Effects of Relaxation Reagents on the Relative Widths of Lines in Spin Multiplets

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Summary Differential line width effects in n.m.r. spin multiplets, which display splittings caused by quadrupolar nuclei, have been produced by a relaxation reagent for a number of cases (^{13}CD, ^{1}H^{10}B, ^{1}H^{11}B), and their origin has been rationalised on a generalised random field model.

ALTHOUGH relaxation reagents for T_1 have become popular for sensitivity enhancement at natural abundance and for quenching of the nuclear Overhauser effect, for example with ^{13}C,[1] ^{15}N,[2] and ^{29}Si,[3] little quantitative work has been done on the changes produced in the relaxation times. Levy has recently measured changes in T_1 produced by relaxation reagents[4a] and has explained differential effects at the ^{13}C nuclei of the borneol molecule in terms of dipolar interactions in a co-ordination complex,[4b] as for lanthanide shift reagents.[5] Bacon and Reeves have studied both T_1 and T_2 for thallium resonances in the presence of dissolved oxygen.[6]

We have observed *differential* T_2 effects between the central and outermost components of spin multiplets, if they arise from quadrupolar nuclei, in the presence of relaxation reagents. For example the ^{13}C resonance of ^{13}CDCl$_3$ is normally an approximately 1 : 1 : 1 triplet, because

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of coupling with D ($I = 1$), with some slight extra broadening of the outer lines. In a solution which is 0·08M in $Cr(acac)_3$ (acac = acetylacetonate), however, the relative peak heights are very different: 1·0:0·8:1·0. The line widths are 3·8 and 4·5 Hz relative to an operational line width, under the instrumental conditions used, of 2 Hz when the reagent is absent. Changes in the quadrupolar relaxation mechanism for ^{13}C arising from coupling to D cannot be held responsible, since the broadening effects in a triplet should be more pronounced for the outer lines.

An explanation for our results may be found in the generalised random isotropic field model, defined by a Hamiltonian of the type $\mathscr{H}'(t) = \mathbf{I}\cdot\mathbf{H}(t)$ [where $\mathbf{H}(t)$ is the randomly varying field] summed over the nuclei. The general model is neutral on the point of mechanism but two simple cases may be considered: a scalar model, and a long range dipole–dipole model.[7]

In the scalar model, in which a complex between the paramagnetic reagent and the compound is visualised, $\mathbf{H}(t)$ is replaced by $A(t)\mathbf{S}$ [or alternatively by $A\mathbf{S}(t)$] where A is a hyperfine constant, and the nuclei are relaxed by a modulated hyperfine interaction. Considering the deuterium spin states (1, 0, −1) and the electron states (α_e and β_e), one can expect such processes as

$$\alpha_e,1\rangle \longleftrightarrow \beta_e,0\rangle \text{ and } \alpha_e,0\rangle \longleftrightarrow \beta_e, -1\rangle.$$

The lifetimes of the $0\rangle$ states are thus shortened twice as much as the lifetimes of the $1\rangle$ and $-1\rangle$ states, which leads to broadening of the central components of the ^{13}C multiplet. In the C–D example the factors are 2:1 if the effects are much more important for D than for ^{13}C (case 1), 1·5:1 if the effects are equal (case 2), and 1:1 if the ^{13}C effects dominate (case 3). For CD_2 and CD_3 units larger ratios should be possible: 2:2:1 and 4:3·3:2·3:1 respectively for case 1; 1·66:1·66:1 and 3·7:2·8:2:1 respectively for case 2. The absence of an effect could be due to a lack of complex formation or to the occurrence of case 3.

The alternative 'classical' model regards the electron spins as producing, intermolecularly, random isotropic fluctuating fields at the nuclei by dipole–dipole effects. The extent of the differential line width effect is determined by the relation between the fluctuations at the two centres, which are characterised by their relative sizes (asymmetry parameter) and correlation[8] (conditions which are the counterparts of the requirements for cases 1 and 2 above).

So far we have observed the effect only for the simplest cases involving one quadrupolar nucleus. On the other hand a variety of 'spin $\frac{1}{2}$' nuclei has been surveyed. Specifically the cases are $^{13}CDCl_3$, $^{13}CDBr_3$, $^{10}BH_4^-$, $^{11}BH_4^-$, $^{11}BF_4^-$ and $^{14}NH_4^+$, with $Cr(acac)_3$ as reagent. The effects are on the limit of detection for the last two cases. Our failure to observe an effect for other cases, notably $(CD_3)_2CO$, CD_3OD, and CD_3I can be rationalised on the basis of the scalar model by comparison with the ENDOR interpretations of Richards and his co-workers.[9] They found large positive enhancements for the ^{13}C signals of $^{13}CDCl_3$ and $^{13}CHBr_3$ in the presence of a paramagnetic radical excited with microwave radiation, which were explained on the basis of dominant scalar contributions to T_1, but, on the other hand, large negative enhancements for acetone and methanol which are typical of dipolar effects.

Comparisons of the effect of the relaxation reagents on T_1 and T_2 should be useful in determining the nature of these interactions more fully, and such studies are of considerable importance also for the lanthanide shift reagents for which T_2 and shift effects have been employed[10] (and advocated[11]) in concert. The use also of selectively deuteriated materials with observation of the ^{13}C triplets so produced may prove an interesting ancillary procedure.

We thank Miss E. Hughes and Sig. Arnone for spectral measurements, the Consiglio Nazionale delle Ricerche for a N.A.T.O. Visiting Professorship (to E.W.R.), and the S.R.C.

(*Received, 26th November* 1973; *Com.* 1622.)

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