Electronic Spin Relaxation in Dimeric Iron(III) Complexes

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Summary The temperature-dependence of the Mössbauer spectra of dimeric iron(III) complexes can be explained by spin–spin intermolecular relaxation.

IN a comparison[1] between monomeric and dimeric iron(III) compounds, the view was expressed that the Mössbauer spectra of the dimeric compounds (e.g. [Fe salen]$_2$O or [Fe salen Cl]$_2$) indicate fast intramolecular relaxation. We have been studying the Mössbauer spectra of several such dimeric compounds[2,3] which have an intramolecular antiferromagnetic exchange interaction between the two $S = 5/2$ iron ions. The spectrum for all of these is a normal symmetric quadrupole doublet at 4·2° K, becoming asymmetric at higher temperatures in a manner typical of a spin relaxation time which is comparable with the nuclear precession times. We show here how these results may be explained by intermolecular, but not intramolecular, relaxation.

Because of the strong intramolecular exchange each molecule will be in a state characterised by $\langle S^{T}, S_{z}^{T}=M^{T}|$ where S^{T} is the resultant of the spins S^{1} and S^{2} of the two ions. Each such state is a static admixture of $\langle S_{z}^{1},S_{z}^{2}|$ states, and as fluctuations of the hyperfine field at a nucleus can only take place by fluctuations in S_{z} of the ion containing that nucleus, this must involve fluctuations between different $\langle S^{T},S_{z}^{T}|$ states. By conservation of angular momentum, this can only take place *via* spin flips involving the $\langle S^{T},M^{T}|$ states of different molecules and not by intramolecular relaxation.

The $S^{T} = 1$ manifold has an energy greater than that of the $S^{T} = 0$ ground state by $2J$, so that at temperatures T less than *ca.* $|J|/1{\cdot}8\,k$ °K (with J in cm.$^{-1}$) only the $S^{T} = 0$ state is significantly populated and there can be no magnetic hyperfine interaction so that the spectrum must be a symmetric quadrupole doublet. This is why [Fe salen Cl]$_2$ ($J = -\ 7{\cdot}5$ cm.$^{-1}$)[4] gives a symmetric spectrum[2] for T less than *ca.* 6° K, whereas the [Fe salen]$_2$O ($J = -\ 95$ cm.$^{-1}$)[5] spectrum [1] is symmetric for $T = 80°$ K; relaxation processes are irrelevant.

Molecules with $S^{T} \neq 0$ and $M^{T} \neq 0$ have non-zero hyperfine fields at each nucleus and the asymmetry in the spectra at temperatures high enough for these states to be populated must be due to relaxation effects. The ($2S^{T} + 1$)-degeneracy of each S^{T} manifold will be split by crystal fields. Because this splitting will be different for each manifold, the only spin flips satisfying energy conservation will be those between molecules with the same S^{T} but different M^{T}, so that the relaxation times for those ions in each S^{T} manifold may be considered independently and will depend on the population of the manifold in a manner similar to that for ferric chlorohaemin.[6] We believe that the dominant reason for the increased asymmetry as the temperature is raised is that the manifolds with larger S^T, which are populated at higher temperatures, will have larger magnetic hyperfine fields, and hence larger precessional times so that the effects of relaxation will become greater. The half-width ratio of 0·97 observed[7,8] for [Fe salen]$_2$O at 298° K is small, as expected, since *ca.* 57% of $M^T = 0$ states are occupied at room temperature, and is consistent with the asymmetry observed for [Fe salen Cl]$_2$ at the same value for $|J|/kT$, *i.e.*, 24° K.

We are now carrying out quantitative calculations of the relaxation broadening using a model similar to that of Blume[6] but extended to apply to the intermolecular relaxation of dimeric compounds.[2] A fuller account of the theory together with a more detailed study of the temperature-dependence of the spectra is to be published.[8]

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