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AN EVALUATION OF THE Fe57m NUCLEAR QUADRUPOLE MOMENT

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## Abstract

A value for the  $\text{Fe}^{57\text{m}}$  nuclear quadrupole moment of  $0.175 \pm 0.02$  has been determined from a comparison of the quadrupole splittings in the Mössbauer data of ferrocene and the pure nuclear quadrupole resonance of  $\text{Co}^{59}$  in cobalticinium perchlorate. The value is in good accord with recent calculations of  $\text{Fe(II)}$  complexes in the solid state.

## INTRODUCTION

The evaluation of the electric nuclear quadrupole moment,  $Q$ , of the 14.4 keV state of  $\text{Fe}^{57\text{m}}$  has received considerable attention in the literature in the past.<sup>1-6</sup> The determination of  $Q$  from Mössbauer data has led to values from 0.1 b derived from Fe(II) compounds<sup>3</sup> to a high value of 0.46 b derived from Fe(III) compounds.<sup>4</sup> Recently, Nozik and Kaplan<sup>1</sup> evaluated the Mössbauer data for  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$  and calculated a value of 0.20 b. Earlier, a substantially higher value of 0.28 b was derived by Ingalls<sup>2</sup> from this compound by essentially a ligand field approach. The differences between the two calculations arise from first, a difference in the computed lattice effects and second, from an inclusion of covalency in one treatment and the neglect of it in another. An accurate appraisal of the  $\text{Fe}^{57\text{m}}$   $Q$  must come eventually from a full molecular orbital treatment of some neutral covalent Fe complex. Direct measurement of the  $\text{Fe}^{57\text{m}}$  quadrupole coupling constant and magnetic hyperfine interaction seems unlikely at this point in view of the very short, 100 nsec., half-life of the 14.4 keV state.<sup>7</sup>

It is the purpose of this communication to present a value for the  $\text{Fe}^{57\text{m}}$  nuclear quadrupole moment by analogy to the  $\text{Co}^{59}$  nuclear quadrupole moment. This will be accomplished by showing the physical and chemical analogy in the bonding between di- $\pi$ -cyclopentadienyl  $\text{Co(III)}$  and di- $\pi$ -cyclopentadienyl  $\text{Fe(II)}$ . It is important to point out that the reliability of the present values of the Fe moment rest on the evaluation of both the lattice contribution to the field gradient and a correct evaluation of the valence electron contributions. In di- $\pi$ -cyclopentadienyl  $\text{Fe(II)}$ , more

commonly known as ferrocene, there is no lattice contribution since the molecule is neutral.<sup>8</sup> It is known<sup>9</sup> that induced-dipole interactions can at most contribute less than 1% of the total field gradient in unfavorable cases. In di- $\eta$ -cyclopentadienyl Co(III), more commonly known as cobalticinium, there is a lattice contribution to the field gradient. Although the crystal structure of cobalticinium perchlorate has not been reported, it is safe to assume that the point charge sum over the anions in cations, i.e. the lattice sum contribution, is insufficient to contribute appreciably to either the magnitude or direction of  $q_{zz}$ . The very small coupling constants which have been found in  $\text{Co}[\text{NH}_3]_6\text{Cl}_3$ <sup>10</sup> and  $\text{Coen}_3\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ <sup>11</sup> attributable only to lattice effects are less than 2% of the coupling constants found in cobalticinium perchlorate. This includes the Sternheimer<sup>12</sup> factor  $(1-\gamma_\infty)$ .

A molecular electronic interpretation of the coupling constant in these molecules is straight forward. In a valence bond<sup>13</sup> or a molecular orbital<sup>14</sup> approach the coupling constant arises from an imbalance of valence electrons. In either complex there is the possibility of having 3d, 4s and 4p electrons participating in the bonding. Since s electrons do not contribute to the field gradient we need only directly consider 3d and 4p electrons. Utilizing equations<sup>15</sup> relating the field gradient to the fine structure splitting and using Slater's method<sup>16</sup> for determining to Co effective nuclear charge seen by 3d and 4p electrons in the configuration  $(\text{Ar})3d^6 4p^1$  it can be shown that the field gradient arising from one 4p electron is at least three times smaller than that from a 3d electron. In all probability the ratio in Co would be around  $5 \pm 1$ . This can be estimated<sup>17</sup> from differences in the cobalt and copper magnetic

hyperfine interaction. From the transformation properties of the 4p electrons in the molecular  $D_{5d}$  symmetry and estimates of the 4p population in octahedral Co(III) complexes from recent calculations,<sup>18</sup> 0.1 of an electron per 4p orbital, it can be shown that the total contribution to the field gradient from 4p electrons would be only 0.02 that from a single 3d electron. Thus, equation 1 can be written for the quadrupole

$$q_{zz}^{\text{molecular}} = q_{zz}^{\text{atomic}} (\#_{3d_{z^2}} + \#_{3d_{\epsilon/2}} - \#_{3d_{\delta}} - 0.02) \quad (1)$$

coupling constant for cobalticinium or ferrocene. The value for the field gradient contribution of one Co  $3d_{z^2}$  electron can be calculated using the quadrupole coupling constant obtained from the  ${}^4F_{9/2}$  state measured by Co atomic beam spectroscopy.<sup>19</sup> The value of the Co<sup>59</sup> nuclear quadrupole moment,  $Q$ , can be extracted from equation  $Q$  of  ${}^4F_{9/2}$  state by utilizing the  $\langle r^{-3} \rangle$  obtained from the magnetic hyperfine coupling constant measured<sup>19</sup> in this state. Thus one obtains simultaneously and independently  $q$  and  $Q$  for Co. No Sternheimer correction  $R$ , which is believed to be small, was made. Using the quadrupole coupling constant in the  ${}^4F_{9/2}$  state and the measured nuclear quadrupole moment for Co<sup>59</sup> it can be shown that Co  $q_{zz} = -9.53 \times 10^{15}$  esu/cm<sup>2</sup>. The field gradient for a 3d electron in Fe can be calculated from the ratios of the various  $[r^{-3}]$  values tabulated in the literature.<sup>20</sup>  $q_{zz}$  for Fe is calculated in this manner as  $-8.08 \times 10^{15}$  esu/cm<sup>2</sup>.

The population of the  $3d_{z^2}$  orbital in both ferrocene and cobalticinium can safely be assumed to be equaled to two electrons. Explicit evaluation of the overlap integral<sup>21</sup> in ferrocene between cyclopentadienyl orbitals and the  $3d_{z^2}$  orbital yields a value of only 0.01; thus, the  $a_{1g}$  MO is for all practical purposes a pure  $3d_{z^2}$  wave function.



Using the available quadrupole coupling constants determined for cobalticinium perchlorate<sup>22</sup> and the Mössbauer data for ferrocene<sup>23,24</sup> equations 2 and 3 can be written for the quadrupole coupling constant of

$$q_{zz}^{CP_2Co^+} / q_{zz}^{Co. 3d} = -0.595 = (1.98 + \#_{3d\epsilon}/2 - \#_{3d\delta}) \quad (2)$$

$$[2(\gamma \pm 3/2 \rightarrow \pm 1/2) / eq_{zz}^{Fe 3d}] [1/Q_{Fe^{57m}}] = (1.98 + \#_{3d\epsilon}/2 - \#_{3d\delta}) \quad (3)$$

these two molecules in terms of their 3d $\epsilon$  and 3d $\delta$  populations.<sup>25</sup> In the case of ferrocene one must include the uncertainty of the Fe<sup>57m</sup> nuclear quadrupole moment. Figure 1 shows a graphic solution of equation 2 and 3 for cobalticinium and ferrocene for values of Q(Fe<sup>57m</sup>) equal to 0.1, 0.2 and 0.3 b. It is clear that there are many possible solutions, only one of which is correct. Fortunately, a fairly reliable solution to this dilemma can be found in a comparison of the uv and visible spectra<sup>26,27</sup> of the respective molecules. It is apparent from Table 1 that the uv and visible spectra of the isoelectronic cobalticinium and ferrocene are sufficiently similar to presuppose that the 3d orbital coefficients and consequently, the orbital populations, are within 2-5% and 10% of each other respectively. It is known that a few per cent change in the MO coefficients can result in electron volt changes in the energy of the MOs. This would result, therefore, in a large difference in the spectra between these two compounds. Furthermore, it is entirely reasonable to suppose from a covalency point of view that the cobalt to cyclopentadienyl and the Fe to cyclopentadienyl bonds are within at least 10% of each other. If we assume that the bonding is identical in these two compounds, bearing in mind that such an assumption introduces a possible cumulative error

of 15%, one can calculate a value of the  $\text{Fe}^{57\text{m}}$  nuclear quadrupole moment as  $0.175 \pm 0.02$  barn. This value is entirely in accord with the most recent value of 0.2 barn, calculated by Nozik and Kaplan.<sup>1</sup> It should be pointed out that the 0.175 value is only a working value insofar as it relies on the similarity of bonding in two isoelectronic compounds. It should be interesting to see whether or not this value can account in a satisfactory manner for the quadrupole splittings obtained from Mössbauer spectra in other Fe(II) and Fe(III) complexes.

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Table I

## Visible and UV Spectra

Transition	$(C_5H_5)_2CoClO_4^a$	$(C_5H_5)_2Fe^b$
$\gamma_1$ (cm <sup>-1</sup> ) <sup>c</sup>	38,400	41,700
$\gamma_2$ (cm <sup>-1</sup> )	32,700	30,800
$\gamma_3$ (cm <sup>-1</sup> )	24,700	22,700

(a) Taken from Reference 26.

(b) Taken from Reference 27.

(c) Charge transfer band.

REFERENCES

1. A. J. Nozik and M. Kaplan, Phys. Rev., 159, 273 (1967).
2. R. Ingalls, Phys. Rev., 133, A 787 (1964).
3. C. E. Johnson, W. Marshall and G. J. Perlow, Phys. Rev., 126, 1503 (1962).
4. G. Burns, Phys. Rev., 124, 524 (1961).
5. H. Eicher, Z. Physik, 171, 582 (1963).
6. A. Abragam and F. Boutron, Compt. Rend., 252, 2404 (1961).
7. G. W. Wertheim, Mössbauer Effect: Principles and Applications, Academic Press, N.Y., 1964, pg. 13.
8. J. D. Dunitz, L. E. Orgel and A. Rich, Acta. Cryst., 9, 373 (1956).
9. T. P. Das and E. L. Hahn, Solid State Phys., Suppl., 1, (1958).
10. T. Sugawara, J. Phys. Soc. Japan, 14, 858 (1959).
11. B. A. Scott and R. A. Bernheim, J. Chem. Phys., 44, 2004 (1966).
12. R. M. Sternheimer, Phys. Rev., 84, 244 (1951); 86, 316 (1952); 95, 736 (1954); 130, 1423 (1963).
13. C. H. Townes and B. P. Dailey, J. Chem. Phys., 17, 782 (1949).
14. F. A. Cotton and C. B. Harris, Proc. Natl. Acad. Sci. U.S., 56, 12 (1966).
15. C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill, N.Y., 1955.
16. J. C. Slater, Phys. Rev., 36, 57 (1930).
17. V. S. Korol'kov and A. G. Makhanev, Optika i Spektroskopiya, 12, 87 (1962).
18. H. Basch, A. Viste, and H. B. Gray, J. Chem. Phys., 44, 10 (1966).

19. D. v. Ehrenstein, H. Kopfermann and S. Penselin, Z. Physik, 159, 230 (1960).
20. J. Fidone, Nuovo Cimento, 11, 736 (1959).
21. J. D. Dunitz and L. E. Orgel, J. Chem. Phys., 23, 954 (1955).
22. J. Voitländer, H. Klocke, R. Longino and H. Thieme, Naturwiss., 49, 491 (1962).
23. G. K. Wertheim and R. H. Herber, J. Chem. Phys., 38, 2106 (1963).
24. U. Zahn, P. Kienle and H. Eicher, Z. Physik, 166, 220 (1962).
25.  $3d\epsilon$  refers to the  $3d_{xz}$  and  $3d_{yz}$  electron while  $3d\delta$  refers to the  $3d_{x^2-y^2}$  and  $3d_{xy}$  electrons. The Z-direction is coincident with the  $C_5$  axis.
26. G. Wilkinson, J. Am. Chem. Soc., 74, 6148 (1952).
27. G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *ibid.*, 74, 2125 (1952).

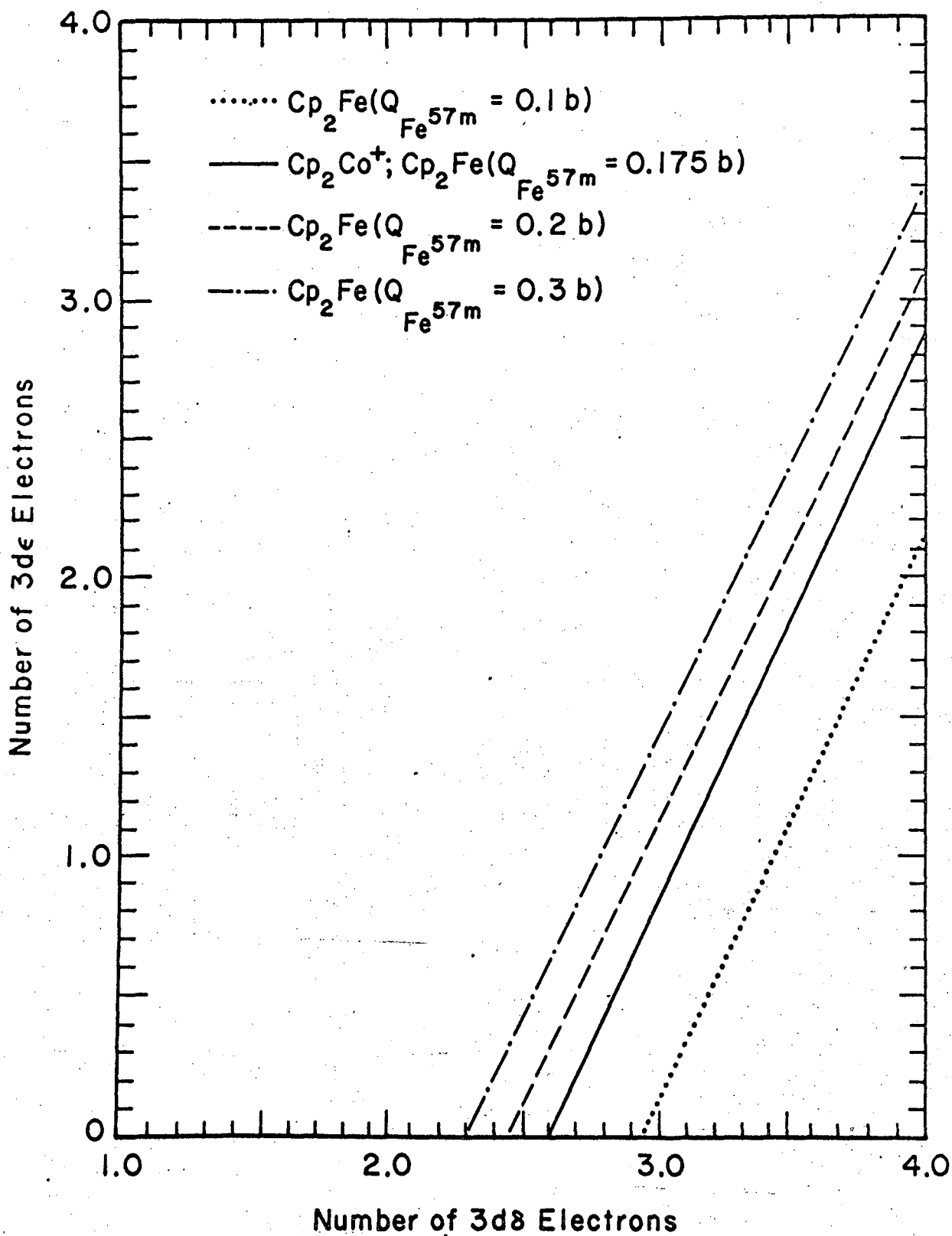


Figure 1. Solutions for the field gradients and  $\text{Fe}^{57m}Q$  from Equations 2 and 3.

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