Effect of Correlation Time on the Sign of the Overhauser Effect in Liquids

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MEASUREMENTS of the nuclear electron Overhauser effect on solutions of free radicals in fluorinated solvents often reveal nuclear polarization of opposite sign to that expected for dipolar coupling between the electrons and the fluorine nuclei; the nuclear resonance is enhanced rather than reversed.[1,2] This effect arises from scalar coupling, as well as dipolar coupling between the electrons and the nuclei. The variation of nuclear polarization with $\omega_e \tau_c$ (where ω_e is the angular electron resonance frequency and τ_c is the correlation time) for various strengths of scalar coupling have been calculated by Hubbard[3] for two models. The first model assumes that the dipolar coupling is modulated by random diffusion, and that the scalar coupling occurs while the molecules are briefly stuck together. The scalar coupling constant is therefore A_{ij} or 0. The sticking time must be assumed to be short so as not to invalidate the postulate of random diffusion for the particles. In the second model the random diffusion is again assumed, but the scalar coupling is assumed to vary with distance according to a steep exponential function.

Hubbard has given plots of the enhancement factor, ρ, as a function of $(\omega_e \tau_c)^{\frac{1}{2}}$ and of ξ, the ratio of scalar to dipolar coupling.

Experiments on various fluorinated solvents at 3,000 gauss and 12,500 gauss can be fitted to the diffusion model but not to the sticking model used by Hubbard. A combination of diffusion for dipolar coupling and Abragam's sticking model[4] for scalar coupling can also be fitted,[5] but the sticking time required proves to be comparable with the diffusional correlation time, so that the use of random diffusion seems hardly justified.

The fluorine resonances of solutions of tri-t-butyl phenoxide in *p*-difluorobenzene, of 1,1,1-trichloro-2,2,2-trifluoroethane, and of benzotrifluoride are negatively polarised at values of ω_e corresponding to 9 KMc./sec. and positively polarised at 35 KMc./sec. These results can be fitted to Hubbard's calculations, which for particular values of ξ predict a change of sign of ρ as $\omega_e \tau_c$ increases. This result could be checked by changing τ_c at fixed ω_e, if we assume that ξ remains constant.

For translational diffusion, an increase of viscosity increases τ_c, and although the exact relationship depends on the system, the value of τ_c often varies linearly with the viscosity. Alternatively the temperature can be changed; an increase of temperature shortens τ_c with an activation energy of 2—4 Kcal./mole.[6,7]

A solution of tri-t-butylphenoxy-radical in *p*-difluorobenzene shows a negative nuclear polarisation at 3,300 gauss ($\omega_{e/} 2\pi = 9{\cdot}2$ KMc./sec.)

When $\omega_e\tau_c$ is increased by working at higher magnetic fields, 12,500 gauss, a positive polarisation is obtained. Furthermore, if at 3,300 gauss, τ_c is increased by lowering the temperature, while ω_e remains constant, a positive polarisation is also obtained as expected, which becomes negative again as the temperature rises.

Addition of liquid paraffin at room temperature, by increasing τ_c, can also cause the nuclear polarisation to change sign from negative to positive. An increase of temperature can then shorten τ_c enough to change the nuclear polarisation back, once again, to a negative value.

These results are all in accordance with Hubbard's theory. For solutions of the same radical in hexafluorobenzene however, previous results have indicated that the scalar coupling, and hence ξ, has a value corresponding to a curve for ρ which at these frequencies is almost independent of $\omega_e\tau_c$.[2] Addition of four times its volume of carbon disulphide, which lowers the viscosity, changed the enhancement at 3,300 gauss from strongly positive to a weakly negative value. Furthermore, at very low values of ω_e, the enhancement is also negative.[4,8] Our interpretation of the results for this compound must therefore either be incorrect or be based on the wrong model.

Similar changes in the sign of fluorine nuclear polarisations have been described by Imbaud and Berthet[9] which occur when the temperature is changed, or on dilution with other materials. In these cases, the authors have suggested that a three-spin effect may be responsible, but it seems more probable that the change of correlation time is the important factor. Triple irradiation experiments on the systems described above gave no indication of any three spin effect.[10]

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