

# NMR Chemical Shift for 4d<sup>n</sup> System (II). Calculation of the Pseudo Contact Shift for a 4d<sup>1</sup> System in a Strong Crystal Field Environment of Octahedral Symmetry

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NMR shift arising from the electron orbital angular momentum and the electron spin dipolar-nuclear spin angular momentum interactions has been investigated for a 4d<sup>1</sup> system in a strong crystal field of octahedral symmetry. To examine the NMR shift for a 4d<sup>1</sup> system in a strong crystal field of octahedral symmetry, we derive a general expression for  $\Delta B/B$  using a nonmultipole expansion technique. From this expression all the multipolar terms are determined. For the 4d<sup>1</sup> system in a strong crystal field of octahedral symmetry the exact solution for NMR shift,  $\Delta B$ , is compared with the multipolar results.  $\Delta B/B$  for the 4d<sup>1</sup> system is also compared with that for the 3d<sup>1</sup> system. It is found that the  $1/R^7$  term contributes dominantly to the NMR shift. However, there is good agreement between the nonmultipole and multipolar results for  $R$ -values larger than 0.2 nm for the 4d<sup>1</sup> system but for  $R$ -values larger than 0.4 nm for the 3d<sup>1</sup> system.

## 1. Introduction

For a decade considerable interest has been focussed on the NMR shifts arising from 3d<sup>n</sup> and 4f<sup>n</sup> systems<sup>1</sup> and in the use of lanthanide ions as NMR shift reagents<sup>2</sup>. The NMR shift in 3d<sup>n</sup> and 4f<sup>n</sup> paramagnetic systems has been interpreted as arising through the Fermi contact interaction between the electron bearing nucleus and the NMR nucleus<sup>3</sup>. For this case a simplified form of the expression for the NMR shift,  $\Delta B$ , was derived (4),

$$\frac{\Delta B}{B} = -\frac{a \mu_B}{3g_N \mu_N} \left\{ \frac{2}{\lambda} (g-1)(g-2) + (g-1)g \frac{J(J+1)}{kT} \right\} \quad (1)$$

where

$$g = 1 + \{J(J+1) - L(L+1) + S(S+1)\} / [2J(J+1)] \\ \lambda = \pm \zeta / 2S$$

Here  $\zeta$  is the spin-orbit coupling constant and only the  $(2S+1)L_J$  ground state was considered with no bonding effects.

In the other cases<sup>5</sup> the NMR shifts have been interpreted as arising dominantly through pseudo contact interactions. The expression for NMR shifts first given by McConnell and Robertson<sup>6</sup>, adopting the dipolar approximation, was extended by Kurland and McGravey<sup>7</sup> in terms of the magnetic susceptibility components,  $\chi_{\alpha\alpha}$ ,

$$\frac{\Delta B}{B} = -\frac{1}{3R^3} \left\{ \left[ \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy}) \right] (3 \cos^2 \theta - 1) + \frac{3}{2}(\chi_{xx} - \chi_{yy}) \sin^2 \theta \cos 2\phi \right\} \quad (2)$$

This expression has been used extensively in interpreting the pseudo contact shift in paramagnetic 3d<sup>n</sup> and 4f<sup>n</sup> systems. Using the dipolar approximation expressed in terms of the magnetic susceptibility components, Bleaney derived an equation for the NMR shift<sup>8</sup>,  $\Delta B$ , which may be written as<sup>4</sup>,

$$\frac{\Delta B}{B} = \frac{N \mu_B^2 g^2 (2L+1-4S) [3X(X-1) - 4J(J+1)(L+1)]}{24 \sqrt{5} (2L+1)(2L-1)(2L-1) \sqrt{\pi} R^3 k^2 T^2} \\ \times (1 - 3 \cos^2 \theta) a^2 \quad (3)$$

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$$X = J(J+1) + L(L+1) - S(S+1)$$

In equation (3),  $l=3$ ,  $a_l^0$  is a crystal field parameter,  $N$  is the Avogadro constant. This equation can be applied to 4f<sup>n</sup> systems. As far as we are aware no previous attempt has been made to determine the exact solution of the NMR shift arising from the 4d-electron angular momentum and the 4d-electron spin dipolar-nuclear spin angular momentum interactions and, in addition, to compare the results with the multipolar approximations which may be expressed as<sup>9</sup>

$$\frac{\Delta B}{B} = \sum_{L=2}^K \sum_{M=0}^L (A_{LM} \cos M\phi + B_{LM} \sin M\phi) P_L^M(\cos \theta) / R^{L+1} \quad (4)$$

where  $K=2(2l+1)$  for a specific  $l$ -electron,  $P_L^M(\cos \theta)$ , the associated Legendre polynomials and the coefficients  $A_{LM}$  and  $B_{LM}$  measure the anisotropy in the multipolar magnetic susceptibilities of the molecule. The purpose of this work is to develop a method for calculating the NMR shift for a 4d<sup>1</sup> system in a strong crystal field environment of octahedral symmetry, adopting the nonmultipole expansion method<sup>10</sup> and to compare this exact results with the multipolar NMR results. This enable us to explore the limitations of the multipolar expansion method in interpreting the NMR shifts in 4d<sup>1</sup> transition metal complexes. We also compare the NMR shift for a 4d<sup>1</sup> system with that of a 3d<sup>1</sup> system in a strong crystal field environment of octahedral symmetry.

## 2. Theory

The hamiltonian representing the various interactions we shall consider in this paper may be expressed as

$$\mathcal{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + V(r) + J\mathbf{I} \cdot \mathbf{S} \\ + \mu_B (\mathbf{I} + 2\mathbf{S}) \cdot \mathbf{B} + \mathcal{H}_{hf} \quad (5)$$

where  $V(r)$  is a crystal field term and

$$\mathcal{H}_{hf} = \frac{\mu_0}{4\pi} g_N \mu_B \mu_N \left\{ \frac{2\mathbf{I}_N \cdot \mathbf{I}}{r_N^3} + g_S \left[ \frac{3(\mathbf{r}_N \cdot \mathbf{S}) \mathbf{r}_N \cdot \mathbf{I}}{r_N^5} - \frac{\mathbf{S} \cdot \mathbf{I}}{r_N^3} \right] \right\} \quad (6)$$

Here  $r$  and  $r_N$  are electron radius vector about the electron-bearing atom and the nucleus with nuclear spin angular mo-

mentum  $I$ , respectively. The quantity  $B$  is the applied magnetic field and the other terms have their usual meaning. In this paper  $g_S$ , the free electron  $g$  value, is taken to be equal to exactly 2. Since we are examining the interaction of a 4d electron centered at O in a strong crystal field of octahedral symmetry (refer to 1st series of this work.), we shall express the required wave functions as

$$\begin{aligned} |4d_{yz}\rangle &= \left(\frac{\beta^9}{21\pi}\right)^{\frac{1}{2}} yzr \exp(-\beta r) \\ |4d_{xz}\rangle &= \left(\frac{\beta^9}{21\pi}\right)^{\frac{1}{2}} xzr \exp(-\beta r) \\ |4d_{xy}\rangle &= \left(\frac{\beta^9}{21\pi}\right)^{\frac{1}{2}} xy r \exp(-\beta r) \end{aligned} \quad (7)$$

where  $\beta = 2.8481/a_0^{11}$ .

To determine the NMR shift of a 4d<sup>1</sup> system in liquid solution, the principal values  $\sigma_{xx}$ ,  $\sigma_{yy}$  and  $\sigma_{zz}$  of the NMR screening tensor,  $\sigma$ , are determined by considering the magnetic field,  $B$ , interaction as parallel to the  $x$ ,  $y$  and  $z$  axes and averaged assuming a Boltzmann distribution. The contribution to the NMR shift,  $\Delta B$ , is given by

$$\Delta B = \frac{1}{3} B(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \quad (8)$$

where

$$\begin{aligned} \sigma_{\alpha\alpha} &= \left(\frac{\partial^2 \langle \mathcal{H}_{hf} \rangle}{\partial \mu_\alpha \partial B_\alpha}\right)_{\mu=B=0} \\ \mu &= g_N \mu_N I \end{aligned} \quad (9)$$

The term  $\langle \mathcal{H}_{hf} \rangle$  refers to the Boltzmann average of the hyperfine interaction represented by equation (6),

$$\langle \mathcal{H}_{hf} \rangle = \frac{\sum_i \langle \phi_i | \mathcal{H}_{hf} | \phi_i \rangle \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} \quad (10)$$

where  $\phi_i$  are the eigenfunctions of the spin-orbit coupling and magnetic field interactions and  $E_i$  the corresponding eigenvalues. To evaluate the hyperfine interaction matrix elements,  $\langle \phi_i | \mathcal{H}_{hf} | \phi_i \rangle$ , we adopt the calculated hyperfine integrals for 4d orbitals<sup>12</sup>. In a strong crystal field of octahedral symmetry, the NMR shift for a 4d<sup>1</sup> system is given by

$$\frac{\Delta B}{B} = -\frac{\mu_0}{4\pi} \frac{\mu_B^2}{kT} \left\{ \frac{d(R) + [1 - \exp(3\zeta/2kT)](kT/\zeta)S(R)}{1 + 2 \exp(3\zeta/2kT)} \right\} \quad (11)$$

where

$$\begin{aligned} d(R) &= \frac{8\sqrt{\pi}}{147} Y_{00}(\theta, \phi) E(t) \\ &+ \frac{11520}{t^5} \sqrt{\frac{\pi}{21}} \left[ \frac{1}{2} \sqrt{\frac{7}{3}} Y_{40}(\theta, \phi) \right. \\ &+ \left. \frac{1}{2} \sqrt{\frac{5}{6}} (Y_{4-4}(\theta, \phi) + Y_{44}(\theta, \phi)) \right] H(t) \\ &+ \frac{15206400}{7t^7} \sqrt{\frac{\pi}{26}} \left[ \frac{1}{2\sqrt{2}} Y_{60}(\theta, \phi) \right. \\ &- \left. \sqrt{\frac{7}{4}} (Y_{6-4}(\theta, \phi) + Y_{64}(\theta, \phi)) \right] J(t) \end{aligned}$$

$$\begin{aligned} S(R) &= -\frac{40\sqrt{\pi}}{441} Y_{00}(\theta, \phi) M(t) \\ &- \frac{5120}{t^5} \sqrt{\frac{\pi}{21}} \left[ \frac{1}{2} \sqrt{\frac{7}{3}} Y_{40}(\theta, \phi) \right. \\ &+ \left. \frac{1}{2} \sqrt{\frac{5}{6}} (Y_{4-4}(\theta, \phi) + Y_{44}(\theta, \phi)) \right] N(t) \\ &- \frac{10137600}{7t^7} \sqrt{\frac{\pi}{26}} \left[ \frac{1}{2\sqrt{2}} Y_{60}(\theta, \phi) \right. \\ &- \left. \sqrt{\frac{7}{4}} (Y_{6-4}(\theta, \phi) + Y_{64}(\theta, \phi)) \right] J(t) \quad (12) \\ E(t) &= \beta^3 e^{-t} \left( \frac{1}{3} \frac{t^6}{6!} + \sum_{n=0}^5 \frac{t^n}{n!} \right) \\ H(t) &= \beta^3 \left\{ 1 - e^{-t} \left( \frac{8}{9} \frac{t^{11}}{11!} + \sum_{n=0}^{10} \frac{t^n}{n!} \right) \right\} \\ J(t) &= \beta^3 \left\{ 1 - e^{-t} \left( \frac{13}{11} \frac{t^{13}}{13!} + \sum_{n=0}^{12} \frac{t^n}{n!} \right) \right\} \\ M(t) &= \beta^3 e^{-t} \left( -\frac{2}{15} \frac{t^6}{6!} + \sum_{n=0}^5 \frac{t^n}{n!} \right) \\ N(t) &= \beta^3 e^{-t} \left( \frac{4}{3} \frac{t^{11}}{11!} \right) \end{aligned}$$

Since this expression for  $\Delta B/B$  is applicable for all values of  $R$  we may determine from equation (11) the case when  $R \rightarrow 0$ , namely,

$$\frac{\Delta B}{B} \rightarrow \frac{4\beta^3 \mu_B^2}{441kT} \left\{ \frac{3-5[1-\exp(3\zeta/2kT)]kT/\zeta}{1+2\exp(3\zeta/2kT)} \right\} \frac{\mu_0}{4\pi} \quad (13)$$

When  $R$  is large, the terms in equation (11) involving the polar coordinates of the NMR nucleus may be expressed in terms of  $1/R^5$  and  $1/R^7$ ,

$$\begin{aligned} d(R) &= \frac{1}{R^5} \frac{360}{\beta^2} \sqrt{\frac{\pi}{21}} \left\{ \frac{1}{2} \sqrt{\frac{7}{3}} Y_{40}(\theta, \phi) \right. \\ &+ \left. \frac{1}{2} \sqrt{\frac{5}{6}} [Y_{4-4}(\theta, \phi) + Y_{44}(\theta, \phi)] \right\} \\ &+ \frac{1}{R^7} \frac{118800}{7\beta^4} \sqrt{\frac{\pi}{26}} \left\{ \frac{1}{2\sqrt{2}} Y_{60}(\theta, \phi) \right. \\ &- \left. \frac{\sqrt{7}}{4} [Y_{6-4}(\theta, \phi) + Y_{64}(\theta, \phi)] \right\} \\ S(R) &= -\frac{1}{R^7} \frac{79200}{7\beta^4} \sqrt{\frac{\pi}{26}} \left\{ \frac{1}{2\sqrt{2}} Y_{60}(\theta, \phi) \right. \\ &- \left. \frac{\sqrt{7}}{4} [Y_{6-4}(\theta, \phi) + Y_{64}(\theta, \phi)] \right\} \quad (14) \end{aligned}$$

In equation (12), (13) and (14), the symmetry of the system is reflected in the analytical form for  $\Delta B/B$ , namely, only those combinations of the spherical harmonics  $Y_{lm}(\theta, \phi)$  that transform as the irreducible representation  $A_{1g}$  of the octahedral group occur.

### 3. Results and Discussion

The calculated NMR shifts along the  $x$ ,  $y$  and  $z$  axes for a 4d<sup>1</sup> system in a strong crystal field environment of octahedral symmetry are listed in Table 1. Here we choose  $\beta = 2.8481/a_0$ , the spin-orbit coupling constant as  $1030 \text{ cm}^{-1}$ . These parameter values are similar to those for  $\text{Mo}^{5+}$  ion. The temperature is taken as  $T = 300 \text{ K}$ . As shown in Table 1,  $\Delta B/B$  for specific  $R$ -values along the  $\langle 100 \rangle$ ,  $\langle 010 \rangle$  and  $\langle 001 \rangle$  axes for a 4d<sup>1</sup> system in a strong crystal field environments of octahedral symmetry are consistent with each other. This result represents an isotropic NMR shielding for a 4d<sup>1</sup> system

**TABLE 1:**  $\Delta B/B$ (ppm) for Specific  $R$ -values for a  $4d^1$  System along the  $x$ ,  $y$  and  $z$  axes in a Strong Crystal Field Environment of Octahedral Symmetry

$R$ (nm)	$\Delta B/B$ (ppm)		
	$\langle 100 \rangle$ axis	$\langle 010 \rangle$ axis	$\langle 001 \rangle$ axis
0.05	-92044.3724	-92044.3724	-92044.3724
0.1	-879.2927	-879.2927	-879.2927
0.15	-60.9222	-60.9233	-60.9233
0.2	-8.4320	-8.4320	-8.4320
0.25	-1.7866	-1.7866	-1.7866
0.3	-0.5036	-0.5036	-0.5036
0.35	-0.1732	-0.1732	-0.1732
0.4	-0.0689	-0.0689	-0.0689
0.45	-0.0307	-0.0307	-0.0307
0.5	-0.0149	-0.0149	-0.0149

**TABLE 2:**  $\Delta B/B$  (ppm) for Specific  $R$ -Values for a  $4d^1$  System in a Strong Field Environment of Octahedral Symmetry

$R$ (nm)	$\Delta B/B$ (ppm)		
	$\langle 100 \rangle$ axis	$\langle 110 \rangle$ axis	$\langle 111 \rangle$ axis
0.05	-92044.3724	147206.3179	-162486.2417
0.1	-879.2927	1216.9444	-1401.0489
0.15	-60.9233	91.3902	-100.1516
0.2	-8.4320	13.3953	-14.5252
0.25	-1.7869	2.8466	-3.0761
0.3	-0.5036	0.7963	-0.8561
0.35	-0.1732	0.2712	-0.2897
0.4	-0.0689	0.1069	-0.1132
0.45	-0.0307	0.0469	-0.0493
0.5	-0.0149	0.0225	-0.0234

Parameters used;  $\zeta=1030\text{cm}^{-1}$ ,  $\beta=2.8481/a_0$  and  $T=300\text{K}$ .**TABLE 3:** A Comparison of the Exact values of  $\Delta B/B$  (ppm) using Equation (11) with the Multipolar Terms for Specific  $R$ -values along  $\langle 100 \rangle$  Axis

$R$ (nm)	$\Delta B/B$ (ppm)			
	$1/R^5$	$1/R^7$	sum of all multipolar terms	exact from eq. (11).
0.05	-219.5464	-91038.5742	-91258.1206	-92044.3724
0.1	-48.7723	-775.3416	-824.1140	-879.2927
0.15	-2.8949	-56.6456	-59.4506	-60.9233
0.2	-0.1837	-8.2277	-8.4114	-8.4320
0.25	-0.0410	-1.7456	-1.7866	-1.7869
0.3	-0.0161	-0.4876	-0.5036	-0.5036
0.35	-0.0074	-0.1657	-0.1732	-0.1732
0.4	-0.0038	-0.0651	-0.0689	-0.0689
0.45	-0.0021	-0.0285	-0.0307	-0.0307
0.5	-0.0012	-0.0136	-0.0149	-0.0149

along the  $x$ ,  $y$  and  $z$  axes in a strong crystal field of octahedral symmetry. The calculated NMR shifts,  $\Delta B/B$ , along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  axes for specific  $R$ -values are tabulated in Table 2. As expected, the NMR shift,  $\Delta B/B$ , decreases in magnitude rapidly as  $R$  increases. Along the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  axes,  $\Delta B/B$  is negative for all values of  $R$ , while along the  $\langle 110 \rangle$  axis,  $\Delta B/B$  is positive. The NMR results for a  $4d^1$  system using equation (11) and the corresponding multipolar terms,  $1/R^5$  and  $1/R^7$ , given by

**TABLE 4:** A Comparison of  $\Delta B/B$ (ppm) using Equation(11) with the Multipolar Terms for Specific  $R$ -values Along the  $\langle 110 \rangle$  Axis.

$R$ (nm)	$\Delta B/B$ (ppm)			
	$1/R^5$	$1/R^7$	sum of all multipolar terms	exact from eq. (11).
0.05	54.8866	147937.6831	147992.5697	147206.3179
0.1	12.1931	1259.9301	1272.1232	1216.9444
0.15	0.7237	92.0492	92.7729	91.3902
0.2	0.0459	13.3700	13.4159	13.3953
0.25	0.0103	2.8366	2.8469	2.8466
0.3	0.0040	0.7923	0.7963	0.7963
0.35	0.0019	0.2693	0.2712	0.2712
0.4	0.0010	0.1058	0.1067	0.1067
0.45	0.0005	0.0464	0.0469	0.0469
0.5	0.0003	0.0222	0.0225	0.0225

Parameters used;  $\zeta=1030\text{cm}^{-1}$ ,  $\beta=2.8481/a_0$  and  $T=300\text{K}$ .**TABLE 5:** A Comparison of  $\Delta B/B$  (ppm) using Equation (11) with the Multipolar Terms for Specific  $R$ -values along the  $\langle 111 \rangle$  Axis

$R$ (nm)	$\Delta B/B$ (ppm)			
	$1/R^5$	$1/R^7$	sum of all multipolar terms	exact from eq. (11)
0.05	146.3643	-161846.3342	-161699.9899	-162486.2417
0.1	32.5149	-1378.3851	-1345.8702	-1401.0489
0.15	1.9300	-100.7034	-98.7734	-100.1561
0.2	0.1224	-14.6270	-14.5046	-14.5252
0.25	0.0274	-3.1033	-3.0759	-3.0761
0.3	0.0107	-0.8668	-0.8561	-0.8561
0.35	0.0050	-0.2946	-0.2897	-0.2897
0.4	0.0025	-0.1157	-0.1132	-0.1132
0.45	0.0014	-0.0507	-0.0493	-0.0493
0.5	0.0008	-0.0243	-0.0234	-0.0234

Parameters used;  $\zeta=1030\text{cm}^{-1}$ ,  $\beta=2.8481/a_0$  and  $T=300\text{K}$ .**TABLE 6:**  $\Delta B/B$  (ppm) for Specific  $R$ -values for a  $3d^1$  System in a Strong Crystal Field Environment of Octahedral Symmetry

$R$ (nm)	$\Delta B/B$ (ppm)			
	$\langle 100 \rangle$ axis	$\langle 001 \rangle$ axis	$\langle 110 \rangle$ axis	$\langle 111 \rangle$ axis
0.05	-783171.9483	-783171.9483	1154326.66	-1187769.763
0.1	-8824.8011	-8824.8011	9118.2366	-8378.6768
0.15	-935.3065	-935.3065	572.9484	-403.5502
0.2	-215.3654	-215.3654	107.8626	-23.6982
0.25	-67.9963	-67.9963	33.4199	5.8437
0.3	-26.0932	-26.0932	12.3354	5.6731
0.35	-11.5494	-11.5493	5.0923	3.6171
0.4	-5.7325	-5.7325	2.3340	2.2015
0.45	-3.1050	-3.1050	1.1761	1.3570
0.5	-1.8008	-1.8008	0.6421	0.8592

Parameters used;  $\zeta=154\text{cm}^{-1}$ ,  $\beta=4/3a_0$  and  $T=300\text{K}$ .

equation (4) are shown in Table 3, 4 and 5. A comparison of the multipolar terms with the exact solution given by equation (11) show that the first multipolar term,  $1/R^5$  in this case, is inadequate to describe the NMR shift for all values of  $R$ . When the  $1/R^7$  term is included, there is good agreement between the nonmultipole and multipolar results for  $R$  values larger than 0.2 nm. It is interesting to note that along the  $\langle 111 \rangle$  axis, the  $1/R^5$  term gives values opposite in sign to that of the  $1/R^7$  term. In addition, the results show that the NMR

TABLE 7: A Comparison of the Exact Values of  $\Delta B/B$  (ppm) with the Multipolar Terms for Specific R-values for a 3d<sup>1</sup> System in a strong Crystal field of O<sub>h</sub> Symmetry.

(a) Along  $\langle 100 \rangle$  axis

R (nm)	$\Delta B/B$ (ppm)			exact values
	$1/R^5$	$1/R^7$	sum of all multipolar terms	
0.05	-698476.9775	-83197.2342	-781674.2117	-783171.9483
0.1	-5488.3463	-2828.9029	-8317.2492	-8824.8011
0.15	-345.7988	-480.4265	-826.2253	-935.3065
0.2	-55.9411	-141.1062	-197.0472	-215.3654
0.25	-14.3482	-50.9938	-65.3420	-67.9863
0.3	-4.5484	-21.1516	-25.7045	-26.0493
0.35	-1.6416	-9.8659	-11.5076	-11.5494
0.4	-0.6595	-5.0682	-5.7277	-5.7325
0.45	-0.2913	-2.8131	-3.1044	-3.1050
0.5	-0.1396	-1.6612	-1.8008	-1.8008

(b) Along the  $\langle 110 \rangle$  axis

R(nm)	$\Delta B/B$ (ppm)			Exact values
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	
0.05	1135025.088	20799.3085	1155824.397	1154326.66
0.1	8918.5628	707.2257	9625.7885	9118.2366
0.15	561.9230	120.1066	682.0296	572.9484
0.2	90.9042	35.2765	126.1807	107.8626
0.25	23.3158	12.7484	36.0642	33.4199
0.3	7.3912	5.2890	12.6804	12.3354
0.35	2.6676	2.4665	5.1341	5.0923
0.4	1.0717	1.2670	2.3388	2.3340
0.45	0.4733	0.7033	1.1766	1.1761
0.5	0.2269	0.4153	0.6421	0.6421

(c) Along the  $\langle 111 \rangle$  axis

R(nm)	$\Delta B/B$ (ppm)			Exact values
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	
0.05	-1241736.849	55464.8228	-1186272.026	-1187769.763
0.1	-9757.0602	1885.9353	-7871.1249	-8378.6768
0.15	-614.7534	320.2843	-294.4690	-403.5502
0.2	-99.4508	94.0708	-5.3799	-23.6982
0.25	-25.5079	33.9959	-8.4880	5.8437
0.3	-8.0861	14.1040	6.0179	5.6731
0.35	-2.9184	6.5773	3.6589	3.6171
0.4	-1.1725	3.3788	2.2063	2.2015
0.45	-0.5179	1.8754	1.3576	1.3570
0.5	-0.2482	1.1074	0.8593	0.8592

Parameters used;  $\zeta=154 \text{ cm}^{-1}$ ,  $\beta=4/3a_0$  and  $T=300 \text{ K}$ .

shift arising from the electron angular momentum, and the electron spin dipolar-nuclear spin angular momentum interactions in a 4d<sup>1</sup> system in a strong crystal field environment of octahedral symmetry is large for significant distances between the NMR nucleus and 4d-electron bearing atom. For distances less than 0.35 nm it should not be neglected.

The calculated NMR shifts for a 3d<sup>1</sup> system in a strong crystal field environment of octahedral symmetry, using the equation derived by Golding and Stubbs (13), are listed in Table 6 and 7. Here we choose  $\beta=4/3a_0$ , the spin-orbit coupling constant as  $154 \text{ cm}^{-1}$ . These parameter values correspond to those for Ti<sup>3+</sup> ion. The temperature is chosen as  $T=300 \text{ K}$ . As shown in Table 6-7, a similar trend for the NMR results with the 4d<sup>1</sup> system appears in a 3d<sup>1</sup> system in a strong crystal field of octahedral symmetry. However, the NMR shifts in magnitude increase significantly in the 3d<sup>1</sup> system in a strong crystal field environment of octahedral symmetry and along the  $\langle 111 \rangle$  axis, the NMR shift changes sign for R-values larger than 0.25 nm. As shown in Table 7(c), the  $1/R^5$  term gives the negative shift while the  $1/R^7$  term gives the positive shift. The contribution of  $1/R^7$  term to  $\Delta B/B$  is bigger than that of  $1/R^5$  term for R-values larger than 0.25 nm. From Table 7, we can find that for a 3d<sup>1</sup> system in a strong crystal field of octahedral symmetry, there is good agreement between the nonmultipole and multipolar results for R-values larger than 0.4 nm. These are different from the NMR results for a 4d<sup>1</sup> system. This calculation can be applied to investigate the NMR shift for 4d<sup>n</sup> system. However, no experimental value of  $\Delta B/B$  has been reported for 4d<sup>1</sup> and 3d<sup>1</sup> systems.

## References

- (1) G. A. Webb, Ann. Rept. on NMR Spectroscopy, **6A**, 1 (1975).
- (2) A. F. Cockerill, G. L. O. Davies, R. C. Harden and D. M. Rackham, *Chem. Revs.*, **73**, 553 (1973).
- (3) W. B. Lewis, J. A. Jackson and R. J. Taube, *J. Chem. Phys.*, **36**, 694 (1962).
- (4) R. M. Golding, R. O. Pascual and S. Ahn, *J. Magn. Res.*, **46**, 406 (1982).
- (5) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969); B. Bleaney, C. M. Dobson, B. A. Levine, B. B. Martin, R. J. P. Williams and A. V. Xavier, *Chem. Commun.*, 791 (1972).
- (6) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).
- (7) R. J. Kurland and B. R. ReGravey, *J. Magn. Res.*, **2**, 286 (1970).
- (8) B. Bleaney, *J. Magn. Res.*, **8**, 91 (1972).
- (9) P. J. Stiles, *Nucl. Phys.*, **29**, 1271 (1975).
- (10) R. M. Golding and L. C. Stubbs, *Proc. Roy. Soc.*, **A354**, 223 (1977).
- (11) E. Clementi, D. L. Raimondi and W. P. Reinhart, *J. Chem. Phys.*, **47**, 1300 (1968).
- (12) S. Ahn and H. C. Suh, Submitted to *Bull. Korean Chem. Soc.* for publication.
- (13) L. C. Stubbs, Unpublished Thesis (PhD. The University of New South Wales, 1978).