

CALCULATION OF NUCLEAR MAGNETIC RESONANCE
SPECTRA IN THE PRESENCE OF EXCHANGING SPINS

abstract

The appearance of nuclear magnetic resonance spectra of systems of nuclei in which exchange of magnetic environment occurs, both for intra- and inter-molecular cases, has been related to the exchange rate, yielding methods whereby parameters of kinetic and thermodynamic interest may be easily obtained. Computer programs have been written for the IBM 7094 which compute the spectra for certain simple systems of exchanging nuclei.

I. EFFECT OF EXCHANGING NUCLEI ON THE APPEARANCE OF MAGNETIC RESONANCE SPECTRA: INTRAMOLECULAR EXCHANGE

INTRODUCTION

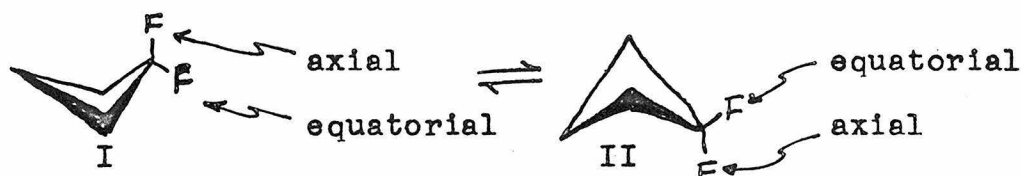
The modified form of the Arrhenius equation (1) is useful for obtaining activation energies. Its use depends on being able

$$k = AT^n e^{-E_a/RT} \quad (1)$$

to measure k at various temperatures and then making an appropriate plot whereby E_a can be obtained. Nuclear magnetic resonance (NMR) and electron paramagnetic resonance have been successfully employed to determine rate constants for rapid and reversible reactions by interpreting the spectrum as a function of k at different temperatures.¹

¹Frost and Pearson, Kinetics and Mechanism, John Wiley & Sons, Inc., New York (1961). (2nd edition) pg. 276

To see how this can be accomplished consider the following simple example:



It is a well known fact that cyclobutanes possess a "folded" config-

uration,² with conversion between the two identical forms occurring rapidly at room temperature. The effect of this inversion

²J.B. Lambert and J.D. Roberts, JACS, **85**, 3710 (1963).

in the case of 1,1 difluoro-cyclobutane is to exchange the magnetic environment of the axial and equatorial fluorines. At a low enough temperature the conversion between the two identical forms (I & II) takes place only very slowly. The NMR spectrum of the fluorines (with the protons being spin decoupled) is that of a typical AB system. It is convenient to define a mean lifetime, τ , of the molecule between exchanges which occur between the magnetic environments of the two fluorines. Obviously $k = 1/\tau$. Tau, along with the magnetic parameters obtained in the limit $\tau = \text{infinity}$, can be used to describe the resulting spectrum as the temperature is varied, giving rise to different exchange rates. For small values of tau (fast exchange) we would expect a single peak, representing the AB system being averaged to an A_2 system. Intermediate cases of exchange demonstrate what is appropriately termed exchange broadening. See figure 1.

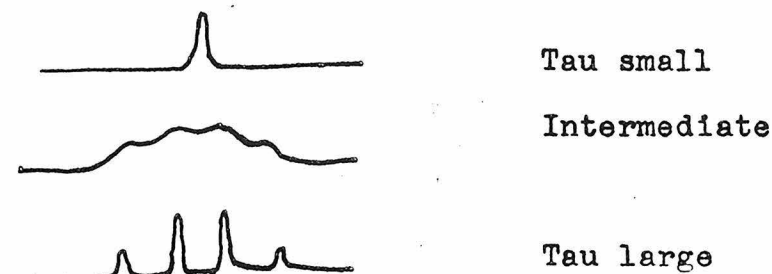


Figure 1

Inclusion of an exchange term in the Bloch equations has been considered by numerous authors³ and the investigation of the

³H.S. Gutowsky and C.H. Holm, J.Chem.Phys., **25**, 1228 (1956).
(and references cited in this article)

resulting influence on the spectrum has been carried out. This method is somewhat cumbersome if not unfeasible in its application to more than two uncoupled exchanging spins.

Recent treatments of the problem as suggested by Kaplan⁴ and developed in more detail by Alexander⁵ are based on a consideration of the motions of the nuclear spin-density matrix for the spin system.

⁴J.I. Kaplan, J.Chem.Phys., 29, 462 (1958).

⁵S.Alexander, J.Chem.Phys., 37, 967 (1962).

The treatment employed in (5) is basically that which is employed in this paper to calculate spectra as a function of the exchange rate. Another good reference to this work is the Ph.D. Thesis of Dr. G.M. Whitesides (1963), which contains a good review and interpretation of (5). (5) contains a number of errors which are corrected in this work. As an example of the method of calculation employed the AB case will be considered in detail.

THEORY AND CALCULATIONS: TWO EXCHANGING SPINS

The time variation of the density matrix is given by

$$\left(\frac{d\rho}{dt}\right)_{\sim} = \left(\frac{d\rho}{dt}\right)_{\sim \text{relaxation}} + \left(\frac{d\rho}{dt}\right)_{\sim \text{exchange}} + i[\rho, H] \quad (2)$$

where

$\left(\frac{d\rho}{dt}\right)_{\sim \text{relax.}}$ is a phenomenological term inserted to make the formulation consistent with the original Bloch equations.

$$\left(\frac{d\rho}{dt}\right)_{\sim \text{relax.}} = \frac{1}{T_1}(\rho_0 - \rho)_{\text{DIAGONAL TERMS}} - \frac{1}{T_2}(\rho)_{\text{OFF DIAGONAL TERMS}} \quad (3)$$

$\frac{1}{T_1}$ = rate constant for restoration of thermal equilibrium among the populations of the energy levels following a perturbation.

$\frac{1}{T_2}$ = rate constant for the process restoring the normal induced magnetization in the xy plane after a perturbation. (The primary magnetic field, H_0 , is taken in the z-direction, so the normal induced magnetization is zero in the xy plane.)

$\rho_0 = \rho$ at thermal equilibrium.

The exchange term is given by:

$$\left(\frac{d\rho}{dt}\right)_{\text{exchange}} = \frac{\rho_{\text{after exchange}} - \rho}{\tau} = \frac{\tilde{P}\tilde{P}^{-1}\rho - \rho}{\tau} = \frac{\tilde{P}\rho\tilde{P}^{-1} - \rho}{\tau} \quad (4)$$

where $\tilde{P}$ = exchange operator ($\tilde{P}\tilde{P}=1 \Rightarrow \tilde{P}=\tilde{P}^{-1}$)

For the basis functions we take (AB case):

$$\begin{aligned} \phi_1 &= \alpha\alpha & \phi_3 &= \beta\alpha \\ \phi_2 &= \alpha\beta & \phi_4 &= \beta\beta \end{aligned} \quad (5)$$

The effect of exchange is given by:

$$\begin{aligned} \tilde{P}\phi_1 &= \alpha\alpha = \phi_1 \\ \tilde{P}\phi_2 &= \beta\alpha = \phi_3 \\ \tilde{P}\phi_3 &= \alpha\beta = \phi_2 \\ \tilde{P}\phi_4 &= \beta\beta = \phi_4 \end{aligned} \Rightarrow \tilde{P}\phi = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \end{pmatrix} = \begin{pmatrix} \phi_1 \\ \phi_3 \\ \phi_2 \\ \phi_4 \end{pmatrix} \quad (6)$$

The Hamiltonian is written in a co-ordinate system rotating with angular frequency ω in the xy plane about the z axis.

$$\underline{H} = \underline{H}^{(0)} + \underline{H}^{(1)} + \underline{H}^{(*)} \quad (7)$$

$$\underline{H}^{(0)} = \sum_i \underline{I}_z(i) [\gamma H_0 (1 - \sigma(i)) - \omega] \quad (8)$$

$$\underline{H}^{(1)} = \sum_{i < j} J_{ij} \underline{I}_z(i) \cdot \underline{I}_z(j) \quad (9)$$

$$\underline{H}^{(*)} = \sum_i \gamma H_1 \underline{I}_x(i) \quad (10)$$

(7) is the total Hamiltonian. (8) describes the interaction of the spins with the static field. (9) describes the interaction of the spins with one another. (10) describes the interaction of the spins with the rotating field (which appears as a constant

vector in the rotating co-ordinate system). (10) is usually neglected in the calculation of magnetic resonance spectra.

Alexander⁵ has shown quite generally that to a good approximation we can take:

$$\langle \phi_k^* | [\rho, H^{(1)}] | \phi_j \rangle \cong \begin{matrix} \Delta M = M_j - M_k = +1 \\ + \\ 2C \langle \phi_k^* | \sum_i I_x(i) | \phi_j \rangle \\ \Delta M = -1 \end{matrix} \quad (11)$$

where $C = \gamma^2 \hbar H_0 H_1 / 2NKT$

The resulting spectrum is described by the Trace of $(I^+ \rho)$, this being the average value of the induced magnetization in the xy plane. For the AB case,

$$\text{Trace } (I^+ \rho) = \text{Tr}(I^+ \rho) = \rho_{21} + \rho_{31} + \rho_{42} + \rho_{43} \quad (12)$$

Performing the required manipulations we can relate these elements (12) by the following equations (the matrix equation (2) yields 16 linear equations):

$$\frac{d\rho_{21}}{dt} = \frac{\rho_{31} - \rho_{21}}{\tau} - \frac{\rho_{21}}{T_2} + i(-\Delta - \delta/2)\rho_{21} + i(-\gamma/2)\rho_{31} + iC = 0 \quad (13)$$

$$\frac{d\rho_{31}}{dt} = \frac{\rho_{21} - \rho_{31}}{\tau} - \frac{\rho_{31}}{T_2} + i(-\Delta + \delta/2 + \gamma/2)\rho_{31} + i(-\gamma/2)\rho_{21} + iC = 0 \quad (14)$$

$$\frac{d\rho_{42}}{dt} = \frac{\rho_{43} - \rho_{42}}{\tau} - \frac{\rho_{42}}{T_2} - i(\Delta - \delta/2 + \gamma/2)\rho_{42} + i(\gamma/2)\rho_{43} + iC = 0 \quad (15)$$

$$\frac{d\rho_{43}}{dt} = \frac{\rho_{42} - \rho_{43}}{\tau} - \frac{\rho_{43}}{T_2} - i(\Delta + \delta/2 + \gamma/2)\rho_{43} + i(\gamma/2)\rho_{42} + iC = 0 \quad (16)$$

Where

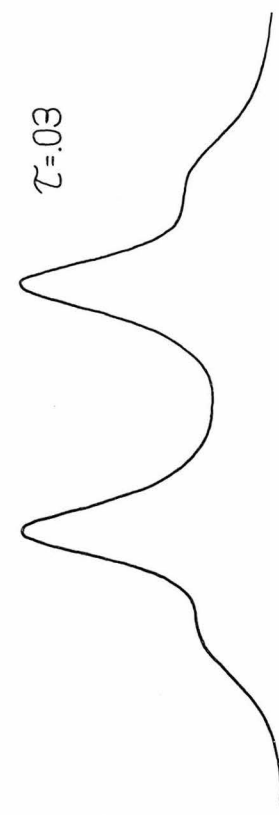
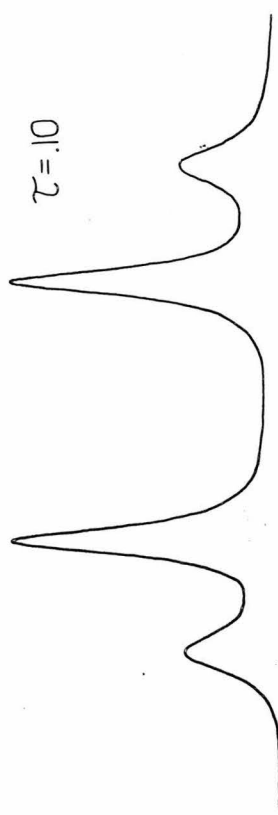
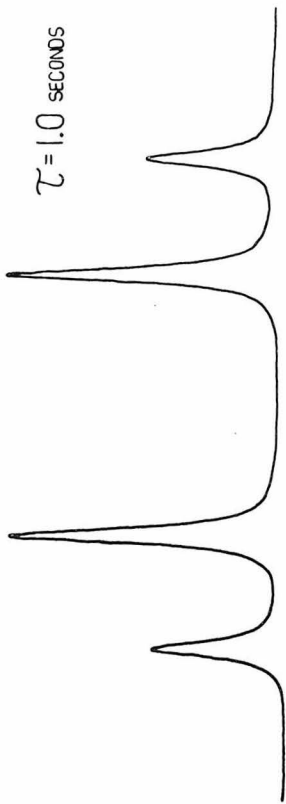
J = coupling between A and B

δ = $\gamma H_0 (\sigma(2) - \sigma(1))$

Δ = $\omega - \frac{\gamma H_0}{2} (2 - \frac{1}{2}\sigma(1) - \sigma(2))$

$\sigma(i)$ = nuclear shielding constant of nucleus i

If we assume that the spectrum is observed under conditions of slow passage we can set the LHS of the above equations (13-16) equal to zero and solve for the ρ_{ij} of interest. This has been done and the



$\Delta\nu_{AB} = 45.0$ cps
 $J_{AB} = 14.5$ cps

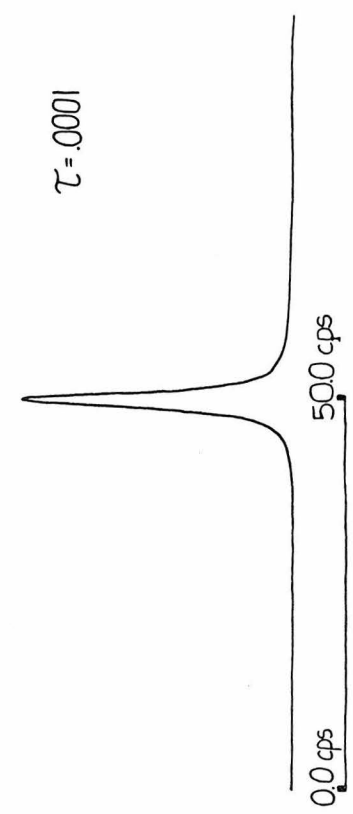
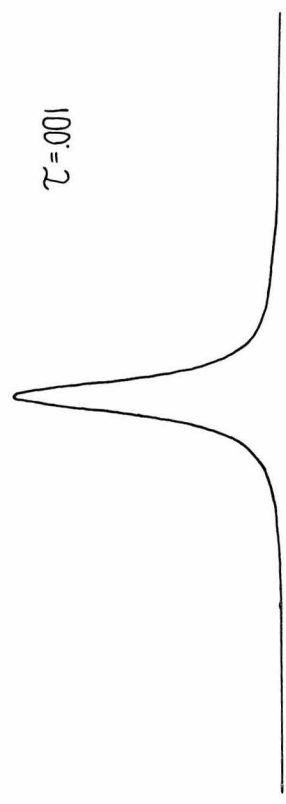
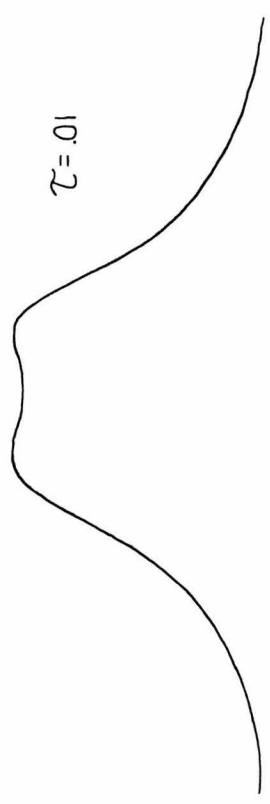


FIGURE 2. Effect of intramolecular exchange on a typical AB spectrum. The value of T_2 employed is .16 cps.

aid of an IBM 7094 computer has been enlisted to obtain plots of the spectra as a function of τ . Figure 2 illustrates the effect which exchanging nuclei have on the observed spectrum for the AB case. This program gives a method whereby kinetic data can be easily obtained. Isotopic substitution in conjunction with spin decoupling can reduce many exchange problems to the AB case. The possibility of including more spins in such a calculation is considered in the next section.

CALCULATIONS: THREE SPIN CASE - TWO EXCHANGING SPINS COUPLED TO A THIRD NUCLEUS

An attempt to calculate the full observed spectrum for three nuclei, two of which are exchanging, has been attempted, but with little success. The treatment was carried out for an ABC system with the A and B nuclei exchanging. The calculations follow the same general procedure as is outlined in the previous section. The initial calculations were done with the following basis set:

$$\begin{array}{ll} \phi_1 = \alpha\alpha\alpha & \phi_5 = \alpha\beta\beta \\ \phi_2 = \alpha\alpha\beta & \phi_6 = \beta\alpha\beta \\ \phi_3 = \alpha\beta\alpha & \phi_7 = \beta\beta\alpha \\ \phi_4 = \beta\alpha\alpha & \phi_8 = \beta\beta\beta \end{array} \quad (17)$$

The ρ_{jk} necessary to describe the spectrum can be calculated from the system of linear equations obtained from Alexander's treatment. The elements of the density matrix which describe the spectrum fall into three groups which may each be solved separately. The first consists of the ρ_{jk} which connect the $I_z = +3/2$ with the three $I_z = +1/2$ states. This constitutes three of the ρ_{jk} . Similarly the three ρ_{jk} elements which connect the $I_z = \pm 3/2$ with the $I_z = \pm 1/2$ state can be readily calculated. The nine elements of ρ which

connect the $I_z = \pm 1/2$ functions do not lend themselves readily to solution. To solve the nine equations it would be necessary to break up the ρ_{jk} into real and imaginary parts, thus yielding eighteen equations which would take the 7094 a minimum of 10 seconds and an average of about 15 seconds to solve using the available programs for the solution of linear equations. The minimum number of points for a good plot is between two and three hundred. Each spectrum thus would utilize about one hour of 7094 time (\$300) which would not be justified.

An attempt was made to select another basis set in which the calculations would be simpler. Ideally one would want the coefficient matrix for the system of linear equations obtained to come out diagonal, but this is generally not possible. It is possible, however, to reduce the number of off-diagonal elements in the coefficient matrix. This is done by using the basis set in which the functions are either symmetric or anti-symmetric with respect to the exchanging spins. This gives the exchange matrix a form which results in the $1/\tau$ dependence being entirely along the diagonal in the coefficient matrix. The basis functions for which this was done are the following:

$$\begin{aligned}
 \phi_1 &= \alpha\alpha\alpha & \phi_5 &= \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\beta \\
 \phi_2 &= \alpha\alpha\beta & \phi_6 &= \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)\beta \\
 \phi_3 &= \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)\alpha & \phi_7 &= \beta\beta\alpha \\
 \phi_4 &= \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\alpha & \phi_8 &= \beta\beta\beta
 \end{aligned} \tag{18}$$

While this basis set helps to simplify the equations somewhat it still does not permit an easy reduction of the system of 9 related equations connecting $I_z = \pm 1/2$. It is of no help to use the basis functions for which $\underline{H}$ is diagonal. This complicates the exchange matrix considerably.

The complete spectrum for the three spin case was thus not calculated. A program was written for the 7094 which calculates the three transitions between $I_z = +1/2$ and $I_z = +3/2$. It should be possible to obtain tau from the experimental spectra by consideration of these three transitions alone, as can be seen in the sample calculation given in figure 3. The upper spectra in figure 3 are calculated from basis set (17) using the following equations which were obtained from (2):

$$\begin{aligned} (-1/T_2 + i\Delta C + iJ'_{BC} + iJ'_{AC})\rho_{21} - iJ'_{BC}\rho_{31} - iJ'_{AC}\rho_{41} + iC &= 0 \\ -iJ'_{BC}\rho_{21} + (-1/T_2 - 1/T_2 + iJ'_{BC} + i\Delta_B + iJ'_{AB})\rho_{31} + (1/T_2 - iJ'_{AB})\rho_{41} + iC &= 0 \\ -iJ'_{AC}\rho_{21} + (1/T_2 - iJ'_{AB})\rho_{31} + (-1/T_2 - 1/T_2 + i\Delta_A + iJ'_{AB} + iJ'_{AC})\rho_{41} + iC &= 0 \end{aligned} \quad (19)$$

where

$$\begin{aligned} T_2(I^+ \rho) &= \rho_{21} + \rho_{31} + \rho_{41} \quad (\text{for the three transitions considered}) \\ \Delta A &= \omega - \omega_A \\ J'_{AB} &= J_{AB}/2 \end{aligned}$$

For groups of nuclei greater than three the calculations become impractical. It is possible, however, following approximations suggested in reference 5 to get information from the peak half-widths which yields the exchange rate.

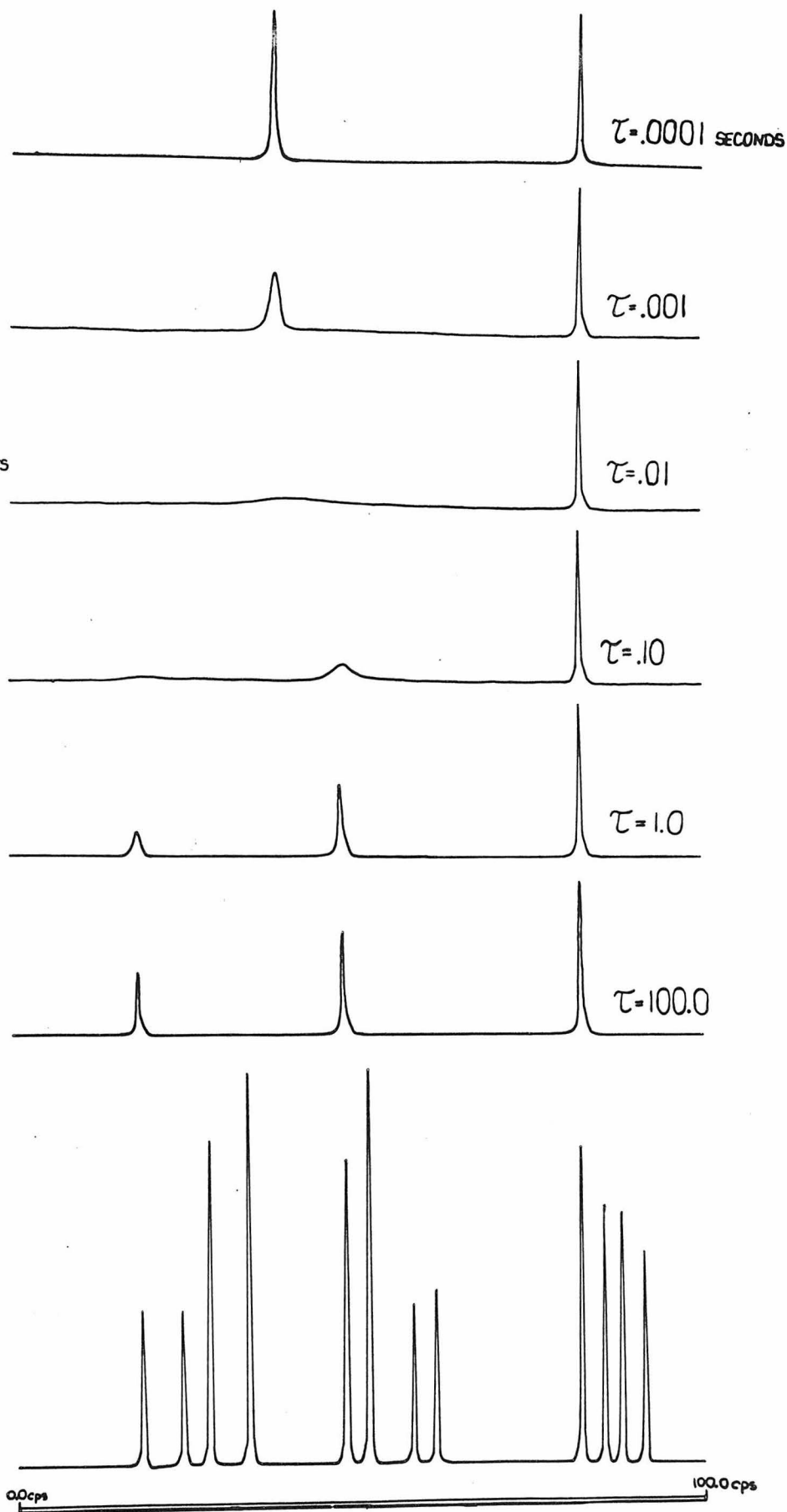
CALCULATION OF LINE WIDTHS OF NMR SPECTRA IN THE PRESENCE OF EXCHANGING SPINS

We can write the equation giving the time dependence of the density matrix describing an ensemble of interacting spins as a sum of three terms:

FIGURE 3

EFFECT OF NUCLEI EXCHANGE
ON THE THREE TRANSITIONS
BETWEEN THE $F_{\alpha} = +\frac{1}{2}$ AND
 $F_{\alpha} = -\frac{1}{2}$ STATES FOR A 3-SPIN
ABC SYSTEM IN WHICH A
AND B ARE EXCHANGING.
THE UPPER SPECTRA
REPRESENT THE THREE
 $F_{\alpha} = +\frac{1}{2}$ TO $F_{\alpha} = -\frac{1}{2}$ TRANSITIONS
FOR VARIOUS VALUES OF τ ,
THE PRE-EXCHANGE LIFETIME.
THE LOWER FIGURE IS THE
FULL SPECTRUM IN THE ABSENCE
OF EXCHANGE EFFECTS,
CALCULATED USING THE
FOLLOWING PARAMETERS:

CHEMICAL SHIFTS	COUPLING CONSTANTS
$\nu_A = 20.5 \text{ cps}$	$J_{AB} = 7.5 \text{ cps}$
$\nu_B = 40.7$	$J_{AC} = 4.6$
$\nu_C = 65.8$	$J_{BC} = 2.4$



$$\frac{d\rho}{dt} = i[\rho, H] + \left(\frac{d\rho}{dt}\right)_{\text{exchange}} + \left(\frac{d\rho}{dt}\right)_{\text{relaxation}} \quad (20)$$

In a rotating co-ordinate system this becomes:

$$\frac{d\rho}{dt} = \left\{ \frac{P\rho P - \rho}{T_1} \right\}_{\text{exchange}} + \left\{ \frac{\rho_0 - \rho}{T_1} \right\}_{\text{relaxation}} - \frac{\rho_{op}}{T_2} \quad (21)$$

where

$$+ i(\omega_0 - \omega) [\rho, \sum_j I_z(j)] + i[\rho, H_s] + i\omega_1 [\rho, \sum_j I_x(j)]$$

ω = angular frequency of rotation

$\omega_0 = \gamma H_0$

$\omega_1 = \gamma H_1$

$H_s = \sum_j \delta_j I_z(j) + \sum_{j < k} J_{jk} I(j) \cdot I(k)$ {measured in frequency units}

δ_j = chemical shift of nucleus j in the applied field H_0 .

Using this notation we can write the equation governing a single term, ρ_{mn} , of the density matrix. m and n are states of the system for which the magnetic quantum number (M) differs by unity. ρ_{mn} thus describes a transition of the system between states m and n with the transition energy being given by $\omega_{mn} = E_m - E_n$ (m and n are thus eigenstates of the system and H_s is diagonal). To find the equation for ρ_{mn} it is necessary to find $(P\rho P)_{mn}$. This is obtained by straightforward matrix multiplication and is given by

$$(P\rho P)_{mn} = \sum_{k,l} P_{mk} \rho_{kl} P_{ln} \quad (22)$$

The expression for $\frac{d\rho_{mn}}{dt}$ is then given by:

$$\frac{d\rho_{mn}}{dt} = +i(\omega_0 - \omega) \rho_{mn} + i\omega_{mn} \rho_{mn} + \left\{ \sum_{k,l} \frac{P_{mk} \rho_{kl} P_{ln} - \rho_{mn}}{T_1} \right\} - \frac{\rho_{mn}}{T_2} \quad (23)$$

The final term of (21), $i\omega_1 [\rho, \sum_j I_x(j)]$, has been omitted in the above equation as it is negligible in comparison to H_s . (This term is used as the driving term for a system of linear equations in the event that the LHS of (21) is considered approximately equal to zero.) In the limit of slow exchange, coalescence of lines does

not occur and broadening effects are observed. In the limit of slow exchange we can make approximations by considering the terms of the summation in (23). First we can factor out ρ_{mn} to get:

$$\sum_{k,l} P_{mk} \rho_{kl} P_{ln} = \rho_{mn} \left(\sum_{k,l} P_{mk} \frac{\rho_{kl}}{\rho_{mn}} P_{ln} \right) \quad (24)$$

Then we note that all of the non-zero elements of the exchange matrix must be between states which have the same magnetic quantum number. This is because exchange cannot effect a spin inversion which is necessary for a change in M. Thus the term will be non-zero only for ρ_{kl} in which k and l have the same magnetic quantum numbers as m and n, respectively. Such a ρ_{kl} would describe a transition between states of the same quantum number as ρ_{mn} . Since this would (considering the weak coupling case for simplicity) represent a different spin inversion than that for the transition described by ρ_{mn} we would expect ρ_{kl} to have a small amplitude in the neighborhood of ρ_{mn} . This amounts to assuming that $\tau |\omega_{mn} - \omega_{kl}| > 1$ and permits us to rewrite (24) as:

$$\sum_{k,l} P_{mk} \frac{\rho_{kl}}{\rho_{mn}} P_{ln} \approx P_{mm} P_{nn} \quad (25)$$

Using this in (23) we have:

$$\frac{d\rho_{mn}}{dt} = - \left[-i(\omega_0 - \omega + \omega_{mn}) + \frac{1 - P_{mm}P_{nn}}{\tau} + \frac{1}{T_2} \right] \rho_{mn} \quad (26)$$

(26) describes a line with resonance at $\omega_0 + \omega_{mn}$ and with an effective relaxation time given by

$$\left(\frac{1}{T_2} \right)_{\text{eff.}} = \left\{ \frac{1 - P_{mm}P_{nn}}{\tau} + \frac{1}{T_2} \right\} \quad (27)$$

The density matrix treatment gives the same result as the Bloch equations, and describes the transitions with lines of Lorentzian shape.⁶ The half width for a Lorentzian line shape function

⁶See Pople, Schneider, and Bernstein, High Resolution NMR, page 37 for a discussion of the line shapes derived from the Bloch formulation.

is given by

$$(\Delta\omega)_{1/2} = \frac{1}{\pi T_2)_{eff}}$$

where $(\Delta\omega)_{1/2}$ is the width at half height (in cps) and

$T_2)_{eff}$ is the effective relaxation time in seconds.

Thus we have

$$(\Delta\omega)_{1/2} = \frac{1}{\pi} \left(T_2 + \frac{1 - P_{mm}P_{nn}}{\tau} \right) \quad (28)$$

and knowing the half width we can calculate tau. T_2 can be eliminated by calculating $P_{mm}P_{nn}$ for different transitions. The problem of obtaining tau thus reduces to the problem of calculating the exchange matrix P for the representation in which the Hamiltonian (H_s) is diagonal.

The exchange matrix in the representation of I_z has already been calculated and is given by:

$$P = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad (29)$$

To calculate the exchange matrix in the case of the representation in which H_s is diagonal (designated by P') we must first diagonalize the Hamiltonian and then obtain the eigenvectors for the problem.

The widely used NMRIT computer program written by Dr. J.D. Swalen to calculate complex NMR spectra can give us just the matrix we need. It performs the following operation on the Hamiltonian in the representation of I_z :

$$\tilde{S}^{-1} \tilde{H} \tilde{S} = \tilde{\Lambda} \text{ where}$$

$$H_{jk} = \langle \phi_j^* | H_S | \phi_k \rangle$$

$$H_S = \text{Hamiltonian} = H^{(0)} + H^{(1)}$$

$\tilde{S}$ = transformation matrix. Its columns will be eigenvectors of H_S .

$\tilde{\Lambda}$ = diagonal matrix in which the elements are the stationary state energies of the system.

Since $\tilde{P}$ transforms in the same way as does $\tilde{H}$ we have:

$$\tilde{P}' = \tilde{S}^{-1} \tilde{P} \tilde{S} \quad (30)$$

To check the assumptions involved the AB case is again considered as an example:

$$\phi = \begin{pmatrix} \alpha & \alpha \\ \alpha & \beta \\ \beta & \alpha \\ \beta & \beta \end{pmatrix} \quad S = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta & 0 \\ 0 & \sin \theta & \cos \theta & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad (31)$$

$$\theta \text{ is defined by } \sin 2\theta = \frac{J_{AB}}{\sqrt{D_{AB}^2 + J_{AB}^2}}$$

Then, since S is Hermetian and normalized, we have

$$S^{-1} = \tilde{S} \quad (\text{transpose of } S)$$

yielding

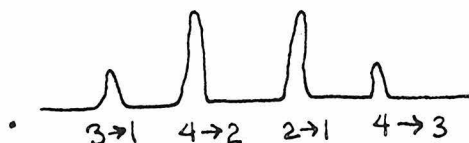
$$\tilde{P}' = \begin{pmatrix} 1 & & & \\ & \cos \theta & \sin \theta & \\ & -\sin \theta & \cos \theta & \\ & & & 1 \end{pmatrix} \begin{pmatrix} 1 & & & \\ & 0 & 1 & \\ & 1 & 0 & \\ & & & 1 \end{pmatrix} \begin{pmatrix} 1 & & & \\ & \cos \theta & -\sin \theta & \\ & \sin \theta & \cos \theta & \\ & & & 1 \end{pmatrix} = \begin{pmatrix} 1 & & & \\ & 2\sin \theta \cos \theta & \cos^2 \theta - \sin^2 \theta & \\ & \cos^2 \theta - \sin^2 \theta & -2\cos \theta \sin \theta & \\ & & & 1 \end{pmatrix} \quad (32)$$

For the broadening of ρ_{mn} (describing the $m \rightarrow n$ transition) we calculate $\frac{1 - \rho_{mm} \rho_{nn}}{\tau}$:

ρ_{mn}	$\frac{1 - P_{mm}P_{nn}}{\tau}$
$4 \rightarrow 3$	$\frac{1 + 2 \sin \theta \cos \theta}{\tau}$
$2 \rightarrow 1$	$\frac{1 - 2 \sin \theta \cos \theta}{\tau}$
$4 \rightarrow 2$	$\frac{1 - 2 \sin \theta \cos \theta}{\tau}$
$3 \rightarrow 1$	$\frac{1 + 2 \sin \theta \cos \theta}{\tau}$

(33)

The numbering of transitions as related to the spectrum is as follows:



The outside peaks broaden faster than the inner peaks. This agrees with what is experimentally observed in spectra when A and B are exchanging. The expression for the half width given above (28) has been used to calculate tau from a set of spectra which were computed from the complete treatment of the AB case (equations 13 - 16). The results are tabulated in TABLE I, along with the tau calculated using Gutowsky's³ formula which relates the peak positions to exchange rates.

The Gutowsky and Holm³ method (derived from the Bloch equations) states the following:

$$\nu_e = \frac{1}{2\pi \tau} \sqrt{4\pi^2 \nu^2 \tau^2 - 8} \quad (34)$$

where

ν_e = observed difference in chemical shifts

ν = difference in chemical shifts in absence of exchange

τ has units of seconds

ν is in cps

TABLE I

CALCULATION OF TAU VALUES FROM COMPUTED SPECTRA^a

Tau used to compute spectrum (seconds)	Tau calculated from spectrum by Gutowsky-Holm equation. (seconds)	Peak half widths		Tau calculated from half widths	
		2→1 (cps)	4→3 (cps)	2→1 (seconds)	4→3 (seconds)
.05	.043	2.65	4.36	.044	.050
.07	.067	1.85	3.36	.064	.066
.10	.097	1.32	2.35	.094	.096
.20	.37	.71	1.22	.198	.196
.50	b	.38	.59	.495	.490

- a) Parameters used were $\Delta\nu_{AB} = 30.0$ cps $J_{ab} = 10.0$ cps $T_2 = 1.$ sec.
- b) Could not be calculated. This method breaks down except for a short range of tau when the peaks are collapsing.

Outside of this range (for tau less than .05) the lines collapsed and the half widths could not be measured. For tau greater than 1.00 it would not be possible to calculate the half widths very accurately, and the Gutowsky-Holm method also breaks down, as noted in footnote (b) above. The applicability of the half-width method of obtaining exchange rates is not limited to two nuclei, but is easily extended to any number of nuclei with (30). There is no problem with viscous broadening or absence of relaxation data, provided that the exchange broadening is a factor of two or so larger than other effects. Line widths due to relaxation, viscous broadening, etc., can be approximated as the same for all transitions. Then, choosing two peaks which have different broadening ($\frac{1-P_{mm}P_{nn}}{\tau}$), the natural line widths could be eliminated from equation (28) and

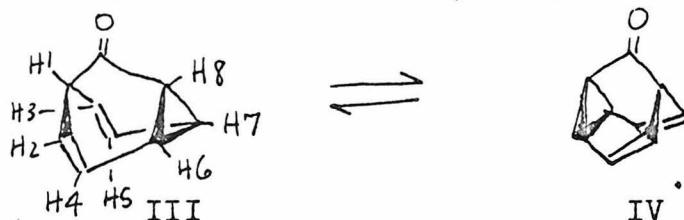
tau calculated.

A computer program is presently being written to calculate $S^{-1}PS$. P is being considered for a general type of exchange:

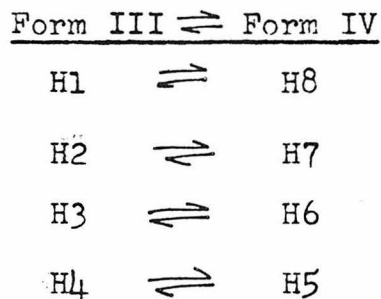
$$P_{\text{total}} = \prod_{i,j \text{ pairs}} P_{ij}$$

P_{ij} = exchange operator for nuclei pair i,j

As a possible example for the application of this general program, consider the degenerate Cope rearrangement of tricyclo (3.3.1.0^{4,6}) nona-2,7-diene-9-one (barbaralone, III).



The exchange of magnetic environment which occurs is as follows:



Tau could thus be calculated for barbaralone at different temperatures and the activation energy computed.

II. EFFECT OF EXCHANGING NUCLEI ON THE APPEARANCE OF MAGNETIC RESONANCE SPECTRA: CHEMICAL EXCHANGE

INTRODUCTION

The problem of interpreting features of magnetic resonance spectra with more than one molecular species in the sample being considered is further complicated by exchange of nuclei between two or more species or between non-equivalent sites in a single species (chemical exchange). A number of different simple cases where chemical exchange occurs are listed in TABLE II.

TABLE II
DIFFERENT CASES OF CHEMICAL EXCHANGE

CASE	CONDITIONS	EXAMPLE
I	Chemical exchange between two species, neither of which is coupled to other spins ^a	$R-OH \rightleftharpoons H^+$
II	Chemical exchange between two molecules of the same species, the exchanging nucleus not coupled with the rest of the molecule	$\begin{array}{c} R-OH \\ \uparrow \downarrow \\ H^+ \end{array}$
III	Same as I except the exchanging nucleus is coupled to a second nucleus at one of the sites	$\begin{array}{c} R \\ \\ H-C-OH \\ \\ R' \end{array} \quad \uparrow \downarrow \quad H^+ \quad \text{or} \quad \begin{array}{c} R \\ \\ N^H-H \\ \\ R' \end{array} \quad \uparrow \downarrow \quad H^+$
IV	Same as II except the exchanging nucleus is coupled to a second nucleus	$\begin{array}{c} R \\ \\ H-C-OH \\ \\ R' \end{array} \quad \uparrow \downarrow \quad \begin{array}{c} R \\ \\ H-C-H \\ \\ R' \end{array} \quad \text{or} \quad \begin{array}{c} R \\ \\ N-H \\ \\ R' \end{array} \quad \uparrow \downarrow \quad \begin{array}{c} R \\ \\ N-H \\ \\ R' \end{array}$
V	Intramolecular chemical exchange between several sites in the same molecule	$\begin{array}{c} OH \cdots O \\ \diagdown \quad \diagup \\ CH_3-C \quad C-CH_3 \\ \quad \quad \quad \\ \quad \quad \quad H \end{array}$

a) R and R' are groups which either contain nuclei which are not coupled to the system of interest, or by appropriate experiments can have their influence removed from the spectrum.

Cases I and II are best treated by the modified Bloch equations proposed by McConnell⁷ and discussed in most of the recent literature on the applications of magnetic resonance (see for instance ref. 6, pg. 218). As has been mentioned the solution of the modified Bloch

⁷H.M. McConnell, J.Chem. Phys., 28, 430 (1958)

equations becomes somewhat involved with more than two sites. In a series of recent papers by S. Forsen and R.A. Hoffman⁸ a method^{is discussed} for

⁸S. Forsen and Ragnar A. Hoffman, J.Chem.Phys., 39, 2892 (1963) and 40, 1189 (1964).

obtaining rate constants for exchange of type V by saturating signals of nuclei at one site, and relating the recovery time of the signal at other sites to the relaxation time, which is in turn related to the exchange rate of nuclei between the two sites. For exchange of type III and IV, where coupling exists, a theory similar in many respects to that employed in the calculations for intra-molecular exchange has also been developed by Alexander.⁹

⁹S.Alexander, J.Chem.Phys., 37, 974 (1962).

The application of the method which is put forth in (9) has been employed to calculate the spectra for exchange of type III and IV. Kaplan^{4,10}

¹⁰J. Kaplan, J.Chem.Phys., 28, 278 (1958).

has also treated the problem of chemical exchange for case IV making the assumption that the concentration of the single species is much larger than the concentration of the species containing the two coupled nuclei. His method involves a solution of the density matrix equation, but he is in many ways less straightforward in his

treatment than is Alexander⁹, especially with regards to the inclusion of relaxation effects which are responsible for the line shapes in the absence of exchange. The general method of calculation will first be given, and then applications of the method which have been made to two cases of chemical interest will be discussed. The treatment given here differs slightly from that in (9) with the hope of making the procedure a little clearer, especially for the chemist whose background in quantum mechanics is not as wide as is necessary to be able to interpret Alexander's work. In some ways the treatment given here is more general than that in (9), where in order to use the relationships derived one must work in the representation of I_z .

THEORY

We will consider two species in solution. The extension to more than two species is straightforward, though not highly practical. Each of the species in solution is described by a separate density matrix (in the notation used here a superscript to the right of a quantity describes the species which that quantity is related to):

$$\begin{aligned} \text{Species 1} & - \rho^1 \\ \text{Species 2} & - \rho^2 \end{aligned} \tag{35}$$

We assume that some part of species 1 is exchanging reversibly with some part of system 2 in such a manner as to leave the configuration of both species unchanged following an exchange. We define τ^1 and τ^2 , the correlation times for species 1 and 2, respectively. τ^1 and τ^2 are related to the relative concentrations of species 1 (C^1) and species 2 (C^2) in the following manner:

$$\frac{\tau^1}{\tau^2} = \frac{C^1}{C^2} \tag{36}$$

The equations describing the time dependence of the density matrices

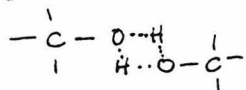
can again be described as in the previous section:

$$\frac{d\rho^1}{dt} = i[\rho^1, H^1] + \left(\frac{d\rho^1}{dt}\right)_{\text{exchange}} + \left(\frac{d\rho^1}{dt}\right)_{\text{relaxation}} \quad (37)$$

$$\frac{d\rho^2}{dt} = i[\rho^2, H^2] + \left(\frac{d\rho^2}{dt}\right)_{\text{exchange}} + \left(\frac{d\rho^2}{dt}\right)_{\text{relaxation}} \quad (38)$$

The commutator relationships and the relaxation terms are evaluated in the same fashion as for intramolecular exchange with the exception that species 1 has its characteristic relaxatimes (T_1^1 & T_2^1) which may or may not be the same as those for species 2.

The treatment of chemical exchange differs from that of intramolecular exchange only in that the form of the exchange matrix is now more complicated. At the point of exchange, for instance,



we have a "collision complex" of species 1 and 2. This complex can be described by taking the direct product of the two density matrices. The formalism of the direct product is simply a method whereby all of the states of the complex can be represented as products of the states of the two species. Supposing we have

$$\rho^1 = \begin{pmatrix} \rho_{11}^1 & \rho_{12}^1 & \rho_{13}^1 & \rho_{14}^1 \\ \rho_{21}^1 & \rho_{22}^1 & \rho_{23}^1 & \rho_{24}^1 \\ \rho_{31}^1 & \rho_{32}^1 & \rho_{33}^1 & \rho_{34}^1 \\ \rho_{41}^1 & \rho_{42}^1 & \rho_{43}^1 & \rho_{44}^1 \end{pmatrix} \quad (39)$$

and

$$\rho^2 = \begin{pmatrix} \rho_{11}^2 & \rho_{12}^2 \\ \rho_{21}^2 & \rho_{22}^2 \end{pmatrix} \quad (40)$$

then for $\rho^1 \times \rho^2$, the direct product of ρ^1 with ρ^2 we have

$$\rho^1 \times \rho^2 = \begin{pmatrix} \rho_{11}^1 \times \rho^2 & \rho_{12}^1 \times \rho^2 & \dots & \rho_{14}^1 \times \rho^2 \\ \rho_{21}^1 \times \rho^2 & \dots & \dots & \dots \\ \vdots & \dots & \dots & \dots \\ \rho_{41}^1 \times \rho^2 & \dots & \dots & \rho_{44}^1 \times \rho^2 \end{pmatrix} \quad (41)$$

where $\rho_{ij}^1 \times \rho^2$ = direct product of ρ_{ij}^1 with ρ^2 . Since ρ_{ij}^1 is one dimensional, we have simply:

$$\rho_{ij}^1 \times \rho^2 = \begin{pmatrix} \rho_{ij}^1 \rho_{11}^2 & \rho_{ij}^1 \rho_{12}^2 \\ \rho_{ij}^1 \rho_{21}^2 & \rho_{ij}^1 \rho_{22}^2 \end{pmatrix}$$

As can be seen the result of the direct product of an $n \times n$ matrix with an $m \times m$ matrix is a third matrix with dimensions $nm \times nm$.

The basis functions for the two systems are given by

Species 1 - φ^1

Species 2 - φ^2

We have for the basis functions of the collision complex, then,

$\varphi^1 \times \varphi^2$. If $\varphi^1 = \begin{pmatrix} \phi_1^1 \\ \phi_2^1 \\ \phi_3^1 \\ \phi_4^1 \end{pmatrix}$ and

$\varphi^2 = \begin{pmatrix} \phi_1^2 \\ \phi_2^2 \end{pmatrix}$

then

$$\varphi^1 \times \varphi^2 = \begin{pmatrix} \phi_1^1 \times \begin{pmatrix} \phi_1^2 \\ \phi_2^2 \end{pmatrix} \\ \phi_2^1 \times \begin{pmatrix} \phi_1^2 \\ \phi_2^2 \end{pmatrix} \\ \phi_3^1 \times \begin{pmatrix} \phi_1^2 \\ \phi_2^2 \end{pmatrix} \\ \phi_4^1 \times \begin{pmatrix} \phi_1^2 \\ \phi_2^2 \end{pmatrix} \end{pmatrix} = \begin{pmatrix} \phi_1^1 \phi_1^2 \\ \phi_1^1 \phi_2^2 \\ \phi_2^1 \phi_1^2 \\ \vdots \\ \phi_4^1 \phi_2^2 \end{pmatrix}$$

Any matrix which defines some aspect of the collision complex is defined on the basis set $\varphi^1 \times \varphi^2$. We will later do this with the exchange matrix P.

Consider the nature of the density matrices with which we are working. The high temperature limit of the thermal equilibrium value of the density matrix is given by:

$$\rho_0 = \exp \left\{ -\frac{\hat{H}}{kT} \right\} / \text{Tr} \exp \left\{ -\frac{\hat{H}}{kT} \right\} \quad (44)$$

$\exp \left\{ -\frac{\hat{H}}{kT} \right\}$ is a matrix with $\left\{ \exp \left(-\frac{\hat{H}}{kT} \right) \right\}_{ij}$ being calculated by expanding the exponential in a power series and evaluating it between states i and j .¹¹

¹¹ Slichter, Principles of Magnetic Resonance, presents a discussion of exponential operators on page 23.

We can expand the numerator and denominator of (44) in a power series:

$$\rho_0 = \frac{\underline{\epsilon} - \frac{\hat{H}}{kT} + \frac{1}{2!} \left(\frac{\hat{H}}{kT} \right)^2 - \dots}{\text{Trace} \left\{ \underline{\epsilon} - \frac{\hat{H}}{kT} + \frac{1}{2!} \left(\frac{\hat{H}}{kT} \right)^2 - \dots \right\}} \quad (45)$$

where $\underline{\epsilon}$ = a unit matrix of the same dimensions as ρ_0 . In the high temperature limit, we have:

$$\hbar H \ll kT \quad (\text{measuring } H \text{ in frequency units})$$

Thus

$$\text{Trace} \left\{ \underline{\epsilon} - \frac{\hat{H}}{kT} + \dots \right\} \approx \text{Trace}(\underline{\epsilon}) = N$$

where N = order of $\underline{\epsilon}$. Then

$$\rho_0 = \frac{\underline{\epsilon}}{N} - \frac{\hat{H}}{NkT} + \text{higher order terms} \quad (46)$$

The off diagonal elements of the density matrix (non-thermal equilibrium) are small deviations from unity such that we can write, quite generally,

$$\rho = \frac{\underline{\epsilon}}{N} + \rho' \quad (47)$$

We note that $\underline{\epsilon}$ commutes with the Hamiltonian, such that

$$[\rho, H] = \frac{1}{N} [\rho', H] \quad (48)$$

Also, since ϵ/N is a constant, irrespective of time,

$$\frac{d\rho}{dt} = \frac{1}{N} \frac{d^+ \rho}{dt} = \frac{1}{N} [\rho, H] + \left(\frac{d\rho}{dt} \right)_{exc} + \left(\frac{d\rho}{dt} \right)_{relax} \quad (49)$$

We are now in a position to consider the form of the exchange term. $\rho_1 \times \rho_2$, as we have noted, describes the collision complex.

In terms of the expanded density matrices, this is taken as:

$$\rho_1 \times \rho_2 = \left(\frac{\epsilon^1}{N^1} + \frac{\rho^1}{N^1} \right) \times \left(\frac{\epsilon^2}{N^2} + \frac{\rho^2}{N^2} \right) = \frac{1}{N^1 N^2} (\epsilon^1 \times \epsilon^2 + \epsilon^1 \times \rho^2 + \rho^1 \times \epsilon^2 + \dots) \quad (50)$$

We again want $\left(\frac{d\rho}{dt} \right)_{exc}$ to be of the form:

$$\left(\frac{d\rho}{dt} \right)_{exchange} = \frac{\rho^1(\text{after exchange} - \rho^1)}{\tau^1} \quad (51)$$

$$\left(\frac{d\rho^2}{dt} \right)_{exchange} = \frac{\rho^2(\text{after exchange} - \rho^2)}{\tau^2} \quad (52)$$

Since we have $\rho^1 \times \rho^2$ to describe the collision complex we must consider the effect of exchange on $\rho^1 \times \rho^2$:

$$(\rho^1 \times \rho^2)_{\text{after exchange}} = P(\rho^1 \times \rho^2) \quad (53)$$

where

$$P_{ij} = ([\rho^1 \times \rho^2]_i^* | \hat{P} | [\rho^1 \times \rho^2]_j) \quad (54)$$

P exchanges the spin functions of the nuclei which participate in the exchange process. Then, since $\rho^1 \times \rho^2$ is defined on $\underline{\rho^1} \times \underline{\rho^2}$, we have

$$\begin{aligned} (\rho^1 \times \rho^2)_{\text{after exchange}} &= P(\rho^1 \times \rho^2)P \\ &= P(\epsilon^1 \times \epsilon^2 + \epsilon^1 \times \rho^2 + \rho^1 \times \epsilon^2)P \end{aligned} \quad (55)$$

+ higher order terms

Species 1, following collision and exchange with species 2, becomes independent of species 2. The exchange process can be simply considered as exchanging the spin functions of the parts of species 1 and 2 which exchange with each other. The probability of finding species 1 in some given state following exchange depends on the statistical appearance of that state (considering the exchanging part of the molecule only) in molecule 2. Thus, following exchange we must average the final states of species 1 over all of the states of species 2 (and vice versa). Using the contraction operator Ω defined by Alexander, then, we have:

$$\begin{aligned} (\rho^1)_{\text{aft. exchange}} &= \Omega^2 (P \rho_1 \times \rho_2 P) \\ (\rho^2)_{\text{aft. exchange}} &= \Omega' (P \rho_1 \times \rho_2 P) \end{aligned} \quad (56)$$

The Ω^2 & Ω' are defined such that they average the final states of species 1 and 2, respectively, over all of the states of 2 and 1, respectively:

$$(\rho^1)_{\varphi_i^1 \varphi_j^1} (\text{after exchange}) \equiv \langle \varphi_i^1 | \Omega^2 (P \rho^1 \times \rho^2 P) | \varphi_j^1 \rangle \quad (57)$$

Performing the averaging, we have:

$$\langle \varphi_i^1 | \Omega^2 (P \rho^1 \times \rho^2 P) | \varphi_j^1 \rangle = \frac{\sum_{\varphi_k^2} \langle \varphi_i^1 \varphi_k^2 | P \rho^1 \times \rho^2 P | \varphi_j^1 \varphi_k^2 \rangle}{\sum_{\varphi_k^2} \langle \varphi_k^2 | \rho^2 | \varphi_k^2 \rangle} \quad (58)$$

$$\text{where } T_n(\rho^2) = \sum_{\varphi_k^2} \langle \varphi_k^2 | \rho^2 | \varphi_k^2 \rangle = 1 \quad (\text{by assumption of normalization of the matrix}) \quad (59)$$

$\langle \varphi_i^1 \varphi_k^2 | P \rho^1 \times \rho^2 P | \varphi_j^1 \varphi_k^2 \rangle$ is merely the matrix element of $P \rho^1 \times \rho^2 P$ between states $\varphi_i^1 \varphi_k^2$ & $\varphi_j^1 \varphi_k^2$ in the space of $\varphi^1 \times \varphi^2$. Summing this over the φ_k^2 is the same as taking a "partial trace" and acts to decompose the direct product. Taking the trace over the φ^2 decomposes the direct product into the representation of φ^1 . Likewise, taking the trace over

the ψ^1 decomposes the direct product into the representation of ψ^2 . This decomposition does not involve any more work than adding up the appropriate elements of the transformed direct product, $P\rho^1 \times \rho^2 P$, but is perhaps best explained by the two examples in the next sections. The traces are defined simply as

$$T_n^2(\rho^1 \times \rho^2 P) = \sum_{i,j,k} \langle \psi_i^1 \psi_k^2 | P \rho^1 \times \rho^2 P | \psi_j^1 \psi_k^2 \rangle = (\rho^1)_{\psi_i^1 \psi_j^1} \text{ (after exchange)} \quad (60)$$

or in matrix notation as:

$$\begin{aligned} \rho^1 \text{ (after exchange)} &= T_n^2(P\rho^1 \times \rho^2 P) \\ \rho^2 \text{ (after exchange)} &= T_n^1(P\rho^1 \times \rho^2 P) \end{aligned} \quad (61)$$

Putting everything together gives for the exchange term:

$$\left(\frac{d\rho^1}{dt} \right)_{\text{exchange}} = \frac{T_n^2(P\rho^1 \times \rho^2 P) - \rho^1}{\tau} = \frac{\frac{1}{N^2} T_n^2(P[\rho^1 \times \epsilon^2 + \epsilon^1 \times \rho^2 + \epsilon^1 \times \epsilon^2]P) - \rho^1}{\tau^1}$$

But $T_n^2(P\epsilon^1 \times \epsilon^2 P) = N^2 \epsilon^1$, so

$$\begin{aligned} \left(\frac{d\rho^1}{dt} \right)_{\text{Exchange}} &= \frac{1}{N^2} \frac{T_n^2[P(\rho^1 \times \epsilon^2 + \epsilon^1 \times \rho^2)P] - \rho^1}{\tau^1} \\ \left(\frac{d\rho^2}{dt} \right)_{\text{Exchange}} &= \frac{\frac{1}{N^2} T_n^1[P(\rho^1 \times \epsilon^2 + \epsilon^1 \times \rho^2)P] - \rho^2}{\tau^2} \end{aligned} \quad (62)$$

The relaxation terms are given by:

$$\begin{aligned} \left(\frac{d\rho^1}{dt} \right)_{\text{relax.}} &= \left\{ \frac{\rho_0^1 - \rho^1}{T_1^1} \right\} - \left\{ \rho^1 \left[\frac{1}{T_2^1} - \frac{1}{T_1^1} \right] \right\} \\ &= \left\{ \frac{\rho_0^1 - \rho^1}{N^1 T_1^1} \right\}_{\text{Diag}} - \left\{ \frac{\rho^1}{N^1 T_2^1} \right\}_{\text{off Diag.}} \end{aligned} \quad (63)$$

(and similarly for $\left(\frac{d\rho^2}{dt} \right)_{\text{relax}}$)

We can now write the overall equations for the density matrices:

$$N^1 \frac{d\rho^1}{dt} = \frac{d^+\rho^1}{dt} = i[\rho^1, H^1] + \frac{T_1^2}{N^2} \underbrace{[P^+\rho^1 \epsilon^2 P + P\epsilon^1 x^+\rho^2 P]}_{\tau^1} - \rho^1 + \left(\frac{\rho_0^1 - \rho^1}{T_1^1} \right)_{\text{DIAG}} - \left(\frac{\rho^1}{T_2^1} \right)_{\text{OFF DIAG}} \quad (64)$$

$$N^2 \frac{d\rho^2}{dt} = \frac{d^+\rho^2}{dt} = i[\rho^2, H^2] + \frac{T_2^1}{N^1} \underbrace{[P^+\rho^1 \epsilon^2 P + P\epsilon^1 x^+\rho^2 P]}_{\tau^2} - \rho^2 + \left(\frac{\rho_0^2 - \rho^2}{T_1^2} \right)_{\text{DIAG}} - \left(\frac{\rho^2}{T_2^2} \right)_{\text{OFF DIAG}} \quad (65)$$

Henceforth the superscript + will be dropped, but it must be remembered that we have

$$\begin{aligned} \rho^1 &= \epsilon^1/N^1 + \rho^1/N^1 \\ \rho^2 &= \epsilon^2/N^2 + \rho^2/N^2 \end{aligned} \quad (66)$$

so that the total magnetization induced in the xy plane is given

$$\text{by } C_1 \overline{\langle I_{x+iy} \rangle^1} + C_2 \overline{\langle I_{x+iy} \rangle^2} = C_1 T_1 \left(I^+ \left\{ \frac{\epsilon^1}{N^1} + \frac{\rho^1}{N^1} \right\} \right) + C_2 T_2 \left(I^+ \left\{ \frac{\epsilon^2}{N^2} + \frac{\rho^2}{N^2} \right\} \right) \quad (67)$$

and since I^+ has no diagonal elements,

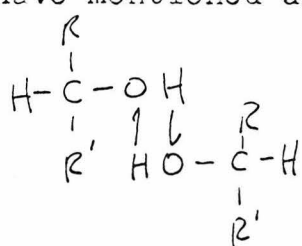
$$= \frac{C_1}{N^1} T_1 (I^+ \rho^1) + \frac{C_2}{N^2} T_2 (I^+ \rho^2)$$

Thus the $1/N^1$ and $1/N^2$ appear as scaling factors. The C^1 and C^2 (concentrations of the species) appear also as obvious scaling factors.

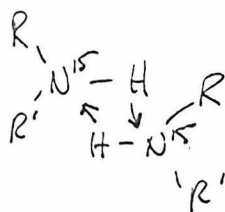
CALCULATIONS: I. CHEMICAL EXCHANGE OF ONE NUCLEUS COUPLED TO A SECOND BETWEEN MOLECULES OF THE SAME SPECIES

This is the simplest case involving coupling which can be treated by the above equations, since it involves solving only one of the equations (64 & 65). Examples of this type of exchange

which have^{been} mentioned are:



and



(R & R' are not coupled to the observed system)

We have in this problem:

$$\rho' = \rho^2 \equiv \rho$$

$$\tau' = \tau^2$$

Thus we can write (with primes indicating one of the two identical molecules):

$$\frac{d\rho}{dt} = i[\rho, H] + \frac{T_2'}{N'} \frac{[P(\rho' \times \epsilon + \epsilon' \times \rho)P] - \rho}{\tau} \quad (69)$$

$$+ \left(\frac{P_0 - P}{T_1} \right)_{\text{DIAG}} - \left(\frac{P}{T_2} \right)_{\text{OFF DIAG}}$$

Aside from the exchange term this equation (69) has the

same appearance as the intramolecular AB exchange problem. The exchange term can be obtained as follows. We use the same basis set as in the AB intramolecular problem:

$$\begin{array}{ll} \phi_1 = \alpha\alpha & \phi_3 = \beta\alpha \\ \phi_2 = \alpha\beta & \phi_4 = \beta\beta \end{array} \quad (70)$$

Assume that nucleus 1 ($\phi_1 = \alpha(1)\alpha(2)$) is exchanging between the primed and unprimed molecules. For $\phi \times \phi$ we have:

$$\phi \times \phi = \begin{pmatrix} \alpha\alpha\alpha\alpha \\ \alpha\alpha\alpha\beta \\ \alpha\alpha\beta\alpha \\ \vdots \\ \beta\beta\beta\beta \end{pmatrix} = \begin{pmatrix} \Theta_1 \\ \Theta_2 \\ \vdots \\ \Theta_{16} \end{pmatrix} \quad (71)$$

The effect of the exchange operator can be readily seen:

$$\begin{aligned} P_{39} &= (\Theta_3 | P | \Theta_9) \\ &= (\alpha\alpha\beta\alpha | P | \beta\alpha\alpha\alpha) \\ &= (\alpha\alpha\beta\alpha | \alpha\alpha\beta\alpha) = 1 \end{aligned} \quad (72)$$

$\epsilon' \times \rho + \rho' \times \epsilon$ is found by adding the two direct products and is given by:

$$\epsilon' \times \rho + \rho' \times \epsilon = \quad (74)$$

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	$\rho_{11} + \rho_{11}$	ρ_{12}	ρ_{13}	ρ_{14}	ρ_{12}				ρ_{13}				ρ_{14}			
2	ρ_{21}	$\rho_{22} + \rho_{11}$	ρ_{23}	ρ_{24}		ρ_{12}				ρ_{13}				ρ_{14}		
3	ρ_{31}	ρ_{32}	$\rho_{33} + \rho_{11}$	ρ_{34}			ρ_{12}				ρ_{13}				ρ_{14}	
4	ρ_{41}	ρ_{42}	ρ_{43}	$\rho_{44} + \rho_{11}$				ρ_{12}				ρ_{13}				ρ_{14}
5	ρ_{21}				$\rho_{11} + \rho_{22}$	ρ_{12}	ρ_{13}	ρ_{14}	ρ_{23}				ρ_{24}			
6		ρ_{21}			ρ_{21}	$\rho_{22} + \rho_{22}$	ρ_{23}	ρ_{24}		ρ_{23}				ρ_{24}		
7			ρ_{21}		ρ_{31}	ρ_{32}	$\rho_{33} + \rho_{22}$	ρ_{34}			ρ_{23}				ρ_{24}	
8				ρ_{21}	ρ_{41}	ρ_{42}	ρ_{43}	$\rho_{44} + \rho_{22}$				ρ_{23}				ρ_{24}
9	ρ_{31}				ρ_{32}			$\rho_{11} + \rho_{33}$	ρ_{12}	ρ_{13}	ρ_{14}	ρ_{34}				
10		ρ_{31}				ρ_{32}		ρ_{21}	$\rho_{22} + \rho_{33}$	ρ_{23}	ρ_{24}		ρ_{34}			
11			ρ_{31}				ρ_{32}	ρ_{31}	ρ_{32}	$\rho_{33} + \rho_{33}$	ρ_{34}				ρ_{34}	
12				ρ_{31}				ρ_{32}	ρ_{41}	ρ_{42}	ρ_{43}	$\rho_{44} + \rho_{33}$				ρ_{34}
13	ρ_{41}				ρ_{42}			ρ_{43}				$\rho_{11} + \rho_{44}$	ρ_{12}	ρ_{13}	ρ_{14}	
14		ρ_{41}				ρ_{42}			ρ_{43}			ρ_{21}	$\rho_{22} + \rho_{44}$	ρ_{23}	ρ_{24}	
15			ρ_{41}				ρ_{42}				ρ_{43}	ρ_{31}	ρ_{32}	$\rho_{33} + \rho_{44}$	ρ_{34}	
16				ρ_{41}				ρ_{42}				ρ_{43}	ρ_{41}	ρ_{42}	ρ_{43}	$\rho_{44} + \rho_{44}$

The calculation of $P[\rho' \times \epsilon + \epsilon' \times \rho]P$ involves two matrix multiplications. Because of the form of P this is done by first interchanging the proper rows and then the proper columns to give:

$$P[\rho' \times \epsilon + \epsilon' \times \rho]P = \quad (75)$$

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	$2\rho_{11}$	ρ_{12}	ρ_{13}		ρ_{12}		ρ_{14}		ρ_{13}	ρ_{14}						
2	ρ_{21}	$\rho_{22} + \rho_{11}$		ρ_{13}		ρ_{12}		ρ_{14}	ρ_{23}	ρ_{24}						
3	ρ_{31}		$\rho_{33} + \rho_{11}$		ρ_{32}		ρ_{34}				ρ_{13}	ρ_{14}				
4		ρ_{31}	ρ_{21}	$\rho_{33} + \rho_{22}$		ρ_{32}		ρ_{34}			ρ_{23}	ρ_{24}				
5	ρ_{21}				$\rho_{11} + \rho_{22}$	ρ_{12}	ρ_{24}						ρ_{13}	ρ_{14}		
6		ρ_{21}		ρ_{23}	ρ_{21}	$2\rho_{22}$		ρ_{24}					ρ_{23}	ρ_{24}		
7	ρ_{41}		ρ_{43}		ρ_{42}		$\rho_{11} + \rho_{44}$	ρ_{12}							ρ_{13}	ρ_{14}
8		ρ_{41}		ρ_{43}		ρ_{42}	ρ_{21}	$\rho_{22} + \rho_{44}$							ρ_{23}	ρ_{24}
9	ρ_{31}	ρ_{32}						$\rho_{33} + \rho_{11}$	ρ_{34}	ρ_{13}		ρ_{12}		ρ_{14}		
10	ρ_{41}	ρ_{42}						$\rho_{43} + \rho_{11}$	ρ_{11}		ρ_{13}		ρ_{12}		ρ_{14}	
11			ρ_{31}	ρ_{32}				ρ_{31}		$2\rho_{33}$	ρ_{34}	ρ_{32}		ρ_{34}		
12			ρ_{41}	ρ_{42}					ρ_{31}	ρ_{43}	$\rho_{33} + \rho_{44}$		ρ_{32}		ρ_{34}	
13					ρ_{31}	ρ_{32}		ρ_{21}		ρ_{23}		$\rho_{22} + \rho_{33}$	ρ_{34}	ρ_{24}		
14					ρ_{41}	ρ_{42}			ρ_{21}		ρ_{23}	ρ_{43}	$\rho_{22} + \rho_{44}$	ρ_{24}		
15							ρ_{31}	ρ_{32}	ρ_{41}	ρ_{43}		ρ_{42}		$\rho_{33} + \rho_{44}$	ρ_{34}	
16							ρ_{41}	ρ_{42}		ρ_{41}		ρ_{43}		ρ_{42}	ρ_{43}	$2\rho_{44}$

The circled elements indicate the trace to find ρ_{21} (after exchange) which is taken over the primed elements.

The elements enclosed in a triangle are the trace over the unprimed elements to find ρ_{21} (after the exchange). Since both molecules involved in the exchange are the same the equations for the primed molecule are identical with those for the unprimed molecule with the exception of the labeling.

Then with $N = N' = 4$, we have:

$$\begin{aligned} \left(\frac{d\rho_{21}}{dt} \right)_{\text{exc.}} &= \frac{1}{4} \left\{ \tau_1' \frac{[P(\rho' \times E + E' \times \rho)]_{21}}{\tau} - \rho_{21} \right\} \\ &= \frac{1}{4} \left\{ \frac{\rho_{21} + \rho_{21} + \rho_{43} + \rho_{43}}{\tau} - \rho_{21} \right\} = \frac{\rho_{43} - \rho_{21}}{2\tau} \end{aligned}$$

Similarly,

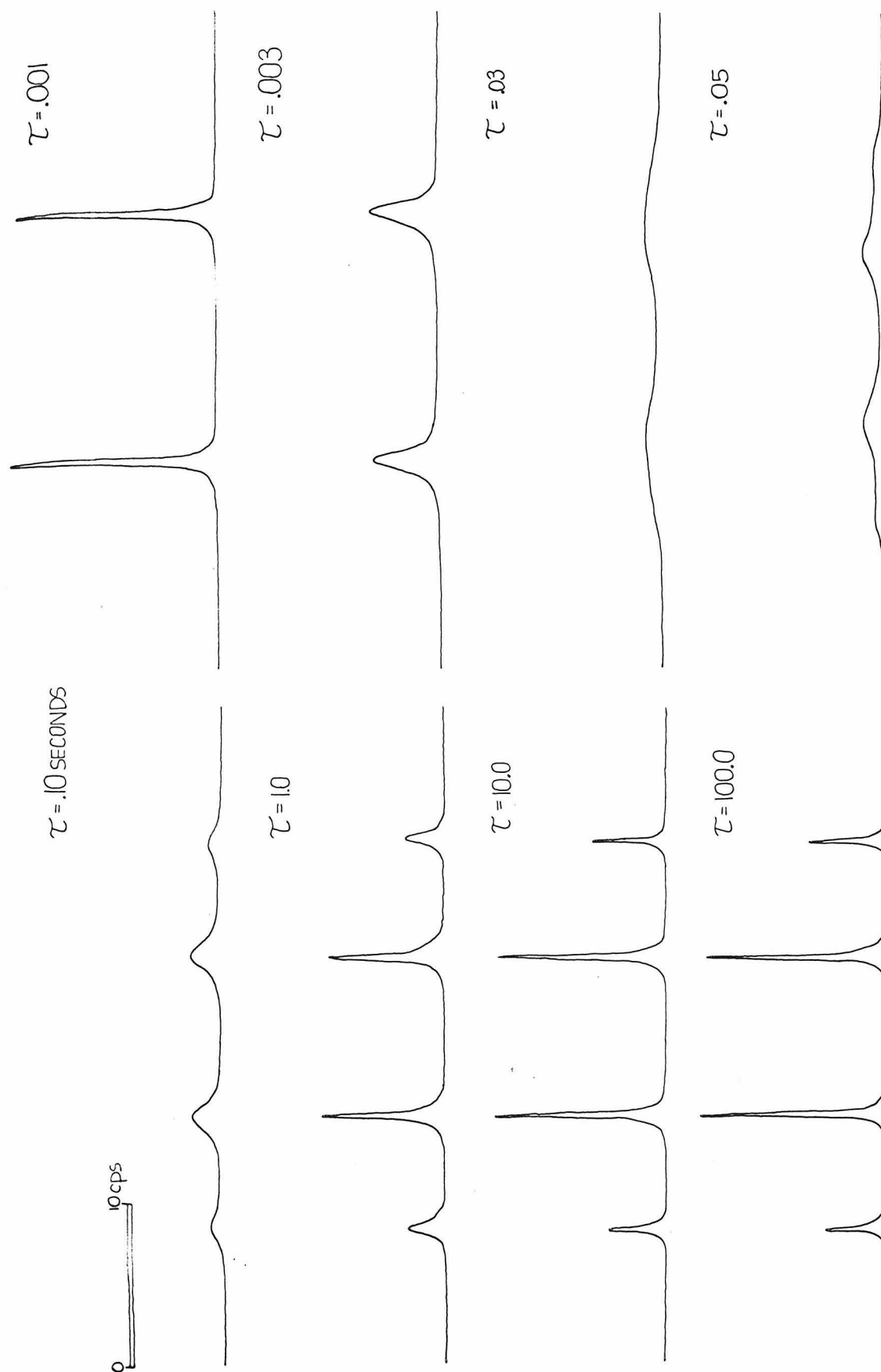
$$\begin{aligned} \left(\frac{d\rho_{31}}{dt} \right)_{\text{exc.}} &= \frac{\rho_{42} - \rho_{31}}{2\tau} \\ \left(\frac{d\rho_{42}}{dt} \right)_{\text{exc.}} &= \frac{\rho_{31} - \rho_{42}}{2\tau} \\ \left(\frac{d\rho_{43}}{dt} \right)_{\text{exc.}} &= \frac{\rho_{21} - \rho_{43}}{2\tau} \end{aligned} \quad (76)$$

The rest of the problem is treated as in the AB intramolecular exchange case which permits us to immediately write the full equations by inserting the exchange terms (76) in equations (13-16):

$$\begin{aligned} \frac{\rho_{43} - \rho_{21}}{2\tau} - \frac{\rho_{21}}{\tau_2} + i(-\Delta - \delta/2 + J/2)\rho_{21} + i(-J/2)\rho_{31} + iC &= 0 \\ \frac{\rho_{42} - \rho_{31}}{2\tau} - \frac{\rho_{31}}{\tau_2} + i(-\Delta + \delta/2 + J/2)\rho_{31} + i(-J/2)\rho_{21} + iC &= 0 \\ \frac{\rho_{31} - \rho_{42}}{2\tau} - \frac{\rho_{42}}{\tau_2} - i(\Delta - \delta/2 + J/2)\rho_{42} + i(J/2)\rho_{43} + iC &= 0 \\ \frac{\rho_{21} - \rho_{43}}{2\tau} - \frac{\rho_{43}}{\tau_2} - i(\Delta + \delta/2 + J/2)\rho_{43} + i(J/2)\rho_{42} + iC &= 0 \end{aligned} \quad (77)$$

These equations have been programmed on the IBM 7094, with a sample set of resulting plotted spectra being displayed in figure 4.

The influence of this type of exchange on the magnetic resonance spectrum is obvious from the features of the spectra. For large values of tau (slow exchange) the spectrum is of the normal AB type. For small values of tau (fast exchange) the spectrum appears sharp and decoupled due to the short lifetime of the nucleus A on any given molecule. Intermediate rates cause broadening of the spectral lines.



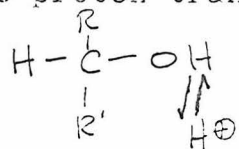
$$\Delta \nu_{AB} = 15 \text{ cps}$$

$$J_{AB} = 7 \text{ cps}$$

FIGURE 4. Chemical exchange of the A nuclei between two molecules of the same species in an AB system. ($T_2 = 1.0$ sec.)

CALCULATIONS: II. CHEMICAL EXCHANGE OF A SINGLE NUCLEUS WITH ONE OF TWO COUPLED NUCLEI

Examples of this type of exchange are quite common, usually occurring when some proton transfer reaction takes place in solution.



For this calculation I am going to employ the same notation and basis functions as used by Kaplan in reference (10). So that the results of Alexander's method can be compared with the equations derived by Kaplan.

Basis set for species 1 (two nonequivalent nuclei):

$$\begin{aligned} \varphi_1' &= \alpha\alpha & \varphi_3' &= p\alpha\beta + r\beta\alpha \\ \varphi_2' &= p(\beta\alpha - r\alpha\beta) & \varphi_4' &= \beta\beta \end{aligned} \quad (78)$$

Basis set for species 2 (a single proton):

$$\varphi_1^2 = \alpha \quad \varphi_2^2 = \beta \quad (79)$$

Products of φ_i^1 with φ_j^2 will be taken with the first two members of the product belonging to φ_i^1 and the third to φ_j^2 . For instance,

$$\alpha\alpha\alpha = (\alpha\alpha)(\alpha) = \varphi_1' \varphi_1^2 \quad (80)$$

The exchange matrix is easily calculated. It is defined on the basis set $\varphi^1 \times \varphi^2$, given by:

$$\varphi^1 \times \varphi^2 = \begin{pmatrix} \varphi_1' \varphi_1^2 \\ \varphi_1' \varphi_2^2 \\ \varphi_2' \varphi_1^2 \\ \varphi_2' \varphi_2^2 \\ \varphi_3' \varphi_1^2 \\ \varphi_3' \varphi_2^2 \\ \varphi_4' \varphi_1^2 \\ \varphi_4' \varphi_2^2 \end{pmatrix} = \begin{pmatrix} \theta_1 \\ \theta_2 \\ \theta_3 \\ \theta_4 \\ \vdots \\ \theta_8 \end{pmatrix} \quad (81)$$

For P, we have:

$$P = \begin{array}{c|cccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ \hline 1 & 1 & & & & & & & \\ 2 & & & -r & & p & & & \\ 3 & & -r & p^2 & & pr & & & \\ 4 & & & & r^2 & & -pr & p & \\ 5 & & p & pr & & r^2 & & & \\ 6 & & & & -pr & & p^2 & r & \\ 7 & & & & p & & r & & \\ 8 & & & & & & & & 1 \end{array} \quad (82)$$

A typical element of P is calculated by the following method.

P exchanges nucleus 2 of species 1 with the single nucleus of species 2.

$$\begin{aligned} (\Theta_S | \hat{P} | \Theta_2) &= (\varphi_3' \varphi^2 | \hat{P} | \varphi_1' \varphi_2^2) \\ &= (p_{\alpha\beta\alpha} + n_{\beta\alpha\alpha} | \hat{P} | \alpha\alpha\beta) \\ &= (p_{\alpha\beta\alpha} + n_{\beta\alpha\alpha} | \alpha\beta\alpha) = P \end{aligned} \quad (83)$$

It may well be noted that the exchange matrix is symmetric, requiring that one need only calculate terms on one side of the diagonal.

We have two equations to consider in this example:

$$\begin{aligned} \frac{dp^1}{dt} &= i[p^1, H^1] + \frac{T_1^2}{N^2} \frac{[Pp^1 \times \epsilon^2 P + P\epsilon^1 \times p^2 P]}{\tau^1} - p^1 \\ &\quad + \left(\frac{p_0^1 - p^1}{T_1^1} \right)_{\text{diag.}} - \left(\frac{p^1}{T_2^1} \right)_{\text{off. diag.}} \end{aligned} \quad (84)$$

$$\begin{aligned} \frac{dp^2}{dt} &= i[p^2, H^2] + \frac{T_1^1}{N^1} \frac{[Pp^2 \times \epsilon^2 P + P\epsilon^1 \times p^2 P]}{\tau^2} - p^2 \\ &\quad + \left(\frac{p_0^2 - p^2}{T_1^2} \right)_{\text{diag.}} - \left(\frac{p^2}{T_2^2} \right)_{\text{off. diag.}} \end{aligned} \quad (85)$$

The various matrices of interest have the following forms:

$$\begin{aligned} \epsilon^1 &= \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & 1 & \\ & & & 1 \end{pmatrix} & \rho^1 &= \begin{pmatrix} \rho_{11}^1 & \dots & \rho_{14}^1 \\ \vdots & & \vdots \\ \rho_{41}^1 & & \rho_{44}^1 \end{pmatrix} \\ \epsilon^2 &= \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix} & \rho^2 &= \begin{pmatrix} \rho_{11}^2 & \rho_{12}^2 \\ \rho_{21}^2 & \rho_{22}^2 \end{pmatrix} \end{aligned} \quad (86)$$

The spectrum is described by:

$$c^1 T_R(I^1 \rho^1) + c^2 T_R(I^2 \rho^2) = c^1 [(\rho+r) \rho_{21}^1 + (\rho+n) \rho_{43}^1 + (\rho+m) \rho_{31}^1 + (\rho-r) \rho_{42}^1] + c^2 [\rho_{21}^2]$$

Only the elements of ρ of interest will be retained in the calculation.

Doing this, we have for $\rho^1 \times \epsilon^2 + \epsilon^1 \times \rho^2$:

$$\rho^1 \times \epsilon^2 + \epsilon^1 \times \rho^2 =$$

	1	2	3	4	5	6	7	8
1								
2	A							
3	B							
4		B	A					
5	C							
6		C			A			
7			D		E			
8				D		E	A	

(87)

We have made the following substitutions:

$$\begin{aligned} \rho_{21}^2 &= A & \rho_{42}^1 &= D \\ \rho_{21}^1 &= B & \rho_{43}^1 &= E \\ \rho_{31}^1 &= C & & \end{aligned} \quad (88)$$

Performing the matrix multiplications we obtain

$$P(p'x\epsilon^2 + \epsilon'x p^2)P =$$

	1	2	3	4	5	6	7	8
1								
2	$-rB$ $+pC$							
3	$-rA$ $+p^2B$ $+prC$							
4		Ar^3 $-p^3rA$ $-rpD + Ep^2$	$-r^3B$ $+pr^2C +$ $p^3D + prE$		$r^2pB - pr^2C$ $+ p^2rD$ $+ Er^2p$			
5	$pA + prB$ $+ r^2C$							
6		$pr^2A +$ $Ap^3 +$ $Epr -$ r^2D	$pr^2B +$ $p^2rC +$ $rp^2D +$ pr^2E		$-p^2rB +$ $Cp^3 +$ $pr^2D +$ Er^3			
7		$-Arp$ $+ Apr$	$-pr^3B$ $+ p^3A$ $- r^2C$ $+ pr^2A$		$Bp^2 + ADr$ $+ Cpr$ $+ Ar^3$			
8				r^2D $-prE$ $+ pA$		$-Dpr$ $+ Ep^2$ $+ rA$	$Dp + Er$	

(89)

We can now decompose the transformed collision complex matrix into the various elements of interest:

$$\left\{ T_{11}^2 [P(p'x\epsilon^2 + \epsilon'x p^2)P] \right\}_{21}^1 = -rA + p^2B + prC - Ar^3 - p^2rA - rpD + Ep^2 \quad (90)$$

$$\left\{ \begin{array}{c} " \\ " \end{array} \right\}_{31}^1 = pA + prB + r^2C + pr^2A + Ap^3 - r^2D + Epr \quad (91)$$

$$\left\{ \begin{array}{c} " \\ " \end{array} \right\}_{42}^1 = -prB + p^3A - r^2C + pr^2A + r^2D - prE + pA \quad (92)$$

$$\left\{ \begin{array}{c} " \\ " \end{array} \right\}_{43}^1 = Bp^2 + Ap^2r + Cpr + Ar^3 - Dpr + Ep^2 + rA \quad (93)$$

$$\left\{ T_{11}^1 [P(p'x\epsilon^2 + \epsilon'x p^2)P] \right\}_{21}^2 = -rB + pC - r^3B + pr^2C + p^3D + p^2rE - p^2rB + Cp^3 + pr^2D + Er^3 + Dp + Er \quad (94)$$

Using the fact that $p^2 + r^2 = 1$ (see (97)) we can simplify the above and substitute the density matrix elements back into the relationships to obtain:

$$\begin{aligned}
 \rho_{21}^2 (\text{after exchange}) &= \frac{r(\rho_{43}' - \rho_{21}') + p(\rho_{42}' + \rho_{31}')}{2} \\
 \rho_{21}' (\quad) &= \frac{-2r\rho_{21}^2 + pr(\rho_{31}' - \rho_{42}') + p^2(\rho_{43}' + \rho_{21}')}{2} \\
 \rho_{31}' (\quad) &= \frac{2p\rho_{21}^2 + pr(\rho_{43}' + \rho_{21}') + r^2(\rho_{31}' - \rho_{42}')}{2} \quad (95) \\
 \rho_{42}' (\quad) &= \frac{2p\rho_{21}^2 + pr(\rho_{43}' + \rho_{21}') + r^2(\rho_{42}' - \rho_{31}')}{2} \\
 \rho_{43}' (\quad) &= \frac{2r\rho_{21}^2 + pr(\rho_{31}' - \rho_{42}') + p^2(\rho_{43}' + \rho_{21}')}{2}
 \end{aligned}$$

With the derivation of the above we have obtained the information needed for the exchange terms in (84) and (85). The calculations are done in the representations in which H^1 and H^2 are diagonal. We thus have:

$$\begin{aligned}
 i[\rho^l, H^l]_{mn} &= i \langle \phi_m^{l*} | \rho^l H^l - H^l \rho^l | \psi_n^l \rangle \\
 &= -i \langle E_n^l - E_m^l - \omega \rangle \rho_{mn}^l \\
 &= -i (\omega_{mn}^l - \omega) \rho_{mn}^l \quad (96)
 \end{aligned}$$

From the table on page 121 of reference (6) we obtain the first four of the following relations:

$$\begin{aligned}
 \omega_{21}' &= E_1' - E_2' = (\frac{1}{2})(\nabla^2 + J^2)^{1/2} + \frac{1}{2}J \\
 \omega_{31}' &= E_1' - E_3' = -\frac{1}{2}(\nabla^2 + J^2)^{1/2} + \frac{1}{2}J \\
 \omega_{42}' &= E_2' - E_4' = -\frac{1}{2}(\nabla^2 + J^2)^{1/2} - \frac{1}{2}J \\
 \omega_{43}' &= E_3' - E_4' = (\frac{1}{2})(\nabla^2 + J^2)^{1/2} - \frac{1}{2}J \\
 \omega_{21}^2 &= E_1^2 - E_2^2 = \omega_3
 \end{aligned} \quad (97)$$

where ∇ = difference in chemical shift in species 1
 ω_3 = chemical shift of species 2

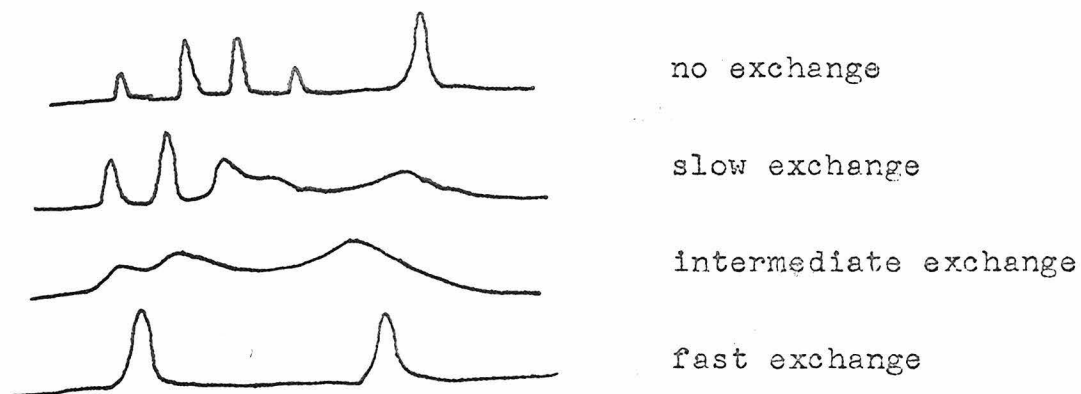
$$\rho^2 = \frac{1}{2} \left(1 + \left(1 + \frac{J^2}{\omega^2} \right)^{-1/2} \right) \quad -39-$$

$$\rho^2 = \frac{1}{2} \left(1 - \left(1 + \frac{J^2}{\omega^2} \right)^{-1/2} \right)$$

The zero of frequency is taken arbitrarily at the center of the spectrum of species 1 in the absence of exchange. All of the values of the parameters in (97) are taken to be in radians per second.

We can now write the elements of interest from the matrix equations (84) and (85) for the system being considered. The driving term comes again from the commutator of ρ with $H(t)$ as in the case of intramolecular exchange and the time derivative on the LHS of the equations (85) and (84) has again been set equal to zero, assuming slow passage conditions. The full equations are thus given in TABLE III, pg. 40.

The equations in TABLE III agree with those derived by Kaplan,¹⁰ who uses a quite different method to obtain them. The equations which Kaplan offers are the complex conjugates of those in TABLE III. This is not a discrepancy since from the definition of the density matrix we have $\rho_{ij} = \rho_{ji}^*$, and for the spectrum Kaplan takes the real part of $\text{Trace}(I^+ \rho)$, while we take the imaginary part. Kaplan has solved these equations by assuming the concentration of species 2 to be infinite. A computer program is being written which solves them in general, for any concentration of either species. The results can probably be predicted as follows:



$$\frac{p^2(\rho_{21}' + \rho_{43}') + pr(\rho_{31}' - \rho_{42}') - 2r\rho_{21}'^2 - 2\rho_{21}'}{2\tau'} + i\rho_{21}'(w - w_{21}') + iC(p - r) = 0$$

$$\frac{p^2(\rho_{21}' + \rho_{34}') + pr(\rho_{31}' - \rho_{42}') + 2r\rho_{21}'^2 - 2\rho_{43}'}{2\tau'} + i\rho_{43}'(w - w_{43}') + iC(p + r) = 0$$

$$\frac{pr(\rho_{21}' + \rho_{43}') + r^2(\rho_{31}' - \rho_{42}') + 2p\rho_{21}'^2 - 2\rho_{31}'}{2\tau'} + i\rho_{31}'(w - w_{31}') + iC(p + r) = 0$$

$$\frac{-pr(\rho_{21}' + \rho_{43}') - r^2(\rho_{31}' - \rho_{42}') + 2p\rho_{21}'^2 - 2\rho_{42}'}{2\tau'} + i\rho_{42}'(w - w_{42}') + iC(p - r) = 0$$

$$\frac{p(\rho_{31}' + \rho_{42}') - r(\rho_{21}' - \rho_{43}') - 2\rho_{21}'^2}{2\tau^2} - \frac{\rho_{21}'^2}{\tau^2} + i\rho_{21}'^2(w - w_{21}'^2) + iC = 0$$

TABLE III. Equations involving density matrix elements of interest in the case when one of two coupled nuclei is exchanging with a single nuclei of a second species.

CONCLUSION AND DISCUSSION

A number of simple cases of nuclei exchange in species which contain nuclei of magnetic interest (spin $+\frac{1}{2}$) have been analyzed in detail using the method outlined by Alexander.^{5,9} A large number of cases in which exchange of magnetic environment between different nuclei occurs can be reduced to one of these simple cases by appropriate and judicious choice of compounds and substituents. Spin decoupling experiments can also serve to simplify the spectrum such that it can be compared to one of the simple systems which have been analyzed.

Computer programs have been written for the IBM 7094 (Fortran IV language used) which plot the spectra as a function of the relaxation time, exchange rate, and magnetic parameters (coupling constants and chemical shifts).

An example of the kinetic studies to which this technique has been applied will appear in a forthcoming article by Dr. F. Mallory, in which the rearrangement of various substituted benzofurazan oxides (figure 5) was studied.

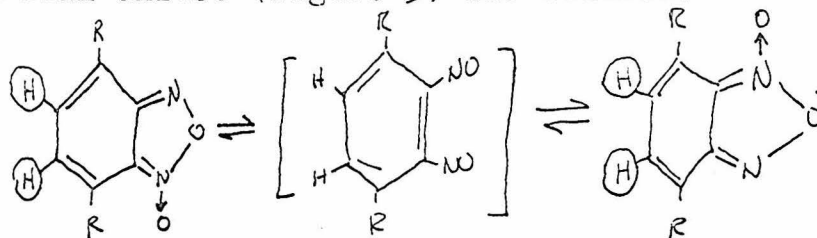


Figure 5

The circled protons exchange their magnetic environment, giving spectra similar to those shown in figure 2. The rate constants at different temperatures were obtained by fitting the experimental spectra with those calculated by the computer program. Activation energies were measured from Arrhenius plots.

In cases of intramolecular exchange where the system cannot be reduced to a simple one it may still be possible to apply (28) to obtain fairly good kinetic data from the peak half widths.

APPENDIX: Computer Programs

I. Moment Calculations: NMREX 150A

This program is discussed in my April 20, 1964 research report. The binary deck and source deck are held by the computing center. A Fortran IV listing is here included.

<u>INPUT CARDS</u>	<u>COLUMNS</u>	<u>DATA</u>	<u>DECIMAL</u>
Card 1	1-3	NPROB (no. of problem)	NO
	4	NTYPE = 1 for reading moments = 2 for reading freq. and int.	NO
	5-7	NTRAN = No. of cards with transitions (or segments of spectrum) listed. ((999)) max.	NO
	8-9	NA = no. of nuclei in group A (low field)	NO
	10-11	NB	NO
	12-13	NC	NO
Card 2 (if NTYPE=2)	1-12	$\langle (\Delta\nu)^2 \rangle$ moments relative to the mean	YES
	13-24	$\langle (\Delta\nu)^3 \rangle$ "	YES
	25-36	$\langle (\Delta\nu)^4 \rangle$ "	YES
Card 2 (if NTYPE=1) Through Card NTRAN+1	1-12	Frequency of transition (or segment)	YES
	13-24	Intensity "	YES
Final Card	1-3	999 (Calls end of program)	NO

C NMR MOMENT PROGRAM JD ROBERTS 4/29/64
C THE FOLLOWING PROGRAM CALCULATES CHEMICAL SHIFTS FROM MOMENT
C INFORMATION. PROGRAM WILL WORK FOR 3 GROUPS OR 3 GROUPS BY
C SETTING NC=C
C NPROB = PROBLEM NUMBER = 999 FOR NO PROBLEM
C TYPE = 1 FOR READING CARDS = 2 FOR READING MOMENTS
C MOMENTS READ MUST BE FOR THE FIRST MOMENT = 0.000
C NTRAN = NUMBER OF TRANSITIONS READ FROM CARDS
C NA NB NC = NUMBER OF NUCLEI IN EACH GROUP
C ANY FREQUENCIES MAY BE USED IN DATA WITHOUT AFFECTING THE
C ACCURACY WITH WHICH THE PROGRAM WORKS.
C DIMENSION FREQ(999), PH(999), XIT(4), NC(4)

25 READ(5,1) NPROB, NTYPE, NTRAN, NA, NB, NC

1 FORMAT(I3,I1,I3,3I2)
IF(NPROB-999) 2,600,2
2 WRITE(6,3) NPROB
3 FORMAT(///22H NUMBER OF PROBLEM IS , I3//)
WRITE(6,881)
881 FORMAT(39H FREQUENCY AND INTENSITY OF LINES USED)
FREQC = C.C
DEL1 = C.0
IF(NTYPE-1) 100,100,101
100 SUM = C.0

DO 6 I = 1,NTRAN
READ(5,4) FREQ(I),PH(I)
WRITE(6,321) FREQ(I) , PH(I)
SUM = SUM + PH(I)
6 CONTINUE
4 FORMAT(2F12.7)
321 FORMAT(2F15.4)
ASUM = .5*SUM
PSUM = C.0
DO 7 I = 1,NTRAN
PSUM = PSUM+ PH(I)
K = I

IF(PSUM-ASUM)7,9,9

7 CONTINUE

9 FREQC = FREQ(K)

C THE FOLLOWING SETS FREQ(K) = 0.0 IN THE DATA

DO 10 I=1,NTRAN
10 FREQ(I) = FREQ(I) - FREQC

DEL1=C.0

DEL2 = C.0

DEL3 = C.0

DEL4 = C.0

DO 11 I = 1,NTRAN

DEL1 = DEL1 + FREQ(I)*PH(I)

DEL2 = DEL2 + FREQ(I)*FREQ(I)*PH(I)

DEL3 = DEL3 + FREQ(I)*FREQ(I)*FREQ(I)*PH(I)

DEL4 = DEL4 + FREQ(I)*FREQ(I)*FREQ(I)*FREQ(I)*PH(I)

11 CONTINUE

DEL1 = DEL1/SUM

DEL2 = DEL2/SUM

DEL3 = DEL3/SUM

DEL4 = DEL4/SUM
DELS = DEL2 - DEL1*DEL1
DELQ = DEL3- 3.*DEL2*DEL1 + 2.*DEL1**3
DELF = DEL4 - 4.*DEL3*DEL1 + 6.*DEL2*DEL1**2 -3.*DEL1**4
GO TO 102

101 READ(5,12) DELS, DELQ, DELF
12 FORMAT(3F12.4)

102 CONTINUE

C XA IS NEG SHIFT REL TO DEL1 AS ZERO

C XB IS PCS OR NEG

C XC IS PCSITIVE SHIFT IN THIS PROGRAM RELATIVE TO DEL1 AS ZERO

AN = NA

BN = NB

CN = NC

CAR = AN+BN+CN

DELS = CAR*DELS

DELQ = CAR*DELQ

DELF = CAR*DELF

XB = 0.0

XAL = -SQRT(DELS/AN)

XCL = SQRT(DELS/CN)

XA = XAL

XC = XCL

IF(NC) 85,85,84

84 CCNTINUE

XIT(1) = 1.0

XIT(2) = .10

XIT(3) = .01

XIT(4) = .001

NO(1) = 1000

NO(2) = 100

NO(3) = 100

NO(4) = 100

DO 175 I = 1,4

CCR = XIT(I)

NN = NO(I)

DO 185 J = 1,NN

COMP = AN*XA*XA + BN*XB*XB + CN*XC*XC

IF(COMP-DELS) 110,140,120

110 XC = XC + CCR

IF(XC-XCL) 140,140,139

139 XC = XC-CCR

GO TO 140

120 XC = XC-CCR

IF(XC)138,140,140

138 XC = XC+ CCR

140 XB = (-XA*AN - XC*CN)/BN

IF(XB-XC) 791,792,793

793 XB = XC

GO TO 792

791 IF(XB-XA) 794,792,792

794 XB = XA

792 CCNTINUE

COMP = AN*XA**3 + BN*XB**3 + CN*XC**3

IF(COMP- DELQ) 179,180,181

179 XA = XA + COR

```

IF(XA) 180,180,186
186 XA = XA-CCR
GO TO 180
181 XA = XA - CCR
IF(XA-XAL) 178,180,180
178 XA = XA + CCR
180 XB = (-XA*AN - XC*CN)/BN
IF(XB-XC) 391,392,393
393 XB = XC
GO TO 392
391 IF(XB-XA) 394,392,392
394 XB = XA
392 CONTINUE
185 CCNTINUE
175 CCNTINUE
GO TO 1111
85 XA = -SQRT((BN*DELS)/(AN*CAR))
XB = SQRT((AN*DELS)/(BN*CAR))
XC = 0.0
1111 CONTINUE
SK = AN*XA**4 + BN*XB**4 + CN*XC**4
SL = (DELF-SK)*2.
COAB = ((XA-XB)**2)*AN*BN
COAC = ((XA-XC)**2)*AN*CN
CCBC = ((XB-XC)**2)*BN*CN
CHA = XA + DEL1 + FRECC
CHB = XB + DEL1 + FRECC
CHC = XC + DEL1 + FRECC
WRITE(6,533)
533 FORMAT(39F CHEMSHIFT NUMBER OF NUCLEI /)
WRITE(6,501) CHA, NA, CHB, NB, CHC, NC
501 FORMAT(11H SPECIES A , F12.4 , 16/11H SPECIES B , F12.4, 16/
1 11H SPECIES C , F12.4,16///)
WRITE(6,193) SL, COAB,COAC,CCBC
193 FORMAT(/64H THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING
1CCNSTANTS //2H ,F12.4,1H=,1H ,F12.4,9HJAB**2 + , F12.4,
1 9HJAC**2 + , F12.4,7HJBC**2 )
GO TO 25
600 CONTINUE
STOP
END

```

Research Report

Jack Beauchamp

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ABSTRACT

Computer programs have been written for the Burroughs 220 and the IBM 7094 which use the moment equations of Anderson and McConnell to obtain spectral parameters. Chemical shifts can be obtained for up to three groups of nuclei. The 7094 program yields a relation between the coupling constants.

CONTENTS:

GENERAL DISCUSSION OF PROBLEM. . . .	1
BURROUGHS 220 PROGRAM	3
IBM 7094 Program	5

I. GENERAL DISCUSSION OF PROBLEM:

The theory of spectral moments as applied to NMR spectra has been developed by Anderson and McConnell.¹

¹Anderson, W.A., and H.M. McConnell; J. Chem. Phys., 26, 1496 (1957)

An excellent review of this paper can be found in Pople, Schneider, and Bernstein, High Resolution Nuclear Mag. Res., page 156.

The nth moment of the spectrum is defined by

$$\langle \nu^n \rangle = \frac{\sum_{j,k} (\nu_{jk})^n I_{jk}}{\sum_{j,k} I_{jk}} \quad \begin{array}{l} I = \text{intensity} \\ \nu_{jk} = \text{frequency of transition} \end{array}$$

The different line positions relative to the mean are defined by

$$\Delta \nu = \nu - \langle \nu \rangle$$

Then, using the relationships

$$\langle \Delta \nu \rangle = 0$$

$$\langle (\Delta \nu)^2 \rangle = \langle \nu^2 \rangle - \langle \nu \rangle^2$$

$$\langle (\Delta \nu)^3 \rangle = \langle \nu^3 \rangle - 3\langle \nu^2 \rangle \langle \nu \rangle + 2\langle \nu \rangle^3$$

$$\langle (\Delta \nu)^4 \rangle = \langle \nu^4 \rangle - 4\langle \nu^3 \rangle \langle \nu \rangle + 6\langle \nu^2 \rangle \langle \nu \rangle^2 - 3\langle \nu \rangle^4$$

This formula is wrong in PSB.

the following relationships can be derived:

$$\begin{aligned} \langle \Delta \nu \rangle &= N^{-1} \sum_i \Delta \nu_i = 0 \\ \langle (\Delta \nu)^2 \rangle &= N^{-1} \sum_i (\Delta \nu_i)^2 \\ \langle (\Delta \nu)^3 \rangle &= N^{-1} \sum_i (\Delta \nu_i)^3 \end{aligned} \quad \left\{ \begin{array}{l} \langle (\Delta \nu)^4 \rangle = N^{-1} \left[\sum_i (\Delta \nu_i)^4 + \frac{2}{3} I(I+1) \sum_{i,j} (\Delta \nu_i \Delta \nu_j)^2 J_{ij}^2 \right] \end{array} \right.$$

Where:

N = total # of nuclei

$\Delta \nu_i$ = chemical shift of nucleus i

J_{ij} = coupling between nuclei i and j

For systems of the type $A_n B_m$ we have the following equations:

N_A = # of nuclei in group A

N_B = # of nuclei in group B

$$N_A (\Delta \nu_A) + N_B (\Delta \nu_B) = 0$$

$$N_A (\Delta \nu_A)^2 + N_B (\Delta \nu_B)^2 = \langle (\Delta \nu)^2 \rangle (N_A + N_B)$$

Yielding:

$$\langle \Delta \nu_B \rangle^2 = \langle (\Delta \nu)^2 \rangle \frac{N_A}{N_B}$$

$$\langle \Delta \nu_A \rangle^2 = \langle (\Delta \nu)^2 \rangle \frac{N_B}{N_A}$$

If all the couplings between the nuclei of the different groups are equal we have the following equation which permits us to obtain J_{AB} .

$$\begin{aligned} \langle (\Delta \nu)^4 \rangle (N_A + N_B) &= N_A \langle \Delta \nu_A \rangle^4 + N_B \langle \Delta \nu_B \rangle^4 \\ &+ \frac{1}{2} N_A N_B (\Delta \nu_A - \Delta \nu_B)^2 J_{AB}^2 \end{aligned}$$

If all couplings between the different groups are not equal, then the above must be reconsidered as:

$$\begin{aligned} \langle (\Delta \nu)^4 \rangle (N_A + N_B) &= N_A \langle \Delta \nu_A \rangle^4 + N_B \langle \Delta \nu_B \rangle^4 \\ &+ \frac{1}{2} \sum_{i>j} (\Delta \nu_i - \Delta \nu_j)^2 J_{ij}^2 \end{aligned}$$

Thus for an $A_n B_m$ system of nuclei we can obtain the chemical shifts of the two species as well as the coupling between the groups unless more than one distinct coupling exists (which is often the case.) In the latter case it is still possible to relate the couplings to the fourth moment of the spectrum.

The problem is not so easily soluble in a system in which three groups of nuclei are present. We have the following relationships between the chemical shifts:

$$0 = N_A \langle \Delta \nu_A \rangle + N_B \langle \Delta \nu_B \rangle + N_C \langle \Delta \nu_C \rangle$$

$$N \langle (\Delta \nu)^2 \rangle = N_A \langle \Delta \nu_A \rangle^2 + N_B \langle \Delta \nu_B \rangle^2 + N_C \langle \Delta \nu_C \rangle^2$$

$$N \langle (\Delta \nu)^3 \rangle = N_A \langle \Delta \nu_A \rangle^3 + N_B \langle \Delta \nu_B \rangle^3 + N_C \langle \Delta \nu_C \rangle^3$$

The couplings between groups can be related by an equation similar to (4). Discussion of this relationship is found in the section under the IBM 7094 program. The system of equations above (5) yields a sixth degree polynomial if solved by elimination of two variables. The six roots give 6 sets of results, not all of which are meaningful. This method of solution has been rejected in favor of an iterative solution to the problem with the following being quite reasonably assumed to limit the number of possible solutions:

$$\begin{aligned}\Delta Y_A & \text{ is negative} \\ \Delta Y_B & \text{ is negative or positive} \\ \Delta Y_C & \text{ is positive}\end{aligned}$$

and

$$\Delta Y_A \leq \Delta Y_B \leq \Delta Y_C$$

The ΔY_i 's are obtained by the following iterative method:

- (1) Calculate limits to $\Delta Y_{A,C}$ by

$$\begin{aligned}0 \geq \Delta Y_A & \geq \frac{\pm}{\Delta Y_A} \left\langle \frac{N}{N_A} (\Delta Y)^2 \right\rangle^{1/2} \\ 0 \leq \Delta Y_C & \leq \frac{\pm}{\Delta Y_C} \left\langle \frac{N}{N_C} (\Delta Y)^2 \right\rangle^{1/2}\end{aligned}$$

(Use the non-zero limits as iterative starting points for ΔY_A and ΔY_C . Start with $\Delta Y_B = 0$.)

- (2) Compute $N_A (\Delta Y_A)^2 + N_B (\Delta Y_B)^2 + N_C (\Delta Y_C)^2$ and compare this to $\langle (\Delta Y)^2 \rangle \cdot N$.
If greater ΔY_C is decreased; if less ΔY_C is increased.

- (3) ΔY_B is calculated from: $\Delta Y_B = \frac{1}{N_B} (-N_A \Delta Y_A - N_C \Delta Y_C)$

- (4) Compute $N_A (\Delta Y_A)^3 + N_B (\Delta Y_B)^3 + N_C (\Delta Y_C)^3$ and compare this to $\langle (\Delta Y)^3 \rangle \cdot N$.

If greater then ΔY_A is decreased (remember this is a negative quantity, so $|\Delta Y_A|$ is increased); if less then ΔY_A is increased.

- (5) ΔY_B is calculated from: $\Delta Y_B = \frac{1}{N_B} (-N_A \Delta Y_A - N_C \Delta Y_C)$

- (6) Go back to (2) and repeat. This is continued until the values do not change more than a prescribed amount over a single iteration.

check has been added which keeps ΔY_B between ΔY_A and ΔY_C

II. BURROUGHS 220 PROGRAM:

Using the above treatment a computer program was written for the Burroughs 220. This program calculates only the chemical shifts for three groups of nuclei if the moments $\langle(\Delta\nu)^2\rangle$ and $\langle(\omega\nu)^3\rangle$ are read into the computer. The tape is read in as follows:

- (1) Paper tape read into cell 0000
- (2) Tape Halts
- (3) Paper tape read into cell 1000
- (4) Tape Halts
- (5) Rewind tape

The data must be entered manually at the console. All data must be in floating point form. The form for this is

S 1 1 1 2 3 4 5 6 7 8

where the number represented is

S = sign = 1 for -, 0 for +

number = $\pm .12345678 \times 10^{1j-50}$

In other words,

-525.4 = 15352540000

1.0 = 051100000000

The data is entered in the following locations

Cell	Data
0001	NA
0002	NB
0003	NC
0004	$\langle(\Delta\nu)^2\rangle$
0005	$\langle(\omega\nu)^3\rangle$

The program is started at cell 0000. The part of the program in cell 1000 on was used to check the program. It can be used to check output against the program. It uses the chemical shifts as data to calculate the moments and then transfers to the first part of the program to calculate the chemical shifts. Many different sets of input data have been checked in the program with no resulting problems. The data is entered into the part of the program in cell 1000 as follows

Cell	Data
1001	NA
1002	NB
1003	NC
1004	ΔV_A
1005	ΔV_B
1006	ΔV_C

The program is then started at cell 1000. The results are printed out as follows:

Input data: ANS NA NB NC ΔV_A ΔV_B ΔV_C

This is the input data (in cells 1001 on) and is not printed if the first part of the program is used alone. The output of the first part of the program is as follows:

THE SHIFTS ARE

ΔV_A ΔV_B ΔV_C

A sample of both outputs is here attached

ANS
5110000000. 5110000000 5110000000
THE SHIFTS ARE
-5319999995 5225000000 5317499999

The program iterates until the chemical shifts are less than $\pm .005$ cps during a single iteration.

III. IBM 7094 PROGRAM:

The 7094 program is written to employ the techniques outlined in section I. This program can take either the computed moments or the transition frequencies and intensities. For the transitions the peaks of the spectrum may be divided up in small segments, as long as the same interval of frequency is used for the entire spectrum, and all peaks are treated similarly. Segmenting of the peaks is, of course, a more practical method for spectra in which there are a considerable number of overlapping peaks. It does require a lot of careful measurement on the spectrum.

INPUT CARDS

Card 1

Cols	Data
1-3	NPROB = problem no. = 999 for no problem Last card must have 999.
4	Type = 1 for reading frequencies and intensities = 2 for reading moments
5-7	NTRAN = no. of cards with transitions on them. 999 maximum.
8-9	NA
10-11	NB
12-13	NC

If TYPE = 1

Cards 2 through NTRAN + 1

Cols	
1-12	Frequency in cps of transitions. Decimals must be punched.
13-24	Transition intensity

The frequencies used in no way affect the accuracies of the calculations.

If TYPE = 2

Card 2 contains

Cols	Data	
1-12	$\langle (\Delta\nu)^2 \rangle$	decimal must be punched
13-24	$\langle (\Delta\nu)^3 \rangle$	" " " "
25-36	$\langle (\Delta\nu)^4 \rangle$	If this is not supplied the relation given between the coupling constants will be meaningless.

The last card should be

Cols	
1-3	999

The form of the output is as follows:

PROB NO. $\frac{1}{2}$	CHEMSHIFT	NUMBER OF NUCLEI
SPECIES A	ν_A	NA
SPECIES B	ν_B	NB
SPECIES C	ν_C	NC

THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING CONSTANTS

$$\left\{ 2 \langle (\Delta\nu)^4 \rangle - N_A \Delta\nu_A^4 - N_B \Delta\nu_B^4 - N_C \Delta\nu_C^4 \right\} = \left\{ N_A N_B (\nu_A - \nu_B)^2 \right\} \overbrace{J_{AB}^{**2}}^{= J_{AB}^2} + \left\{ N_A N_C (\nu_A - \nu_C)^2 \right\} J_{AC}^{**2} + \left\{ N_B N_C (\nu_B - \nu_C)^2 \right\} J_{BC}^{**2}$$

The contents of the brackets $\{ \}$ appear as numbers in the actual output. If all couplings between any two groups of nuclei are not equivalent then the RHS of the relation between the coupling constants can be reinterpreted by the program user in light of the original equations.

NMR MOMENT PROGRAM (NMREX 150A), cont:

SAMPLE CALCULATIONS

Attached are six sample calculations of different systems which were used to check the program. The results are remarkably good. The first sheet is the input data for the Wiberg program. The data from the Wiberg program was then put into the moment program, the results of which are found on the second and subsequent sheets. In some cases the data is rounded off to .1 cps and intensities are measured to 1% of the full height of the more intense peaks of the spectrum with the results still being quite good. The plotted spectrum from the input data is included to show how complicated a spectrum would have been observed in the actual case.

①

NUMBER OF PROBLEM IS 1
FREQUENCY AND INTENSITY OF LINES USED

28.9500	0.0050
38.6300	0.2950
42.3000	0.6450
42.6300	0.9940
44.3400	0.1880
46.3000	0.3880
48.3400	2.4330
49.6900	2.8670
53.6900	0.1800
55.9800	2.0610
58.0200	0.1220
61.6900	0.8690
63.3700	0.5290
67.0400	0.0380
69.0800	0.3870

W(1)=	45.00
W(2)=	48.00
W(3)=	61.00
A(1, 2)=	3.40
A(1, 3)=	7.20
A(2, 3)=	6.50

Input DATA

①

	CHEMSHIFT	NUMBER OF NUCLEI
SPECIES A	45.0123	1
SPECIES B	47.9955	1
SPECIES C	61.0047	1

THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING CONSTANTS

$$20488.2336 = 8.8998JAB^{**2} + 255.7593JAC^{**2} + 169.2399JBC^{**2}$$

NUMBER OF PROBLEM IS 1
FREQUENCY AND INTENSITY OF LINES USED

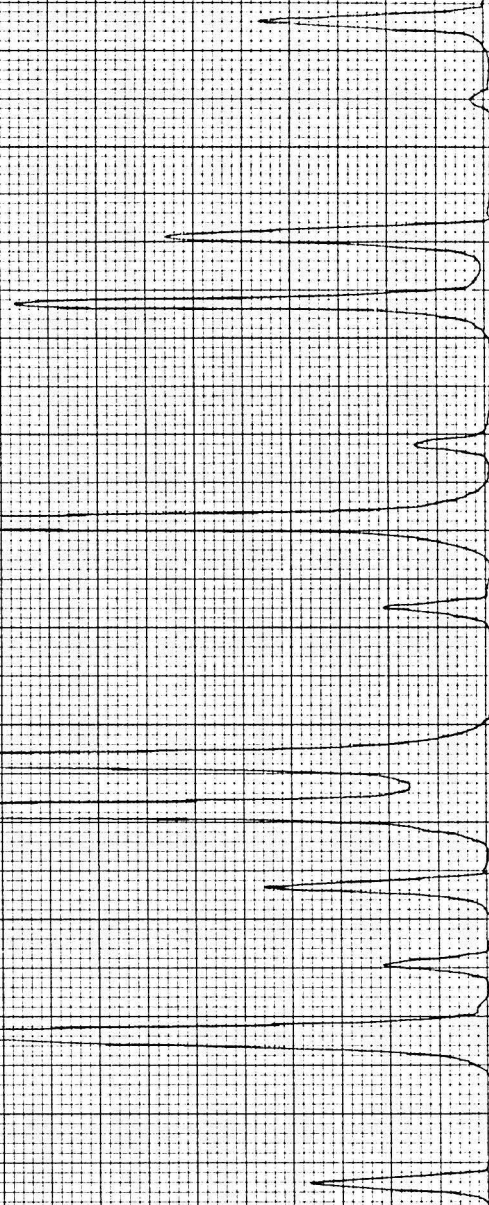
29.0000	0.0100
38.6000	0.3000
42.3000	0.6500
42.6000	1.0000
44.3000	0.1900
46.3000	0.3900
48.3000	2.4300
49.7000	2.8700
53.7000	0.1800
56.0000	2.0600
58.0000	0.1200
61.7000	0.8700
63.4000	0.5300
67.0000	0.0400
69.1000	0.3900

①

	CHEMSHIFT	NUMBER OF NUCLEI
SPECIES A	44.8578	1
SPECIES B	48.0730	1
SPECIES C	61.0201	1

THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING CONSTANTS

$$21158.0745 = 10.3375JAB^{**2} + 261.2222JAC^{**2} + 167.6293JBC^{**2}$$



1

②

Input DATA

②
W(1)= 26.70
W(2)= 43.20
W(3)= 45.80
A(1, 2)= 12.50
A(1, 3)= 6.40
A(2, 3)= 3.70

NUMBER OF PROBLEM IS 2

FREQUENCY AND INTENSITY OF LINES USED

15.0300	0.3220
19.5800	0.2290
21.9200	0.2000
26.2700	0.4070
28.6100	0.7190
33.1600	2.1270
35.6900	0.3950
40.1600	2.8540
42.3800	2.2830
46.8600	0.2680
46.9300	0.4940
49.2600	0.8230
51.4000	0.7430
53.7400	0.1300
67.5100	0.0050

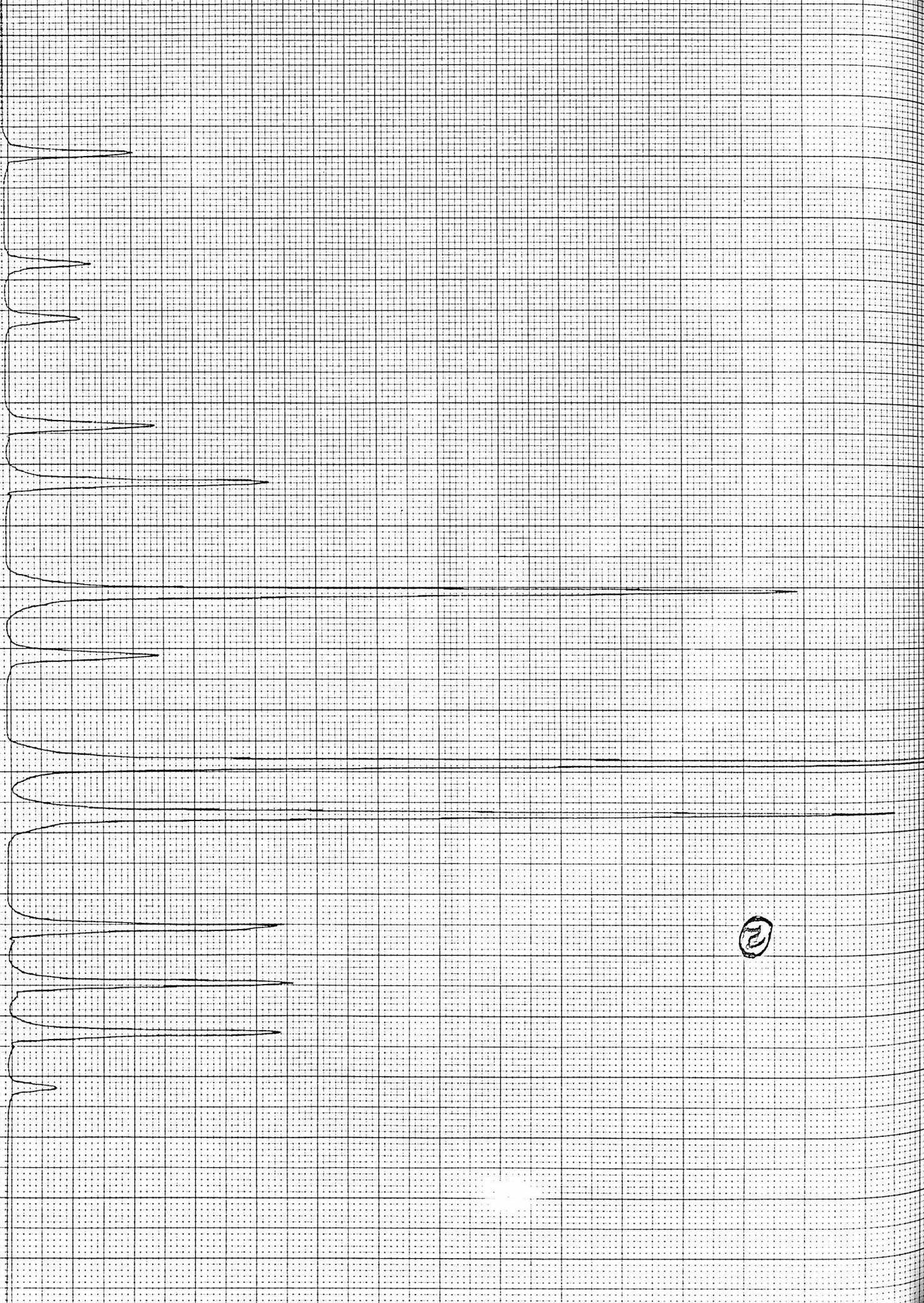
CHEMSHIFT NUMBER OF NUCLEY

SPECIES A	26.6991	1
SPECIES B	43.1890	1
SPECIES C	45.8130	1

②

THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING CONSTANTS

57736.2939= 271.9168JAB**2 + 365.3384JAC**2 + 6.8850JBC**2



③

Input Data

③

W(1)= 24.70
W(2)= 24.70
W(3)= 29.90
A(1, 2)= 12.00
A(1, 3)= 5.50
A(2, 3)= 5.50

NUMBER OF PROBLEM IS 3

FREQUENCY AND INTENSITY OF LINES USED

15.0600	0.0150
19.1000	0.3010
23.2200	1.1390
25.8600	2.8460
26.1800	3.6840
27.2500	2.6990
29.9000	1.0000
34.3400	0.1620
36.9900	0.1540

CHEMSHIFT NUMBER OF NUCLEI

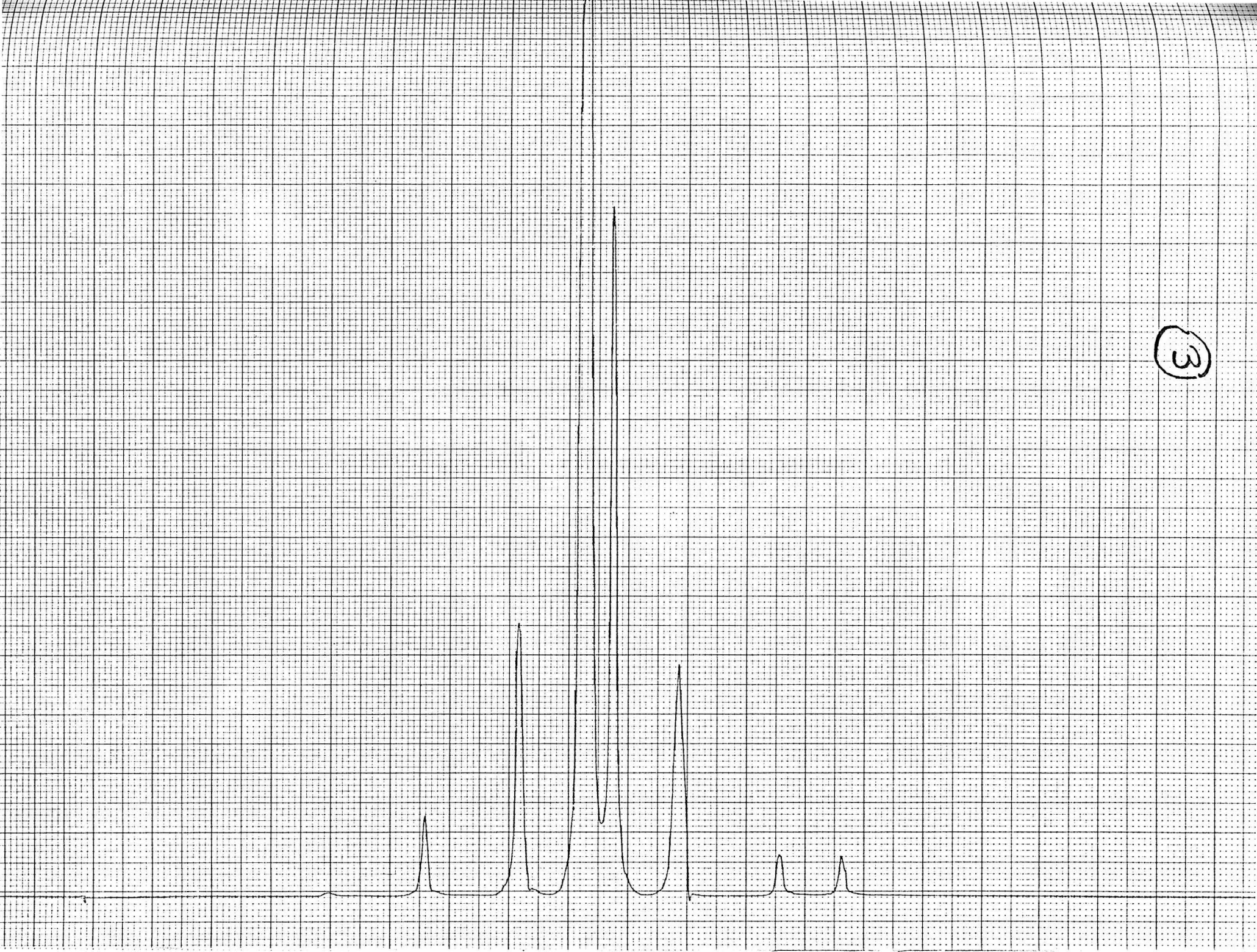
SPECIES A	24.6971	2
SPECIES B	29.8593	1
SPECIES C	26.4312 00.0000	0

← ignore this number if 0 nuclei in group.

THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING CONSTANTS

1642.3291= 54.1257JAB**2 + 0. JAC**2 + 0. JBC**2

3



4

Input Data

W(1)= 21.80
W(2)= 35.60
W(3)= 35.60
W(4)= 48.90
A(1, 2)= 4.50
A(1, 3)= 4.50
A(1, 4)= 1.60
A(2, 3)= 12.00
A(2, 4)= 4.90
A(3, 4)= 4.90

NUMBER OF PROBLEM IS 4
FREQUENCY AND INTENSITY OF LINES USED

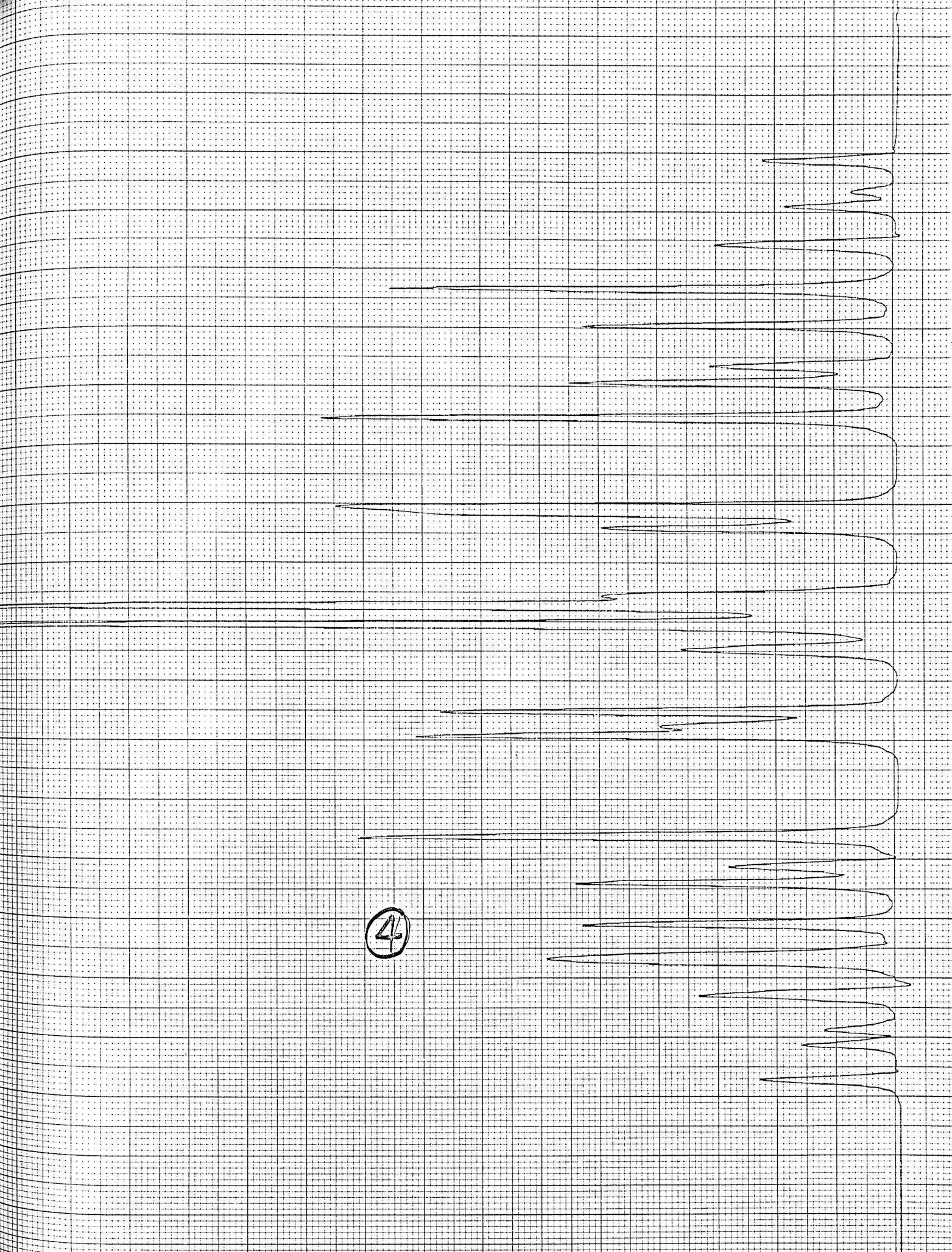
15.8300	0.4690
17.3400	0.3100
17.9900	0.2500
19.3700	0.6770
20.9800	0.9410
21.2600	0.8080
22.5800	1.0590
24.3100	1.0630
24.9600	0.5650
26.2900	1.8440
30.5700	1.5850
30.9700	0.6360
31.6200	1.5210
34.1200	0.7520
35.2900	3.3290
36.1200	3.3850
36.5600	0.8030
39.3900	0.9870
40.0400	1.3130
40.3200	1.7250
44.2000	1.9460
45.7100	1.0820
46.3600	0.6350
48.1200	1.0590
49.7200	0.9410
49.7500	0.7520
51.6400	0.6260
53.4200	0.3650
54.0700	0.1500
55.4000	0.4310

CHEMSHIFT NUMBER OF NUCLEI

SPECIES A	21.8030	1
SPECIES B	35.6021	2
SPECIES C	48.8972	1

THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING CONSTANTS

18039.0488= 380.8306JAB**2 + 734.0962JAC**2 + 353.5196JBC**2



4

5

Input Data

5

W(1)=	18.50
W(2)=	26.40
W(3)=	76.50
A(1, 2)=	12.00
A(1, 3)=	7.50
A(2, 3)=	7.50

NUMBER OF PROBLEM IS 5

FREQUENCY AND INTENSITY OF LINES USED

5.8400	0.1540
12.5100	0.1720
17.5500	1.6040
19.3700	1.5420
24.5800	2.0700
27.6200	2.1320
31.4400	0.1480
39.3300	0.1790
69.5600	1.3040
76.5900	1.0060
77.4500	0.9380
88.4900	0.7520

5

CHEMSHIFT NUMBER OF NUCLEI

SPECIES A	19.6411	1
SPECIES B	25.1785	1
SPECIES C	77.5397	1

THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING CONSTANTS

569574.9063= 30.6625JAB**2 + 3352.2537JAC**2 + 2741.7034JBC**2

5

6

Input Data

W(1)=	25.00
W(2)=	25.00
W(3)=	40.50
W(4)=	58.30
A(1, 2)=	6.50
A(1, 3)=	4.70
A(1, 4)=	10.50
A(2, 3)=	4.70
A(2, 4)=	10.50
A(3, 4)=	8.20

NUMBER OF PROBLEM IS 1
FREQUENCY AND INTENSITY OF LINES USED

-14.1500	0.0010
-12.6100	0.0020
1.7300	0.0010
4.5600	0.0180
12.4100	0.0060
15.1500	0.9900
17.8600	1.2160
21.2300	1.6650
22.3800	1.8630
25.2000	1.3400
26.7500	1.8130
30.4200	3.0790
30.4900	0.4480
31.6700	3.8140
35.5000	0.5820
36.5700	0.6670
39.5400	3.1620
41.0900	0.5100
41.8800	0.1790
43.7000	1.4180
46.0100	0.7950
47.1600	2.5210
47.4000	0.0210
49.6800	0.5460
55.1000	1.4180
56.2200	0.6440
57.2200	1.0910
63.3000	0.5820
66.1100	0.7060
66.6600	0.4670
71.5600	0.0160
74.7000	0.3750
85.3700	0.0020

CHEMSHIFT NUMBER OF NUCLEI

SPECIES A	24.9946	2
SPECIES B	40.5333	1
SPECIES C	58.3078	1

THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING CONSTANTS

276706.6133= 482.9018JAB**2 + 2219.5366JAC**2 + 315.9326JBC**2

(6)

NUMBER OF PROBLEM IS 1

FREQUENCY AND INTENSITY OF LINES USED

4.5600	0.0180
15.1500	0.9900
17.8600	1.2160
21.2300	1.6650
22.3800	1.8630
25.2000	1.3400
26.7500	1.8130
30.4200	3.0790
30.4900	0.4480
31.6700	3.8140
35.5000	0.5820
36.5700	0.6670
39.5400	3.1620
41.0900	0.5100
41.8800	0.1790
43.7000	1.4180
46.0100	0.7950
47.1600	2.5210
47.4000	0.0210
49.6800	0.5460
55.1000	1.4180
56.2200	0.6440
57.2200	1.0910
63.3000	0.5820
66.1100	0.7060
66.6600	0.4670
71.5600	0.0160
74.7000	0.3750

CHEMSHIFT NUMBER OF NUCLEI

SPECIES A	25.0321	2
SPECIES B	40.4826	1
SPECIES C	58.3132	1

THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING CONSTANTS

269201.4180 = 477.4370JAB**2 + 2215.2594JAC**2 + 317.9286JBC**2

6

NUMBER OF PROBLEM IS 1

FREQUENCY AND INTENSITY OF LINES USED

15.1500	0.9900
17.8600	1.2160
21.2300	1.6650
22.3800	1.8630
25.2000	1.3400
26.7500	1.8130
30.4200	3.0790
30.4900	0.4480
31.6700	3.8140
35.5000	0.5820
36.5700	0.6670
39.5400	3.1620
41.0900	0.5100
41.8800	0.1790
43.7000	1.4180
46.0100	0.7950
47.1600	2.5210
49.6800	0.5460
55.1000	1.4180
56.2200	0.6440
57.2200	1.0910
63.3000	0.5820
66.1100	0.7060
66.6600	0.4670
74.7000	0.3750

CHEMSHIFT NUMBER OF NUCLEI

SPECIES A	25.0770	2
SPECIES B	40.3948	1
SPECIES C	58.2893	1

THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING CONSTANTS

262836.2344= 469.2692JAB**2 + 2206.1070JAC**2 + 320.2118JBC**2

6

NUMBER OF PROBLEM IS 1
FREQUENCY AND INTENSITY OF LINES USED

15.2000	0.9900
17.9000	1.2200
21.2000	1.6700
22.4000	1.8600
25.2000	1.3400
26.8000	1.8100
30.4000	3.0800
30.5000	0.4500
31.7000	3.8100
35.5000	0.5800
36.6000	0.6700
39.5000	3.1600
41.1000	0.5100
41.9000	0.1800
43.7000	1.4200
46.0000	0.8000
47.2000	2.5200
49.7000	0.5500
55.1000	1.4200
56.2000	0.6400
57.2000	1.0900
63.3000	0.5800
66.1000	0.7060
66.7000	0.4700
74.7000	0.3800

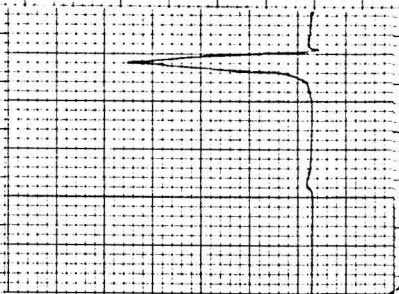
CHEMSHIFT NUMBER OF NUCLEI

SPECIES A	25.0942	2
SPECIES B	40.3832	1
SPECIES C	58.3165	1

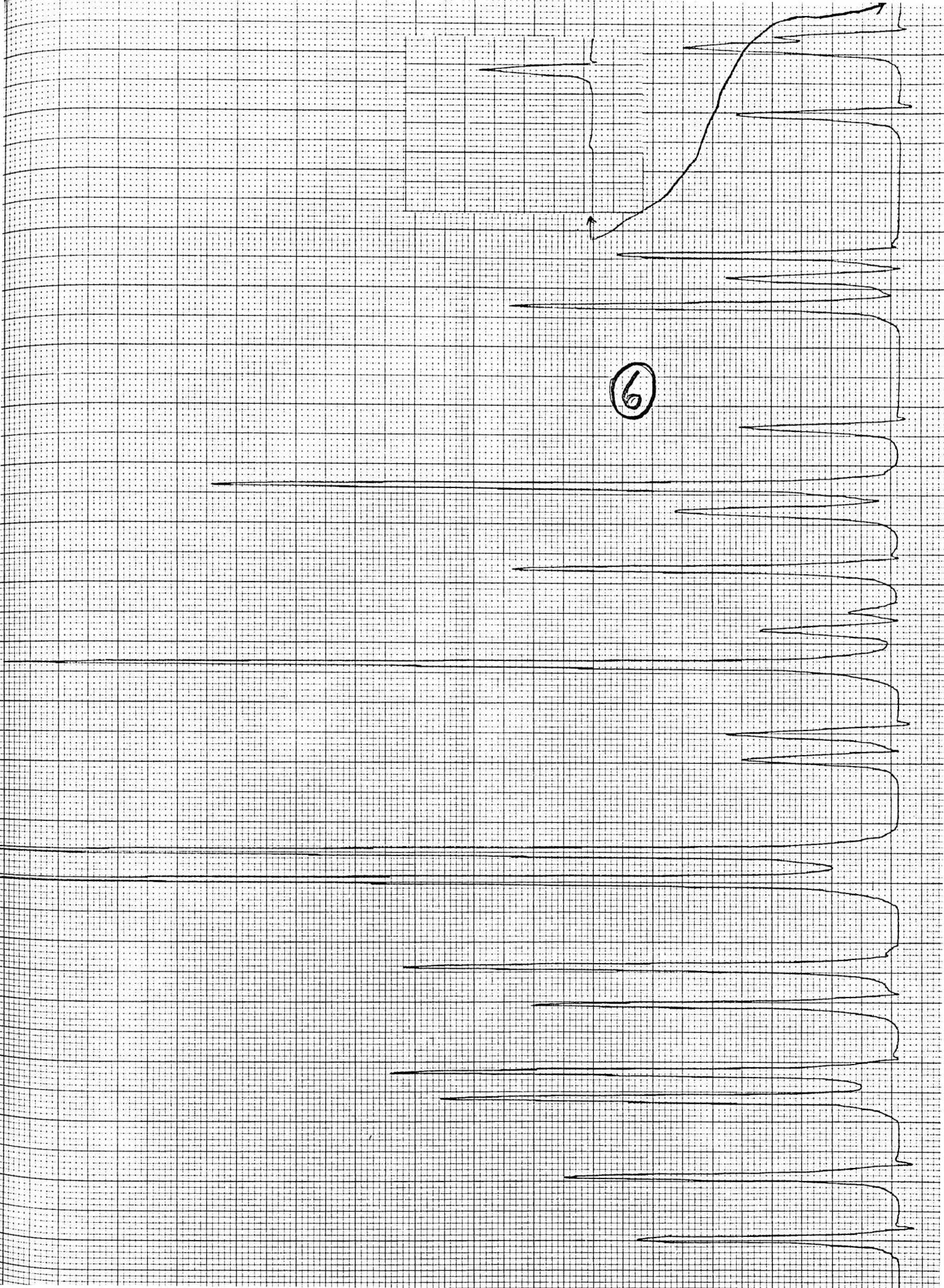
6

THE FOLLOWING RELATION EXISTS BETWEEN THE COUPLING CONSTANTS

263093.2422 = 467.5114JAB**2 + 2207.4417JAC**2 + 321.6005JBC**2



6



This program solves the equations presented on page (5) of the thesis. A plot is supplied which represents the observed spectrum as a function of the input parameters. The output lists are inclusive of all the data going into each plot.

The next card can be the same as card 1 with another problem

•

Final card 1-3 999 - Calls end of program NO

PROGRAM FOR CALCULATING NMR SPECTRA (AB CASE)
WITH A AND B EXCHANGING

```

C
C
COMPLEX SPEC,DEN,ANUM,S
DIMENSION PLT(1500)
DATA FAL / 6CH AB CASE NUCLEI EXCHANGE
$
950 READ(5,2) N1,N2,RT,VA,VB,CO,ALIM,BLIM
C N1 = PROBLEM NUMBER
C N2 = NUMBER OF VALUES OF TAU SUPPLIED
C RT = RELAXATION TIME (T2) IN SECONDS
C VA VB CO ARE CHEM SHIFT AND COUPLING IN CPS
WRITE(6,3) N1
2 FORMAT(I3,I2,F7.4,5F12.4)
3 FORMAT(19H PROBLEM NUMBER IS , I3/)
IF(N1-999) 181,180,180
181 CONTINUE
S = (0.,1.)
WRITE(6,4) VA,VB,CC,RT,ALIM,BLIM
C ALIM AND BLIM ARE LEFT AND RIGHT PLOT FREQUENCIES IN CPS
4 FORMAT(21H SPECTRAL PARAMETERS /14H CHEMSHIFT A ,F12.3,4H CPS/
$ 14H CHEMSHIFT B ,F12.3,4H CPS/14H JAB ,F12.3,4H CPS//
$18H RELAXATION TIME ,F12.6,8H SECONDS//18H LEFT PLOT FREQ ,
$ F12.3/18H RIGHT PLOT FREQ ,F12.3//)
WRITE(6,6)
6 FORMAT(28H VALUES OF TAU USED IN PLOTS )
WID = (BLIM-ALIM)/1500.
WID = WID*6.28318
CO = CO*6.28318
VA = VA*6.28318
VB = VB*6.28318
DIF = (VA-VB)/2.
CC = CC/2.
DO 169 J = 1,N2
READ(5,1) TAU
1 FORMAT(F12.7)
WRITE(6,5) TAU
5 FORMAT(8H TAU = , F12.6,8H SECONDS)
TOP = 0.0
T = -1./TAU - 1./RT
DO 69 N = 1,1500
SPEC = (0.,0.)
SH = N
SH = SH*WID
W = ALIM*6.28318 + SH
DEL = -(VA+VB)/2. + W
DO 101 K = 1,2
CO = -CO
DEN = (T+S*(DEL+DIF-CO))*(T+S*(DEL-DIF-CO))-(1./TAU+S*CO)**2
ANUM = -S*(2./RT+4./TAU) + 4.*CO - 2.*DEL
SPEC = SPEC + ANUM/DEN
101 CONTINUE
PLT(N) = AIMAG(SPEC)
PLT(N) = ABS(PLT(N))
TOP = AMAX1(TOP,PLT(N))
69 CONTINUE

```

TCP = TCP*5./3.

BCT = -TCP/3.

CALL CPLCT(PLT,1500,1500,FAL,TOP,BOT,J)

169 CONTINUE

GC TC 95C

180 STOP

END

ABC * EXCHANGE PROGRAM (A and B exchanging intramolecularly)
NMREX 004A

This program solves and plots the equations on page 9 of the thesis. Provisions are made for calculating only one problem at a time, with any number of tau values.

<u>INPUT CARDS</u>	<u>COLUMN</u>	<u>DATA</u>	<u>DECIMAL</u>
Card 1	1-2	N1 = no. of values of tau supplied	NO
	3-7	ALIM - left plot frequency (cps)	YES
	8-12	BLIM - right plot frequency	YES
	13-23	SHA = chemical shift of nucleus A (cps)	YES
	24-34	SHB	YES
	35-45	SHC	YES
	46-52	CAB = coupling between A and B (cps)	YES
	53-59	CAC	YES
	60-66	CBC	YES
	67-72	RT = T_2 in seconds	YES
Card 2 through Card N1+1	1-12	Tau (in seconds)	YES

_____ no further cards needed. Due to the number of points used in the plot, the spectra may be a little "rough."

```

C 3 SPIN ABC CASE INTRCMOLECULAR AB EXCHANGE
C COMPLETES THE THREE UPPER TRANSITIONS
C INPUT DATA SHOULD BE IN CPS
  READ(5,1) N1,ALIM,BLIM,SFA,SHB,SHC,CAB,CAC,CBC,RT
1  FCRMAT(I2,2F5.2,3F11.4,3F7.3,F6.3)
  COMPLEX SA, SB, SC, SD, SE, SF, SG, SH, SAP, SBP, SCP, DEN
  DIMENSION PLT1(500), PLT2(500), PLT3(500)
  CAB = .5*CAB*6.28318
  CAC = .5*CAC*6.28318
  CBC = .5*CBC*6.28318
  SFA = 6.28318*SFA
  SHB = 6.28318*SHB
  SHC = 6.28318*SHC
  DO 2 J = 1,N1
    READ(5,3) TAU
  2  FCRMAT(F12.7)
    SA = (0.,-1.)*(1./RT) - CBC - CAC
    SB = (0.,-1.)*(1./TAU + 1./RT) - CBC - CAB
    SC = (0.,-1.)*(1./TAU + 1./RT) - CAB - CAC
    SD = (0.,1.)*(1./TAU) + CAB
    RA = CBC
    RB = CAC
    WIC = (BLIM-ALIM)*6.28318
    WIC = WIC/500.
    DO 4 I = 1,500
      SHIFT = I
      SHI = SHIFT*WIC + ALIM*6.28318
      DELA = SHI - SFA
      DELB = SHI - SHB
      DELC = SHI - SHC
      SAP = SA - DELC
      SBP = SB - DELB
      SCP = SC - DELA
      DEN = SAP*(SBP*SCP - SD*SD) - RA*(RA*SCP - RB*SD) + RB*(RA*SD -
$    RB*SBP)
      SF = (SBP*SCP - SD*SD) - RA*(SCP - SD) + RB*(SD - SBP)
      SF = SF/DEN
      SG = SAP*(SCP - SD) - RA*SCP + RB*SD + RB*(RA - RB)
      SG = SG/DEN
      SH = SAP*(SBP - SD) - RA*(RA - RB) + RA*SD - RB*SBP
      SH = SH/DEN
      PLT1(I) = AIMAG(SF)
      PLT2(I) = AIMAG(SG) + .1
      PLT3(I) = AIMAG(SH) + .2
  4  CONTINUE
  DATA FAL / 60H      ABC COMPUTER PROGRAM FOR THREE TRANSI.
$
  A = 3.0
  B = -1.00
  DO 987 KJ = 1,500
987 PLT1(KJ) = PLT1(KJ) + PLT2(KJ) + PLT3(KJ)
  CALL CPLCT(PLT1,500,500,FAL,A,B,J)
  2  CONTINUE
  STOP
  END

```


AB CHEMICAL EXCHANGE PROGRAM - NMREX 003A

This program solves and plots the equations on page 32 of the thesis. Only one problem at a time may be run and up to 10 tau values plotted. (the number of tau values should be an even number as two spectra are plotted on each sheet.) The zero of frequency is at the center of the AB spectrum.

<u>INPUT CARDS</u>	<u>COLUMNS</u>	<u>DATA</u>	<u>DECIMAL</u>
Card 1	1-2	N1 = number of values of tau supplied	NO
	3-14	D = $\frac{1}{2}$ of chemical shift difference	YES
	15-26	ALIM = left plot frequency	YES
	27-38	BLIM = right plot frequency	YES
	39-50	RT = T ₂ in secs	YES
	51-62	CO- coupling in cps	YES
Card 2 through N1+1	1-12	Tau - values to be employed with the above data	YES

no further cards needed

```

C      CHEMEX PROGRAM FOR CHEMICAL EXCHANGE OF NUCLEI
C      PLOTS UP TO 10 TAU VALUES TWO PER PLOT
C      ASK TO HAVE OUTPUT PLOTTED IN CYCLES OF TWO PER PAGE
C      2*CC IS CHEM SHIFT DIFFERENCE IN PROGRAM
C      S IS CMGA MINUS CMGA ZERO
C      CC IS COUPLING CONSTANT BETWEEN THE TWO NUCLEI
C      N1 IS THE NUMBER OF PLOTS DESIRED SHOULD BE AN EVEN NUMBER
C      ALIM AND BLIM ARE LEFT AND RIGHT PLOT FREQUENCIES
C      RT IS THE RELAXATION TIME IN SECONDS
      COMPLEX A,U1,U2,AAM,AAP,BBP,BBM
      COMPLEX CSQRT
      COMPLEX SPEC
      DIMENSION PLOT(300)
      DIMENSION PLT(10,300)
      DIMENSION TOP(10)
      READ(5,119) N1,C,ALIM,BLIM,RT,CO
119    FORMAT(I2,5F12.4)
      C = .5CC*C*6.28318
      CC = CC*6.28318
      CC 69 N= 1,N1
      TOP(N) = C.C
      READ(5,222) TAU
222    FORMAT(F12.7)
C      WID IS TO BE RADIAN PER POINT IN THE SPECTRUM OF 300 POINTS
      WID = BLIM - ALIM
      WID = WID/300.
      WID = WID*6.28318
      AX = .25*CC**4 + CC*CO*D*D - (C*D)/(TAU*TAU)
      IF(AX) 31,31,32
31     A = (C.,1.)*SQRT(-AX)
      GO TO 33
32     A = (1.,0.)*SQRT(AX)
33     U1 = CSQRT(C*D + .5*CC*CC - .25/(TAU*TAU) + A)
      U2 = CSQRT(C*D + .5*CC*CC - .25/(TAU*TAU) - A)
      AAM = 1. - CC*CC/(2.*A)
      AAP = 1. + CC*CC/(2.*A)
      BBP = (1. + (4.*C*D - CC*CC)/(2.*A))/(2.*TAU*U1)
      BBM = (1. - (4.*C*D - CC*CC)/(2.*A))/(2.*TAU*U2)
      TT = -1./(2.*TAU) - 1./RT
      CO 96 K = 1,300
      ASS = K
      DEL = ASS-150.
      DEL = DEL*WID
      SPEC = (AAM - (C.,1.)*BBP)/(DEL - U1 + (C.,1.)*TT)
      SPEC = SPEC + (AAM + (C.,1.)*BBP)/(DEL + U1 + (C.,1.)*TT)
      SPEC = SPEC + (AAP - (C.,1.)*BBM)/(DEL - U2 + (C.,1.)*TT)
      SPEC = SPEC + (AAP + (C.,1.)*BBM)/(DEL + U2 + (C.,1.)*TT)
      PLT(N,K) = AIMAG(SPEC)
      TOP(N) = AMAX1(TOP(N),PLT(N,K))
96    CONTINUE
69    CONTINUE
      TOPC = 0.0
      CC 169 J = 1,N1
      TOPC = AMAX1(TOPC,TOP(J))
169   CONTINUE
  
```

```

C  ALL PARTS OF PROGRAM CCNE IN RADIANS  INPUT IS IN CPS
DATA  FAL/ 6CH  AB COMPUTER PROGRAM FOR CHEMICAL EXCHANGE
$
TCPC = TCPC/.4
TOPC = 3.48
BOT = 0.C
CCN = 1.C
CC 196 L= 1,N1
CCN = -CCN
IF(CCN) 1,1,2
1  BCTP = .C5*TCPC
GO TO 111
2  BCTP = TCPC*11./2C.
111  CC 112 K1 = 1,3CC
PLCTC(K1) = BCTP + PLT(L,K1)
112  CONTINUE
CALL CPLCT(PLCTC,3CC,300,FAL,TOPO,BOT,L)
196  CONTINUE
STOP
END

```

NMREX 150A - MOMENT CALCULATION PROGRAM

Programmer: _____ Extension: _____

Charge number: _____ Date: _____

Timing: Allow 1 minute plus 3 seconds per problem. Round off the time to the next highest integral number of minutes.

Time: _____

CARD 1	Columns	Data
	1-3	_____ Number of problem
	4	_____ = 2 for reading frequency and intensity data (999 cards maximum) NTYPE
	5-7	_____ =1 for reading moments Number of cards with frequency and intensity data (999 maximum)
	8-9	_____ Number of nuclei in group A (low freq.)
	10-11	_____ Number of nuclei in group B (intermed. freq.)
	12-13	_____ Number of nuclei in group C (high freq.)

CARD 2 depends on whether NTYPE = 1 or 2

IF NTYPE = 1

Card 2	Columns	Data
	1-12	_____ Second moment relative to the mean
	13-24	_____ Third moment relative to the mean
	25-36	_____ Fourth moment relative to the mean (if this is not supplied the relation between the coupling constants will be meaningless)

IF NTYPE = 2

Card 2	Columns	Data
on (up to 999 cards)	1-12	Frequency of transition or segment
	13-24	Intensity of "

Final Card after all problems: Cols. 1-3 999