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NUCLEAR MAGNETIC DOUBLE RESONANCE EXPERIMENTS
ON CHEMICALLY EXCHANGING MOLECULES

A THESIS

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SUMMARY

A theoretical and experimental study of nuclear magnetic double resonance experiments on chemically exchanging molecules is carried out in this thesis. The compounds $\text{CCl}_3\text{CH}_2\text{OH}$ and CH_3OH are used to illustrate the results. The $\text{CCl}_3\text{CH}_2\text{OH}$ compound is treated as an AX_2 spin system, and the CH_3OH compound as an AX_3 system.

The Gutowsky, McCall, and Slichter, as well as the McConnell extension of the Bloch equations are compared and cast in a convenient probability formulation. Explicit line shape formulas are obtained for AX_2 and AX_3 systems in which the A nucleus undergoes chemical exchange.

Theoretical intensity expressions are derived for frequency sweep double resonance experiments in which an X transition is irradiated by the strong rf field, H_2 . The expressions are derived using a model based upon energy level populations. This double resonance technique provides a method for investigating slow self-exchange processes between the same molecules. The line shape technique is valid only if the exchange rate is fast compared with the experimental line width. The analysis takes into account possibilities of multiplet structure and arbitrary amplitudes of the strong rf field. The above results are illustrated with the compound $\text{CCl}_3\text{CH}_2\text{OH}$ for an AX_2 spin system. The exchange rate of $\text{CCl}_3\text{CH}_2\text{OH}$ is varied by complexing with dimethylsulfoxide. The exchange rate of CH_3OH is changed by temperature variation.

Experiment and theory are in qualitative agreement, but not in

satisfactory quantitative agreement. This is believed due to experimental difficulties associated with the strong rf field used in the double resonance experiments. The large signal produced by the strong rf tended to overload the detector and distort the NMR spectra. The results indicate that the chemical exchange has the same effect as the spin-lattice relaxation in driving the perturbed spin system toward the Boltzmann distribution.

CHAPTER I

INTRODUCTION

In a weakly coupled spin system,¹ several modifications of the Bloch equations² have been used to investigate proton exchange between different sites. One such set of equations, the GMS equations, was obtained from the modified Bloch equations solved by Gutowsky, McCall, and Slichter.³ The GMS approach was extended by Gutowsky and Saika,⁴ and Grunwald, Loewenstein, and Meiboom,⁵ and Luz, Gill, and Meiboom.⁶ Starting from a different point of view, McConnell⁷ introduced a modification of the Bloch equations known as the McConnell equations by assuming that the magnetization could be transferred between different sites in a manner analogous to that of ordinary chemical exchange. If there is a steady state and no saturation, the McConnell equations reduce to the GMS equations.

In strongly coupled systems the nuclear spin density matrix master equation was used by Alexander^{8,9} to investigate chemical exchange.

In addition to the above steady state line shape methods, other techniques were introduced. McConnell and Thompson¹⁰ used adiabatic fast passage to measure exchange rates. Nonequilibrium nuclear spin magnetization equations were derived to calculate exchange rate constants. Forsén and Hoffman^{11,12} have determined the rate constants and spin-lattice relaxation times at chemically shifted sites by double resonance experiments.

The purpose of this thesis is to study nuclear magnetic double resonance experiments on chemically exchanging molecules. The double resonance experiments discussed in this thesis are related to those of Forsén and Hoffman.^{11,12} Forsén and Hoffman consider only chemically shifted peaks, and therefore studied exchange between different compounds. They also confined their studies to complete saturation by the strong rf field. In this thesis, multiplet structure is considered and self-exchange involving one compound is investigated. Also, expressions are derived for intermediate saturation strengths for the strong rf field.

In Chapter II, an explicit probability notation is introduced to compare the GMS and McConnell extensions of the Bloch equations to chemical exchange. Explicit line shape formulas are derived for AX_2 and AX_3 spin systems¹ in which the A nucleus undergoes chemical exchange. The AX_2 formulas are applied to CCl_3CH_2OH , and the AX_3 formulas to CH_3OH .

A theoretical description of the combined effect of double resonance saturation and chemical exchange on the multiplet structure of CCl_3CH_2OH and CH_3OH is presented in Chapter III. This provides a method for determining the average time interval between chemical exchange when the exchange is too slow to affect the line shapes. The strong rf is used to perturb the weakly coupled spin system from the Boltzmann distribution, but the chemical exchange and spin-lattice relaxation decrease this deviation. This has been investigated in CCl_3CH_2OH and CH_3OH as a function of proton exchange rate. The experimental results are compared with theoretical predictions in Chapter IV.

CHAPTER II

DEPENDENCE OF LINE SHAPES ON CHEMICAL EXCHANGE

The GMS³ and McConnell⁷ extensions of the Bloch equations to chemical exchange are compared in this chapter. An explicit probability notation is introduced in making the comparison. Explicit line shape formulas are derived for AX_2 and AX_3 spin systems¹ in which the A nucleus undergoes chemical exchange. The AX_2 formulas will be applied to CCl_3CH_2OH , and the AX_3 formulas to CH_3OH .

Let τ be defined as the average time interval between chemical exchange. The probability factor, f_{ab} , is defined as the probability of a proton transferring from site b to site a during a chemical exchange. Actually, f_{ab} is equal to the probability of a proton leaving site b times the probability of this proton arriving at site a. The GMS equations assume a steady state and no rf saturation. They are derived as follows.

The Bloch equations¹ for the transverse magnetization at site a in a coordinate system rotating with an angular velocity of $-\omega_1$ are

$$\frac{dm_{xa}}{dt} + \Delta\omega_a m_{ya} = -\frac{m_{xa}}{T_2} \quad (1)$$

and

$$\frac{dm_{ya}}{dt} - \Delta\omega_a m_{xa} = -\frac{m_{ya}}{T_2} - 2\pi V_1 m_0 \quad (2)$$

In equations (1) and (2), T_2 is the transverse relaxation time, m_{xa} and m_{ya} are the components of magnetization per molecule along the x and y axes of the rotating coordinate system, and m_0 is the thermal equilibrium magnetization per molecule at site a. If there is no rf saturation, the magnetization per molecule along the z axis at site a is equal to m_0 . The observing rf field \vec{H}_1 is given in the laboratory frame by

$$\vec{H}_1 = 2\pi V_1 \cos \omega_1 t \hat{i} - 2\pi V_1 \sin \omega_1 t \hat{j}$$

where V_1 is the amplitude of \vec{H}_1 in cps, ω_1 is the angular frequency in radians per second, and \hat{i} and \hat{j} are unit vectors along the laboratory x and y axes, respectively. The frequency deviation $\Delta\omega_a$ is defined by $\Delta\omega_a = \omega_a - \omega_1$, where ω_a is the resonance frequency of site a in radians per second.

Now, g_a is defined as the complex magnetization per molecule at site a and equals $m_{xa} + i m_{ya}$. The steady state magnetization¹ per molecule at site a, $\langle \bar{g}_a \rangle$, due to chemical exchange is obtained from (1) and (2) by first time averaging with a weight factor of $\frac{1}{\tau} e^{-t/\tau}$, and then averaging over initial conditions. It is given by

$$\langle \bar{g}_a \rangle = \frac{-2\pi i V_1 m_{0a} \tau}{1 + \alpha_a \tau} + \frac{\langle g_{0a} \rangle}{1 + \alpha_a \tau} \quad (3)$$

In equation (3), $\langle g_{0a} \rangle$ = average initial value and $\alpha_a = \frac{1}{T_2} - i \Delta\omega_a$.

Set n equal to the number of exchange sites. In this thesis, sites corresponding to coincident transitions will be treated as separate sites

even though their resonance frequencies are equal. Then

$$\langle g_{0a} \rangle = \sum_{b \neq a} f_{ab} \langle \bar{g}_b \rangle + (1 - \sum_{b \neq a} f_{ba}) \langle \bar{g}_a \rangle \quad (4)$$

For convenience, $-\sum_{b \neq a} f_{ba}$ is denoted by f_a which equals the probability of a proton leaving site a and going to any other site. The sign of f_a is negative since the proton leaves site a. Then, equation (3) becomes

$$\langle \bar{g}_a \rangle (1 + \alpha_a \tau) = -2\pi i V_1 m_0 \tau + \sum_{b \neq a} f_{ab} \langle \bar{g}_b \rangle + (1 + f_a) \langle \bar{g}_a \rangle \quad (5)$$

or

$$\left(\frac{f_a}{\tau} - \alpha_a \right) \langle \bar{g}_a \rangle + \frac{1}{\tau} \left(\sum_{b \neq a} f_{ab} \langle \bar{g}_b \rangle \right) = 2\pi i V_1 m_0$$

Equation (5) also can be derived from the McConnell equations.⁷

For no rt saturation, the McConnell equations are

$$\frac{dM_{xa}}{dt} + \Delta\omega_a M_{ya} = -\frac{M_{xa}}{T_2} + \frac{f_a M_{xa}}{\tau} + \frac{1}{\tau} \sum_{b \neq a} f_{ab} M_{xb} \quad (6)$$

and

$$\frac{dM_{ya}}{dt} - \Delta\omega_a M_{xa} = -\frac{M_{ya}}{T_2} + \frac{f_a M_{ya}}{\tau} + \frac{1}{\tau} \sum_{b \neq a} f_{ab} M_{yb} - 2\pi V_1 M_0 \quad (7)$$

All terms are defined as before except for M_{xa} , M_{ya} , and M_0 which are components of the total magnetization at site a along the x, y, and z axes of the rotating coordinate system, respectively. Define $\langle \bar{G}_a \rangle$ equal to the total complex magnetization at site a and set it equal to $M_{xa} + i M_{ya}$. Adding (6) to $i \times$ (7), the following equation is obtained.

$$\frac{d \langle \bar{G}_a \rangle}{dt} + \langle \bar{G}_a \rangle \alpha_a = - 2\pi i V_1 M_0 + \frac{f_a \langle \bar{G}_a \rangle}{\tau} + \frac{1}{\tau} \sum_{b \neq a} f_{ab} \langle \bar{G}_b \rangle \quad (8)$$

At the steady state, equation (8) becomes

$$\left(\frac{f_a}{\tau} - \alpha_a \right) \langle \bar{G}_a \rangle + \frac{1}{\tau} \sum_{b \neq a} f_{ab} \langle \bar{G}_b \rangle = 2\pi i V_1 m_0 \quad (9)$$

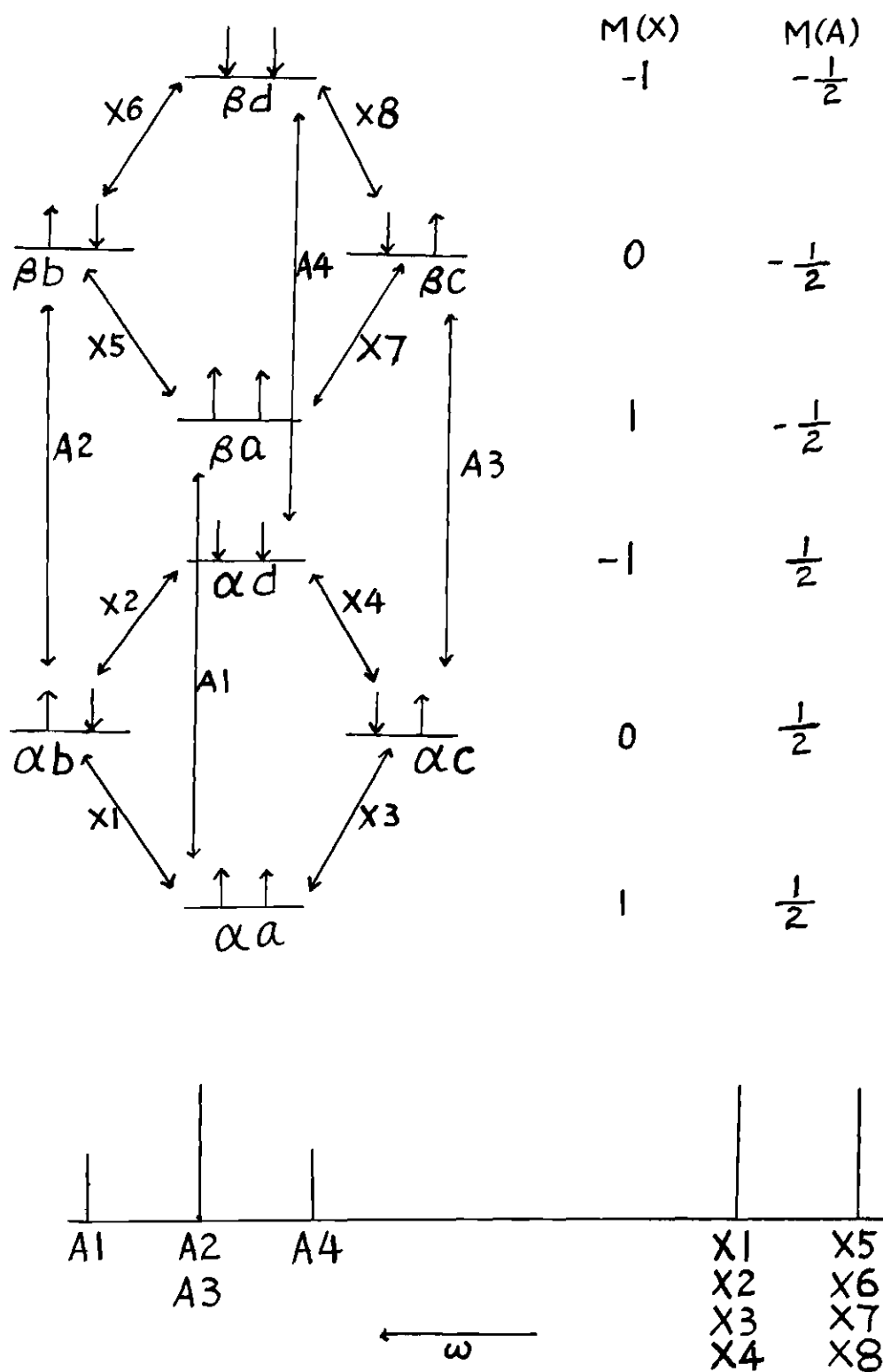
If n' is defined as the number of molecules per cc, then $\langle \bar{g}_a \rangle$ is equal to $\frac{\langle \bar{G}_a \rangle}{n'}$. Therefore, when equation (9) is divided by n' , it becomes

$$\left(\frac{f_a}{\tau} - \alpha_a \right) \langle \bar{g}_a \rangle + \frac{1}{\tau} \sum_{b \neq a} f_{ab} \langle \bar{g}_b \rangle = 2\pi i V_1 m_0 \quad (10)$$

Equation (10) is exactly the same as equation (5). Hence, there exist n linear equations for n unknown complex magnetizations. After these n unknowns are solved for the total complex magnetization per molecule over n sites, g is set equal to $\sum_a^n \langle \bar{g}_a \rangle$. The detected NMR signal is proportional to the imaginary part of g .

Equations (5) or (10) will now be used to calculate the spectra for an AX_2 and an AX_3 spin system where A is undergoing chemical exchange.

First, consider an AX_2 system. A schematic energy level diagram and spectrum for an AX_2 spin system are shown in Figure 1. The magnetic quantum number for the A proton is denoted by $M(A)$, and the total magnetic quantum number for the two X protons is denoted by $M(X)$. The value of $M(A)$ and $M(X)$ for each state is given on the right hand side of the figure. The A proton states are denoted by α and β , where $M(A)$ equals

Figure 1. Energy Level Diagram for AX_2 System

$\frac{1}{2}$ for α and $-\frac{1}{2}$ for β . The states for the two X protons are denoted by a, b, c, and d, where $M(X)$ equals 1 for a, etc. The combined spin function for the state of the A and X protons equals the product of the A and X spin functions. The set of arrows by the symbol for each state represents the X spin function for that state.

There are four A transitions corresponding to the selection rule¹ $\Delta M(A) = \pm 1$, and $\Delta M(X) = 0$. They are labeled A1, A2, A3, and A4 in the spectrum and correspond to $M(X) = -1, 0, 0$, and 1, respectively. The A2 and A3 transitions are coincident.

There are eight X transitions corresponding to the selection rule¹ $\Delta M(A) = 0$ and $\Delta M(X) = \pm 1$. They are labeled by X1 through X8 on the energy level diagram and spectrum. The transitions X1 through X4 are coincident, and the transitions X5 through X8 are coincident.

The lines A1, A2, A3, and A4 correspond to four exchange sites for the A proton. The A lines correspond to the following transitions:

Line	Transition
A1	$\alpha\alpha - \beta\alpha$
A2	$\alpha\beta - \beta\beta$
A3	$\alpha\alpha - \beta\alpha$
A4	$\alpha\beta - \beta\beta$

These four sites will be denoted by a, b, c, and d, respectively, in the following. The corresponding complex magnetizations will be denoted by g_a , g_b , g_c , and g_d .

Using equations (5) and (10)

$$\left(\frac{f_a}{\tau} - \alpha_a\right) \langle \bar{g}_a \rangle + \frac{1}{\tau} \left(f_{ab} \langle \bar{g}_b \rangle + f_{ac} \langle \bar{g}_c \rangle + f_{ad} \langle \bar{g}_d \rangle\right) \quad (11)$$

$$= 2\pi i V_1 m_0$$

By definition, f_{ab} is equal to the probability of a proton leaving site b times the probability of this proton arriving at site a. The probability of a proton leaving site b during an exchange is equal to three-fourths. This result is obtained from the following reasoning. The proton which leaves site b in molecule 1 can go to four sites in molecule 2: a, b, c, and d. If the proton goes to site b in molecule 2, there has been no net transfer of protons out of site b. If the proton goes to sites a, c, or d in molecule 2, there has been a net transfer of protons out of site b. The probability of a proton which has definitely left site b arriving at site a is equal to one-third. This is because there are three sites a, c, and d to which the proton can go. Therefore, f_{ab} is equal to $\frac{3}{4} \times \frac{1}{3} = \frac{1}{4}$. In the same way, $f_{ac} = f_{ad} = \frac{1}{4}$. Since f_a is equal to $-\sum_{b \neq a} f_{ba}$, $f_a = -\frac{1}{4} - \frac{1}{4} - \frac{1}{4} = -\frac{3}{4}$. Equation (11) becomes

$$\left(\frac{-3}{4\tau} - \alpha_a\right) \langle \bar{g}_a \rangle + \frac{1}{\tau} \left(\frac{\langle \bar{g}_b \rangle}{4} + \frac{\langle \bar{g}_c \rangle}{4} + \frac{\langle \bar{g}_d \rangle}{4}\right) = 2\pi i V_1 m_0 \quad (12)$$

or

$$\left(-\frac{3}{4\tau} - \alpha_a\right) \langle \bar{g}_a \rangle + \frac{1}{\tau} \left(\frac{\langle \bar{g}_b \rangle}{2} + \frac{\langle \bar{g}_d \rangle}{4}\right) = 2\pi i V_1 m_0 \quad (13)$$

In (12), $\langle \bar{g}_c \rangle$ is equal to $\langle \bar{g}_b \rangle$ because the sites c and d correspond to coincident transitions. Using the same method, the complex magnetization equations at sites b and d are

$$\frac{\langle \bar{g}_a \rangle}{4\tau} - \frac{1}{\tau} \left(\frac{1}{2} + \alpha_b \right) \langle \bar{g}_b \rangle + \frac{1}{4\tau} \langle \bar{g}_d \rangle = 2\pi i V_1 m_0 \quad (14)$$

and

$$\frac{\langle \bar{g}_a \rangle}{4\tau} + \frac{1}{2\tau} \langle \bar{g}_b \rangle - \left(\frac{3}{4\tau} + \alpha_d \right) \langle \bar{g}_d \rangle = 2\pi i V_1 m_0 \quad (15)$$

The complex magnetizations, $\langle \bar{g}_a \rangle$, $\langle \bar{g}_b \rangle$, and $\langle \bar{g}_d \rangle$ can be obtained from equations (13), (14), and (15). The NMR signal for the triplet is proportional to the imaginary part of g , where g is equal to $\langle \bar{g}_a \rangle + 2 \langle \bar{g}_b \rangle + \langle \bar{g}_d \rangle$. The explicit expression for g is equal to

$$\frac{\text{numerator}}{\text{denominator}} \quad (16)$$

where numerator = $2\pi V_1 m_0 \times 64\tau \times \left\{ \tau \left(1 + \frac{\tau}{T_2} \right) (3\Delta\omega_a + 2\omega_b + 3\omega_d) \right.$

$$\left. + \left[4 \left(1 + \frac{2\tau}{T_2} + \frac{\tau^2}{T_2^2} \right) - \tau^2 (\Delta\omega_b \Delta\omega_d + 2\Delta\omega_a \Delta\omega_d + \Delta\omega_a \Delta\omega_b) \right] i \right\}$$

and

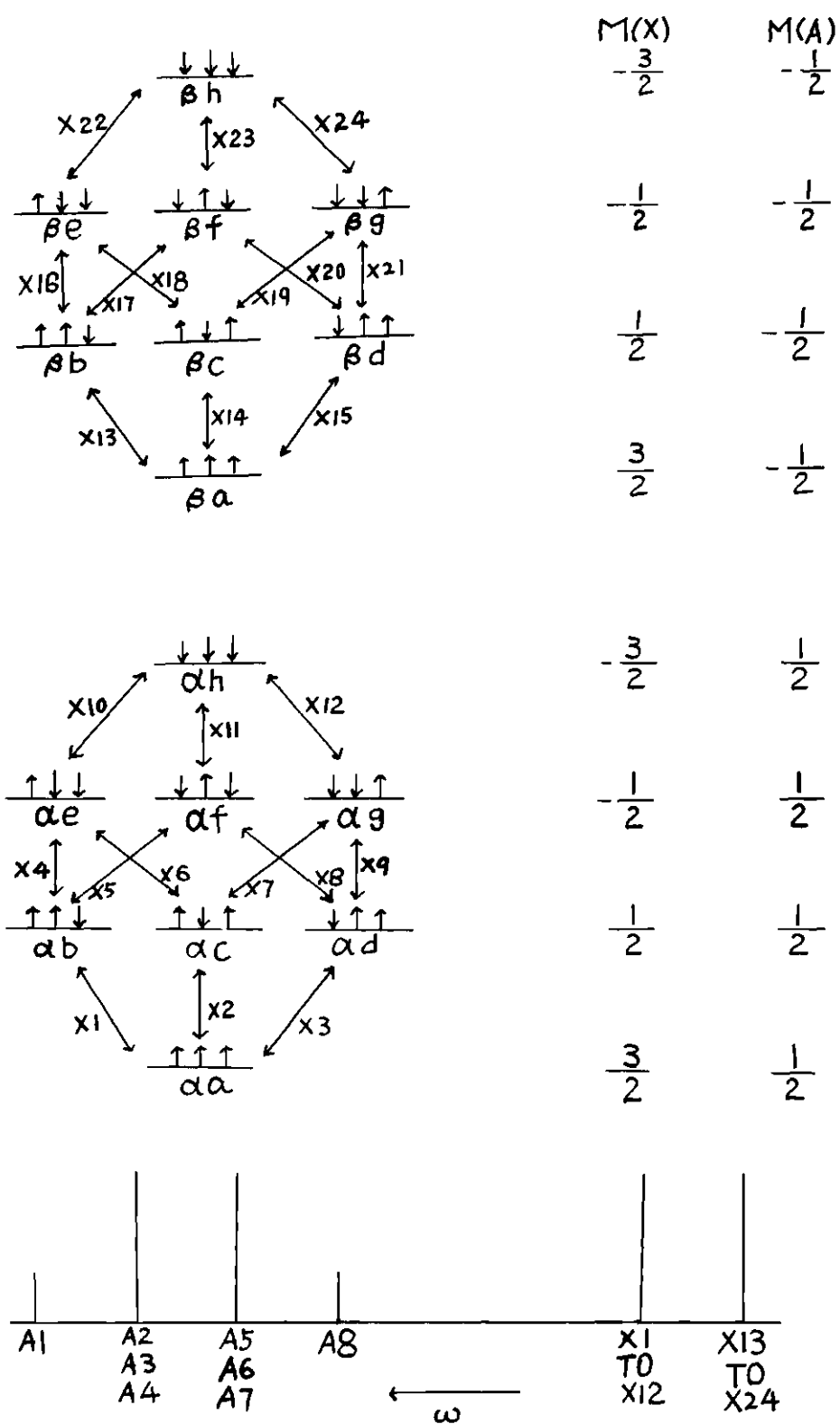
$$\text{denominator} = - \frac{64\tau}{T_2} - \frac{128\tau^2}{T_2^2} + 48\tau^2 \Delta\omega_b (\Delta\omega_a + \Delta\omega_d) + 32\tau^2 \Delta\omega_a \Delta\omega_d$$

$$- \frac{64\tau^3}{T_2^3} + \frac{64\tau^3}{T_2} (\Delta\omega_a \Delta\omega_b + \Delta\omega_a \Delta\omega_d + \Delta\omega_d \Delta\omega_b) - [\tau (7\Delta\omega_a + 3\Delta\omega_b + 7\Delta\omega_d)$$

$$- \frac{\tau^2}{T_2} (80\Delta\omega_a + 80\Delta\omega_d + 96\Delta\omega_b) - \frac{64\tau^3}{T_2^2} (\Delta\omega_a + \Delta\omega_b + \Delta\omega_d)$$

$$+ 64\tau^3 \Delta\omega_a \Delta\omega_b \Delta\omega_d] i$$

The AX_3 system can be treated in a similar way. In Figure 2, all

Figure 2. Energy Level Diagram for AX_3 System

of the symbols are defined in a similar way as Figure 1. There are eight transitions: A1, A2, A3, A4, A5, A6, A7, and A8 for proton A and hence eight sites. The symbols for the eight sites are a, b, c, d, e, f, g, and h, and the complex magnetizations at these sites are g_a , g_b , g_c , g_d , g_e , g_f , g_g , and g_h , respectively. Using equations (5) or (10), there are the following four independent linear equations.

$$-(8\alpha_a\tau + 7) \langle \bar{g}_a \rangle + 3 \langle \bar{g}_b \rangle + 3 \langle \bar{g}_e \rangle + \langle \bar{g}_h \rangle = 16 i \tau V_1 m_0 \quad (17)$$

$$\langle \bar{g}_a \rangle - (8\alpha_b\tau + 5) \langle \bar{g}_b \rangle + 3 \langle \bar{g}_e \rangle + \langle \bar{g}_h \rangle = 16 i \tau V_1 m_0 \quad (18)$$

$$\langle \bar{g}_a \rangle + 3 \langle \bar{g}_b \rangle - (8\alpha_e\tau + 5) \langle \bar{g}_e \rangle + \langle \bar{g}_h \rangle = 16 i \tau V_1 m_0 \quad (19)$$

and

$$\langle \bar{g}_a \rangle + 3 \langle \bar{g}_b \rangle + 3 \langle \bar{g}_e \rangle - (8\alpha_h\tau + 7) \langle \bar{g}_h \rangle = 16 i \tau V_1 m_0 \quad (20)$$

The total complex magnetization for the quartet, g , is equal to $\langle \bar{g}_a \rangle + 3 \langle \bar{g}_b \rangle + 3 \langle \bar{g}_e \rangle + \langle \bar{g}_h \rangle$, where $\langle \bar{g}_a \rangle$, $\langle \bar{g}_b \rangle$, $\langle \bar{g}_e \rangle$, and $\langle \bar{g}_h \rangle$ can be obtained from equations (17), (18), (19), and (20). The NMR signal for the quartet is proportional to the imaginary part of g . The explicit expression for g is equal to

$$\frac{\text{numerator}}{\text{denominator}} \quad (21)$$

$$\begin{aligned} \text{where numerator} = & 2\pi V_1 m_0 \times 512 \left\{ 8\tau^4 \left[\frac{1}{T_2} \times (\Delta\omega_a + \Delta\omega_b + \Delta\omega_e + \Delta\omega_h) \right. \right. \\ & + \frac{1}{T_2^2} \times (\Delta\omega_e + \Delta\omega_b + 3\Delta\omega_h + 3\Delta\omega_a) - (\Delta\omega_a \Delta\omega_b \Delta\omega_e + \Delta\omega_e \Delta\omega_h \Delta\omega_b \\ & \left. \left. + 3\Delta\omega_a \Delta\omega_e \Delta\omega_h + 3\Delta\omega_a \Delta\omega_b \Delta\omega_h) \right] + \frac{\tau^3}{T_2} \times (88\Delta\omega_a + 72\Delta\omega_b + 72\Delta\omega_e + 88\Delta\omega_h) \right\} \end{aligned}$$

$$\begin{aligned}
& + \tau^2 (14\Delta\omega_a + 8\Delta\omega_b + 8\Delta\omega_e + 14\Delta\omega_h) + \left[32\tau + \frac{64\tau^4}{T_2^3} - \frac{8\tau^4}{T_2} \times (4\Delta\omega_a\Delta\omega_b \right. \\
& + 4\Delta\omega_a\Delta\omega_e + 6\Delta\omega_a\Delta\omega_h + 2\Delta\omega_b\Delta\omega_e + 4\Delta\omega_b\Delta\omega_h + 4\Delta\omega_e\Delta\omega_h) + \tau^3 \left(\frac{160}{T_2^2} \right. \\
& - 26\Delta\omega_a\Delta\omega_b - 32\Delta\omega_a\Delta\omega_e - 30\Delta\omega_a\Delta\omega_h - 14\Delta\omega_b\Delta\omega_e - 32\Delta\omega_b\Delta\omega_h - 26\Delta\omega_e\Delta\omega_h) \\
& \left. + \frac{128\tau^2}{T_2} \right] i \}
\end{aligned}$$

and

$$\begin{aligned}
\text{denominator} = & -1024 - 4096\tau^4 \left[\frac{1}{T_2^4} - \frac{1}{T_2^2} \times (\Delta\omega_a\Delta\omega_b + \Delta\omega_a\Delta\omega_e + \Delta\omega_b\Delta\omega_e \right. \\
& + \Delta\omega_h\Delta\omega_a + \Delta\omega_h\Delta\omega_b + \Delta\omega_e\Delta\omega_h) + (\Delta\omega_a\Delta\omega_b\Delta\omega_e\Delta\omega_h) \left. \right] - 64 \times 8\tau^3 \left[\frac{24}{T_2^3} - \frac{1}{T_2} \right. \\
& \times (12\Delta\omega_e\Delta\omega_h + 14\Delta\omega_e\Delta\omega_b + 12\Delta\omega_h\Delta\omega_b + 12\Delta\omega_a\Delta\omega_e + 10\Delta\omega_a\Delta\omega_h + 12\Delta\omega_a\Delta\omega_b) \left. \right] \\
& - 64\tau^2 \left(\frac{208}{T_2^2} - 35\Delta\omega_e\Delta\omega_h - 49\Delta\omega_b\Delta\omega_e - 32\Delta\omega_a\Delta\omega_e - 32\Delta\omega_h\Delta\omega_b - 25\Delta\omega_a\Delta\omega_h \right. \\
& - 35\Delta\omega_a\Delta\omega_b) - \frac{1}{T_2} \times (6144\tau) + i \left\{ 4096\tau^2 \left[\frac{1}{T_2^3} (\Delta\omega_a + \Delta\omega_b + \Delta\omega_e + \Delta\omega_h) \right. \right. \\
& - \frac{1}{T_2} (\Delta\omega_h\Delta\omega_a\Delta\omega_b + \Delta\omega_a\Delta\omega_e\Delta\omega_h + \Delta\omega_b\Delta\omega_e\Delta\omega_h) \left. \right] + \frac{1}{T_2^2} \times (7\Delta\omega_b + 5\Delta\omega_h \\
& + 7\Delta\omega_e + 5\Delta\omega_a) - 7\Delta\omega_e\Delta\omega_h\Delta\omega_b - 5\Delta\omega_a\Delta\omega_e\Delta\omega_h - 7\Delta\omega_a\Delta\omega_b\Delta\omega_e - 5\Delta\omega_b\Delta\omega_h\Delta\omega_a \left. \right] \\
& + \frac{64\tau^2}{T_2} \times (122\Delta\omega_e + 98\Delta\omega_h + 122\Delta\omega_b + 98\Delta\omega_a) + 8\tau (190\Delta\omega_a + 266\Delta\omega_b \\
& + 190\Delta\omega_h + 266\Delta\omega_e) \left. \right\}
\end{aligned}$$

CHAPTER III

COMBINED EFFECT OF DOUBLE RESONANCE SATURATION
AND CHEMICAL EXCHANGE ON MULTIPLY STRUCTURE

In this chapter, expressions will be derived for frequency sweep nuclear magnetic double resonance experiments on AX_2 and AX_3 spin systems in which A is undergoing chemical exchange. It will be assumed that one of the X lines is irradiated by the strong rf field \underline{H}_2 while the spectrum is scanned with a weak observing rf field \underline{H}_1 . In the laboratory frame

$$\underline{H}_1 = 2\pi V_1 (\hat{i} \cos \omega_1 t - \hat{j} \sin \omega_1 t)$$

and

$$\underline{H}_2 = 2\pi V_2 (\hat{i} \cos \omega_2 t - \hat{j} \sin \omega_2 t)$$

where V_1 and V_2 are the amplitudes of \underline{H}_1 and \underline{H}_2 in cps, respectively, ω_1 and ω_2 are the angular frequencies of \underline{H}_1 and \underline{H}_2 in radians per second, respectively, and \hat{i} and \hat{j} are unit vectors along the X and Y laboratory axes, respectively. The analysis will assume that the only effect of \underline{H}_2 is to saturate the irradiated X transitions. Double resonance splittings¹³ due to \underline{H}_2 will be neglected.

Consider an AX_n system.¹ The A spin states will be denoted by Greek letters, e.g. α , β , etc. The X spin states will be denoted by Latin letters, e.g. a, b, etc. The spin state of the combined AX_n system will be denoted by product of Latin and Greek letters, e.g. αa . The population of state αa equals the fraction of molecules in state αa

and will be denoted by $P_{\alpha a}$. At thermal equilibrium, the population of state αa is given by the Boltzmann distribution¹⁴

$$P_{\alpha a}^0 = \frac{1}{N} - \frac{\omega_{\alpha a} \hbar}{N k T}$$

where N = number of spin states

$\omega_{\alpha a}$ = energy of state αa in units of radians per second

k = Boltzmann constant

T = temperature in °K.

The energy¹ of state αa is given by

$$\omega_{\alpha a} = -\omega_{OA} M(A)_{\alpha} - \omega_{OX} M(X)_a + 2\pi J M(A)_{\alpha} M(X)_a$$

where ω_{OA} is the Larmor frequency of the A proton

ω_{OX} is the Larmor frequency of the X protons

$M(A)_{\alpha}$ is the magnetic quantum number of the A proton in state α

$M(X)_a$ is the total magnetic quantum number of the X protons in state a

J is the coupling constant in cps.

For an A transition, $\Delta M(A) = -1$, and $\Delta M(X) = 0$. For an X transition, $\Delta M(X) = 0$, and $\Delta M(X) = -1$.

Let us introduce some notation. Consider an A line labeled by A1. Suppose this corresponds to the transition $\alpha a \rightarrow \beta a$ in Figure 1. Then, the intensity of the line A1 will be proportional to $MA1$, the Z component of magnetization in units of $n\hbar$ for site A1, where

$$MA1 = \frac{1}{2} (P_{\alpha a} - P_{\beta a})$$

n' = number of molecules per cc

r = magnetogyric ratio.

At thermal equilibrium

$$MA1^0 = \frac{1}{2} (P_{\alpha a}^0 - P_{\beta a}^0)$$

In a similar manner, the line X1, corresponding to an X transition

$\alpha a \rightarrow \alpha b$ in Figure 1, is proportional to MX1, where

$$MX1 = \frac{1}{2} (P_{\alpha a} - P_{\alpha b})$$

At thermal equilibrium

$$MX1^0 = \frac{1}{2} (P_{\alpha a}^0 - P_{\alpha b}^0)$$

It will be convenient for our purposes to work with the difference quantities, $\Delta MA1$, etc., where

$$\Delta MA1 = MA1 - MA1^0$$

In the following, equations of motion for $\Delta MA1$, etc. will be derived assuming that

$$\frac{d(\Delta MA1)}{dt} = \left(\frac{d\Delta MA1}{dt} \right)_{\text{ex}} + \left(\frac{d\Delta MA1}{dt} \right)_{\text{irr}} + \left(\frac{d\Delta MA1}{dt} \right)_{\text{relx}}$$

where

$\left(\frac{d\Delta MA1}{dt} \right)_{\text{ex}}$ is the contribution due to chemical exchange

$\left(\frac{d\Delta MA1}{dt} \right)_{\text{irr}}$ is the contribution due to irradiation by H_2

$\left(\frac{d\Delta MA1}{dt} \right)_{\text{relx}}$ is the contribution due to relaxation

First, the contribution due to chemical exchange is considered.

The rate of change of population of state αa due to chemical exchange is

given by

$$\left(\frac{dP_{\alpha a}}{dt}\right)_{\text{ex}} = \left(\sum_{\alpha=1}^{N_e} P_{\alpha a}\right) \left(\frac{1}{\tau}\right) \left(\sum_{a=1}^{N_n} P_{\alpha a}\right) - \frac{1}{\tau} P_{\alpha a} \quad (22)$$

where

N_e = number of states of A proton

N_n = number of states of X proton

N = number of states of AX_n spin system = $N_e N_n$

$\sum_{\alpha=1}^{N_e} P_{\alpha a}$ = probability that a proton enters molecule 1 with the X proton in spin state a

$\sum_{a=1}^{N_n} P_{\alpha a}$ = probability that an A proton leaves molecule 2 in spin state α

$P_{\alpha a}$ = probability of molecules having A proton in state α and X protons in state a

τ = average time interval between chemical exchange

If the populations are not in thermal equilibrium, $P_{\alpha a}$ can be replaced by $\left(\frac{1}{N} - \frac{\omega_{\alpha a} \hbar}{N k T} + \chi_{\alpha a}\right)$ in equation (22) where $\chi_{\alpha a}$ is the deviation of the population from the Boltzmann distribution.

Expanding

$$\begin{aligned} \left(\frac{d\left(\frac{1}{N} - \frac{\omega_{\alpha a} \hbar}{N k T} + \chi_{\alpha a}\right)}{dt}\right)_{\text{ex}} &= \left[\sum_{\alpha=1}^{N_e} \left(\frac{1}{N} - \frac{\omega_{\alpha a} \hbar}{N k T} + \chi_{\alpha a}\right)\right] \times \left(\frac{1}{\tau}\right) \\ &\times \left[\sum_{a=1}^{N_n} \left(\frac{1}{N} - \frac{\omega_{\alpha a} \hbar}{N k T} + \chi_{\alpha a}\right)\right] - \left(\frac{1}{\tau}\right) \left(\frac{1}{N} - \frac{\omega_{\alpha a} \hbar}{N k T} + \chi_{\alpha a}\right) \end{aligned}$$

Neglecting terms which are second order in $\frac{1}{T}$ and $\chi_{\alpha a}$

$$\begin{aligned}
\left(\frac{dx_{\alpha a}}{dt}\right)_{\text{ex}} &= \frac{1}{\tau} \left[\frac{1}{N} + \frac{1}{N_e} \sum_{\alpha=1}^{N_e} x_{\alpha a} + \frac{1}{N_n} \sum_{a=1}^{N_n} x_{\alpha a} \right. \\
&\quad \left. - \frac{\hbar}{N k T} \left(\frac{1}{N_e} \sum_{\alpha=1}^{N_e} \omega_{\alpha a} + \frac{1}{N_n} \sum_a^{N_n} \omega_{\alpha a} \right) - \frac{1}{N} - x_{\alpha a} + \frac{\hbar}{N k T} \omega_{\alpha a} \right] \\
&= \frac{1}{\tau} \left[\frac{1}{N_e} \sum_{\alpha=1}^{N_e} x_{\alpha a} + \frac{1}{N_n} \sum_{a=1}^{N_n} x_{\alpha a} - x_{\alpha a} \right] \\
&\quad - \frac{\hbar}{N k T} \left[\frac{1}{N_e} \sum_{\alpha=1}^{N_e} \omega_{\alpha a} + \frac{1}{N_n} \sum_{a=1}^{N_n} \omega_{\alpha a} - \omega_{\alpha a} \right]
\end{aligned}$$

where

$$\begin{aligned}
\sum_{\alpha=1}^{N_e} \omega_{\alpha a} &= - \sum_{\alpha=1}^{N_e} \omega_{\text{OA}} M(A)_{\alpha} - N_e \omega_{\text{OX}} M(X)_a = - N_e \omega_{\text{OX}} M(X)_a \\
\sum_{a=1}^{N_n} \omega_{\alpha a} &= - N_n \omega_{\text{OA}} M(A)_{\alpha} - \sum_{a=1}^{N_n} \omega_{\text{OX}} M(X)_a = - N_n \omega_{\text{OA}} M(A)_{\alpha}
\end{aligned}$$

Therefore

$$\left(\frac{dx_{\alpha a}}{dt}\right)_{\text{ex}} = \frac{1}{\tau} \left[\frac{1}{N_e} \sum_{\alpha=1}^{N_e} x_{\alpha a} + \frac{1}{N_n} \sum_{a=1}^{N_n} x_{\alpha a} - x_{\alpha a} \right] \quad (23)$$

Equation (23) is the general formula for evaluating the population changes due to chemical exchange. This equation may also be obtained from Alexander's^{8,9} density matrix formulation of chemical exchange by assuming weakly coupled systems.

Now, consider the AX_2 system.¹ The energy level diagram is given in Figure 1. Using equation (23), the population changes at different

levels are

$$\left(\frac{dx_{\alpha a}}{dt}\right)_{ex} = \frac{1}{\tau} \left[\frac{1}{2} (x_{\alpha a} + x_{\beta a}) + \frac{1}{4} (x_{\alpha a} + x_{\alpha b} + x_{\alpha c} + x_{\alpha d}) - x_{\alpha a} \right] \quad (24)$$

$$= \frac{1}{\tau} \left[\frac{1}{2} (x_{\beta a} - x_{\alpha a}) + \frac{1}{4} (x_{\alpha a} + x_{\alpha b} + x_{\alpha c} + x_{\alpha d}) \right]$$

$$\left(\frac{dx_{\beta a}}{dt}\right)_{ex} = \frac{1}{\tau} \left[\frac{1}{2} (x_{\alpha a} - x_{\beta a}) + \frac{1}{4} (x_{\beta a} + x_{\beta c} + x_{\beta b} + x_{\beta d}) \right] \quad (25)$$

$$\left(\frac{dx_{\alpha b}}{dt}\right)_{ex} = \frac{1}{\tau} \left[\frac{1}{2} (x_{\beta b} - x_{\alpha b}) + \frac{1}{4} (x_{\alpha a} + x_{\alpha b} + x_{\alpha d} + x_{\alpha c}) \right] \quad (26)$$

$$\left(\frac{dx_{\beta b}}{dt}\right)_{ex} = \frac{1}{\tau} \left[\frac{1}{2} (x_{\alpha b} - x_{\beta b}) + \frac{1}{4} (x_{\beta a} + x_{\beta b} + x_{\beta c} + x_{\beta d}) \right] \quad (27)$$

$$\left(\frac{dx_{\alpha c}}{dt}\right)_{ex} = \frac{1}{\tau} \left[\frac{1}{2} (x_{\beta c} - x_{\alpha c}) + \frac{1}{4} (x_{\alpha a} + x_{\alpha b} + x_{\alpha c} + x_{\alpha d}) \right] \quad (28)$$

$$\left(\frac{dx_{\beta c}}{dt}\right)_{ex} = \frac{1}{\tau} \left[\frac{1}{2} (x_{\alpha c} - x_{\beta c}) + \frac{1}{4} (x_{\beta a} + x_{\beta b} + x_{\beta c} + x_{\beta d}) \right] \quad (29)$$

$$\left(\frac{dx_{\alpha d}}{dt}\right)_{ex} = \frac{1}{\tau} \left[\frac{1}{2} (x_{\beta d} - x_{\alpha d}) + \frac{1}{4} (x_{\alpha a} + x_{\alpha b} + x_{\alpha c} + x_{\alpha d}) \right] \quad (30)$$

and

$$\left(\frac{dx_{\beta d}}{dt}\right)_{ex} = \frac{1}{\tau} \left[\frac{1}{2} (x_{\alpha d} - x_{\beta d}) + \frac{1}{4} (x_{\beta a} + x_{\beta b} + x_{\beta c} + x_{\beta d}) \right] \quad (31)$$

The A signals correspond to $\Delta M(A) = -1$ and $\Delta M(X) = 0$. The X signals correspond to $\Delta M(A) = 0$ and $\Delta M(X) = -1$. Therefore, for the transition between αa and βa

$$\frac{1}{2} \left(\frac{dx_{\alpha a}}{dt}\right)_{ex} - \frac{1}{2} \left(\frac{dx_{\beta a}}{dt}\right)_{ex} = \left(\frac{d \frac{1}{2}(x_{\alpha a} - x_{\beta a})}{dt}\right)_{ex} = \left(\frac{d\Delta M A 1}{dt}\right)_{ex} \quad (32)$$

$$= \frac{1}{\tau} \left\{ \frac{1}{2} (x_{\beta a} - x_{\alpha a}) + \frac{1}{4} \left[\frac{1}{2} (x_{\alpha a} - x_{\beta a}) + \frac{1}{2} (x_{\alpha b} - x_{\beta b}) \right] \right\}$$

$$\begin{aligned}
& + \frac{1}{2} (x_{\alpha c} - x_{\beta c}) + \frac{1}{2} (x_{\alpha d} - x_{\beta d}) \Big] \Big\} \\
& = \frac{1}{\tau} \left\{ -\frac{3}{4} (x_{\alpha a} - x_{\beta a}) \times \frac{1}{2} + \frac{1}{4} \left[\frac{1}{2} (x_{\alpha b} - x_{\beta b}) + \frac{1}{2} (x_{\alpha c} - x_{\beta c}) \right. \right. \\
& \quad \left. \left. + \frac{1}{2} (x_{\alpha d} - x_{\beta d}) \right] \right\} \\
& = \frac{1}{\tau} \left\{ -\frac{3}{4} (\Delta MA1)_{ex} + \frac{1}{4} [(\Delta MA2)_{ex} + (\Delta MA3)_{ex} + (\Delta MA4)_{ex}] \right\} \\
& = \frac{1}{\tau} \left[-\frac{3}{4} (\Delta MA1)_{ex} + \frac{1}{2} (\Delta MA2)_{ex} + \frac{1}{4} (\Delta MA4)_{ex} \right]
\end{aligned}$$

where

$$\begin{aligned}
\frac{1}{2} (x_{\alpha a} - x_{\beta a}) &= (\Delta MA1)_{ex}, \quad \frac{1}{2} (x_{\alpha b} - x_{\beta b}) = (\Delta MA2)_{ex}, \quad \frac{1}{2} (x_{\alpha c} - x_{\beta c}) \\
&= (\Delta MA3)_{ex}, \quad \text{and} \quad \frac{1}{2} (x_{\alpha d} - x_{\beta d}) = (\Delta MA4)_{ex}. \quad \text{Also, } (\Delta MA2)_{ex} \text{ is equal}
\end{aligned}$$

to $(\Delta MA3)_{ex}$ because the A_2 and A_3 transitions are coincident.

In the same way, the following equations are derived

$$\left(\frac{d\Delta MA2}{dt} \right)_{ex} = \frac{1}{\tau} \left[-\frac{1}{2} (\Delta MA2)_{ex} + \frac{1}{4} (\Delta MA1)_{ex} + \frac{1}{4} (\Delta MA4)_{ex} \right] \quad (33)$$

$$\left(\frac{d\Delta MA4}{dt} \right)_{ex} = \frac{1}{\tau} \left[-\frac{3}{4} (\Delta MA4)_{ex} + \frac{1}{4} (\Delta MA1)_{ex} + \frac{1}{2} (\Delta MA2)_{ex} \right] \quad (34)$$

$$\left(\frac{d\Delta MX1}{dt} \right)_{ex} = \frac{1}{2\tau} \left[-\frac{1}{2} (x_{\alpha a} - x_{\alpha b}) + \frac{1}{2} (x_{\beta a} - x_{\beta b}) \right] \quad (35)$$

$$= \frac{1}{2\tau} \left[-(\Delta MX1)_{ex} + (\Delta MX5)_{ex} \right]$$

and

$$\begin{aligned}
 \left(\frac{d\Delta MX5}{dt} \right)_{\text{ex}} &= \frac{1}{2\tau} \left[\frac{1}{2} (x_{\alpha a} - x_{\alpha b}) - \frac{1}{2} (x_{\beta a} - x_{\beta b}) \right] \\
 &= \frac{1}{2\tau} \left[(\Delta MX1)_{\text{ex}} - (\Delta MX5)_{\text{ex}} \right]
 \end{aligned} \tag{36}$$

where

$$\begin{aligned}
 \frac{1}{2} (x_{\alpha a} - x_{\alpha c}) &= (\Delta MX1)_{\text{ex}}, \quad \frac{1}{2} (x_{\alpha b} - x_{\alpha d}) = (\Delta MX2)_{\text{ex}}, \quad \frac{1}{2} (x_{\alpha a} - x_{\alpha c}) \\
 &= (\Delta MX3)_{\text{ex}}, \quad \frac{1}{2} (x_{\alpha c} - x_{\alpha d}) = (\Delta MX4)_{\text{ex}}, \quad \frac{1}{2} (x_{\beta a} - x_{\beta b}) = (\Delta MX5)_{\text{ex}}, \\
 \frac{1}{2} (x_{\beta b} - x_{\beta d}) &= (\Delta MX4)_{\text{ex}}, \quad \text{and} \quad \frac{1}{2} (x_{\beta a} - x_{\beta c}) = (\Delta MX7)_{\text{ex}}, \\
 \frac{1}{2} (x_{\beta h} - x_{\beta f}) &= (\Delta MX8)_{\text{ex}}. \quad \text{Also, } (\Delta MX1)_{\text{ex}}, (\Delta MX2)_{\text{ex}}, (\Delta MX3)_{\text{ex}},
 \end{aligned}$$

and $(\Delta MX4)_{\text{ex}}$ are equal because they correspond to coincident transitions, and $(\Delta MX5)_{\text{ex}}$, $(\Delta MX6)_{\text{ex}}$, $(\Delta MX7)_{\text{ex}}$, and $(\Delta MX8)_{\text{ex}}$ are equal because they correspond to coincident transitions.

The population changes due to chemical exchange have been discussed above. Now, the population changes due to irradiation and relaxation are considered. In the AX_2 system, X1, X2, X3, and X4 are irradiated by H_2 . The population changes at αa due to irradiation induced X1 transitions are assumed to be¹⁶

$$\begin{aligned}
 \left(\frac{dx_{\alpha a}}{dt} \right)_{\text{irr}} &= \pi^2 V_2^2 | \langle \alpha a | I_+(X) + I_-(X) | \alpha b \rangle |^2 (P_{\alpha a}^0 - P_{\alpha b}^0) \\
 &\quad + x_{\alpha a} - x_{\alpha b} \times g(\nu - \nu_{ab}) = -I_{ab}
 \end{aligned} \tag{37}$$

where V_2 = amplitude of H_2

$P_{\alpha a}^0 - P_{\alpha b}^0$ = difference of population between αa and αb states at thermal equilibrium

$x_{\alpha a} - x_{\alpha b}$ = difference of population deviation from thermal equilibrium between αa and αb states

$g(\nu - \nu_{ab})$ = line shape function normalized to 1 on the cps scale
 $- I_{ab}$ = the population changes in the αa state due to H_2

In the following it will be assumed that the relaxation of the A and X protons is due to uncorrelated randomly fluctuating magnetic fields caused by the molecular motions of the molecules.¹⁷ Assuming this relaxation mechanism, the selection rules for relaxation are identical to the selection rules for rf induced transitions.¹⁷ The thermal transition probability per unit time for A relaxation transitions [$\Delta M(A) = \pm 1$, $\Delta M(X) = 0$] will be denoted by W_A . The thermal transition probability per unit time for X relaxation transitions [$\Delta M(A) = 0$, $\Delta M(X) = \pm 1$] will be denoted by W_X . It can be shown that $W_A = \frac{1}{2T_A}$ and $W_X = \frac{1}{2T_X}$, where T_A is the longitudinal relaxation time and T_X is the longitudinal relaxation time of the X protons.¹⁷ Then, the population changes due to relaxation and rf irradiation are easily written down by inspection from Figure 1. They are described by the following equations.¹⁸

$$\left(\frac{dx_{\alpha a}}{dt}\right)_{\text{relx}} + \left(\frac{dx_{\alpha a}}{dt}\right)_{\text{irr}} = W_X(x_{\alpha b} + x_{\alpha c}) + W_A x_{\beta a} - (2W_X + W_A) x_{\alpha a} - 2I_{ab} \quad (38)$$

$$\begin{aligned} \left(\frac{dx_{\alpha b}}{dt}\right)_{\text{relx}} + \left(\frac{dx_{\alpha b}}{dt}\right)_{\text{irr}} &= W_X(x_{\alpha a} + x_{\alpha d}) + W_A x_{\beta b} - (2W_X + W_A) x_{\alpha b} + I_{ab} - I_{bd} \\ &= W_X(x_{\alpha a} + x_{\alpha d}) + W_A x_{\beta b} - (2W_X + W_A) x_{\alpha b} \end{aligned} \quad (39)$$

$$\left(\frac{dx_{\alpha c}}{dt}\right)_{\text{relx}} + \left(\frac{dx_{\alpha c}}{dt}\right)_{\text{irr}} = W_X(x_{\alpha a} + x_{\alpha d}) + W_A x_{\beta c} - (2W_X + W_A) x_{\alpha c} + I_{ac} - I_{cd} \quad (40)$$

$$= W_X(x_{\alpha a} + x_{\alpha d}) + W_A x_{\beta c} - (2W_X + W_A) x_{\alpha c}$$

$$\left(\frac{dx_{\alpha d}}{dt}\right)_{\text{relx}} + \left(\frac{dx_{\alpha d}}{dt}\right)_{\text{irr}} = W_X(x_{\alpha b} + x_{\alpha c}) + W_A x_{\beta d} - (2W_X + W_A) x_{\alpha d} + 2I_{ab} \quad (41)$$

where $I_{ab} = I_{bd} = I_{ac} = I_{cd}$

$$\left(\frac{dx_{\beta a}}{dt}\right)_{\text{relx}} = W_X(x_{\beta b} + x_{\beta c}) + W_A x_{\alpha a} - (2W_X + W_A) x_{\beta a} \quad (42)$$

$$\left(\frac{dx_{\beta b}}{dt}\right)_{\text{relx}} = W_X(x_{\beta a} + x_{\beta d}) + W_A x_{\alpha b} - (2W_X + W_A) x_{\beta b} \quad (43)$$

$$\left(\frac{dx_{\beta c}}{dt}\right)_{\text{relx}} = W_X(x_{\beta a} + x_{\beta d}) + W_A x_{\alpha c} - (2W_X + W_A) x_{\beta c} \quad (44)$$

and

$$\left(\frac{dx_{\beta d}}{dt}\right)_{\text{relx}} = W_X(x_{\beta b} + x_{\beta c}) + W_A x_{\alpha d} - (2W_X + W_A) x_{\beta d} \quad (45)$$

The A signals correspond to $\Delta M(A) = -1$ and $\Delta M(X) = 0$, and the X signals correspond to $\Delta M(A) = 0$ and $\Delta M(X) = -1$. Thus, the relaxation and irradiation contributions to the equation of motion of ΔM_A are found to be

$$\left(\frac{d\frac{1}{2}(x_{\alpha a} - x_{\beta a})}{dt}\right)_{\text{relx}} + \left(\frac{d\frac{1}{2}(x_{\alpha a} - x_{\beta a})}{dt}\right)_{\text{irr}} = \left(\frac{d\Delta M_A}{dt}\right)_{\text{relx}} + \left(\frac{d\Delta M_A}{dt}\right)_{\text{irr}} \quad (46)$$

$$= \frac{1}{2} [W_X(x_{\alpha b} - x_{\beta a}) + W_X(x_{\alpha c} - x_{\beta c}) - (2W_X + 2W_A)(x_{\alpha a} - x_{\beta a}) - 2I_{ab}]$$

$$\begin{aligned}
&= W_X(\Delta MA2)_{\text{relx}} + W_X(\Delta MA3)_{\text{relx}} - (2W_X + 2W_A)(\Delta MA1)_{\text{relx}} - I_{ab} \\
&= 2W_X(\Delta MA2)_{\text{relx}} - 2(W_X + W_A)(\Delta MA1)_{\text{relx}} - I_{ab}
\end{aligned}$$

where $\frac{1}{2}(\chi_{\alpha a} - \chi_{\beta a})_{\text{relx}} = (\Delta MA1)_{\text{relx}}$, $\frac{1}{2}(\chi_{\alpha a} - \chi_{\beta a})_{\text{irr}} = (\Delta MA1)_{\text{irr}}$,

$\frac{1}{2}(\chi_{\alpha b} - \chi_{\beta b})_{\text{relx}} = (\Delta MA2)_{\text{relx}}$, $\frac{1}{2}(\chi_{\alpha b} - \chi_{\beta b})_{\text{irr}} = (\Delta MA2)_{\text{irr}}$,

$\frac{1}{2}(\chi_{\alpha c} - \chi_{\beta c})_{\text{relx}} = (\Delta MA3)_{\text{relx}}$, $\frac{1}{2}(\chi_{\alpha c} - \chi_{\beta c})_{\text{irr}} = (\Delta MA3)_{\text{irr}}$,

and $\frac{1}{2}(\chi_{\alpha d} - \chi_{\beta d})_{\text{relx}} = (\Delta MA4)_{\text{relx}}$, $\frac{1}{2}(\chi_{\alpha d} - \chi_{\beta d})_{\text{irr}} = (\Delta MA4)_{\text{irr}}$

Again, $(\Delta MA2)_{\text{relx}}$ is equal to $(\Delta MA3)_{\text{relx}}$ because they correspond to coincident transitions. In the same way, the following equations are derived

$$\left(\frac{d\Delta MA2}{dt}\right)_{\text{relx}} + \left(\frac{d\Delta MA2}{dt}\right)_{\text{irr}} = W_X(\Delta MA1)_{\text{relx}} + W_X(\Delta MA4)_{\text{relx}} - (2W_X + 2W_A)(\Delta MA2)_{\text{relx}} \quad (47)$$

$$\left(\frac{d\Delta MA4}{dt}\right)_{\text{relx}} + \left(\frac{d\Delta MA4}{dt}\right)_{\text{irr}} = 2W_X(\Delta MA2)_{\text{relx}} - 2(W_X + W_A)(\Delta MA4)_{\text{relx}} + I_{ab} \quad (48)$$

$$\left(\frac{d\Delta MX1}{dt}\right)_{\text{relx}} + \left(\frac{d\Delta MX1}{dt}\right)_{\text{irr}} = W_A(\Delta MX5)_{\text{relx}} - (2W_X + W_A)(\Delta MX1)_{\text{relx}} - I_{ab} \quad (49)$$

$$\left(\frac{d\Delta MX5}{dt}\right)_{\text{relx}} + \left(\frac{d\Delta MX5}{dt}\right)_{\text{irr}} = W_A(\Delta MX1)_{\text{relx}} - (2W_X + W_A)(\Delta MX5)_{\text{relx}} \quad (50)$$

where $\frac{1}{2}(\chi_{\alpha a} - \chi_{\alpha b})_{\text{relx}} + \frac{1}{2}(\chi_{\alpha a} - \chi_{\alpha b})_{\text{irr}} = (\Delta MX1)_{\text{relx}} + (\Delta MX1)_{\text{irr}}$,

$\frac{1}{2}(\chi_{\beta a} - \chi_{\beta b})_{\text{relx}} + \frac{1}{2}(\chi_{\beta a} - \chi_{\beta b})_{\text{irr}} = (\Delta MX5)_{\text{relx}} + (\Delta MX5)_{\text{irr}}$, and

$(\Delta MX1)_{\text{relx}}$, $(\Delta MX2)_{\text{relx}}$, $(\Delta MX3)_{\text{relx}}$, and $(\Delta MX4)_{\text{relx}}$ are equal be-

cause they correspond to the coincident transitions, and $(\Delta MX5)_{\text{relx}}$, $(\Delta MX6)_{\text{relx}}$, $(\Delta MX7)_{\text{relx}}$, and $(\Delta MX8)_{\text{relx}}$ are equal for the same reason.

The population changes due to chemical exchange have been described by equations (32) to (36), and the population changes due to relaxation and irradiation are expressed by equations (46) to (50). The three effects are combined together as follows

(32) plus (46)

$$\frac{d(\Delta MA1)}{dt} = \left(\frac{d\Delta MA1}{dt}\right)_{\text{ex}} + \left(\frac{d\Delta MA1}{dt}\right)_{\text{relx}} + \left(\frac{d\Delta MA1}{dt}\right)_{\text{irr}} \quad (51)$$

$$= \left(-\frac{3}{4\tau} - 2W_X - 2W_A\right)(\Delta MA1) + \left(\frac{1}{2\tau} + 2W_X\right)(\Delta MA2) + \frac{1}{4\tau}(\Delta MA4) - I_{ab}$$

(33) plus (47)

$$\frac{d(\Delta MA2)}{dt} = \left(\frac{d\Delta MA2}{dt}\right)_{\text{ex}} + \left(\frac{d\Delta MA2}{dt}\right)_{\text{relx}} + \left(\frac{d\Delta MA2}{dt}\right)_{\text{irr}} \quad (52)$$

$$= \left(\frac{1}{4\tau} + W_X\right)(\Delta MA1) - \left(2W_X + 2W_A + \frac{1}{2\tau}\right)(\Delta MA2) + \left(\frac{1}{4\tau} + W_X\right)(\Delta MA4)$$

(34) plus (48)

$$\frac{d(\Delta MA4)}{dt} = \left(\frac{d\Delta MA4}{dt}\right)_{\text{ex}} + \left(\frac{d\Delta MA4}{dt}\right)_{\text{relx}} + \left(\frac{d\Delta MA4}{dt}\right)_{\text{irr}} \quad (53)$$

$$= \frac{1}{4\tau}(\Delta MA1) + \left(\frac{1}{2\tau} + 2W_X\right)(\Delta MA2) - \left(\frac{3}{4\tau} + 2W_X + 2W_A\right)(\Delta MA4) + I_{ab}$$

(35) plus (49)

$$\frac{d(\Delta MX1)}{dt} = \left(\frac{d\Delta MX1}{dt}\right)_{\text{ex}} + \left(\frac{d\Delta MX1}{dt}\right)_{\text{relx}} + \left(\frac{d\Delta MX1}{dt}\right)_{\text{irr}} \quad (54)$$

$$= -\left(2W_X + W_A + \frac{1}{2\tau}\right)(\Delta MX1) + \left(W_A + \frac{1}{2\tau}\right)(\Delta MX5) - I_{ab}$$

(36) plus (50)

$$\begin{aligned} \frac{d(\Delta MX5)}{dt} &= \left(\frac{d\Delta MX5}{dt} \right)_{\text{ex}} + \left(\frac{d\Delta MX5}{dt} \right)_{\text{relx}} + \left(\frac{d\Delta MX5}{dt} \right)_{\text{irr}} \\ &= \left(W_A + \frac{1}{2\tau} \right) (\Delta MX1) - \left(2W_X + W_A + \frac{1}{2\tau} \right) (\Delta MX5) \end{aligned} \quad (55)$$

At the steady state, equations (51) to (55) become

$$\left(-\frac{3}{4\tau} - 2W_X - 2W_A \right) (\Delta MA1) + \left(\frac{1}{2\tau} + 2W_X \right) (\Delta MA2) + \frac{1}{4\tau} (\Delta MA4) = I_{\text{ab}} \quad (56)$$

$$\left(\frac{1}{4\tau} + W_X \right) (\Delta MA1) - \left(2W_X + 2W_A + \frac{1}{2\tau} \right) (\Delta MA2) - \left(\frac{1}{4\tau} + W_X \right) (\Delta MA4) = 0 \quad (57)$$

$$\frac{1}{4\tau} (\Delta MA1) + \left(\frac{1}{2\tau} + 2W_X \right) (\Delta MA2) - \left(\frac{3}{4\tau} + 2W_X + 2W_A \right) (\Delta MA4) = -I_{\text{ab}} \quad (58)$$

$$- \left(2W_X + W_A + \frac{1}{2\tau} \right) (\Delta MX1) + \left(W_A + \frac{1}{2\tau} \right) (\Delta MX5) = I_{\text{ab}} \quad (59)$$

and

$$\left(W_A + \frac{1}{2\tau} \right) (\Delta MX1) - \left(2W_X + W_A + \frac{1}{2\tau} \right) (\Delta MX5) = 0 \quad (60)$$

Then, the changes in the A proton signal intensity corresponding to $(\Delta MA1)$, $(\Delta MA2)$, and $(\Delta MA4)$ are obtained from three linear equations: (56), (57), and (58).

$$(\Delta MA1) = \frac{I_{\text{ab}} \begin{vmatrix} 1 & \frac{1}{2\tau} + 2W_X & \frac{1}{4\tau} \\ 0 & -2W_X - 2W_A - \frac{1}{2\tau} & \frac{1}{4\tau} + W_X \\ -1 & \frac{1}{2\tau} + 2W_X & -\frac{3}{4\tau} - 2W_X - 2W_A \end{vmatrix}}{\begin{vmatrix} -\frac{3}{4\tau} - 2W_X - 2W_A & \frac{1}{2\tau} + 2W_X & \frac{1}{4\tau} \\ \frac{1}{4\tau} + W_X & -2W_X - 2W_A - \frac{1}{2\tau} & \frac{1}{4\tau} + W_X \\ \frac{1}{4\tau} & \frac{1}{2\tau} + 2W_X & -\frac{3}{4\tau} - 2W_X - 2W_A \end{vmatrix}} \quad (61)$$

$$= I_{ab} (TA1)$$

where (TA1) is the ratio of two determinants. In the same way

$$(\Delta MA2) = I_{ab} (TA2) \quad (62)$$

and

$$(\Delta MA4) = I_{ab} (TA4) \quad (63)$$

The intensity changes in X proton doublet corresponding to $(\Delta MX1)$ and $(\Delta MX5)$ are obtained from equations (59) and (60).

Then

$$(\Delta MX1) = I_{ab} \begin{vmatrix} 1 & W_A + \frac{1}{2\tau} \\ 0 & -2W_X - W_A - \frac{1}{2\tau} \end{vmatrix} = I_{ab} (TX1) \quad (64)$$

$$= \begin{vmatrix} -2W_X - W_A - \frac{1}{2\tau} & W_A + \frac{1}{2\tau} \\ W_A + \frac{1}{2\tau} & -2W_X - W_A - \frac{1}{2\tau} \end{vmatrix}$$

and

$$(\Delta MX5) = I_{ab} \begin{vmatrix} -2W_X - W_A - \frac{1}{2\tau} & 1 \\ W_A + \frac{1}{2\tau} & 0 \end{vmatrix} = I_{ab} (TX5) \quad (65)$$

$$= \begin{vmatrix} -2W_X - W_A - \frac{1}{2\tau} & W_A + \frac{1}{2\tau} \\ W_A + \frac{1}{2\tau} & -2W_X - W_A - \frac{1}{2\tau} \end{vmatrix}$$

where (TX1) and (TX5) are the ratios of determinants. It is important to realize that (TX1) and (TX5) are negative.

From equations (37) and (64), I_{ab} can be calculated as follows

$$I_{ab} = \frac{T_2(MA1)^0 V_2^2 \pi^2}{1 + 4\pi^2 T_2^2 (\nu - \nu_{ab})^2 - T_2(TX1) V_2^2 \pi^2}$$

At resonance, $\nu - \nu_{ab} = 0$. Hence

$$I_{ab} = \frac{T_2(MA1^0) V_2^2 \pi^2}{1 - T_2(TX1) V_2^2 \pi^2} \quad (66)$$

The quantity $R(A1)$ for line A1 will be defined as the fractional intensity deviation from thermal equilibrium. Then

$$R(A1) = \frac{(\Delta MA1)}{(MA1^0)} \quad (67)$$

From equations (61), (66), and (67)

$$\begin{aligned} R(A1) &= \frac{(\Delta MA1)}{(MA1^0)} = \frac{I_{ab}(TA1)}{(MA1^0)} \\ &= \frac{T_2 V_2^2 \pi^2 (MA1^0)}{1 - \pi^2 T_2^2 V_2^2 (TX1)} \times \frac{(TA1)}{(MA1^0)} \\ &= \frac{T_2 V_2^2 \pi^2 (TA1)}{1 - T_2 \pi^2 V_2^2 (TX1)} \end{aligned} \quad (68)$$

Then, τ can be determined by comparing the experimental value of $R(A1)$ with the theoretical value of $R(A1)$ calculated from equation (68). This provides a method to determine τ .

Equation (68) is also valid for an AX_3 system. However, $(TA1)$ and $(TX1)$ will be different. In order to evaluate $(TA1)$ and $(TX1)$, the following equations are used

$$- \left[3W_X + 2W_A + \frac{7}{8\tau} \right] (\Delta MA1) + \left(3W_X + \frac{3}{8\tau} \right) (\Delta MA2) + \frac{3}{8\tau} (\Delta MA5) \quad (69)$$

$$+ \frac{1}{8\tau} (\Delta MA8) = \frac{3}{2} I_{ab}$$

$$\left(W_X + \frac{1}{8\tau} \right) (\Delta MA1) - \left[3W_X + 2W_A + \frac{5}{8\tau} \right] (\Delta MA2) + \left(2W_X + \frac{3}{8\tau} \right) \quad (70)$$

$$\times (\Delta MA5) + \frac{1}{8\tau} (\Delta MA8) = \frac{I_{ab}}{2}$$

$$\left(\frac{1}{8\tau} \right) (\Delta MA1) + \left(2W_X + \frac{3}{8\tau} \right) (\Delta MA2) - \left(3W_X + 2W_A + \frac{5}{8\tau} \right) (\Delta MA5) \quad (71)$$

$$+ \left(W_X + \frac{1}{8\tau} \right) (\Delta MA8) = - \frac{I_{ab}}{2}$$

$$\left(\frac{1}{8\tau} \right) (\Delta MA1) + \left(\frac{3}{8\tau} \right) (\Delta MA2) + \left(3W_X + \frac{3}{8\tau} \right) (\Delta MA5) \quad (72)$$

$$- \left(3W_X + 2W_A + \frac{7}{8\tau} \right) (\Delta MA8) = \frac{3}{2} I_{ab}$$

$$\left(-6W_X - W_A - \frac{1}{2\tau} \right) (\Delta MX1) + \left(W_A + \frac{1}{2\tau} \right) (\Delta MX13) = I_{ab} \quad (73)$$

and

$$\left(W_A + \frac{1}{2\tau} \right) (\Delta MX1) + \left(-6W_X - W_A - \frac{1}{2\tau} \right) (\Delta MX13) = 0 \quad (74)$$

Using methods similar to those given for the AX_2 system

$$(TA1) = \frac{1.5 \times (6W_X + 2W_A + \frac{1}{\tau})}{(3W_X + 2W_A + \frac{1}{\tau}) (5W_X + 2W_A + \frac{1}{\tau}) - 3W_X^2} \quad (75)$$

and

$$(TX1) = \frac{- (6W_X + W_A + \frac{1}{2\tau})}{(6W_X + W_A + \frac{1}{2\tau})^2 - (W_A + \frac{1}{2\tau})^2} \quad (76)$$

All of the equations derived are applicable to weakly coupled spin systems. If strongly coupled spin systems are considered, they must be described by the density matrix formalism.

CHAPTER IV

NUCLEAR MAGNETIC DOUBLE RESONANCE EXPERIMENTS

ON 2,2,2-TRICHLOROETHANOL AND METHANOL

Experimental Methods

Double Resonance

A standard Varian V-4300 NMR spectrometer was used to record frequency sweep double resonance spectra of $\text{CCl}_3\text{CH}_2\text{OH}$ and CH_3OH . Phase sensitive detection of audio sidebands was accomplished using a field-frequency lock system modeled after that described by Noggle.¹⁹ A General Radio 1107-A interpolation oscillator driven by a synchronous motor was used to provide audio frequency modulation for H_1 , the observing field. The modulation for H_2 was provided by a Hewlett-Packard 204-B oscillator. The output of the 204-B was amplified by a General Radio 1201-B unit amplifier and then attenuated by a Hewlett-Packard 350-D attenuator. The low field sidebands were used for the field-frequency lock, observing, and double resonance signals.

Variable Temperature Addition to Probe

A Varian Model V-4340 Variable Temperature NMR Probe Accessory was used. The temperature was controlled by first passing dry nitrogen gas through a copper tube coil immersed in liquid nitrogen and then through the Probe Accessory. A copper-constantan thermocouple was used to measure the temperature. The thermocouple EMF was read on an L & N Galvanometer. The sample spinning and magnetic field homogeneity were

greatly affected by the changes in temperature.

Sample Preparation

All reagents were stock material. The methanol was 12 percent by volume in CCl_4 . Tetramethylsilane (TMS) was five percent by volume in the methanol sample and was used for the field-frequency locking loop. The 2,2,2-trichloroethanol samples were prepared with 70 percent, 40 percent, 20 percent, and seven percent by volume of $\text{CCl}_3\text{CH}_2\text{OH}$ in dimethylsulfoxide (DMSO). Although the amount of TMS which dissolved in the DMSO was quite small, it was enough for the lock loop. The multiplet structure in $\text{CCl}_3\text{CH}_2\text{OH}$ and CH_3OH gradually disappeared after the sample stood for a few days. This is probably due to the dissolving of impurities from the sample tube glass. Therefore, the samples were freshly prepared and kept in dry ice during the experimental period. The variation of temperature for the methanol sample was limited by the freezing point of CCl_4 , -23°C .

Experimental Results

Single Resonance Experiments

The compound, $\text{CCl}_3\text{CH}_2\text{OH}$, was chosen as an example of an AX_2 system.

The triplet and doublet in the spectra correspond to the hydroxyl group and methylene group, respectively. Dimethylsulfoxide strongly complexes with this alcohol because of the three beta chlorine atoms. This provides a convenient way for varying τ for proton exchange in $\text{CCl}_3\text{CH}_2\text{OH}$ at room temperature. One simply adjusts the ratio of $\text{CCl}_3\text{CH}_2\text{OH}$ to DMSO. The samples contain two percent TMS by volume for the lock loop.

Thus, a series of samples of $\text{CCl}_3\text{CH}_2\text{OH}$ was made with different concentrations in DMSO.

The coupling constant for this compound is 7.2 cps. The chemical shift for 70 percent $\text{CCl}_3\text{CH}_2\text{OH}$ by volume in DMSO is 148 cps. The chemical shift is changed to about 160 cps when the concentration of $\text{CCl}_3\text{CH}_2\text{OH}$ is 20 percent by volume in DMSO.

Equation (16) was used to predict the theoretical spectra of the triplet for different values of τ . The calculation was programmed in ALGOL for the Burroughs B5500 of the Georgia Institute of Technology's Rich Electronic Computer Center. In Figure 3, the theoretical spectra of the hydroxyl triplet are on the left and the experimental spectra are on the right. The frequency decreases from left to right in the spectra. The value of τ was determined by matching the theoretical and experimental spectra. The reciprocal half width, T_2 , was assumed to be 1.9 seconds for the theoretical calculations. This value was obtained by measuring the half width of the nonexchanging TMS. The values of τ for $\text{CCl}_3\text{CH}_2\text{OH}$ in different concentrations are listed in Table 1. The value of τ for seven percent $\text{CCl}_3\text{CH}_2\text{OH}$ could not be determined by this technique because the dominant contribution to the line shape is due to magnetic field inhomogeneity. The value of two seconds for τ was obtained by the double resonance technique to be described later.

The compound methanol was chosen as an example of an AX_3 system. The quartet and doublet in the spectra are the hydroxyl group and methyl group signals, respectively. The compound was dissolved in CCl_4 in order to slow down the proton exchange enough for the multiplet splitting to appear. A sample which was 12 percent by volume in CCl_4 was prepared.

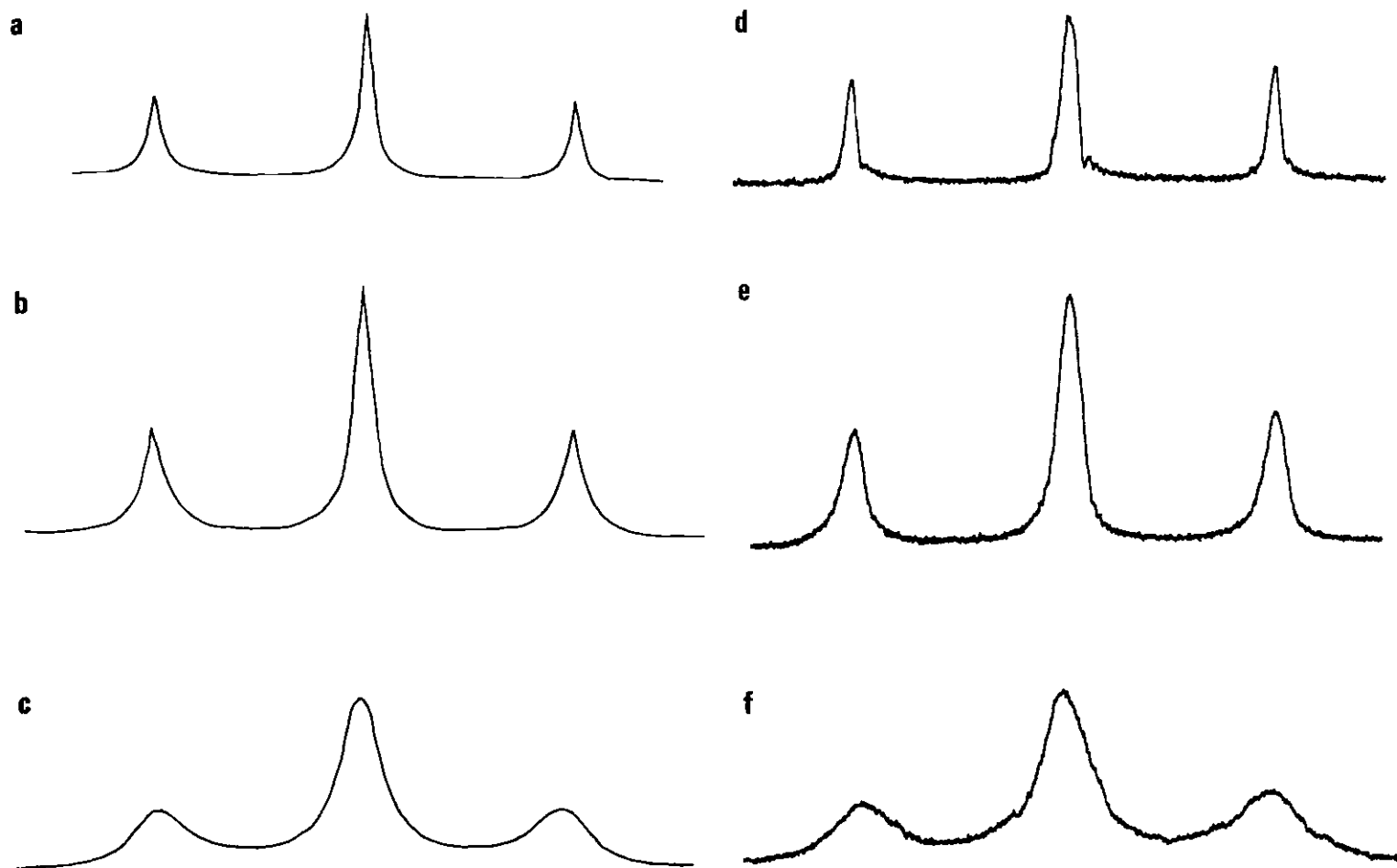


Figure 3. Experimental and Theoretical Spectra of $\text{CCl}_3\text{CH}_2\text{OH}$ for Different τ . The spectra on the left are theoretical spectra. The spectra on the right are experimental spectra. The value of τ for traces a and d is 1.0 second. The value of τ for traces b and e is 0.40 second. The value of τ for traces c and f is 0.12 second.

Table 1. The Values of τ for $\text{CCl}_3\text{CH}_2\text{OH}$ for Different Concentrations in DMSO

Concentration	7% V	20% V	40% V	70% V
τ (sec)	2.0*	1.0	0.4	0.12

*The value of τ equal to two seconds was obtained from double resonance technique, and the others were obtained from line shape method.

The sample also contained five percent by volume of TMS for the lock loop. The value of τ was varied by changing the sample temperature.

The coupling constant for CH_3OH is 5.2 cps. The chemical shift at 25°C is 72 cps and about 90 cps at -20°C . Equation (21) was used to predict the theoretical spectra of the hydroxyl quartet for different values of τ . The calculation was programmed in ALGOL for the Burroughs B5500. In Figure 4, the theoretical spectra of the hydroxyl quartet are on the left, and the experimental spectra are on the right. The frequency decreases from left to right in the spectra. The value of τ was determined by comparison of the theoretical and experimental spectra. The values of τ for the CH_3OH sample at different temperatures are listed in Table 2.

Double Resonance Experiments

Frequency sweep double resonance experiments for AX_2 and AX_3 systems were carried out in this thesis. First, consider the AX_2 system, $\text{CCl}_3\text{CH}_2\text{OH}$. Refer to Figure 1. If H_2 irradiates X_1 to X_4 , the difference in populations between αa and βa will be decreased. This is because the population in the αa state is reduced by irradiation of H_2 . Therefore, the A_1 peak corresponding to the transition between αa and βa is decreased. On the other hand, the difference of populations between αd and βd will be increased. This is because the population in αd is increased by the irradiation of H_2 . Therefore, the intensity of the A_4 peak corresponding to the transition between αd and βd will be increased. If H_2 is set on X_5 to X_8 , the intensity changes should be reversed. These intensity changes are known as the nuclear Overhauser effect.²⁰ The intensity changes in the triplet caused by irradiating

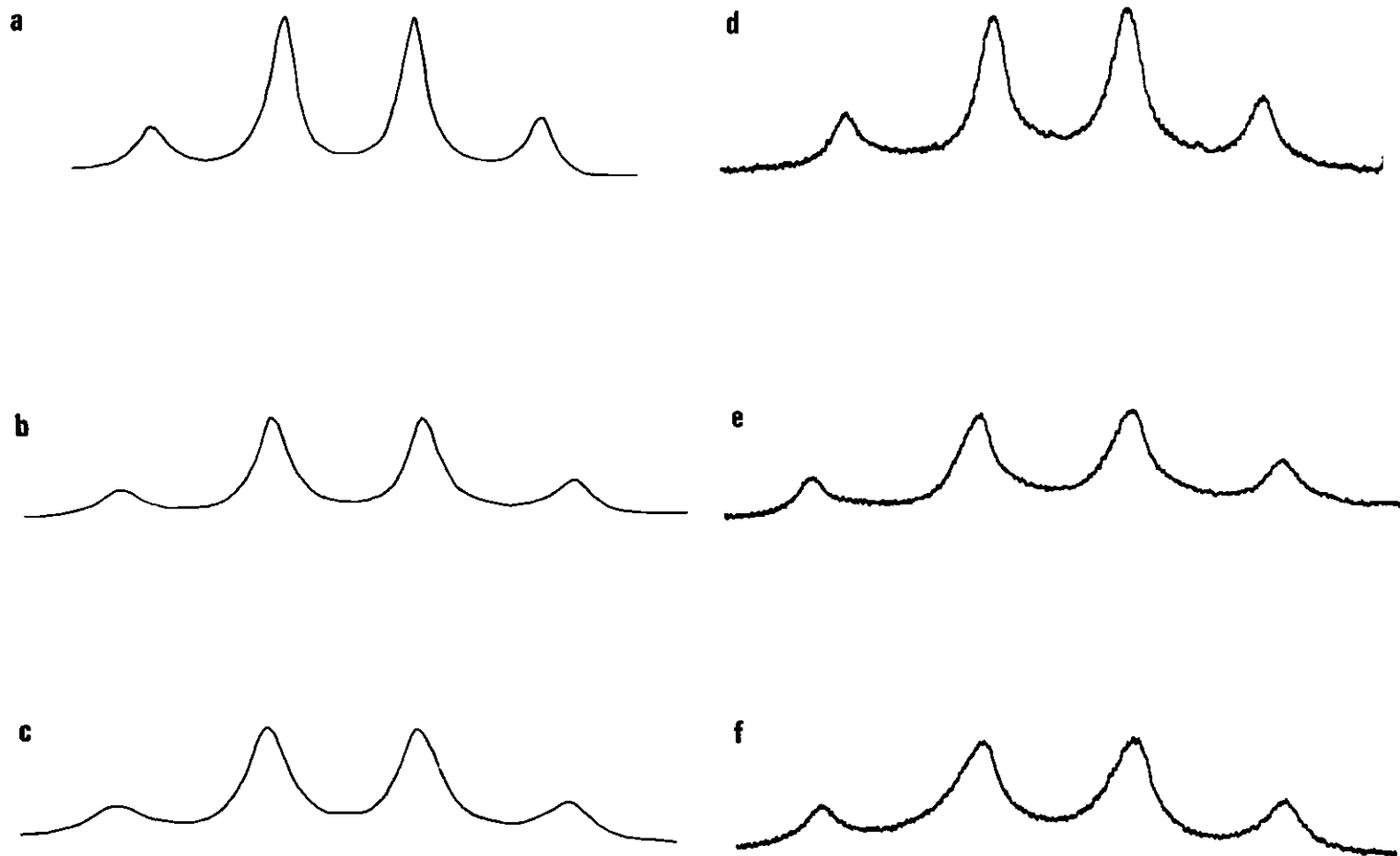


Figure 4. Experimental and Theoretical Spectra of CH_3OH for Different τ . The spectra on the left are theoretical spectra. The spectra on the right are experimental spectra. The value of τ for traces a and d is 0.23 second. The value of τ for traces b and e is 0.20 second. The value of τ for traces c and f is 0.14 second.

Table 2. The Values of τ for 12 Percent CH_3OH by Volume
in CCl_4 at Different Temperatures

Temperature	-20°C	0°C	24°C
τ (sec)*	0.23	0.20	0.14

* The values of τ were obtained from line shape method.

X1 to X4 and X5 to X8 are compared in Figure 9. In the left hand traces, X1 to X4 are irradiated by H_2 . In the right hand traces, X5 to X8 are irradiated. When chemical exchange becomes faster, the Overhauser effect will be decreased. This is predicted by equation (23) and occurs because protons can transfer among the αa , αb , αc , and αd states directly. Thus, when τ becomes shorter, the deviations of the populations of αa and αd from thermal equilibrium decrease. Therefore, chemical exchange causes the intensity changes for A1 and A4 to be reduced. This causes the experimental spectra of the hydroxyl triplet to become more symmetrical. This result is shown in Figure 7.

If relaxations of A and X protons are considered, the Overhauser effect will become smaller when T_A and T_X become shorter. The reason is that αa can relax with βa , αb , and αc . Hence, when T_A and T_X become shorter, they relax faster and the deviations of populations of αa and αd decrease. Therefore, the relaxations of A and X protons cause the intensity changes for A1 and A4 to be reduced. This makes the experimental spectra of the hydroxyl triplet become more symmetrical. Unfortunately, T_A and T_X were not measured in this experiment; therefore, this prediction is not proved experimentally.

The same argument can be applied to the AX_3 system, CH_3OH . In Figure 2, if X1 to X12 are irradiated by H_2 , the intensities of the A1, A2, A3, and A4 peaks will be decreased because the differences of populations between αa and βc , αb and βb , αc and βc , and αd and βd , respectively, are decreased. Meanwhile, the A5, A6, A7, and A8 peaks will be increased because the differences of populations between αe and βe , αf and βf , αg and βg , and αh and βh will be increased. On the other hand,

if X13 to X24 are irradiated by \tilde{H}_2 , the intensity changes will be reversed. The Overhauser effect is affected by chemical exchange and relaxation in the same way as discussed for the CCl_3CH_2OH sample.

The experimental spectra for CH_3OH are shown in Figure 8. In these experiments, X13 to X24 are irradiated by \tilde{H}_2 , and the temperatures are varied. Since the lower limit for the temperature is determined by the freezing point of CCl_4 , $-23^\circ C$, the chemical exchange could not be slowed down very much. Therefore, the change in the Overhauser effect is not very obvious.

The theoretical values of R for CCl_3CH_2OH were calculated from equation (68) by assuming T_2 , T_A , and T_X equal to 2.5 seconds. The values of T_2 , T_A , and T_X chosen here give the best fit of the theory with the experimental values of R . This assumption is reasonable for these samples. The experimental values of R were determined by computing the fractional intensity deviation of the A1 signal. The signal area was measured by an integrating rotor. These experimental values of R are listed in Table 3. In Figure 5, the experimental and theoretical values of R versus V_2 for CCl_3CH_2OH are shown. The value of τ for seven percent CCl_3CH_2OH was chosen as two seconds by comparison of theoretical and experimental values of R in Figure 5. This value is chosen in order to obtain consistency in the theoretical values of R being smaller than experimental values of R .

The theoretical values of R for CH_3OH were calculated by equation (68). By the same reason mentioned before, T_2 , T_A , and T_X are assumed equal to four seconds when τ equals 0.23 second and equal to five seconds when τ equals 0.2 and 0.14 second. The experimental values of R were

Table 3. Overhauser Effect on $\text{CCl}_3\text{CH}_2\text{OH}$ for Different Concentrations in DMSO with Low Frequency Peak of Methylene Doublet Irradiated by Second Strong rf

7% V		20% V		40% V		70% V	
$\tau = 2.0 \text{ sec}$		$\tau = 1.0 \text{ sec}$		$\tau = 0.40 \text{ sec}$		$\tau = 0.12 \text{ sec}$	
V_2	R	V_2	R	V_2	R	V_2	R
(cps)		(cps)		(cps)		(cps)	
0	0	0	0	0	0	0	0
0.11	0.29	0.06	0.14	0.06	0.05	0.06	0.03
0.19	0.36	0.086	0.23	0.27	0.19	0.086	0.05
0.27	0.41	0.11	0.25	0.37	0.23	0.19	0.12
0.37	0.46	0.37	0.40	0.60	0.29	0.37	0.16
0.6	0.51	0.60	0.45	1.10	0.37	0.6	0.18
0.76	0.54	0.96	0.48			1.1	0.2
0.96	0.58						

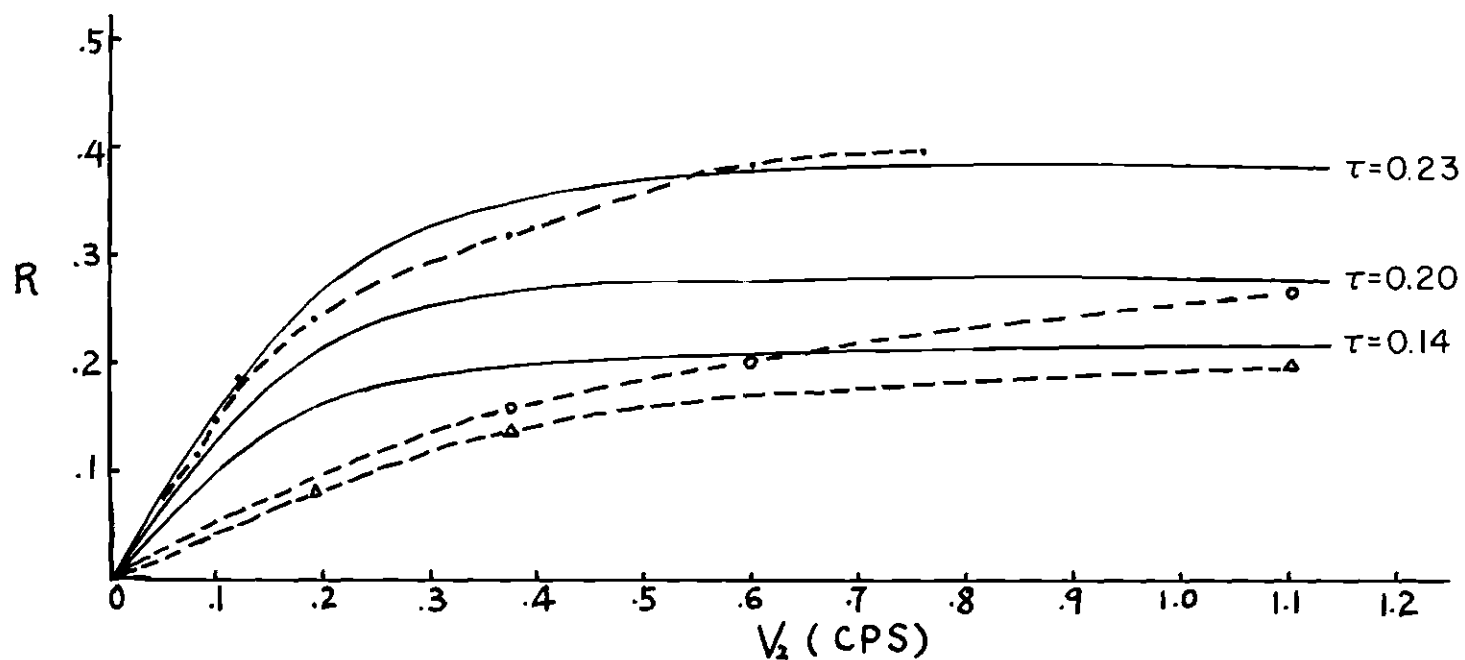


Figure 5. Experimental and Theoretical Values of R versus V_2 for $\text{CCl}_3\text{CH}_2\text{OH}$. The experimental points for 7, 20, 40, and 70 volume % alcohol are represented by \cdot , Δ , $+$, and \circ , respectively. The experimental points for one concentration are connected by dashed curves. The theoretical dependence of R on V_2 is represented by solid curves. The solid curves were computed with T_2 , T_A , and T_X equal to 2.5 seconds and with τ equal to 2.0, 1.0, 0.4, and 0.12 seconds for the 7, 20, 40, and 70 volume % solution, respectively.

determined by computing the fractional intensity deviation of A1 signal. The signal area was measured by an integrating rotor. Equation (69) and equation (70) predict that $R(A1)$ is equal to the sum of $R(A2)$, $R(A3)$, and $R(A4)$. The experimental values of $R(A2)$, $R(A3)$, and $R(A4)$ could not be measured accurately, however, due to the overlapping of peaks. Therefore, this prediction could not be satisfactorily compared with theory. The experimental values of $R(A1)$ are listed in Table 4. The theoretical and experimental values of $R(A1)$ versus V_2 are shown in Figure 6.

In Figure 9, each peak of the hydroxyl triplet in traces d and h is split into a triplet due to the large value of V_2 .¹³ The reason is that there are two more allowed transitions for each peak of original triplet. The spacing between two adjacent peaks of split triplet is equal to V_2 .¹³ Therefore, the measurement of this splitting enabled the value of V_2 to be obtained. A precision attenuator was used to obtain smaller known values of V_2 . As for the methanol sample, each peak of the hydroxyl quartet will be theoretically split into a quartet.¹³ It was not split clearly, however, in the experimental spectra. The reason is that the line width of each peak in the quartet was so large that there was considerable overlap, because the coupling constant is only 5.2 cps. Hence, the split quartet was not clearly resolved. Because of this, the values of V_2 used in the CH_3OH experiments were obtained from the CCl_3-CH_2OH experiments.

The double resonance experiments presented several difficulties. First, when V_2 became large, the receiver saturated and the detector amplification decreased. Second, as V_2 became large, the lock loop became

Table 4. Overhauser Effect on 12 Percent CH_3OH by Volume in CCl_4 for Different Temperatures with Low Frequency Peak of Methyl Doublet Irradiated by Second Strong rf

-20°C		0°C		24°C	
$\tau = 0.23 \text{ sec}$		$\tau = 0.20 \text{ sec}$		$\tau = 0.14 \text{ sec}$	
V_2	R	V_2	R	V_2	R
(cps)		(cps)		(cps)	
0	0	0	0	0	0
0.076	0.12	0.37	0.16	0.19	0.09
0.12	0.19	0.6	0.2	0.37	0.14
0.19	0.24	1.1	0.27	1.1	0.2
0.37	0.32				
0.76	0.4				

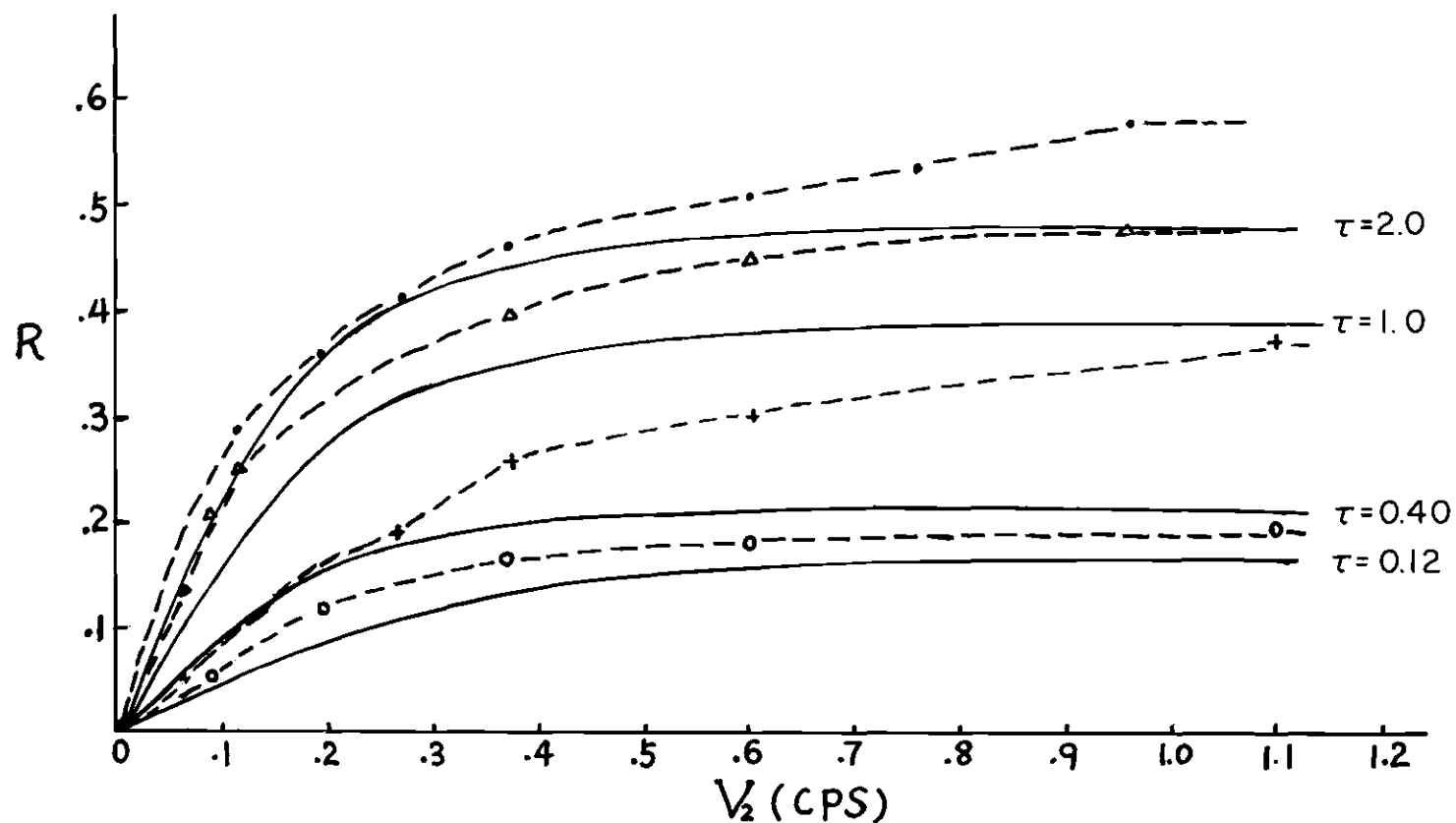


Figure 6. Experimental and Theoretical Values of R versus V_2 for CH_3OH . The experimental points for samples with a temperature of -20°C , 0°C , and 24°C are represented by \cdot , \circ , and Δ , respectively. The experimental points for one temperature are connected by dashed curves. The theoretical dependence of R on V_2 is represented by solid curves. The solid curves for -20°C were computed with T_2 , T_A , and T_X equal to 4 seconds, and with τ equal to 0.23 second. The solid curves for temperatures of 0°C and 24°C were computed with T_2 , T_A , and T_X equal to 5 seconds, and with τ equal to 0.20 and 0.14 second, respectively.

unstable. Third, when the Overhauser effect was small, the measurement of R had a large experimental error. Fourth, when the variable temperature was used, the poor sample spinning aggravated the above difficulties.

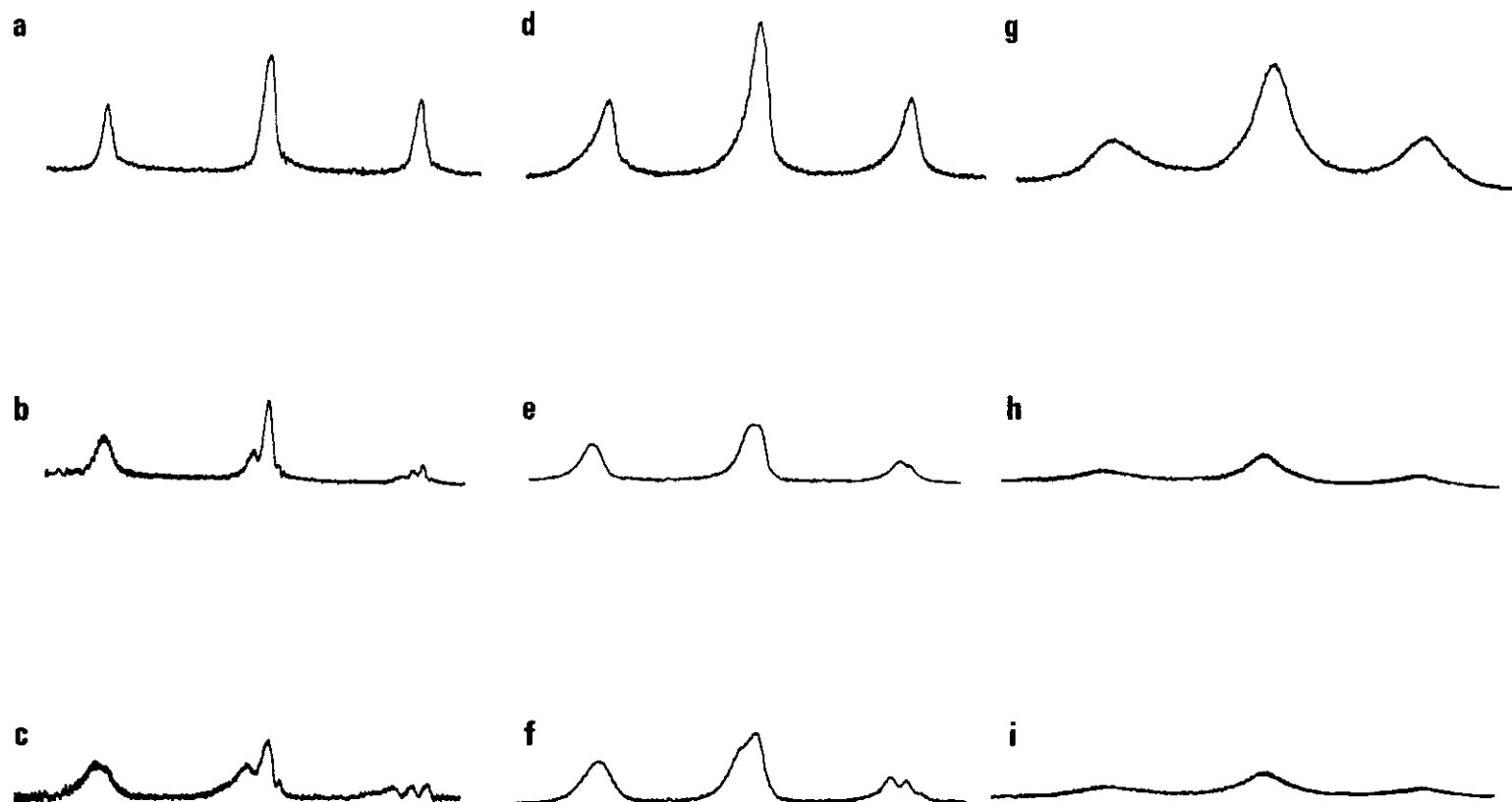


Figure 7. Overhauser Effect on $\text{CCl}_3\text{CH}_2\text{OH}$ for Different Concentration in DMSO. The value of τ is 1.0 second in traces a, b, and c. The value of τ is 0.4 second in traces d, e, and f. The value of τ is 0.12 second in traces g, h, and i. The value of V_2 is 0 cps in traces a, d, and g. The value of V_2 is 0.37 cps in traces b, e, and h. The value of V_2 is 0.6 cps in traces c, f, and i. The frequency decreases from left to right. The low frequency peak of the methylene doublet is irradiated by second strong rf.

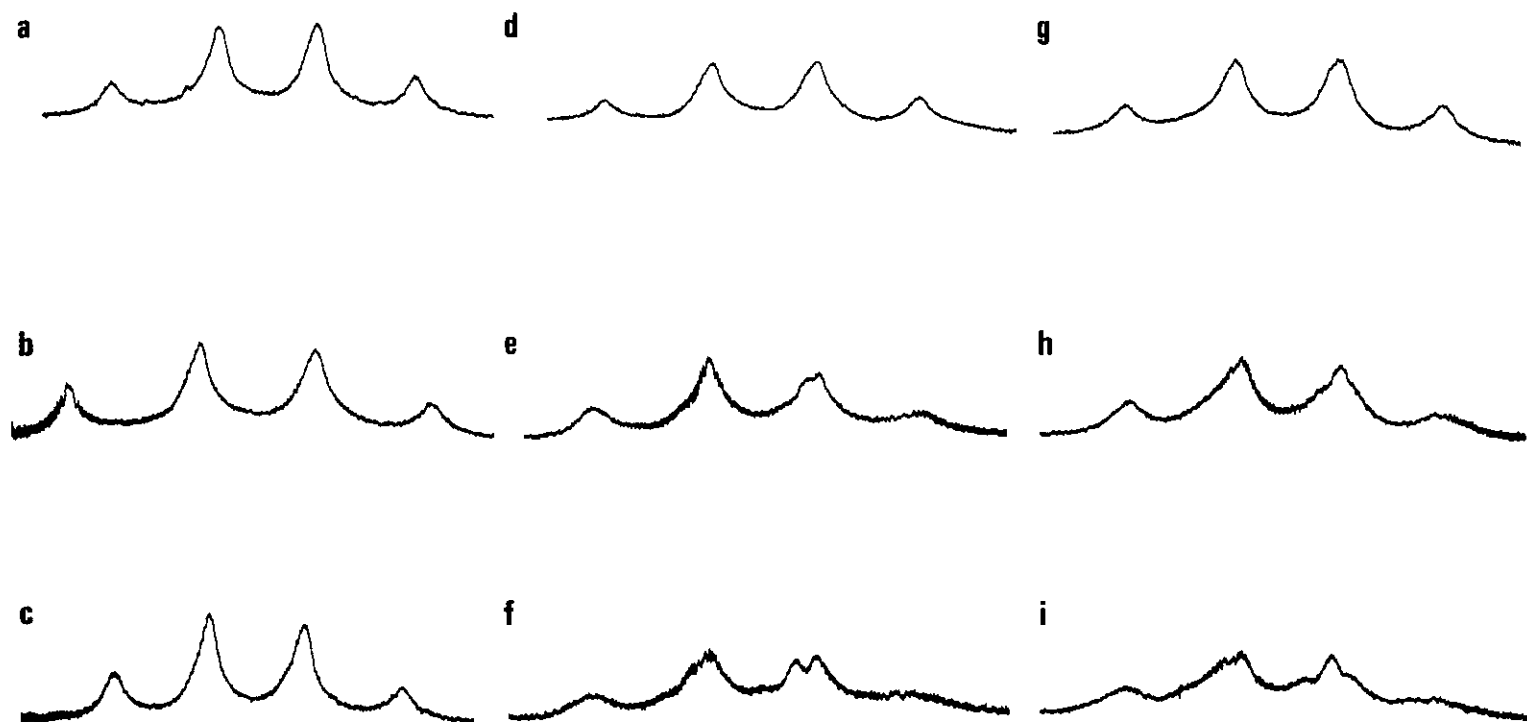


Figure 8. Overhauser Effect on CH_3OH at Different Temperatures. The value of τ is 0.23 second in traces a, b, and c. The value of τ is 0.20 second in traces d, e, and f. The value of τ is 0.14 second in traces g, h, and i. The value of V_2 is 0 cps in traces a, d, and g. The value of V_2 for traces b, e, and h is 0.19, 0.6, and 0.37 cps, respectively. The value of V_2 for traces c, f, and i is 0.37, 1.1, and 1.1 cps, respectively. The frequency decreases from left to right. The low frequency peak of methyl doublet is irradiated by second strong rf.

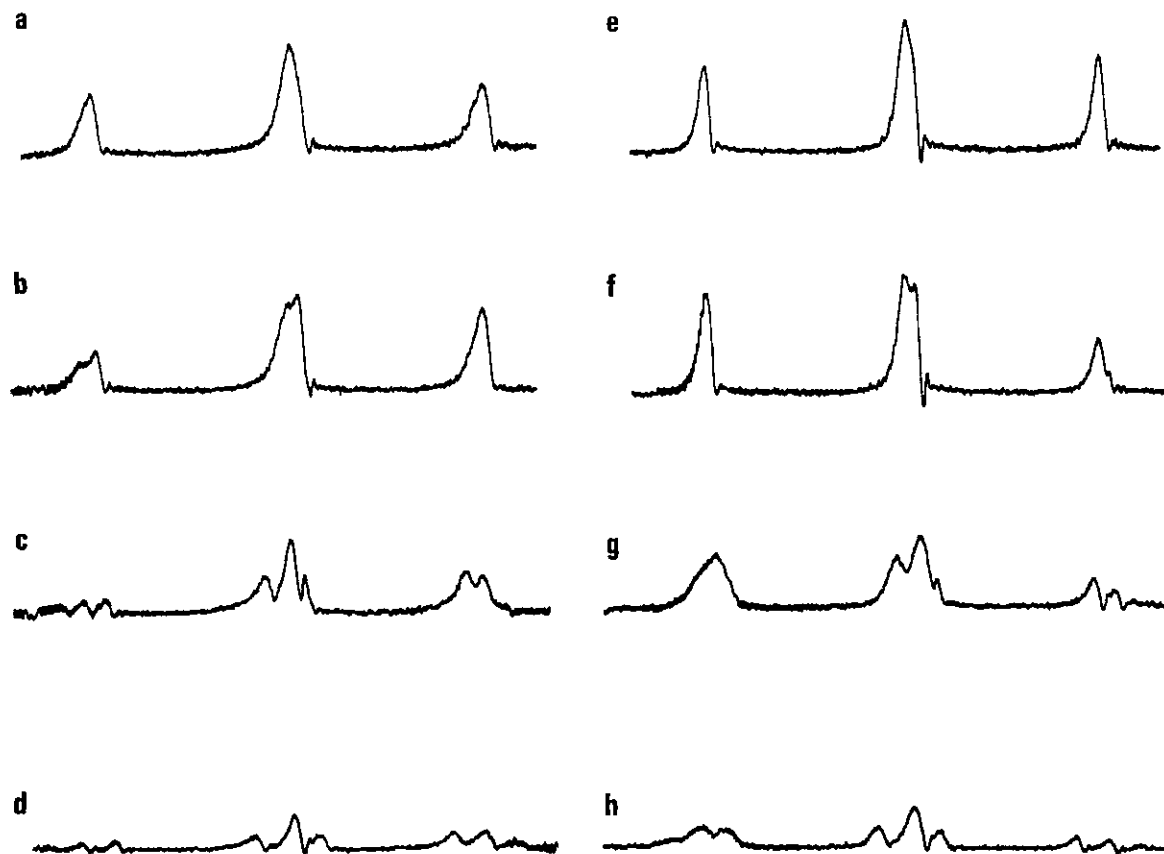


Figure 9. Comparison of Overhauser Effect on $\text{CCl}_3\text{CH}_2\text{OH}$ When τ Equals 2.0 Seconds. The high frequency peak of the methylene doublet is irradiated by second strong rf in traces a, b, c, and d. The low frequency peak of the methylene doublet is irradiated by second strong rf in traces e, f, g, and h. In traces a and e, V_2 equals 0 cps. In traces b and f, V_2 equals 0.11 cps. In traces c and g, V_2 equals 0.6 cps. In traces d and h, V_2 equals 1.2 cps.

CHAPTER V

DISCUSSION

Using equations (16) and (21), the theoretically predicted line shapes are consistent with the experimental spectra. Hence, by the comparison of line shapes between theoretical and experimental spectra, the average time interval between chemical exchange can be determined. However, this method is suitable only if τ is less than one second. The reason is that the line width is determined by field inhomogeneity if τ is longer than one second.

One of the motivations of this thesis was to provide a double resonance experiment to determine τ when it is longer than one second. In Figures 5 and 6, however, the quantitative agreement between the theoretical and experimental values of R is not satisfactory. This is probably because of the experimental difficulties mentioned in the last chapter.

However, these double resonance experiments have indicated the general aspects of the combined effect of chemical exchange and double resonance saturation. In Figures 5 and 6, as τ becomes shorter, the Overhauser effect decreases. This implies that the chemical exchange does play the role of driving the spin system toward the Boltzmann distribution. Hence, as the chemical exchange becomes faster, the Overhauser effect decreases. In Figure 7, the experimental spectra for $\text{CCl}_3\text{CH}_2\text{OH}$ show this phenomenon. As τ becomes shorter, the unsymmetrical

hydroxyl triplet becomes more symmetrical since the chemical exchange has decreased the deviation of populations from Boltzmann distribution. In Figure 8, the same effect is shown for the hydroxyl quartet of CH_3OH . Since the chemical exchanges are always fast within the limited temperature range used for CH_3OH , the Overhauser effect in CH_3OH is not so obvious as that for $\text{CCl}_3\text{CH}_2\text{OH}$.

The following method is suggested as an alternative method of measuring T_A , T_X , and τ . If X1 is saturated by H_2 , equation (55) becomes

$$\frac{d(\Delta\text{MX5})}{dt} = - \left(W_A + \frac{1}{2\tau} \right) (\text{MX1}^0) - \left(2W_X + W_A + \frac{1}{2\tau} \right) (\Delta\text{MX5})$$

This can be rewritten as

$$\frac{dR(X5)}{dt} = - \left(W_A + \frac{1}{2\tau} \right) - \left(2W_X + W_A + \frac{1}{2\tau} \right) R(X5)$$

or

$$\frac{dR(X5)}{dt} = - C - K R(X5) \quad (77)$$

$$\text{where } K = 2W_X + W_A + \frac{1}{2\tau} = \frac{1}{T_X} + \frac{1}{2T_A} + \frac{1}{2\tau} \quad (78)$$

$$C = W_A + \frac{1}{2\tau} = \frac{1}{2T_A} + \frac{1}{2\tau} \quad (79)$$

$$\text{MX1}^0 = \text{MX5}^0, \text{ and } R(X5) = \frac{\Delta\text{MX5}}{\text{MX5}^0}$$

Equation (77) can be integrated as follows, using the fact that $R(X5) = 0$ when $t = 0$. Then

$$\int_{O+C}^{KR(X5)+C} \frac{d[K R(X5) + C]}{[K R(X5) + C]} = - \int_0^t K dt$$

$$\ln [K R(X5) + C] = - K t + \ln C$$

$$\ln [R(X5) + \frac{C}{K}] = - K t + \ln \frac{C}{K}$$

and

$$\ln [R(X5) - R(X5)(\infty)] = - K t + \ln [- R(X5)(\infty)] \quad (80)$$

where $R(X5)(\infty)$ is $R(X5)$ at the steady state and is equal to $-\frac{C}{K}$. The value of K can be obtained from the slope of $\ln [R(X5) + \frac{C}{K}]$ versus the time elapsed after application of the saturating rf. Thus, after $X1$ is saturated, $R(X5)$ decays to the steady state value of $-\frac{C}{K}$. The value of $\frac{C}{K}$ is obtained from a steady state measurement of $R(X5)$.

If $A2$ and $A4$ are saturated by H_2 , equation (51) becomes

$$\frac{d(\Delta MA1)}{dt} = \left(-\frac{3}{4\tau} - 2W_X - 2W_A\right)(\Delta MA1) - \left(\frac{1}{2\tau} + 2W_X\right)(MA2^0) - \frac{1}{4\tau} (MA4^0)$$

This can be rewritten as

$$\frac{dR(A1)}{dt} = - \left(\frac{3}{4\tau} + 2W_X + 2W_A\right) R(A1) - \left(\frac{3}{4\tau} + 2W_X\right)$$

or

$$\frac{dR(A1)}{dt} = - K' R(A1) - C' \quad (81)$$

$$\text{where } K' = \frac{3}{4\tau} + 2W_X + 2W_A = \frac{3}{4\tau} + \frac{1}{T_X} + \frac{1}{T_A} \quad (82)$$

$$C' = \frac{3}{4\tau} + 2W_X = \frac{3}{4\tau} + \frac{1}{T_X} \quad (83)$$

$$MA1^0 = MA2^0 = MA4^0, \text{ and } R(A1) = \frac{\Delta MA1}{MA1^0}$$

Equation (81) can be integrated as follows, using the fact that $R(A1) = 0$ when $t = 0$.

Then

$$\int_{0+C'}^{K'R(A1)+C'} \frac{d[K'R(A1) + C']}{[K'R(A1) + C']} = - \int_0^t K' dt$$

$$\ln [K'R(A1) + C'] = -K't + \ln C$$

$$\ln [R(A1) + \frac{C'}{K'}] = -K't + \ln C'$$

and

$$\ln [R(A1) - R(A1)(\infty)] = -K't + \ln [-R(A1)(\infty)] \quad (84)$$

where $R(A1)(\infty)$ is $R(A1)$ at the steady state and is equal to $-\frac{C'}{K'}$. The value of K' can be obtained from the slope of $\ln [R(A1) - R(A1)(\infty)]$ versus the time elapsed after application of the saturating rf. Thus, after $A2$ and $A4$ are saturated, $R(A1)$ decays to the steady state value of $-\frac{C'}{K'}$. The value of $\frac{C'}{K'}$ is obtained from a steady state measurement of $R(A1)$.

Since K , $\frac{C}{K}$, K' , and $\frac{C'}{K'}$ can be measured, T_A , T_X , and τ can be expressed in terms of K , C , K' , and C' from equations (78), (79), (82), and (83). The explicit formulas are as follows.

$$T_A = \frac{1}{K' - C'} \quad (85)$$

$$T_X = \frac{1}{K - C} \quad (86)$$

and

$$\tau = \frac{1}{2C - K' + C'} \quad (87)$$

Therefore, T_A , T_X , and τ can be obtained from equations (85), (86), and (87).

This technique would allow all of the parameters used in this thesis to be independently measured. This would enable the theory developed in this thesis to be tested without using adjustable parameters.

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^{*} Abbreviations used herein follow the form of Chemical Abstracts, 50, 1 J (1956).

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