# Interpretation of Experimental Mössbauer Quadrupole Splittings of Iron Pentacyanide Complexes Using Molecular Orbital Theory*

Alfred Trautwein

Fachbereich Angewandte Physik, Universität des Saarlandes, Saarbrücken, W.-Germany

Frank E. Harris

Department of Physics, University of Utah, Salt Lake City, Utah, USA

Istvan Dézsi

Central Research Institute for Physics, Budapest, Hungary

Semiempirical self-consistent-field molecular-orbital calculations are carried out for six iron-pentacyanide complexes and are used to interpret their experimental Mössbauer quadrupole splittings. Probable orientations are identified for the $C_6H_5^-$ and $NO_2^-$ groups in $Fe(CN)_5NOC_6H_5^{-3}$ and $Fe(CN)_5NO_2^{-4}$. Calculations on $Fe(CN)_5NO^{-2}$ and $Fe(CN)_5NO^{-3}$ can simultaneously be brought into agreement with experiment by reparametrization to make the NO group more positively charged. All the calculations indicate the importance of including all the Fe 3d and 4p orbitals in the calculations and of considering neighboring-atom effects.

The present communication describes the interpretation of experimental Mössbauer quadrupole splittings in several iron-pentacyanide complexes, using theoretical results derived from semiempirical self-consistent-field molecular-orbital calculations. The calculational methods have previously been reported in detail [1] and have been applied to the Mössbauer spectra of a set of iron-oxygen complexes [2]. The compounds presently under study include the diamagnetic clusters $Fe(CN)_5NOC_6H_5^{-3}$, $Fe(CN)_5NO_2^{-4}$, $Fe(CN)_5H_2O^{-3}$, $Fe(CN)_5NH_3^{-3}$, $Fe(CN)_5NO^{-2}$, and the paramagnetic $(S = 1/2)$ $Fe(CN)_5NO^{-3}$. All these compounds exhibit covalent bonding to varying degrees and therefore may appropriately be handled by methods based on molecular-orbital theory rather than by crystal-field methods.

The experimental quadrupole splittings of all the above compounds are temperature-independent over a wide temperature range, and we therefore felt justified in limiting our calculations to self-consistent-field studies which ignore the effect of low-lying excited electronic states. From the calculated electronic structures we determined quadrupole splittings, including both the effect of the

field gradient along the quantization axis, $V_{zz}$, and the effect of departures from axial symmetry as described by the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. We included contributions from the Fe valence-electron distribution and from other atoms, as indicated by Eqs. (1)–(3):

$$\Delta E_Q = \frac{1}{2} e Q V_{zz} \left(1 + \frac{1}{3} \eta^2\right)^{\frac{1}{2}} \tag{1}$$

$$V_{zz} = e \left\{ (1 - R)_{3d} \langle r^{-3} \rangle_{3d} \sum_{3d} P_{3d,3d} f_{3d} \right.$$
$$+ (1 - R)_{4p} \langle r^{-3} \rangle_{4p} \sum_{4p} P_{4p,4p} f_{4p} \tag{2}$$
$$\left. + (1 - \gamma_\infty) \sum_a \frac{q_a}{e} (3z_a^2 - r_a^2)/r_a^5 \right\}$$

$$\eta = \frac{e}{V_{zz}} \left[ (1 - R_{3d}) \langle r^{-3} \rangle_{3d} (P_{3d_{yz},3d_{yz}} - P_{3d_{xz},3d_{xz}}) \frac{6}{7} \right.$$
$$+ (1 - R)_{4p} \langle r^{-3} \rangle_{4p} (P_{4p_y,4p_y} - P_{4p_x,4p_x}) \frac{6}{5} \tag{3}$$
$$\left. + (1 - \gamma_\infty) \sum_a 3 \frac{q_a}{e} (x_a^2 - y_a^2)/r_a^5 \right\}.$$

The calculated electronic structure affects the values of $V_{zz}$ and $\eta$ through the bond-order matrix elements $P_{3d,3d}$ and $P_{4p,4p}$ and through the net atomic charges $q_a$. The 3d and 4p summations in Eqs. (2) und (3) are over the indicated set of Fe orbitals, the "a" summation is over all atoms other than Fe, and $x_a$, $y_a$, $z_a$, $r_a$ refer to coordinates of atom "a". The quantities $\langle r^{-3} \rangle$ are the radial factors resulting from taking the expectation value of $(3z^2 - r^2)/r^5$. The $\langle r^{-3} \rangle_{3d}$ were taken from estimates [3] based on Clementi's [4] atomic Hartree-Fock wave-functions: 4.49 a.u. for Fe configuration $3d^7$, 5.09 a.u. for $3d^6$, and 5.73 a.u. for $3d^5$. The actual value of $\langle r^{-3} \rangle_{3d}$ was determined for each calculation from its calculated 3d orbital occupancy by interpolation between the foregoing values. The Sternheimer shielding corrections [5] were taken as $(1 - R)_{3d} = 0.68$ and $(1 - \gamma_\infty) = 10.1$. For Fe 4p electrons the quantity $(1 - R) \langle r^{-3} \rangle$ was taken to be 1/3 of the corresponding quantity for Fe 3d electrons [6, 7]. The nuclear quadrupole moment $Q$ was taken to be $+0.21\,b$, consistently with our previous work [1, 2, 6] and the findings of other authors [9]. Finally, the quantities $f_{3d}$ and $f_{4p}$ describe factors dependent upon the specific orbitals. These factors are $f_{3z^2-r^2} = -4/7$, $f_{xy} = f_{x^2-y^2} = +4/7$, $f_{xz} = f_{yz} = -2/7$, $f_z = -4/5$, $f_x = f_y = -2/5$.

The molecular geometries for which calculations were made are described in Table 1. Table 2 gives the bond-order matrix elements and net atomic charges needed for making the quadrupole-splitting calculations according to Eqs. (1)–(3). In Table 3 we compare experimental quadrupole splittings with those calculated in the present work. Because the present calculations might have been affected by the neglect of two-center off-diagonal $P_{a,b}$ contributions neglected in Eqs. (2) and (3), we repeated some of the calculations without the neglect of off-diagonal $P_{a,b}$. We found that the values listed in Table 3 remained nearly unaltered.

Table 1. Geometries used for iron-pentacyanide complexes. Geometry for $Fe(CN)_5^{-3}$ based on $Na_2Fe(CN)_5NO \cdot H_2O$ (see Ref. [1]). Symmetry axis of $Fe(CN)_5^{-3}$ taken in $z$ direction

| Compound | 6$^{th}$ ligand | Geometry of 6$^{th}$ ligand in cartesian coordinates (Å) relative to Fe | Comments |
|---|---|---|---|
| I. $Fe(CN)_5NOC_6H_5^{-3}$ | $NOC_6H_5$ | N: (0, 0, 1.63)<br>O: (0, 0, 2.42)<br>$C_1$: (−0.986, 0, 2.616)<br>$C_2$: (−1.476, +0.49, 3.106)<br>$C_3$: (−1.476, −0.49, 3.106)<br>$C_4$: (−2.457, +0.49, 4.087)<br>$C_5$: (−2.457, −0.49, 4.087)<br>$C_6$: (−2.947, 0, 4.577)<br>$H_1$: (−1.476, +2.06, 3.106)<br>$H_2$: (−1.476, −2.06, 3.106)<br>$H_3$: (−2.457, +2.06, 4.087)<br>$H_4$: (−2.457, −2.06, 4.087)<br>$H_5$: (−4.046, 0, 5.676) | Coordinates of benzol (Ref. [14])<br>Fe-N distance same as in $Fe(CN)_5NO^{-2}$<br>N−O distance same as in $Fe(CN)_5NO^{-2}$<br>N−C distance in $NOC_6H_5$ from compounds like $C_6H_4N_2O_4$ (Ref. [14]) |
| II. $Fe(CN)_5NO_2^{-4}$ | $NO_2^-$ | $O_1$: (0.742, 0.742, 2.519)<br>$O_2$: (−0.742, −0.742, 2.519)<br>N: (0, 0, 1.960) | Coordinates of $NO_2^-$ from compounds containing $NO_2$ (Ref. [14])<br>Fe−N distance from $Ag[Co(NO_2)_4(NH_3)_2]$ (Ref. [14]) |
| III. $Fe(CN)_5H_2O^{-3}$ | $H_2O$ | O: (0, 0, 2.09)<br>$H_1$: (0, 0.8, 2.618)<br>$H_2$: (0, −0.8, 2.618) | Coordinates of $H_2O$ (Ref. [14])<br>Fe−O distance from $FeCl_2 \cdot 4H_2O$ (Ref. [15]) |
| IV. $Fe(CN)_5NH_3^{-3}$ | $NH_3$ | N: (0, 0, 1.96)<br>$H_1$: (0.955, 0, 2.289)<br>$H_2$: (−0.477, 0.827, 2.289)<br>$H_3$: (−0.477, −0.827, 2.289) | N−H distance from $NH_3$ (Ref. [16])<br>$NH_3$ angles same as those for $CH_3$ in $CH_3CH_2Br$ (Ref. [14])<br>Fe−N distance from Co−N compounds (Ref. [14]) |
| V. $Fe(CN)_5NOC_6H_5^{-3}$ | $NOC_6H_5$ | | Same as Compound I but with $C_6H_5^-$ rotated by 90° around the N−$C_1$−$C_6$−$H_5$ axis |
| VI. $Fe(CN)_5NO_2^{-4}$ | $NO_2^-$ | | Same as Compound II but with $NO_2^-$ rotated by 45° around the $z$ axis. |
| VII. $Fe(CN)_5NO^{-2}$ | $NO^+$ | N: (0, 0, 1.63)<br>O: (0, 0, 2.76) | Coordinates (Ref. [1]) |
| VIII. $Fe(CN)_5NO^{-3}$ | NO | N: (0, 0, 1.63)<br>O: (0.386, 0, 2.69) | |

Table 2. Bond-order matrix elements $P_{a,a}$ for iron orbitals and atomic charges $q_a$ for the iron-pentacyanide complexes specified in Table 1. Data calculated by SCF MO as described in Ref. [1]

| $P_{a,a}$ | I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|
| $a = d_{x^2-y^2}$ | 0.99 | 0.97 | 0.96 | 0.95 | 1.05 | 0.97 | 1.03 | 0.98 |
| $d_{3z^2-r^2}$ | 0.80 | 0.87 | 0.77 | 0.76 | 0.86 | 0.87 | 0.85 | 0.86 |
| $d_{xz}$ | 1.80 | 1.67 | 1.78 | 1.79 | 1.80 | 1.55 | 1.51 | 1.76 |
| $d_{yz}$ | 1.56 | 1.67 | 1.78 | 1.79 | 1.21 | 1.79 | 1.51 | 1.60 |
| $d_{xy}$ | 1.74 | 1.70 | 1.70 | 1.69 | 1.78 | 1.70 | 1.77 | 1.72 |
| $s$ | 0.15 | 0.15 | 0.15 | 0.14 | 0.13 | 0.15 | 0.11 | 0.14 |
| $p_z$ | 0.29 | 0.25 | 0.17 | 0.20 | 0.27 | 0.25 | 0.20 | 0.22 |
| $p_x$ | 0.23 | 0.24 | 0.24 | 0.23 | 0.22 | 0.24 | 0.22 | 0.24 |
| $p_y$ | 0.22 | 0.24 | 0.24 | 0.23 | 0.20 | 0.24 | 0.22 | 0.24 |
| Atomic charges $q_a$ (units of e):[a] | | | | | | | | |
| Fe | +0.033 | +0.029 | 0 | 0 | +0.153 | +0.033 | +0.100 | −0.035 |
| +x | −0.271 | −0.287 | −0.266 | −0.274 | −0.207 | −0.280 | −0.217 | −0.270 |
| −x | −0.268 | −0.287 | −0.266 | −0.276 | −0.159 | −0.280 | −0.217 | −0.270 |
| +y | −0.264 | −0.261 | −0.266 | −0.275 | −0.192 | −0.266 | −0.217 | −0.285 |
| −y | −0.264 | −0.261 | −0.266 | −0.275 | −0.192 | −0.266 | −0.217 | −0.264 |
| +z | −0.103 | −0.088 | −0.157 | −0.029 | −0.067 | −0.089 | −0.140[b] | 0 |
| −z | −0.258 | −0.250 | −0.244 | −0.254 | −0.190 | −0.251 | −0.211 | −0.250 |

[a] $\pm x$, $\pm y$, $\pm z$ refer to atoms coordinated to Fe in approximately the indicated directions.
[b] charge of oxygen in $NO^+$ is $+0.473$.

Table 3. Experimental and theoretical quadrupole splittings for the iron-pentacyanide complexes specified in Table 1. $\Delta E_Q$, theor. is calculated by Eqs. (1)–(3) as described in the text

|  | I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|
| $\Delta E_Q$, exp. (mm/sec) | 1.32[a] ±0.03 | 0.85[a] ±0.03 | 0.75[a] ±0.03 | 0.65[a] ±0.03 | | | 1.726[b] 1.82[c] 1.90[d] | 1.25[e] |
| $\Delta E_Q$, theor. (mm/sec) | 1.24 | 0.71 | 0.68 | 0.64 | 2.55 | 1.11 | 1.84 | 1.17 |

[a] Dezsi, I., Molnar, B., Srolay, T., Iaszberesyi, I.: Chem. Phys. Letters **18**, 598 (1973); Dezsi, I., Molnar, B., Srolay, T.: Chem. Phys. Letters (to be published).
[b] Danon, J., Iannarella, L.: J. Chem. Phys. **47**, 382 (1967); value from $Fe(CN)_5NO^{-2}$ (solid).
[c] Reference [13]; value from $Fe(CN)_5NO^{-2}$ (in $H_2O$).
[d] Reference [13]; value from $Fe(CN)_5NO^{-2}$ (in N, N-dimethylformamide).
[e] Reference [13]; value from $Fe(CN)_5NO^{-3}$ (in $H_2O$).

For Compounds I to IV we find good agreement between experimental and calculated quadrupole splittings, thereby confirming our use of the semiempirical parameter set we have previously applied to several iron-containing [1, 2, 6, 10] and non-iron-containing [11] compounds. Compounds V and VI are identical respectively to Compounds I and II, except that in V and VI the non-axial ligands

($C_6H_5^-$ and $NO_2^-$) have been rotated relative to their positions in I and II. Our results show that this rotation has a substantial effect upon the Fe $3d$ charge density, and in particular changes the $P_{3d,3d}$ values to such an extent that the calculated quadrupole splittings have moved away from their corresponding experimental values. We therefore conclude that the orientations of $C_6H_5^-$ and $NO_2^-$ relative to the iron-pentacyanide complex are described better by Compounds I and II than by V and VI.

We have previously [1] studied $Fe(CN)_5NO^{-2}$ (Compound VII), using the same semiempirical parameter set as for Compounds I–VI. We found then that the NO group was predicted to be nearly neutral, and our calculated Fe $3d$ and Fe $4p$ atomic orbital occupancies led to a quadrupole splitting which was about 30 % larger than the experimental value. Since it appears that the actual environment of the NO group, not fully included in our calculations, would cause it to have an appreciable positive charge, we repeated our calculations on Compound VII, decreasing the Hückel $\alpha$ parameters for this group until the theoretical and experimental quadrupole splittings agreed. The NO group then had net charge $+0.613e$. We then applied this altered parameter set to $Fe(CN)_5NO^{-3}$ (Compound VIII). We found the electron added in going from Compound VII to Compound VIII to be distributed about 70 % on the NO and nearly 30 % on the Fe, in agreement with the calculations of Manoharan and Gray [12]. However, we did not use the axially symmetric molecular geometry adopted by Manoharan and Gray, as magnetic hyperfine splitting of Mössbauer patterns indicate that there must be some rhombic distortion of the $Fe(CN)_5NO^{-3}$ compound, giving rise to a nonzero asymmetry parameter <0.5 [13]. Since this asymmetric distortion of the electronic charge density about the $z$ axis is probably due to bending of the Fe–N–O chain, we made calculations for a bent geometry as indicated in Table 1. We then obtain a calculated quadrupole splitting in agreement with the experimental value.

Summarizing our study of the $3d^7$ compounds investigated here, we find that the electric field gradient is substantially influenced not only by the Fe $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbital occupancies as sometimes described in the literature, but also by the $3d_{3z^2-r^2}$ and $3d_{x^2-y^2}$ occupancies. These latter occupancies cancel in their effect on the field gradient only if they are equal (as in typical crystal-field studies), and they are not constrained to be equal in typical molecular-orbital calculations. The field gradient is also significantly affected by departures of the electronic distribution from axial symmetry, by the net charges of the surrounding atoms, and to some extent by effects of Fe $4p$ occupancy.

## References

1. Trautwein, A., Harris, F. E.: Theoret. Chim. Acta (Berl.) **30**, 45 (1973)
2. Trautwein, A., Kreber, E., Gonser, U., Harris, F. E.: J. Phys. Chem. (1974)
3. Weissbluth, M., Maling, J. E.: J. Chem. Phys. **47**, 4166 (1967)
4. Clementi, E.: I.B.M. J. Res. Develop. Suppl. **9**, 2 (1965)
5. Sternheimer, R. M.: Phys. Rev. **130**, 1423 (1963)

6. Trautwein, A., Harris, F. E.: Phys. Rev. B **7**, 4755 (1973)
7. de Vries, J. L. K. F., Kreijzers, C. P., de Boer, E.: Inorg. Chem. **11**, 1343 (1972)
8. McNab, T. K., Micklitz, H., Barrett, P. H.: Phys. Rev. B **4**, 3787 (1971)
9. Sharma, R. R.: Phys. Rev. Letters **26**, 563 (1971)
10. Trautwein, A., Maeda, Y., Harris, F. E., Formanek, H.: Theor. Chim. Acta (Berl.) (submitted for publication)
11. Rein, R., Clarke, G. A., Harris, F. E.: Quantum aspects of heterocyclic compounds in chemistry and biochemistry. The Jerusalem symposia on quantum chemistry and biochemistry. II. Jerusalem: Israel Academy of Sciences and Humanities 1970
12. Manoharan, P. T., Gray, H. B.: J. Am. Chem. Soc. **87**, 3340 (1965)
13. Osterhuis, W. T., Lang, G.: J. Chem. Phys. **50**, 4381 (1969)
14. Tables of interatomic distances and configurations in molecules and ions. Sutton, L. E. (Ed.). (London: Chem. Soc. 1958
15. Penford, B. R., Grigor, J. H.: Acta Cryst. **12**, 850 (1959)
16. Pauling, L.: The nature of the chemical bond, p. 226. New York: Cornell University Press 1960

Prof. Dr. A. Trautwein
Universität des Saarlandes
Fachbereich 12.1
Werkstoffphysik und Werkstofftechnologie
D-6600 Saarbrücken,
Federal Republic of Germany