CHEMISTRY LETTERS, pp. 281-286, 1972. Published by the Chemical Society of Japan

PSEUDOCONTACT SHIFT IN Eu(III) COMPLEXES. II. A SIMPLE THEORY FOR COMPLEXES OF C_{3h}, D_{3h} OR C_{3v} POINT SYMMETRY

Ushio SAKAGUCHI, Akira YAMASAKI, and Shizuo FUJIWARA
Department of Chemistry, Faculty of Science, The University of Tokyo
Hongo, Tokyo

An approximate equation has been obtained for the pseudocontact shift in tris-chelated europium(III) complexes with C_{3h} , D_{3h} or C_{3v} symmetry. The crystal field energies have been calculated as a first-order perturbation on the spin-orbit levels.

I. The Eu(III) ion

The ground term of a tripositive europium ion is ^7F and the spin-orbit coupling splits this term into seven levels $^7F_J(J=0,1,2,...,6)$. The energy levels of these multiplets have been determined(1,4) at about 370 and 1100 cm^{-1} for the $^7F_1$ and $^7F_2$ levels respectively, with the $^7F_0$ state as a ground level. The (2J+1)-fold degeneracy of a level is wholly or partially lifted by the action of the crystal field.

As a first approximation to the tris-chelated complex of Eu(III), let us take the C_{3h}, D_{3h} or C_{3v} symmetry for the crystal potential. The Hamiltonian of the system may be written as

$$\mathcal{H} = \mathcal{H}_f + V_c \qquad \text{...(1)}$$

here $\mathcal{H}_f$ is the free ion Hamiltonian and V_c is the crystal potential. The eigenfunctions of $\mathcal{H}_f$ can be labelled by J and J_z values as $|JJ_z\rangle$. Since V_c has no matrix element between $^7F_0$ and $^7F_1$ states, we shall use the first order perturbation theory to obtain the crystal field energies(1). Thus the crystal potential of C_{3h} or D_{3h} symmetry can be written, within a manifold of a given J value, as(2)

$$V_c=A_2^0\langle r^2\rangle\langle J||\alpha||J\rangle O_2^0 +A_4^0\langle r^4\rangle\langle J||\beta||J\rangle O_4^0 +A_6^0\langle r^6\rangle\langle J||\gamma||J\rangle O_6^0 +A_6^6\langle r^6\rangle\langle J||\gamma||J\rangle O_6^6 \quad \text{....(2)}$$

where $A_2^0\langle r^2\rangle$ etc. are adjustable crystal field parameters, $\langle J||\alpha||J\rangle$ etc. are Stevens proportionality constants, and O_2^0 etc. the angular momentum operators. The explicit forms of these operators and constants can be found in refs.(1) and (2).

Hereafter we shall consider only ${}^7F_0$, ${}^7F_1$ and ${}^7F_2$ levels because other levels are higher in energy so that their contribution to the susceptibility is negligibly small. Under the influence of the V_c, these multiplets break up into a series of doublet $|J\pm M>$ and singlet $|J0>$ energy levels. To first order in the crystal field , the energies of these levels are given by

$$\begin{aligned} &E(|00>)=0 \\ &E(|10>)=\Delta_1+V_{10}=\Delta_1+2A_2^0<r^2>/5 \\ &E(|1\pm1>)=\Delta_1+V_{11}=\Delta_1-A_2^0<r^2>/5 \end{aligned} \qquad \ldots\ldots(3)$$

where Δ_1 is the separation between the ${}^7F_C$ and ${}^7F_1$ states in the absence of the crystal field, and

$$\begin{aligned} &E(|20>)=\Delta_2+V_{20}=\Delta_2+22A_2^0<r^2>/105-16A_4^0<r^4>/21 \\ &E(|2\pm1>)=\Delta_2+V_{21}=\Delta_2+11A_2^0<r^2>/105+32A_4^0<r^4>/63 \\ &E(|2\pm2>)=\Delta_2+V_{22}=\Delta_2-22A_2^0<r^2>/105-8A_4^0<r^4>/63 \end{aligned} \qquad \ldots\ldots(4)$$

here Δ_2 is the ${}^7F_2$ energy in a free ion.

This energy level scheme remains unchanged even in a crystal field of C_{3v} symmetry. This can be seen as follows. The potential $V_c(C_{3v})$ contains extra terms proportional to $<J||\beta||J>O_4^3$ and to $<J||\gamma||J>O_6^3$ in addition to the V_c described by eq.(1)$^{(12)}$. But the matrix elements of these terms are zero in the manifold of a constant J, so the final result eq.(19) holds also for complexes of C_{3v} symmetry.

II. The Zeeman effect

We shall first consider the parallel Zeeman effect. The Hamiltonian is

$$\mathcal{H}_z=\beta H(L_z+2S_z) \qquad \ldots\ldots(5)$$

H being the applied magnetic field. The ${}^7F_0$ level shows of course no first order Zeeman splitting, but the second order Zeeman energy arises through coupling with the ${}^7F_1(J_z=0)$ level.

$$E(|00>)=-4\beta^2H^2/(\Delta_1+V_{10}) \qquad \ldots\ldots(6)$$

Similarly the second order Zeeman energy of the ${}^7F_1(J_z=0)$ level is

$$E(|10>)=+4\beta^2H^2/(\Delta_1+V_{11})-3\beta^2H^2/(\Delta_2+V_{20}-V_{10}) \qquad \ldots\ldots(7)$$

The energies of the ${}^7F_1(J_z=\pm1)$ levels are obtained as

$$E(|1\pm1>)=\pm(3/2)\beta H-9\beta^2H^2/4(\Delta_2+V_{21}-\Delta_1-V_{11}) \qquad \ldots\ldots(8)$$

The perpendicular Zeeman effects are calculated in an analogous way to yield

$$\begin{aligned}
E(|00\rangle) &= -4\beta^2H^2/(\Delta_1+V_{11})\\
E(|10\rangle) &= 9\beta^2H^2/4(V_{10}-V_{11}) - 9\beta^2H^2/4(\Delta_2+V_{21}-\Delta_1-V_{10})\\
E(|11\rangle) &= 2\beta^2H^2/(\Delta_1+V_{11}) + 9\beta^2H^2/8(V_{11}-V_{10}) + 3\beta^2H^2/8(\Delta_1+V_{11}-\Delta_2-V_{20}) \qquad \cdots\cdots\cdots\cdots(9)\\
&\quad +9\beta^2H^2/4(\Delta_1+V_{11}-\Delta_2-V_{22})\\
E(|1\,\text{-}1\rangle) &= (\text{ibid})
\end{aligned}$$

III. Anisotropy in susceptibility

The Van Vleck equation for susceptibility(3) can be used to obtain the anisotropy in susceptibility.

$$\chi_{ii} = \frac{\Sigma\Sigma\,((E_{nm}^{(1)})^2/kT - 2E_{nm}^{(2)})\,\exp(-E_n^0/kT)}{\Sigma\,\exp(-E_n^0/kT)} \qquad \cdots\cdots\cdots\cdots(10)$$

Neglecting the Boltzmann contribution from the excited $^7F_2$ state, we get

$$\chi_{\parallel} = \beta^2\varepsilon\{\frac{8}{\Delta_1+V_{10}} + (\frac{-8}{\Delta_1+V_{10}} + \frac{6}{\Delta_2+V_{20}-\Delta_1-V_{10}})\exp(-(\Delta_1+V_{10})/kT)$$

$$+2(\frac{9/4}{kT} + \frac{9/2}{\Delta_2+V_{21}-\Delta_1-V_{11}})\exp(-(\Delta_1+V_{11})/kT)\} \qquad \cdots\cdots\cdots\cdots(11)$$

and

$$\chi_{\perp} = \beta^2\varepsilon\{\frac{8}{\Delta_1+V_{11}} + (\frac{-9/2}{V_{10}-V_{11}} + \frac{9/2}{\Delta_2+V_{21}-\Delta_1-V_{10}})\exp(-(\Delta_1+V_{10})/kT)$$

$$+2(\frac{-4}{\Delta_1+V_{11}} + \frac{-9/4}{V_{11}-V_{10}} + \frac{3/4}{\Delta_2+V_{20}-\Delta_1-V_{11}} + \frac{9/2}{\Delta_2+V_{22}-\Delta_1-V_{11}})\exp(-(\Delta_1+V_{11})/kT)\} \qquad \cdots\cdots(12)$$

with

$$\varepsilon = \{1 + \exp(-(\Delta_1+V_{10})/kT) + 2\exp(-(\Delta_1+V_{11})/kT)\}^{-1} \qquad \cdots\cdots\cdots\cdots(13)$$

Since the crystal field splitting of $^7F_2$ state is much smaller than the separation between the $^7F_1$ and $^7F_2$ states(1,4), we can approximate eqs.(11) and (12) as

$$\chi_{\parallel} \simeq \beta^2\varepsilon\{\frac{8}{\Delta_0} + (\frac{-8}{\Delta_0} + \frac{6}{\Delta_2-\Delta_0})\exp(-\Delta_0/kT) + 2(\frac{9/4}{kT} + \frac{9/2}{\Delta_2-\Delta_1})\exp(-\Delta_1/kT)\} \qquad \cdots\cdots(14)$$

and

$$\chi_{\perp} \simeq \beta^2\varepsilon\{\frac{8}{\Delta_1} + (\frac{-9/2}{\Delta_0-\Delta_1} + \frac{9/2}{\Delta_2-\Delta_0})\exp(-\Delta_0/kT) +$$

$$+2(\frac{-4}{\Delta_1} + \frac{-9/4}{\Delta_1-\Delta_0} + \frac{3/4}{\Delta_2-\Delta_1} + \frac{9/2}{\Delta_2-\Delta_1})\exp(-\Delta_1/kT)\} \qquad \cdots\cdots\cdots\cdots(15)$$

here for convenience we have changed the notation from Δ_1+V_{10}, Δ_1+V_{11} and $\Delta_1+\Delta_2+V_{2i}$ ($i=0,1,2$) to Δ_0, Δ_1, and Δ_2, respectively(see Fig. 1).

$$\chi_{\parallel}-\chi_{\perp} \simeq \beta^2\varepsilon\Big\{ \Big(\frac{8}{\Delta_0} - \frac{8}{\Delta_1}\Big) + \Big(\frac{-8}{\Delta_0} + \frac{3/2}{\Delta_2-\Delta_0} + \frac{9/2}{\Delta_0-\Delta_1}\Big)\exp(-\Delta_0/kT)$$

$$+ \Big(\frac{9/2}{kT} + \frac{8}{\Delta_1} + \frac{9/2}{\Delta_1-\Delta_0} + \frac{-3/2}{\Delta_2-\Delta_1}\Big)\exp(-\Delta_1/kT)\Big\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(16)$$

In cases where the crystal field splitting of the $^7F_1$ state is small compared with the spacing between the $^7F_1$ and $^7F_2$ states, we can further approximate eq.(16) as

$$\chi_{\parallel}-\chi_{\perp} \simeq \beta^2\varepsilon\Big\{\Big(\frac{8}{\Delta_0} - \frac{8}{\Delta_1}\Big) + \Big(\frac{-8}{\Delta_0} + \frac{9/2}{\Delta_0-\Delta_1}\Big)\exp(-\Delta_0/kT) + \Big(\frac{9/2}{kT} + \frac{8}{\Delta_1} + \frac{9/2}{\Delta_1-\Delta_0}\Big)\exp(-\Delta_1/kT)\Big\}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(17)$$

IV. Pseudocontact shift

If we adopt the point dipole model as described by McConnell and Robertson(6), the pseudocontact shift can be given by the following equation(7).

$$\Delta H/H = (1-3\cos^2\theta)(\chi_{\parallel}-\chi_{\perp})/R^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(18)$$

Substituting eq.(17) into the above, we obtain an approximate expression for the pseudocontact shift in Eu(III) complexes.

$$\frac{\Delta H}{H} \simeq \frac{(1-3\cos^2\theta)}{R^3}\beta^2\{ 1 + \exp(-\Delta_0/kT) + 2\exp(-\Delta_1/kT)\}^{-1}$$

$$\times\Big\{\Big(\frac{8}{\Delta_0} - \frac{8}{\Delta_1}\Big)-\Big(\frac{8}{\Delta_0} + \frac{9/2}{\Delta_1-\Delta_0}\Big)\exp(-\Delta_0/kT) + \Big(\frac{9/2}{kT} + \frac{8}{\Delta_1} + \frac{9/2}{\Delta_1-\Delta_0}\Big)\exp(-\Delta_1/kT)\Big\} \quad \ldots\ldots(19)$$

In eq.(19), R is the distance between the central Eu(III) ion and the proton of interest, θ the angle between the C_3 axis of the complex and the R vector, and Δ_0 and Δ_1 are the energies of the $^7F_1(J_z=0)$ and $^7F_1(J_z=\pm1)$ levels, respectively, as measured from the ground state $^7F_0$(see Fig. 1).

As is evident from eq.(19), the temperature dependence of the pseudocontact shift of the Eu(III) complex with C_{3h} , D_{3h} or C_{3v} symmetry is quite different from the Curie behavior. Although the magnetic characters of the crystal field levels in tris-chelated Eu(III) complexes have not been well recognized(4,5), the dominant terms at higher temperatures may be the latter terms and at low temperatures the first term may dominate. The shift is expected to reach asymptotically

$$\frac{\Delta H}{H} \longrightarrow \frac{(1-3\cos^2\theta)}{R^3}\beta^2\left(\frac{8}{\Delta_0}-\frac{8}{\Delta_1}\right) \qquad \cdots\cdots (20)$$

at low temperatures($kT \ll \Delta_0$ or Δ_1).

Figure 2 shows the temperature dependence of the pseudocontact shift predicted by the approximate eq.(19), assuming that $\Delta_0=350\ \mathrm{cm}^{-1}$, $\Delta_1=600\ \mathrm{cm}^{-1}$(4,5), $\theta=60^\circ$ and R=6, 7,8 Å(8-11).

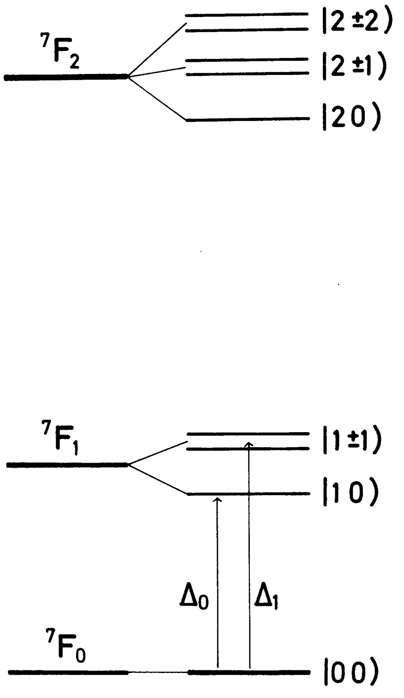

Figure 1. The crystal field splitting of the lower multiplets in Eu(III) ion.

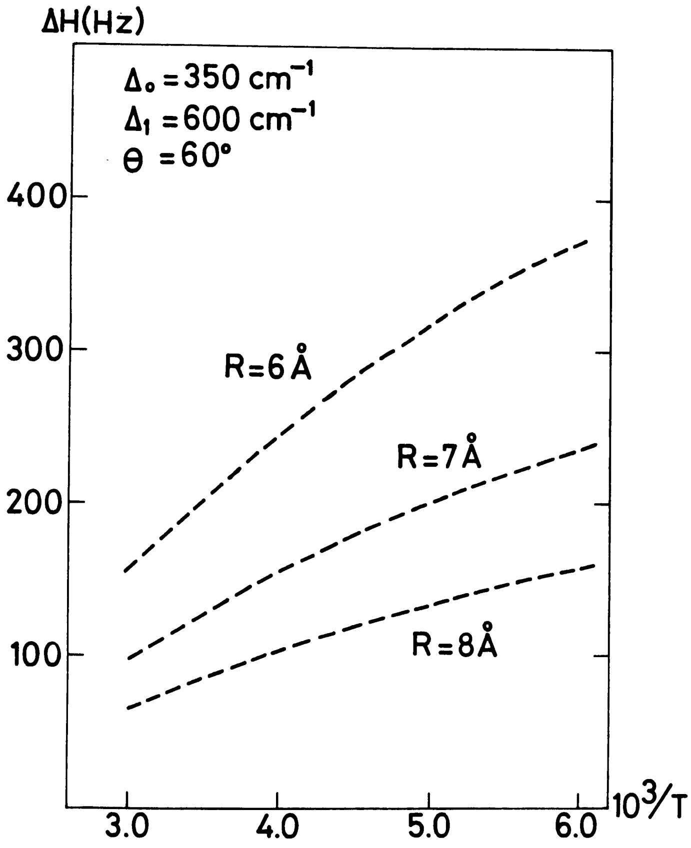

Figure 2. The calculated temparature dependence of the pseudocontact shift (eq.(19)) , the resonance frequency being assumed to be 100 MHz.

References.

* Part I of this series, Ushio Sakaguchi, Masayuki Kunugi, Toshio Fukumi, Shin'ichi Tadokoro, Akira Yamasaki, and Shizuo Fujiwara, Chemistry Letters(in press).

(1) B.R.Judd, Mol.Phys.,2,407(1959).

(2) A.Abragam and B.Bleaney,"Electron Paramagnetic Resonance of Transition Ions" Oxford(1970).

(3) J.H.Van Vleck,"Theory of Electric and Magnetic Susceptibilities", Oxford University Press, London(1932).

(4) E.V.Sayre and S.Freed, J.Chem.Phys.,24,1213(1956).

(5) C.Brecher, H.Samelson and A.Lempicki, J.Chem.Phys.,42,1081(1965).

(6) H.M.McConnell and R.E.Robertson, ibid.,29,1361(1958).

(7) R.J.Kurland and B.R.McGarvey, J.Mag.Resonance,2,286(1970).

(8) C.S.Erasmus and J.C.A.Boeyens, Acta Cryst.,B26,1843(1970).

(9) W.DeW.Horrocks,Jr., J.P.Sipe III, and J.R.Luber, J.Amer.Chem.Soc.,93,5258(1971).

(10) J.A.Cunningham, D.E.Sands, and W.F.Wagner, Inorg.Chem.,6,499(1967).

(11) T.Phillips II, D.E.Sands, and W.F.Wagner, ibid.,7,2295(1968).

(12) B.G.Wybourne,"Spectroscopic Properties of Rare Earths", John Wiley&Sons,Inc., N.Y.(1965).

(Received February 7, 1972)