COMMUNICATIONS TO THE EDITOR

A Further Study on the NMR Chemical Shift for a 3d[1] System in a Strong Crystal Field Environment of Octahedral Symmetry with a Threefold Axis of Quantization

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The hamiltonian representing the various interaction in a strong crystal field environment of octahedral symmetry may be expressed as

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi e_0 r} + V(\underset{\sim}{r}) + \zeta \underset{\sim}{l}\cdot\underset{\sim}{S} + \mu_B(\underset{\sim}{l}+2\underset{\sim}{S}) + H_{NJ} \quad (1)$$

where

$$H_{NJ} = \frac{\mu_0}{4\pi} g_N \mu_B \mu_N \{\frac{2\underset{\sim}{l}_N\cdot\underset{\sim}{I}}{r_N 3} + g_e(\frac{3(\underset{\sim}{r}_N\cdot\underset{\sim}{S})\underset{\sim}{r}_N\cdot\underset{\sim}{I}}{r_N^5} - \frac{\underset{\sim}{S}\cdot\underset{\sim}{I}}{r_N^3})\} \quad (2)$$

and when a threefold axis is chosen as the axis of quantization

$$V(\underset{\sim}{r}) = a_4\{\frac{1}{3}\sqrt{\frac{7}{3}}Y_{40}(\theta,\phi) - \frac{1}{3}\sqrt{\frac{10}{3}}[Y_{4-3}(\theta,\phi) - Y_{43}(\theta,\phi)]\} \quad (3)$$

Here $\underset{\sim}{r}$ and r_N are the electron radius vectors about the electron-bearing atom and the nucleus with nuclear spin angular momentum $\underset{\sim}{I}$, respectively. The quantity $\underset{\sim}{B}$ is the applied magnetic field, $V(\underset{\sim}{r})$ is the crystal field potential of octahedral symmetry when a threefold axis is chosen as the axis of quantizaiton and a_4[2] is the required crystal field parameter for the 3d electron system. The other symbols have their usual meaning. In this paper g_e, the free electron g value is taken to be equal to exactly 2.

When a threefold axis is chosen as the axis of quantization, the axial wave functions with t_2 symmetry may be expressed, in$|m\pm>$ notation, as[3]

$$\phi_0^{\pm} = |3d_z 2^{\pm}>$$

$$\phi_1^{\pm} = \sqrt{\frac{2}{3}}|2^{\pm}> - \sqrt{\frac{1}{3}}|-1^{\pm}>$$

$$\phi_2^{\pm} = \sqrt{\frac{2}{3}}|-2^{\pm}> + \sqrt{\frac{1}{3}}|1^{\pm}> \quad (4)$$

To determine the NMR chemical shift arising from the 3d orbital angular momentum and the 3d ellectron spin dipolar-nuclear spin dipolar-nuclear spin angular momentum interaction for a 3d[1] system in a strong crystal field environment of octahedral symmetry when a threefold axis is chosen as the axis of quantization, the principal values of the NMR screening tensor σ_{xx}, σ_{yy} and σ_{zz}, are determined by considering the magnetic field interaction as pararell to the x, y and z axes and averaged assuming a Boltzmann distribution. It follows that the contribution to the NMR chemical shift, ΔB, is given by

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

where

$$\sigma_{\alpha\alpha} = (\frac{\partial^2 <H_{NJ}>}{\partial\mu_\alpha \partial B_\alpha})_{\underset{\sim}{\mu}=\underset{\sim}{B}=0} \quad (5)$$

where

$$\underset{\sim}{\mu} = g_N \mu_N \cdot \underset{\sim}{I}$$

$<H_{NJ}>$ refers to the Boltzmann average of the hyperfine interaction represented by equation (2). The NMR chemical shift arising from the 3d electron orbital angular momnetum and the 3d electron spin dipolar-nuclear spin angular momentum interaction, when a three-fold axis is chosen as the axis of quantization, is given by

$$\Delta B/B = -\frac{\mu_0}{4\pi}\frac{\mu_B^2}{KT}\{\frac{d(\underset{\sim}{R}) + [1-\exp(3\zeta/2KT)]KT/\zeta S(\underset{\sim}{R})}{1+2\exp(3\zeta/2KT)}\} \quad (6)$$

where

$$d(\underset{\sim}{R}) = \frac{16\sqrt{\pi}}{105}Y_{oo}(\Theta,\Phi)J(t) - \frac{7168}{t^6}Y_3E(t) - \frac{921600}{t^7}Y_6M(t)$$

$$S(\underset{\sim}{R}) = -\frac{16\sqrt{\pi}}{63}Y_{oo}(\Theta,\Phi)P(t) + \frac{7168}{t^6}Y_3G(t) - \frac{614400}{t^7}Y_6M(t)$$

where

$$Y_3 = \sqrt{\frac{\pi}{21}}\{\frac{1}{3}\sqrt{\frac{7}{3}}Y_{40}(\Theta,\Phi) - \frac{1}{3}\sqrt{\frac{10}{3}}[4_{4-3}(\Theta,\Phi) - Y_{43}(\Theta,\Phi)]\}$$

$$Y_6 = \sqrt{\frac{\pi}{26}}\{\frac{4\sqrt{2}}{9}Y_{60}(\Theta,\Phi) + \frac{1}{9}\sqrt{\frac{35}{3}}[Y_{6-3}(\Theta,\Phi) - Y_{63}(\Theta,\Phi)]$$

$$+\frac{1}{9}\sqrt{\frac{77}{6}}[Y_{6-6}(\Theta,\Phi) + Y_{66}(\Theta,\Phi)]\}$$

$$M(t) = \beta^t\{1 - e^{-t}\sum_{n=0}^{11}\frac{t^n}{n!}\}$$

Table 1. The NMR Chemical Shift for a $3d^1$ System in a Strong Crystal field Environment of Octahedral Symmetry when Threefold Axis is Chosen as the Quantization Axis. (ζ = 154cm^{-1}, β = 4/3a_0 and T = 300K)

R(nm)	<001>	<100>	<010>	<110>	<111>
0.05	−1417.465	−1466.051	−1445.746	−1455.899	−1428.524
0.10	−402.246	−463.234	−395.726	−429.480	−394.346
0.15	−61.262	−87.121	−30.603	−58.862	−43.453
0.20	−1.378	−9.935	18.533	4.299	9.577
0.25	4.137	0.724	12.292	6.508	8.617
0.30	3.007	1.226	5.618	3.422	4.493
0.35	1.833	0.782	2.480	1.631	2.246
0.40	1.104	0.461	1.159	0.810	1.180
0.45	0.679	0.276	0.587	0.431	0.661
0.50	0.429	0.171	0.321	0.246	0.392

Table 2. A Comparison of the Exact Value of $\Delta B/B$(ppm) Using Equation (6) with the Multipolar Terms for Specific R-Values

(2a) Along the <001> Axis

R(nm)	$1/R^5$	$1/R^7$	sum of all multipolar terms	From eq.(6)
0.05	96.937	−16.877	80.060	−1417.465
0.1	161.408	−56.111	105.296	−402.247
0.2	40.608	−23.663	16.945	−1.378
0.3	7.004	−3.651	3.353	3.008
0.4	1.690	−0.581	1.109	1.104
0.5	0.554	−0.124	0.430	0.430
0.6	0.223	−0.035	0.188	0.188
0.7	0.103	−0.012	0.091	0.091

(2b) Along the <100> Axis

R(nm)	$1/R^5$	$1/R^7$	sum of all multipolar terms	From eq.(6)
0.05	36.351	−4.878	31.473	−1466.052
0.1	60.528	−16.219	44.308	−463.235
0.2	15.228	−6.840	8.388	−9.935
0.3	2.626	−1.055	1.571	1.226
0.4	0.352	−0.075	0.277	0.277
0.5	0.129	−0.018	0.111	0.111
0.6	0.056	−0.006	0.050	0.050
0.7	0.038	−0.003	0.035	0.035

(2c) Along the <010> Axis

R(nm)	$1/R^5$	$1/R^7$	sum of all multipolar terms	From eq.(6)
0.05	36.351	15.327	51.778	−1445.747
0.1	60.528	51.289	111.816	−395.727
0.2	15.228	21.228	36.857	18.534
0.3	2.626	3.337	5.964	5.619
0.4	0.634	0.531	1.164	1.159
0.5	0.208	0.113	0.321	0.321
0.6	0.083	0.032	0.115	0.115
0.7	0.039	0.011	0.049	0.049

(2d) Along the <110> Axis

R(nm)	$1/R^5$	$1/R^7$	sum of all multipolar terms	From eq.(6)
0.05	36.351	5.274	41.425	−1455.899
0.10	60.527	17.535	78.062	−429.481
0.20	15.228	7.395	22.625	4.299
0.30	2.626	1.141	3.767	3.422
0.40	0.634	0.181	0.815	0.810
0.50	0.208	0.039	0.246	0.246
0.60	0.083	0.011	0.094	0.094
0.07	0.039	0.004	0.042	0.042

(2e) Along the <111> Axis

R(nm)	$1/R^5$	$1/R^7$	sum of all multipolar terms	From eq.(6)
0.05	70.021	−1.021	69.000	−1428.524
0.10	116.591	−3.394	113.197	−394.346
0.20	29.333	−1.431	27.901	9.578
0.30	5.059	−0.221	4.838	4.493
0.40	1.220	−0.035	1.185	1.181
0.50	0.400	−0.008	0.392	0.392
0.60	0.161	−0.002	0.159	0.159
0.70	0.074	−0.001	0.054	0.054

$$E(t) = \{1 - e^{-t}(\frac{8}{11}\frac{t^9}{9!} + \sum_{n=0}^{8}\frac{t^n}{n!})\}$$

$$J(t) = \beta^2 e^{-t}(\frac{2}{9}\frac{t^4}{4!} + \sum_{n=0}^{3}\frac{t^n}{n!})$$

$$G(t) = \beta^2 e^{-t}(\frac{16}{33}\frac{t^9}{9!})$$

$$P(t) = \beta^2 e^{-t}(-\frac{4}{45}\frac{t^4}{4!} + \sum_{n=0}^{3}\frac{t^n}{n!}) \quad \text{with } t = 2\beta R \tag{6a}$$

For the case of the free atom, the expression (6) may take the form given by

$$\Delta B/B = -\frac{\mu_0}{4\pi}\frac{\mu_\beta^2}{KT}\frac{8\beta^3}{315}\{\frac{3-5[1-\exp(3\zeta/2KT)]KT/\zeta}{1+2\exp(3\zeta/2KT)}\} \tag{6b}$$

Table 3. The Temperature Dependence of $\Delta B/B$(ppm) at Various of R Expressed in Terms of the Coefficients in a Strong Crystal Field Environment of Octahedral Symmetry when Threefold Axis is Chosen as the Quantization Axis. ($\zeta = 154cm^{-1}$, $\beta = 4/3a_0$)

R(nm)	axis	A(ppm)	B(ppm·K)	C(ppm·K²)
0.10		3.016	-151104.964	8864269.841
0.20		23.407	-4091.950	-1013419.422
0.30	<001>	4.760	398.385	-275368.236
0.40		1.045	253.580	-71226.016
0.50		0.312	113.164	-23486.317
0.10		-39.474	-167323.153	12085475.757
0.20		6.136	-4655.555	-52275.372
0.30	<100>	1.597	214.869	-98555.688
0.40		0.367	116.394	-26658.403
0.50		0.118	44.347	-8471.374
0.10		-71.901	-137105.688	12027322.672
0.20		-7.539	8087.561	-76797.118
0.30	<010>	-0.513	2181.078	-102339.329
0.40		0.032	429.026	-27259.999
0.50		0.040	113.999	-8943.946
0.20	<110>	-0.701	1716.030	-64539.811
0.20	<111>	8.646	2263.367	-599140.710

When R is large

$$d(\underset{\sim}{R}) = -\frac{1}{R^5}\left(\frac{224}{\beta^2}\ Y_3\right) - \frac{1}{R^7}\left(\frac{7200}{\beta^4}Y_4\right)$$

$$S(\underset{\sim}{R}) = \frac{1}{R^5}\left(\frac{224}{\beta^2}Y_3\right) - \frac{1}{R^7}\left(\frac{4800}{\beta^4}Y_4\right)$$

When a threefold axis is chosen as the axis of quantization, the calculated NMR chemical shift for a 3d¹ system in a strong crystal field environment of octahedral symmetry using equation (6) along the x, y and z axes is listed Table 1. Here we choose $\beta = 4/3a_0$, the spin-orbit coupling constant $\zeta = 154cm^{-1}$ and the temperature T = 300K. As shown in Table 1, the NMR chemical shift for specific R-values for a 3d¹ system in a strong crystal field environment of octahedral symmetry along the x, y and z axis has different values, and the NMR chemical shift, $\Delta B/B$(ppm), decreases in magnitude rapidly as R increases. $\Delta B/B$ changes sign when $R \simeq 0.15$ nm along the <010>, <110> and <111> and $R \simeq 0.2$ nm along the <0.01> and <100> axes, the values being negative for smaller R values and positive for greater R values.

When a threefold axis is chosen as the axis of quantization, a comparison of the exact values of $\Delta B/B$(ppm) calculated by equation (6) with the multipolar terms for specific R-values shows that when $R \simeq 0.20$ nm the constant term contributes dominantly to the NMR chemical shift and when $R \simeq 0.20$ nm the major contribution arises from $1/R^5$, and along the <001>, <100> and <111> axes the $1/R^5$ term gives values opposite in sign to that of the $1/R^7$, while along the <010>, and <110> axes the $1/R^5$ and $1/R^7$ terms gives values equal in sign. It is interesting to note that the exact solution given by equation (6) for a 3d¹ system in a strong crystal field environment of octahedral symmetry is in good agreement with the multipolar results when R>0.40 nm. In addition, Table 2 shows that the NMR chemical shift arising from the 3d electron orbital angular momentum and 3d electron spin dipolar-nuclear angular momentum interaction in a 3d¹ system in a strong crystal field environment of octahedral symmetry is large for significant distances between the NMR nucleus and the 3d electron bearing atom. For less than 0.40 nm it should not be neglected.

It is usual to correlate the temperature dependence of $\Delta B/B$(ppm) to the expression

$$\Delta B = a\langle S_z\rangle + b(\chi_\parallel - \chi_\perp) \tag{7}$$

The fitting of the data at a ligand position over a temperature range 200 to 400K from equation (6) could be expressed as

$$\Delta B/B = A + B/T + C/T^2 \tag{8}$$

where the 1/T term arises fromt he Fermi contact term and the $1/T^2$ term from pseudo contact term. Therefore the temperature dependence of $\Delta B/B$(ppm) for a 3d¹ system in a strong crystal field environment of octahedral symmetry, when a threefold axis is chosen as the axis of quantization, at ligand along the z, x and y axes, may be expressed, respectively, as

$$\Delta B/B = 23.407 - 4091.95/T - 1013420/T^2$$
$$\Delta B/B = 6.136 - 4655.56/T - 52275.3/T^2$$
$$\Delta B/B = -7.539 + 8087.56/T - 76797.1/T^2 \tag{9}$$

These results show that each term in equation (9) contributes significantly to the value of the NMR chemical shift and equation (9) is of the form given by equation (8). However, the ratio A/B differs markedly from the expected value of -32/105 and so we may not use equation (7) to interpret the origin of the NMR chemical shift. The major contribution to the NMR chemical shift however arises from the $1/T^2$ term but the contributions of other two terms are significant as shown in Table 3.

It is necessary to mention at this moment that this work has already been carried out, since it is found however that some of the result are not correctly expressed,[7] we rederive the general formula for a 3d¹ system in a strong crystal field environment of octahedral symmetry when a threefold axis is chosen as the axis of quantization and recalculate the NMR chemical shift. We extend further this work to investigate the temperature dependence of $\Delta B/B$ from equation (6).

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