Spin Decoupling using Pulsed Radiofrequency Magnetic Fields

By R. S. MILNER and D. W. TURNER

(*Organic Chemistry Laboratories, Imperial College, London, S.W.7*)

INTERNUCLEAR spin decoupling by continuous irradiation of one nuclear resonance while observing others has been widely applied to determination of molecular structure and spectrum analysis.[1] More recently discontinuous irradiation techniques have been employed in spectrum analysis.[2,3] It does not seem to be generally appreciated that under certain conditions the naive attribution of decoupling to a reduction of the life-time of spin states gives useful results and can predict behaviour towards pulsed decoupling at low duty ratios.

A pulse of duration t at the exact nuclear resonant radiofrequency rotates a nucleus about the radiofrequency field vector through an angle $\theta = \gamma H_2 t$ where the symbols have their usual significance. Such a rotation can be represented by an exponential operator[4] $\Omega = \exp\{iI_y\theta\}$ which mixes the spin states of the nucleus, so that

$$\Omega|m'\rangle = \sum_{m=-I}^{m=+I} c_{mm'}|m\rangle$$

After such a pulse the probabilities of finding the spin state changed or unchanged are, respectively,

$$P_{m'\to m} = \sum_{mm} c^*_{mm'}c_{mm'} \text{ and } P_{m'\to m'} = c^*_{m'm'}c_{m'm'}$$

If a sequence of pulses is applied with repetition frequency ν it is easily shown that the mean life-time of a spin state is given by $\tau_{m'} = 1/\nu P_{m\to m}$. In particular, for $I = \frac{1}{2}$

$$\tau_{+\frac{1}{2}} = \tau_{-\frac{1}{2}} = 1/\nu\sin^2(\theta/2)$$

and for $I = 1$

$$\tau_{+1} = \tau_{-1} = 4/\nu(\sin^2\theta - 2\cos\theta + 2)$$
$$\tau_0 = 1/\nu\sin^2\theta$$

From this it is seen that, for both states in the $I = \frac{1}{2}$ case and for the $m = \pm 1$ states in the $I = 1$ case, when $\theta = (2n+1)\pi$ the lifetimes are minima. The lifetime of the $I = 1$, $m = 0$ state has minima for $\theta = (2n+1)\pi/2$ and maxima for $\theta = n\pi$. It follows that a sequence of $(2n+1)\pi$ pulses will produce optimum decoupling, since the outer members of a multiplet collapse to a central position and, with coupling to a $I = 1$ nucleus, the centre line is unaffected. More noteworthy, however, is the prediction that for $\theta = 2n\pi$, $\tau \to \infty$ in all cases, and that in this region τ will be a sensitive function of θ. Application of a low duty ratio sequence of $2n\pi$ pulses should thus produce a virtually unaltered spectrum provided that $\nu > J$.

Figure 1a-l shows the methyl proton resonance spectrum of the tetraethylammonium ion recorded

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[1] See for example J. D. Baldeschweiler and E. W. Randall, *Chem. Rev.*, **1963**, **63**, 81.

[2] R. Hoffman, B. Gestblom, and S. Forsen, *J. Chem. Phys.*, 1964, **40**, 3734.

[3] S. L. Gordon and J. D. Baldeschweiler, *J. Chem. Phys.*, 1964, **41**, 571.

[4] E. Feenberg and G. E. Pake, "Notes on the Quantum Theory of Angular Momentum," Addison-Wesley, Mass., 1953, p. 12.

during irradiation of the ^{14}N ($I = 1$) resonant frequency[5] with pulses of varying length. Figure 1m shows the normal undecoupled spectrum and Figure 1n that with continuous decoupling for comparison. Complete decoupling for $t = 5{\cdot}98$msec and $t = 17{\cdot}48$msec. ($\theta = 1{\cdot}1\pi$ and $3{\cdot}2\pi$) is seen and the reappearance of the triple structure ($J_{\text{N-H}} = 1{\cdot}83$ c./sec. and $J_{\text{H-H}} = 7{\cdot}2$ c./sec.) for $t = 11{\cdot}5$msec. and $t = 23{\cdot}0$msec. ($\theta = 2{\cdot}2\pi$ and $4{\cdot}25\pi$) is clearly visible. The angles quoted here were calculated by using values of H_2, the rotating r.f. field, measured by an inductive pick-up coil and may be subject to errors of $\pm 10\%$. Internuclear modulation present at other pulse durations is apparently associated with nitrogen relaxation processes occurring during the interpulse period.

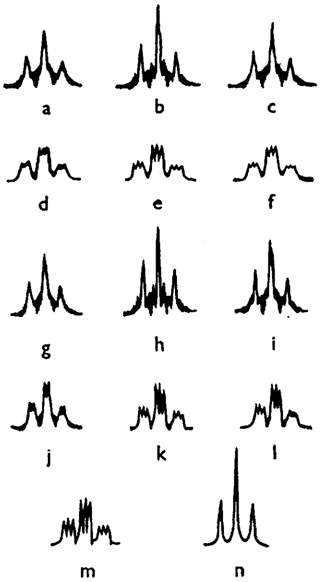

Figure 1. *Methyl proton resonances in tetraethylammonium chloride in* D_2O *in the presence of pulsed double irradiation at the* ^{14}N *resonance frequency. Pulse repetition interval* τ ($= 1/\nu$) $= 0{\cdot}2003$ *sec. Pulse duration in msec*: (*a*) 4·52, (b) 5·98, (c) 7·46, (d) 10·00, (e) 11·51, (f) 13·00, (g) 16·00, (h) 17·48, (i) 19·00, (j) 21·48, (k) 22·99, (l) 24·45, (m) 0 (*normal spectrum*), (n) ∞ (*continuous decoupling*).

This form of decoupling experiment offers some practical advantages. Decoupling effects equal to those obtained with the same peak power level applied continuously can be had for a much reduced mean power dissipation, which is of value when nuclei of low gyromagnetic ratio are studied in conductive solutions. In addition, receiver muting during the "on" period offers some advantages in terms of signal to noise ratio. It can also be shown that the rapid variation of τ with θ near $\theta = 2n\pi$ enables radiofrequency field magnitudes to be measured (in terms of the pulse duration) to within $\pm 1\%$. Finally our observations warn that in using time discontinuous double irradiation the choice of duty ratio is not an arbitrary one.

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[5] J. A. Glasel, D. W. Turner and L. M. Jackman, *Proc. Chem. Soc.*, 1961, 426.

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