The Pseudocontact Shift for a $3d^9$ System in a Strong Crystal Field Environment of Tetragonally Distorted Tetrahedral Symmetry

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A general expression adopting a nonmultipole expansion method is derived for pseudocontact contribution to the NMR chemical shift arising from the electron orbital angular momentum and electron spin dipolar-nuclear spin angular momentum interaction of $3d^9$ system in a strong crystal field of tetragonally distorted tetrahedral symmetry. From this expression all the multipolar term are determined and the exact solution of $\Delta B/B$(ppm) is compared with the multipolar term. The $1/R^5$ term in the multipolar terms contributes dominantly to the NMR chemical shift but the other terms are certainly significant except that of the $\langle 111 \rangle$ axis. In addition, an analysis of the temperature dependence of the NMR chemical shift further illustrates that considerable care must be taken in interpeting NMR results in paramagnetic system.

Introduction

The pseudocontact(dipolar) shift which affords information related to geometrical structure has widely been accepted as a main contributor to the isotropic shift. In recent theoretical work the nonmultipole expansion method has been mainly adopted for the acculate calculation of pseudocontact shift and its contribution to NMR chemical shifts of $3d(3d^1, 3d^2)^{1-5}$, $4d(4d^1, 4d^2)^{6-10}$, and f^{13} systems[11,12] in several symmetries, respectively.

Up to our knowledge no attempt has been made to calculate the NMR chemical shift for $3d^n$ systems in a strong crystal field of tetragonally distorted tetrahedral symmetry. The purpose of this work is to derive a general formula for the exact calculation of the electron orbital angular momentum and the electron spin dipolar-nuclear spin angular momentum interactions, adopting the nonmultipole expansion method, and to calculate its contribution to NMR chemical shifts of a $3d^9$ system in a strong crystal field of tetragonally distorted tetrahedral symmetry. Also, to enable a ready comparison of the results derived in this work to the results that would be gained using the multipole expansion method or the point-dipole approximation, tables are included comparing the three methods. Finally an analysis of the temperature dependence of the exact solution is performed to interpret the origin of the NMR chemical shift.

Theory

The hamiltonian representing the various interactions may be expressed as

$$H = -\frac{h^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} + V(\underline{r}) + \zeta\underline{l}\cdot\underline{s} + \delta(l_z^2 - 2)$$

$$+ \mu_B(\underline{l} + 2\underline{s}) \cdot \underline{B} + H_{hft} \tag{1}$$

where

$$H_{hf} = \frac{\mu_0}{4\pi}g_N\mu_B\mu_N\left\{\frac{2\,\underline{l}_N\cdot\underline{I}}{r_N^3} + g_s\left[\frac{3(\underline{r}_N\cdot\underline{s})\,r\sim_N\cdot\underline{I}}{r_N^5} - \frac{\underline{s}\cdot\underline{I}}{r_N^3}\right]\right\} \tag{2}$$

and

$$V(r) = A_{32}r^3\{Y_{32}(\theta, \phi) - Y_{3-2}(\theta, \phi)\}$$

$$+ A_{40}r^4[Y_{40}(\theta, \phi) + (5/14)^{1/2}\{Y_{4-4}(\theta, \phi) + Y_{44}(\theta, \phi)\}] \tag{3}$$

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 I, respectively. The quantity $\underline{B}$ is the applied magnetic field, $V(\underline{r})$ is the crystal field potential of tetragonal symmetry, and A_{32} and A_{40} are the crystal field parameters.[13] The other symbols have their usual meaning. In this work the free electron g value, g_s, is taken to be equal to exactly 2.

In order to solve our problem, we may use the basis function involving $4p$ orbitals because it was reported that the correct $3d$ wave functions to use in the construction of the tetrahedral state are then given by the admixture of the $4p$ orbital into the $3d$ orbital formulated through the first-order perturbation procedure[13,15,16] as

$$|t_2i\rangle = |3dt_2i\rangle - b|4pi\rangle, \quad i = yz, xz, xy. \tag{4}$$

where

$$b = \frac{C}{E(4p) - E(3d)}\langle 4p_i|xyz|3dt_{2i}\rangle$$

with C is a constant.

It was also reported that using a point-charge model,[13] the value of b is about 8×10^{-2}. The intermixing of $|3d\rangle$ and $|4p\rangle$ atomic orbitals is thus the about 10 percent in this approximation. In this work b is chosen to be a parameter. However, since these wave functions are degenerate, we may choose any orthogonal set of linear combinations, so we take the basis set of wave functions as

$$\phi_0 = \frac{1}{\sqrt{2}}(|3d_2\rangle - |3d_{-2}\rangle) + b_1|4p_0\rangle,$$

$$\phi_1 = -|3d_1 + b_1|4p_{-1}\rangle, \text{ and}$$

$$\phi_2 = -|3d_{-1} + b_1|4p_1\rangle \tag{5}$$

where $b_1 = -ib$.

The $^2T_2$ ground state is separated into three Kramer's doublets by the spin-orbit coupling interaction and the tetragonal field components. The magnetic field interaction, $\mu_B(\underline{l} + 2\underline{s}) \cdot \underline{B}$, is then added and treated as a perturbation to yield new eigenfunctions, $|\Psi_n\rangle$, and the corresponding eigenvalues, E_n.

To determine the NMR chemical shift we shall calculate the principal values σ_{xx}, σ_{yy}, and σ_{zz} of the NMR screening tensor 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 shift, ΔB, is given by

$$\Delta B = B(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3, \tag{6}$$

where

$$\sigma_{\alpha\alpha} = \left[\frac{\partial^2}{\partial \mu_\alpha \partial B_\alpha} \left(\frac{\sum_i \langle \Psi_i | H_{hf} | \Psi_i \rangle \exp(-E_i/kT)}{\sum_i \exp(-E_i/kt)} \right) \right]_{\underline{u} = \underline{B} = 0}, \tag{7}$$

with

$$\mu = g_N \mu_N I.$$

The term H_{hf} is the hamiltonian given in Eq. (2). The NMR shift for the $3d^9$ system in a strong crystal field environment of tetragonally distorted tetrahedral symmetry is calculated by

$$\frac{\Delta B}{B} = -\frac{\mu_0}{4\pi} \frac{\mu_B^2}{3kT} \left\{ \frac{\sum_{i=1}^3 (A_i + B_i kT) \exp(-E_i/kT)}{2 \sum_{i=1}^3 \exp(-E_i/kT)} \right\} \tag{8}$$

Here the eigenvalues and the corresponding eigenfuntions by the spin-orbit and distortion interactions are given by

$$\varepsilon_1 = \zeta_C/4 + \delta/2 + X/2, \quad \psi_1^+ = a\phi_1^+ + a_1\phi_0^-,$$
$$\psi_1^- = a\phi_2^- + a_1\phi_0^+,$$
$$\varepsilon_2 = \zeta_C/4 + \delta/2 - X/2, \quad \psi_2^+ = a_1\phi_1^+ - a\phi_0^-,$$
$$\psi_2^- = a_1\phi_2^- - a\phi_0^+,$$
$$\varepsilon_3 = -\zeta_C/2 - \delta \qquad \psi_3^+ = \phi_2^+,$$
$$\psi_3^- = \phi_1^-, \tag{9}$$

where

$$X^2 = (9/4)\zeta_c^2 - 3\delta\zeta_c + 9\delta^2, \quad a^2 = 1/2 + 1/2(\zeta_c/2 - 3\delta)X^{-1},$$
$$a_1^2 = 1/2 - 1/2(\zeta_c/2 - 3\delta)X^{-1}, \quad aa_1 = -(\zeta_c/\sqrt{2})X^{-1},$$
$$\zeta_c = \zeta_d + b_1^2 \zeta_p$$

and δ is equal to one-third of Δ which is the usual meaning of the distortion parameter. A_i and B_i may be expressed in terms of spherical harmonics,

$$A_i = a_1^{(i)}\sqrt{2\pi/91} [Y_{6-4}(\Theta, \Phi) + Y_{64}(\Theta, \Phi)] + a_2^{(i)}\sqrt{\pi/13} Y_{60}(\Theta, \Phi)$$

$$+ a_3^{(i)}\sqrt{2\pi/35} [Y_{4-4}(\Theta, \Phi) + Y_{44}(\Theta, \Phi)] + a_4^{(i)}\sqrt{\pi} Y_{40}(\Theta, \Phi)$$

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

$$B_i = b_1^{(i)}\sqrt{2\pi/91} [Y_{6-4}(\Theta, \Phi) + Y_{64}(\Theta, \Phi)] + b_2^{(i)}\sqrt{\pi/13} Y_{60}(\Theta, \Phi)$$

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

$m \backslash i$	1	2	3
1	a^4	a_1^4	0
2	$a^3a_1/\sqrt{2}$	$-aa_1^3/\sqrt{2}$	0
3	$a^2a_1^2/2$	$a^2a_1^2/2$	0
4	$\sqrt{2}(1-a_1^2)aa_1^3$	$-\sqrt{2}(1-a_1^2)a^3a_1$	0

Not. a and a_1 are defined in Eq. (9).

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

	1	2	3
1	$\dfrac{(1+b_1^2)(a^4+a_1^4)}{(\varepsilon_1-\varepsilon_2)}$	$\dfrac{(1+b_1^2)(a^4+a_1^4)}{(\varepsilon_2-\varepsilon_1)}$	0
2	$\dfrac{aa_1(a^2-a_1^2)}{\sqrt{2}(\varepsilon_1-\varepsilon_2)}$	$\dfrac{aa_1(a^2-a_1^2)}{\sqrt{2}(\varepsilon_2-\varepsilon_1)}$	0
3	$\dfrac{a^2a_1^2}{(\varepsilon_1-\varepsilon_2)}$	$\dfrac{a^2a_1^2}{(\varepsilon_2-\varepsilon_1)}$	0
4	$\dfrac{(1-b_1^2)a^2}{(\varepsilon_1-\varepsilon_3)}$	$\dfrac{(1-b_1^2)a_1^2}{(\varepsilon_2-\varepsilon_3)}$	$(1-b_1^2)\left[\dfrac{a^2}{(\varepsilon_3-\varepsilon_1)}+\dfrac{a_1^2}{(\varepsilon_3-\varepsilon_2)}\right]$
5	$\dfrac{aa_1}{\sqrt{2}(\varepsilon_1-\varepsilon_3)}$	$-\dfrac{aa_1}{\sqrt{2}(\varepsilon_2-\varepsilon_3)}$	$\dfrac{1}{\sqrt{2}}\left[\dfrac{aa_1}{(\varepsilon_3-\varepsilon_1)}+\dfrac{aa_1}{(\varepsilon_3-\varepsilon_2)}\right]$
6	$-\dfrac{(1+b_1^2)a_1^2}{(\varepsilon_1-\varepsilon_3)}$	$\dfrac{(1+b_1^2)a^2}{(\varepsilon_2-\varepsilon_3)}$	$(1-b_1^2)\left[\dfrac{a_1^2}{(\varepsilon_3-\varepsilon_1)}+\dfrac{a^2}{(\varepsilon_3-\varepsilon_2)}\right]$

Not. a, a_1 and ε defined in Eq. (9).

$$+ b_3^{(i)}\sqrt{2\pi/35} [Y_{4-4}(\Theta, \Phi) + Y_{44}(\Theta, \Phi)] + b_4^{(i)}\sqrt{\pi} Y_{40}(\Theta, \Phi)$$

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

here the coefficients $a_i^{(i)}$ and $b_i^{(i)}$ for $i = 1-3$ are functions of the internuclear separation, R, and the spin-orbit coupling constant, ζ. The coefficients $a_l^{(i)}$ and $b_l^{(i)}$ may be expressed in terms of the matrices $g_m^{(i)}$ and $h_m^{(i)}$ and two matrices c_{lm} and d_{lm} of radial dependence,

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

$$b_l^{(i)} = \sum_{m=1}^6 d_{lm}(t) h_m^{(i)}, \tag{11}$$

where $t = 2\beta R$, or $2\beta_1 R$. The matrix elements $g_m^{(i)}$ and $h_m^{(i)}$ are represented in Table 1 and 2, and the matrix elements $c_{lm}(t)$ and $d_{lm}(t)$ are given in Table 3 and 4, respectively. They are given in terms of series which are linear combinations of the radial integrals[17]. In order to investigate angular and radial dependence of NMR chemical shifts arising from the electron-nuclear interaction, we choose $\langle 001 \rangle$, $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ axes.

RESULTS AND DISCUSSION

In this work we have investigated, the NMR chemical shift arising from the $3d$ and $4p$ electron orbital angular momentum and the $3d$ and $4p$ electron spin dipolar-nuclear spin angular momentum interactions for a $3d^9$ system in a strong crystal

Table 3. The Matrix Elements $c_{lm}(t)$

$C_{lm}(t)$	$C_{lm}(t)$ for $R \longrightarrow \infty$
$c_{11} = 0$	0
$c_{21} = (64/231)S_1$	$7200/R^7\beta^4$
$c_{31} = 0$	0
$c_{41} = (32/3465)(22f_1 + F_4) + (16/3675)b^2 M_2$	$(72b^2 - 96)/R^5\beta^2$
$c_{51} = -(16/63)(t_1 + T_4) - (8/2205)b^2(7m_2 + 5M_8)$	$-16/R^3$
$c_{61} = -(16/315)(7n_1 + N_1) + (8b^2/1575)(5m_1 + M_1)$	0
$c_{12} = (32/33)(2 + b^2)S_1$	$25200(2 + b^2)R^7\beta^4$
$c_{22} = -(64/231)S_1$	$-7200/R^7\beta^4$
$c_{32} = (16/33)[F_8 + (1 + b^2)F_3]$	$560(1 + b^2)/R^5\beta^2$
$c_{42} = (672/3465)F_{10} + (16b^2/3675)(3 - b^2)M_2$	$8(16 + 27b^2 - 9b^4)/R^5\beta^2$
$c_{52} = (8/315)[12T_3 + (1 + b^2)(5T_1 - 12T_3 - 5T_5)] + (4/2205)b^2[-12M_5 + (1 + b^2)(12M_5 + M_6 + 11M_9)]$	0
$c_{62} = -(32/105)N_1 - (48/1575)(2 + b^2)b^2 M_1$	0
$c_{13} = -(80/33)S_1$	$-63000/R^7\beta^4$
$c_{23} = (32/231)(1 - 2b^2)S_1$	$3600(1 - 2b^2)/R^7\beta^4$
$c_{33} = (16/99)[(1 + b^2)(11f_1 - 3F_3) + (3 - b^2)F_8]$	$-1120(1 + b^2)/R^5\beta^2$
$c_{43} = -(8/3465)[(1 + b^2)(-44f_1 + 4F_4) + 64F_9 + 84(1 - b^2)F_{10}] - (8b^2/3675)(1 - 7b^2)M_2$	$-4(64 - 41b^2 + 63b^4)R^5\beta^2$
$c_{53} = (32/315)[(1 + b^2)(15t_1 - 10T_4 + 5T_5 + 12T_3) + 20T_1 - 12(1 - b^2)T_3]$ $+ (8/2205)b^2[-(1 + b^2)(7m_2 + M_6/2 - 5M_8) - 12b^2 M_5 + 33M_9 - 11b^2 M_9]$	$4(24 + 23b^2 + 7b^4)/R^3$
$c_{63} = (16/315)[-21(1 + b^2)n_1 + (3 - 5b^2)N_1] + (8/1575)b^2[-25(1 + b^2)m_1 + (15 - b^2)M_1]$	0
$c_{14} = (4/33)S_1$	$3150/R^7\beta^4$
$c_{24} = -(8/231)S^1$	$-900/R^7\beta^4$
$c_{34} = -(2/99)(22f_1 + 8F_8)$	$140/R^5\beta^2$
$c_{44} = -(4/3465)(66f_1 - 32F_9) - (16/3675)b^2 M_2$	$8(7 - 9b^2)/R^5\beta^2$
$c_{54} = -(8/63)(t_1 + T_1) + (4/2205)b^2(7m_2 - 11M_9)$	$-8(1 + b^2)/R^3$
$c_{64} = (16/315)(7n_1 + N_1) + (8/1575)b^2(7m_1 - M_1)$	0

Note. Radial series are listed elsewhere (17) and appendix.

Table 4. The Matrix Elements $d_{lm}(t)$

$d_{lm}(t)$	$d_{lm}(t)$ for $R \longrightarrow \infty$
$d_{11} = (8/33)S_1$	$6300/R^7\beta^4$
$d_{21} = -(16/231)S_1$	$-1800/R^7\beta^4$
$d_{31} = -(4/99)(11f_1 - 3F_8)$	$140/R^5\beta^4$
$d_{41} = -(8/1155)(11f - 7F_{10}) + (16/3675)b^2 M_2$	$96b^2/R^5\beta^2$
$d_{51} = -(8/315)(5t_1 - 3T_3) - (4/2205)b^2(7m_2 + 3M_5)$	0
$d_{61} = (8/315)(14n_1 - 3N_1) - (4/1575)b^2(10m_1 + 3M_1)$	0
$d_{12} = (8/33)(7 - 3b^2)S_1$	$6300(7 - 3b^2)/R^7\beta^4$
$d_{22} = -(16/231)(3 + b^2)S_1$	$1800(3 + b^2)/R^7\beta^4$
$d_{32} = (8/99)[11(1 + b^2)f_1 + 6F_8 + 2(1 - b^2)(3F_3 + 2F_8)]$	$280(1 - 3b^2)/R^7\beta^2$
$d_{42} = (16/3465)[33(1 + b^2)f_1 + 42F_{10} - 16(1 - b^2)F_9] + (16/3675)b^2(5 - b^2)M_2$	$8(2 + 31b^2 - 9b^4)/R^5\beta^2$
$d_{52} = (8/315)[10(1 + b_2)t_1 + 12T_3 + (1 - b^2)(15T_1 - 12T_3 - 5T_5)] + (4/2205)b^2[14(1 + b^2)m_2$ $- 12M_5 + (1 - b^2)(12M_5 + M_6 + 33M_9)]$	$16(1 - b^2)/R^3$
$d_{62} = -(32/315)[7(1 + b^2)n_1 + 3N_1 + (1 - b^2)N_1] + (4/1575)b^2[5(1 + b^2)m_1 - (1 + 2b^2)M_1]$	0
$d_{13} = (8/33)(1 + 3b^2)S_1$	$6300/R^7\beta^4$
$d_{23} = -(48/231)(3 + b^2)S_1$	$-21600(3 + b^2)/R^7\beta^4$
$d_{33} = (8/99)[11(1 - b^2)f_1 + 4(3 + b_2)F_8 - 6(1 + b_2)F_3$	$-280(3 + b^2)/R^5\beta^2$
$d_{43} = -(16/3465)[-(110 + 77b^2)f_1 - 2(3 + b^2)(F_4 + 8F_9)] + (32/3675)b^2(2 + b^2)M_2$	$8(8 + b^2 + 36b^4)/R^5\beta^2$
$d_{53} = (8/315)[40t_1 + 10(3 + b^2)(T_1 + T_4) - (1 + b^2)(5T_1 - 5T_5 - 12T_3)]$	$90/R^3$

$$+ (4/2205)b^2[56m_2 + 2(3+b^2)(5M_8 + 11M_9) - (1+b^2)(18M_5 + M_6 + 33M_9)]$$

$d_{63} = (16/315)[(7+9b^2)n_1 - (3+b^2)N_1] - (8/1575)b^2[5m_1(1+3b^2) - 2M_1(2+b^2)]$ 0

$d_{14} = 0$ 0

$d_{24} = (64/231)S_1$ $7200/R^7\beta^4$

$d_{34} = 0$ 0

$d_{44} = (8/3465)(23F_1 - 19F_7) + (16/3675)b^2M_2$ $-8(4-9b^2)/R^5\beta^2$

$d_{54} = -(8/63)(T_1 + T_5) + (4/2205)b^2(M_6 - 11M_9)$ $-8(1+b^2)/R^3$

$d_{64} = -(16/315)N_1 + (8/1575)b^2M_1$ 0

$d_{15} = (16/33)(1+b^2)S_1$ $12600(1+b^2)/R^7\beta^4$

$d_{25} = -(32/231)(3-b^2)S_1$ $3600(3-b^2)/R^7\beta^4$

$d_{35} = (8/99)(1+b^2)(11f_1 + 3F_8)$ $280(1+b^2)/R^5\beta^2$

$d_{45} = (8/3465)[6(1+b^2)(11f_1 + 7F_{10}) - (1-b^2)(23F_1 - 19F_7)] - (4/3675)b^2(1-7b^2)M_5$ $2(11-5b^2)/R^5\beta^2$

$d_{55} = (8/315)[10(1+b^2)t_1 + 6(1+b^2)T_3 + 3(1-b^2)(T_1 + T_5)]$ $16(4+b^2-5b^4)/5R^3$
$\qquad + (4/2205)b^2[14(1+b^2)m_2 - 6(1+b^2)M_5 - (1-b^2)(M_6 - 11M_9)]$

$d_{65} = -(32/315)[7(1+b^2)n_1 + (13+14b^2)N_1] + (4/315)b^2[20(1+b^2)m_1 - (7+5b^2)M_1]$ 0

$d_{16} = -(8/33)S_1$ $-6300/R^7\beta^4$

$d_{26} = (16/231)S_1$ $1800/R^7\beta^4$

$d_{36} = -(4/99)(11f_1 + 3F_8)$ $140/R^5\beta^2$

$d_{46} = -(8/1155)(11f_1 + 7F_{10}) - (16/3675)b^2M_2$ $-8(1+9b^2)R^5\beta^2$

$d_{56} = -(8/315)(5t_1 + 3T_3) - (4/2205)b^2(7m_2 - 3M_5)$ $4(1+b^2)/R^3$

$d_{66} = (8/315)(14n_1 + 3N_1) - (4/1575)b^2(10m_1 - 3M_1)$ 0

Note. Radial series are listed in the elsewhere (17) and appendix.

Table 5. $\Delta B/B$(ppm) for Specific R-Values for a $3d^9$ System in a Strong Crystal Field of Tetragonally Distorted Tetrahedral Symmetry ($\delta = 1660$ cm^{-1}, $\zeta = -830$ cm^{-1}, $\zeta_1 = -1280$ cm^{-1}, $\beta = 4.4002/a_0$, $\beta_1 = 1.3770/a_0$, and $T = 330$ K)

R(nm) \ axis	$\langle 001 \rangle$	$\langle 100 \rangle$ (or $\langle 010 \rangle$)	$\langle 110 \rangle$ (or $\langle \bar{1}10 \rangle$)	$\langle 111 \rangle$	$\langle 11\bar{2} \rangle$
			(a) $b=0$ (Eq. 4)		
0.05	-41090.1610	-1657.2934	-1179.5435	9220.7592	-13325.1510
0.10	-5439.6329	1415.5310	1634.8821	843.7777	-1993.0222
0.15	-1469.8131	549.0708	592.6717	100.1606	-628.3814
0.20	-591.5237	250.5403	260.1817	22.4472	-226.2754
0.30	-168.5110	78.1949	79.8498	2.8310	-80.2003
0.40	-70.0340	33.5700	33.9727	0.6614	-34.0406
			(b) $b=0.1$ (Eq. 4)		
0.05	-41035.0710	-1636.9301	-1124.5204	9156.0049	-13302.4970
0.10	-5424.0777	1412.3563	1632.1480	838.8863	-1987.2919
0.15	-1465.3890	547.6047	591.0973	99.6418	-616.6073
0.20	-589.7489	249.8419	261.4422	22.3382	-265.5071
0.30	-168.0109	77.9709	79.6190	2.8180	-79.9674
0.40	-69.8273	33.4730	33.8741	0.6585	-33.9415
			(c) $b=1$ (Eq. 4)		
0.05	25.5828	-116.8908	-116.8908	-14.4540	33.0376
0.10	45.2527	-38.6229	-38.6229	7.0063	34.9652
0.15	16.9463	-10.8597	-10.8597	1.0608	10.3296
0.20	7.6542	-4.3946	-4.3946	0.2522	4.2685
0.30	2.3747	-1.2621	-1.2621	0.0332	1.2455
0.40	1.0176	-0.5265	-0.5265	0.0079	0.5226

field environment of tetragonally distorted tetrahedral symmetry. The calculated NMR chemical shifts a $3d^9$ system using Eq. (8) along the $\langle 001 \rangle$, $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ and $\langle 11\bar{2} \rangle$ axes are given in Table 5. Here we choose the spin orbit couping constants, ζ_{3d} as -830 cm^{-1} and $\zeta_{4p} = -1280$ cm^{-1}, $\beta = 4.4002/a_0$, $\beta_1 = 1.3770/a_0$, and the distortion parameter $\delta = 1660$ cm^{-1}, which are the appropriate values for the Cu^{2+} ion[18,19].

Table 6. A Comparison of the Exact Values of $\Delta B/B$ (ppm) Using Eq. (8) with the Multipolar Terms for Specific R Values Along the $\langle 001 \rangle$ Axis

R(nm)	$1/R^3$	$1/R^5$	$1/R^7$	Sum of multipolar terms	Exact
		(a) $b=0$ (Eq. 4)			
0.05	−24187.8300	−20602.2740	7227.7513	−37562.3530	−41090.1610
0.10	−4371.3777	−1438.4052	374.2708	−5435.5122	−5439.6329
0.15	−1301.4141	−192.6661	24.2690	−1469.8112	−1469.8131
0.20	−549.0432	−45.7248	3.2442	−591.5237	−591.5237
0.30	−162.6795	−6.0214	0.1898	−168.5110	−168.5110
0.40	−68.6304	−1.4289	0.0253	−79.0340	−70.0340
		(b) $b=0.1$ (Eq. 4)			
0.05	−24151.0240	−20526.4810	7162.8505	−37514.6550	−41035.0710
0.10	−4358.6758	−1432.2171	370.9101	−5419.9828	−5424.0777
0.15	−1297.6094	−192.8288	24.0511	−1465.3871	−1465.3890
0.20	−547.4380	−45.5260	3.2151	−589.7489	−589.7489
0.30	−162.2039	−3.9952	0.1882	−168.0109	−168.0109
0.40	−68.4298	−1.4227	0.0251	−69.8273	−69.8273
		(c) $b=1$ (Eq. 4)			
0.05	118.5305	−56.5155	0.0000	62.0151	25.5828
0.10	63.4903	−18.1756	0.0000	45.3147	45.2527
0.15	19.6737	−2.7276	0.0000	16.9462	16.9463
0.20	8.3027	−0.6486	0.0000	7.6542	7.6542
0.30	2.4601	−0.0854	0.0000	2.3747	2.3747
0.40	1.0378	−0.0203	0.0000	1.0176	1.0176

Table 7. A Comparison of the Exact Values of $\Delta B/B$ (ppm) Using Eq. (8) with the Multipolar Terms for Specific R Values Along the $\langle 001 \rangle$ Axis

R(nm)	$1/R^3$	$1/R^5$	$1/R^7$	Sum of multipolar terms	Exact
		(a) $b=0$ (Eq. 4)			
0.05	12093.9150	−9820.5106	−402.8893	1870.5153	−1657.2934
0.10	2185.6889	−745.1745	−20.8626	1419.6517	1415.5310
0.15	650.7070	−100.2815	−1.3528	549.0727	549.0708
0.20	274.5219	−23.8005	−0.1808	250.5403	250.5403
0.30	81.3397	−3.1342	−0.0106	78.1949	78.1949
0.40	34.3152	−0.7438	−0.0014	33.5700	33.5700
		(b) $b=0.1$ (Eq. 4)			
0.05	12075.5120	−9787.3570	−404.6691	1883.4860	−1636.9301
0.10	2179.3379	−741.9319	−20.9548	1416.4512	1412.3563
0.15	648.8047	−99.8393	−1.3588	547.6066	547.6047
0.20	273.7190	−23.6955	−0.1816	249.8419	249.8419
0.30	81.1019	−3.1204	−0.0116	77.9709	77.9709
0.40	34.2149	−0.7405	−0.0014	33.4730	33.4730
		(c) $b=1$ (Eq. 4)			
0.05	−59.2652	−21.1933	0.0000	−80.4586	−116.8908
0.10	−31.7451	−6.8159	0.0000	−38.5610	−38.6229
0.15	−9.8369	−1.0228	0.0000	−10.8597	−10.8597
0.20	−4.1514	−0.2432	0.0000	−4.3936	−4.3936
0.30	−1.2300	−0.0320	0.0000	−1.2621	−1.2621
0.40	−0.5189	−0.0076	0.0000	−0.5265	−0.5265

The results for a $3d^9$ system using Eq. (8) and the corresponding dipolar term $1/R^3$ and multipolar terms, $1/R^5$, and $1/R^7$, are shown in Tables 6 to 9. The NMR chemical shifts along the $\langle 100 \rangle$ and $\langle 110 \rangle$ axes are very similar to those for a $3d^1$ system in a strong crystal field environment of tetragonal symmetry when a fourfold axis is chosen as the quantization axis. When the mixing coefficient, b is 0.1, the NMR chemical shift decreases in magnitude rapidly as R

Table 8. A Comparison of the Exact Values of $\Delta B/B$ (ppm) Using Eq. (8) with the Multipolar Terms for Specific R Values Along the $\langle 110 \rangle$ Axis

R(nm)	$1/R^3$	$1/R^5$	$1/R^7$	Sum of multipolar terms	Exact
		(a) $b=0$ (Eq. 4)			
0.05	12093.9150	−5631.1947	−4114.4553	2348.2652	−1179.5435
0.10	2185.6889	−333.6294	−213.0566	1639.0028	1634.8821
0.15	650.7070	−44.2180	−13.8153	592.6736	592.6717
0.20	274.5216	−10.4931	−1.8468	262.1817	262.1817
0.30	81.3397	−1.3818	−0.1081	79.8489	79.8498
0.40	34.3152	−0.3279	−0.0144	33.9729	33.9729
		(b) $b=0.1$ (Eq. 4)			
0.05	12075.5120	−5607.5039	−4072.1124	2395.8957	−1124.5204
0.10	2179.3379	−332.2309	−210.8640	1636.2429	1632.1480
0.15	648.8047	−44.0323	−13.6731	591.0993	591.0973
0.20	273.7190	−10.4490	−1.8278	261.4422	261.4422
0.30	81.1019	−1.3760	−0.1070	79.6190	79.6190
0.40	34.2149	−0.3265	−0.0143	33.8741	33.8741
		(c) $b=1$ (Eq. 4)			
0.05	−59.2653	−21.1933	0.0000	−80.4586	−116.8908
0.10	−31.7451	−6.8159	0.0000	−38.5610	−38.6229
0.15	−9.8369	−1.0228	0.0000	−10.8597	−10.8597
0.20	−4.1514	−0.2432	0.0000	−4.3946	−4.3946
0.30	−1.2300	−0.0320	0.0000	−1.2621	−1.2621
0.40	−0.5189	−0.0076	0.0000	−0.5265	−0.5265

Table 9. A Comparison of the Exact Values of $\Delta B/B$ (ppm) Using Eq. (8) with the Multipolar Terms for Specific R Values Along the $\langle 111 \rangle$ Axis

R(nm)	$1/R^3$	$1/R^5$	$1/R^7$	Sum of multipolar terms	Exact
		(a) $b=0$ (Eq. 4)			
0.05	0.0000	8942.9544	3805.6153	12748.5680	9220.7592
0.10	0.0000	650.8343	197.0641	847.8983	843.7777
0.15	0.0000	87.3842	12.7783	100.1625	100.1606
0.20	0.0000	20.7390	1.7082	22.4472	22.4472
0.30	0.0000	2.7311	1.1000	2.8310	2.8310
0.40	0.0000	0.6481	0.0133	0.6614	0.6614
		(b) $b=0.1$ (Eq. 4)			
0.05	0.0000	8911.3767	3765.0443	12676.4210	9156.0049
0.10	0.0000	648.0180	194.9633	842.9813	838.8863
0.15	0.0000	87.0016	12.6421	99.6437	99.6418
0.20	0.0000	20.6482	1.6900	22.3382	22.3382
0.30	0.0000	2.7191	0.0989	2.8180	2.8180
0.40	0.0000	0.6453	0.0132	0.6585	0.6585
		(c) $b=1$ (Eq. 4)			
0.05	0.0000	21.9782	0.0000	21.9782	−14.4540
0.10	0.0000	7.0683	0.0000	7.0683	7.0063
0.15	0.0000	1.0607	0.0000	1.0607	1.0608
0.20	0.0000	0.2522	0.0000	0.2522	0.2522
0.30	0.0000	0.0332	0.0000	0.0332	0.0332
0.40	0.0000	0.0079	0.0000	0.0079	0.0079

increases. Along the $\langle 111 \rangle$ axis, $\Delta B/B$ is positive for all values of R, while along the $\langle 001 \rangle$ $\Delta B/B$ is negative for all values of R and along the $\langle 100 \rangle$ and $\langle 110 \rangle$ axes, $\Delta B/B$ changes sign around 0.1 nm, the values being negative for smal-

ler R values and positive for greater R values as shown in Table 5 ($b=0.1$).

The NMR results of Table 5 ($b=1$) show that along the $\langle 100 \rangle$ and $\langle 110 \rangle$ axes, $4p$ atomic orbitals contribute negati-

vely to the NMR chemical shifts, while in the case of the other axes contribute positively to NMR chemical shift. Table 5 shows the relative contribution of the $3d$ and $4p$ atomic orbital to the NMR chemical shift dependent upon each intermixing coefficient b. When b is 0.1, $3d$ atomic orbital contribution to the NMR chemical shift dominates for the given R values.

The comparison of the multipolar terms with the exact solution of $\Delta B/B$ given by Eq. (8) shows that the major contribution to the NMR chemical shift arises from the $1/R^3$ term but the other terms ($1/R^5$, $1/R^7$) contribute significantly to the values of the NMR chemical shift along all directions except $\langle 111 \rangle$ axis. Here it is necessary to mention that along the $\langle 111 \rangle$ axis the $1/R^3$ term is zero, while along the $\langle 100 \rangle$ and $\langle 110 \rangle$ axes the $1/R^3$ term is positive, but along the $\langle 001 \rangle$ $1/R^3$ term is negative when the mixing coefficient, b is 0 or 0.1, while in the case of $b=1$ the sign is the reverse for all R values. These are shown in Tables 6 to 9.

In addition, the contribution of $1/R^5$ term to the NMR chemical shift along the $\langle 100 \rangle$, $\langle 001 \rangle$, and $\langle 110 \rangle$ axes is negative, while along the $\langle 111 \rangle$ axes the contribution of the $1/R^5$ term is positive for all R values. We observe also that the $\langle 001 \rangle$ axis the $1/R^7$ term gives values opposite in sign to the $1/R^5$ term. Finally, the sum of all multipolar terms along the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ axes is positive, while along the $\langle 001 \rangle$ axis that of $\sum_{i=1}^{3} \frac{1}{R^{2i+1}}$ terms is negative when $b=0$ or 0.1, but the sign is the reverse when $b=1$ for all R values except along the $\langle 111 \rangle$ axis. We find that the exact solution of $\Delta B/B$ is exactly in agreement with multipolar results when $R \geq 0.2$ nm, while with the point-dipole results the exact results is significantly different in the R values shorter than 0.2 nm.

We examine next the temperature dependence of the NMR chemical shift calculated from exact solution and compare the results with the usually used approximate equations as follows[11]:

$$\frac{\Delta B}{B} = C_0 + C_1/T + C_2/T^2 \qquad (12)$$

In Eq. (12) the $1/T$ term arises from the Fermi contact term (FC) and $1/T^2$ term from the pseudocontact (PC) term. This expression may be applied to a $3d^9$ system in a strong crystal field environment of tetragonally distorted tetrahedral symmetry because only the crystal field is changed. The NMR chemical shift over the temperature range from 200 K to 400 K obtained from the exact solution of $\Delta B/B$ may be fitted almost precisely to an expression of the form given by Eq. (12).

The values C_0, C_1 and C_2 depend markedly on the location of the NMR nucleus some values are given in Table 10. The dominant contribution to $\Delta B/B$ expressed in the form of Eq. (12) is the $1/T$ term. The temperature dependence of NMR shift arising from the interaction described by Eq. (2) would mirror closely the Fermi contact interaction and not pseudocontact interaction. Hence a temperature-dependence analysis based on Eq. (12) may lead to an incorrect interpretation of the origin of the NMR chemical shift.

Finally, the calculated $\Delta B/B$ in the $3d^9$ system coming from the interactions expressed by Eq. (2), by using nonmultipole expansion method provides an excellent check with

Table 10. The Temperature Dependence of $\Delta B/B$ (ppm) at Various Values of R Expressed in Terms of the Coefficients in Eq. (12) ($\delta = 1660$ cm^{-1}, $\zeta = -830$ cm^{-1} and $\zeta_1 = 1280$ cm^{-1}, $\beta = 4.4002/a_0$ and $\beta_1 = 1.3770/a_0$, $b = 0.1$)

R(nm)	Axis	C_0 (ppm)	$C_1 \times 10^{-2}$ (ppm K)	$C_2 \times 10^{-4}$ (ppm K^2)
0.10	$\langle 001 \rangle$	1209.7904	-20438.0556	1613.8582
0.20		145.9155	-2258.2523	154.2258
0.30		42.3936	-645.2524	41.9903
0.40		17.7245	-268.4549	17.3477
0.50		9.0167	-136.5352	9.0066
0.20	$\langle 100 \rangle$ (or $\langle 010 \rangle$)	-65.2320	959.6661	-44.8012
0.20	$\langle 110 \rangle$ (or $\langle \bar{1}10 \rangle$)	-66.3795	1005.4121	-66.0130
0.20	$\langle 111 \rangle$	-3.1260	79.1435	-82.9828
0.20	$\langle 11\bar{2} \rangle$	68.9750	-1025.2622	65.6055

errors coming from the point-dipole and multipole expansion approximations.

Appendix

Radial Series

(a) General Formulars

$$M_j = u_2 + (2-A)v_1 + Av_3$$

where $A = \mu/5$

Parameter values for the M_j series are listed in the following tables:

M_j	M_3	M_5	M_6	M_7	M_8	M_9
μ	6	3	-18	16/3	36/3	54/11

(b) Specific Formulars

$$m_1 = v_1 + w_0$$

$$m_2 = v_1 + w_2$$

$$M_1 = u_2 + 2v_1 + w_0$$

$$M_2 = u_2 + 2v_3 + w_4$$

$$M_4 = u_2 + 2v_3 + w_2$$

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Diffusion Controlled Alkylation of Aromatic Compounds in Cation-Exchanged ZSM-5 Zeolites

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Using uniform flat plate-like samples of ZSM-5 zeolites, diffusion coefficients were measured volumetrically for the diffusion of xylene, ethyltoluene and diethylbenzene by direct measurement of sorption rate. Toluene disproportionation over H(100)-, K(72)- and Cs(82)-ZSM-5 at 773 K and toluene methylation, toluene ethylation and ethylbenzene ethylation over Cs(75)-ZSM-5 at 623 K were carried out. The selective formation of para xylene during the toluene disproportionation, presumably due to the increased tortuosity over Cs-ZSM-5, could be explained by smaller diffusion coefficient in Cs-ZSM-5 than in K- and H-ZSM-5. The para selectivity increased in the order; toluene methylation<toluene ethylation<ethylbenzene ethylation. As the chain length of the alkyl substituent in dialkylbenzenes is increased, the para selectivity of the products was improved. It may be attributed to the differences in the ratios of diffusion coefficient of para products to that of ortho ones. Diffusion coefficient of *m*-xylene was about 1 order of magnitude smaller than that of *o*-xylene.

Introduction

When the size and shape of the molecules approach to those of the intracrystalline structure of zeolites, molecular shape selectivity can be observed. Molecular shape selectivity can arise due to large differences in the diffusivities of reactant or product molecules in the intracrystalline channels and to the differences in size and structure of the reaction intermediate. Shape-selective catalysis was first demonstrated by Weisz over CaA zeolite[1]. Recent developments in molecular shape-selective catalysis in zeolites have been reviewed by Weisz[2], Csicsery[3] and Derouane[4]. We reported the diffusive properties of cyclohexanes in ZSM-5 zeolites[5] and para-selectivities in the alkylation of toluene with ethanol over cation exchanged ZSM-5 and ZSM-8 zeolites[6,7].

The framework of ZSM-5 type zeolites contains two types of intersecting channels. The straight channels running parallel to the *b*-axis [010] of orthorhombic unit cell have about 5.4×5.6Å free diameter. The sinusoidal channels along *a*-axis [100] interconnected by straight channels have somewhat smaller openings[8]. The typical shape of ZSM-5 crystals is reported to be a platelet shape with the (010) surface being

the plate surface[9].

Molecular shape selective properties of ZSM-5 type zeolites can be modified by ion exchange. This study involves the investigation of para-selectivities of toluene disproportionation over H-, K- and Cs-exchanged ZSM-5 zeolites and toluene methylation, toluene ethylation and ethylbenzene ethylation over Cs-ZSM-5. Measurement of diffusion coefficient of *o*-, *m*- and *p*-isomers of xylene, ethyltoluene and diethylbenzene made it possible to interprete the para-shape selectivity resulting from diffusional restriction by exchanged cation and the kinetic diameter of aromatics. For measurement of diffusion coefficients, we synthesized the ZSM-5 crystallites of flat plate-like structure.

Experimental

Synthesis of ZSM-5 Zeolites. For the synthesis of Al-free ZSM-5 samples, colloidal silica (29% SiO_2, Snowtex, Nissan Chem.) was added to the aqueous solution of 10% tetrapropylammonium hydroxide (TPAOH, Tokyo Kasei) as organic base, as described in the literature[10]. For Na-ZSM-5, sodium aluminate (35% Al_2O_3, Kanto Chem.) was dissolved