^{57}Fe Mössbauer Parameters of Two Crystal Polymorphs of Fc$^+$AsF$_6^-$ and the Sign of the Quadrupole Splitting in the Ferrocenium Ion

Rolfe H. Herber,[*,a] **Israel Nowik,**[a] **Dario Braga,**[b] **and Marco Polito**[b]

[a]*Racah Institute of Physics, the Hebrew University, 91904 Jerusalem, Israel*
[b]*Department of Chemistry "G.Ciamician" University of Bologna, 40126 Bologna, Italy*

Temperature-dependent ^{57}Fe Mössbauer effect spectroscopy has been used to characterize the hyperfine and dynamical properties of the metal atom in two crystallographic forms of ferrocenium hexafluoroarsenate. The temperature dependence of the recoil-free fraction and the spin-lattice relaxation rates have been determined over the interval 89<T<300 K and shows a small difference between the two crystallographic forms. The sign of the quadrupole splitting parameter in the Fc$^+$ cation has been elucidated in a transverse magnetic field experiment at room temperature.

1. Introduction

Salts of the ferrocenium ion, Fc$^+$, were among the first organometallic compounds characterized by Mössbauer effect (ME) spectroscopy,[1,2] and its hyperfine parameters have played a central role in arriving at the correct description of the bonding interaction between the metal atom and its ligands. It is well known that this ion can exhibit polymorphism in the solid state. In a recent study, Braga et al.[3,4] have described the successful isolation of both monoclinic (M) and trigonal (T) Fc$^+$AsF$_6^-$ using the technique of heteromolecular seeding. The two polymorphs have distinctly different crystallographic properties. The T form exists in space group $P3_121$ with three formula units per unit cell, whereas the M form exists in space group $P2_1$/c with Z=4. Both of these crystallographic modifications are blue. The only other crystallographic study reported in the literature is that of Fc$^+$SbF$_6^-$, a deep red compound reported by Hendrickson et al.[5]

In the present study, temperature dependent ^{57}Fe ME spectroscopy has been used to determine the hyperfine parameters of the M and T form of Fc$^+$AsF$_6^-$ and elucidate the metal atom dynamics in the two forms. In addition, a room temperature transverse magnetic field has been applied to Fc$^+$AsF$_6^-$ to further elucidate the sign of the quadrupole hyperfine interaction in the cation.

2. Experimental

Samples. Microcrystalline powder samples of the M and T form of the subject compounds were prepared as previously reported [3,4] by the Bologna group, mixed with BN to assure random crystallite orientation, and transferred to plastic sample holders. These, in turn, were mounted in a suitable cryostat and examined in transmission geometry as a function of temperature as described earlier.

ME Spectroscopy. The ME transmission spectroscopy was carried out using a ^{57}Co in Rh source at room temperature as previously detailed.[6] Temperature monitoring and control over the period of data accumulation (typically 7 to 20 hours) showed that the reported temperatures were constant to better than ±0.2 K. Spectrometer calibration was effected using a 20 mg/cm^2 α-Fe foil at room temperature, and all isomer shifts

are reported with respect to the centroid of such spectra.

Magnetic Field Experiments. Transmission geometry experiments in a transverse magnetic field of 2.13 T were performed on a finely powdered sample of Fc$^+$AsF$_6^-$ using a Newport Instruments Model 369 electromagnet slightly above room temperature (due to resistive magnet heating), with a current of 6–7 ampers at 55 volts. The magnet gap was ~ 8 mm and the powdered sample was confined in a brass sample holder having an area of 6×10 mm^2.

3. Results and Discussion

Variable temperature experiments. a representative ME spectrum of the M form of Fc$^+$AsF$_6^-$ at room temperature (~ 296 K) is shown in the upper trace of Figure 1 and is typical of spectra showing spin-lattice relaxation, as reported earlier.[7] The ME spectra of Fc$^+$PF$_6^-$ have qualitatively the same appearance, and the data analysis was carried out on the two forms of the hexafluoroarsenates, assuming a simple spin-lattice relaxation resonance. The temperature dependence of the isomer
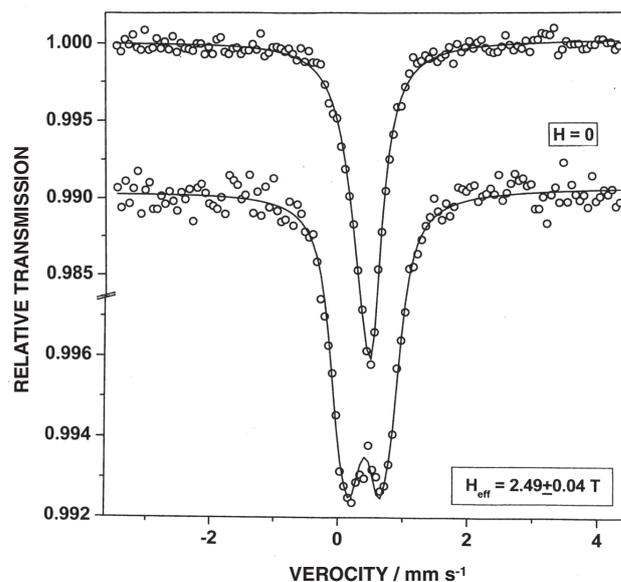

Figure 1. ^{57}Fe Mössbauer spectra of the monoclinic form of Fc$^+$AsF$_6^-$ at room temperature. The upper trace is in zero external field, the lower trace in a 2.13 T transverse magnetic field. The isomer shift scale is with respect to the centroid of a room temperature α-Fe absorber spectrum in identical geometry.

*Corresponding author. E-mail: HERBER@VMS.HUJI.AC.IL Fax:972 2 6586347

shifts (IS) for the two $Fc^+AsF_6^-$ forms is summarized graphically in Figure 2 and shows that this parameter is the same for both forms within experimental error. The temperature dependencies of the recoil-free fraction, which scales directly with the temperature dependency of the area under the resonance curve for an optically "thin" absorber, are shown in Figure 3. Both data sets show curvature over the accessible temperature range, but the data suggest a slightly "softer" lattice (as deduced from $-d\ln A/dT$ of the iron atom) for the T form as compared to the M form. However, not wishing to over-interpret the ME data, it is worth noting that the Fe–ring carbon bond distances at 293 K are identical (within experimental error) for the M form (2.080 ± 0.018 Å) and the T form (2.079 ± 0.008 Å) as extracted from the X-ray crystallographic data.

The collapse of the well-resolved quadrupole splitting in the parent ferrocene [QS at room temperature = 2.41(2) mm s^{-1}] when the neutral compound is subjected to a one-electron oxidation has been reported extensively in the literature.[8,9] The QS hyperfine interaction in the $Fc^+AsF_6^-$ cation is clearly negative [QS = $-0.133(12)$ mm s^{-1}], as deduced from the χ^2 values obtained in the fitting procedure. The broad resonance line envelope observed for the Fc^+ cation is due to spin lattice relaxation, and a relative relaxation rate for the M and T forms of the hexafluoroarsenate salt can be calculated using spin 1/2 relaxation theory[10] to fit the spectra. Such relaxation rates are only relative since the magnitude of the magnetic hyperfine field due to the unpaired electron is not known. The data, summarized in Figure 4 suggest both a temperature-dependent spin-lattice relaxation rate, as observed earlier, as well as a slightly faster rate for the T form than for the M form, although the error limits, especially at the higher temperature, make this conclusion somewhat tenuous.

ME spectra of $Fc^+BF_4^-$ (no crystallographic form specified) were reported in an early study by Zahn et al.[1] who reported an IS of 0.25 ± 0.04 and a QS of 0.37 ± 0.04 mm s^{-1} at room temperature. Despite the employment of a ^{57}Co in stainless steel (Sandvik 2R2) source, these authors were able to resolve the broad resonance line envelope into two components, with the line at lower velocity having the greater intensity. In the present study, the zero-field ME spectrum of $Fc^+BF_4^-$ was analyzed using a relaxation algorithm, employing the Nowik-Wickman Mössbauer spectra relaxation formalism[11] and resulted in a value of IS=0.400 ± 0.006 and a QS of -0.133 ± 0.012 mm s^{-1} at room temperature, in only modest agreement with the earlier results. The sign of the QS is consistent with those reported earlier in related ferrocenium cations.[12]

The lower trace of Figure 1 shows the ME absorption spectrum of the M form of $Fc^+AsF_6^-$ in a transverse magnetic field using the data analysis algorithm which has recently been developed in this laboratory.[13] The QS is negative in the cation, as has been observed for similar ferrocenoid complexes,[13] and the effective magnetic field is larger than the nominal applied field (determined from similar studies with diamagnetic complexes) by $H_{eff}-H_{ext} = 3.6$ kOe. The induced hyperfine field is produced by the electron vacancy in the 3d electron shell as has been reported in other nominally Fe(III) complexes.[14] This induced hyperfine field is given by $H_{eff}-H_{ext} = (\mu_B H_{ext}/k_B T) H_{hf}$, which yields $H_{hf} = +720$ kOe. Such a positive large field is generally interpreted[15] in terms of orbital contributions to the hyperfine field acting on the nucleus.

4. Summary and Conclusions

Two crystallographically distinct forms of ferrocenium hexafluoroarsenate have been studied by temperature-dependent ^{57}Fe ME spectroscopy to elucidate the influence of the crystal form on the hyperfine and dynamical parameters of the iron atom. Within experimental error, the IS parameter is the same for both forms over the temperature interval $87<T<295$

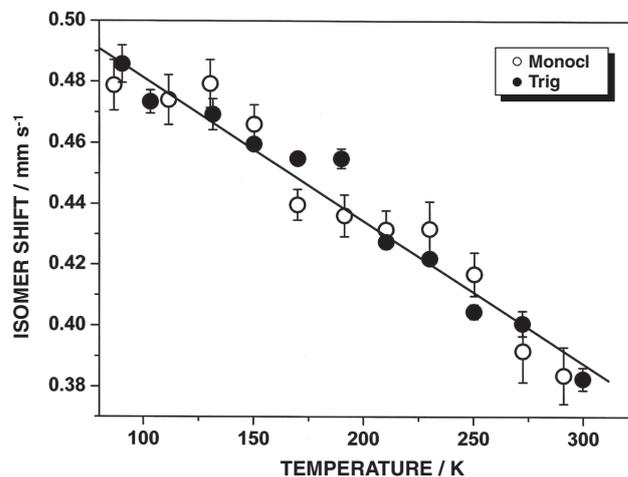**Figure 2.** The temperature dependence of the isomer shift for the T form (filled data points) and the M form (open data points) of $Fc^+AsF_6^-$.
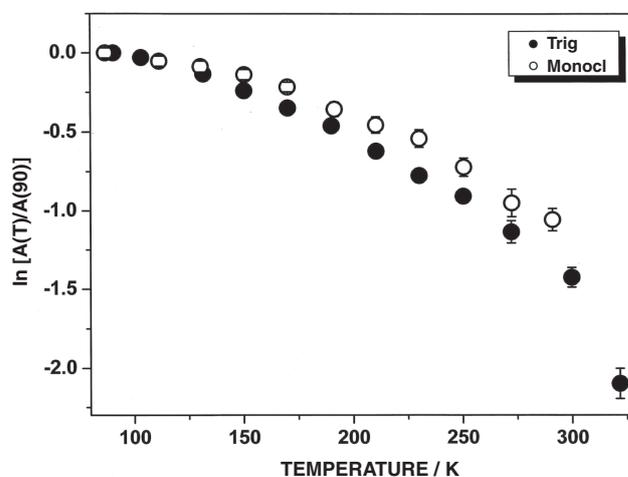

Figure 3. The temperature dependence of the recoil-free fraction (normalized to the 90 K data points) for the T form (filled data points) and M form (open data points) of $Fc^+AsF_6^-$.
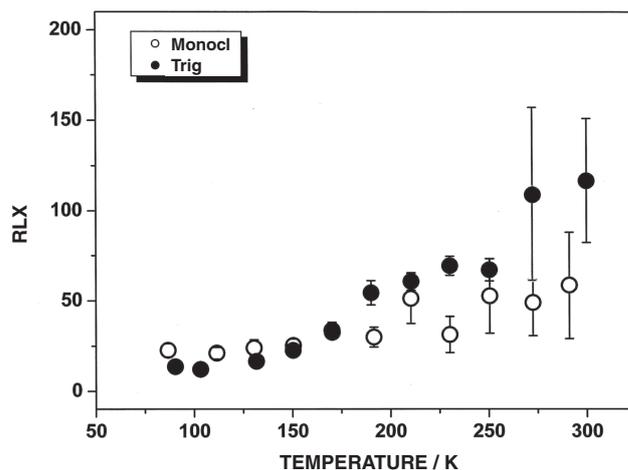

Figure 4. Temperature dependence of the spin-lattice relaxation rates for the two polymorphic forms of $Fc^+AsF_6^-$. The data are normalized to the 90 K data points as discussed in the text.

K, but the temperature dependence of the recoil-free fraction and the spin-lattice relaxation rate appear to differ between the two forms. The sign of the quadrupole splitting in the monoclinic form is negative, in contrast to its positive sign in the neutral (diamagnetic) precursor.

57Fe Mössbauer Parameters of Two Crystal Polymorphs

J. Nucl. Radiochem. Sci., Vol. 7, No. 1, 2006 **15**

References

(1) U. Zahn, P. Kienle, and H. Eicher, Z. Phys. **166**, 220 (1962).
(2) R. H. Herber and G. K. Wertheim, *The Mössbauer Effect* (2nd. Int. Conf. Saclay, France, Sept. 1961); G. K. Wertheim and R. H. Herber, J. Chem. Phys. **9**, 2106 (1963) and references therein.
(3) D. Braga, G. Cojazzi, D. Paolucci, and F. Grepioni, Chem. Commun. **38**, 1 (2001).
(4) D. Braga, G. Cojazzi, D. Paolucci, and F. Grepioni, Cryst. Eng. Comm. **3**, 159 (2001).
(5) D. Hendrickson, A. L. Rheingold, and M. B. Allen, private comm. to Cambridge Crystallographic Data Centre, 1996.
(6) R. H. Herber, A. R. Kudinov, P. Zanello, I. Nowik, D. S. Perekalin, V. I. Meshcheryakov, K. S. Lyssenko, M. Corsini, and S. Fedi, Eur. J. Inorg. Chem. *in print.*
(7) I. Nowik and R. H. Herber, Inorg. Chim. Acta **310**. 191 (2000).
(8) R. L. Collins, J. Chem. Phys. **42**, 1072 (1965).
(9) N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy*, Chapman Hall Ltd. London, 1971, p 233 and references therein.
(10) H. H. Wickman and G. K. Wertheim. *Chemical Applications of Mössbauer Spectroscopy*, Eds. V. I. Gol'danskii and R. H. Herber, Academic Press, New York, 1968, p 548 and references therein.
(11) I. Nowik and H. H. Wickman, Phys. Rev. Lett. **17**, 949 (1966); see also the discussion in N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy*, Chapman Hall Ltd. London, 1971, p 72 and references therein.
(12) H. Schottenberger, K. Wurst, U. J. Griesser, R.K.R Jetti, G. Laus, R. H. Herber, and I. Nowik, J. Am. Chem. Soc. **127**, 6795 (2005).
(13) I. Nowik and R. H. Herber, to be published.
(14) K. Ono, M. Shinohara, A. Ito, N. Sakai, and M. Suenaga, Phys. Rev. Lett. **24**, 770 (1970).
(15) H. Andres, E. L. Baminaar, J. M. Smith, N. A. Eckert, P. C. Holland, and E. Münck, J. Am. Chem. Soc. **124**, 3012 (2002).