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TRANSIENT NUTATIONS IN NUCLEAR MAGNETIC DOUBLE RESONANCE.  
ASSIGNMENT OF TRANSITIONS TO AN ENERGY LEVEL DIAGRAM

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Transient Nutations in Nuclear Magnetic Double Resonance.  
Assignment of Transitions to an Energy Level Diagram

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ABSTRACT

A nuclear magnetic double resonance technique is described which permits the assignment of transitions of complex high resolution spectra to the appropriate energy level diagram. A monitoring radiofrequency ( $H_1$  at  $\omega_1$ ) is maintained at exact resonance for a chosen line in the spectrum with the level  $H_1$  set well above saturation, while a second radiofrequency ( $H_2$  at  $\omega_2$ ) of about the same strength is swept through the entire spectrum. A transient nutation of the type described by Torrey (Phys. Rev., 76, 1059, (1949)) is detected whenever  $\omega_2$  passes through a line that shares an energy level with the monitored transition. This is attributed to the sudden transfer of spin population to the common energy level as result of population inversion across the connected transition caused by adiabatic passage through resonance. The new magnetization vector then precesses around  $H_1$  in the rotating frame of reference, giving the characteristic decaying oscillation first observed by Torrey. This transient oscillation is positive-going when the two connected transitions span an interval  $\Delta m = 2$  (the 'progressive' configuration), and negative-going when they span an interval  $\Delta m = 0$  (the 'regressive' configuration), thus making a clear distinction between these two possibilities. The technique is illustrated by transient double resonance experiments on 2-chlorothiophene.

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## 1. INTRODUCTION

The first step in the analysis of complex high resolution nuclear magnetic resonance spectra is almost invariably the assignment of the observed transitions to an appropriate energy level diagram. Since the frequencies and intensities of the observed lines necessarily obey certain sum rules,<sup>1</sup> trial and error methods have often been employed. Alternatively, when reasonably good estimates can be made of the shielding and spin coupling parameters, computer methods can be used to calculate the theoretical spectrum (and the assignment of the theoretical transitions) which can then be matched to the experimental spectrum in order to deduce the assignments.<sup>2</sup>

A more direct procedure was made possible by the advent of double resonance<sup>3</sup> and double quantum methods<sup>4</sup> designed to identify connected transitions (those that share the same energy level) in an unambiguous fashion. Connected transitions can have just two configurations: progressive, spanning an interval  $\Delta m = 2$ , and regressive, where the two terminal levels have the same magnetic quantum number. Observation of a double quantum line identifies pairs of progressively connected transitions while the double resonance technique splits into doublets<sup>5</sup> all transitions that are connected with the irradiated line, identifying the progressive or regressive cases from the observed line profiles or from the sense of the asymmetry of the doublets when the irradiation field is slightly offset from exact resonance.<sup>3</sup>

A distinction may be drawn between the two principal effects of 'spin tickling' - the splitting described above and the intensity changes brought about by population rearrangements when  $H_2$  is allowed to saturate a given transition or invert the populations of two energy levels by adiabatic rapid passage<sup>6</sup>. Population rearrangement through saturation of a given transition can be thought of as a manifestation of the general Overhauser effect.<sup>7</sup> The details of the resulting

intensity changes depend on the relaxation mechanisms that are operative in the particular molecule under consideration--where the spin-lattice relaxation times are known, the electrical circuit analogy proposed by Bloch<sup>8</sup> can be used to predict these intensity changes, as for example in the quartet of acetaldehyde when one of the methyl doublet components is saturated.<sup>9</sup> In the limit that the dominant mechanism is relaxation of all nuclei by some influence external to the molecule, and where the irradiated nucleus has a much shorter relaxation time than any coupled nuclei, the intensity changes are particularly simple<sup>10</sup> being given by the equalization of the populations of the irradiated transition without any appreciable rearrangement by 'leakage' through other transitions. When the irradiated transition is not degenerate the result is simply an increase in the intensity of a progressively connected transition by one half, and a 50% decrease in the intensity of a regressively connected transition.

Unfortunately for the general application of such Overhauser experiments for the assignment of transitions to an energy level diagram, such approximations are not always valid, and moreover it is possible for intensity changes to appear on transitions that are not directly connected with the irradiated line. The method may, however, be applied to the much more restricted goal of separating out transitions that belong to energy levels of different symmetry classes.<sup>11</sup>

The way out of this dilemma is through the use of transitory double resonance methods<sup>12</sup> such that the population changes are observed just after the perturbation has been applied but within a time that is short compared with the relevant spin-lattice relaxation times, before any appreciable 'leakage' of population can occur. For example, Hoffman<sup>12</sup> has shown that it is possible to contrive a field-sweep

double irradiation experiment where a given transition is saturated and then the intensity changes of a second transition examined after an interval that is still short compared with the spin lattice relaxation times. The expected intensity changes then approximate the simple ~ 50% changes of the 'no leakage' limit, if the irradiated line is not degenerate.<sup>13</sup> The delay between perturbation and observation avoids the complication of detecting splittings on the observed line through 'spin tickling'.

These two effects of double irradiation, line splitting and intensity changes, since they often occur together can mutually interfere and complicate the determination of energy level assignments. For example, in frequency sweep spin tickling experiments, line splittings are sought and the intensity changes usually ignored. An alternative sweep mode where the observing rf field is set to monitor the peak of a chosen line while the perturbing rf field is swept through the whole spectrum<sup>14</sup>, suffers considerably because of the two interfering effects. Splitting of the monitored line when a connected transition is irradiated produces a dip on the recorder pen, but intensity changes due to population rearrangements can cause the pen to go either up or down, often masking the effect of the splitting. This difficulty is compounded by the fact that a slight misadjustment of the monitoring frequency to one side of the center of the peak can result in a response that first rises and then falls, merely as a consequence of the splitting of the monitored line and not through the influence of population changes. Moreover, the line width differences usually used to distinguish progressive and regressive configurations are easily obscured by the grosser changes produced by population disturbances and their usually slow recovery.

The aim of the present investigation is to devise a convenient method of observing the effects of population rearrangements without interference from line splitting, in order to assign the transitions of a complex spectrum to an energy



level diagram.

## 2. DETECTION OF TRANSIENT POPULATION CHANGES

### 2.1 Torrey Oscillations Induced by $H_1$

Suppose that a chosen line in the spectrum, with transition matrix element  $\lambda_{pq}$  at frequency  $\omega_{pq}$  is monitored by a radiofrequency field  $H_1$  of angular frequency  $\omega_1$ , held at exact resonance by the usual internally locked field-frequency control system.<sup>3</sup> Transient population changes may be induced by sweeping a second rf field  $H_2$  (of angular frequency  $\omega_2$ ) through the entire spectrum. On the principle that the observed response should be strong and rapid,  $H_1$  is purposely set much higher than the level used for steady-state experiments where saturation has to be avoided. As a result, transient nutations of the type described by Torrey<sup>15</sup> are observed whenever  $H_1$  is suddenly switched on, the nutation frequency being unaffected by relaxation in the limit  $\gamma H_1 \lambda_{pq} \gg T_2^{-1}$ , being given by

$$\Omega = \left[ \gamma^2 H_1^2 \lambda_{pq}^2 + (\omega_0 - \omega_1)^2 \right]^{\frac{1}{2}} = \gamma H_{\text{eff}} \quad (1)$$

In the present experiment the offset from resonance ( $\omega_0 - \omega_1$ ) is negligibly small for all parts of the line and the observed frequency reduces to  $\gamma H_1 \lambda_{pq}$ . It is convenient to define  $K$  as the height of the peak excursion of this oscillatory signal.

In a frame of reference rotating with angular frequency  $\omega_1$ , the magnetization vector precesses about the effective field  $H_{\text{eff}}$  (which is identical with  $H_1 \lambda_{pq}$  in the present experiment) and is subject to both spin-spin and spin-lattice relaxation, being damped with a time constant given by

$$\frac{1}{T} = \frac{1}{2} \left[ \frac{1}{T_1} + \frac{1}{T_2} \right] \quad (2)$$

This characteristic damped oscillation is readily distinguished from the 'wiggles' observed in many conventional NMR spectra by the fact that the oscillation is of constant frequency.

## 2.2 Torrey Oscillations Induced by Population Transfer

The present experiment hinges on the fact that a Torrey oscillation may be initiated not only by the sudden application of  $H_1$  but also by any sudden population transfer to the levels  $p$  or  $q$  while  $\omega_{pq}$  is being monitored by  $H_1$ . Assume for the purpose of simplicity that only homonuclear double resonance is to be treated, so that in the absence of a saturating rf field there will be the same equilibrium population difference  $\Delta \approx -\frac{1}{2}N_0(E_p - E_q)/kT \ll 1$  across each transition. (The extension to heteronuclear double resonance, where  $(E_p - E_q)$  depends on the particular nucleus under consideration, is straightforward.)

Consider an energy level system in which four levels,  $p$ ,  $q$ ,  $r$ , and  $s$  are arranged such that  $\omega_{pq}$  and  $\omega_{qr}$  are progressive connected transitions and  $\omega_{pq}$  and  $\omega_{ps}$  are regressive connected transitions. Without loss of generality the monitored line  $\omega_{pq}$  may be taken to be a transition of a nucleus  $A$ , and  $\omega_{qr}$  and  $\omega_{rs}$  may be transitions of another nucleus  $M$ . Let the steady-state spin populations be  $P_p$ ,  $P_q$ ,  $P_r$ , and  $P_s$  after the application of a saturating rf field to transition  $\omega_{pq}$ . Then  $P_p = P_q$  but the populations  $P_r$  and  $P_s$  will depend on the details of the relaxation processes in the particular molecule under consideration. They will be calculated in Section 2.3 for certain assumptions about the relaxation.

If the radiofrequency  $\omega_2$  is now swept through  $\omega_{qr}$  in such a way as to satisfy the adiabatic rapid passage conditions (3) and (4) the populations of the levels  $q$  and  $r$  may be inverted.<sup>6</sup>

$$\gamma H_2 \lambda_{qr} \gg \frac{1}{H_2 \lambda_{qr}} \cdot \frac{dH_0}{dt} \quad (3)$$

$$\frac{1}{H_2 \lambda_{qr}} \frac{dH_0}{dt} \gg \frac{1}{T_1}, \frac{1}{T_2} \quad (4)$$

Note that, since  $T_1 \geq T_2$ , this also requires that the saturation parameter  $S_{qr}$  be large

$$S_{qr} = \gamma^2 H_2^2 \lambda_{qr}^2 T_1 T_2 \gg 1 \quad (5)$$

This sudden population transfer provides level q with a population excess over level p and a Torrey oscillation is induced which starts out in a positive direction and reaches a peak excursion proportional to  $P_r - P_p$ . It will be shown in the next Section that  $P_r$  is always greater than  $P_p$ , consequently this response is always positive.

If the radiofrequency is swept through the regressively connected transition  $\omega_{ps}$ , and if the adiabatic conditions (3) and (4) are still fulfilled for the transition matrix element  $\lambda_{ps}$  (which may be very different from  $\lambda_{qr}$  in a strongly coupled system), the populations  $P_p$  and  $P_s$  may be inverted. This makes level p more highly populated than level q, so that the net magnetization vector is along the -Z axis and is consequently carried into the -Y direction in the first quarter cycle of the nutation about  $H_1$ , giving rise to an oscillatory signal that starts in the negative direction reaching a peak excursion proportional to  $P_q - P_s$ . The experiment thus draws a clear distinction between progressive and regressive connected transitions from the sense of the observed transient oscillations.

### 2.3 Population Distributions in the Presence of a Saturating rf Field

Several different relaxation mechanisms may be considered for the protons of a molecule in the liquid state. However, under certain assumptions it is possible to set limits on the possible spin populations  $P_s$  and  $P_r$  when  $H_1$  is allowed to saturate the transition  $\omega_{pq}$ . Consider the case where  $\omega_{pq}$ ,  $\omega_{qr}$ , and  $\omega_{ps}$  are transitions of a weakly coupled three spin system AMX. It will be assumed that the thermal relaxation times of all the transitions of a given nucleus are the same; this is not essential to the argument that follows but appears to be the case most likely to be encountered in practice.

Bloch's electrical circuit analogy<sup>8</sup> is the general method used to calculate the steady-state spin populations in the presence of the applied rf field  $H_1$ . These are established through the balance between the pumping influence of the rf field and the interaction with the thermal motions of the lattice which tends to try to reestablish a Boltzmann distribution of spin populations. In this analogy, the spin population in a given level in excess of the Boltzmann population attributable to that level is compared with the electrical potential at a junction of an electrical circuit. The relaxation time of a given transition is the analogue of electrical resistance, and the flow of spins under the influence of the rf field is the equivalent of the electric current. Application of Kirchhoff's laws then permits the evaluation of the current distribution and hence the required potentials and the steady-state populations. (In the simpler cases considered below where one particular relaxation path is dominant the solution may often be obtained by inspection.)

### Independent Relaxation

In the absence of any rf field the normalized populations would be as shown in Fig. 1 (a). If A, M, and X are assumed to relax independently of one another and if the relaxation of the M nuclei is much more rapid than all other relaxation, then when  $\omega_{pq}$  is saturated  $P_p = P_q$  and Boltzmann distributions are established across all four M transitions resulting in the steady-state populations illustrated in Fig. 1 (b). Adiabatic passage through either the progressive transition  $\omega_{qr}$  or the regressive transition  $\omega_{ps}$  therefore generates a Torrey oscillation at the frequency  $\omega_{pq}$  with a peak excursion of  $+K$  or  $-K$  units respectively (i.e. equal in magnitude to that observed when  $H_1$  was suddenly switched on). This, in fact, constitutes the lower limit for the amplitude of the response due to passage through a progressive connected transition, and an upper limit for the amplitude of the response due to passage through a regressive connected transition, on the assumption of independent relaxation.

The other limits of the amplitude of the Torrey oscillations may be illustrated by the case where all nuclei relax independently but the relaxation of X nuclei dominates the other relaxation rates. The steady-state spin populations indicated in Fig. 1 (c) will be established such that  $P_p = P_q$  and Boltzmann distributions are maintained across all X transitions. Adiabatic passage through the progressive connected transition  $\omega_{qr}$  would then induce a Torrey oscillation at the monitored line of amplitude  $+\frac{3}{2}K$ , while adiabatic passage through the regressive connected transition  $\omega_{ps}$  would yield an oscillation of amplitude  $-\frac{1}{2}K$ . The same results for the strengths of the responses would be obtained in the case that relaxation of the A nucleus is much more rapid than other relaxation paths.

An example of a particular relaxation pattern that falls within these limits is that of independent relaxation where all A, M, and X transitions relax equally

efficiently. The result is the population distribution illustrated in Fig. 1 (d). The response due to inversion of the population of the progressive transition  $\omega_{qr}$  would have a peak excursion  $+\frac{19}{14} K$  (i.e., within the limits  $+K$  to  $+\frac{3}{2} K$ ), while population inversion of the regressive transition  $\omega_{ps}$  would induce a response of amplitude  $-\frac{9}{14} K$  (i.e. within the limits  $-\frac{1}{2}K$  to  $-K$ ). Note that for all the cases where A, M, and X relax independently, the sum of the absolute magnitudes of the progressive and regressive responses is  $2K$ .

These treatments have all assumed weak coupling between the three nuclei; in the strong coupling (ABC) limit it is no longer possible to consider one nucleus relaxing much faster than the others, because of the mixing of eigenstates. The analysis is then correspondingly more complicated, but the solution for the amplitudes of the responses would tend to lie well inside the limits calculated for the weak coupling case.

#### Intramolecular Relaxation

Two special cases must now be considered that fall outside the general assumption of independent relaxation. If dipole-dipole interaction between nuclei A and M within the same molecule is the dominant relaxation mechanism, then the most effective relaxation path would be across the  $\Delta m = 2$  (double-quantum) transitions. Fig. 1 (e) illustrates the even more extreme case where this is the only effective relaxation path, and steady-state populations are established such that there is a Boltzmann distribution across each AM double-quantum transition. The amplitude of the response due to the progressive connected transition  $\omega_{qr}$  now falls above the previously calculated upper limit for progressive responses for the assumption of independent relaxation. It can be shown that this new value  $2K$  constitutes an absolute upper limit independent of the relaxation mechanism, provided that the transitions are not degenerate<sup>13</sup> and that only one saturating rf field is present. Hence, all responses obtained by adiabatic passage through a progressive connected

transition have amplitudes between  $K$  and  $2K$ .

The other special case is that of spin-spin interaction between A and M nuclei as the dominant relaxation mechanism. This would tend to maintain a Boltzmann distribution across the two  $\Delta m = 0$  transitions, holding these populations essentially equal as indicated in Fig. 1 (f). The magnitude of the response obtained by adiabatic passage through the regressive transition  $\omega_{ps}$  then falls below the lower limit calculated for independent relaxation. In this extreme case, which is an absolute lower limit, the observed response could become vanishingly small. This spin-spin coupling mechanism requires that there be a large Fourier component of the correlation spectrum at the very low frequency  $J_{AM}$ , and it would therefore seem unlikely to constitute the dominant relaxation process in more than a very small fraction of molecules studied. One example is liquid HF with the chemical exchange rate adjusted to fall in the required frequency range by careful exclusion of moisture.<sup>16</sup>

#### 2.4 Identification of Connected Transitions

It may be concluded from the previous section that unless the details of the relaxation mechanisms in the molecule under study are known, the strengths of the Torrey oscillations cannot be predicted with any accuracy. Furthermore, unless the inequalities (3) and (4) are satisfied by the experimental conditions for all of the relevant transition matrix elements, the relative strengths of the responses will vary. This problem is considered in more detail in Section 4.1. Fortunately, for the purpose of identifying connected transitions, this intensity information is only relevant inasmuch as it guarantees a finite response and ensures that the sense of the response correctly identifies the progressive and regressive configurations. The sharp leading edge of the Torrey oscillation locates the frequency of the perturbed line in the spectrum. This is a rather precise method

because the time required to reach the first peak of the oscillation is only  $\pi/(2\gamma H_1 \lambda_{pq})$ , in practice about 1-2 seconds, and at the sweep rates actually used this corresponds to a horizontal movement of only 0.03 - 0.06 cps.

The Torrey oscillations are detected only a short time (of the order 1 second) after  $\omega_2$  passes through the center frequency of a connected transition. This greatly diminishes the possibility of a 'false' resonance - a response at the frequency of a transition that is not directly connected with the monitored line, through a two-stage population transfer - since the rate of 'leakage' would be expected to be very slow, being determined by the relevant spin-lattice relaxation time. Some weak responses of this type were just discernable in practice, but their slow rise and fall together with the absence of an oscillatory component clearly distinguished them from the 'real' signals of connected transitions.

The large value of the saturation parameter for the monitored line

$$S_{pq} = \gamma^2 H_1^2 \lambda_{pq}^2 T_1 T_2 \gg 1 \quad (6)$$

ensures that the steady-state signal, which constitutes the 'base-line' in the double resonance experiment, is weak compared with the amplitude of the transient responses. Consequently any dip in the base-line due to splitting of the monitored line attributable to spin tickling must also be correspondingly small, and in practice has been found to be completely obscured by the large transient responses caused by population transfer.

Optimization of the experimental responses tends to establish the approximate condition

$$\gamma H_1 \lambda_{pq} \approx \gamma H_2 \lambda_{qx} \quad (7)$$



although this is not at all critical (the transition matrix elements  $\lambda_{qx}$  differ considerably from line to line). This is strongly reminiscent of the requirement in Hahn's double resonance experiments<sup>17</sup> where the equalization of the nutation frequencies of two spin systems in a solid permits rapid cross-relaxation and the establishment of a common spin temperature. However, Hahn's experiment requires that the spin systems be effectively isolated from the lattice (in practice the whole experiment is completed in a time that is short compared with the shortest spin-lattice relaxation time) and this appears to rule out the possibility of explaining the present experiments by this mechanism.

### 3. EXPERIMENTAL

Essentially identical experimental results have been obtained on two separate NMR instruments, both Varian HR 60 spectrometers modified for field-frequency stabilization through a servo loop operating on the dispersion-mode signal from internal tetramethylsilane (TMS).<sup>18</sup> The experimental details have been described elsewhere.<sup>3,9</sup> By examination of the signal corresponding to the side of a sharp resonance, it can be shown that such a regulator holds the variations of the field-frequency ratio within 1 part in  $10^9$  or better.

Conventional single and double resonance spectra are recorded by sweeping the frequency of a modulation sideband used to generate  $\omega_1$ , being demodulated in a variable frequency synchronous detector. The frequency sweep ( $\omega_2$ ) spectra described above simply involve the transfer of the motor drive from this oscillator to another oscillator used to generate a third modulation sideband that can be swept through the whole spectrum. Audiofrequency oscillators with a linear frequency scale are used and the output voltage is compensated for the normal falloff of modulation index with frequency.

The effective rf field strengths of the modulation sidebands (e.g.  $\gamma H_2 \lambda_{qx}$ ) were calibrated by measurement of the splitting  $\mathcal{G}$  observed on a regressive connected transition in a spin tickling experiment.<sup>3</sup>

$$\mathcal{G} = \gamma H_2 \lambda_{qx} / 2\pi \text{ cps} \quad (8)$$

and by the use of a constant centerband rf field and a precision attenuator to drive the field modulation coils. This calibration can be cross-checked for the monitoring rf field by noting the frequency  $F$  of the Torrey nutation during the transient responses<sup>15</sup>

$$F = \gamma H_1 \lambda_{pq} / 2\pi \text{ cps} \quad (9)$$

A typical value of  $\mathcal{G}$  was 0.16 cps, a value very close to the experimentally observed full line width at half maximum (caused by magnetic field inhomogeneity). A typical sweep rate was 2 cps/min; although faster sweeps with higher rf power would make the inequalities (3) and (4) more easily satisfied, the slower sweep speeds have the advantage that the transient oscillations have longer to decay before the next response is reached.

It was found that the best results were obtained when  $\omega_1$  was adjusted to the peak of a chosen resonance line with extreme care (a low, non-saturating rf level  $H_1$  was used during this procedure). Careful optimization of the magnetic field inhomogeneity, and the audiofrequency phase shift to give pure absorption mode, were two other factors that appeared to have a marked influence on the quality of the transient responses.

A new technique was introduced to carry out certain pulsed double resonance experiments described in Section 4.1, and to measure the spin-spin relaxation time

of one of the experimental lines by the Carr-Purcell technique, and the spin-lattice relaxation time by a series of  $\pi$ ,  $\pi/2$  pulse sequences.<sup>19</sup> This involves pulsing the effective rf field of a modulation sideband by gating the audiofrequency used for modulating the magnetic field. In this way  $\pi$  and  $\pi/2$  pulses may be obtained with high precision with only very simple modifications to the spectrometer. The effective rf field strengths  $H_1$  and  $H_2$  were kept so weak that only one line of the spectrum was appreciably affected by the pulse; this corresponds to pulse widths of the order of 1 second. The  $\pi/2$  phase shift of the effective rf field during the first pulse of the Carr-Purcell sequence according to the modification suggested by Meiboom<sup>20</sup> was obtained through a  $\pi/2$  phase shift of the audiofrequency signal. The technique shows some promise for selective pulse experiments in high resolution spectra.

#### 4. RESULTS

The proposed method of energy level assignment by observation of transient population rearrangements has been illustrated by the analysis of an 'unknown' unsymmetrical three spin system, the ABC spectrum of 2-chlorothiophene. The single resonance spectrum is shown in Fig. 2(b). Twelve strong lines can be discerned together with two weak 'combination' lines (1) and (15) that were confirmed by recording spectra at a high rf level.

##### 4.1 The Adiabatic Passage Conditions

The amplitudes of the observed Torrey oscillations depend not only on the steady-state populations  $P_r$  and  $P_s$  but also on how well the inequalities (3) and (4) are satisfied. An approximate value of the spin-lattice relaxation time of a typical transition (line 3) was measured by application of several sequences of  $\pi$ ,  $\pi/2$  pulses<sup>19</sup>, and the spin-spin relaxation time by the application of a  $\pi/2$  pulse followed by a series of  $\pi$  pulses timed so as to create a train of spin echoes<sup>19, 20</sup> with the modification described in Section 3. These gave  $T_1 \approx$

31 sec and  $T_2 \approx 26$  sec. At the sweep rate used in practice (2 cps/min) and with the experimental setting  $\gamma H_2 \lambda_{qr} / 2\pi = 0.16$  cps for a typical line, the ratios of the left-hand to right-hand sides of the inequalities (3) and (4) were both about 5 : 1. This ratio is not sufficient to avoid detectable losses in magnetization both by the failure to follow the effective field in the rotating frame and by relaxation. Although these conditions could be improved by increasing the rf field  $H_2$  and the sweep rate, time must be allowed after each transient response for the reestablishment of the steady-state spin populations before a second adiabatic passage, and this sets a practical upper limit on the permissible sweep rate.

In a typical response (at the frequency of line 13 due to passage through line 2) the peak excursion of the transient oscillation was somewhat less than half that to be expected for a 'perfect' adiabatic passage on the assumption of independent relaxation of all nuclei with equal relaxation times. A computer program for the numerical solution of the Bloch equations for non-stationary conditions<sup>21</sup> was used to calculate the motion of the net magnetization vector during adiabatic passage under the conditions employed experimentally. The projection of this motion on the XZ and YZ planes is shown in Fig. 3. In an ideal adiabatic passage experiment the locus would be a semicircle in the XZ plane (dispersion mode), followed by relaxation along the vertical axis towards +Z, with no component at any time in the YZ plane (absorption mode). Clearly in reality the magnetization vector has lagged behind the effective field  $H_{eff}$ , resulting in a slight precessional motion about  $H_{eff}$  and some absorption mode signal, while relaxation has attenuated the length of the vector.<sup>22</sup> In accordance with the amplitude of the observed Torrey oscillation, the maximum negative excursion of the Z component of magnetization was -0.47.

The program also permits the calculation of the frequency difference between the exact center of resonance and the point at which the maximum negative Z component of magnetization is obtained. In this example it amounted to about 0.1 cps, which is probably the largest contribution to the error involved in locating the line position by observation of the population transfer.

The amplitude of the Torrey oscillation compared quite well with that obtained when an rf pulse was used to invert the populations. The rf field strength was set such that  $\gamma H_2 \lambda_{qr} \tau = \pi$  radians, and the width  $\tau$  was adjusted to equal  $H_2 \lambda_{qr} \left( \frac{dH_0}{dt} \right)^{-1}$  sec, the time required to pass through resonance in the adiabatic passage experiment (so that relaxation losses should be about the same). However, the comparison cannot be carried too far since the pulse experiment (unlike adiabatic passage) is subject to loss in magnetization through the dephasing effects of spatial inhomogeneity in  $H_2$ .

Since the inequalities (3) and (4) involve the transition matrix elements  $\lambda_{qr}$ , the efficiency of population inversion (and hence the relative intensity of the corresponding response) varies from line to line during a sweep through the spectrum at constant  $H_2$ . Lines with extreme values of  $\lambda_{qr}$ , for example the weak "combination lines", are particularly affected, and it may be necessary to reinvestigate the spectrum at a higher level of  $H_2$  in order to enhance these responses.

## 4.2 Transient Double Resonance Experiments

Double resonance spectra were examined by monitoring ten of the strong lines in turn, the positions of the transient responses indicating the connected transitions, and the sense of the oscillations identifying the progressive and regressive configurations. The results are summarized in Table I. Note that each monitored line should have a total of either five connected transitions (three progressive and two regressive) or six connected transitions (two progressive and four regressive). This observation helps to decide which transitions terminate on the  $m = \pm 3/2$  quantum levels.

As soon as it is realized that transitions 8 and 9 are unresolved it becomes a simple matter to construct the energy level diagram shown schematically in Fig. 4, for the problem is highly overdetermined.

Two typical double resonance spectra are illustrated in Figs. 2 (a) and 2 (c) in which lines (3) and (13) have been monitored. Note that as  $\omega_2$  sweeps through  $\omega_1$  the usual beat pattern is generated, but in addition  $\omega_2$  disturbs the population distribution across the monitored transition and a nutation signal may be observed superimposed on the trailing edge of the beat pattern. Responses from transitions that have a small transition matrix element, such as line (1) in Fig. 2 (a) or line (15) in Fig. 2 (c) were considerably enhanced by increasing the rf level  $H_2$ , as illustrated in the insets (d) and (e). A similar compensation for small transition matrix elements by increasing  $H_2$  is a common device in the equivalent spin tickling experiment.<sup>3</sup>

Even if the weak responses (1) and (15) had not been detected, the distinction between the two progressive and three regressive responses in each double resonance trace is so clear, that the monitored lines (3) and (13) can be unambiguously

assigned to transitions between  $m = \frac{1}{2}$  and  $m = -\frac{1}{2}$  quantum levels. In general, the recognition of the number and type of connected transitions may sometimes lead directly to a key assignment. For example, four or more responses in an AA'BB' system would immediately indicate that the monitored line belonged to the symmetric set of energy levels.

#### 4.3 Chemical Shift and Spin Coupling Parameters of 2-Chlorothiophene

Once the observed transitions have been assigned to an energy level diagram the iterative program MARIP 1 of Reilly and Swalen<sup>2</sup> converges rapidly. Rather arbitrary starting parameters were used ( $\nu_A = 400$  cps,  $\nu_B = 405$  cps,  $\nu_C = 410$  cps,  $J_{AB} = J_{BC} = J_{AC} = 2$  cps) and good convergence was obtained long before 50 iterations had been completed, yielding the parameters:

$$\nu_A = 397.41 \pm 0.01 \text{ cps}$$

$$\nu_B = 401.84 \pm 0.01 \text{ cps}$$

$$\nu_C = 407.14 \pm 0.02 \text{ cps}$$

$$J_{AB} = \pm 3.71 \pm 0.01 \text{ cps}$$

$$J_{BC} = \pm 1.45 \pm 0.02 \text{ cps}$$

$$J_{AC} = \pm 5.65 \pm 0.01 \text{ cps}$$

The greatest discrepancy between an observed and a calculated transition frequency was 0.03 cps.

From the magnitudes of the spin coupling constants, proton A would be assigned to position 4 of the thiophene ring, proton B to position 3, and proton C to position 5. The observed and calculated spectra are compared in Fig. 5. For a meaningful comparison of intensities it was found necessary to detune the receiver coil to minimize radiation damping effects, and to use a very weak rf field to avoid preferential saturation of lines with large transition matrix elements.<sup>21</sup>

## 5. CONCLUSION

The proposed method of assigning transitions to an energy level diagram by observation of transient nutations has the advantage over the analogous spin tickling experiment in that the distinction between the progressive and regressive configurations is perhaps clearer and less likely to be obscured by overlapping lines. In a similar way to the spin tickling experiment it could also be used to determine the relative signs of spin coupling constants in weakly coupled spectra of three or more non-equivalent spins, or to locate transitions that are hidden by overlying resonances. Weak signals such as those of  $^{13}\text{C}$  nuclei could also be detected indirectly by transient double resonance, provided that the  $^{13}\text{C}$  satellites in the proton spectrum are detectable.

Several authors<sup>10-12</sup> have employed population changes due to double irradiation to give information about energy level diagrams. Some of these methods depend for their applicability on assumptions about the relaxation mechanisms<sup>10</sup> or are likely to be complicated by line splitting effects due to spin tickling. The present experiment essentially avoids these two pitfalls, and in this sense achieves the same result as Hoffman's 'transitory selective irradiation' experiments<sup>12</sup>, but in the more convenient frequency sweep mode and without the need for establishing a precise time sequence for the various irradiations.

It should be possible to extend the technique to population inversions involving more than one transition, either simultaneously, in the case of degenerate transitions, or sequentially, by the use of two or more perturbing rf fields. The latter experiment, which might for example involve one adiabatic passage and one rf pulse of  $\pi$  radians, might be employed to relate coupling constant signs in three-spin systems where one coupling is vanishingly small.<sup>12</sup>



The technique might also be exploited to examine relaxation mechanisms by using the amplitude of the transient responses as a measure of the steady-state populations established in the presence of a saturating rf field  $H_1$ . It would have the advantage that the saturation would be achieved by the application of a radio frequency field  $H_1$  held at exact resonance (rather than being swept through resonance), thus all transients could be allowed to die away before the measurements are made. For this application it would be necessary to make quite sure that the adiabatic conditions are adequately fulfilled for the second rf field  $H_2$ .

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## FIGURE CAPTIONS

1. The steady-state spin populations established on the energy levels of a weakly coupled three spin system when a saturating rf field  $H_1$  is applied to the transition  $\omega_{pq}$ . The edges of the 'cube' represent transitions and the corners energy levels.

(a) A Boltzmann distribution for  $H_1 = 0$ . (b) and (c) Independent relaxation where the relaxation rate of one nucleus (double lines) dominates the rest. (d) Independent relaxation with all rates equal. (e) Double-quantum transitions as the most effective relaxation path. (f) Relaxation dominated by spin-spin interaction. The relative strengths of the transient responses excited by inversion of the populations across a progressive connected transition ( $\omega_{qr}$ ), or a regressive connected transition ( $\omega_{ps}$ ), are indicated below each diagram.

2. The nuclear magnetic resonance spectrum of 2-chlorothiophene at 60 Mc/sec (center trace). The transient nutations in the top trace were obtained by monitoring line 3 with an rf field  $\omega_1$  while sweeping a second rf field  $\omega_2$  through the entire spectrum at a rate of 2 cps/min. The two positive responses identify the progressive connected transitions 5 and 14, while the four negative responses locate the regressive connected transitions 1, 7, 8, and 12. A similar experiment is illustrated in the bottom trace where line 13 was monitored, and progressive responses obtained from lines 2 and 11, and regressive responses from lines 4, 7, 8, and 15. The weak response from line 1 in the top trace was improved (inset 'd') by doubling the rf field strength  $H_2$ , and the very weak response from line 15 in the bottom trace enhanced (inset 'e') by quadrupling  $H_2$ .

3. Motion of the tip of the net magnetization vector during adiabatic passage, calculated by numerical solution of the Bloch equations. The parameters correspond to a typical experimental set:  $T_1 = 31$  sec,  $T_2 = 26$  sec,  $\gamma H_2 \lambda_{qr} / 2\pi = 0.16$  cps, sweep rate = 2 cps/min. The rf field  $H_2$  is applied along the X axis, the effective field  $H_{eff}$  moving from +Z to -Z in the XZ plane. For reasons of clarity the locus is shown in projection on the XZ plane (absorption mode) and the YZ plane (dispersion mode). Since the adiabatic conditions are not adequately fulfilled, the magnetization vector lags behind the effective field and begins a precessional motion around it, while relaxation losses reduce the length of the vector.

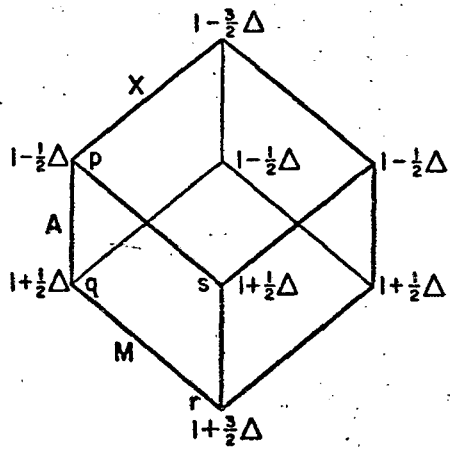
4. Schematic representation of the energy level diagram appropriate to the transitions of 2-chlorothiophene, obtained by consideration of the transient double resonance results summarized in Table I. The broken lines represent 'combination lines' which tend to zero intensity in the weak coupling limit. The numbering is that of Fig. 2.

5. Comparison of the observed 60 Mc/sec spectrum of 2-chlorothiophene with a computer simulated spectrum employing the parameters  $\nu_A = 397.41$  cps,  $\nu_B = 401.84$  cps,  $\nu_C = 407.14$  cps,  $J_{AB} = \pm 3.71$  cps,  $J_{BC} = \pm 1.45$  cps,  $J_{AC} = \pm 5.65$  cps, obtained after 50 iterative cycles. The line shape used in the calculated spectrum was essentially Gaussian with a full width at half-height of 0.14 cps. Considerable care was taken to avoid radiation damping and selective saturation effects in the experimental spectrum; the sweep rate was 1 cps/min.

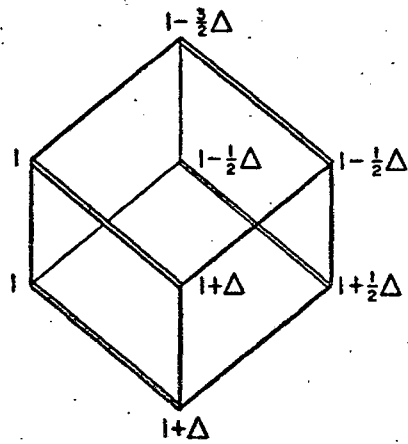
TABLE I

Summary of the transient double resonance responses observed for 2-chlorothiophene. Lines numbered as indicated in Fig. 2. Lines 8 and 9 are unresolved; a response at this frequency has been designated 8\*.

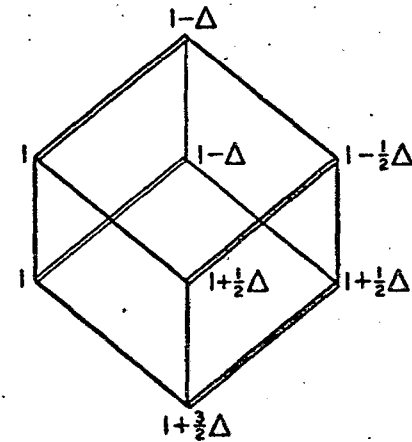
| Monitored Transition | Progressive Transitions | Regressive Transitions |
|----------------------|-------------------------|------------------------|
|                      | (positive response)     | (negative response)    |
| 2                    | 7, 13, 15               | 5, 10                  |
| 3                    | 5, 14                   | 1, 7, 8*, 12           |
| 4                    | 10, 11                  | 1, 8*, 13              |
| 6                    | 8*, 12, 15              | 11, 14                 |
| 7                    | 2, 14                   | 1, 3, 13, 15           |
| 10                   | 1, 4, 8*                | 2, 5                   |
| 11                   | 4, 8*, 13               | 6, 14                  |
| 12                   | 5, 6                    | 3, 8*, 15              |
| 13                   | 2, 11                   | 4, 7, 8*, 15           |
| 14                   | 1, 3, 7                 | 6, 11                  |



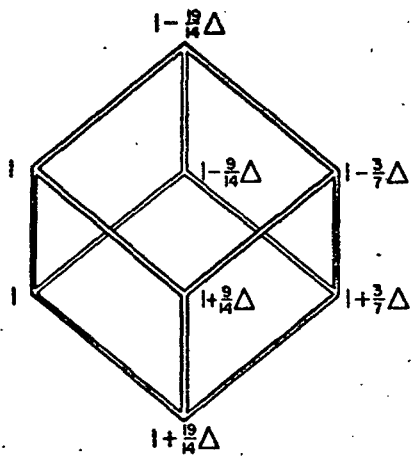
a UNPERTURBED POPULATIONS



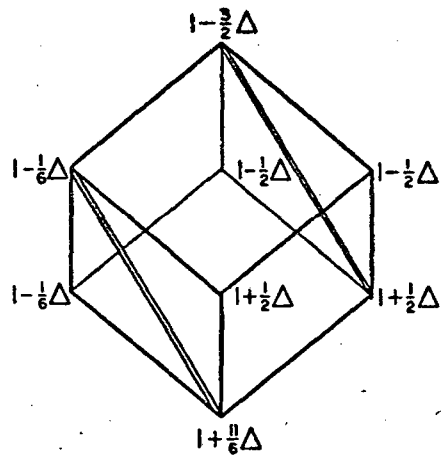
b PROGRESSIVE +K  
REGRESSIVE -K



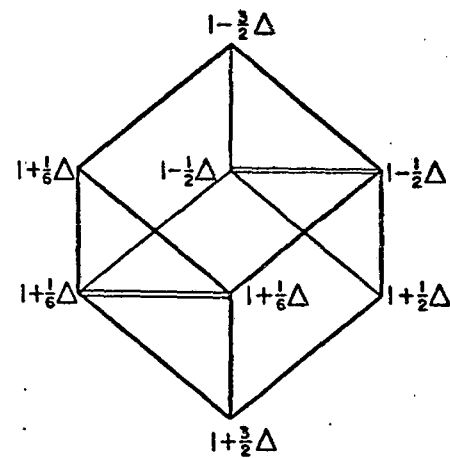
c PROGRESSIVE + $\frac{3}{2}$ K  
REGRESSIVE - $\frac{1}{2}$ K



d PROGRESSIVE + $\frac{19}{24}$ K  
REGRESSIVE - $\frac{9}{24}$ K



e PROGRESSIVE +2K  
REGRESSIVE - $\frac{2}{3}$ K



f PROGRESSIVE + $\frac{4}{3}$ K  
REGRESSIVE 0

FIG 1

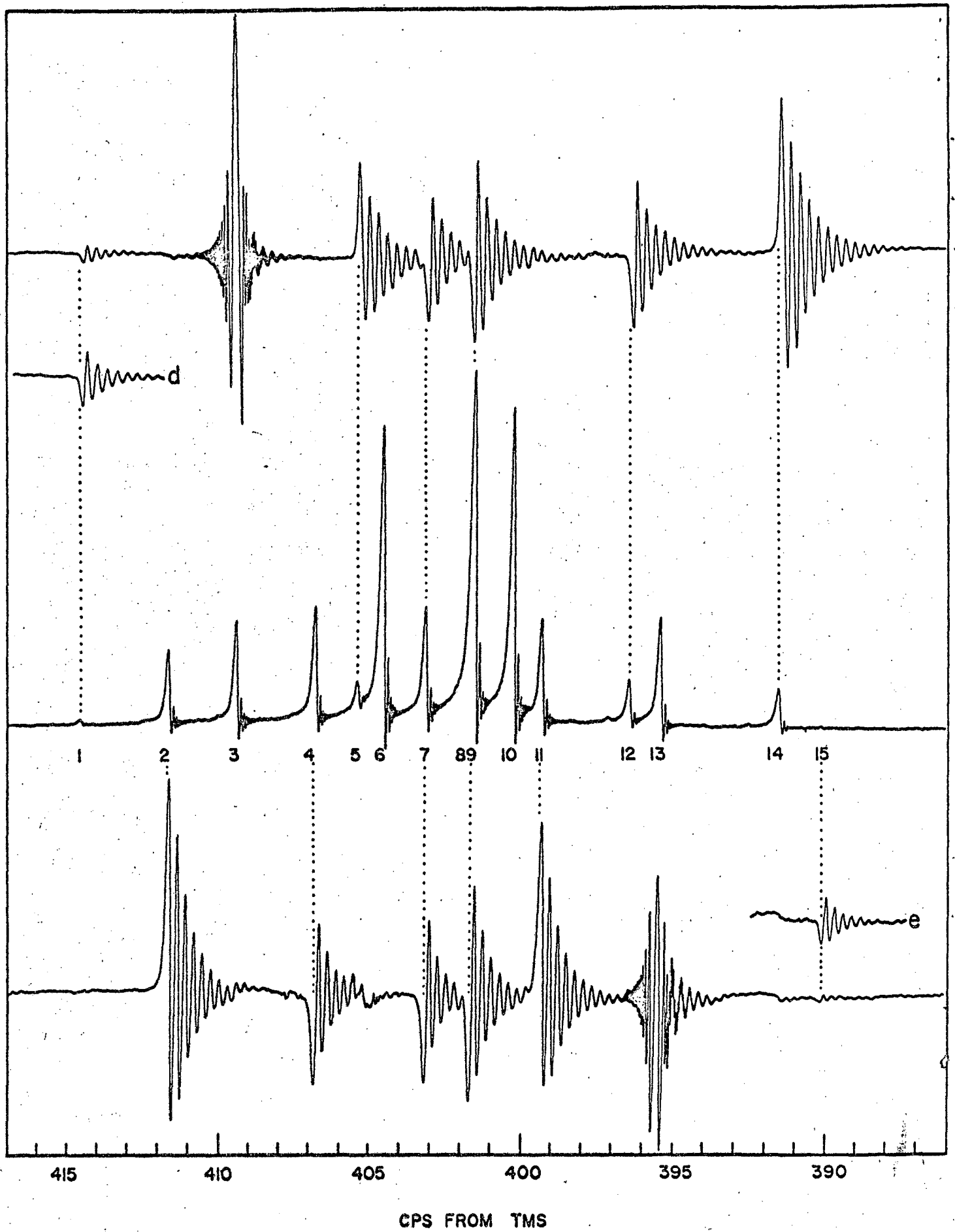


Fig 2



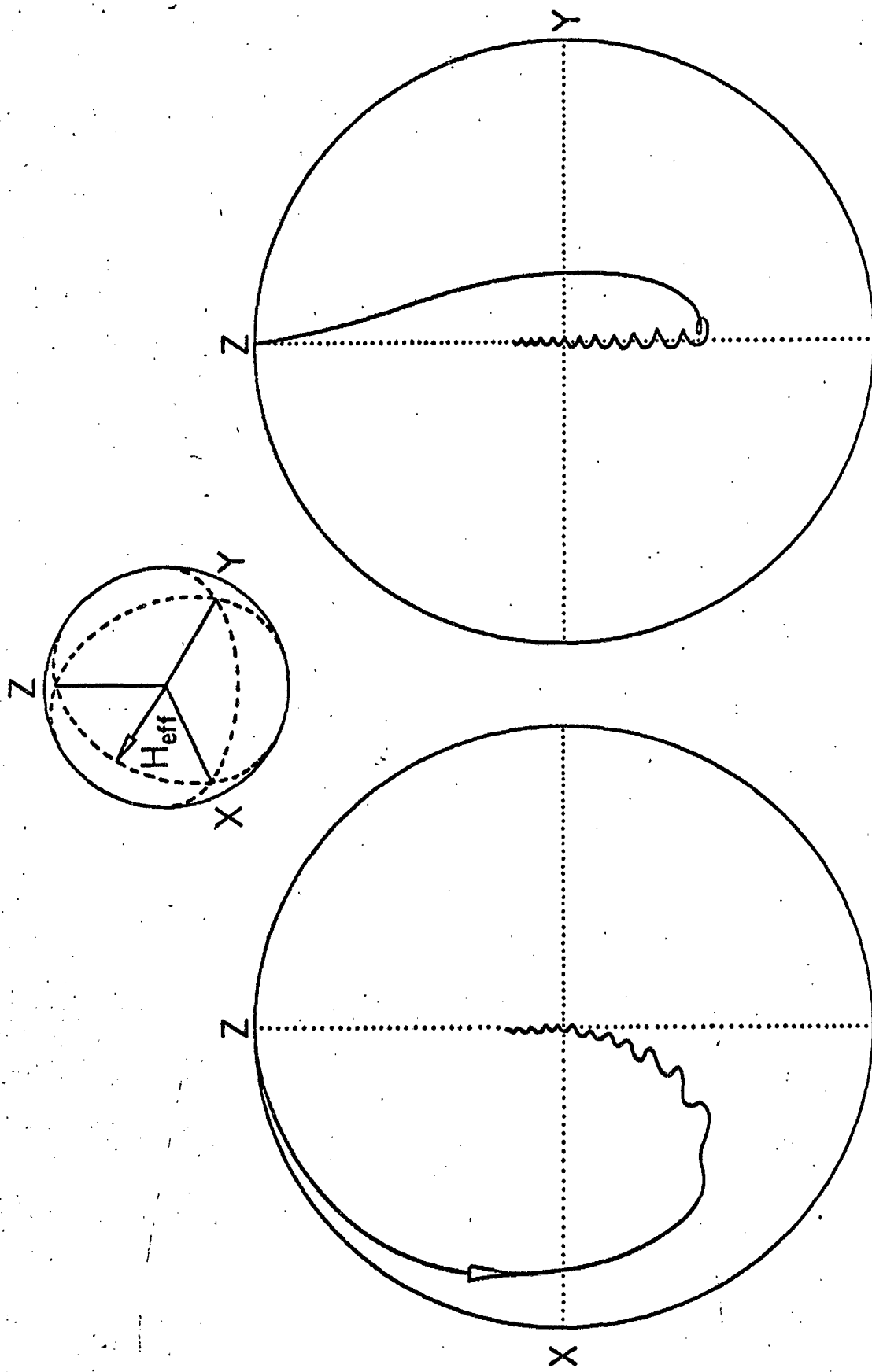


Fig 3

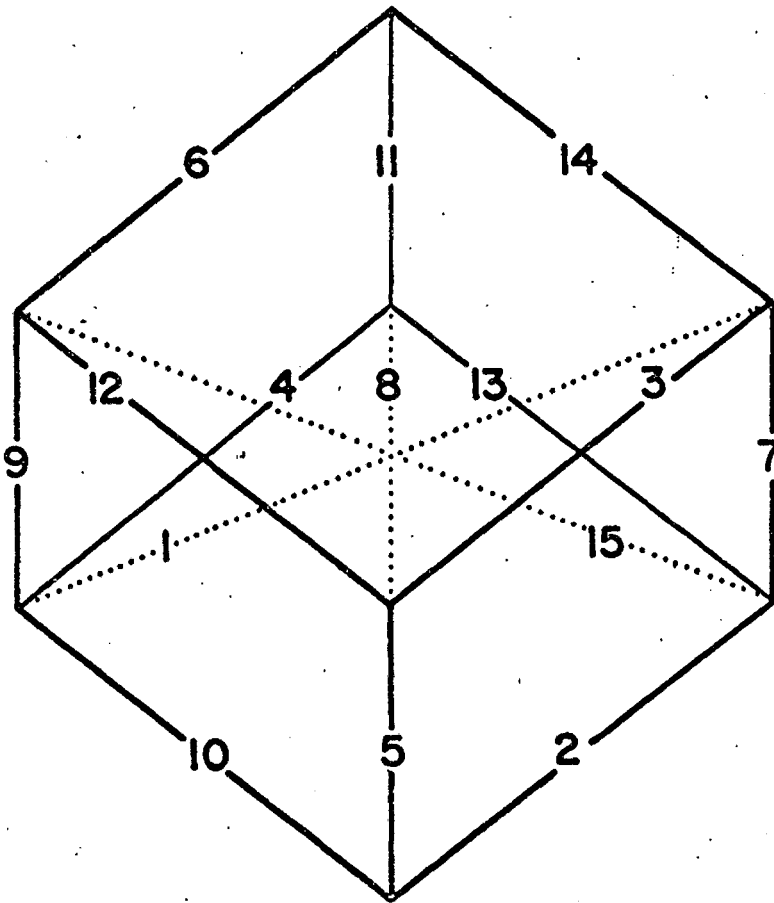


Fig 4

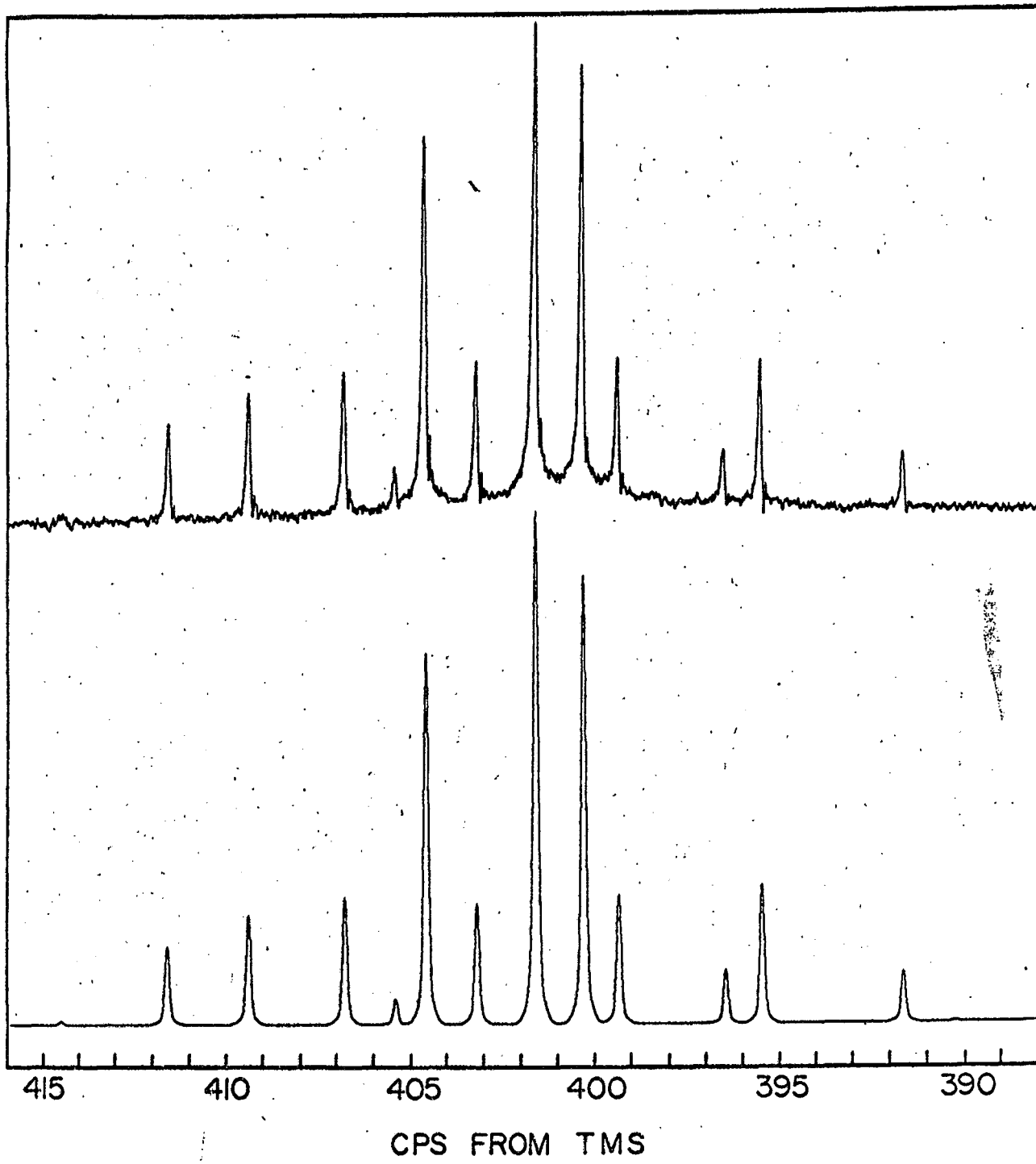


Fig 5

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