Volume 14, number 5 CHEMICAL PHYSICS LETTERS 1 July 1972

NMR BANDSHAPE STUDIES OF NUCLEAR SPIN RELAXATION

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Received 16 March 1972

It is shown that bandshape studies of saturation of NMR continuous wave spectra can yield detailed information regarding nuclear magnetic relaxation, especially for complex spin systems. The AB case of 2-chloroacrylonitrile is discussed as an example.

High-resolution continuous-wave (cw) NMR spectral analysis is normally concerned [1] with extracting chemical shift and coupling constant information from transition frequencies and intensities. Bandshapes are used mainly [2] for obtaining rate constant data in cases of magnetic site exchange. Relaxation information has only normally been obtained from bandshapes in special cases (see, for example, ref. [3]), e.g., (i) T_2 values from linewidths, or (ii) T_1 values for a quadrupolar nucleus (from linewidths or resonances of spin-$\frac{1}{2}$ nuclei coupled to the quadrupolar nucleus). In other cases relaxation data has usually been obtained from pulsed NMR work [4], or from non-equilibrium cw methods [5] such as saturation recovery. The study of relaxation by the progressive saturation cw method has been used only to a very limited extent, normally only for simple first-order spectra. This fact appears to be mainly due to the discouraging experimental situation in the early days of NMR (see, for example, ref. [6], p. 85). The method has, however, considerable advantages, arising from the fact that measurements are done at equilibrium in the continuous presence of rf radiation (in contrast to all other methods of studying relaxation). This renders the interpretation of the results easier than for non-equilibrium methods (ref. [6], p. 527); in particular it makes simulation of the observed spectra feasible [7,8]. Such simulation can be carried out for a variety of relaxation models, and comparison of experimental and theoretical spectra will then yield information about the relaxation mechanisms occurring. Iterative fitting of the theoretical shape to the observed shape by computer becomes possible, and the parameters governing the relaxation may be accurately obtained.

Modern instrumentation has improved experimental aspects in several ways. The high instrument stability obtained by the field/frequency locking procedure allows bandshapes to be accurately obtained with considerable scale expansion, even at high values of the radiofrequency magnetic field, B_1, and even at the slow sweep rates necessary for equilibrium conditions. The advent of digital recorders and on-line computers means that bandshape information can be obtained conveniently for analysis by computer either on-line or off-line to the spectrometer. In addition the increased resolution of modern spectrometers implies that more bandshapes are seen to be relaxation-dominated rather than inhomogeneity-dominated.

It has been shown that information about magnetic site exchange is best obtained [9] by bandshape analysis for cases where the spectra are relatively complex and thus more sensitive to spectral parameters. We believe the same situation obtains for bandshape studies of relaxation, and consequently we have examined the spectra of an AB spin system under saturation conditions. We are interested in determining relaxation mechanisms and the parameters governing relaxation. The determination of overall T_1 and T_2 values by pulsed methods is commonplace but these parameters are of only limited use in obtaining detailed information about relaxation in complex spin systems. It is now feasible to obtain data about relaxation of specific lines in a complex spectrum by Fourier transform methods [4], though the non-equilibrium nature of these experiments complicates interpretation. It is also possible to obtain effective T_1 and T_2 values for each line in a spectrum [6,8], provided there is no overlap of lines, by continuous-wave saturation experiments using the simple line approximation [6]. However the complete set of specific T_1 and T_2 values comprise more parameters than is necessary to describe the relaxation. It seems to us therefore that complete bandshape analysis on the basis of given relaxation models provides the best approach to the problem.

We therefore suggest the following general procedure. Bandshapes are measured and recorded digitally, for a range of B_1 values. (The measurement of B_1 by the Torrey oscillation method [10] is straightforward.) Spectral shapes are then simulated using density matrix theory and Redfield relaxation formalism, for different relaxation mechanisms (or for a mixture) as a function of the parameters determining them. (These parameters are directly related to the spectral densities, which in turn are Fourier transforms of the relaxation correlation functions [7].) Iterative fitting can then be employed to optimise the values of the parameters. The range of B_1 values allows for consistency checks.

We have chosen to study 2-chloroacrylonitrile (0.05 ml in 0.2 ml D_2O plus 0.65 ml acetone-d_6 plus 0.1 ml acetone), which has an AB proton spin system. The sample was doped with a paramagnetic ion (10.8 mg $NiCl_2.6H_2O$) in order (i) to provide a known relaxation mechanism, and (ii) to broaden the lines sufficiently to render the effect of field and frequency inhomogeneities negligible. We then attempted to fit the spectra using, firstly a random-field relaxation model, and secondly, an intramolecular dipole–dipole model.The intention was to distinguish between the two mechanisms and to obtain the parameters. One procedure used was to fit the spectra to each model in turn (optimising the parameters) for a relatively low value of B_1 (but one which still causes some saturation). The parameters were then used to predict bandshapes at a substantially higher value of B_1. Fig. 1 shows that the spectra are reasonably consistent with the random-field model, but not with the intramolecular dipole–dipole one. This result was, of course, expected, since double resonance experiments have shown ([11] but see also [12]) the random-field mechanism to be dominant even for an undoped sample; the doping further ensures its dominance.

The random-field mechanism depends on three parameters [7]. These may be quoted as (i) the root-mean-square random field at nucleus A, F_A, (ii) the asymmetry parameter determining the difference between F_A and F_B, and (iii) the correlation factor, q, between the random fields at A and B. Our best values

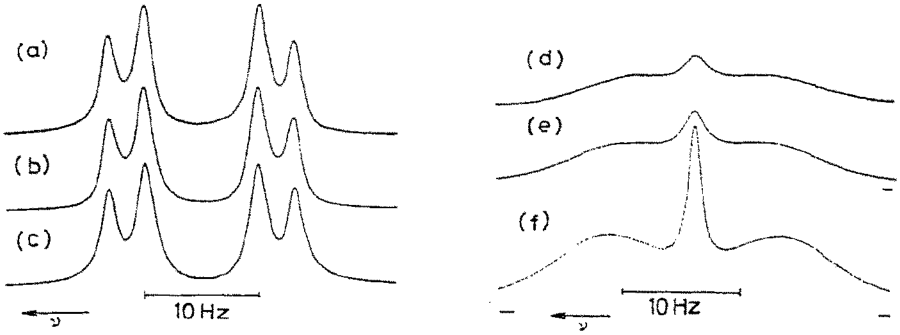

Fig. 1: 100 MHz PMR spectra of 2-chloroacrylonitrile. The three spectra at the left are for B_1 = 11.0 nT (little saturation). The three spectra at the right for B_1 = 110 nT (much saturation, involving the appearance of the double quantum line). (a) and (d) are observed spectra. (b) and (e) are spectra computed under the assumption of random-field relaxation, with parameters such as to fit the B_1 = 11.0 nT spectrum. (c) and (f) are spectra computed under the assumption of intramolecular dipolar relaxation, with parameters such as to fit the B_1 = 11.0 nT spectrum. No inhomogeneity corrections have been applied. The small horizontal markers in (e) and (f) indicate the true baselines.

of F_A and q (without homogeneity corrections) are:

$$F_A = 1.05\ s^{-1/2}\ , \quad q = 0.44\ .$$

We find the asymmetry parameter to be zero within experimental error, a not unexpected result. The root-mean-square deviation between experimental and theoretical spectra is of the order of the experimental noise level, ca. 2.0 mm, for cases where the maximum intensity is ca. 12 cm. Allowance was made in the computation for phase errors. The iteration involved horizontal position and vertical scaling factors as well as the relaxation parameters. The spectra were obtained using a Varian HA100 instrument in the field/frequency lock mode; they were digitised and output to paper tape via a Varian 620/i computer, and analysed off-line with an ICL 1905E computer. We have experimented with deconvolution corrections [7] for inhomogeneity effects, but the changes in the parameters are relatively small. These experiments will be reported in detail in a full paper later.

A notable feature of the spectra is the sensitivity of the double quantum transition to the nature of the relaxation mechanism. This arises mainly because the intramolecular dipolar mechanism allows relaxation between the $\alpha\alpha$ and $\beta\beta$ energy levels, whereas the random-field mechanism does not [6]. Double quantum transitions have been used previously in spectral analysis (see for example, ref. [13]), but not, so far as we are aware, to distinguish between relaxation mechanisms, as here. A further notable feature is that the lines in the spectrum overlap considerably under saturation, and line-interaction terms become important [8]. The simple line approximation [6] is not satisfactory.

We believe our studies show that bandshape analysis of progressively-saturated cw NMR spectra can distinguish between relaxation mechanisms and can yield accurate values of the fundamental relaxation parameters. These parameters may well take their place beside chemical shifts and coupling constants as important molecular quantities giving information about structure, motion and environment. They are more fundamental than T_1 and T_2 values. We suggest that more complex spin systems may readily be studied by an extension of the techniques developed. The main limitation at the moment is computation time (ca. 2500 sec central processor unit time for a typical iteration sequence on the case studied).

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