FOURIER TRANSFORM STUDIES OF NUCLEAR SPIN RELAXATION

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ABSTRACT

The transient response to a radiofrequency impulse is known to be the Fourier transform of the slow-passage nmr spectrum. In high resolution nmr spectroscopy the Fourier transform method represents a considerable acceleration of the rate of acquiring data from samples with many component lines, and when coupled with time-averaging techniques, it provides a significant enhancement in spectrometer sensitivity. The improved time resolution of this technique can be exploited to monitor dynamic nmr phenomena such as chemical exchange or spin relaxation effects. Spin–lattice relaxation times of the individual lines of a high resolution spectrum have been studied by the inversion-recovery method and by the Fourier transform analogue of progressive saturation. Spin–spin relaxation measurements utilize the spin-echo pulse sequence of Carr and Purcell or the forced transitory precession technique of Solomon. In each case the experiment is done under complete computer control and the results are presented in the form of a 'three-dimensional' diagram of intensities as a function of frequency and elapsed time.

1. INTRODUCTION

When a nuclear spin system is subjected to a short pulse of radiofrequency energy near the nuclear resonance condition, a radiofrequency free precession signal which persists for a finite time after the excitation pulse may be detected in the receiver coil. The decay rate of this free precession signal is determined partly by relaxation effects and partly (often predominantly) by mutual interference between signal components due to the spatial inhomogeneity of the applied static field H_0, and in a typical high resolution nmr spectrometer this time constant T_2^* is of the order of 1 second.

The information contained in the slow passage spectrum (the frequency domain) may also be derived from the free induction signal (the time domain), one form representing the Fourier transform of the other[1]. This property of gathering signal information from all parts of the spectrum simultaneously gives pulse excitation a decided advantage over the conventional sweep mode in terms of the signal-to-noise ratio that may be attained in a given elapsed time[2]. This has been exploited to enhance the sensitivity of high resolution nmr spectrometers by about an order of magnitude, and has had a

particular impact in the important field of carbon-13 spectroscopy of compounds with natural isotopic abundance (1·1 %).

More recently the idea of using the free induction signal as a 'snapshot' of the high resolution spectrum has enabled time-dependent nmr phenomena to be studied with greatly improved 'resolution' in the time domain[3]. Previously, the investigation of such transient effects by conventional sweep methods had to be limited to very narrow spectral regions, in the limit the monitoring of a single line, in order to minimize the variations that occurred during the passage from one line to the next. Pulse excitation followed by Fourier transformation of the free induction signal eliminates this problem—the small changes in nmr parameters that occur during a single free induction decay result in only trivial changes in the transformed spectrum, the important point being that all spectral components are affected in the same way. The technique is thus well-suited to the observation of time-dependent nmr phenomena, including the study of chemical exchange by magnetization transfer, spectra of unstable chemical species, chemically-induced nuclear polarization, transient Overhauser effects, and nuclear spin–spin and spin–lattice relaxation. These last two applications will be examined in some detail.

2. SPIN–LATTICE RELAXATION

When M_z, the component of nuclear spin magnetization along the direction of the applied field, is perturbed from its thermal equilibrium value M_0, it recovers towards M_0 along an exponential with time constant T_1, the spin–lattice relaxation time. For the liquid samples used in high resolution nmr, the mechanisms responsible for this exchange of energy with the environment include the magnetic dipole–dipole interaction with other nuclear spins or with the electron spins of paramagnetic impurities, the coupling of the nuclear spins with the fields generated by the rotational motion of the molecular framework, the effect of chemical shift anisotropy modulated by molecular tumbling, and quadrupolar interaction with fluctuating electric field gradients for nuclei with spin greater than 1/2. Where the dipolar mechanism is known to be dominant it can be used to deduce information about internuclear distances or to infer something about molecular structure; all these mechanisms provide information about molecular motion.

2.1 Inversion-recovery

The clasic method of studying spin–lattice relaxation is the 'inversion-recovery' technique[4]. The initial perturbation is a 180° radiofrequency pulse which aligns the nuclear magnetization along the $-Z$ direction of the rotating reference frame. After a delay t seconds during which the magnetization begins to recover towards the $+Z$ direction the length of the vector is sampled by a 90° pulse which turns the magnetization into the XY plane where it induces a free precession signal S_t. Fourier transformation of this signal results in a spectrum where each line has partially recovered from its initial inverted condition to an extent determined by its characteristic spin–lattice relaxation rate. After a suitable waiting period, T seconds, to permit all

nuclear spin populations to return to thermal equilibrium, the 180°–90° pulse sequence is repeated with a different value of the interval t, and thus a series of spectra are generated as a function of t, showing the time development of all the spectral lines.

The waiting period T is usually taken to be at least three times the longest relaxation time to be measured, and since it is the factor which determines the time required to complete the series of measurements, it can result in prohibitively long experiments when extensive time averaging is required for sensitivity reasons[5]. An estimate of T is required before setting up the experiment, and if this estimate is too short the long relaxation times will be underestimated, while if it is too long the experiment will require an excessive amount of instrument time.

The evaluation of T_1 requires a determination of S_∞, the thermal equilibrium magnetization, corresponding to the signal strength observed as $t \to \infty$, in other words the signal excited by an isolated 90° pulse. The recovery curve is described by

$$S_\infty - S_t = 2S_\infty \exp(-t/T_1) \tag{1}$$

In applications that necessitate time averaging of several identical free induction decays, it is advantageous to determine S_∞ as soon as possible after S_t in order to minimize the effects of slow drifts of spectrometer gain or resolution. The two measurements are therefore alternated in the pulse sequence:

$$[\ldots T \ldots 90°(S_\infty) \ldots T \ldots 180° \ldots t \ldots 90°(S_t) \ldots]_n$$

The two free induction signals are substracted ($S_\infty - S_t$) and after Fourier transformation this gives spectra where the signals start with large positive values and decay exponentially to zero[6]. This elimination of inverted signals tends to simplify the display in cases where there are several lines relaxing at different rates.

Carbon-13 spectroscopy provides some interesting examples of the application of spin–lattice relaxation measurements. In carbon-13 spectra that have not been decoupled from protons, it is not possible to describe the recovery of the individual lines by means of a single exponential, since the relaxation involves both protons and carbon-13 nuclei[7]. However the usually accepted mode of operation involves complete decoupling through incoherent irradiation of the protons[8], and under these conditions the recovery of each individual carbon-13 line follows a pure exponential, giving the characteristic spin–lattice relaxation time.

The aromatic carbon-13 nuclei of acenaphthene serve to illustrate the use of the inversion-recovery technique. The carbon-13 spectrum of acenaphthene has been assigned by Jones *et al.*[9] according to the results of selective proton decoupling, relying on the proton assignments made by Dewar and Fahey[10]. An ambiguity in the assignment of C11 and C12 was resolved through nuclear Overhauser measurements[11] which indicated a negligible effect for one carbon site (assigned therefore to C11) and an enhancement factor of 1.3 for the other (C12). The same factors that are responsible for the low nuclear Overhauser effect would be expected to reflect a small dipolar contribution to the spin–lattice relaxation rate.

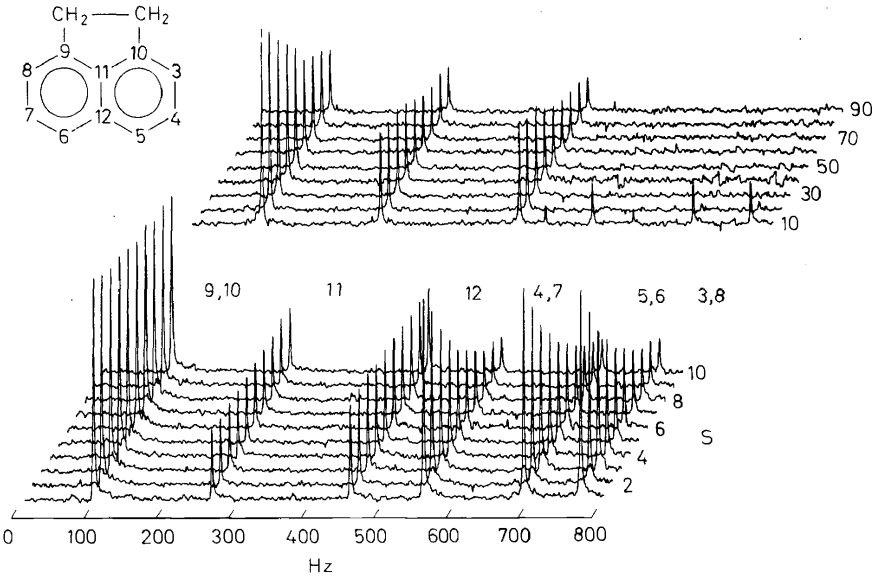

Figure 1. Spin–lattice relaxation results for the aromatic carbon-13 nuclei of acenaphthene measured by the inversion-recovery technique, modified to display the difference magnetization ($S_\infty - S_t$) directly. The spectra have been stacked as a function of the time interval between 180° and 90° pulses. Since the nuclei in the quaternary sites relax much more slowly than those with directly attached protons, it was necessary to record a second set of spectra with the time scale expanded by a factor ten. The total instrument time was about 58 hours, determined mainly by the waiting period $T = 400$ s employed for the upper set of spectra.

Figure 1 illustrates the results of the spin–lattice relaxation measurements, showing the spectrum of the ring carbon nuclei as a function of the time t between 180° and 90° pulses. Each trace represents the Fourier transform of 40 free induction decays with the waiting period T set at 400 seconds. The most striking feature of these results is the much more rapid relaxation of the CH carbon nuclei, presumably due to the dipolar coupling to the directly attached proton. The quaternary carbons relax over an order of magnitude more slowly. If it can be assumed that the dipolar interaction with protons is still a major relaxation mechanism, the inverse sixth power dependence of the relaxation effect on internuclear distance would seem to confirm the assignment of C11 and C12, made on the basis of nuclear Overhauser measurements[11], since C11 is separated by three chemical bonds from the nearest protons. The C11 nucleus is also protected from intermolecular interactions, and it is to be noted that although this is one of the longest carbon-13 relaxation times reported, the sample had not been degassed to remove paramagnetic oxygen. The experimental relaxation times are listed in *Table 1*.

2.2 Progressive saturation

The acenaphthene measurements bring out the principal drawback of the inversion-recovery method when applied to weak nuclei with long relaxation

Table 1. Experimental results for the spin–lattice relaxation times (T_1) of the aromatic carbon-13 nuclei of acenaphthene (numbered as in *Figure 1*).

Lines	9,10	11	12	4,7	5,6	3,8
Inversion-recovery T_1, s	66 ± 4	112 ± 10	73 ± 5	5·3 ± 0·2	5·5 ± 0·2	5·4 ± 0·2
Progressive saturation						
(a) from peak heights T_1, s	64 ± 6	118 ± 12	72 ± 7	5·1 ± 0·2	5·5 ± 0·2	5·1 ± 0·2
(b) by integration T_1, s	62 ± 3	103 ± 22	76 ± 8	5·1 ± 0·5	5·4 ± 0·7	5·3 ± 0·5

The experimental errors of the inversion-recovery results were estimated from the semilogarithmic plots by drawing lines with extreme slopes through the error bars. The progressive saturation error estimates were made from the peak noise amplitude for the peak-height measurements, but for the integrated intensities represent standard deviations of many results.

times—a very long time may be required to complete the experiment. The experimental problem is compounded by the need for an estimate of the longest relaxation time before the experiment can be set up, in order to establish a suitable waiting period for return to thermal equilibrium. Often a trial experiment must be run simply to determine the approximate values of the relaxation times.

There is an alternative method of measuring spin–lattice relaxation times that is better suited to spectra that require repeated averaging of the free induction signal for reasons of sensitivity; moreover the experiment can be planned in such a way that relatively quick initial measurements will indicate a suitable choice of timing parameters to match the relaxation rates of the sample when these are not known at the outset. This technique is the analogue of the progressive saturation method[6] well known in continuous-wave magnetic resonance[12]. The nuclear spin system is excited by a repeated sequence of 90° pulses, and allowed to reach a steady-state condition where the effect of the pulses is just balanced by spin–lattice relaxation. There are three basic conditions which should be satisfied.

(a) Sufficient time must be allowed to elapse after the first pulses of the sequence for the steady-state condition to be properly established. Under normal conditions this requirement is satisfied after three or four pulses.

(b) There must be negligible transverse components of magnetization remaining at the time the next pulse in the sequence is applied. This is not ensured by field inhomogeneity alone since this tends to be refocussed by the effect of the pulses, as in the spin echoes described by Hahn. Several techniques may be used to inhibit these spin echoes; for carbon-13, noise decoupling is very effective in preventing refocussing.

(c) The longitudinal component of magnetization immediately after the pulse should be negligible; this is the condition for 'saturation'. This implies that the pulse length has been correctly set for 90°, and that the radiofrequency level during the pulse is sufficiently high that off-resonance effects can be neglected†.

† Pulse flip angles different from 90° may be used, but this complicates the interpretation of the results. See reference 6.

When these three conditions are satisfied, the signal strength S_t observed with a pulse interval t seconds, is related to the asymptotic signal S_∞ that is observed when the pulse interval is long compared with the relevant relaxation time, by the equation

$$S_\infty - S_t = S_\infty \exp(-t/T_1) \tag{2}$$

Thus by following the individual signal intensities in the transformed spectra as a function of the pulse interval t, the characteristic spin–lattice relaxation times can be obtained.

2.3 The 'Rapid Method' for spin–lattice relaxation

Often the determination of T_1 by the methods described in Sections 2.1 and 2.2 demands a prohibitively long time, when in fact all that is needed is an indication of the trend of relaxation times within a given molecule, or simply the information that one nucleus relaxes significantly faster than another. The progressive saturation technique is readily adapted to the rapid determination of approximate spin–lattice relaxation times of inherently weak signals. For the purposes of sensitivity enhancement many identical free induction signals can be acquired relatively quickly in the steady-state pulse regime. The most time-consuming measurement, that of S_∞, may be dispensed with altogether, and in the limit the experiment may be reduced to the determination of just two values of S_t. Let the two measurements be represented by S_a and S_b, and suppose that time a is always shorter than time b. Then from equation 2,

$$R = \frac{S_a}{S_b} = \frac{1 - \exp(-a/T_1)}{1 - \exp(-b/T_1)}. \tag{3}$$

The ratio of signal intensities is thus uniquely related to the spin–lattice relaxation time T_1, and this relationship is readily displayed graphically (*Figure 2*) as a family of curves for various choices of the times a and b. The selection of these times is important in determining the accuracy of the derived T_1 values, since the greater the slope of the curve, the larger the proportional error in the derived relaxation time for a given experimental error in the measurements of S_a and S_b. This figure may be used as a set of universal curves by scaling the times a and b and the T_1 axis in the same proportion.

When a molecule is to be examined where there is no prior estimate available for the spin–lattice relaxation times, an arbitrary choice of the times a and b must be made for the initial experiment. Often a would be chosen as the normal acquisition time for the transient free induction signal, a time of the order of one second for spectra of resolution of the order of 1 Hz, while b might be selected to be ten times longer by introducing a suitable delay after acquisition and before the next pulse. The ratio of S_a/S_b that is then observed may not be suitable for estimating T_1, but it will indicate how a and b should be readjusted for a repeat experiment aimed at an accurate determination of T_1. If the initial measurement of S_a/S_b falls below about 0.2, the pulse intervals are too short for an accurate determination of T_1, partly because the signal S_a is so weak that its measured intensity is very susceptible to noise, and

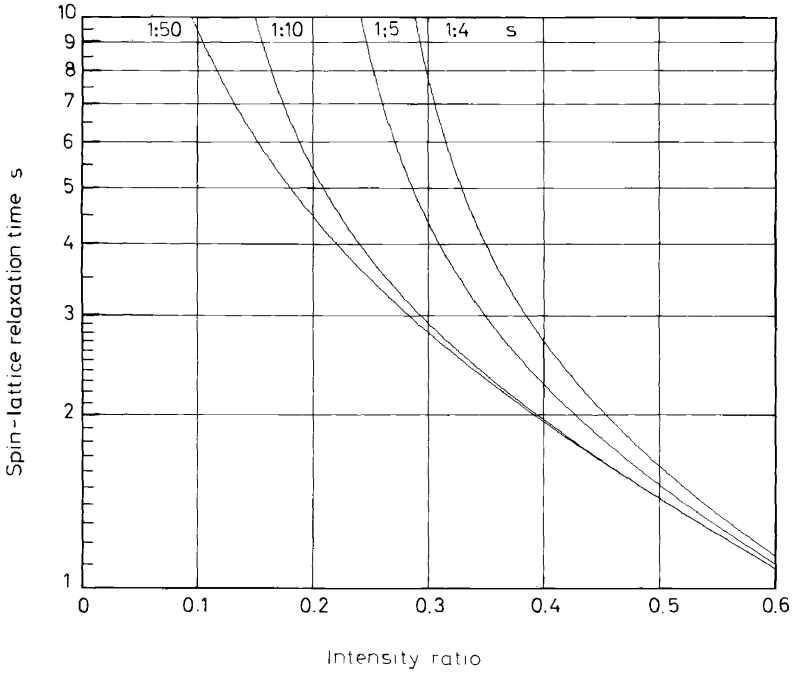

Figure 2. Calculated curves for predicting spin–lattice relaxation times from the intensity ratio S_a/S_b of a given line observed in two progressive saturation experiments performed with pulse intervals a and b seconds. The four branches represent $a = 1$ s, $b = 4$, 5, 10 and 50 s. The diagram may be used for other ranges of relaxation times by scaling the pulse intervals and the relaxation time in the same proportion.

partly because the slope of the curve increases in this region, introducing relatively large uncertainties in the derived T_1 value. When the pulse intervals a and b are increased so as to bring the intensity ratio within the approximate range 0.2 to 0.6, the reliability improves considerably. However a further increase beyond the point where the shorter pulse interval a becomes comparable with T_1 involves a significant increase in the total time expended in obtaining the spectra—time that would be better employed averaging more transients at shorter settings of a and b. The family of curves tends to merge into a single curve beyond this point since the signal S_b then approximates S_∞. Finally, if the pulse intervals are chosen to be so long in comparison with T_1 that the intensity ratio S_a/S_b exceeds about 0.9, the curve turns down again and becomes asymptotic to the T_1 axis, and the derived T_1 values are extremely sensitive to the exact value of S_a/S_b. For these reasons *Figure 2* has not been carried beyond $S_a/S_b = 0.6$. For spectra where there is a wide range of relaxation rates, more than one pair of measurements may have to be made, but often a judicious choice of *three* times a, b and c, will permit a very wide range of relaxation times to be studied.

The errors involved in the determination are a function both of the intensity errors due to the presence of noise on the signal (peak heights or integrated intensities may be used), and of the suitability of the selected

values of the times a and b. Another source of error is introduced if the 90° pulse condition is not properly adjusted or if off-resonance effects cannot be entirely neglected because of the finite strength of H_1. This general problem has been analyzed elsewhere[6]; in the present form of the progressive saturation experiment the result is that for an imperfect 90° pulse, equation 3 must be modified,

$$\frac{S_a}{S_b} = \frac{1 - \exp(-a/T_1)}{1 - \exp(-b/T_1)} \cdot \frac{1 - k\exp(-b/T_1)}{1 - k\exp(-a/T_1)}. \tag{4}$$

The small numerical factor k represents the ratio of the Z-component of magnetization immediately after the pulse to the Z-component immediately before the pulse. For an ideal pulse $k = 0$, and in most practical cases k may be kept below ± 0.1. The largest error occurs when the times a and b are chosen at extremes of the relaxation curve where $a \ll T_1 \ll b$, in which case equation 4 may be approximated by

$$\frac{S_a}{S_b} = \frac{1 - \exp(-a/T_1)}{1 - \exp(-b/T_1)} \cdot \frac{1}{1 - k}. \tag{5}$$

Thus the upper limit of the error in the intensity ratio S_a/S_b is a fraction k.

The proposed 'rapid method' for spin–lattice relaxation has been illustrated with a series of measurements on acenaphthene, in order to permit a direct comparison with the inversion-recovery results. Only the relatively narrow spectrum of the aromatic carbon atoms was examined, using an acquisition time of two seconds. Initial values for the pulse interval were therefore chosen to be 2 and 20 seconds. The spectra obtained are shown in the two lower traces of *Figure 3*. It can be seen at once that the methine carbons (at the high-field end) all give ratios of S_a/S_b near 0.3, which is near the optimum region for estimating these relaxation times, whereas the three quaternary carbons give ratios S_a/S_b that are too low, with large uncertainties in the value of S_a because the signal is so weak. These results suggested the choice of a third setting of the pulse interval $c = 200$ seconds, which resulted in the top trace of *Figure 3* which gave intensity ratios S_b/S_c more suited to the slow relaxation of these three carbon sites. The derived spin–lattice relaxation times are compared with the results from inversion-recovery experiments in *Table 1*. The error estimates for the progressive saturation results are based on the observed noise level in the experimental traces and a calculation of the extent to which this influences the derived relaxation time when the curves of *Figure 2* are employed. Since the inversion-recovery values represent means of three separate determinations of the recovery curve with ten measurements of $S_\infty - S_t$ on each curve, these are believed to be the more reliable. The progressive saturation values represent the means of three series of experiments like the one illustrated in *Figure 3*, and it is gratifying to note the agreement within the expected experimental error.

A comparison of peak height measurements with integrated area determinations indicated that although the latter would be expected to provide more reliable values, it occasionally produced a reading that was inconsistent with the peak height measurement and the relaxation time derived from

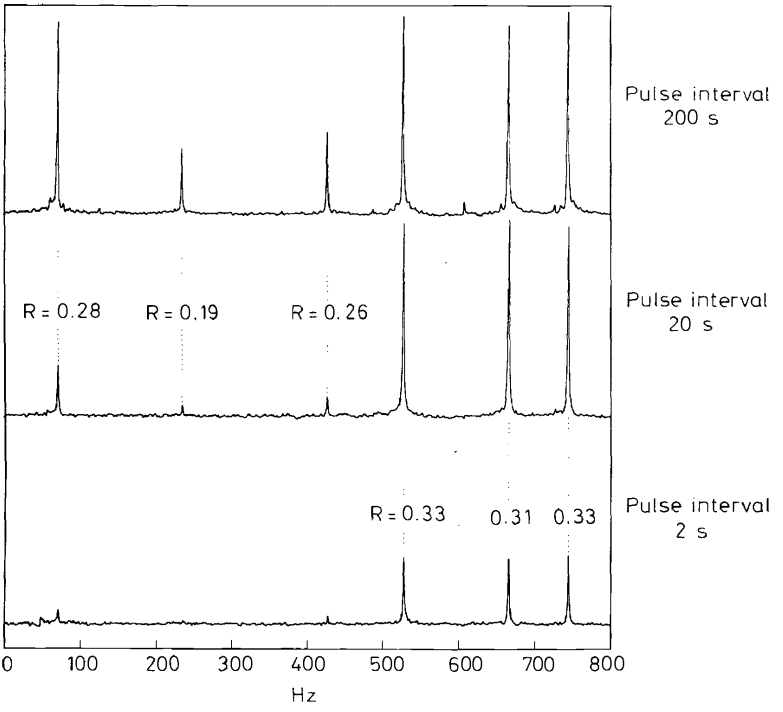

Figure 3. An illustration of the 'rapid method' for determining spin–lattice relaxation times by progressive saturation experiments at only three settings of the pulse interval (2, 20 and 200 s). The spectra represent the aromatic carbon–13 resonances of acenapthene (see *Figure 1* for the assignment). The total instrument time expended on these results was about four hours. The curves of *Figure* 2 were used to predict the relaxation times from the intensity ratios $R = S_2/S_{20}$ (methine carbons) and S_{20}/S_{200} (quaternary carbons). The results are compared with the inversion-recovery measurements in *Table 1*.

inversion-recovery. Note, for example, the result for line 11 in *Table 1*. The integrations (which were carried out digitally) were felt to be more susceptible to difficulties associated with defining the baseline in the presence of noise and nearby resonance signals, a problem that might have been solved with a more sophisticated computer routine for determining the baseline. The peak heights were measured simply with respect to a baseline drawn by the operator. Some care was exercised to ensure that the recorder pen response was adequate for proper reproduction of signals of different intensities.

3. SPIN–SPIN RELAXATION

At first sight it would appear that the Fourier transform method should be equally applicable to spin–spin relaxation of individual lines, through transformation of the free precession signal at various points along a spin-echo train of the kind described by Carr and Purcell[13]. There is however one serious drawback when dealing with nuclei that exhibit homonuclear spin–spin coupling (for example, ^{1}H, ^{19}F or ^{31}P). The amplitude of the spin

echoes does not simply decay monotonically according to the relevant spin–spin relaxation times, but is also modulated, often in a very complex fashion[14, 15].

The effect is best visualized by reference to a very simple case, that of two non-equivalent nuclei A and X, separated by a sufficiently large chemical shift δ_{AX} that the scalar coupling J_{AX} may be described by first-order theory ($|\delta_{AX}| \gg |J_{AX}|$). Consider the motion of the A magnetization in a frame of reference rotating about the Z direction at the mean precession frequency of A and X; the motion of the X magnetization can be deduced by symmetry considerations. The initial 90° pulse of the Carr–Purcell sequence[13] at time zero produces a transverse component of magnetization directed along the Y axis (*Figure 4a*), which when left free to precess breaks up into two components that both precess rapidly away from the Y axis at a rate determined

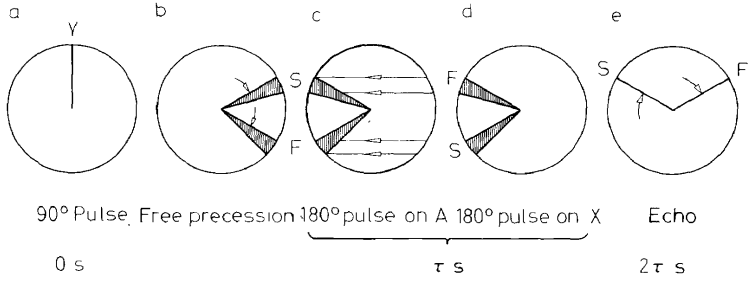

Figure 4. Schematic representation of the source of J-modulation of spin echoes in a Carr–Purcell sequence for a two-spin system (AX) in a frame of reference rotating at the mean frequency of A and X. (a) The initial 90° pulse aligns the A magnetization along the Y axis. (b) It precesses freely through many cycles, the fast (F) and slow (S) components diverging due to their frequency difference J_{AX}, and spreading out due to magnet field inhomogeneity. (c) The next pulse turns all the vectors through 180° about the Y axis. (d) It also inverts the spin states of the X nucleus, interchanging the labels of the fast and slow components of the A magnetization. (e) As a result, the chemical shift and field inhomogeneity effects are refocussed at $t = 2\tau$, but the divergence due to J_{AX} continues unchanged, reducing the observed echo amplitude by $\cos(2\pi J_{AX}\tau)$.

by $\delta_{AX}/2$, while diverging slowly at a rate determined by J_{AX}, and becoming diffuse at a rate determined by the extent of field inhomogeneities over the sample. This is illustrated in *Figure 4b*, where the two components have been identified with F for fast and S for slow. The effect of the refocussing pulse applied at time τ is to turn these vectors through 180° about the Y axis, producing mirror image inversion with respect to the YZ plane (*Figure 4c*), an operation which would normally cause perfect refocussing of chemical shift, spin–spin coupling and field inhomogeneity effects at time 2τ. However the 180° pulse has one important additional effect: it inverts the spin states of the second nucleus X, which interchanges the fast and slow vectors in the diagram (*Figure 4d*). For this reason the divergence due to the J coupling is not refocussed but persists unchanged throughout the entire time interval 2τ, resulting in an echo with amplitude reduced by a factor $\cos(2\pi J_{AX}\tau)$. For a repeated train of echoes this corresponds to a modulation at the frequency $J_{AX}/2$. Note that a *hetero*nuclear coupling does not induce echo

modulation since the X nucleus then does not experience the effect of the 180° pulses. For molecules with more than two spins of the same species, the echo modulation becomes correspondingly more complex, and if in addition the first-order approximation is not satisfied, then further complications arise[15].

One method of circumventing this problem is to operate with very high pulse repetition rates compared with the largest chemical shift difference between coupled nuclei, that is,

$$2\pi|\delta_{AX}|\tau \ll 1 \tag{6}$$

where $(2\tau)^{-1}$ is the repetition rate of the 180° pulses; then the echo modulation disappears[16]. This may be visualized by recognizing that the Fourier spectrum of the pulsed radiofrequency contains a series of sidebands separated by the pulse repetition frequency, and that at high repetition rates these are all so far away from resonance that the H_1 field behaves more like a continuous irradiation. (At these high pulse rates, any individual echo in the train would be of too short a duration to yield a high resolution spectrum after Fourier transformation; the pulse train would have to be interrupted to permit an adequately long sampling of the free induction signal.)

This argument suggests that a rather different experimental technique might be better suited to studies of transverse relaxation in spectra with homonuclear spin–spin coupling. This is the 'forced transitory precession' or 'spin locking' experiment first proposed by Redfield[17], and applied to liquid samples by Solomon[18]. After an initial 90° pulse, the transverse magnetization is held aligned ('locked') along the Y direction of the rotating frame by a continuous radiofrequency field H_1 which is strong compared with all frequency offsets from resonance, and is shifted in phase by 90° with respect to the radiofrequency used for the 90° pulse. In the presence of this field the transverse magnetization decays with a characteristic time constant known as the 'spin–lattice relaxation time in the rotating frame', $T_{1\rho}$. At the end of a variable spin-locking time t seconds the field H_1 is interrupted, and the remaining transverse component of magnetization monitored in the form of a free induction decay. Fourier transformation of this signal generates a spectrum where each line has decayed in amplitude by $\exp(-t/T_{1\rho})$, where $T_{1\rho}$ is the characteristic transverse relaxation time, essentially equal to the spin–spin relaxation time for most liquid samples[18].

A complication arises when this technique is combined with heteronuclear decoupling (which has become almost indispensible for carbon-13 studies). Since carbon-13 relaxation is normally determined by interaction with protons, there is the possibility of energy transfer between protons and carbon if the precession frequency of protons about H_2 in the 100 MHz rotating frame becomes equal to the precession frequency of carbon-13 nuclei about H_1 in the 25 MHz frame, $\gamma_H H_2 = \gamma_C H_1$[19]. If the proton irradiation field H_2 is made incoherent (the accepted practice for carbon-13 spectroscopy) it is no longer possible to avoid the 'rotating frame resonance condition' and the transverse magnetization exhibits a spuriously fast decay rate, giving a false value for $T_{1\rho}$. In order to obtain the results reported below, this problem

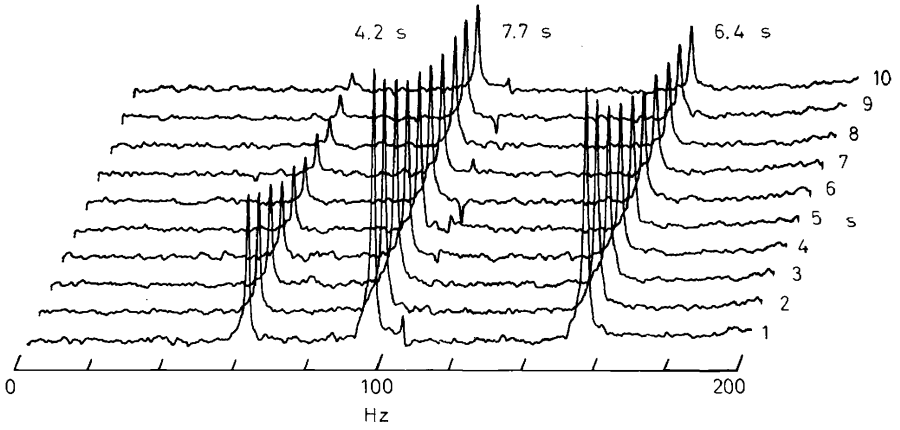

Figure 5. Transverse relaxation of the three carbon-13 sites of *o*-dichlorobenzene studied by a spin-locking experiment, with special precautions to avoid rotating frame resonance effects. The low-field signal (from carbon directly bonded to chlorine) shows much faster transverse than longitudinal relaxation, attributed to spin coupling to ^{35}Cl and ^{37}Cl nuclei, while the other resonances give $T_{1\rho}$ values essentially equal to T_1.

was circumvented by operating the proton decoupler in the coherent mode during the spin-locking period at such a level as to avoid resonance in the rotating frame. This ensured the enhancement of the carbon-13 signals through the nuclear Overhauser effect. However in order to simplify the observed spectra, the decoupler was switched to the incoherent mode during the acquisition of the transient free induction signals (at this time H_1 was extinguished and no rotating frame resonance could occur). The mode switching of the decoupler was controlled by a small laboratory computer which formed part of the Fourier transform accessory.

This spin-locking technique has been applied to the study of the transverse relaxation of carbon-13 nuclei in *o*-dichlorobenzene[20]. For reasons of symmetry there are just three non-equivalent carbon-13 resonances which have been assigned by coherent off-resonance proton decoupling. The spin–lattice relaxation times measured by the inversion-recovery method gave $T_1 > 66$ s for the carbon with no directly attached protons, $T_1 = 7.8 \pm 0.8$ s for the next carbon atoms around the ring, and $T_1 = 6.4 \pm 0.6$ s for the carbon atoms furthest from the chlorine. The results of the spin-locking experiments, which are illustrated in *Figure 5*, indicate essentially equal values for $T_{1\rho}$ except for the carbon nuclei directly bound to chlorine, where spin coupling to the rapidly relaxing ^{35}Cl and ^{37}Cl nuclei causes very rapid transverse relaxation, with $T_{1\rho} = 4.2 \pm 0.4$ s.

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