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## NMR Chemical Shift for $4d^n$ System (IV). Calculation of NMR Chemical Shift for $4d^2$ System in a Strong Crystal Field Environment of Octahedral Symmetry

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The NMR chemical shift arising from 4d electron orbital angular momentum and 4d electron spin dipolar-nuclear Spin angular momentum interactions for a  $4d^2$  system in a strong crystal field environment of octahedral symmetry has been investigated when the four fold axis is taken as the quantization axis. The NMR results are compared with the multipolar shift at various R-values and we find that the exact results are in agreement with the multipolar shift when  $R \geq 0.20$  nm. We also separate the NMR shift into the contribution of the  $1/R^5$  and  $1/R^7$  terms. It is found that the contribution of the  $1/R^5$  term to the NMR shift is dominant than the contribution of the  $1/R^7$  term. Temperature dependence analysis shows that the  $1/T^2$  term is the dominant contribution to the NMR shift for a  $4d^2$  system but the contribution of the  $1/T$  term may not negligible. The similar results are obtained for a  $4d^1$  system from the temperature dependence analysis.

### 1. Introduction

In the past decade a great deal of interest has been focussed on NMR chemical shifts in paramagnetic systems.<sup>1-9</sup> NMR shift in paramagnetic systems was first interpreted in terms of the dipolar shift.<sup>10,11</sup> Attention has however been focussed on the higher multipolar terms<sup>12-14</sup> to illustrate the octapole contribution to the pseudo contact chemical shift. Recently, the non-multipole expansion method has been developed to elucidate the NMR chemical shifts in paramagnetic systems arising from the Fermi contact interaction and the electron orbital angular momentum and the electron spin dipolar-nuclear spin angular momentum interactions.<sup>5-8</sup> In interpreting the NMR chemical shift,  $\Delta B$ , obtained from the NMR spectra of paramagnetic molecules, it has been contrary to consider the Fermi contact interaction<sup>15</sup> and the dipolar term. The contribution of the former to the NMR chemical shift may be expressed as

$$\Delta B = a \langle S_z \rangle / g_N \mu_N \quad (1)$$

where  $a$  is the hyperfine interaction constant, The latter term was derived by Bleaney<sup>17</sup> using the dipolar approximation expressed in terms of magnetic susceptibility components of Kurland and McGravey.<sup>11</sup> For a  $4d^2$  system in a strong crystal field environment of octahedral symmetry the term in eq. (1) may be expressed<sup>16, 17</sup> as

$$\langle S_z \rangle = -\frac{\mu_B B}{3KT} \left\{ \frac{(g-\gamma)}{(2-\gamma)} J(J+1) + \frac{2KT(g-\gamma)(g-2)}{(2-\gamma)} \right\} \quad (2)$$

and

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

where only the  $(2s+1)L$  ground state has been considered with no bonding effects.

The dipolar term may be written as

$$\frac{\Delta B}{B} = \frac{\sqrt{5}}{40\sqrt{\pi}} \frac{a_0^2}{a_0^2} \frac{(2l+1-4S) \{3X(X-1) - 4J(J+1)(L+1)\}}{(2l+3)(2l-1)(L-1)} \frac{(1-3\cos^2\theta)}{R^2 K^2 T^2} \quad (3)$$

and

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

In eq. (3),  $\ell = 2$ ,  $a_0$  is a crystal field parameter and  $N$  is the Avogadro number. The quantity  $R$  is the distance between the NMR nucleus and electron bearing atom and  $\theta$  is the angle between the principal  $z$  axis and the  $R$  vector.

The temperature dependence of the NMR chemical shift was investigated<sup>18, 19</sup> and the separation of the Fermi contact term from the pseudo contact term by temperature dependence assuming  $T^{-1}$  for Fermi contact and Bleaney's  $T^{-2}$  for the pseudo contact term has been attempted.<sup>20</sup> Assuming the ligand field splitting are small compared to  $KT$ , Bleaney derived that the NMR shift predominantly has  $T^{-2}$  character, with a small  $T^{-1}$  contribution and a very small temperature independent term for all lanthanides.<sup>17</sup> In this case a method was developed to analyze a range of NMR shifts for a series of lanthanide complexes as a linear combination of eq. (2) and (3).<sup>21</sup> In this work the linear combination of the Fermi contact and the pseudo contact terms is applied to  ${}^3T_1$  ground state for a  $4d^2$  system in a strong crystal field of octahedral symmetry to analyze a range of NMR chemical shifts.

Since it was reported that the ground state of  $4d^2$ ,  $4d^3$ ,  $4d^4$ ,  $4d^5$ , and  $4d^7$  are  ${}^3T_1$ ,  ${}^4A_2$ ,  ${}^3T_2$  and  ${}^3E$  in a strong crystal field of octahedral symmetry, respectively, we expect that the electronic structure of  $4d^2$  system is different from those of  $4d^n$  system, where  $n = 1, 3, 4, 5$  and  $7$ . First, we choose a  $4d^2$  system to examine the NMR chemical shift in a strong crystal field environment of octahedral symmetry and the NMR results are to be compared with the multipolar results. The NMR Chemical shift is analyzed in terms of the contributions of  $1/R^5$  and  $1/R^7$  terms.

As far as we are aware no attempt has been made to determine the exact solution of the NMR shift arising from the 4d-electron orbital angular momentum and the 4d-electron spin dipolar-nuclear spin angular momentum interaction for a  $4d^2$  system. In this work we wish to determine, by a nonmultipole expansion, the NMR chemical shift in analytical form for a  $4d^2$  system in strong crystal field environment of octahedral symmetry to determine the magnitude and sign of the various electron-nuclear hyperfine interactions, detailed information about the electronic structure and distribution of electrons around the electron bearing nucleus when fourfold axis is chosen as the quantization axis.

The purpose of this work is to derive a general expression for the NMR chemical shift and to determine the NMR chemical shift for a  $4d^2$  system in a strong crystal field environment of octahedral symmetry, adopting the general formula. We also separate the contribution of Fermi contact and pseudo contact terms to the NMR chemical shift by temperature dependence analysis.

## 2. Theory

The hamiltonian representing the various interaction needed to consider in this work may be written as

$$H = \sum_{i=1}^2 \left\{ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Z_i e^2}{4\pi\epsilon_0 r_{e_i}} + V_i(r_{e_i}) + \zeta_i \mathbf{l}_i \cdot \mathbf{s}_i + \mu_B (l_i + 2s_i) \right\}$$

$$+ \frac{e^2}{|r_1 - r_2|} + H_{hy} \quad (4)$$

Where

$$V = \sum_{i=1}^2 V_i(r_{e_i}) = a_0 \left\{ \frac{1}{2} \sqrt{\frac{7}{3}} Y_{40}(\theta, \Phi) + \frac{1}{2} \sqrt{\frac{5}{6}} [Y_{44}(\theta, \Phi) + Y_{4-4}(\theta, \Phi)] \right\} \quad (5)$$

and

$$H_{hy} = \frac{\mu_0}{4\pi} g_N \mu_B \mu_N \left\{ \frac{2\mathbf{l}_N \cdot \mathbf{I}}{r_N^3} + g_s \left[ \frac{3(\mathbf{r}_N \cdot \mathbf{s}) r_N \cdot \mathbf{I}}{r_N^5} - \frac{\mathbf{s} \cdot \mathbf{I}}{r_N^3} \right] \right\} \quad (6)$$

Here  $r$ , and  $r_N$  are the electron radius vectors about the electron-bearing atom and the nucleus with nuclear spin angular momentum  $I$ , respectively. The quantity  $B$  is the applied magnetic field,  $V$  is the crystal field potential of octahedral symmetry and  $a_0$  is the required crystal field parameter. The other symbols have their usual meaning. In this paper  $g_s$ , free electron  $g$  value, is taken to be equal to exactly 2.

To determine the NMR chemical shift for a  $4d^2$  system in a strong crystal field of octahedral symmetry, we adopt the electronic wave functions for the  $4d$  electron in real forms given by

$$\begin{aligned} |4d_{yz}\rangle &= \left(\frac{\beta^3}{21\pi}\right)^{\frac{1}{2}} yzr \exp(-\beta r) \\ |4d_{zx}\rangle &= \left(\frac{\beta^3}{21\pi}\right)^{\frac{1}{2}} zxr \exp(-\beta r) \\ |4d_{xy}\rangle &= \left(\frac{\beta^3}{21\pi}\right)^{\frac{1}{2}} xy r \exp(-\beta r) \end{aligned} \quad (7)$$

A  $4d^2$  system in a strong crystal field environment of octahedral symmetry results in a  ${}^3T_1$  ground state whose energy is given by<sup>22</sup>

$$E({}^3T_1) = -\frac{4}{5} \Delta + A - 5B \quad (8)$$

where  $A$  and  $B$  are the Racah parameters and  $\Delta$  the crystal field parameter. Mixing due to the coulomb repulsion interaction between the  ${}^3T_1$  state of the  $t_2^2$  configuration and the  ${}^3T_1$  state of  $e^1 t_2^1$  configuration was ignored. The spin-orbit coupling interactions splits this  ${}^3T_1$  ground state into three levels whose eigenvalues are  $-\zeta/2$ ,  $\zeta/2$  and  $\zeta$ , respectively. The corresponding eigenfunctions are given by<sup>23, 24</sup>

$$\begin{aligned} |{}^3T_1 1 1\rangle &= |(-1^+ \zeta_1^+) \rangle \\ |{}^3T_1 1 0\rangle &= \frac{1}{\sqrt{2}} \{ |(-1^+ \zeta_1^-) \rangle + |(-1^- \zeta_1^+) \rangle \} \\ |{}^3T_1 1 -1\rangle &= |(-1^- \zeta_1^-) \rangle \\ |{}^3T_1 0 1\rangle &= |(1^+ \zeta_1^+) \rangle \\ |{}^3T_1 0 0\rangle &= \frac{1}{\sqrt{2}} \{ |(1^+ -1^-) \rangle + |(1^- -1^+) \rangle \} \\ |{}^3T_1 0 -1\rangle &= |(1^- -1^-) \rangle \\ |{}^3T_1 -1 1\rangle &= |(1^+ \zeta_1^+) \rangle \\ |{}^3T_1 -1 0\rangle &= \frac{1}{\sqrt{2}} \{ |(1^+ \zeta_1^-) \rangle + |(1^- \zeta_1^+) \rangle \} \\ |{}^3T_1 -1 -1\rangle &= |(1^- \zeta_1^-) \rangle \end{aligned} \quad (9)$$

where the numerals in the kets  $|{}^3T_1 a b\rangle$  indicate the effective  $M_L$  and  $M_S$  quantum numbers, respectively.

The magnetic field interaction was then treated as a perturbation to yield new eigenfunctions  $|\psi_n\rangle$  and corresponding eigenvalues  $E_n$ . The principal values  $\sigma_{aa}$  of the NMR shielding tensor are determined by considering the magnetic field interac-

tion parallel to the  $x$ ,  $y$  and  $z$  directions and then averaged assuming a Boltzmann distribution. The contribution to the NMR chemical shift is given by<sup>6</sup>

$$\Delta B = \frac{1}{3} B (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \quad (10)$$

where

$$\sigma_{\alpha\alpha} = \left( \frac{\partial^2 \langle H_{hy} \rangle}{\partial \mu_{\alpha} \partial B_{\alpha}} \right)_{\mu=B=0} \quad (11)$$

In eq. (11),

$$\langle H_{hy} \rangle = \frac{\sum_i \langle \psi_i | H_{hy} | \psi_i \rangle \exp(-E_i/KT)}{\sum_i \exp(-E_i/KT)}$$

and

$$\mu = g_N \mu_N I$$

The NMR chemical shift for a 4d<sup>2</sup> system in a strong crystal field environment of octahedral symmetry are calculated, adopting the required hyperfine integrals,<sup>25</sup> as outlined in the previous paragraph. The NMR chemical shift is given by

$$\frac{\Delta B}{B} = -\frac{2}{3} \frac{\mu_0}{4\pi} \frac{\mu_B^2}{KT} \left\{ \frac{\sum_{i=1}^3 (A_i + B_i KT/\zeta) \exp(-E_i/KT)}{\sum_{i=1}^3 d_i \exp(E_i/KT)} \right\} \quad (12)$$

where

$$d_1 = 5, d_2 = 3, d_3 = 1, E_1 = -\zeta/2, E_2 = \zeta/2 \text{ and } E_3 = \zeta.$$

with

$$A_1 = - (17/98) \sqrt{\pi} Y_{00}(\theta, \phi) A_1(t) - (15120/t^5) Y_4 D_1(t) + (8553600/t^7) Y_6 S(t)$$

$$A_2 = - (4/98) \sqrt{\pi} Y_{00}(\theta, \phi) A_2(t) + (2160/t^5) Y_4 D_2(t) - (8553600/t^7) Y_6 S(t)$$

$$B_1 = (33/98) \sqrt{\pi} Y_{00}(\theta, \phi) B_1(t) + (38880/t^5) Y_4 E_1(t) - (34214400/3t^7) Y_6 S(t)$$

$$B_2 = (27/98) \sqrt{\pi} Y_{00}(\theta, \phi) B_2(t) - (38880/t^5) Y_4 E_2(t) + (102643200/7t^7) Y_6 S(t)$$

$$B_3 = - (30/49) \sqrt{\pi} Y_{00}(\theta, \phi) B_3(t) - (46080/t^5) Y_4 E_3(t) - (68428800/7t^7) Y_6 S(t)$$

where

$$Y_4 = (\pi/21)^{1/2} \left[ (7/12)^{1/2} Y_{40}(\theta, \phi) + (5/24)^{1/2} \{ Y_{4-4}(\theta, \phi) + Y_{44}(\theta, \phi) \} \right]$$

$$Y_6 = (\pi/26)^{1/2} \left[ (1/8)^{1/2} Y_{60}(\theta, \phi) - (7/4)^{1/2} \{ Y_{6-4}(\theta, \phi) + Y_{64}(\theta, \phi) \} \right]$$

$$A_1(t) = \beta^3 e^{-t} \{ (1/17) (t^6/6!) + \sum_{n=0}^5 (t^n/n!) \}$$

$$A_2(t) = \beta^3 e^{-t} \{ - (1/4) (t^6/6!) + \sum_{n=0}^5 (t^n/n!) \}$$

$$S(t) = \beta^3 [1 - e^{-t} \{ (13/11) (t^{13}/13!) + \sum_{n=0}^{12} (t^n/n!) \}]$$

$$D_1(t) = \beta^3 [1 - e^{-t} \{ (21/8) (t^{11}/11!) + \sum_{n=0}^{10} (t^n/n!) \}]$$

$$D_2(t) = \beta^3 [1 - e^{-t} \{ (8/3) (t^{11}/11!) + \sum_{n=0}^{10} (t^n/n!) \}]$$

$$E_1(t) = \beta^3 [1 - e^{-t} \{ (16/27) (t^{11}/11!) + \sum_{n=0}^{10} (t^n/n!) \}]$$

$$E_2(t) = \beta^3 [1 - e^{-t} \{ (16/9) (t^{11}/11!) + \sum_{n=0}^{10} (t^n/n!) \}]$$

$$E_3(t) = \beta^3 e^{-t} (t^{11}/11!)$$

$$B_1(t) = \beta^3 e^{-t} \{ (4/33) (t^6/6!) + \sum_{n=0}^5 (t^n/n!) \}$$

$$B_2(t) = \beta^3 e^{-t} \{ - (4/9) (t^6/6!) + \sum_{n=0}^5 (t^n/n!) \}$$

$$B_3(t) = \beta^3 e^{-t} \{ - (2/15) (t^6/6!) + \sum_{n=0}^5 (t^n/n!) \} \quad (13)$$

When  $R$  is large,

$$A_1 = - (945/2\beta^2 R^5) Y_4 + (66825/7\beta^4 R^7) Y_6$$

$$A_2 = (675/\beta^2 R^5) Y_4 - (66825/7\beta^4 R^7) Y_6$$

$$B_1 = (1215/\beta^2 R^5) Y_4 - (267300/7\beta^4 R^7) Y_6$$

$$B_2 = - (1215/\beta^2 R^5) Y_4 + (801900/7\beta^4 R^7) Y_6$$

$$B_3 = - (534600/7\beta^4 R^7) Y_6 \quad (14)$$

Since this expression for  $\Delta B/B$  is applicable for all values of  $R$  we may determine from eq. (12) the case when  $R \rightarrow 0$

$$\frac{\Delta B}{B} \rightarrow \frac{\mu_0}{4\pi} \frac{\beta^3}{680 KT} \times \left[ \frac{(737 - 3456KT/\zeta) + (891 - 3546KT/\zeta) \exp(-\zeta/KT) + 12672KT/\zeta}{5 + 3 \exp(-\zeta/KT) + \exp(-3\zeta/2KT)} \right] \quad (15)$$

In eqs. (12)~(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  $A_1, a_1$  of the octahedral group<sup>26</sup> occur.

### 3. Results and Discussion

The calculated NMR shift for specific  $R$ -values for a 4d<sup>2</sup> system in a strong crystal field environment of octahedral symmetry are listed in Table 1 and a comparison is given at different values of  $R$  along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  axes using eq. (12). Here we choose the spin orbit coupling constant,  $\zeta$ , as 800 cm<sup>-1</sup>.  $\beta = 3.111/a_0$  and the temperature as  $T = 300K$ .

As shown in Table 1, the NMR chemical shift,  $\Delta B/B$ , decreases in magnitude rapidly, as  $R$  increase. Along the  $\langle 100 \rangle$  axis  $\Delta B/B$  is negative for all values of  $R$  while  $\Delta B/B$  is positive along the  $\langle 111 \rangle$  axis except  $R < 0.10$  nm. However, along the  $\langle 110 \rangle$  axis  $\Delta B/B$  changes sign around  $R \approx 0.20$  nm, the values being negative for small  $R$  values and positive for greater  $R$  values.

As shown in Table 2, a comparison of the multipolar terms with the exact solution obtained from eq. (12) shows that the  $1/R^5$  term contributes dominantly to the NMR chemical shift for a 4d<sup>2</sup> system in a strong crystal field environment of octahedral symmetry and there is in agreement between the exact solution and the multipolar terms when  $R \geq 0.25$  nm. It is interesting to note that along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  axes, the  $1/R^5$  term gives values opposite to that of the  $1/R^7$  term.

Separation of the Fermi contact and the pseudo contact shift has been performed by the temperature dependence analysis of  $\Delta B/B$  for the 4d<sup>2</sup> system in a strong crystal field environment of octahedral symmetry. The temperature dependence for  $\Delta B/B$  is based on Bleaney's theoretical analysis<sup>17</sup> and may be expressed as

TABLE 1:  $\Delta B/B$ (ppm) for Specific  $R$ -values for a 4d<sup>2</sup> System in a Strong Crystal Field Environment of Octahedral Symmetry when the Fourfold Axis is Chosen as the Quantization Axis

$R$ (nm)	$\Delta B/B$ (ppm)		
	$\langle 100 \rangle$	$\langle 110 \rangle$	$\langle 111 \rangle$
0.05	-5901.580	-4133.560	-3406.850
0.10	-1230.180	-372.277	222.288
0.15	-234.158	-15.862	97.588
0.20	-61.708	4.482	26.382
0.25	-21.164	2.977	8.883
0.30	-8.712	1.532	3.616
0.35	-4.088	0.882	1.685
0.40	-2.116	0.443	0.869
0.45	-1.186	0.256	0.484
0.50	-0.701	0.157	0.286

**TABLE 2: A Comparison of the Exact Values of  $\Delta B/B(\text{ppm})$  with the Multipolar Terms for Specific R-Values**(2a). Along the  $\langle 100 \rangle$  axis

R(nm)	$\Delta B/B(\text{ppm})$			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	From eq.(12)
0.05	-2029.540	292.533	-1737.010	-5901.580
0.10	-1278.610	282.041	-996.569	-1230.180
0.15	-279.336	49.788	-229.548	-234.158
0.20	-69.563	7.910	-61.653	-61.708
0.25	-22.846	1.683	-21.163	-21.164
0.30	-9.182	0.470	-8.712	-8.712
0.35	-4.248	0.160	-4.088	-4.088
0.40	-2.179	0.063	-2.116	-2.116
0.45	-1.209	0.028	-1.182	-1.182
0.50	-0.714	0.013	-0.701	-0.701

(2b). Along the  $\langle 110 \rangle$  axis

R(nm)	$\Delta B/B(\text{ppm})$			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	From eq.(12)
0.05	507.385	-475.366	32.018	-4132.560
0.10	319.653	-458.317	-138.665	-372.277
0.15	69.834	-80.906	-11.072	-15.683
0.20	17.391	-12.854	4.537	4.482
0.25	5.711	-2.734	2.977	2.977
0.30	2.295	-0.764	1.532	1.532
0.35	1.062	-0.260	0.802	0.802
0.40	0.545	-0.102	0.443	0.443
0.45	0.302	-0.045	0.258	0.258
0.50	0.178	-0.021	0.157	0.157

(2c). Along the  $\langle 111 \rangle$  axis

R(nm)	$\Delta B/B$			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	From eq.(12)
0.05	821.992	-64.260	757.733	-3406.850
0.10	517.855	-61.954	455.901	222.288
0.15	113.135	-10.937	102.198	97.588
0.20	28.184	-1.738	26.437	26.382
0.25	9.253	-0.370	8.883	8.883
0.30	3.719	-0.103	3.616	3.616
0.35	1.721	-0.035	1.685	1.685
0.40	0.882	-0.014	0.869	0.869
0.45	0.490	-0.006	0.484	0.484
0.50	0.289	-0.003	0.286	0.286

$$\Delta B/B = b_0 + b_1/T + b_2/T^2 \quad (16)$$

where

$$b_0/b_1 = -32/105$$

As described in the introduction we use a linear combination of the NMR chemical shift approximate expression arising from the Fermi contact interaction and the point-dipole approximation of the interaction represented by a hamiltonian (3), because the  $b_1/T$  term arise from the Fermi contact term and the  $b_2/T^2$  term the pseudo contact term.

**TABLE 3: The Temperature Dependence of  $\Delta B/B(\text{ppm})$  at Various Values of  $(R, \theta, \phi)$  Expressed in Terms of the Coefficients**(3a). For a  $4d^2$  system,  $\zeta = 800 \text{ cm}^{-1}$ ,  $\beta = 3.111/a_0$ 

R(nm)	axis	$b_0(\text{ppm})$	$b_1(\text{ppm/K}) \times 10^2$	$b_2(\text{ppm/K}^2) \times 10^3$
0.10	$\langle 100 \rangle$	283.706	-4777.472	7104.495
0.20	$\langle 100 \rangle$	20.328	-262.904	505.366
0.30	$\langle 100 \rangle$	2.947	-37.490	75.643
0.40	$\langle 100 \rangle$	0.721	-9.134	18.707
0.50	$\langle 100 \rangle$	0.240	-3.029	6.246
0.30	$\langle 110 \rangle$	-0.444	6.221	-8.849
0.30	$\langle 111 \rangle$	-1.234	15.619	32.019

(3b). For a  $4d^1$  system,  $\zeta = 500 \text{ cm}^{-1}$ ,  $\beta = 3.2679/a_0$ 

R(nm)	axis	$b_0(\text{ppm})$	$b_1(\text{ppm/K}) \times 10^2$	$b_2(\text{ppm/K}^2) \times 10^3$
0.10	$\langle 100 \rangle$	-496.016	761.024	-6712.620
0.20	$\langle 100 \rangle$	-15.856	44.844	-418.082
0.30	$\langle 100 \rangle$	-1.810	5.818	-54.654
0.40	$\langle 100 \rangle$	-0.406	1.372	-12.926
0.50	$\langle 100 \rangle$	-0.130	0.448	-4.229
0.20	$\langle 110 \rangle$	9.911	-13.089	114.310
0.20	$\langle 111 \rangle$	5.700	-17.904	168.671

The temperature dependence of the NMR chemical shift at various values of  $(R, \theta, \phi)$  may be expressed in terms of the coefficients in eq. (16) and is listed in Table 3a. The NMR results over the temperature range from 200 to 360K from the exact solution of  $\Delta B/B$  given by eq. (12) may be fitted almost precisely to an expression of form given by eq. (16). We find that the values of  $b_0$ ,  $b_1$  and  $b_2$  depend markedly on the location of the NMR nucleus. The major contribution to the NMR chemical shift arises from the  $1/T^2$  term but the other two terms are certainly significant. In this case although the angular and R dependence of  $\Delta B/B$  follow very closely the expected  $(3\cos^2\theta - 1)/R^3$  function, the temperature dependence is not simply proportional to  $1/T^2$ . The temperature dependence analysis of  $\Delta B/B$  for a  $4d^1$  system shows that the same trend as for the  $4d^2$  system can be observed but the contribution of  $1/T$  term to the NMR chemical shift is slightly smaller.

This work may be applied to determine the NMR chemical shift the hyperfine tensor components and contribution of dipolar and multipolar terms to the NMR shift for  $4d^n$  systems. We can also determine how much the Fermi contact and pseudo contact interaction contribute to the NMR chemical shift from the temperature dependence analysis.

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## The Effect of Pressure on the Solvolysis of Benzylchlorides(I). *p*-Methylbenzyl Chloride in Ethanol-Water Mixtures

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Rate Constants for the solvolysis of *p*-methylbenzyl chloride in various ethanol-water mixtures were studied at 30 and 40°C under various pressures up to 1600 bar. The rates of reaction were increased with increasing temperature and pressure, and decreased with increasing solvent composition of ethanol mole fraction. From the rate constants, the values of the activation parameters ( $\Delta V^\ddagger$ ,  $\Delta\beta^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) were evaluated. The values of  $\Delta V^\ddagger$  and  $\Delta\beta^\ddagger$  exhibit the extremum behavior at about 0.30 mole fraction of ethanol. This behavior is discussed in terms of solvent structure variation (electrostriction). From the relation between the reaction rate and the dielectric constant of solvent or the number of water molecule participated in the transition state, it could be postulated that the reaction proceeds through  $S_N1$  mechanism.

### Introduction

In recent years, the effect of pressure on the rates of organic reactions in binary solvent mixtures has been extensively studied<sup>1-4</sup>. Rate measurements of reactions under high pressure allow us to estimate activation volumes,  $\Delta V^\ddagger$ , by means of the following expression;

$$(\partial \ln k / \partial P)_T = -\Delta V^\ddagger / RT \quad (1)$$

where  $\Delta V^\ddagger$  is the difference in partial molal volume between initial state and transition state. An examination of the pressure effect on the kinetic rates can give a great deal of information about the transition states of the reactions. Moreover the measurement and the interpretation of activation volumes have become a useful tool in the study of reaction mechanisms in binary solvent mixtures<sup>5</sup>. Whally<sup>6</sup> has reviewed the significance of activation volumes in the determination of reaction mechanism, and has suggested that the volume of activation is probably easier to rationalize in terms of reaction mechanism than the other important parameters of activation,  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$

and  $\Delta S^\ddagger$ .

Laidler and Martin<sup>7</sup> have been concentrated on the effect of the change in solvent composition on the activation volumes for the solvolysis of *p*-methylbenzyl chloride in acetone-water mixtures under high pressure.

The results are interpreted on the view that the mechanisms are  $S_N2(1)$ . However, since the solvolysis considered in our analysis were carried out in ethanol-water mixtures, a direct comparison cannot be made with the acetone-water results.

Hyne and his co-workers<sup>8</sup> have investigated the behavior of the activation volume,  $\Delta V^\ddagger$ , and the temperature dependence of the activation volume,  $(\partial \Delta V^\ddagger / \partial T)_P$ .

In this study, we calculated various pseudo thermodynamic quantities from the rate constants and discussed in terms of solvent structure variation of initial state and transition state (Electrostriction), because these parameters are essential for getting detailed information about the transition states of the solvolysis reactions. In order to determine the reaction mechanism of *p*-methylbenzyl chloride in various mole fractions of ethanol-