

The NMR Pseudocontact Shift of Tetrahedral and Pseudo-Tetrahedral Complex of Cu(II)

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The NMR dipolar shift in tetrahedral and tetragonally-distorted tetrahedral complexes for Cu(II) has been calculated adopting nonmultipole expansion method. The exact solution of $\Delta B/B$ (ppm) is exactly in agreement with multipolar results when R, the distance between the paramagnetic ion and the nucleus, is larger than 0.2 nm. The major contribution to the dipolar shift arises from $1/R^3$ term but the other terms, $1/R^5$ and $1/R^2$, contribute significantly to the pseudocontact shift when R is shorter than 0.5 nm. The shift is mainly due to the 3d orbitals and sensitive to distortion parameters at short range of R.

Introduction

The NMR dipolar shift which affords information related to geometrical structure has widely been accepted as a main contributor to the isotropic shift. The dipolar shift has also been called the pseudocontact shift in literature. The non-multipole expansion method has been mainly used for the accurate calculation of dipolar shift and its contribution to NMR chemical shifts of $3d(3d^1, 3d^2)$, $1-5$ $4d(4d^1, 4d^2)$, $6-10$ and (4f and 5f) systems^{11,12} in several symmetries, respectively.

In the treatment of the dipolar shift in transition metal complexes and lanthanide shift reagents, most researchers have used a simplified set of equations to analyze their experimental results. For axially symmetric complexes the dipolar shift is normally given in the form¹³⁻¹⁵:

$$(\Delta B/B)_D = -DP(3 \cos^2\theta - 1)R^{-3} \quad (1)$$

where DP is related to the atomic susceptibility, R is the distance between the paramagnetic ion and the nucleus, and θ is the angle between the vector R and the z axis. Eq. (1) is the first term in a multipole expansion and is correct only if R is much larger than the size of the metal d orbital of the electron. When R is not large enough, the expression for the dipolar term becomes more complex as has been shown in the work of Golding.^{1,3,16,17}

In this paper, we will calculate the exact pseudocontact shift of complex of Cu(II) in tetrahedral and pseudo tetrahedral symmetry using the nonmultipole expansion method and Eq. (1) will be compared with exact values. Also, to enable a ready comparison of the results in this work to the results that would be gained using the multipole expansion method, tables are included comparing the these methods. Finally we will investigate the effect of distortion parameters on pseudocontact shift in this system.

Theory

The hamiltonian representing the various interactions may be expressed as

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + V(r) + \delta(l_z^2 - 2) + \zeta l \cdot s + \mu_B(l + 2s) \cdot B + H_M \quad (2)$$

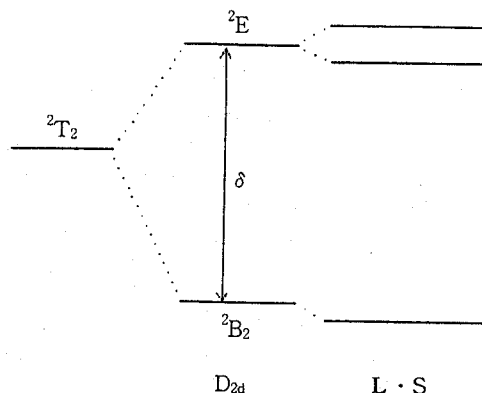


Figure 1. Distortion and spin-orbit coupling of the 2T_2 energy level of CuCl_4^{2-} .

where

$$H_M = \frac{\mu_0}{4\pi} g_N \mu_B \mu_N \left\{ \frac{2I_N \cdot I}{r_N^3} + g_s \left[\frac{3(r_N \cdot s)r_N \cdot I}{r_N^5} - \frac{s \cdot I}{r_N^3} \right] \right\} \quad (3)$$

and

$$V(r) = A_{32} r^3 \{Y_{32}(\theta, \phi) - Y_{3-2}(\theta, \phi)\} + A_{40} r^4 \{Y_{40}(\theta, \phi) + (5/14)^{1/2} \{Y_{4-4}(\theta, \phi) + Y_{44}(\theta, \phi)\}\} \quad (4)$$

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, $V(r)$ is the crystal field potential of tetrahedral symmetry, and A_{32} and A_{40} are the crystal field parameters.¹⁸ The other symbols have their usual meaning. The tetrahedral complex approximates to D_{2d} symmetry, suffering a tetragonal compression of the tetrahedral coordination shell like CuCl_4^{2-} . A qualitative diagram of the term splittings is illustrated in Figure 1. 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 functions involving 3d and 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^{18,20,21} as

$$|t_{2i}\rangle = |3d_{t_{2i}}\rangle - b|4p_i\rangle, \quad i=yz, xz, xy. \quad (5)$$

where

$$b = \frac{C}{E(4p) - E(3d)} \langle 4p_x | xyz | 3d_{2yz} \rangle$$

with C is a constant.

It was also reported that using a point-charge model,¹⁸ 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. Since these wave functions are degenerate, we may choose an orthogonal set of linear combinations, so we take the basis set of wave functions as

$$\begin{aligned} \phi_0 &= 1/(2)^{1/2} (|3d_2\rangle - |3d_{-2}\rangle) + b_1|4p_0\rangle, \\ \phi_1 &= -|3d_1\rangle + b_1|4p_{-1}\rangle, \text{ and} \\ \phi_2 &= |3d_{-1}\rangle + b_1|4p_1\rangle \end{aligned} \quad (6)$$

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 as shown in Figure 1. The magnetic field interaction, $\mu_B(I+2s) \cdot B$, is then added and treated as a perturbation to yield new eigenfunctions, $|\Psi_n\rangle$, and the corresponding eigenvalues, E_n . To determine the pseudocontact 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

$$\Delta B = B(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3, \quad (7)$$

where

$$\sigma_{\alpha\alpha} = \left[\frac{\partial^2}{\partial \mu_\alpha \partial B_\alpha} \left(\frac{\sum_i \langle \psi_i | H_M | \psi_i \rangle \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} \right) \right]_{\mu=B=0} \quad (8)$$

with

$$\mu = g_N \mu_N I$$

The term H_M is the hamiltonian given in Eq. (3). The pseudocontact shift for the $3d^9$ system in a strong crystal field environment of tetrahedral symmetry is calculated by

$$\frac{\Delta B}{B} = -\frac{\mu_0}{4\pi} \frac{\mu_B^2}{3kT} \left\{ \frac{\sum_{i=1}^3 (A_i + B_i/kT) \exp(-E_i/kT)}{2 \sum_{i=1}^3 \exp(-E_i/kT)} \right\} \quad (9)$$

Here the eigenvalues and the corresponding eigenfunctions by the spin-orbit coupling are given by

$$\begin{aligned} \varepsilon_1 &= \zeta_s/4 + X/2, & \phi_1^+ &= a\phi_1^+ + a_1\phi_0^-, \\ & & \phi_1^- &= a\phi_2^- + a_1\phi_0^+, \\ \varepsilon_2 &= \zeta_s/4 - X/2, & \phi_2^+ &= a_1\phi_1^+ - a\phi_0^-, \\ & & \phi_2^- &= a_1\phi_2^- - a\phi_0^+, \\ \varepsilon_3 &= -\zeta_s/2, & \phi_3^+ &= \phi_2^+ \\ & & \phi_3^- &= \phi_1^- \end{aligned} \quad (10)$$

Table 1. $\Delta B/B$ (ppm) of Cu(II) complex for specific R values in a strong crystal field of tetrahedral symmetry at T=300 K

R (nm)	$\langle 001 \rangle$	$\langle 100 \rangle$	$\langle 110 \rangle$	$\langle 111 \rangle$
	b=0			
0.10	289.8045	-2126.1031	-954.7088	1657.5261
0.15	292.5819	-446.3943	-227.3730	184.4998
0.20	159.4058	-154.1815	-96.3579	39.9364
0.30	55.3332	-37.7813	-29.6157	4.8955
0.40	24.5860	-14.7188	-12.7353	1.1315
0.50	12.8843	-7.2409	-6.5840	0.3662
	b=0.1			
0.10	306.7498	-2142.5718	-953.3583	1662.2935
0.15	297.7599	-450.1060	-228.5369	185.0739
0.20	161.5858	-155.5428	-97.0998	40.0670
0.30	55.9836	-38.1427	-29.8942	4.9121
0.40	24.8527	-14.8607	-12.8574	1.1354
0.50	13.0239	-7.3135	-6.6501	0.3675
	b=1.0			
0.10	17.0022	-29.8116	-29.8116	9.2174
0.15	6.8821	-6.7587	-6.7587	1.4108
0.20	4.3698	-2.9682	-2.9682	0.3558
0.30	1.4384	-0.8827	-0.8227	0.0458
0.40	0.6311	-0.3388	-0.3388	0.0107
0.50	0.3272	-0.1715	-0.1715	0.0036

where

$$\begin{aligned} X^2 &= (9/4)\zeta_s^2, \quad a^2 = 1/2 + (\zeta_s/4)X^{-1}, \quad a_1^2 = 1/2 - (\zeta_s/4)X^{-1}, \\ aa_1 &= -(\zeta_s/\sqrt{2})X^{-1}, \quad \zeta_s = \zeta_d + b_1^2\zeta_p \end{aligned}$$

Here, A_i and B_i may be expressed in terms of spherical harmonics, which is included several matrix elements that have been reported before in earlier paper.^{21,22} In order to investigate angular and radial dependence of pseudocontact shifts arising from the electron-nuclear interaction, we choose $\langle 001 \rangle$, $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ axes.

Results and Discussion

In this work we have investigated the dipolar 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, e.g. complex of Cu(II), in a strong crystal field environment of tetrahedral symmetry and tetragonally-distorted tetrahedral symmetry.²¹ The calculated pseudocontact shift of tetrahedral and pseudo-tetrahedral (D_{2d}) Cu(II) complexes using Eq. (9) along the $\langle 001 \rangle$, $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ axes are given in Tables 1 and 2. Here we choose the spin-orbit coupling constants, ζ_{3d} as -827.7 cm^{-1} and $\zeta_{4p} = -925 \text{ cm}^{-1}$, $\beta = 4.4002/a_0$, $\beta_1 = 1.3770/a_0$, and the distortion parameter $\delta = 5000 \text{ cm}^{-1}$, which are the appropriate values for the Cu(II) ion in Cs_2CuCl_4 .^{23,24}

As R increases, the pseudocontact shift is decreased dramatically in both tables. When b is 0.1, the sign of $\Delta B/B$ is opposite for all values of R between tetrahedral and tetragonally-distorted tetrahedral symmetry except $\langle 111 \rangle$ axis as shown in Tables 1 and 2. We find that the exact solution of $\Delta B/B$ is exactly in agreement with the multipolar result

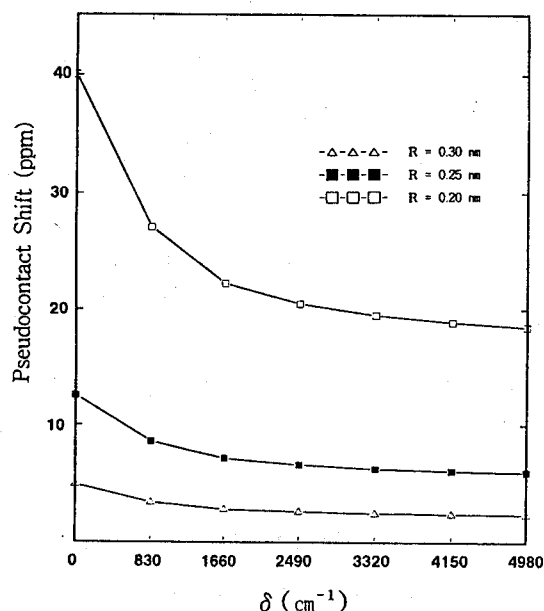
Table 2. B/B(ppm) of Cu(II) complex for specific R values in strong crystal field of pseudo-tetrahedral symmetry at T=300 K and $\delta=5000\text{ cm}^{-1}$

R (nm)	$\langle 001 \rangle$	$\langle 100 \rangle$	$\langle 110 \rangle$	$\langle 111 \rangle$
b=0				
0.10	-5662.3340	1685.4982	1757.6754	666.6238
0.15	-1548.6289	614.7516	629.3492	81.5238
0.20	-627.0076	274.9612	278.8717	18.5482
0.30	-179.5269	84.6242	85.1812	2.3671
0.40	-74.7579	36.1541	36.2898	0.5554
0.50	-38.0387	18.6172	18.6622	0.1811
b=0.1				
0.10	-5644.2540	1679.4702	1751.9639	664.0173
0.15	-1543.2774	612.5365	627.1362	81.2364
0.20	-624.8034	273.9738	277.8810	18.4862
0.30	-178.8903	84.3215	84.8777	2.3595
0.40	-74.4922	36.0250	36.1604	0.5537
0.50	-37.9034	18.5508	18.5957	0.1805
b=1.0				
0.10	64.0052	-46.0553	-46.0553	7.4349
0.15	22.1831	-13.3545	-13.3529	1.0079
0.20	9.8370	-5.4568	-5.4568	0.2392
0.30	3.0159	-1.5789	-1.5789	0.0315
0.40	1.2873	-0.6605	-0.6605	0.0075
0.50	0.6626	-0.3368	-0.3368	0.0025

Table 3. A comparison of the exact values of $\Delta B/B$ (ppm) using Eq. (9) with the multipolar terms for specific R values when b is chosen to be $b=0.1$, T=300 K, and $\delta=5000\text{ cm}^{-1}$

R (nm)	$1/R^3$	$1/R^5$	$1/R^7$	Sum of multipolar terms	exact
$\langle 001 \rangle$					
0.10	-4662.2253	-1334.4205	356.0988	-5640.5470	-5644.2540
0.20	-585.5438	-42.3464	3.0867	-624.8034	-624.8034
0.30	-173.4945	-5.5765	0.1807	-178.8903	-178.8903
0.40	-73.1930	-1.3233	0.0241	-74.4922	-74.4922
0.50	-37.4748	-0.4336	0.0051	-37.9034	-37.9034
$\langle 100 \rangle$					
0.10	2331.1126	-569.5094	-78.4260	1683.1772	1679.4702
0.20	292.7719	-18.1183	-0.6798	273.9738	273.9738
0.30	86.7472	-2.3860	-0.0398	84.3215	84.3215
0.40	36.5965	-0.5662	-0.0053	36.0250	36.0250
0.50	18.7374	-0.1855	-1.1138	18.5508	18.5508
$\langle 111 \rangle$					
0.10	0	549.6534	118.0721	667.7243	664.0173
0.20	0	17.4629	1.0235	18.4862	18.4862
0.30	0	2.2996	0.0599	2.3595	2.3595
0.40	0	0.5457	0.0080	0.5537	0.5537
0.50	0	0.1788	0.0017	0.1805	0.1805

when $R \geq 0.2\text{ nm}$, while the exact result is significantly different to the point-dipole result when R is shorter than 0.2 nm . In order to compare the contributions of d and p orbitals

**Figure 2.** The effect of distortion parameter on pseudocontact shift along the $\langle 111 \rangle$ axis when b is chosen to be $b=0.1$.

to the shift we also calculated the pseudocontact shift of d orbital ($b=0$) and p orbital ($b=1$) contributions as listed in the Table 1 and 2. The NMR results of Table 1 ($b=1$) show that along the $\langle 100 \rangle$ and $\langle 110 \rangle$ axes, $4p$ atomic orbitals contribute negatively to the pseudocontact shifts, while in the case of the other axes contribute positively to pseudocontact shifts.

In the D_{2d} symmetry, $4p$ atomic orbitals inversely contribute compared to $3d$ atomic orbitals to pseudocontact shifts except $\langle 111 \rangle$ axis. Tables 1 and 2 show the relative contribution of the $3d$ and $4p$ atomic orbitals to the pseudocontact shift dependent upon each intermixing coefficient b . When b is 0.1, the shift is mainly due to $3d$ atomic orbitals for the given R values. In other words, p orbitals do not contribute in a significant manner to the dipolar shift. Thus, we can ignore the effect of p atomic orbital in Eq. (5) for R values larger than 0.3 nm .

The results for pseudo-tetrahedral Cu(II) complex using Eq. (9) and the corresponding multipolar terms $1/R^3$, $1/R^5$, and $1/R^7$, are shown in Table 3. A comparison of the multipolar terms with the exact solution of $\Delta B/B$ given by Eq. (9) shows that the major contribution to the pseudocontact shift arises from the $1/R^3$ term but the other terms, $1/R^5$ and $1/R^7$, contribute significantly to the values of the pseudocontact shift along all directions except $\langle 111 \rangle$ axis. Here it is necessary to mention that along the $\langle 111 \rangle$ axis θ is chosen to be 54.74° , $3 \cos^2 \theta - 1 = 0$ in Eq. (1), which is referred to as the magic angle. These results in $1/R^3$ term are zero in Table 3. Along the $\langle 001 \rangle$ axis the contribution of $1/R^3$ term to the pseudocontact shift is negative, while along the $\langle 100 \rangle$ axis that of $1/R^3$ term is positive when the mixing coefficient, b is 0.1. In addition, we observe that the first term, $1/R^3$ is inadequate to describe accurately the NMR pseudocontact shift for $R \leq 0.5\text{ nm}$. When the $1/R^5$ and $1/R^7$ terms are included, there is good agreement when $R \geq 0.2\text{ nm}$. Thus, we can approximately use the Eq. (1) instead of the nonmultipole expansion method when R is larger than

0.5 nm.

We studied the effect of a distortion parameter on a pseudocontact shift along the $\langle 111 \rangle$ axis as given in Figure 2. Pseudocontact shifts depend on distortion parameter, δ and R values. We observe that the distortion parameter is more effective on pseudocontact shifts at short R values. But it is little effective to the pseudocontact shift when R is larger than 0.3 nm. Distortion parameters make contribution significantly to dipolar shifts until δ is 1660 cm^{-1} . But when δ is larger than 1660 cm^{-1} , pseudocontact shifts are little affected by δ values even though at short range of R.

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