Steady-state and Transient Overhauser Effect with Three Spins

By D. F. S. NATUSCH and R. E. RICHARDS

(*Physical Chemistry Laboratory, South Parks Road, Oxford*)

IN a solution containing a free radical in a diamagnetic solvent the spin–lattice relaxations of the unpaired electrons in the free radicals and of the nuclei of the solvent molecules are coupled by dipolar, and sometimes scalar, coupling.[1] When the electron resonance is saturated marked changes in the nuclear polarisation can occur; for dipolar coupling the difference between the populations of the nuclear energy levels is reversed and greatly increased resulting in a strong negative n.m.r. signal. Scalar coupling, however, tends to give an enhanced positive signal.[2]

If the solution contains two distinguishable types of nuclei their coupling to the electrons may be different and there is the possibility that a "three-spin" effect can modify the results of a double resonance experiment.[3] In this case the electrons may pump the nuclei A into an inverted population while the relaxation of A may polarise the B nuclei. Because the magnetic moments of the two nuclei are usually of the same sign, dipolar coupling between A and B nuclei results in a positive polarisation of B greater than the equilibrium value. This effect can either add to or oppose the change in polarisation caused by nuclei B coupling directly to the electron.

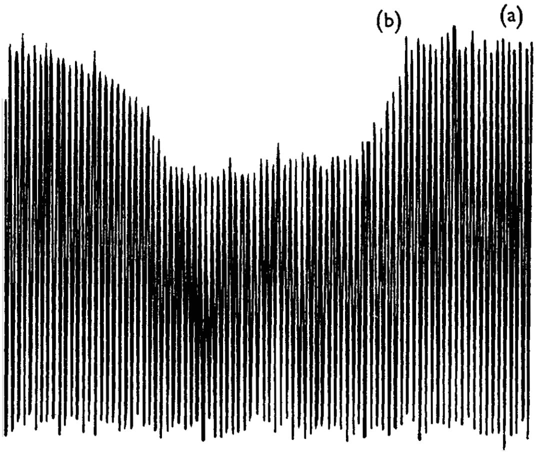

FIGURE 1. ^{19}F *Resonance of a 50/50 solution of* C_6H_6 *and* C_6F_6.

The presence of a "three-spin" effect may be demonstrated by a triple resonance experiment. The electron resonance is saturated and the resonance of nucleus B is observed both when that of nucleus A is saturated and when it is not. The vertical lines in Figure 1 represent repeated traversals (about 1½ second intervals) of the fluorine resonance in a 50/50 mixture of benzene and hexafluorobenzene containing a very low concentration ($\sim 5 \times 10^{-4}$M) of tri-t-butylphenoxyl radical. Microwave power at 9·125 Kmc./sec. has been applied to the electron resonance and the fluorine resonances at (a) are positively enhanced about 20 times. At (b) the proton resonance was strongly excited and the fluorine polarisation is diminished. When the proton irradiation is removed the fluorine resonance returns to its enhanced value.

In this case the fluorine resonance is positively enhanced by coupling to the electron because scalar coupling predominates.[4] In addition, relaxation of the strongly inverted proton polarisation causes a further positive polarisation of the fluorines by internuclear dipolar coupling. This additional effect is reduced when the proton resonance is saturated.

Under suitable conditions the transient effect of "three-spin" coupling can give useful information about spin coupling in solution. Figure 2 shows the fluorine resonances of a solution of tri-t-butylphenoxyl ($\sim 5 \times 10^{-4}$M) in *p*-difluorobenzene in which the relaxation time of the protons is relatively long compared with that of the fluorines. The initial signal (a) is inverted (b) when the electron resonance is saturated but this signal decays (c) to a smaller value as the relaxation of the strongly inverted proton population pumps the fluorine resonance in a positive direction. When the electron irradiation is removed the fluorine signal becomes positive again (d) but is enhanced by coupling to the protons. As the proton polarisation returns to its equilibrium value the fluorine population ceases to be pumped and decays also to its equilibrium value (e).

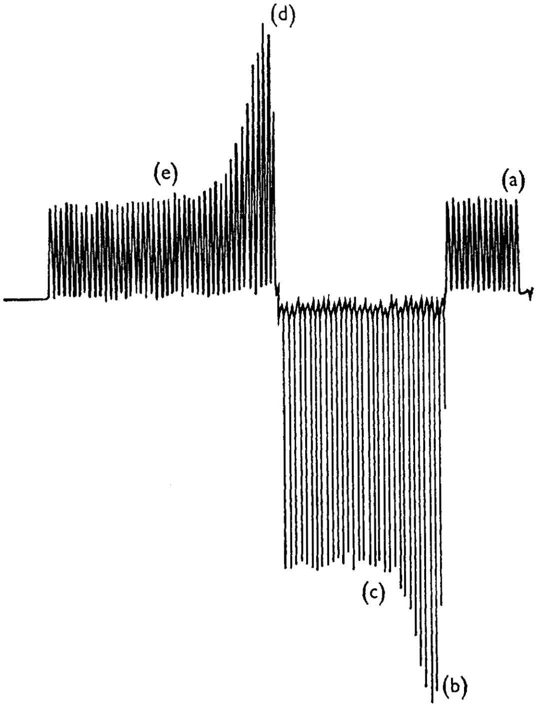

FIGURE 2. ^{19}F *Resonance of* p-*difluorobenzene.*

The quantitative theory of the steady state and transient responses of such a three-spin system has been applied to this and other systems and will be described in a forthcoming publication.

(*Received, February 7th,* 1966; *Com.* 076.)

[1] A. Abragam, "Principles of Nuclear Magnetism", Oxford Univ. Press, 1961, p. 289.

[2] R. E. Richards and J. W. White, *Proc. Roy. Soc.*, 1965, *A*, **283**, 459.

[3] R. E. Richards and J. W. White, *Proc. Chem. Soc.*, 1962, 119.

[4] R. A. Dwek, J. G. Kenworthy, D. F. S. Natusch, R. E. Richards, and D. J. Shields, *Proc. Roy. Soc.*, 1966, in the Press.