Title
FAR IHFRARED SPECTRA OF SEVERAL Fe(III) COMPLEXES WITH SPIN S=3/2

Authors
Brackett, G.C.
Richards, P.L.
Wickman, H.H.

Publication Date
1970-04-01

Submitted to Chemical Physics Letters

UCRL-19185
Preprint

c.2

FAR INFRARED SPECTRA OF SEVERAL Fe(III) COMPLEXES WITH SPIN S=3/2

G. C. Brackett, P. L. Richards, and H. H. Wickman

April 1970

AEC Contract No. W-7405-eng-48

34

DISCLAIMER

Far Infrared Spectra of Several Fe(III) Complexes with Spin S=3/2

G. C. Brackett and P. L. Richards

Department of Physics, University of California
and
Inorganic Materials Research Division
Lawrence Radiation Laboratory
Berkeley, California 94720

and

H. H. Wickman

Bell Telephone Laboratories
Murray Hill, New Jersey 07974

ABSTRACT

The far infrared transmission spectra of seven bis (N, N dialkyl dithiocarbamato) Fe(III) halides have been measured at 4.2°K in applied magnetic fields up to 52 kOe. The paramagnetic spectra are closely consistent with the spin Hamiltonian $\mathcal{H}=g\mu_B\bar{H}\cdot\bar{S} + D[S_z^2 - S(S+1)/3] + E[S_x^2 - S_y^2]$ for $S=3/2$, $E/D<<1$, and values of D between - 2.35 and +8.15 cm^{-1}. The zero field ferromagnetic resonance of $((C_2H_5)_2NCS_2)_2$ FeCl in the ordered state was observed at 3.85 cm^{-1}.

We have measured the far infrared transmission spectra of a series of penta-coordinate Fe(III) complexes, the bis (N, N dialkyl dithiocarbamato) Fe(III) halides: $(R_2NCS_2)_2FeX$. The iron atom in these compounds lies approximately at the centroid of a rectangular prism which has a base of four sulfur atoms and a halide at the apex.[1] Measurements of magnetic susceptibility,[1,2] EPR,[3] and Mössbauer effect[4] have shown that the Fe(III) electronic ground multiplet is consistent with the spin Hamiltonian

$$\mathcal{H} = g\mu_B \bar{H}\cdot\bar{S} + D[S_z^2 - S(S+1)/3] + E[S_x^2 - S_y^2] \qquad (1)$$

with the unusual intermediate-spin value S=3/2, and parameters g=2.00 $|D| > 1\ cm^{-1}$, and E << D. Our far infrared measurements have enabled us to investigate the validity of the spin Hamiltonian approximation, and to directly obtain values for the axial crystal field parameter D.

The far infrared measurements were made over the frequency interval 3-50 cm^{-1}, using the techniques of Fourier transform spectroscopy.[5] The Michelson interferometer and sample dewar employed have been recently described elsewhere.[6] Spectra were obtained for polycrystalline samples immersed in liquid helium at temperatures between 1.3 and 4.2°K; magnetic fields up to 52 kOe were applied by a superconducting solenoid. The spectra for all seven compounds studied showed magnetic field-dependent absorptions due to magnetic dipole transitions between states of the paramagnetic ground multiplet. In addition, the ferromagnetic resonance of $((C_2H_5)_2NCS_2)_2$ FeCl in the ordered state was observed.

In the absence of a magnetic field, the eigenstates of the Hamiltonian (1) consist of two Kramer's doublets separated by the zero field splitting $\Delta = 2D\sqrt{1+3(E/D)^2}$. If D>0, the ground doublet is chiefly characterized by $S_z = \pm 1/2$; if D < 0, the level system is inverted. In an applied

magnetic field H ⊥ z, the $S_z = \pm 1/2$ doublet splits with $g_\perp = 4$ and the $S_z = \pm 3/2$ doublet splits quadratically in H. A plot of the absorption line positions derived from far infrared data for a sample with crystallites arranged in approximately this orientation[7] is shown in Fig. 1. The curves represent a "best fit" of the Hamiltonian to the observed spectrum; the values of D and E were chosen to fit the zero field splitting and the ground doublet Zeeman splitting. Although the overall fit is excellent, the positions of the high frequency transitions differ from the predictions by more than the experimental error (0.1 cm^{-1} in this case). This discrepancy cannot be explained by imperfect alignment of the crystallites. It is more likely due to effects of the small admixture of higher states which are not included in (1). The "high-frequency" far infrared transitions are particularly sensitive to effects of this kind.

Most of the other compounds studied had small crystallite sizes, which prevented the construction of oriented samples. In order to compare their experimental powder absorption spectra with the predictions of the spin Hamiltonian, a computer program was written to calculate the powder average absorption coefficient as a function of frequency for a specified D, E, temperature T, linewidth, and applied field H. It was assumed that the direction of the external magnetic field and the direction of propagation of the far infrared radiation were randomly oriented with respect to the crystalline axes; this approximation is consistent with the experimental conditions.[8] The g-factor was taken to be isotropic with a value g=2.0, and a Gaussian lineshape, due to site inhomogeneities,

was fitted to the zero field spectrum. The computed spectra were quite complex, and were relatively insensitive to the value of E chosen. Accurate comparison of the predicted spectra with the observations were complicated by the breadth of the absorption lines and the difficulty of determining the non-electronic background spectrum. However, the computed relative intensities and frequencies of absorption maxima as well as the qualitative lineshape agreed closely with experiment. Data for a powdered compound are compared with the powder average calculations in Fig. 2. The value of D used was determined from the zero field splitting, and E was obtained from the EPR result: $E/D=0.036$.

One of the compounds investigated, $((C_2H_5)_2NCS_2)_2FeCl$, has been shown[2] to be a ferromagnet with a transition temperature $T_c=2.43°K$. No sharp zero field absorption was observed for this compound in the paramagnetic state, presumably because of exchange broadening. Such broadening is likely in this compound, since the Heisenberg exchange coupling parameter J is of the same order as D.

A zero field ferromagnetic resonance was observed for $T\leq 2.3°K$. At T=0, a simple classical argument shows that the zero field resonance frequency $\nu_o(T=0)=2DS$. This argument, exact in the limit of large spin S, must be corrected by the factor[9] $\eta=[1-1/(2S)]$. Therefore, for spin $S=3/2$, $\nu_o=2D$. The frequency $\nu_o(T)$ tends to zero in a regular fashion[10] as T approaches T_c. Our measurements of ν_o between 1.3 and 2.3°K, however, showed a progressive broadening of the resonance and a decrease of only ~0.05 cm^{-1}. Therefore, we have taken $|2D|=\nu_o(T=1.3°K)=3.85\ cm^{-1}$ for this compound. The sign of D was obtained from Mössbauer effect results.

The values of D obtained for the seven compounds investigated are listed in Table I. The values for the compounds which have not been discussed were obtained from the zero field splitting, assuming E=0. The sign of D was also found from the spectra. A comparison of Fig. 1 (D>0) with Fig. 2 (D<0) illustrates the two cases. The qualitative differences between the two spectra are caused by the effect of thermal population on the transition strengths; the population depends upon the level sequence and therefore upon the sign of D. The sign of D found from examination of the far infrared spectra is in agreement with previous Mössbauer effect results.

The similarity of the chemical and macroscopic properties of the bis dithiocarbamates indicates that they form an isostructural series obtained by substitution of either the halide ligand or the alkyl groups located at the periphery of the molecule. In order to study the variation of D with such ligand substitutions, we compare the change in the zero field splitting Δ when the halide ligand is changed from Br to Cl for a fixed bidentate dithiocarbamate ligand. This quantity, $\Delta_{Br}-\Delta_{Cl}$, is also listed in Table I.

For the first two pairs of compounds, $\Delta_{Br}-\Delta_{Cl}$ is approximately independent of the alkyl ligand; preliminary results indicate that a similar value will be found for the isopropyl derivatives. This observation suggests that the effect of alkyl group substitution upon Δ is either small or relatively independent of the halide ligand. However, $\Delta_{Br}-\Delta_{Cl}$ for the pyrrolidinyl derivatives is quite different, which implies that the bonding in these complexes varies markedly from that in the other compounds.

We may compare these observations with results for a series of related compounds. Magnetic susceptibility measurements have been made[11] on tris (dialkyl dithiocarbamato) Fe(III) complexes [$(R_2NCS_2)_3Fe$] with different alkyl groups. With the exception of the tris pyrrolidyl complex, these compounds have temperature-dependent moments which lie between the octahedrally allowed low and high spin states. The tris pyrrolidyl complex, however, shows only high spin behavior.[12]

These striking differences in both the tris and bis dithiocarbamate complexes may be due to a greater degree of π bonding for pyrrolidinyl ligands, owing to a pseudo ring structure including the nitrogen atom. If this is the case, we would expect a very different spin density at the peripheral protons in alkyl derivatives compared with pyrrolidinyl derivatives. Such NMR data for the bis complexes are not available at present, but results reported for several tris compounds[13] show that the effective contact interaction for tris pyrrolidyl is significantly smaller than the corresponding contribution in the tris alkyls.

Finally, we compare the values of D for these compounds with the quadrupole splitting ΔE_Q, also listed in Table I, obtained from Mössbauer effect measurements. Since both ΔE_Q and D depend upon the strength and asymmetry of the ligand field, we might expect a correlation between them. For example, this comparison has been made[14] for Fe(III) porphyrins, which have ground multiplets described by (1) for S=5/2. The porphyrin data suggest an approximately linear variation of ΔE_Q with D, passing through the origin. Our data clearly eliminates such a possibility for the dithiocarbamates, but does not discriminate against other possible zero-intercept functions. For instance, the data can be fit

to a saturating function of D with either even or odd parity. Mössbauer effect and far infrared measurements on the fluoride and iodide complexes would help to clarify this point.

We wish to acknowledge many helpful discussions with G. Harris concerning techniques for computing powder average spectra, and with K. Tsushima concerning magnetic torques in axial systems.

This work was performed under the auspices of the U.S. Atomic Energy Commission.

FIGURE CAPTIONS

Fig. 1 Data for a sample of $((C_2H_5)_2NCS_2)_2FeBr$ oriented with the applied field approximately perpendicular to the z-axis. The points indicate the frequencies of maximum absorption, the bars the experimental width at half maximum. The curves are the predicted transitions of Eq. (1) with D=+7.50 cm^{-1}, E=0.50 cm^{-1}, and the angle between H and the z-axis $\theta_H \sim 3\pi/8$. The resolution interval is 0.50 cm^{-1}.

Fig. 2 Data for a powdered sample of $((i\text{-}C_3H_7)_2NCS_2)_2FeCl$. The curves plot the frequencies of the principal computed powder absorption maxima for D=-2.35 cm^{-1} and E=0.08 cm^{-1}. The resolution interval is 0.20 cm^{-1}.

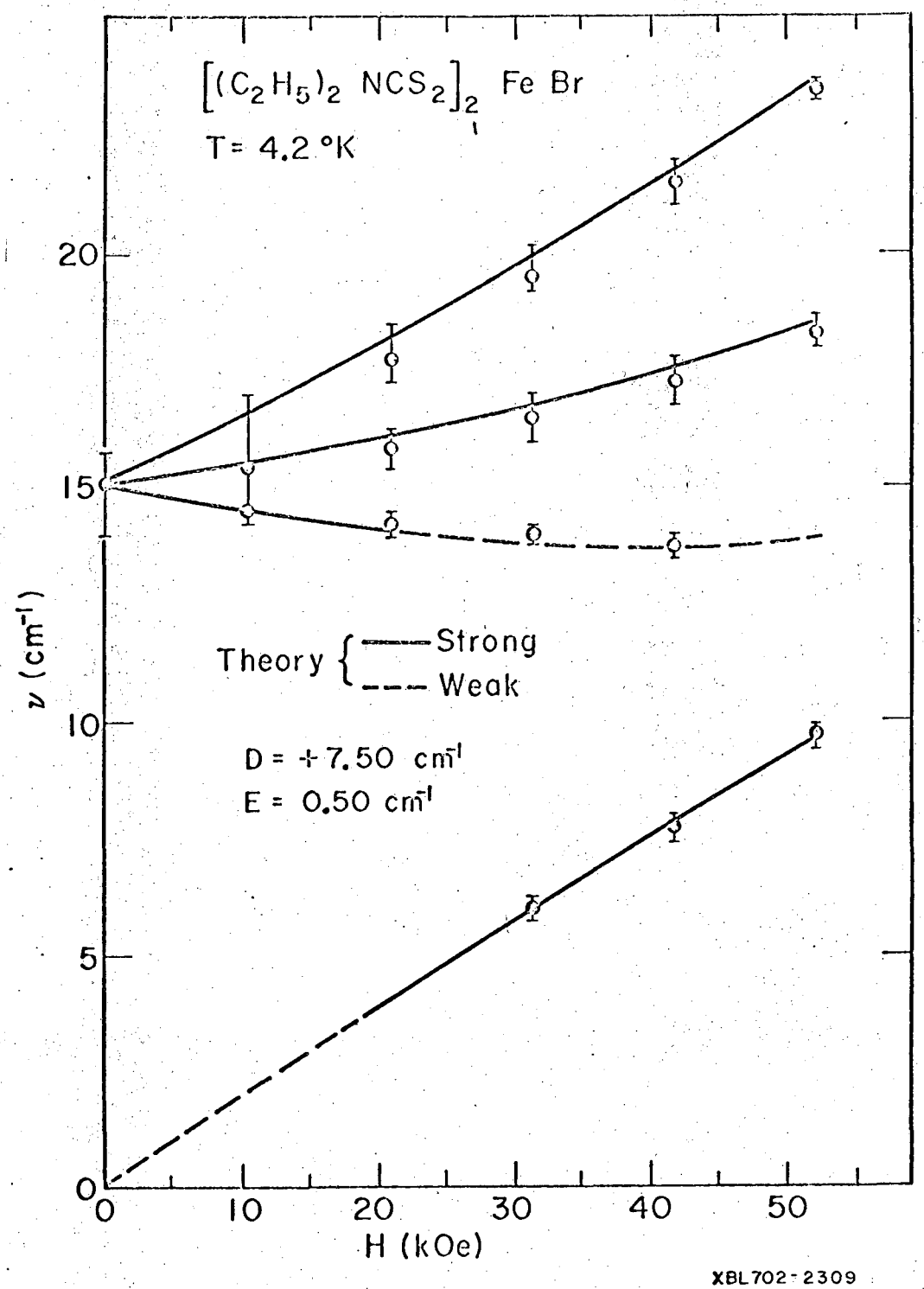
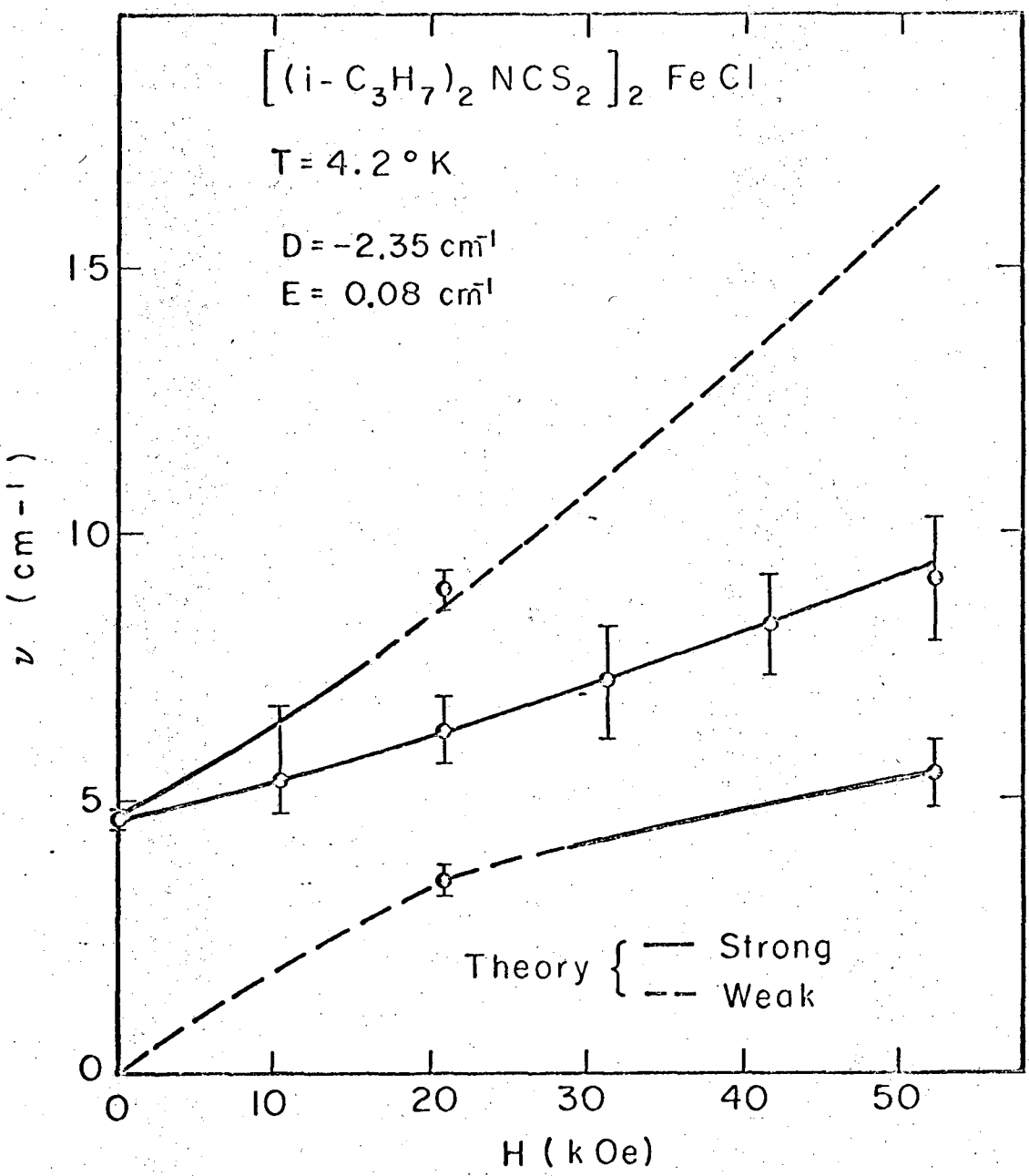

$[(C_2H_5)_2\ NCS_2]_2$ Fe Br
T = 4.2 °K
Theory { Strong
Weak
D = +7.50 cm⁻¹
E = 0.50 cm⁻¹
ν (cm⁻¹)
H (kOe)
0
5
10
15
20
0
10
20
30
40
50
XBL702-2309

fig. 1



XBL6912-6385

fig. 2

TABLE I.

$(R_2NCS_2)_2$ Fe X

Ligands		D (cm^{-1})	$\Delta_{Br}-\Delta_{Cl}$ (cm^{-1})	ΔE_Q (cm/sec)
$R=CH_3$	X=Br	+7.30	18.80	0.290
$R=CH_3$	X=Cl	-2.10		0.266
$R=C_2H_5$	X=Br	+7.50	18.95	0.288
$R=C_2H_5$	X=Cl	-1.93		0.268
$R=i\text{-}C_3H_7$	X=Cl	-2.35		0.268
NR_2=pyrrolidyl	X=Br	+8.17	11.1	0.277
NR_2=pyrrolidyl	X=Cl	+2.60		0.268

REFERENCES

1. B. F. Hoskins, R. L. Martin, and A. H. White, Nature 211, 627 (1966).

2. H. H. Wickman, A. M. Trozzolo, H. J. Williams, G. W. Hull, and F. R. Merritt, Phys. Rev. 155, 563 (1967).

3. H. H. Wickman and F. R. Merritt, Chem. Phys. Letters 1, 117 (1967).

4. H. H. Wickman and A. M. Trozzolo, Symp. of the Faraday Society 1, 21 (1967).

5. Spectroscopic Techniques for Far Infrared, Submillimetre and Millimetre Waves, D. H. Martin ed., (North-Holland Publishing Co., 1967).

6. R. R. Joyce and P. L. Richards, Phys. Rev. 179, 375 (1969).

7. At low temperatures, crystallites containing paramagnetic ions whose ground multiplet is described by (1) are subject to a torque due to the interaction of the low temperature ionic moment with an external magnetic field. This torque tends to align each crystallite with one of the axes of (1) parallel to the external field. This torque can be quite large: for the compound of Fig. 1, the maximum torque per unit volume in a 52 kOe applied field is 8.65×10^5 dyne/cm^2, and the torque tends to rotate the crystallites toward $H \perp z$.

8. Care was taken in the experiments involving powdered samples to eliminate crystallite alignment due to the magnetic torque.

9. R. J. Joenk and R. M. Bozorth, Proceedings of the International Conference on Magnetism, Nottingham, 1964, p. 493.

10. C. Zener, Phys. Rev. 96, 1335 (1954).

11. A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, Proc. Roy. Soc. A280, 235 (1964).

12. Our far infrared measurements on this compound are consistent with

the Hamiltonian (1) for S=5/2, D= -2.15 cm^{-1}, and E=0.24 cm^{-1}.

13. R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin, and A. H. White, J. Chem. Phys. 45, 2688 (1966).

14. W. S. Caughey, H. Eberspaecher, W. H. Fuchsman, S. McCoy, and J. O. Alben, "Pi-Interactions in Metalloporphyrins and Hemeproteins," a paper presented March 28, 1967 at the Conference on Prospectives of Pi-Interactions in Biological Science, N.Y. Academy of Sciences. To be published in the Annals of the N.Y. Academy of Sciences.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720