron atom.

The results obtained in this work indicate that the Jahn-Teller effect on the g -factor value and splitting of the e_{1g}^* level should also be taken into consideration. The dynamic nature of the Jahn-Teller effect determines the transitions of the metal atom between the naphthalene nuclei. Such transitions are not observed in the complexes in the ${}^1A_{1g}$ state [5,8].

In addition to the arene complexes having second order symmetry axes studied earlier [4], we have studied a paramagnetic complex containing the diphenyl ligand, $\text{C}_6\text{H}_5\text{—C}_6\text{H}_5$ ($g_{\parallel} = 2.25$ and $g_{\perp} = 2.006$), which, however, showed no noticeable differences from the other complexes.

Most EPR studies of the Jahn-Teller effect have dealt with crystals. Studies of frozen solutions put forth the problem of interaction between the molecule studied and the environment. The observed averaging of g -factors by the tunnelling mechanism in $\text{C}_{10}\text{H}_8\text{FeC}_5\text{H}_5$ leads to actual rotations of the molecule, which differs from pseudorotations in crystals involving shifts of distortions over the complex axes [1,2]. One may suggest that tunnelling induced rotations of the $\text{C}_{10}\text{H}_8\text{FeC}_5\text{H}_5$ molecule create a cavity in a frozen solvent having some free volume.

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