NMR Lineshape Theory of Superimposed Intermolecular Spin Exchange Reactions and Its Application to the System Acetic Acid/Methanol/Tetrahydrofuran-\textit{d}_8

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The density matrix equations describing the NMR lineshape of tightly coupled spin systems in the presence of intermolecular spin exchange have been recast in a form which is convenient for kinetic studies. The lineshape equation is expressed as a function of pseudo-first-order group exchange rate constants, \( k_{rs}(i) \), of the spin group \( i \) between the environments \( r \) and \( s \), of which \( i \) is an integral part. Thus, NMR lineshapes are easily calculated even if different exchange reactions such as \( AB + BD \rightleftharpoons AC + BD \), \( AB + A^*C \rightleftharpoons A^*B + AC \), \( AB + A^*B \rightleftharpoons A^*B + AB^* \), \( AB + CD \rightleftharpoons ABC + D \), etc., are present in the sample. The use of the \( k_{rs}(i) \) avoids the assumption of reaction mechanisms at the stage of extracting the kinetic data from the NMR lineshape. The presence of any particular reaction set appears as a result of special relations between the \( k_{rs}(i) \). The utility of this formulation of the lineshape equation is illustrated by the example of the slow intermolecular proton exchange in the system methanol/acetic acid/tetrahydrofuran-\textit{d}_8.

INTRODUCTION

The NMR lineshape of high-order spin systems that undergo intermolecular exchange reactions must be described by a quantum mechanical density matrix formalism (1). Such a description, valid for special intermolecular exchange reactions, was given by Kaplan (2) and Alexander (3). The theory was later formulated in Liouville space by Binsch (4). A more general formalism was then proposed by Kaplan and Fraenkel (5) which provides a good physical insight into all approximations which must be used in calculating NMR lineshapes affected by the presence of intermolecular exchange.

The theory describes the exchange of the reactants as a permutation of spins in a combined spin system formed by the reactions, for example,

\[
AB + CD \rightleftharpoons ABCD \rightleftharpoons ACBD \rightleftharpoons AC + BD,
\]  \[1\]

or

\[
AB + CD \rightleftharpoons ABCD \rightleftharpoons ABC + D.
\]  \[2\]

For every reaction mechanism a different lineshape equation must be set up. If one deals with practical kinetic problems such as the intermolecular proton exchange...
one generally finds very complicated reaction schemes. For example, reactions [1] and [2] may be superimposed or may be accompanied by side reactions, such as

\[
\begin{align*}
\text{AB} + A^*C & \rightleftharpoons A^*B + AC, \\
\text{AB} + AC & \rightleftharpoons A_2B + C, \\
\text{AB} + A^*B^* & \rightleftharpoons A^*B + AB^*, \\
\text{AB} + AB & \rightleftharpoons A_2B + B.
\end{align*}
\]

The spin systems CD and BD are involved in similar reactions. For actual lineshape calculations one, therefore, always has to take into account the superposition of all sorts of exchange reactions. From a kinetic point of view it is preferable to separate the determination of kinetic data and the discussion of reaction mechanisms. Therefore, the lineshape equation should be formulated free from assumptions on reaction mechanisms which could lead to an overinterpretation of the NMR spectra. For example, if the concentrations of species AC and BD in reaction [1] or the concentrations of ABC and D in reaction [2] are too low to be detectable by NMR, the resulting lineshape of the signals of AB and CD can be equally well reproduced by each of the corresponding lineshape equations given by Kaplan and Fraenkel (5). Similarly, it is not possible to distinguish between reactions [3] and [4] or between [5] and [6] if the concentration of AB₂ is very low.

The aim of this paper is to propose a kinetic formulation of the lineshape equation which avoids assumptions on reaction mechanisms in the stage of lineshape simulations. This is done by introducing pseudo-first-order group exchange rate constants, \(k_r(i)\), of the spin group \(i\) between the environments or subsystems \(r\) and \(s\) of which \(i\) is an integral part. These constants are the elementary information the spectra provide. One need only consider those subsystems which give nonzero NMR signals. The presence of any particular exchange reaction or the superposition of any reactions appears as a result of special relations between the group exchange rate constants. The notation of Binsch (4) has proved convenient for computer use and will be used here.

The advantage of the formulation of the lineshape equation presented here will be demonstrated by the example of slow intermolecular proton exchange in the system methanol/acetic acid/tetrahydrofuran-d₈.

**THEORY**

The NMR absorption intensity \(Y(\omega)\) of a sample which consists of several subsystems \(r\) with mole fractions \(p_r\) is given according to Kaplan and Fraenkel (5) by

\[
Y(\omega) \sim \text{Imag} \left( \sum_r p_r \, \text{Tr}_r (I_r^\tau \rho') \right).
\]
power and high-temperature limits must be used. In the “permutation of indices method” of Kaplan and Fraenkel (5) the \( \rho' \) are evaluated directly, whereas Alexander (3) evaluates the quantities \( \rho'' \) which are related to \( \rho' \) by

\[
\rho' = N_r^{-1} (\epsilon' + \rho''),
\]

where \( \epsilon' \) is the unit matrix and \( N_r \) the number of spin states in subsystem \( r \) which contains \( l \) spins,

\[
N_r = 2^l.
\]

By combination of Eqs. [7] and [8] one obtains

\[
Y(\omega) \sim \text{Imag} \left( \sum_r p_r N_r^{-1} \text{Tr}_r (I_r \rho'') \right)
\]

since

\[
\text{Tr}_r (I_r \epsilon') = 0.
\]

One may use either Eq. [7] or Eq. [10]. According to Binsch (4), it is very convenient to arrange the elements of the density matrix in a column vector. Then one obtains from Eq. [7] or Eq. [10]

\[
Y(\omega) \sim \text{Imag}(P^{\text{row}} \rho^{\text{col}}) = \text{Imag}(P^{\text{row}} \rho^{\text{icol}}).
\]

The elements of the row vector, \( P \), are given by

\[
P_m = P_{\mu,\nu} = p_r \langle \mu_r | I_r^- | \nu_r \rangle,
\]

the elements of \( P' \) by

\[
P'_m = P'_{\mu,\nu} = p_r N_r^{-1} \langle \mu_r | I_r^- | \nu_r \rangle.
\]

Using the notation of Binsch (4), \( \rho^{\text{col}} \) is given according to Kaplan and Fraenkel (5) by

\[
\rho^{\text{col}} = i \mathcal{M}_0^{-1} I^{\text{col}},
\]

where

\[
I_m^\mu = I_m^\nu = N_r^{-1} \langle \mu_r | I_r^- | \nu_r \rangle.
\]

The matrix \( \mathcal{M}_0 \) is given by

\[
\mathcal{M}_0 = -2\pi i \mathcal{L}_0 + \mathcal{R} + \mathcal{E}.
\]

The elements of \( \mathcal{L}_0 \) depend on the Hamiltonian \( \mathcal{H}_0 \), which contains the Zeeman terms and the indirect coupling terms. The term \( \mathcal{R} \) is Redfield’s relaxation operator (4) and \( \mathcal{E} \) the exchange operator which accounts for the explicit time dependence of \( \rho \),

\[
\frac{\partial \rho^{\text{col}}}{\partial t} = \mathcal{E} \rho^{\text{col}}
\]

[11]
or

\[ \frac{\partial \rho^{\text{col}}}{\partial t} = \mathcal{X} \rho^{\text{col}}. \]  

The lineshape equation is then given by

\[ Y(\omega) \sim \text{Re}(P^\text{row} M_0^{-1} I^{-\text{col}}). \]

By simple matrix calculation one can easily show that

\[ Y(\omega) \sim \text{Re}(P^\text{row} M_0^{-1} I^{-\text{col}}), \]

where

\[ M_{0mn} = \frac{N_x}{M_{0n_xn_yz_z}} = \frac{N_x}{M_{0n_xn_yz_z}} = \frac{N_x}{M_{0mn}}. \]

Since

\[ M_{0n_rn_z} = \mathcal{X}_{n_xn_y} \]

for \( r \neq x \),

one obtains for the elements of \( \mathcal{X} \)

\[ \mathcal{X}_{n_xn_y} = \frac{N_x}{M_{0n_xn_yz_z}}. \]

Consider now the general exchange reaction

\[ AB + CD \Leftrightarrow AC + BD. \]

As usual, the spin functions \( \mu_t \) of spin system \( t \) are replaced by the products \( \mu \mu_t \) of the group spin functions, \( \mu \) and \( \mu_t \). The explicit time dependence of \( \rho \) in the presence of reaction [1] has been given by Kaplan and Fraenkel (5)

\[ \frac{\partial \rho^{\prime}_{n_xn_y}}{\partial t} = k_{\text{rx}} \left[ \sum_{n_y} \delta_{n_y} \frac{1}{n_{\mu y}} \rho^{\prime}_{n_xn_y} + \sum_{n_x} \delta_{n_x} \frac{1}{n_{\mu x}} \rho^{\prime}_{n_xn_y} - \rho^{\prime}_{n_xn_y} \right]. \]

Since

\[ \frac{\partial \rho^{\prime}_{n_xn_y}}{\partial t} = 0 \quad \text{for} \quad \mu \neq \nu, \quad \text{and} \quad \mu_t \neq \nu, \]

we write

\[ \frac{\partial \rho^{\prime}_{n_xn_y}}{\partial t} = k_{\text{rx}} \left[ \sum_{n_y} \delta_{n_y} \frac{1}{n_{\mu y}} \rho^{\prime}_{n_xn_y} + \sum_{n_x} \delta_{n_x} \frac{1}{n_{\mu x}} \rho^{\prime}_{n_xn_y} \right. \]

\[ + \left. \sum_{n_x} \delta_{n_x} \frac{1}{n_{\mu x}} \rho^{\prime}_{n_xn_y} - (\delta_{n_x} + \delta_{n_y}) \rho^{\prime}_{n_xn_y} \right]. \]
LINESHAPE FOR SPIN EXCHANGE REACTIONS

For the case $A = D$, i.e., $y = r$ and $x = s$,

$$AB + A^*C \xrightleftharpoons{r \; \chi \; s} A^*B + AC,$$

which was the objective of Alexander (3) and Binsch (4), Eq. [17] reduces to

$$\frac{d\rho_{\mu',\nu',\mu,\nu}}{dt} = k_{rx} \left[ \sum_{\mu} \delta_{\mu',\mu} \frac{1}{m} \rho_{\mu',\mu,\nu,\nu} \right.$$

$$+ \sum_{u_x} \delta_{u_x} \rho_{u_x,\mu,\nu,\nu} - (\delta_{\mu',\mu} + \delta_{\mu,\nu}) \rho'_{\mu',\nu,\nu,\mu} \left. \right].$$

where

$$m = n_{\mu} = n_{\mu_x} = \frac{N_r}{n_{u_x}}, \quad n_{u_x} = \frac{N_x}{n_{u_x}}.$$  \hspace{1cm} [19]

By combining Eqs. [11], [12], [18], and [19] one obtains

$$\frac{d\rho_{\mu',\nu',\mu,\nu}}{dt} = k_{rx} \left[ \sum_{\mu} \delta_{\mu',\mu} \frac{1}{m} \rho_{\mu',\mu,\nu,\nu} \right.$$

$$+ \sum_{u_x} \delta_{u_x} \rho_{u_x,\mu,\nu,\nu} - (\delta_{\mu',\mu} + \delta_{\mu,\nu}) \rho'_{\mu',\nu,\nu,\mu} \left. \right].$$

which is, in principle, Alexander's Eq. [20a] in Ref. (3). In connection with Eq. [10] the Alexander-Binsch formulation of the lineshape equation of reaction [3], therefore, does not contradict the formalism of Kaplan and Fraenkel.

As Binsch (8) has proposed an elegant way of solving equations of the type of Eqs. [13] and [14] we deal here with the evaluation of the explicit time dependence of $\varrho$ in the case of superimposed intermolecular spin exchange reactions.

Consider, for example, the superposition of the reactions

$$AB + CD \xrightleftharpoons{r \; s \; y} AC + BD,$$

$$AB + A^*C \xrightleftharpoons{r \; s} A^*B + AC,$$

$$AB + BD \xrightleftharpoons{r \; y} AB^* + BD,$$

$$AB + AB \xrightleftharpoons{r} A^*B + AB^*$$

The explicit time dependence of $\rho' = \rho_{AB}$ is given by the sum of four terms which can
be evaluated from Eqs. [17] and [18]. One obtains
\[
\frac{\partial \rho'_{\mu,\nu,v,v}}{\partial t} = (k_{rxy} + k_{ry}) \delta_{\mu,\nu} \left[ \frac{1}{n_{\mu}} \sum_{\nu'} \rho^x_{\mu,\nu,v,v} - \rho^r_{\mu,\nu,v,v} \right] \\
+ (k_{rr} + k_{rx}) \delta_{\mu,\nu} \left[ \frac{1}{n_{\mu}} \sum_{\nu'} \rho^x_{\mu,\nu,v,v} - \rho^r_{\mu,\nu,v,v} \right] \\
+ (k_{rxy} + k_{rx}) \delta_{\mu,\nu} \left[ \frac{1}{n_{\mu}} \sum_{\nu'} \rho^x_{\mu,\nu,v,v} - \rho^r_{\mu,\nu,v,v} \right] \\
+ (k_{rr} + k_{ry}) \delta_{\mu,\nu} \left[ \frac{1}{n_{\mu}} \sum_{\nu'} \rho^x_{\mu,\nu,v,v} - \rho^r_{\mu,\nu,v,v} \right]. \tag{21}
\]

The sums of rate constants within parentheses in Eq. [21] can be interpreted in the following way. For example,
\[
k_{ry}(B) = k_{rxy} + k_{ry} = \frac{p_s}{p_r} k_{yr}(B)
\]
may be called the pseudo-first-order rate constant of the exchange of group B between environments AB and BD, and
\[
k_{rr}(B) = k_{rr} + k_{rx}
\]
is the corresponding rate constant of the exchange of group B between different molecules of AB. By defining \(k_{i}(i)\) as the rate constant of the exchange of group \(i\) between \(r\) and \(t\) one obtains
\[
\frac{\partial \rho'_{\mu,\nu,v,v}}{\partial t} = \delta_{\mu,\nu} \sum_i k_{i}^{(2)} \left[ \frac{1}{n_{\mu}} \sum_{\nu'} g_{\mu} \rho^i_{\mu,\nu,v,v} - \rho^r_{\mu,\nu,v,v} \right] \\
+ \delta_{\mu,\nu} \sum_s k_{i}^{(1)} \left[ \frac{1}{n_{\mu}} \sum_{\nu'} g_{\mu} \rho^s_{\mu,\nu,v,v} - \rho^r_{\mu,\nu,v,v} \right], \quad t = r, y, \ldots, s = r, x, \ldots \tag{22}
\]
The quantities \(g_{\mu}\) and \(g_{\nu}\) are statistical weights which allow one to restrict the sums over nondegenerate spin functions if the spin systems contain symmetry. Although Eq. [22] was derived for a special reaction set, one can easily show that the inclusion of other reactions only increases the number of summands within parentheses in Eq. [21] but does not change the expressions within brackets. Therefore, Eq. [15] is valid for all sorts of superimposed reactions, including group transfer
\[
A + CD \rightleftharpoons AC + D
\]
or dissociation recombination
\[
AB \rightleftharpoons A + B,
\]
since an environment A which consists only of one group may formally be treated as AB, where B does not contain any nuclei. According to Eq. [9], the number of spin
states of B is then \( 2^o = 1 \). In order to evaluate the kinetic information from the experimental data one need consider only those environments which produce measurable NMR signals. One is as justified in doing this as in neglecting the intermediates in which the permutation of spins takes place. The type of reaction set present in the sample may then be obtained from special relations between the \( k_{rs}(i) \).

The exchange operator, \( \mathcal{H} \), is easily constructed from Eqs. [11] and [22],

\[
\mathcal{H}_{\mu_1 \nu_1 \mu_2 \nu_2} = k_{rs}(i) \frac{1}{n_{r\mu}} \delta_{u_{r\mu} \delta_{u_{s\mu}}} \delta_{v_{r\mu} \delta_{v_{s\mu}}} - \delta_{u_{r\mu} \delta_{u_{s\mu}}} \delta_{v_{r\mu} \delta_{v_{s\mu}}} \sum_t k_{rt}(i) \\
+ k_{rs}(2) \frac{1}{n_{\mu r}} \delta_{u_{r\mu} \delta_{u_{s\mu}}} \delta_{v_{r\mu} \delta_{v_{s\mu}}} \\
- \delta_{u_{r\mu} \delta_{u_{s\mu}}} \delta_{v_{r\mu} \delta_{v_{s\mu}}} \sum_t k_{rt}(2), \quad r = r, s, \ldots, \tag{23}
\]

where

\[
k_{rs}(i) = \frac{p_r}{p_s} k_{rs}(i). \tag{24}
\]

The elements of \( \mathcal{H}^r \) are obtained from Eq. [24] by replacing the \( n_{r\mu} \) and the \( n_{\mu r} \) by \( n_{u\mu} \) and \( n_{\mu u} \), which is easily verified by combining Eqs. [12], [19], and [23].

EXAMPLE

As an experimental example of superimposed intermolecular spin exchange we take the problem of slow proton exchange in the system methanol/acetic acid/tetrahydrofuran-\( d_3 \).

As reported earlier (7), in this system the rate of proton exchange between acetic acid and methanol becomes so slow at low temperatures that separate signals for the COOH proton of acetic acid and the OH signal of methanol are observed (Fig. 1). The OH signal and the CH\(_3\) signal of methanol even show a spin–spin splitting, indicating an AB\(_3\) spin system. As the temperature increases the fine structure disappears. The coalescence point of the OH signal and the COOH signal is reached only at room temperature using high concentrations.

We must consider two environments here: (1) \( AB = \text{HOCH}_3 \), and (2) \( A = \text{CH}_2\text{COOH} \), where \( B = \text{CH}_3\text{O} \) and \( A = \text{H} \). The NMR lineshape is then a function of the group exchange constants, \( k_{11}(A) \), \( k_{12}(A) = k_{21}(A)p_2/p_1 \), and \( k_{11}(B) \). In a first-order approximation, \( k_{11}(A) \) and \( k_{11}(B) \) are responsible for the collapse of the multiplet structure of the OH and of the CH\(_3\) signal. The coalescence of the lines of the OH signal with the COOH signal arises from \( k_{12}(A) \) and \( k_{21}(A) \).

A computer program was written in order to calculate the NMR shapes. In the first stage, the matrix \( \mathcal{M}_0 \) is constructed from the static and the kinetic parameters. In the second stage, the lineshape is calculated according to the procedure of Binsch (8) via the diagonalization of the frequency-independent part of \( \mathcal{M}_0 \). The subroutines ALLMAT, NVRT, and CONVEC of the intramolecular exchange program of
FIG. 1. Temperature- and concentration-dependent $^1$H 100-MHz NMR spectra of the system acetic acid/methanol/tetrahydrofuran-$d_8$. Upper curve: $C_{\text{CH}_3\text{OH}} = 1.16$ moles/liter, $C_{\text{CH}_3\text{COOH}} = 1.13$ moles/liter, 25°C. Lower curve: $C_{\text{CH}_3\text{OH}} = 0.23$ mole/liter, $C_{\text{CH}_3\text{COOH}} = 0.09$ mole/liter, −78°C.

Binsch and Kleier (9) were used. The magnetic equivalence in the AB$_3$ spin system was treated according to the procedure of Binsch and Kleier (10) by using the appropriate quartet and doublet spin functions which are given in Table 1 using the nomenclature of Emsley et al. (11). The AB$_3$ spin system contains six A, eight B, and two combination transitions, the A system only one transition. Therefore, the dimension of $\mathcal{M}_0$ is 17. The number of spin states of the exchanging group A is two, the corresponding number of the group B is eight. The elements of the imaginary part of $\mathcal{M}_0$ are given in Table 2, which also contains the elements of vector $I^-$. The elements of the exchange operator, $\mathcal{X}$, are listed in Table 3. $\mathcal{M}_0$ contains the Kubo–Sack matrix, $\mathcal{A}$, of Johnson et al. (12) describing the self-exchange reaction Eq. [5] of an AX$_3$ spin system as a limiting case. This is easily shown by taking $k_{12}(A) = k_{21}(A) = 0$, $k_{11}(A) = k_{11}(B) = k$, neglecting the off-diagonal elements in the imaginary part of $\mathcal{M}_0$, and contracting the step matrices by properly adjusting the statistical weights.

### TABLE 1

<table>
<thead>
<tr>
<th>Spin Functions $\mu$ AND $u$</th>
<th>AND Statistical Weights $g_{\mu}$ AND $g_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$</td>
<td>$g_{\mu}$</td>
</tr>
<tr>
<td>AB$_3$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>8</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>
The experimental $^1$H NMR spectra were measured with a Varian HA-100 spectrometer. The rate constants were obtained by fitting the calculated spectra to the experimental spectra which were digitized previously. The samples were prepared in vacuo by condensing known volumes of the dry solvents into the NMR tube which was attached to a vacuum line and sealed off after filling. Figures 2 and 3 show the superimposed calculated and experimental NMR spectra of two samples. Sample 1 (Fig. 2) was prepared very carefully, whereas a trace of sulfuric acid was added to sample 2 (Fig. 3). Because of association shifts arising from hydrogen bonding the positions of the COOH signal and the OH signal depend on the temperature and the concentration. The AB$_3$ character of the methanol spin system is very pronounced in sample 1 (Fig. 2). In Table 4 the kinetic data are listed. For sample 1 the following relations between the group exchange constants hold (A = H, B = CH$_3$O):

$$k_{12}(A) = k_{21}(A)p_2/p_1,$$

$$k_{12}(A) = k_{11}(B),$$

$$k_{11}(A) = 0.$$  

Equation [25] proves that every time a proton is transferred from the methanol site to the acetic acid site a second proton is transferred in the reverse direction, from acetic acid to methanol. Equations [26] and [27] prove that proton transfer from one methanol molecule to another molecule does not take place without passing through
TABLE 3

<table>
<thead>
<tr>
<th>$\xi_{mn}$</th>
<th>$\xi_{mn}$</th>
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<tr>
<td>1</td>
<td>$-7k_{11}(A)/8 - k_{12}(A)$</td>
</tr>
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<td>6</td>
<td>$-7k_{11}(A)/8 - k_{12}(A)$</td>
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<tr>
<td>7</td>
<td>$-7k_{11}(A)/8 - k_{12}(A)$</td>
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</tr>
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<td>$-3k_{11}(A)/4 - k_{12}(A)$</td>
</tr>
<tr>
<td>16</td>
<td>$-3k_{11}(A)/4 - k_{12}(A)$</td>
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<tr>
<td>2</td>
<td>$-k_{11}(B)$</td>
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</tr>
<tr>
<td>17</td>
<td>$k_{21}(A)/4$</td>
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the acetic acid site. A priori, the proton exchange

$$\text{CH}_3\text{COOH} + \text{CH}_3\text{OH}^* \rightleftharpoons \text{CH}_3\text{COOH}^* + \text{CH}_3\text{OH}$$  \[28\]

can take place via an ionic reaction mechanism,

$$\text{CH}_3\text{COOH} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{CH}_3\text{OH}_2^+.$$  \[29\]

with free solvated ion pairs, or via a cyclic mechanism in which the two protons are
FIG. 2. Experimental and calculated $^1$H 100-MHz NMR spectra of sample 1. The broad peak at 367 Hz arises from solvent protons.

FIG. 3. Experimental and calculated $^1$H 100-MHz NMR spectra of sample 2.
TABLE 4
INTERMOLECULAR PROTON GROUP EXCHANGE RATE CONSTANTS, 
\( k_{12}(A) \), \( k_{21}(A) \), \( k_{11}(A) \), \( k_{11}(B) \) in the System 
METHANOL/ACETIC ACID/TETRAHYDROFURAN-d8

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( k_{12}(A) ) ( \text{sec}^{-1} )</th>
<th>( k_{21}(A) ) ( \text{sec}^{-1} )</th>
<th>( k_{11}(A) ) ( \text{sec}^{-1} )</th>
<th>( k_{11}(B) ) ( \text{sec}^{-1} )</th>
<th>( k ) ( \text{sec}^{-1} \text{ m}^{-1} \text{ liter} )</th>
</tr>
</thead>
<tbody>
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\( a \) See text.

\( b \) Sample 1: \( C_{\text{CH}_3\text{COOH}} = 0.045 \text{ mole/liter}, \ C_{\text{CH}_3\text{OH}} = 0.069 \text{ mole/liter}; \) sample 2: \( C_{\text{CH}_3\text{COOH}} = 0.09 \text{ mole/liter}, \ C_{\text{CH}_3\text{OH}} = 0.17 \text{ mole/liter}, \) with a trace of \( \text{H}_2\text{SO}_4. \) \( k \) is the bimolecular exchange rate constant defined by \( k = k_{12}(A)/C_{\text{CH}_3\text{COOH}} = k_{21}(A)/C_{\text{CH}_3\text{OH}}. \)

transferred during one encounter of the reactants:

\[
\text{CH}_3\text{COOH} + \text{CH}_3\text{OH}^* \rightleftharpoons \text{CH}_3\text{COOH}, \text{CH}_3\text{OH}^* \rightleftharpoons \text{CH}_3\text{COOH}^*, \text{CH}_3\text{OH}
\]

\[
\rightleftharpoons \text{CH}_3\text{COOH}^* + \text{CH}_3\text{OH}.
\] [30]

Equations \([29]\) and \([30]\) are special cases of Eqs. \([2]\) and \([1]\). Because of their low concentrations the dissociation products or the intermediates do not appear as a site in the lineshape equation. Therefore, Eq. \([28]\) formally applies both for the ionic and for the cyclic exchange mechanism. Nevertheless, the ionic mechanism of Eq. \([29]\) can be excluded here because the presence of the ionic species is linked with an ionic mechanism of methanol self-exchange,

\[
\text{CH}_3\text{OH}^+ + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OH} + \text{CH}_3\text{OH}^+.
\] [31]

and also with an ionic mechanism of exchange between methanol and acetic acid,

\[
\text{CH}_3\text{OH}^+ + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{OH} + \text{CH}_3\text{C(OH)}_2^+.
\] [32]

Additional side reactions involving the \( \text{CH}_3\text{COO}^- \) anion should also be present. The fact that no methanol self-exchange is found in sample 1 is, therefore, a proof for the cyclic mechanism according to Eq. \([20]\). Such a mechanism is—according to Grunwald et al. \((13)\)—a side reaction of ionic proton exchange in buffered mixtures of alcohols and carboxylic acids.
The situation is different in sample 2, which contained a trace of sulfuric acid. In this sample methanol self-exchange takes place because

\[ k_{12}(A) = \frac{k_{21}(A)p_2}{p_1}, \]
\[ k_{11}(B) = k_{11}(A) + k_{12}(A). \]

This self-exchange arises from the catalyst \(H_2SO_4\), which probably forms \(CH_3OH_2^+\) ions with methanol, and which induces, therefore, proton transfer according to Eq. [31].

Because of the great theoretical (14) and experimental (6, 15) interest in the mechanism of cyclic proton exchange in hydrogen-bonded systems we are carrying out further experiments in this field.

CONCLUSIONS

The example of proton exchange in the system acetic acid/methanol/tetrahydrofuran-\(d_4\) clearly shows the advantage of calculating the NMR lineshape as a function of group exchange rate constants instead of reaction rate constants. No reaction mechanism is excluded a priori, and the discussion of these does not affect the process of the extraction of kinetic data from experimental NMR spectra which are broadened by intermolecular spin exchange processes.

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