A Further Study on the NMR Chemical Shift for a 4d^1 System in a Strong Crystal Field Environment of Octahedral Symmetry

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The various interactions considered in this paper in calculating the NMR chemical shift arising from the 4d orbital angular momentum and the 4d electron spin dipolar-nuclear spin angular momentum interaction may be expressed as

$$H=\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{4\pi e_o r}+V(\underset{\sim}{r})+\xi\,\underset{\sim}{l}\cdot\underset{\sim}{S}+\mu_B(\underset{\sim}{l}+2\underset{\sim}{S})\underset{\sim}{B}+H_{hf} \qquad (1)$$

where

$V(\underset{\sim}{r})$

$$=a_4\left\{\frac{1}{2}\sqrt{\frac{7}{3}}Y_{40}(\theta,\phi)+\frac{1}{2}\sqrt{\frac{5}{6}}[Y_{4-4}(\theta,\phi)+Y_{44}(\theta,\phi)]\right\}^{1)}$$

and

$$H_{hf}=\frac{\mu_0}{4}g_N\mu_B\mu_N\left\{\frac{2\underset{\sim}{l_N}\cdot\underset{\sim}{I}}{r_N^3}+g_s\left[\frac{3(\underset{\sim}{r_N}\cdot\underset{\sim}{S})\underset{\sim}{r_N}\cdot\underset{\sim}{I}}{r_N^5}-\frac{\underset{\sim}{S}\cdot\underset{\sim}{I}}{r_N^3}\right]\right\} \qquad (2)$$

Here $\underset{\sim}{r}$ and $\underset{\sim}{r_N}$ are, respectively, the electron radius vectors about the electron-bearing atom and nucleus with nuclear spin angular momentum $\underset{\sim}{I}$. The quantity $\underset{\sim}{B}$ is the applied magnetic field. $V(\underset{\sim}{r})$ is the crystal field potential of octahedral symmetry and a_4^2 is the required crystal field parameter for 4d electron system. The other symbols have their usual meaning. In this work, g_s, the free electron g value, is taken to be equal to exactly 2.

To determine 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^1 system in a strong crystal field environment of octahedral symmetry the principal values σ_{aa} of the NMR screening tensor are calculated by considering the magnetic field interaction parallel to the x, y and z axes and averaged assuming a Boltzmann distribution. The contribution to the NMR chemical shift, ΔB, is given by[3]

$$\Delta B=B\sigma_{aa}/3 \qquad (3)$$

where

$$\sigma_{aa}=\left(\frac{\delta^2\langle H_{hf}\rangle}{\delta\mu_a\delta B_a}\right)_{\mu=B=0}$$

with

$$\mu=g_N\mu_N I$$

The term $\langle H_{hf}\rangle$ refers to the Boltzmann average of the hyper-fine interaction represented by equation (2). The NMR chemical shift for a 4d^1 system in a strong crystal field environment of octahedral symmetry is given by

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

where

$d(\underset{\sim}{R})$

$$=\frac{12\sqrt{\pi}}{147}Y_{oo}(\Theta,\Phi)E(t)+\frac{17280}{t^5}Y_4H(t)-\frac{22809600}{7t^7}Y_6J(t)$$

$S(\underset{\sim}{R})$

$$=-\frac{20\sqrt{\pi}}{147}Y_{oo}(\Theta,\Phi)M(t)-\frac{7680}{t^5}Y_4N(t)N(t)-\frac{15206400}{7t^7}Y_6J(t)$$

where

Y_4

$$=\sqrt{\frac{\pi}{21}}\left\{\frac{1}{2}\sqrt{\frac{7}{3}}Y_{40}(\Theta,\Phi)+\frac{1}{2}\sqrt{\frac{5}{6}}[Y_{4-4}(\Theta,\Phi)+Y_{44}(\Theta,\Phi)]\right\}$$

Y_6

$$=\sqrt{\frac{\pi}{26}}\left\{\frac{1}{2}\sqrt{\frac{1}{2}}Y_{60}(\Theta,\Phi)-\frac{\sqrt{7}}{4}[Y_{6-4}(\Theta,\Phi)+Y_{64}(\Theta,\Phi)]\right\}$$

Table 1. The NMR Chemical Shift for a 4d^1 System in a Strong Crystal Field of Octahedral Symmetry. (ζ=500cm^{-1}, β=3.2679/a$_0$ and T=300K)

R(nm)	<001>	<100>	<010>	<110>	<111>
0.05	-4701.679	-4701.679	-4701.679	-1920.887	-2032.734
0.10	-551.519	-551.519	-551.519	273.451	-234.919
0.15	-46.595	-46.595	-46.595	48.658	-38.796
0.20	-7.386	-7.386	-7.386	7.639	-5.401
0.25	-1.909	-1.909	-1.909	1.703	-0.907
0.30	-0.657	-0.657	-0.657	0.506	-0.170
0.35	-0.273	-0.273	-0.273	0.184	-0.024
0.40	-0.130	-0.130	-0.130	0.078	0.005
0.45	-0.068	-0.068	-0.068	0.037	0.010
0.50	-0.038	-0.038	-0.038	0.109	0.008

$$E(t)=\beta^3 e^{-t}\left(\frac{1}{3}\frac{t^6}{6!}+\sum_{n=0}^{5}\frac{t^n}{n!}\right)$$

$$H(t)=\beta^3\left\{1-e^{-t}\left(\frac{8}{9}\frac{t^{11}}{11!}+\sum_{n=0}^{10}\frac{t^n}{n!}\right)\right\}$$

$$J(t)=\beta^3\left\{1-e^{-t}\left(\frac{13}{11}\frac{t^{13}}{13!}+\sum_{n=0}^{12}\frac{t^n}{n!}\right)\right\}$$

$$M(t)=\beta^3 e^{-t}\left(-\frac{2}{13}\frac{t^6}{6!}+\sum_{n=0}^{5}\frac{t^n}{n!}\right)$$

$$N(t)=\beta^3 e^{-t}\left(\frac{4}{3}\frac{t^{11}}{11!}\right) \text{ with } t=2\beta R$$

For the case of the free atom we may take R→o to find

$$\frac{\Delta B}{R}\rightarrow -\frac{\mu_0}{4\pi}\frac{2\beta^2}{147}\left\{\frac{3-5[1-\exp(3\zeta/2KT)]KT/\zeta}{1+2\exp(3\zeta/2KT)}\right\} \tag{5}$$

When R is large

$$d(\underset{\sim}{R})=\frac{1}{R^5}\left(\frac{540}{\beta^2}Y_4\right)-\frac{1}{R^7}\left(\frac{178200}{\beta^4}Y_6\right)$$

$$S(\underset{\sim}{R})=-\frac{1}{R^5}\left(\frac{240}{\beta^2}Y_4\right)-\frac{1}{R^7}\left(\frac{118800}{\beta^4}Y_6\right) \tag{6}$$

Table 2. A comparison of the Exact Value of $\Delta B/B$(ppm) Using Equation (4) with the Multipolar Terms for Specific R-values

(2a) Along the <100> Axis

R(nm)	$1/R^5$	$1/R^7$	sum of all multipolar terms	From eq.(4)
0.05	-1714.588	-242.831	-1957.519	-4701.679
0.1	-275.418	-183.123	-458.541	-551.519
0.2	-3.160	-4.219	-7.239	-7.386
0.3	-0.409	-0.249	-0.658	-0.658
0.4	-0.097	-0.032	-0.130	-0.130
0.5	-0.032	-0.007	-0.039	-0.039
0.6	-0.009	-0.001	-0.010	-0.010
0.7	-0.006	0	-0.006	0.006

(2b) Along the <110> Axis

R(nm)	$1/R^5$	$1/R^7$	sum of all multipolar terms	From eq.(4)
0.05	428.673	394.600	823.272	-1920.888
0.1	68.854	297.576	366.430	273.452
0.2	0.790	6.857	7.647	7.640
0.3	0.102	0.405	0.507	0.507
0.4	0.024	0.054	0.078	0.078
0.5	0.008	0.011	0.019	0.019
0.6	0.003	0.003	0.006	0.006
0.7	0.001	0.001	0.003	0.003

(2c) Along the <111> Axis

R(nm)	$1/R^5$	$1/R^7$	sum of all multipolar terms	From eq.(4)
0.05	1143.126	-431.699	711.426	-2032.734
0.1	183.612	-325.553	-141.941	-234.919
0.2	2.107	-7.501	-5.395	-5.401
0.3	0.273	-0.443	-0.170	-0.170
0,4	0.065	-0.06	0.006	0.006
0.5	0.021	-0.012	0.009	0.009
0.6	0.009	-0.003	0.005	0.005
0.7	0.004	-0.001	0.003	0.003

Table 3. The Temperature Dependence of $\Delta B/B$(ppm) at Various of R Expressed in Terms of the Coeficients ($\zeta=500\text{cm}^{-1}$, and $\beta=3.2679a_0$)

R(nm)	axis	A(ppm)	B(ppm·K)	C(ppm·K^2)
0.10	<001>	-578.1688	7293.1479	251237.4250
0.20		-18.2736	4718.6856	-437249.2688
0.30		-2.3893	754.5414	-70816.4113
0.40		-0.5644	189.3803	-17813.7882
0.50		-0.1852	63.9512	-6031.2148
0.20	<110>	43.8326	1292.8309	-136384.6603
0.20	<111>	11.6756	-7536.8862	727913.8958

The calculated NMR chemical shift using equation (4) is listed in Table 1. Here we choose $\beta=3.2679/a_0$, the spin-orbit coupling constant $\zeta=500\text{cm}^{-1}$ and the temperature T=300°K. As expected, for a $4d^1$ system in a strong crystal field einvornment of ochahedral symmetry the NMR chemical shift for specific R-values is consistent with each other. As shown in Table 1, the NMR chemical shift $\Delta B/B$, decreases in magnitude rapidly as R increases. Along the <100> axis, $\Delta B/B$ is negative for all values of R, while along the <110> and <111> axes, $\Delta B/B$ changes sign when R≃0.05 nm and R≃0.40nm, respectively, the values being negative for smaller R values and positive for greater R values. A comparison of the exact values of $\Delta B/B$(ppm) given by equation (4) with the multipolar terms for specific values R values shows that the $1/R^5$ and $1/R^7$ terms contribute almost equally to the NMR chemical shift and along the <111> axis, the $1/R^5$ term gives values opposite in sign to that of the $1/R^7$ term, while along the other axes, the signs of the $1/R^5$ and $1/R^7$ terms are equal.

It is interesting to note that the exact solution given by equation (4) for a $4d^1$ system in a strong crystal field environment of octahedral symmetry is in good agreement with the multipolar results when R⩾0.3 nm. For distances less than 0.30 nm it should not be neglected.

The temperature dependence of the NMR chemical shift may be expressed as[5]

$$\Delta B/B=A+\frac{B}{T}+\frac{C}{T^2} \tag{7}$$

where A/B = -32/105 for the $4f^1$ ion in a crystal field environment of octahedral symmetry. In equation (7) the 1/T and $1/T^2$ terms arise from the Fermi and the pseudo contact interactions.[6] It is found that the NMR chemical results over the temperature range from 200 to 400K from the exact solution of $\Delta B/B$(ppm) given by equation (4) may be fitted almost precisely to an expression of the form given by equation (7). The temperature dependence of the NMR chemical shift at the ligand may be expressed as

$$\Delta B/B=-18.2736+4718.68/T-437249/T^2 \tag{8}$$

The equation (8) indicates that the 1/T term and the $1/T^2$ term contribute significantly to the value of the NMR chemical shift. Although equation (8) is of the form given by equation (7) the ratio A/B differs markedly the expected value and hence the temperature dependence data may not be used to interpret the NMR chemical shift. We also observe from Table 3 that values of A, B and C depend markedly on the location of the NMR nucleus and the dominant contribution to $\Delta B/B$ arises from the $1/T^2$ term but the $1/T$ term is certainly significant.

At this moment it is required to mention that the NMR chemical shift has already been examined and has derived a general mformula for a $4d^1$ system in a strong crystal field environment of octahedral symmetry.[7] It is however found that this formula is not correct, therefore we reexamine the NMR chemical shift for a $4d^1$ system in a strong crystal field environment of octahedral symmetry and derive the correct expression for $\Delta B/B$. We also study further the temperature dependence of $\Delta B/B$.

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A Thermal and a Photochemical Mutarotation of α-(D)-Glucose in Dimethyl Sulfoxide

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Mutarotation of glucose in aqueous solvent has been extensively investigated,[1] but in nonaqueous solvents a few research works have been reported.[2] Recently, Pincock[3] *et al.* have reported the kinetic study of heterogeneous catalysis of glucose mutarotation by standard alumina suspended in dimethyl sulfoxide. In the alumina catalyzed mutarotation, of course, a thermal mutarotation was assumed to be negligiblle at room temperature. This led us to investigate a thermal and a photochemical mutarotation of α-(D)-glucose in dimethyl sulfoxide. Although the mechanisms of glucose mutarotation in DMSO are not thoroughly understood at present, we wish to report the mechanism including thermodynamic parameters, temperature dependence of quantum yield and the relationship between the rate constants and the quantum yields.

Table 1. Thermodynamic Constants for Mutarotation of α-(D)-Glucose in DMSO and H_2O at 30°C. (a) reference (1) data, (b) this work except ΔH

Solvent	ΔH cal. mol^{-1} deg^{-1}	ΔG cal. mol^{-1}	ΔS e.s.u.
H_2O (a)	-270	-327	0.19
DMSO (b)	-270	-315	0.15

Table 2. Activation Energies for Mutarotation of α(D)-Glucose in DMSO and H_2O at 30°C. (a) Kcal. mol^{-1} (b) cal. mol^{-1}. deg^{-1}. (c) references 7 and 8. (d) this work

Solvent	$E_a{}^a$	$\Delta G^{\neq a}$	$\Delta H^{\neq a}$	$\Delta S^{\neq b}$
H_2O (c)	17.24	24.66	17.24	-24.9
	16.09	22.08	16.09	-19.8
DMSO (d) (thermal)	21.28	23.20	20.0	-10.55
DMSO (d) (photo.)	10.28	22.44	9.62	-42.3

Irradiation[4] of α-(D)-glucose in DMSO causes the photomutarotation and the reaction mixture reaches equilibrium at the optical rotation, $[\alpha] = 51°$. During the irradiation, a thermal mutarotation was also observed especially at the elevated temperature and the equilibrium mixture showed optical rotation, $[\alpha] = 54°$.

While the thermal mutarotation was reversible, the photomutarotation was irreversible,[5] so that the two different rate equations[6] were used to evaluate the rate constants (Figure 1 and 2). Although the photo-mutarotation is irreversible, photo-mutarotation reaches equilibrium at the optical rotation, $[\alpha] = 51°$. This equilibrium state may come from that the thermal equilibrium control overrides the irreversible

Table 3. Temperature Dependence of Quantum Yields. (a) Calculated Values Using k_r (photo). (b) Mmol Disappearance vs. Milli Einstein Absorbed

Temp(°C)	k_r (min^{-1}) thermal	k_r (min^{-1}) photo	ϕ^a_{mut} (b)
30	1.06×10^{-4}	3.75×10^{-4}	0.21 (0.20)
40	2.91×10^{-4}	8.69×10^{-4}	0.48 (0.48)
50	1.05×10^{-3}	1.55×10^{-3}	0.86 (0.84)
60	2.09×10^{-3}	2.21×10^{-3}	1.28 (1.25)
70	5.75×10^{-3}	3.30×10^{-3}	1.83 (1.91)