solution were somewhat skew symmetric on an energy scale, while the lowest-energy band for $BiCl_3$ solutions was very close to being symmetric.

The band maximum of TlCl in the melt at 440°C is near the position of the lowest-energy band of Tl^+-doped KCl crystals (approximately 4.95 eV at 442°C).[3] On the other hand, the oscillator strength and half width are significantly greater while the asymmetry is significantly less for the melt than for crystalline KCl:Tl at (or extrapolated to) comparable temperatures.[3,10]

The band of $PbCl_2$ in the melt is close to the lowest-energy band of crystalline KCl:Pb (approximately 4.5 eV at 545°C) but decidedly less asymmetric than the latter.[11]

Only a few spectroscopic details are available on Bi^{3+} in chloride environments. A band has been observed in Bi^{3+}-doped KCl at 3.75 eV,[5] and a band of the $[BiCl_5]^{2-}$ complex in an aqueous medium has been found at 3.79 eV.[12] These bands are close to the lowest-energy band of the molten solutions reported here. A compressed mixture of $BiCl_3$ and KCl powders was reported to have bands at approximately 3.86 and 5.64 eV.[4] The latter band probably relates to the band we observed at 5.4 eV.

Patterson[3] has drawn conclusions about the geometry of Tl^+ centers in KCl from an analysis of the lowest-energy band into Gaussian components. We have made a similar analysis of the melt spectra and find much more of the band intensity to be concentrated into one component with a maximum near that of the composite band than is the case for KCl:Tl or KCl:Pb at comparable temperatures. If one assumes with Patterson that a different center conformation is to be assigned to each Gaussian component (at least if the conformation has cubic symmetry), then it must be concluded either that the conformation of Tl^+ and Pb^{2+} centers in the melt are different from those in KCl or that the distribution of centers among conformations is quite different. Both conclusions are plausible. More specific geometric pronouncements are not possible at present because there are conformations, such as tetrahedral $PbCl_4^{2-}$ that are plausible in the melt but for which there are no absorption data. Information on Bi^{3+} in crystalline chlorides is too meager to permit any statements.

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Nuclear Relaxation Induced by Paramagnetic Ions Having Anisotropic *g* Factors

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The theory of nuclear spin relaxation induced by paramagnetic ions has been worked out and corroborated in some detail for solutions.[1–3] The relaxation equations that appear in the literature are derived by assuming an isotropic electron spin **g** tensor. However, some ions can have large **g** tensor anisotropies when asymmetrically complexed, and the relaxation equations must be modified.[4]

For the case of an axially symmetric **g** tensor with principal values $g_{\|}$, $g_{\perp}$, $g_{\perp}$, we have found that

$$\begin{aligned} T_1^{-1}=T_2^{-1}=&\tfrac{2}{3}\gamma^2\,|\,\beta\,|^2 S(S+1)r^{-6} \\ &\times[\tfrac{1}{3}(g_{\|}^2+2g_{\perp}^2)+g_{\|}^2\cos^2x+g_{\perp}^2\sin^2x]\tau_c \\ &+\tfrac{4}{9}\gamma\,|\,\beta\,|\,S(S+1)Ar^{-3}(g_{\|}-g_{\perp}) \\ &\times(3\cos^2x-1)\tau_c\delta(\tau_c,\tau_e)+\tfrac{2}{3}S(S+1)A^2\tau_e \qquad (1)\end{aligned}$$

in the limit of short, isotropic correlation times, τ_c and τ_e. A is in radians/seconds.

$$[\tau_c^{-1},\ \hbar\tau_e^{-1}\gg|\,g_{\|}-g_{\perp}\,||\,\beta\,|\,H_0,\ g_{\|}\,|\,\beta\,|\,H_0].$$

τ_c and τ_e are defined by

$$\tau_c^{-1}=\tau_S^{-1}+\tau_h^{-1}+\tau_r^{-1};\qquad \tau_e^{-1}=\tau_S^{-1}+\tau_h^{-1}. \qquad (2)$$

τ_S, τ_h, τ_r denote the electron spin relaxation, chemical exchange, and complex rotation times, respectively. $\hat{r}$, the vector distance between the electron and nuclear spin (point) dipoles, makes an angle, x, with respect to the symmetry axis. H_0 denotes the external magnetic field. The first term in Eq. (1) arises from a time modulation of the dipole–dipole interaction, and can vary with orientation by as much as a factor of 4 (1.7) when $g_{\|}^2>g_{\perp}^2(g_{\perp}^2>g_{\|}^2)$. The second term denotes an interference between the exchange, $\hbar A\hat{I}\cdot\hat{S}$, and dipole–dipole terms, and only appears when $\tau_c \sim \tau_e$, whereupon $\delta(\tau_c, \tau_e) \sim 1$. Analogous interference terms have appeared in discussions of electron spin relaxation.[5–8] In most cases either the dipole–dipole or exchange terms will dominate, and the interference term will be negligible. Equation (1) holds when the complex is either tumbling rapidly,

$$\hbar\tau_r^{-1} \gg |g_{\parallel}-g_{\perp}||\beta|H_0$$

or slowly

$$h\tau_r^{-1} \ll |g_{\parallel}-g_{\perp}||\beta|H_0$$

compared with the electron **g** anisotropy Zeeman energy. (The tumbling is assumed always rapid compared with the nuclear relaxation times.)

The short correlation case is frequently encountered, and will generally be of most interest because $T_1 = T_2$, the condition for maximal detection sensitivity, an important consideration when lines are broad. In the cases of intermediate and long correlation times, where τ_c and τ_e are comparable with or larger than the electron-spin Zeeman energy, the relaxation expressions are functions of the electron-spin energy, and consequently are functions of τ_r.[9] A detailed treatment of this case is of doubtful value. Firstly, lines can be very broad, and $T_1 \neq T_2$, which makes high resolution NMR detection and study difficult. Secondly, the relaxation expressions are not expected to be sensitive functions of τ_r. T_1 will be more sensitive than T_2, and T_1, for example, is not expected to change more than a factor of 2 or 3 when going from rapid to slow tumbling. (Analogously small differences between these two extremes are found when considering nuclear contact shifts in solution.)[10] For the case of rapid tumbling compared with the electron spin anisotropy energy, we obtain that

$$\begin{aligned}
T_1^{-1} = {} & \tfrac{2}{5}\gamma^2|\beta|^2 S(S+1) r^{-6} \\
& \times \Big\{ \big[\tfrac{1}{9}(16g_{11}^2+9g_{\perp}^2-4g_{\parallel}g_{\perp})+(g_{\parallel}-g_{\perp})^2\sin^4 x \\
& \quad +\tfrac{7}{3}g_{\parallel}(g_{\perp}-g_{\parallel})\sin^2 x\big]\frac{\tau_c}{1+(\omega_z\tau_c)^2} \\
& \quad +\big[\tfrac{1}{9}(4g_{\parallel}^2+g_{\perp}^2+4g_{\parallel}g_{\perp})-(g_{\parallel}-g_{\perp})^2\sin^4 x \\
& \quad -\tfrac{1}{3}(2g_{\parallel}-5g_{\perp})(g_{\perp}-g_{\parallel})\sin^2 x\big]\frac{\tau_c}{1+(\omega_z\tau_c)^2} \Big\} \\
& +\tfrac{4}{9}S(S+1)\gamma|\beta|A(g_{\parallel}-g_{\perp}) \\
& \times(3\cos^2 x-1)r^{-3}\delta(\tau_c,\tau_e)\frac{\tau_c}{1+(\omega_z\tau_c)^2} \\
& +\tfrac{2}{3}A^2 S(S+1)\frac{\tau_e}{1+(\omega_z\tau_e)^2}\,; \qquad (3)
\end{aligned}$$

$$\begin{aligned}
T_2^{-1} = {} & \tfrac{1}{15}\gamma^2|\beta|^2 S(S+1) r^{-6} \\
& \times \Big\{ \big[\tfrac{1}{3}(12g_{\parallel}^2+8g_{\perp}^2-8g_{\parallel}g_{\perp})+6(g_{\parallel}-g_{\perp})^2\sin^4 x \\
& \quad +(9g_{\parallel}-5g_{\perp})(g_{\perp}-g_{\parallel})\sin^2 x\big]\tau_c \\
& \quad +\big[\tfrac{1}{3}(24g_{\parallel}^2+11g_{\perp}^2+4g_{\parallel}g_{\perp})-3(g_{\parallel}-g_{\perp})^2\sin^4 x \\
& \quad +(3g_{\parallel}+10g_{\perp})(g_{\perp}-g_{\parallel})\sin^2 x\big]\frac{\tau_c}{1+(\omega_z\tau_c)^2} \\
& \quad +\big[\tfrac{1}{3}(4g_{\parallel}^2+g_{\perp}^2+4g_{\parallel}g_{\perp})-3(g_{\parallel}-g_{\perp})^2\sin^4 x \\
& \quad -(2g_{\parallel}-5g_{\perp})(g_{\perp}-g_{\parallel})\sin^2 x\big]\frac{\tau_c}{1+(\omega_I\tau_c)^2} \Big\} \\
& +\tfrac{2}{9}S(S+1)\gamma|\beta|A(g_{\parallel}-g_{\perp}) \\
& \times(3\cos^2 x-1)r^{-3}\delta(\tau_c,\tau_e)\left[\tau_c+\frac{\tau_c}{1+(\omega_z\tau_c)^2}\right] \\
& +\tfrac{1}{3}[A^2 S(S+1)]\left[\tau_e+\frac{\tau_e}{1+(\omega_z\tau_e)^2}\right]. \\
& [\hbar\omega_z=\tfrac{1}{3}(g_{\parallel}+2g_{\perp})|\beta|H_0; \qquad \omega_I=\gamma H_0]. \qquad (4)
\end{aligned}$$

When $g_{\parallel}=g_{\perp}$, Eqs. (3) and (4) reduce to Solomon's equation.[1–3] When τ_c^{-1}, $\tau_e^{-1} \gg \omega_z$, ω_I, we obtain Eq. (1).

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Simple Analytical Formula for the Phase Shifts of Electron Scattering by Given Atomic Fields*

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The purpose of this note is to give a simple practical analytical formula for the phase shifts of electron scattering by a given atomic field of gas electron