Calculation of the NMR Chemical Shift for a 4d¹ System in a Strong Crystal Field Environment of Trigonal Symmetry with a Threefold Axis of Quantization

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The NMR chemical shift arising from 4d electron angular momentum and 4d electron angular momentum and 4d electron spin dipolar-nuclear spin angular momentum interactions for a 4d¹ system in a strong crystal field environment of trigonal symmetry, when the threefold sxis is chosen to be the axis of quantization axis, has been examined. A general expression using the nonmultipole expansion method (exact method) is derived for the NMR chemical shift. From this expression all the multipolar terms are determined. We observe that along the (100), (010), (110), and (111) axes the NMR chemical shifts are positive while along the (001) axis, it is negative. We observe that the dipolar term $(1/R^3)$ is the dominant contribution to the NMR chemical shift except for along the (111) axis. A comparison of the multipolar terms with the exact values shows also that the multipolar results are exactly in agreement with the exact values around $R \geqslant 0.2$ nm. The temperature dependence analysis on the NMR chemical shifts may imply that along the (111) axis the contribution to the NMR chemical shift is dominantly pseudo contact interaction. Separation of the contributions of the Fermi and the pseudo contact interactions would correctly imply that the dipolar interaction is the dominant contribution to the NMR chemical shifts along the (100), (010), (001), and (110) axes, but along the (111) axis the Fermi contact interaction is incorrectly the dominant contribution to the NMR chemical shift.

Introduction

For the past a few decade a considerable interest has been focussed on the NMR chemical shift (pseudo contact shift) arising from 3d[1,2], 4d[3] and 4f¹ systems.[4,5] It was reported that a contribution to the isotropic NMR chemical shift in paramagnetic complexes comes from the Fermi contact interacion, which may be expressed for the case of a transition metal ion in a crystal field of octahedral symmetry with the $^{2S+1}T_1$ or the $^{2S+1}T_2$ as the ground state, by the following equation[6,7]

$$\frac{\Delta B}{B} = -\frac{ah\mu}{3g_N\mu_NKT} \frac{\sum_J (2S+1)<S_z>\exp(-E_J/KT)}{\sum_J (2S+1)\exp(-E_J/KT)} \quad (1)$$

$$\text{where} <S_z> = -\left\{\frac{(g-r)}{(2-r)}gJ\ (J+1)+2\frac{(g-r)\ (g-2)KT}{(2-r)\quad v}\right\} \quad (2)$$

$$\text{and}\ E_J = -\frac{v}{2}J(J+1)$$

In equation(1), g and g_N are the electronic and nuclear Lande g-factors respectively, B the applied magnetic field, T the absolute temperature, μ and μ_N the electronic and nuclear Bohr magneton respectively, K the Boltzmann constant, h Planck's constant and a is the isotropic hyperfine constant. McConnell and Robertson[8] have noted that an anisotropic magnetic moment produce a shift, in addition to the Fermi contact shift, called the pseudo contact shift, they obtained for this shift the expression

$$\frac{\Delta B}{B} = -\mu_B^2 \frac{S\ (S+1)}{3KT}\left(\frac{3\cos^2\theta-1}{R^3}\right)F(g) \quad (3)$$

This relationship was extended by Kurland and McGarvey[9] in terms of the magnetic susceptibility components $X_{\alpha\alpha}$,

$$\frac{\Delta B}{B} = -\frac{1}{3R^3}\{[X_{zz}-\frac{1}{2}(X_{xx}+X_{yy})]\ (3\cos^2\theta-1)$$
$$+\frac{3}{2}(X_{xx}-X_{yy})\sin^2\theta\cos 2\phi\} \quad (4)$$

In equation(4), $\Delta B/B$ is the dipolar term in the general expansion and the dipolar term has been used extensively in interpreting the pseudo contact contribution to NMR chemical shift in paramagnetic molecules. In equations (3) and (4), R is the distance between the paramagnetic center and the NMR nucleus and θ is the angle between the principal axis of the complex and the vector between the paramagnetic center and the NMR nucleus. F(g) is a function of the principal g-values. Recently, attention was concentrated on the higher multipolar expansion terms.[10-12]

The NMR chemical shift at points (R,θ,ϕ) may be expressed as[2]

$$\frac{\Delta B}{B} = \sum_{L=1}^{K}\sum_{M=0}^{L}(A_{LM}\cos M\phi+B_{LM}\sin M\phi)P_L^M(\cos\theta)/R^{L+1} \quad (5)$$

where $K=2(l+1)$ for a specific l-electron, $P_L^M(\cos\theta)$ the associated Legendre polynomials and A_{LM} and B_{LM} measure the anisotropy in the multipolar magnetic susceptibilities of the molecule. It has been reported that the sum of the multipolar expansion terms yields the correct value of $\Delta B/B$, only when R is greater than 0.3 nm. At samller R values the deviation from the correct value may be considerable. To interpret NMR chemical shift in paramagnetic systems arising

from the pseudo contact interaction applicable for any R, the nonmultipole expansion method has been developed[13] and adopted to calculate NMR chemical shifts arising from the electron orbital angular momenttum and the electron spin dipolar–nuclear spin angular momentum interactions in paramagnetic systems.[14]

In this work we examine the NMR chemical shifts arising from the electron orbital angular momentum and electron spin dipolar–nuclear spin angular momentum interactions for a 4d¹ electron system in a strong crystal field of trigonal symmetry using the nonmultipole expansion method and compare the NMR chemical results with those of a 3d¹ system in a strong crystal field environment of trigonal symmetry, when the threefold axis is chosen to be the axis of quantiation.

For the case when the crystal field has a trigonal component along the (111) axis, the NMR chemical shift was examined,[15] adopting the electronic wave functions when the fourfold axis is chosen as the quantization axis. The NMR chemical shift was also determilided in a strong crystal field of trigonal symmetry for a 3d¹ electronic system when the threefold axis is chosen as the quantization axis.[16]

As far as we are aware, no attempt has been made to examine the NMR chemical shift arising from the electron orbital angular momentum and the electron spin dipolar–nuclear spin angular momentum interactions for a 4d¹ electron system in a strong crystal field environment of trigonal symmetry.

Theory

The hamiltonian representing the various interaction in this paper may be written as

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_o r} + V(r) + \zeta \underline{l}\cdot\underline{S} + \delta\,(l_z^2 - 2)$$
$$+ \mu_B\,(\underline{l} + 2\underline{S})\cdot B + H_h \tag{6}$$

where

$$V(\underline{r}) = a_4\,\{\frac{1}{3}\sqrt{\frac{7}{3}}\,Y_{40}\,(\theta,\ \phi) - \frac{1}{3}\sqrt{\frac{10}{3}}\,(Y_{4-3}\,(\theta,\ \phi)$$
$$- Y_{43}\,(\theta,\ \phi))\}^{14,17}$$

and

$$H_h = \frac{\mu_o}{4\pi}g_N\mu_N\,\{\frac{2\underline{l}_N\cdot\underline{I}}{r_N^3} + g_e\,(\frac{3\,(\underline{r}_N\cdot\underline{S})\,\underline{r}_N\cdot\underline{I}}{r_N^5} - \frac{\underline{S}\cdot\underline{I}}{r_N^3})\} \tag{7}$$

Here $\underline{r}$ and $\underline{r}_N$ are the electron radius vectors about the electron-bearing atom and the nucleus with nuclear spin angular momentum $\underline{I}$, respectively. $V(\underline{r})$ is the crystal field potential of octahedral symmetry when the threefold axis is chosen as the quantization axis and a_4 is the required crystal field parameter for 4d electron system. The other symbols have their usual meaning.

When the threefold axis is taken as the quantization axis the axial wave functions with t_2 symmetry may be expressed by[18]

$$\phi_0 = |4d_0\rangle$$

$$\phi_1 = \sqrt{\frac{2}{3}}\,|4d_2\rangle - \sqrt{\frac{1}{3}}\,|4d_{-1}\rangle$$

$$\phi_2 = \sqrt{\frac{2}{3}}\,|4d_{-2}\rangle + \sqrt{\frac{1}{3}}\,|4d_1\rangle \tag{8}$$

In calculation of the NMR chemical shift for a 4d¹ system in a

strong crystal field of trigonal symmetry a crystal field approach is adopted. The spin–orbit coupling and distortion interactions are regarded as a perturbation acting on crystal field potential and solving the perturbation matrix for the axial wave functions leads to the following eigenvalues and the corresponding eigenfunctions.

$$e_1 = \frac{\zeta}{4} - \frac{\delta}{2} - \frac{A}{2}$$

$$\psi_1^+ = a\,|\phi_1^+\rangle + b\,|\phi_0^-\rangle$$

$$\psi_1^- = a\,|\phi_1^-\rangle - b\,|\phi_0^+\rangle$$

$$e_2 = \frac{\zeta}{4} - \frac{\delta}{2} + \frac{A}{2}$$

$$\psi_2^+ = b\,|\phi_1^+\rangle - a\,|\phi_0^-\rangle$$

$$\psi_2^- = b\,|\phi_1^-\rangle + a\,|\phi_0^+\rangle$$

$$e_3 = -\frac{\zeta}{2} + \delta$$

$$\psi_3^+ = |\phi_2^+\rangle$$

$$\psi_3^- = |\phi_2^-\rangle \tag{9}$$

where

$$a^2 = \frac{1}{2} - \frac{1}{2}\,(\frac{\zeta}{2} - 3\delta)/A$$

$$b^2 = \frac{1}{2} + \frac{1}{2}\,(\frac{\zeta}{2} - 3\delta)/A$$

$$ab = \frac{\zeta}{\sqrt{2}\,A}$$

and

$$A^2 = \frac{9}{4}\zeta^2 - 3\delta\zeta + 9\delta^2$$

The magnetic field interaction is then added, and treated as a perturbation to yield new eigenfunctions $|\Psi_n\rangle$ and corresponding eigenvalues, E_n. The principal values σ_{aa} of the NMR screening tensor are determined by considering the magnetic field interaction parallel to the x,y and z directions and averaged assuming a Boltzmann distribution.

The contribution to the NMR chemical shift, ΔB, is given by

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

where

$$\sigma_{aa} = [\frac{\partial^2}{\partial\mu_\sigma\partial B_\sigma}\,(\frac{\langle\Psi_i|H_h|\Psi_i\rangle\exp\,(-E_i/KT)}{\sum_i\exp\,(-E_i/KT)})]_{\mu = B = 0}$$

and $\mu = g_N\mu_N I$

The NMR chemical shift is given by

$$\frac{\Delta B}{B} = \frac{1}{3}\frac{\mu_s^2}{KT}\frac{\mu_o}{4\pi}\frac{\sum\limits_{i=1}^{3}(A_i + B_i KT)\exp\,(-E_i/KT)}{\sum\limits_{i=1}^{3}\exp\,(-E_i/KT)} \tag{11}$$

Table 1. The matrix Elements $g_m^{(i)}$

m	i=1	i=2	i=3
1	a^4	b^4	0
2	$\sqrt{2}a^3b$	$-\sqrt{2}ab^3$	0
3	a^2b^2	b^2a^2	0
4	$-\sqrt{2}ab^3$	$\sqrt{2}a^3b$	0

Table 2. The Matrix Elements $h_m^{(i)}$

m	i		
	1	2	3
1	$(a^4+b^4)/(e_1-e_2)$	$(b^4+a^4)/(e_2-e_1)$	0
2	$a^2b^2/(e_1-e_2)$	$b^2a^2/(e_2-e_1)$	0
3	$-\sqrt{2}\,ab(b^2-a^2)/(e_1-e_2)$	$-\sqrt{2}\,ba(b^2-a^2)/(e_2-e_1)$	0
4	$a^2/(e_1-e_3)$	$b^2/(e_2-e_3)$	$a^2/(e_3-e_1)+b^2/(e_3-e_2)$
5	$\sqrt{2}\,ab/(e_1-e_3)$	$-\sqrt{2}\,ba/(e_2-e_3)$	$\sqrt{2}\,ab\,[1/(e_3-e_1)-1/(e_3-e_2)]$
6	$b^2/(e_1-e_3)$	$a^2/(e_2-e_3)$	$\dfrac{b^2}{(e_3-e_1)}+\dfrac{a^2}{(e_3-e_2)}$

Table 3. The Matrix Elements $C_{lm}(t)^a$

$C_{11}=0$	0
$C_{21}=\dfrac{16}{231}\,S_1$	$59400/R^7\beta^4$
$C_{31}=\dfrac{16}{4851}\,S_1$	$19800/7R^7\beta^4$
$C_{41}=-\dfrac{4}{2079}(2F_8-11f_1)$	$-150/R^5\beta^2$
$C_{51}=\dfrac{16}{72765}(F_4+16F_9-44f_1)$	$120/R^5\beta^2$
$C_{61}=-\dfrac{8}{1323}(2T_1+T_4-9t_2)$	0
$C_{71}=\dfrac{8}{2205}(N_1-7n_1)$	0
$C_{12}=-\dfrac{8}{21}\,S_1$	$-326700/R^7\beta^4$
$C_{22}=-\dfrac{32}{231}\,S_1$	$-118800/R^7\beta^4$
$C_{32}=-\dfrac{112}{4851}\,S_1$	$-19800/R^7\beta^4$
$C_{42}=\dfrac{2}{2079}(7F_8+12F_{15}+5F_{18}+6F_{31})$	$600/R^5\beta^2$
$C_{52}=\dfrac{2}{72765}(23F_1+42F_6+19F_7-24F_{31})$	$-240/7R^5\beta^2$
$C_{62}=-\dfrac{2}{6615}(5T_1+12T_3-5T_5-60T_{17})$	0
$C_{72}=0$	0
$C_{13}=\dfrac{8}{21}\,S_1$	$326700/R^7\beta^4$
$C_{23}=\dfrac{8}{77}\,S_1$	$89100/R^7\beta^4$
$C_{33}=\dfrac{248}{4851}\,S_1$	$306900/R^7\beta^4$
$C_{43}=-\dfrac{2}{2079}(7F_5-2F_8+12F_{15}+5F_{18}$ $+6F_{31}-55f_1)$	$-975/R^5\beta^2$

Table 3. Continued

$C_{53}=-\dfrac{2}{72765}(23F_1+4F_4+42F_6+19F_7$ $+64F_9-432F_{19}-24F_{31}+88f_1)$	$900/R^5\beta^2$
$C_{63}=\dfrac{2}{6615}(25T_1+12T_3+10T_4-5T_5+180T_8$ $-60T_{17}-270t_2)$	$44/R^3$
$C_{73}=\dfrac{4}{735}(N_1-7n_1)$	0
$C_{14}=0$	0
$C_{24}=0$	0
$C_{34}=\dfrac{8}{539}\,S_1$	$89100/7R^7\beta^4$
$C_{44}=\dfrac{2}{63}\,f_1$	$-225/R^5\beta^2$
$C_{54}=\dfrac{8}{24255}(18F_{19}-11f_1)$	$540/R^5\beta^2$
$C_{64}=\dfrac{4}{147}(T_8-t_2)$	0
$C_{74}=\dfrac{8}{2205}(N_1-7n_1)$	0

^{a}The asymptotic expansion for R→∞ for each $C_{lm}(t)$ is given in the right column.

Table 4. The Matrix Elements $d_{lm}(t)$ **(the Asymptotic Expansion for R→∞ for each** $d_{lm}(t)$ **is Given in the Right Column.)**

$d_{11}=0$	0
$d_{21}=-\dfrac{4}{77}\,S_1$	$-44550/R^7\beta^4$
$d_{31}=-\dfrac{16}{1617}\,S_1$	$-59400/R^7\beta^4$
$d_{41}=\dfrac{2}{693}(F_{31}-11f_1)$	$374/R^5\beta^2$
$d_{51}=-\dfrac{8}{24255}(F_{31}-11f_1)$	$-300/7R^5\beta^2$
$d_{61}=\dfrac{4}{441}(T_{17}+3t_2)$	$4/R^3$

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Table 4. Continued

$$d_{71} = \frac{4}{2205}(N_1 + 14n_1) \qquad 0$$

$$d_{12} = \frac{16}{21}S_1 \qquad 653400/R^7\beta^4$$

$$d_{22} = -\frac{8}{231}S_1 \qquad -29700/R^7\beta^4$$

$$d_{32} = \frac{368}{4851}S_1 \qquad 455400/7R^7\beta^4$$

$$d_{42} = -\frac{4}{2079}(7F_5 - 6F_8 + 12F_{15} + 5F_{18} + 3F_{31}) \qquad -900/R^5\beta^2$$

$$d_{52} = -\frac{4}{72765}(23F_1 + 12F_4 + 42F_6 + 19F_7 + 192F_9 - 432F_{19} - 12F_{31} - 396f_1) \qquad -480/7R^5\beta^2$$

$$d_{62} = \frac{4}{6615}(65T_1 + 12T_3 + 30T_4 - 5T_5 + 180T_8 - 30T_{17} - 360t_2) \qquad 8/R^3$$

$$d_{72} = \frac{8}{2205}(2N_1 + 7n_1) \qquad 0$$

$$d_{13} = -\frac{8}{21}S_1 \qquad -326700/R^7\beta^4$$

$$d_{23} = -\frac{32}{231}S_1 \qquad -118800/R^7\beta^4$$

$$d_{33} = -\frac{40}{4851}S_1 \qquad -49500/7R^7\beta^4$$

$$d_{43} = \frac{2}{2079}(7F_5 + 5F_8 + 12F_{15} + 6F_{31} + 33f_1) \qquad 300/R^5\beta^2$$

$$d_{53} = \frac{2}{72765}(23F_1 + 42F_6 + 19F_7 + 216F_{19} - 24F_{31} - 132f_1) \qquad 300/7R^5\beta^2$$

$$d_{63} = -\frac{2}{6615}(5T_1 + 12T_3 - 5T_5 - 90T_8 - 60T_{17} + 90t_2) \qquad 0$$

$$d_{73} = \frac{8}{2205}(N_1 - 7n_1) \qquad 0$$

$$d_{14} = 0 \qquad 0$$

$$d_{24} = \frac{16}{231}S_1 \qquad 59400/R^7\beta^4$$

$$d_{34} = \frac{16}{4851}S_1 \qquad 17800/7R^7\beta^4$$

$$d_{44} = -\frac{4}{2079}(7F_5 - 5F_{18}) \qquad 0$$

$$d_{54} = \frac{4}{72765}(23F_1 - 19F_7 + 64F_9) \qquad 360/7R^5\beta^2$$

$$d_{64} = -\frac{4}{1323}(5T_1 + T_5) \qquad -8/R^3$$

$$d_{74} = \frac{8}{2205}N_1 \qquad 0$$

Table 4. Continued

$$d_{15} = 0 \qquad 0$$

$$d_{25} = -\frac{20}{231}S_1 \qquad -74250/R^7\beta^4$$

$$d_{35} = -\frac{8}{693}S_1 \qquad 9900/R^7\beta^4$$

$$d_{45} = \frac{2}{2079}(7F_5 - 5F_{18} + 3F_{31} + 33f_1) \qquad -75/R^5\beta^2$$

$$d_{55} = -\frac{2}{72765}(23F_1 - 19F_7 + 64F_9 + 12F_{31} + 132f_1) \qquad -120/7R^5\beta^2$$

$$d_{65} = \frac{2}{1323}(5T_1 + T_5 + 6T_{17} - 18t_2) \qquad 0$$

$$d_{75} = -\frac{8}{315}n_1 \qquad 0$$

$$d_{16} = 0 \qquad 0$$

$$d_{26} = \frac{4}{77}S_1 \qquad 44550/R^7\beta^4$$

$$d_{36} = \frac{16}{1617}S_1 \qquad 59400/R^7\beta^4$$

$$d_{46} = -\frac{2}{693}(F_{31} + 11f_1) \qquad 75/R^5\beta^4$$

$$d_{56} = \frac{8}{24255}(F_{31} + 11f_1) \qquad -60/7R^5\beta^4$$

$$d_{66} = -\frac{4}{441}(T_{17} - 3t_2) \qquad 4/R^3$$

$$d_{76} = -\frac{4}{2205}(N_1 - 14n_1) \qquad 0$$

where A_i and B_i may be expressed in terms of spherical harmonics

$$A_i = a_1^{(i)}\sqrt{\frac{\pi}{3003}}\,[Y_{6-6}(\Theta,\Phi) + Y_{66}(\Theta,\Phi)]$$

$$+ a_2^{(i)}\sqrt{\frac{\pi}{1365}}\,[Y_{6-3}(\Theta,\Phi) - Y_{63}(\Theta,\Phi)] + a_3^{(i)}\sqrt{\frac{\pi}{13}}\,Y_{60}(\Theta,\Phi)$$

$$+ a_4^{(i)}\sqrt{\frac{2\pi}{35}}\,[Y_{4-3}(\Theta,\Phi) - Y_{43}(\Theta,\Phi)]$$

$$+ a_5^{(i)}\sqrt{\pi}\,Y_{40}(\Theta,\Phi) + a_6^{(i)}\sqrt{\frac{\pi}{5}}\,Y_{20}(\Theta,\Phi) + a_7^{(i)}\sqrt{\pi}\,Y_{00}(\Theta,\Phi)$$

$$B_i = b_1^{(i)}\sqrt{\frac{\pi}{3003}}\,[Y_{6-6}(\Theta,\Phi) + Y_{66}(\Theta,\Phi)]$$

$$+ b_2^{(i)}\sqrt{\frac{\pi}{1365}}\,[Y_{6-3}(\Theta,\Phi) - Y_{63}(\Theta,\Phi)]$$

$$+ b_3^{(i)}\sqrt{\frac{\pi}{13}}\,Y_{60}(\Theta,\Phi) + b_4^{(i)}\sqrt{\frac{2\pi}{35}}\,[Y_{4-3}(\Theta,\Phi) - Y_{43}(\Theta,\Phi)]$$

$$+b_5^{(i)}\sqrt{\pi}\ Y_{40}\ (\Theta,\ \Phi)+b_6^{(i)}\sqrt{\frac{\pi}{5}}\ Y_{20}\ (\Theta,\ \Phi)+b_7^{(i)}\sqrt{\pi}\ Y_{00}\ (\Theta,\ \Phi)$$

$$(12)$$

for i = 1,2,3.

The coefficients $a_l^{(i)}$ and $b_l^{(i)}$ for $l = 1 \sim 7$ are functions of the internuclear separation R, the spin-orbit coupling constant ζ and the distortion parameter δ. The coefficients $a_l^{(i)}$ and $b_l^{(i)}$ may be expressed in terms of matrices $g_m^{(i)}$ and $h_m^{(i)}$ and two matrices $C_{lm}(t)$ and $d_{lm}(t)$ of radial dependence. These matrices are represented in Table 1, 2, 3 and 4.

$$a_l^{(i)} = \sum_{m=1}^{4} C_{lm}(t)\ g_m^{(i)}$$

$$b_l^{(i)} = \sum_{m=1}^{6} d_{lm}(t)\ h_m^{(i)} \qquad (13)$$

where $t = 2\beta R$.

When the threefold axis is chosen to be the axis of quantization, the calculated NMR chemical shift arising from the electon anqular momentum and electron spin dipolar–nuclear spin angular momentum interactions for a 4d¹ system in a strong crystal field of trigonal symmetry using equation (11) are listed in Table 5. To calculate the NMR chemical shift we adopt the hyperfine integrals published in the previous papers.[19,20]

Results

Interpretation of the NMR chemical shifts. In this work we examine the exact calculated NMR chemical shifts for a 4d¹ system in a strong crystal field environment of trigonal symmetry, when the threefold axis is chosen to be the axis of quantization. We choose the spin–orbit coupling constant, ζ, as 500 cm⁻¹, the distortion parameter, δ, as 500 cm⁻¹, $\beta = 3.2679/a_0$ and the temperature T = 300 K.

As shown in Table 5, the NMR chemical shift decreases in magnitude rapidly as R increase. For a 4d¹ system in a strong crystal field environment of trigonal symmetry and $\frac{\Delta B}{B}$ (ppm) values along the x, y and z axes are different from each other. It also appears that the NMR chemical shifts along the (100), (010), (110) and (111) axes are positive for all values

of R except for R 0.05 nm while along the (001) axis it is negative. In the case of a 3d¹ system in a strong crystal field environment of trigonal symmetry, the NMR chemical shifts are however negative for all values of R along the (100), (010) and (110) axes, while along the (001) and (111) axes, the NMR chemical shifts change a sign around 0.15 nm of R, the values being negative for smaller R values and positive for greater R values.

As the the distortion is increased from 500cm⁻¹ to 5000cm⁻¹, the NMR chemical shift, $\Delta B/B$ decreases in magnitude markedly. The results for a 4d¹ system and the corresponding multipolar terms, $1/R^3$, $1/R^5$ and $1/R^7$, expressed in the matrix elements in table 3 and 4, are shown in Table 6 in a strong crystal field environment of trigonal symmetry when the threefold axis is taken as the quantization axis. Table 6 shows that the contributions of $1/R^3$ and $1/R^7$ terms to the NMR chemical shifts along the (100), (010), and (110) axes are positive for all values of R while that of $1/R^5$ is negative. However, the contributions of all the multipolar terms ($1/R^3$, $1/R^5$ and $1/R^7$) along the (001) axis are negative for all values of R, while along the (111) axis, the contributions of $1/R^3$ and $1/R^5$ to the NMR chemical shifts are positive, but

Table 5(b). ΔB/B(ppm) for Specific R-values for 4d¹ System Along the (110) and (111) Axes in a Strong Crystal Field Environment of Trigonal Symmetry (δ = 500, 5000cm⁻¹)

	ΔB/B(ppm)			
	(110)		(111)	
	500cm⁻¹	5000cm⁻¹	500cm⁻¹	5000cm⁻¹
0.05	− 140.284	45.773	− 390.869	− 8.127
0.10	68.960	18.391	7.204	0.1978
0.15	26.153	6.285	7.527	0.7376
0.20	10.673	2.675	2.513	0.2928
0.25	5.522	1.402	0.9340	0.1153
0.30	3.255	0.8290	0.4009	0.0506
0.35	2.082	0.5302	0.1924	0.0246
0.40	1.411	0.3592	0.1010	0.0131
0.45	0.9998	0.2543	0.0570	0.0074
0.50	0.7337	0.1865	0.0340	0.0044

Table 5(a). $\frac{\Delta B}{B}$ (ppm) for Specific R-values for 4d¹ System Along the x, y and z Axes in a Strong Crystal Field Environment of Trigonal Symmetry (ζ = 500cm⁻¹)

R(nm)	ΔB/B(ppm)					
	(100)		(010)		(001)	
	500cm⁻¹	5000cm⁻¹	500cm⁻¹	5000cm⁻¹	500cm⁻¹	5000cm⁻¹
0.05	160.623	45.897	− 119.945	45.649	− 355.740	12.418
0.10	53.622	18.485	84.298	18.298	− 337.753	− 71.140
0.15	23.819	6.300	28.487	6.271	− 107.796	− 24.133
0.20	10.321	2.677	11.027	2.673	− 34.663	− 8.179
0.25	5.447	1.403	5.596	1.402	− 15.233	− 3.703
0.30	3.234	0.8291	3.276	0.8288	− 8.151	− 2.012
0.35	2.075	0.5303	2.089	0.5302	− 4.911	− 1.222
0.40	1.408	0.3592	1.414	0.3592	− 3.202	− 0.8007
0.45	0.9986	0.2543	1.001	0.2543	− 2.209	− 0.5541
0.50	0.7332	0.1865	0.7343	0.1865	− 1.590	− 0.3998

that of $1/R^7$ is negative for all values of R.

A comparison of the multipolar terms with the exact values given by equation(11) shows that the dipolar term $(1/R^3)$ is the dominant contribution to the NMR chemical shifts. However, the contributions of $1/R^5$ and $1/R^7$ terms may not be negligible for all values of R except for along the (111) axis, where the contribution of $1/R^3$ term to the NMR chemical shifts is almost zero.

In the case of a 3d¹ system in a strong crystal field environment of trigonal symmetry, the contributions of $1/R^3$ term to the NMR chemical shifts along the (100), (010) and (110) axes are negative, while those of $1/R^5$ and I/R^7 terms are positive for all values of R. However, the contributions of $1/R^3$ and $1/R^7$ terms to the NMR chemical shift along the (001) axis is negative, while that of $1/R^5$ is positive for all values of R. But along the (111) axis, the contribution of $1/R^5$ to the NMR chemical shift is positive while that of $1/R^7$ term is negative for all values of R except for $1/R^3$ whose contribution is zero, when the threefold axis is chosen as the quantization axis. It is found that the multipolar results are exactly in agreement with the exact results around $R \geqslant 0.20$ nm.

The temperature dependence of the NMR chemical shift. We examine the temperature dependence of the NMR chemical shift for a 4d¹ system in a strong crystal field environment of trigonal symmetry and then compare the results

with the usually used approximate equation when the threefold axis is chosen to be the axis of the quantization. The temperature dependence of the NMR chemical shift may be expressed as[21,22]

$$\Delta B/B = A + B/T + C/T^2 \tag{14}$$

In equation(14) the $1/T$ term arises from the Fermi contact term and $1/T^2$ term the pseudo contact term. The NMR chemical shifts calculated from equation (11) over the temperature range 200 to 400 K may be fitted almost precisely to an expression of the form given by equation(14). Some values of A, B and C are listed in Table 7. Therefore, the fitting of the values of the NMR chemical shift for a 4d¹ system in a strong crystal field environment of trigonal symmetry to equation(14) over a temperature range 200 to 400 K shows that along the (111) axis the temperature dependence of the NMR chemical shift may be expressed as

$$\Delta B/B = 2.392 + 8.188/T + 8569.360/T^2 \tag{15}$$

when

$$\delta \quad -500 \text{ cm}^{-1} \text{ and as}$$

$$\Delta B/B = 0.560 - 80.180/T + 0.001/T^2 \tag{16}$$

when

$$\delta \quad -5000 \text{ cm}^{-1}$$

Table 6. A Comparison of the Exact Values of $\Delta B/B$(ppm) with the Multipolar Terms for Specific R-values for a 4d¹ System in a Strong Crystal Field Environment of Trigonal Symmetry ($\zeta = 500$ cm⁻¹, $d = 500$ cm⁻¹)

6a) Along (100) Axis

R(nm)	$\Delta B/B$(ppm)				
	$1/R^3$	$1/R^5$	$1/R^7$	sum of all multipolar terms	exact values
0.05	9.607	85.343	57.964	152.914	−160.623
0.10	38.019	−26.789	43.712	54.393	53.622
0.15	26.697	−9.671	6.652	23.678	23.819
0.20	11.816	−2.505	1.007 •	10.318	10.321
0.25	6.058	−0.823	0.213	5.447	5.447
0.30	3.506	−0.331	0.059	3.234	3.234
0.35	2.208	−0.153	0.020	2.075	2.075
0.40	1.479	−0.078	0.008	1.408	1.408
0.45	1.039	−0.043	0.004	0.999	0.999
0.50	0.757	−0.025	0.002	0.733	0.733

6b) Along the (010) Axis

R(nm)	$\Delta B/B$(ppm)				
	$1/R^3$	$1/R^5$	$1/R^7$	sum of all multipolar terms	exact values
0.05	9.607	85.343	98.643	193.592	−119.945
0.10	38.019	−26.788	74.388	85.619	84.298
0.15	26.697	−9.671	11.320	28.346	28.487
0.20	11.816	−2.505	1.714	11.025	11.028
0.25	6.058	−0.824	0.362	5.596	5.596
0.30	3.506	−0.331	0.101	3.276	3.276
0.35	2.208	−0.153	0.034	0.089	2.089
0.40	1.479	−0.079	0.013	1.414	1.414
0.45	1.039	−0.044	0.005	1.001	1.001
0.50	0.757	−0.026	0.002	0.734	0.734

6c) Along the (001) Axis

R(nm)	$\Delta B/B$(ppm)				
	$1/R^3$	$1/R^5$	$1/R^7$	sum of all multipolar terms	exact values
0.05	− 19.213	227.581	− 250.571	− 42.203	− 355.740
0.10	− 76.037	− 71.434	− 188.960	− 336.432	− 337.572
0.15	− 53.393	− 25.788	− 28.754	− 107.937	− 107.796
0.20	− 23.632	− 6.679	− 4.354	− 34.665	− 34.663
0.25	− 12.116	− 2.197	− 0.920	− 15.233	− 15.233
0.30	− 7.011	− 0.883	− 0.256	− 8.151	− 8.151
0.35	− 4.415	− 0.408	− 0.087	− 4.911	− 4.911
0.40	− 2.958	− 0.209	− 0.034	− 3.202	− 3.202
0.45	− 2.077	− 0.116	− 0.015	− 2.209	− 2.209
0.50	− 1.514	− 0.068	− 0.007	− 1.590	− 1.590

6d) Along the (110) Axis

R(nm)	$\Delta B/B$(ppm)				
	$1/R^3$	$1/R^5$	$1/R^7$	sum of all multipolar terms	exact values
0.05	9.607	85.343	78.303	173.253	− 140.284
0.10	38.107	− 26.788	59.050	70.281	68.960
0.15	26.697	− 9.671	8.986	26.012	26.153
0.20	11.816	− 2.505	1.361	10.672	10.674
0.25	6.058	− 0.823	0.287	5.522	5.522
0.30	3.506	− 0.321	0.080	3.255	3.255
0.35	2.208	− 0.153	0.027	2.082	2.082
0.40	1.479	− 0.078	0.010	1.411	1.411
0.45	1.039	− 0.043	0.004	0.999	0.999
0.50	0.757	− 0.025	0.002	0.733	0.733

6e) Along the (111) Axis

R(nm)	$\Delta B/B$(ppm)				
	$1/R^3$	$1/R^5$	$1/R^7$	sum of all multipolar terms	exact values
0.05	0.002	− 23.070	− 54.264	− 77.332	− 390.689
0.10	0.008	49.639	− 40.922	8.525	7.204
0.15	0.005	13.608	− 6.227	7.387	7.527
0.20	0.002	3.451	− 0.942	2.511	2.513
0.25	0.001	1.134	− 0.199	0.936	0.936
0.30	0.000	0.455	− 0.055	0.400	0.400
0.35	0.000	0.210	− 0.018	0.192	0.192
0.40	0.000	0.108	− 0.007	0.101	0.101
0.45	0.000	0.060	− 0.003	0.057	0.057
0.50	0.000	0.035	− 0.015	0.034	0.034

These results indicate that in case of $\delta = 500$ cm^{-1}, the $1/T^2$ term contributes dominantly to the NMR chemical shift, but the contributions of other terms may not be negligible, As shown in Table 7, the last two terms in equation(15) contribute significantly to the NMR chemical shifts along the (100) and (110) axes.

These may imply that along the (111) axis the contribution to the NMR chemical shift is dominantly of the pseudo contact interaction, but along the (100) and (110) axes, the temperature dependence analysis shows incorrectly that the Fermi and pseudo contact interactions contribute significantly to the NMR chemical shift. It appears that when δ is increased to 5000 cm^{-1}, the major contribution to the NMR chemical shift is the $1/T$ term along the (111), (100) and (110) axes. Such the results imply incorrectly that the NMR chemical shift is dominantly of Fermi contact interaction origin.

Separation of the contributions of the Fermi and the

Table 7. The Temperature Dependence of $\frac{\Delta B}{B}$ (ppm) at Various Values of R Expressed in Terms of the Coefficients, when the Threefold Axis is Chosen to be the Axis of Quantization.

7a) $\zeta = 500$ cm⁻¹, $\delta = 500$ cm⁻¹ and $\beta = 3.2679/a_0$

R(nm)	axis	A (ppm)	B (ppm·K)	C (ppm·K²)
0.1	(111)	6.858	−778.115	267911.513
0.2	(111)	2.392	8.188	8569.360
0.3	(111)	0.316	22.626	900.947
0.4	(111)	0.075	7.252	193.934
0.2	(100)	−14.725	7751.795	−72112.476
0.2	(110)	−13.500	7506.583	−77066.585

7b) $\zeta = 500$ cm⁻¹, $\delta = 500$ cm⁻¹ and $\beta = 3.2679/a_0$

R(nm)	axis	A (ppm)	B (ppm·K)	C (ppm·K²)
0.1	(111)	5.598	−1620.155	0.020
0.2	(111)	0.560	−80.180	0.001
0.2	(100)	−2.173	1454.912	−0.001
0.2	(110)	−2.420	1449.052	0.020

Table 8. A Summary of the Results of Fitting a Set of Theoretical Data for ΔB/B(ppm) as Arising from a Sum of the Fermi Contact and Dipolar Interactions as Given by Equation (17) for the case of a 4d¹ System in a Strong Crystal Field of Trigonal Symmetry ($\zeta = 500$ cm⁻¹, $\delta = 500$ cm and R=0.2 nm)

8a) Along the (001) Axis

T(K)	ΔB/B (ppm) exact	contribution from <S,>	contribution from (χ∥−χ⊥)	Total
		ΔB/B (ppm) fitted to equation (17)		
220	−59.98	2.25	−62.34	−60.10
240	−52.10	2.24	−55.21	−52.97
260	−45.41	2.23	−48.66	−45.41
280	−39.67	2.22	−42.72	−40.50
300	−34.66	2.21	−37.39	−35.18
320	−30.27	2.20	−32.63	−30.43
340	−26.37	2.19	−28.40	−26.21
360	−22.88	2.17	−24.65	−22.88
380	−19.76	2.15	−21.33	−19.18
400	−16.93	2.13	−18.39	−16.26

8b) Along the (001) Axis

T(K)	ΔB/B (ppm) exact	contribution from <S,>	contribution from (χ∥−χ⊥)	Total
		ΔB/B (ppm) fitted to equation (17)		
200	22.24	−2.49	24.18	21.69
220	19.01	−2.48	21.54	19.06
240	16.31	−2.48	19.08	16.60
260	14.02	−2.47	16.81	14.34
280	12.04	−2.46	14.76	12.30
300	10.32	−2.45	12.92	10.47
320	8.80	−2.43	11.28	8.84
340	7.46	−2.42	9.81	7.40
360	6.25	−2.40	8.51	6.12
380	5.17	−2.38	7.37	4.99

8c) Along the (010) Axis

T(K)	ΔB/B (ppm) exact	contribution from <S,>	contribution from (χ∥−χ⊥)	Total
		ΔB/B (ppm) fitted to equation (17)		
200	23.00	−0.69	22.18	21.48
220	19.02	−0.69	19.76	19.07
240	16.54	−0.69	17.50	16.81
260	14.43	−0.69	15.42	14.73
280	12.61	−0.69	13.54	12.86
300	11.03	−0.68	11.85	11.17
320	9.63	−0.68	10.34	9.66
340	8.38	−0.67	9.00	8.33
360	7.27	−0.67	7.81	7.14
380	6.26	−0.66	6.76	6.10
400	5.35	−0.66	5.83	5.17

8d) Along the (110) Axis

T(K)	ΔB/B (ppm) exact	contribution from <S,>	contribution from (χ∥−χ⊥)	Total
		ΔB/B (ppm) fitted to equation (17)		
200	22.12	−1.46	23.07	22.61
220	19.02	−1.46	20.56	19.10
240	16.43	−1.46	18.20	16.75
260	14.23	−1.45	16.05	14.52
280	12.33	−1.45	14.09	12.64
300	10.67	−1.44	12.33	10.89
320	9.92	−1.43	10.76	9.32
340	7.92	−1.42	9.36	7.92
360	6.76	−1.41	8.13	6.72
380	5.72	−1.40	7.03	5.63

8e) Along the (111) Axis

T(K)	ΔB/B (ppm) exact	contribution from <S,>	contribution from (χ∥−χ⊥)	Total
		ΔB/B (ppm) fitted to equation (17)		
200	2.65	2.54	0.07	2.61
220	2.61	2.53	0.07	2.60
240	2.58	2.53	0.06	2.59
260	2.55	2.52	0.05	2.57
280	2.53	2.51	0.05	2.56
300	2.51	2.50	0.04	2.54
320	2.50	2.48	0.03	2.52
340	2.49	2.47	3.03	2.50
360	2.48	2.45	0.03	2.47
380	2.47	2.43	0.02	2.45

pseudo contact interactions to the NMR chemical shift. Experimental paramagnetic NMR chemical shifts are usually analyzed in terms of the Femi and the dipolar interactions given by equation(17).

$$\Delta B = a < S_z > + b\,(\chi_\parallel - \chi_\perp) \tag{17}$$

To explore the possible problems of interpretation associated by such a procedure we examine the ΔB/B results over a temperature range and reconsider the data as a set of ex-

perimental results and then analyze the data as arising from a sum of the Fermi and the dipolar interactions given by equation(15).

In this work we choose $<S_z>$ in equation (18) for a 4d^1 system in a crystal field of octahedral symmetry as[23]

$$\Delta B = a<S_z>/g_N\mu_N \qquad (18)$$

The quatities $\chi_\parallel$ and $\chi_\perp$ are determined from expressions in reference(24). The best fit of the theoretical values of $\Delta B/B$(ppm) for a 4d^1 system in a strong crystal field environment of trigonal symmetry to the expression (17) over the temperature range 200 to 400 K is obtained, when the threefold axis is chosen to be the axis of quantization. The results are summarized in Table 8 and 9. As shown in Table 8, the analysis of the data using equation(15) would correctly imply that the dipolar interaction (pseudo contact interaction) is the dominant contribution to the NMR chemical shift along the (001), (010), (100) and (110) axes, but along the (111) axis, the Fermi contact interaction is incorrectly the dominant contribution to the NMR chemical shift. However, the contribution of Fermi contact interaction increases as the temperature increases.

This work may be applied to examine and interprete the NMR chemical shift for 4d^n system in a strong crystal field environment of trigonal symmetry when the threefold axis is chosen to be the axis of quantization. The caculated results may suggest information on the configuration of electrons for 4d^n system in a strong crystal field environment of trigonal symmetry.

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