Simplification of the ^{1}H Nuclear Magnetic Resonance Spectra of partially Oriented Molecules by Partial Deuteriation and Deuterium Decoupling

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Summary A method is described by which hydrogen–deuterium dipolar coupling may be removed from the n.m.r. spectra of partially oriented molecules.

THE n.m.r. spectrum of a molecule which has been partially aligned by dissolving in an anisotropic fluid, may give valuable information on molecular geometry, chemical shift anisotropies, and the sign and anisotropy of spin–spin coupling constants.[1] However, spectra very soon become too complex for analysis when the number of magnetic nuclei exceeds about eight in number. Large numbers of interacting nuclei very soon render a spectrum unmeasurable because of the multiplicity of lines. The same situation can arise in the case of the n.m.r. spectra of isotropic samples where, because of the short-range nature of spin–spin coupling a molecule with many magnetic nuclei gives unresolved absorption bands, but a spectrum is always observable. It would clearly be an advantage to be able to simplify spectra by removing some of the interactions, and in the case of isotropic systems this can often be done by double irradiation. For the case of proton–proton interactions the conventional double-resonance experiment does not lead to spin decoupling for anisotropic samples because the dipole–dipole interactions are almost always larger than the chemical shifts between nuclei, and the spectra are not first-order. This difficulty may be removed by first replacing some hydrogen atoms with deuterium. Deuterium–proton coupling is now a first-order interaction and can be virtually removed by strong irradiation at the resonance frequency of the deuterium, complete decoupling being possible only for spin $\frac{1}{2}$ nuclei. However, the double-resonance experiment is made more difficult in that the deuterium resonances even of a single deuterium nucleus are not grouped around one frequency.[4] The electric quadrupole of the deuterium nucleus interacts with the electric field gradient to produce a splitting in the spectrum which is typically 50 times greater than H–D dipolar interactions. Thus deuterium spectra occur as two groups of transitions separated by several kHz, and in order to produce the decoupling effect it is necessary to irradiate at both these positions simultaneously. This has been achieved by phase modulation of the second r.f. field, so that the frequency spectrum of the decoupling irradiation has strong components at $\pm\nu_{\mathrm{m}}$, the modulation frequency. It has been shown previously that frequency modulated radiofrequencies are more effective in decoupling widely separated resonance than high-power single signals,[2] and it has also been shown that a number of transitions can be simultaneously irradiated by noise modulation of the phase of the irradiating frequency.[3] In deuterium spectra the transitions not only fall into two widely separated groups, but also each group itself can consist of a large number of transitions extending over a range of perhaps 1000 Hz. We have therefore arranged that noise modulation of the frequency can be added to the coherent phase modulation.

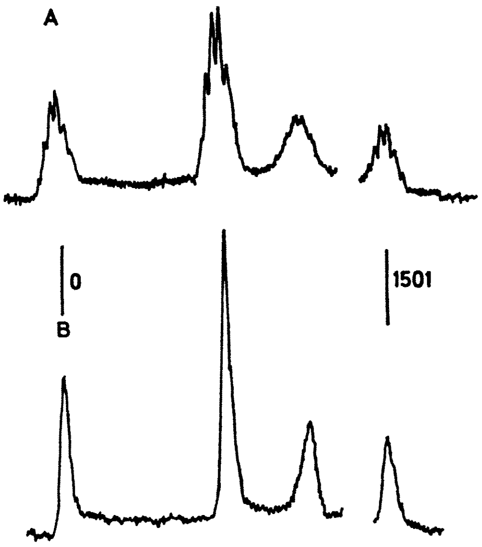

FIGURE. *Spectrum of* CH_3CD_2OH *dissolved in a nematic liquid crystal,* (A) *before, and* (B) *after irradiating at* 15·350 080 *MHz, coherently modulated at* 759 *Hz, and noise modulated at* 434 *Hz. The calibration markers are given in Hz.*

To illustrate the success of this technique we show in the Figure (A) the spectrum of CH_3CD_2OH dissolved in the nematic phase of *N*-(*p*-ethoxybenzylidene)-*p*-n-butylaniline (EBBA). The spectrum is almost entirely first-order and consists of a 1:2:1 triplet for the CH_3 protons with each component split almost equally by the two deuterium nuclei and the OH proton into six lines each. The OH resonance is similarly split by both CH_3 and CD_2 nuclei. The Figure (B) shows the result of irradiating at a frequency of 15·350 080 MHz, coherently modulated with ν_{m} 759 Hz, and with a noise bandwidth of 434 Hz. It is seen that H–D splitting is removed leaving only H–H interactions. The strong double irradiation produces considerable heating of the sample, and cooling must be produced by a flow of cold gas. Under these conditions the lines broaden because of temperature inhomogeneities and hence the decoupled spectrum is not as well resolved as the single-resonance spectrum.

The success of this technique opens up the possibility of obtaining the n.m.r. spectra of partially aligned molecules containing large numbers of protons, provided that the molecule can be partially deuteriated.

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[3] R. R. Ernst, *J. Chem. Phys.*, 1966, **45**, 3845.

[4] Ref. 1, p. 15.