Broadening of N.M.R. Signals of Nuclei Coupled to Fast Relaxing Spin-$\frac{1}{2}$ Nuclei: An Example of T_1 Spin-decoupling

By FRANK BRADY and RAY W. MATTHEWS*
(*Department of Chemistry, The Polytechnic of North London, Holloway, London* N7 8DB)
and MARK J. FORSTER and DUNCAN G. GILLIES*
(*The Bourne Laboratory, Department of Chemistry, Royal Holloway College, University of London, Egham Hill, Egham, Surrey* TW20 0EX)

Summary Broadening effects in the spectra of spin-$\frac{1}{2}$ nuclei, A, coupled to fast relaxing spin-$\frac{1}{2}$ nuclei, X, have been related to the T_1 value of X and hence provide a new method for measuring this parameter at high field on account of enhanced relaxation by the chemical shift anisotropy mechanism.

EVIDENCE is accumulating to show that linewidths of spin-$\frac{1}{2}$ nuclei, A, (*e.g.* A = ^{1}H, ^{13}C, ^{31}P) coupled to fast relaxing spin-$\frac{1}{2}$ nuclei, X, (*e.g.* ^{195}Pt,[1] ^{199}Hg,[2] ^{205}Tl[3]) may be dominated by relaxation at X, particularly at high field. Specification of the relationship between the broadening effects in the A spectrum and relaxation at X provides a new and facile means of determining the spin–lattice relaxation of X.

These lineshape phenomena are examples of the T_1 spin-decoupling effect noted previously[4] for the effect of dissolved oxygen on proton spin–spin multiplets. The spin–lattice relaxation of the X nuclei produces an effect analogous to that of chemical exchange on the multiplet and hence a useful insight may be gained by treating the effect of changes in the X spin-state on the A spectrum of an AX spin system in terms of two-site exchange. Assigning the two A components respectively to the α and β spin states of X, standard exchange equations may be applied noting that the lifetimes of the equally populated spin states, τ_α and τ_β, are related to the transition probability, $W_{\alpha\beta}$, and spin–lattice relaxation of X, T_{1X},[5a] by $\tau_\alpha^{-1} = \tau_\beta^{-1} = W_{\alpha\beta} = (2T_{1X})^{-1}$. The most usual situation corresponds to the slow exchange limit when $\tau_\alpha >> (2\pi J)^{-1}$. In this case the broadening of each A component is just $(\pi\tau_\alpha)^{-1}$ or $(2\pi T_{1X})^{-1}$. Thus the observed line width is given by equation (1), were $(\pi T'_{2A})^{-1}$ is the sum

$$\Delta\nu_{\frac{1}{2}}(A) = (\pi T'_{2A})^{-1} + (2\pi T_{1X})^{-1} \quad (1)$$

of the natural linewidth of A and magnetic field inhomogeneity broadening. The general treatment of Navon and Polak[4] for first-order A_mX_n spectra yields the same result in

the slow exchange limit for the A_mX case, and also provides a means of calculating A-multiplet lineshapes for faster exchange rates, although other formulations of the exchange problem could of course be used.

It should be noted that although scalar relaxation of the second kind[6a] is undoubtedly responsible for the broadening, the usual expressions[6b] for relaxation at A are inappropriate in the case of non-overlapping A-components where the condition[6a] $(2\pi J)^{-1} >> T_{1X}$, implying collapse to a single resonance, clearly does not apply. The situation is analogous, however, to broadened, non-overlapping components of a spin-$\frac{1}{2}$ nucleus coupled to a quadrupolar nucleus (*e.g.* ^1H–^{14}N)[5b] although in this case differential broadening arises from unequal lifetimes of the quadrupolar nuclear spin-states.

The value of $(\pi T'_{2A})^{-1}$ can be obtained from non-coupled signals in the A spectrum and, for some X nuclei (*e.g.* ^{195}Pt, ^{199}Hg), the central uncoupled signal arising from A connected to the 'n.m.r. inactive' isotope of X provides a particularly convenient measure. The ability of equation (1) to yield T_{1X} with accuracy increases with increasing $(2\pi T_{1X})^{-1}$, *i.e.* with increasing relaxation rate of X. The situation will be especially favourable for X nuclei which relax significantly *via* the chemical shift anisotropy (C.S.A.) mechanism and where the A spectra are determined at high magnetic field, B_0, because $(T_{1X})^{-1}$ (C.S.A.) $\propto B_0^2$ [$(\pi T'_{2A})^{-1}$ is essentially field independent]. Equation (2) gives the C.S.A. contribution for the extreme narrowing condition and axial symmetry,[7] and indicates that the applicability of this method for determining T_{1X} also depends on the value of γ_X and the chemical shift anisotropy in the particular molecular species.

$$(T_{1X})^{-1}(\text{C.S.A.}) = (6/7)(T_{2X})^{-1}(\text{C.S.A.}) = (2/15)\gamma_X^2 B_0^2 (\sigma_{\parallel} - \sigma_{\perp})^2 \tau_c \quad (2)$$

Illustrating the use of equation (1) we have obtained $\Delta\nu_{\frac{1}{2}}(H) = 55$ Hz for $Tl(CH_3)_2NO_3$ in D_2O (degassed) at 400 MHz and 300 K. Without allowances for $(\pi T'_{2H})^{-1}$ and the effect of overlapping components coupled to ^{203}Tl and ^{205}Tl (together $<$*ca.* 4 Hz), equation (1) predicts $T_{1(Tl)} =$ *ca.* 2·9 ms in good agreement with a preliminary $T_{1(Tl)}$ for this solution of *ca.* 2·9 ms at 295 K and the same magnetic field.

Where the C.S.A. contribution to relaxation of X is 100%, combination of equations (1) and (2) and neglecting $(\pi T'_{2A})^{-1}$ yields $\Delta\nu_{\frac{1}{2}}(A) = (3/7)\Delta\nu_{\frac{1}{2}}(X)$, where $\Delta\nu_{\frac{1}{2}}(X) = (\pi T_{2X})^{-1}$. For the thallium solution noted above, $\Delta\nu_{\frac{1}{2}}(Tl) =$ *ca.* 140 Hz at 231·5 MHz[3] which is consistent with the predicted value of $(7/3)\Delta\nu_{\frac{1}{2}}(H) = 128$ Hz. The additional broadening in the ^{205}Tl spectrum can be ascribed to the effects of temperature inhomogeneity at high field [temperature coefficient of chemical shift for Tl $(CH_3)_2NO_3$ in $H_2O = 0.44$ p.p.m. K^{-1}].[8] In cases where the relaxation of X is not totally dominated by the C.S.A. mechanism, the relative contributions of other mechanisms (*e.g.* spin rotation) may be ascertained by observation of broadening effects on A as a function of temperature and magnetic field.

We thank the S.R.C. for studentships to F.B. and M.F. and the U.L.I.R.S. WH-400 N.M.R. Service at Queen Mary College for spectra.

(*Received, 10th June* 1981; *Com.* 682.)

[1] J. Y. Lallemand, J. Soulie, and J. C. Chottard, *J. Chem. Soc., Chem. Commun.*, 1980, **436**.
[2] N. S. Ham, E. A. Jeffery, T. Mole, and S. N. Stuart, *Chem. Commun.*, 1967, **254**; A. J. Brown, O. W. Howarth, and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1976, 1589; L. P. Blaauw, A. D. H. Clague, D. G. Gillies, G. R. Hays, and R. Huis, *J. Magn. Reson.*, 1981, **42**, 420.
[3] F. Brady, M. J. Forster, D. G. Gillies, and R. W. Matthews, *Inorg. Nucl. Chem. Lett.*, 1981, **17**, 155.
[4] G. Navon and M. Polak, *Chem. Phys. Lett.*, 1974, **25**, 239.
[5] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959; (a) p. 24; (b) p. 228.
[6] A. Abragam, 'The Principles of Nuclear Magnetism,' Oxford University Press, London, 1961; (a) p. 309; (b) p. 311.
[7] T. C. Farrar and E. D. Becker, 'Pulse and Fourier Transform N.M.R.,' Academic Press, London, 1971, ch. 4.
[8] P. J. Burke, I. D. Cresshull, D. G. Gillies, and R. W. Matthews, *J. Chem. Soc., Dalton Trans.*, 1981, 132.