

Line Width Variations and Partial Virtual Spin Couplings in NMR Spectra of the ABMX and Related Types

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An unusual line width variation has been observed in the 40 Mc/sec proton resonance spectrum of N-methyl-2-pyrrolealdehyde. The line width differences are attributed to unresolved structure caused by partial virtual coupling between the 4-hydrogen and aldehyde proton spins. It is demonstrated that such structure may always arise in spin systems containing at least one pair of strongly coupled nuclei and two or more groups of nuclei that may be weakly spin coupled to that pair. It is also demonstrated that partial virtual couplings may be eliminated by double irradiation (spin decoupling). The 40 Mc/sec and 60 Mc/sec proton resonance spectra of 2-thiophenealdehyde are given as illustrations of these phenomena.

I. INTRODUCTION

Line width variations in a spectrum may be attributed either to time-dependent or to time-independent interactions. If the lifetimes of the different levels in a spectrum are not all equal owing to some specific time-dependent interaction, the natural line widths of the observed transitions will in general not all be the same. The effects of static interactions, on the other hand, may be such as to produce an unresolved fine structure of certain levels and experimentally this structure will appear as line width variations among the observed transitions.

In high-resolution NMR both types of line width variations are well known. Thus chemical exchange as well as specific relaxation mechanisms (in particular quadrupole relaxation) represent time-dependent line broadening interactions. Line broadening by time-independent interactions may in principle be produced by all interactions that contribute to the level structure in the spectrum (chemical shifts, spin couplings and virtual spin couplings¹) provided that the level separation caused by the interaction is comparable in magnitude to or smaller than the (real or apparent) line width of a non-degenerate line.

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The line width effects studied in the present paper are all caused by unresolved — or partly resolved — structure of the kind known as virtual spin coupling.¹ It may be anticipated that similar effects will be more and more commonly observed as resolving power and reproducibility of experimental line shapes become more and more perfected.

II. GENERAL

The simplest spin system capable of displaying the phenomenon of virtual spin coupling is the three-spin system ABX composed of two strongly coupled spin- $\frac{1}{2}$ nuclei, A and B, both of which are weakly spin coupled to a third spin- $\frac{1}{2}$ nucleus, X. In this spin system, the X-part sub-spectrum will display a quartet structure (combination lines excluded) even if one of the possible spin couplings involving nucleus X is vanishingly small: ^{1,2} $J_{AX} = 0$, say. If the spectrum is reasonably first order, one of the splittings in the X-part spectrum will be close in magnitude to the nonvanishing spin coupling (J_{BX}), and the other splitting will then be called a virtual coupling.¹ Both the real and the virtual coupling will produce corresponding splittings in the AB-part of the spectrum.

The phenomenon of virtual spin coupling is only a very particular manifestation of the effects of strong coupling within a group of spins on the multiplet structure in the spectrum of a spin that is weakly coupled to that group. The splittings observed in the X-part of an ABX spectrum will rarely equal the spin couplings that produce them, even though X by definition represents a weakly coupled spin. To see how this comes about it is helpful to decompose the complete ABX spectrum into sub-spectra.^{3,4} The AB-part of the spectrum is a superposition of two in general different AB-type (two-spin) sub-spectra with effective relative chemical shifts

$$(\nu_A^* - \nu_B^*)_{\pm} = \nu_A - \nu_B \pm \frac{1}{2} (J_{AX} - J_{BX}) \quad (1)$$

The degree of mixing in each one of the subspectra may be represented by dimensionless parameters φ_{\pm} . The parameter φ may be regarded as an angle determined by its tangent function: the tangent of (2φ) equals the ratio between J_{AB} and the effective relative chemical shift. Each of the two AB-type sub-spectra corresponds to one definite spin state (α or β) of nucleus X. It is evident therefore, that the degree of mixing between A and B spin states (the strength of the coupling in the AB sub-system) depends on the spin state of nucleus X, *unless* J_{AX} equals J_{BX} .

If, however, the equality

$$J_{AX} = J_{BX} \quad (2)$$

holds, one obtains mixing between A and B spin states that is *independent* of the spin state of X.

In the very particular case when eqn. (2) holds, the ABX spectrum will acquire several first-order features: the two AB-type sub-spectra in the AB-part will become identical except for a mutual frequency displacement of J_{AX} , the combination lines vanish for any strength of the A-B coupling, and the X-part spectrum appears as a 1:2:1 triplet with a splitting that equals J_{AX} , likewise regardless of the degree of mixing between A and B spin states.

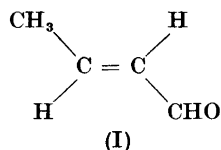
In a general ABX spectrum, in which eqn. (2) is not fulfilled, one obtains six allowed transitions in the X-part of the spectrum. Two of these have unit intensity and represent transitions between "unmixed" states. The four remaining transitions (two of which are usually labelled as combination transitions) do, however all involve a change in the state of the AB-spins as well as that of the X spin. The fact that an X-transition might entail a change in the state of the AB-spins is intuitively obvious from the dependence of the degree of mixing between A and B spin states on the spin state of X, and makes it understandable that the splittings in the X-part multiplet should not be simply related to the spin couplings between X and either one of the A or B spins.

The inclusion of one additional weakly coupled group in the spin system results in a minor but interesting complication. To be specific, let us consider an ABMX system. By use of the "effective Larmor frequency" approach³ one may see that the AB-part of the spectrum will be a superposition of four in general different AB-type (two-spin) sub-spectra with effective relative chemical shifts given by

$$(\nu_A^* - \nu_B^*)_{\pm\pm} = \nu_A - \nu_B \pm \frac{1}{2}(J_{AX} - J_{BX}) \pm \frac{1}{2}(J_{AM} - J_{BM}) \quad (3)$$

The X-part of the spectrum will appear as a superposition of two in general different X-part sub-spectra of an ABX spin system centered at $\nu_X + \frac{1}{2}J_{MX}$ and at $\nu_X - \frac{1}{2}J_{MX}$. Similarly, one obtains two M-part sub-spectra centered at $\nu_M \pm \frac{1}{2}J_{MX}$. The appearance of each M-part sub-spectrum is determined by the spin coupling parameters J_{AM} , J_{BM} , J_{AB} , and by the effective relative chemical shift between A and B according to eqn. (1). If one spin coupling, J_{BM} say, is vanishingly small one might still obtain a virtual spin coupling between M and B in each sub-spectrum.¹ The virtual couplings in the two subspectra would, however, usually be unequal because the extent to which the spin state of M influences the mixing between A and B depends also on the spin state of nucleus X.

The spectrum of *trans*-crotonaldehyde at 40 Mc/sec, published earlier,⁵ offers a clear illustration of such variable virtual long-range coupling. In *trans*-crotonaldehyde (1)



the coupling between the aldehyde proton (M) and the β -ethylenic proton (B) is vanishingly small. The spectrum of the ethylenic protons (A and B) and the aldehyde proton (M) appears as a superposition of four ABM spectra, each one corresponding to a particular value of the magnetic quantum number (m_X) of the methyl group (X_3). The magnitude of the virtual J_{BM} coupling was found to vary⁵ between an unobservably small value when $m_X = +3/2$, so that the effective relative chemical shift becomes equal to

$$|\nu_A - \nu_B| + \frac{3}{2}|J_{AX} - J_{BX}|$$

to the easily resolved value of 0.6 cps when $m_X = -3/2$, so that the effective relative chemical shift becomes equal to

$$|\nu_A - \nu_B| - \frac{3}{2}|J_{AX} - J_{BX}|.*$$

3. EXPERIMENTAL

A sample of N-methyl-2-pyrrolealdehyde was kindly placed at our disposal by Dr. S. Forsén in Stockholm. The 2-thiophenealdehyde sample was the same as that employed in earlier NMR studies of monosubstituted thiophenes.

The single resonance NMR spectra were obtained using a Varian Associates model V 4300 B spectrometer operating at 40.00 Mc/sec and a Varian model A 60 spectrometer operating at 60.00 Mc/sec. The spectra were calibrated using the modulation side-band technique. Audio frequency modulation was obtained by use of a Philips oscillator PP 6050, and the frequencies were measured by use of a Hewlett-Packard electronic counter model 3734A. Double resonance spectra were studied at 40 Mc/sec only, using the V 4300 B spectrometer. The double resonance spectra were recorded in the field sweep mode by operating the Varian V 3521 A integrator in the lower side-band mode. The strong irradiation frequency was generated by frequency modulation of the rf. transmitter using the PP 6050 audio oscillator.

The samples were carefully degassed by bubbling argon gas through the liquid for 10–15 min before sealing the sample tubes.

4. RESULTS AND DISCUSSION

The 40 Mc/sec proton resonance spectrum of N-methyl-2-pyrrolealdehyde in dioxane solution is shown in the upper part of Fig. 1. The different parts of the spectrum were recorded under different conditions; they are assigned as follows: (a) the aldehyde (X) multiplet, (b) the complex band of the strongly coupled protons attached to the 5-position (A) and the 3-position (B), (c) the weakly coupled proton (M) in the 4-position and finally (d) the broadened methyl group resonance.

An interesting feature of the spectrum depicted in Fig. 1 (and actually the one that provided the impetus for the present paper) is the variation in width of the four resolved lines in the band assigned to M. This line width variation is barely noticeable in Fig. 1c, but appears unambiguously in the expanded slow sweep spectrum of Fig. 1e. It is seen that the two central lines in Fig. 1e are significantly broader than the two outer lines. Since it is difficult to find a relaxation process that would selectively broaden the two central lines in the M-part spectrum, an explanation was sought in terms of unresolved structure (*i.e.* a broadening caused by time-independent interactions). It was anticipated that the chemical shift between the ring protons A and B might be small enough to make the spin state of the aldehyde proton X, which is spin coupled with A ($J_{AX} \approx 1$ cps), influence the frequencies of the "mixed" transitions in the M-part spectrum.

To test this hypothesis a theoretical ABMX spectrum was calculated with NMR parameters as listed in the caption of Fig. 2. The calculated M-part

* Actually it is impossible to state with certainty which of the effective A–B chemical shifts that belongs to a particular sign of m_X , since this would require a knowledge of the absolute signs of the spin couplings. The signs given in the text were chosen for definiteness.

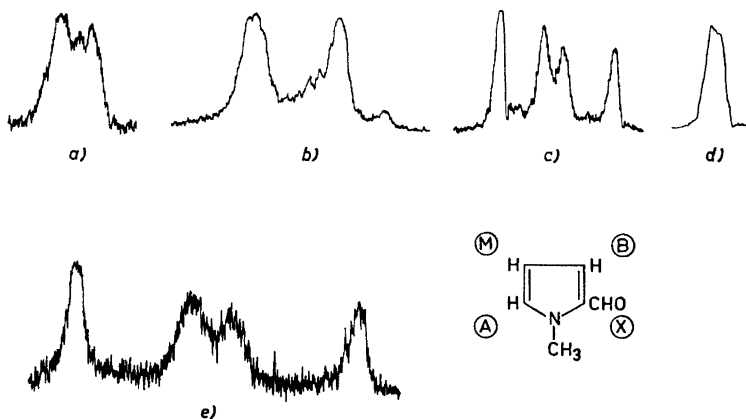


Fig. 1. Proton resonance spectrum at 40 Mc/sec of N-methyl-2-pyrrolealdehyde in dioxane solution. (a) The aldehyde resonance, (b) the resonance of the strongly coupled 3- and 5-ring protons, (c) the resonance of the weakly coupled proton in the 4-position of the pyrrole ring, (d) the methyl group resonance, and (e) an expanded slow sweep recording of the 4-hydrogen spectrum. Note the greater width of the two central lines as compared to the outer lines in spectrum (e).

spectrum of the model spin system is depicted in Fig. 2a. It is seen that the "mixed" transitions (5 and 6 or 7 and 8) in Fig. 2a become nondegenerate even though the spin coupling between M and X was assumed to vanish. The combination transitions (3 and 4 or 9 and 10) are also split by the combined effect of J_{AX} and the near degeneracy of ν_A and ν_B . It is seen, however, that the aldehyde spin X, has no influence on the "unmixed" M-transitions 1,2,11, and 12. The splitting between lines 5 and 6 (or 7 and 8) in Fig. 2a corresponds

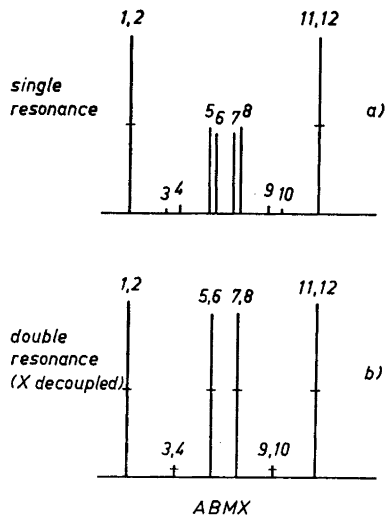


Fig. 2. (a) Schematic M-part spectrum of an ABMX model spin system calculated with the following parameters:

$$\nu_A - \nu_B = 1.6, J_{BX} = J_{MX} = 0, J_{AX} = 1.2, \\ J_{AB} = 1.4, J_{AM} = 5.0, J_{BM} = 3.4$$

ν_M and ν_X are assumed to be large enough to make off-diagonal matrix elements involving couplings to M and X negligible.

(b) The same M-part spectrum as in (a) but calculated for a situation in which X is decoupled from the rest of the spin system by means of a strong irradiation field.

to a virtual long-range coupling between M and X. Thus it is evident that virtual coupling can arise between two weakly coupled groups in a spin system provided that both groups are coupled to at least one pair of strongly coupled spins. Inasmuch as the splitting corresponding to the virtual coupling only arises in some of the otherwise degenerate transitions (*viz.* the "mixed" transitions 5 and 6 or 7 and 8) whereas the "unmixed" transitions remain degenerate, this type of splitting is more appropriately called a partial virtual coupling.

It is difficult to obtain an experimental verification of the above explanation for the greater width of the central lines in the spectrum of Fig. 1e owing to the poor resolution of the line structure. A possible corroboration by means of double resonance was attempted. Application of a strong irradiation field to the aldehyde resonance should result in a quantitation of the aldehyde (X) spin along an axis rotating in the plane perpendicular to the polarizing H_0 field. This would effectively decouple the aldehyde spin from the rest of the spin system — in particular the effect on the resonance of M would be a "collapse" of the partial virtual long-range coupling as indicated schematically in Fig. 2b. A double irradiation experiment of this type was indeed performed. However, the resolution attainable in the double irradiation experiment was not good enough to bring the resulting line narrowing out very clearly and therefore the experimental spectrum has not been reproduced in the present paper.

In order to obtain experimental evidence for the existence of partial virtual long-range coupling it was considered desirable to study the NMR spectrum of a molecule with NMR parameters similar to those of N-methyl-2-pyrrolealdehyde. It was found that pure liquid 2-thiophenealdehyde was appropriate for that purpose.

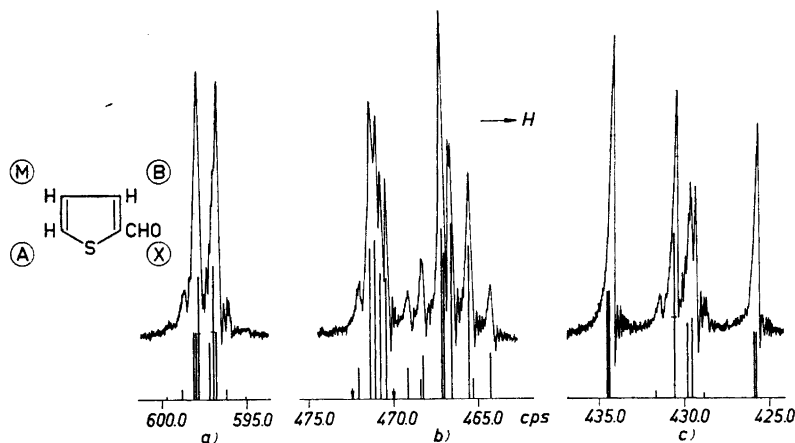


Fig. 3. The proton resonance spectrum at 60.00 Mc/sec of neat 2-thiophenealdehyde containing trace amounts of TMS as internal reference. (a) the X-part (aldehyde proton) resonance, (b) the AB-part (3- and 5- hydrogen) spectrum, (c) the M-part (4-hydrogen) resonance. The theoretical spectrum was calculated by a full ABCX treatment using the parameters listed in the text. Two transitions of very low intensity are located by vertical arrows in the theoretical spectrum of (b).

The 60 Mc/sec proton resonance spectrum of neat 2-thiophenealdehyde containing trace amounts of tetramethylsilane (TMS) as internal standard is depicted in Fig. 3. The three different parts of the spectrum were recorded under identical conditions except for the over all gain which was adjusted to make full use of the recorder paper. Fig. 3a shows the appearance of the X-part (aldehyde) spectrum, Fig. 3b the AB-part due to the strongly coupled 3- and 5-hydrogens, and Fig. 3c the M-part (4-hydrogen) multiplet. The theoretical spectrum included in Fig. 3 was calculated by complete numerical diagonalization of the ABCX Hamiltonian matrix with the parameters (in cps) given below:

$$\begin{array}{llll}
 \nu_A = 467.95 & \nu_B = 469.20 & \nu_M = 430.50 & \nu_X = 597.50 \\
 J_{AB} = 1.25 & J_{AM} = 4.85 & J_{BX} = 3.85 & J_{AX} = 1.20 \\
 J_{BX} = 0.00 & J_{MX} = 0.10 & &
 \end{array}$$

The chemical shifts are given relative to the TMS internal standard. The symbol M for hydrogen 4 should — strictly speaking — have been replaced by C to stress the fact that this proton is not really weakly coupled to the other ring protons. The signs of all couplings are taken as positive even though the spectrum depends significantly only on the sign of J_{AM} relative to that of J_{BM} and on the sign of J_{AX} relative to that of J_{MX} (*cf.* the discussion on relative signs of couplings in ABMX spectra by Nageswara Rao and Puchta Venkateswarlu ⁶). The remaining relative signs are known from earlier work.⁷⁻¹⁰

It is immediately seen that the M-part spectrum in Fig. 3c lacks the mirror image symmetry present in the schematic spectrum of Fig. 2a. The reasons for this dissimilarity are twofold. Firstly, the magnitude of the J_{MX} spin coupling is not completely negligible with the resolution attained in Fig. 3 and secondly, the second order effects of the couplings J_{AM} and J_{BM} result in line shifts and intensity redistributions. The finite value of J_{MX} results in an unresolved splitting of the two outermost lines in the M-part spectrum of Fig. 3c and alters the splittings of the central lines in an asymmetrical fashion (the sense of this asymmetry shows that J_{AX} and J_{MX} have the same sign). The main result of the second order effects of J_{AM} and J_{BM} is an intensity redistribution whereby the low field M-lines increase in intensity at the expense of the high field lines; in addition these second order effects tend to shift the whole M-part spectrum towards higher field.

For the further discussion of Fig. 3 it is helpful to refer to the energy level and transition diagram in Fig. 4, and the caption of that figure. It is seen in Fig. 4 that levels 1 and 8' are the only ones of magnetic quantum number -2 and $+2$, respectively. Consequently, these levels represent "unmixed" states in any spectrum (even in the ABCD limit). As long as the "X-approximation" is well fulfilled (and this is true for the spectrum depicted in Fig. 3) one may safely neglect all mixing between states represented by corners in different cubes. If, in addition, the off-diagonal elements proportional to the spin couplings to nucleus M may be neglected (and this is not perfectly true in the spectrum of Fig. 3) one obtains no mixing between the states represented

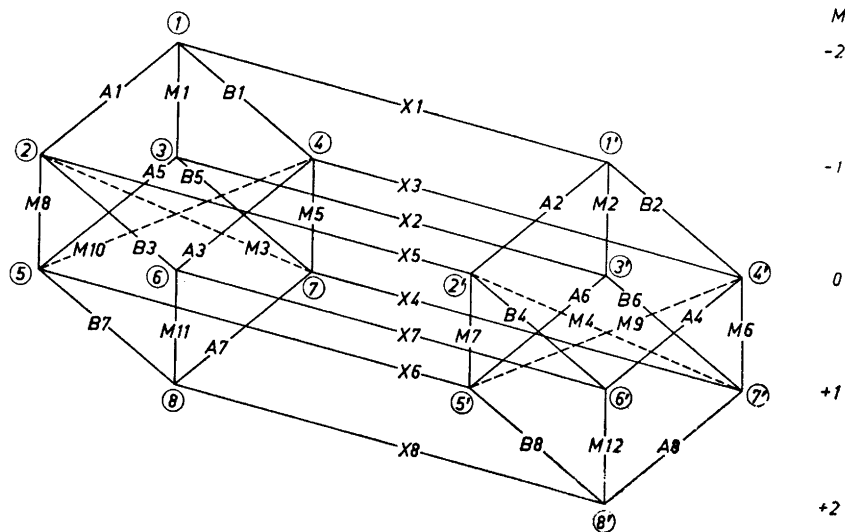


Fig. 4. Energy levels and transitions in an ABMX spectrum. The diagram corresponds to a spin system in which all spin couplings are of the same sign and subject to the inequalities: $J_{BX}, J_{MX} \ll J_{AX} < J_{AB} < J_{BM} < J_{AM}$. The diagram may be visualized as a combination of two cubes tilted so as to have three corners such as those labelled 2, 3, and 4 in a horizontal plane. Each cube belongs to one definite spin state of nucleus X; each corner corresponds to one energy level and each cube edge corresponds to an A, B, or M transition. The combination transitions in the M-part of the spectrum are indicated by dashed body diagonals of the cubes. The X transitions are represented by oblique lines joining the two cubes. For lack of space the four combination transitions in the X-part of the spectrum have been suppressed, (they should be represented by lines joining the following pairs of corners: 2 and 4', 4 and 2', 5 and 7', and 7 and 5').

The AB-part of the ABMX spectrum appears as a superposition of four different AB-type (two-spin) sub-spectra. Each one of these AB-type sub-spectra is represented by the two A transitions and the two B transitions that together span the circumference of a cube surface.

by corners 3, 3', 6, or 6' and any other spin states. When these conditions hold the nuclei M and X are both weakly coupled to the rest of the spin system in the strict sense of this terminology. The transitions M1, M2, M11, and M12 will then all be "unmixed" transitions and become pairwise degenerate if the spin coupling J_{MX} vanishes. When off-diagonal elements involving J_{AM} or J_{BM} have to be taken into account it is no longer necessarily true that lines M1, M2, and M11, M12 become pairwise degenerate even if J_{MX} should vanish.

Not all of the transitions indicated in Fig. 4 are experimentally observed in the spectrum of Fig. 3. The two combination lines M4 and M9 have an intensity less than 0.1 % of the strongest lines and disappear in the background. The four combination transitions observed in the X-part spectrum (Fig. 3a) have on the other hand not been indicated in Fig. 4, but their proper representation is described in the caption.

The analysis of a genuine ABMX spectrum is quite straightforward. General procedures have been given for the analysis of spectra from spin systems in which strong coupling obtains in only one pair of spin- $\frac{1}{2}$ nuclei^{8,11,12} when the problem may be solved in closed form since only 2×2 matrices are involved, and explicit formulae for the ABMX system have been published.^{6,13} The spectrum of Fig. 3 is slightly more complex owing to the finite value of, ν_M but this complication is effectively dealt with by inclusion of second order

Table 1. Transitions in the ABM-part of the 60 Mc/sec proton resonance spectrum of neat 2-thiophenealdehyde.

Line No. (assigned as in Fig. 4)	Transition frequencies			Relative intensities	
	Observed	Calculated		Calculated	
		ABMX 2nd order	ABCX exact	ABMX 2nd order	ABCX exact
B1	472.26 ^a	472.305	472.305	0.008	0.005
B3	470.98	471.027	471.028	1.811	1.823
A1	471.31	471.309	471.308	1.757	1.750
A3	470.03 ^a	470.032	470.031	0.005	0.004
B2	472.05	472.017	472.020	0.294	0.354
B4	470.77	470.738	470.742	1.536	1.457
A2	470.41	470.402	470.398	1.469	1.398
A4	469.13	469.124	469.120	0.279	0.336
B5	468.36	468.385	468.389	0.299	0.212
B7	467.08	467.108	467.113	1.917	1.982
A5	466.62	466.556	466.551	1.985	2.027
A7	465.34	465.279	465.274	0.303	0.224
B6	468.30	468.232	468.236	0.544	0.498
B8	467.02	466.953	466.958	1.619	1.692
A6	465.48	465.516	465.510	1.690	1.742
A8	464.20	464.237	464.232	0.604	0.517
M1	434.65	434.634	434.637	1.257	1.244
M2	434.55	434.530	434.532	1.260	1.248
M3	431.64	431.710	431.718	0.100	0.077
M4	432.44 ^a	432.360	432.370	0.002	0.002
M5	430.75	430.715	430.721	0.917	0.936
M6	430.80	430.748	430.748	1.004	1.014
M7	429.62	429.643	429.644	0.937	0.941
M8	429.90	429.881	429.880	0.871	0.884
M9	427.98 ^a	428.030	428.022	0.000	0.000
M10	429.01	428.890	428.882	0.087	0.067
M11	426.00	425.962	425.964	0.796	0.793
M12	425.87	425.858	425.860	0.777	0.790

^a Transition too weak to be observed. Experimental frequency inferred from rule of repeated spacings.

perturbation corrections according to the formulae given by Reilly and Swalen¹⁴ (listed in Tables I and II of Ref. 14). In Table 1 the experimentally observed transition frequencies (adjusted so as to give the repeated spacings required by the level diagram of Fig. 4) together with the theoretical spectra calculated by complete numerical diagonalization of the ABCX Hamiltonian matrix ("ABCX, exact") as well as by the ABMX formulae including second order perturbation terms ("ABMX, 2nd order"). A comparison of the two calculated spectra with one calculated by neglect of J_{MX} and of the second order effects of the finite value of ν_M * reveals that a major part (0.19 cps) of the experimentally observed splitting between the two M-lines centered at 429.7 cps originates in partial virtual long-range coupling between M and X. The major effect of the real coupling ($J_{MX} = 0.10$ cps) is to increase this splitting by an amount close to the value of J_{MX} , whereas the splitting between the lines at 430.8 cps caused by virtual coupling between M and X is almost cancelled by the real coupling. The effect of the second order perturbation terms is mainly a reduction of both these splittings by *ca.* 0.05 cps.

The actual analysis was performed by successive approximations. Starting values of ν_X , J_{AX} , ν_M , J_{AM} , and J_{BM} , were obtained on inspection of the X-part and M-part spectra, respectively. The values of ν_A , ν_B , and J_{AB} were obtained by analysis of the four AB-type quartets in Fig. 3b. No difficulty was encountered in assigning the AB lines between 464 cps and 468.5 cps, but the appearance of the two low field AB-type quartets — in particular the intensity distribution — was at first considered to be rather puzzling. The cause of this unusual appearance of the AB-type subspectra is to be found in the second order effects of J_{AM} and J_{BM} . The second order perturbation depresses level 2 of Fig. 4 sufficiently to make lines A1 and B3 cross. In this manner the B — B — A — A sequence of transitions prevailing in the other AB-type subspectra is broken and the lowest field AB-type quartet has the line sequence (from low to high field): B1 — A1 — B3 — A3. The second order effects are also responsible for the fact that the splitting between lines B3 and A1 is almost the same as that between lines A2 and B4 even though the effective relative chemical shift in the lowest field AB type quartet 0.15 cps is far less than that of the B2 — B4 — A2 — A4, AB-type, quartet (1.35 cps). It is evident from Table 2 that the perturbation expressions of Reilly and Swalen¹⁴ provide an excellent approximation to the spectrum. The transition frequencies calculated by their formulae deviate by less than 0.01 cps from those obtained by a full ABCX treatment. The relative intensities obtained in the perturbation analysis are not quite as good, but reproduce the observed intensities well within experimental error.

It was anticipated that the splittings of the central lines in the M-part spectrum of 2-thiophenealdehyde would become larger with a smaller relative chemical shift $|\nu_A - \nu_B|$. To verify this prediction a spectrum was recorded at 40.00 Mc/sec. This spectrum is reproduced in Fig. 5. It is seen that the splittings of the two central lines in the M-part spectrum (Fig. 5c) have indeed increased as compared with those of Fig. 3c. The theoretical spectra included

* These calculations follow in a straightforward manner from the formulae given in references. Therefore the details are not reproduced here.

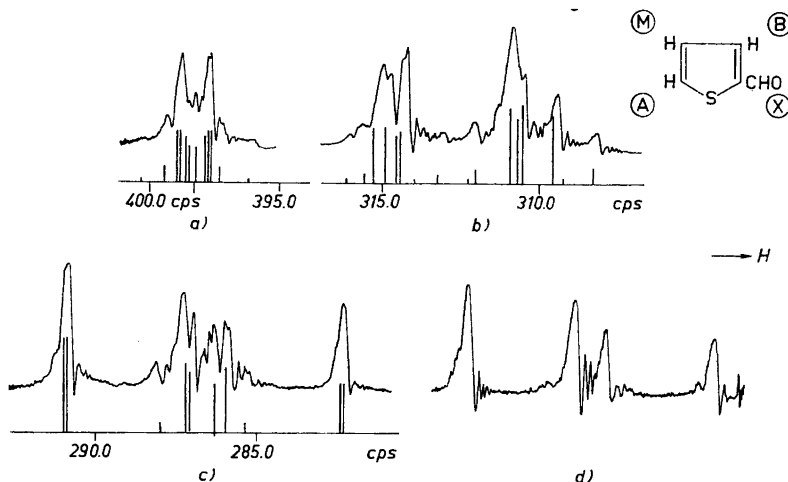


Fig. 5. The proton resonance spectrum at 40.00 Mc/sec of neat 2-thiophenealdehyde containing trace amounts of TMS as internal reference. (a) the X-part spectrum, (b) the AB-part spectrum, (c) the M-part spectrum, (d) the double resonance M-part spectrum recorded with simultaneous spin decoupling of the aldehyde spin. The theoretical spectra included in (a), (b), and (c) were calculated by a full ABCX treatment with parameters as described in the text.

in Figs. 5a–5c were calculated by a full ABCX treatment using the same coupling constants as those derived from the 60 Mc/sec spectrum and with the chemical shifts derived from the 60 Mc/sec spectrum reduced by a factor of 2/3 to account for the reduction in spectrometer frequency. The fit between the calculated and observed spectra is very good, even though the experimental spectrum is slightly distorted by sweep non-linearity. A theoretical 40 Mc/sec spectrum was also calculated by use of the Reilly-Swalen perturbation expressions. The transition frequencies were still quite accurately given by the perturbation formulae, deviating by less than 0.03 cps from those of the ABCX calculation, but the relative intensities obtained by the perturbation formulae are subject to errors as large as 50 %.

Fig. 5 also displays the “collapse” of the splittings caused by virtual (and real) long-range coupling between the aldehyde and 4-hydrogen proton spins obtainable with strong rf. irradiation. The M-part spectrum reproduced in Fig. 5b was recorded with simultaneous irradiation at high rf. power of the aldehyde multiplet at 398 cps. It is seen that the lines in the decoupled spectrum all have the same width, and the M-part spectrum in Fig. 5d has the appearance of a slightly perturbed X-part spectrum of an ABX spin system.

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