A Unified Theory of Exchange Effects on Nuclear Magnetic Resonance Line Shapes

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Abstract: A general theory of line shapes in high-resolution nuclear magnetic resonance spectra of liquids is developed in the framework of the Liouville representation of quantum mechanics. It is shown that both short-memory as well as strong-correlation effects can simultaneously be accounted for in a compact and transparent manner if the full-state vector is projected into a composite Liouville subspace. The equation of motion is governed by a complex non-Hermitian operator that may be broken up into an ordinary Hermitian Liouville operator, a relaxation operator, and an exchange operator. It is demonstrated that the total information content of an unsaturated steady-state nmr spectrum can be contracted into two complex vectors, a radiofrequency-independent "shape vector" and a "spectral vector" which is a trivially simple function of the radiofrequency. A sample calculation for an exchanging three-spin system serves as an illustration of the usefulness of the theory for accurate determinations of rate constants and activation parameters in systems of chemical interest.

The study of dynamic phenomena in chemistry by nuclear magnetic resonance spectroscopy has experienced an impetuous development in recent years. The method is applicable to rate processes with barrier heights between about 5 and 25 kcal/mole and thus conveniently bridges the gap between the realm of the microwave technique and conventional chemical rate determinations. Most applications were concerned with the internal mobility of molecules, such as hindered rotation about bonds, inversion of lone electron pairs, ring inversions, and certain reversible rearrangements.[2] Although such nmr studies have yielded a wealth of valuable qualitative information, the method has unfortunately acquired the reputation of being quantitatively unreliable. It was this latter aspect that provided the motivation for the work to be presented in this paper.

The early theories[3-5] of chemical exchange effects on nmr line shapes were based on modified Bloch[6] equations. Although originally developed for special cases, these theories can easily be generalized.[5] The equations conveniently lend themselves to computer calculations when written in matrix form.[7-10] Equivalent matrix equations have also been derived[11] from the stochastic theory of random Markovian modulations.[12] Since Bloch's phenomenological description of the nuclear magnetic resonance phenomenon presumes an ensemble of independent spins,[13] these classical line-shape theories do, however, not apply to coupled spin systems. A quantum-mechanical treatment, based on the density matrix formalism, was first presented by Kaplan[14] and further developed by Alexander.[15] This theory is limited to cases involving mutual exchanges of nuclear spins. Johnson[16] has recently suggested an elegant modification of the density matrix approach which makes it applicable also to intramolecular processes in which the nuclei move about but do not actually exchange positions with other nuclei. In the present paper we shall show that all previous treatments can be united and formulated in a compact and simple manner if the theory is developed in the Liouville representation[17] of quantum mechanics rather than in the Hilbert space representation.

General Theory

In density matrix theory the equation of motion reads

$$d\rho/dt = -2\pi i[\mathscr{H}, \rho] \tag{1}$$

where $\mathscr{H}$ is the standard high-resolution spin Hamiltonian[15] expressed in frequency units (that is, we set $h = 1$). Instead of arranging the elements of ρ in a square matrix, we may interpret them as components of a state vector $\boldsymbol{\rho}$ in a suitably defined vector space. This vector space has become known as Liouville space.[17] Equation 1 can then be reformulated as

$$d\boldsymbol{\rho}/dt = -i\mathscr{L}\boldsymbol{\rho} \tag{2}$$

where the Liouville operator $\mathscr{L}$ is defined by the elements

$$L_{\mu\nu,\kappa\lambda} = 2\pi[H_{\mu\kappa}\delta_{\nu\lambda} - H_{\lambda\nu}\delta_{\kappa\mu}] \tag{3}$$

We shall assume for the moment that the total system

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[1] The Radiation Laboratory is operated by the University of Notre Dame under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-605.

[2] For a recent review see G. Binsch in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1968, p 97.

[3] H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, 21, 279 (1953); H. S. Gutowsky and A. Saika, *ibid.*, 21, 1688 (1953); H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

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[9] A. Allerhand and E. Thiele, *ibid.*, **45**, 902 (1966).

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[11] R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

[12] (a) P. W. Anderson, *J. Phys. Soc. Japan*, **9**, 316 (1954); (b) R. Kubo and K. Tomita, *ibid.*, **9**, 888 (1954); R. Kubo, *ibid.*, **9**, 935 (1954); *Nuovo Cimento, Suppl.*, **6**, 1063 (1957).

[13] R. K. Wangsness and F. Bloch, *Phys. Rev.*, **89**, 728 (1956); F. Bloch, *ibid.*, **102**, 104 (1956); **105**, 1206 (1957).

[14] J. I. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958); **29**, 462 (1958).

[15] S. Alexander, *ibid.*, **37**, 967, 974 (1962); **38**, 1787 (1963); 40, 2741 (1964).

[16] C. S. Johnson, *ibid.*, **41**, 3277 (1964).

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consists of a large number of noninteracting and uncorrelated subsystems, each subsystem k (molecule) containing n_k identical nuclei with spins 1/2. If all the subsystems k have identical Hamiltonians, the state vector may be represented by the ensemble-averaged density components of a single subsystem. We shall call such a state vector a *primitive-state vector* and the corresponding vector space of dimension 2^{2n_k} a *primitive Liouville space.* If the idealized ensemble contains m different types of subsystems k, it may be represented by a *composite-state vector* in a *composite Liouville space* of dimension $\Sigma_{k=1}^{m}(2^{2n_k})$. The elements of this composite-state vector are defined as the renormalized elements of the constituent primitive-state vectors, the renormalization factors f_k being

$$f_k = mn_k\lambda_k\left(\sum_{k=1}^{m} n_k\right)^{-1} \tag{4}$$

where λ_k represents the relative abundances of the m different types of subsystems k. If all subsystems contain the same number of nuclei, the renormalization factors are simply equal to the fractional populations p_k. The Hamiltonian for the composite system becomes

$$\mathscr{H}^c = \sum_k \mathscr{H}^k \tag{5}$$

where each $\mathscr{H}^k$ acts only on one type of subsystem k; the representation of the Liouville operator

$$\mathscr{L}^c = \sum_k \mathscr{L}^k \tag{6}$$

will therefore appear in block-diagonal form.

In an actual physical system there will of course be interactions between the subsystems. The full density vector would therefore have to be specified in the *interaction Liouville space* of dimension $\Pi_k 2^{2n_k}$.[18] We assume that this vector $\boldsymbol{\rho}$ may be constructed from the components of a vector $\boldsymbol{\rho}^c$ in composite Liouville space ("system of interest") and of a vector $\boldsymbol{\rho}^b$ depending on all the remaining variables of the complete system ("bath"). Under conditions of "short memory," which imply that one particular subsystem remains correlated in time with neighboring subsystems only for short periods, it has in principle already been shown[13,19,20] that the interaction of the system of interest with the bath can be accounted for by including a dissipative term in the equation of motion

$$\mathrm{d}\boldsymbol{\rho}^c/\mathrm{d}t = (-i\mathscr{L}^c + \mathscr{R}^c)\boldsymbol{\rho}^c \tag{7}$$

The representation of the relaxation operator $\mathscr{R}^c$ differs from Redfield's[19] relaxation matrix only in that it is here defined in composite Liouville space. It is now a simple matter to generalize eq 7 to apply also to those cases where strong correlation effects due to slow exchange processes play a dominant role, by writing

$$\mathrm{d}\boldsymbol{\rho}^c/\mathrm{d}t = \mathscr{M}\boldsymbol{\rho}^c = (-i\mathscr{L}^c + \mathscr{R}^c + \mathscr{X}^c)\boldsymbol{\rho}^c \tag{8}$$

The representation of the exchange operator $\mathscr{X}^c$ in the composite Liouville representation can be written down essentially by inspection. Making use of equations derived by Alexander,[15] one obtains for the intramolecular exchange between the magnetic environments r and s

$$X_{\mu_r\nu_r,\kappa_s\lambda_s} = \delta_{\mu\kappa}\delta_{\nu\lambda}[-\delta_{rs}\sum_{t(\neq r)} K_{rt} + (1 - \delta_{rs})K_{sr}] \tag{9}$$

and for the intermolecular exchange

$$X_{\mu_r u_r,\nu_r v_r;\kappa_s x_s,\lambda_s y_s} = \\ [d^{-1}\delta_{\mu\nu}\delta_{\kappa\lambda} - \delta_{\mu\kappa}\delta_{ux}\delta_{\nu\lambda}\delta_{vy}]\delta_{rs}\sum_{t(\neq r)} K_{rt} + \\ n_s^{-1}\delta_{uv}\delta_{xy}(1 - \delta_{rs})K_{rs} \tag{10}$$

where the K_{rs}'s are the first-order or pseudo-first-order rate constants (in sec^{-1}) for transfers from r to s. In eq 10 the Greek indices $\mu\nu(\kappa\lambda)$ refer to the functions of the exchanging group of nuclei in molecule r (s) and the Latin indices uv (xy) to the nonexchanging group in molecule r (s), d denotes the dimension of the Hilbert sub-subspace of the exchanging group, and n_t is the dimension of the Hilbert sub-subspaces of the nonexchanging group of nuclei in molecule t.

Under unsaturated steady-state conditions, eq 8 simplifies to

$$\mathscr{M}\boldsymbol{\rho}^c = 0 \tag{11}$$

which can be written in the more convenient form

$$\mathscr{M}_0\boldsymbol{\rho}^c = -i\boldsymbol{\sigma} \tag{12}$$

where

$$\mathscr{M}_0 = -i\mathscr{L}_0{}^c + \mathscr{R}^c + \mathscr{X}^c \tag{13}$$

$\mathscr{L}_0{}^c$ is the Liouville operator arising from the nuclear Zeeman and spin-coupling Hamiltonians. For intramolecular exchange the vector $\boldsymbol{\sigma}$ has elements

$$\sigma^k{}_{\mu\nu} = Cp_k V_{\mu\nu} \tag{14}$$

where $V_{\mu\nu}$ is equal to 1 if μ and ν refer to spin basis functions that differ by precisely *one* individual spin z component I_z, and zero otherwise; C may be taken as an adjustable scaling factor. The complex magnetization G in the xy plane is obtained from

$$G = \mathbf{I}^- \cdot \boldsymbol{\rho}^c = -i\mathbf{I}^-\mathscr{M}_0{}^{-1}\boldsymbol{\sigma} \tag{15}$$

where $\mathbf{I}^-$ is the row vector constructed from the elements of the lowering operator $\mathbf{I}^- = \Sigma_i I_i{}^-$. The absorption line-shape function Y is extracted from eq 15 as the imaginary part of G

$$Y = \mathrm{Im}(G) = \mathrm{Im}(-i\mathbf{I}^-\mathscr{M}_0{}^{-1}\boldsymbol{\sigma}) \tag{16}$$

or, multiplying eq 15 for convenience by i, as the negative real part of $G' = iG$

$$Y = -\mathrm{Re}(G') = -\mathrm{Re}(\mathbf{I}^-\mathscr{M}_0{}^{-1}\boldsymbol{\sigma}) \tag{17}$$

Many of the elements of the vectors $\mathbf{I}^-$ and $\boldsymbol{\sigma}$ are zero. Both vectors therefore represent projections of the composite Liouville space into smaller subspaces. Inspection of the block-diagonal representations of the Hamiltonians and the Liouville operator reveals that the dimensionality of eq 15 can be reduced to $\Sigma_k w_k$, where w_k is the maximum number of possible transitions for a particular spin system in the magnetic environment (or molecule) k. For diagonal relaxation matrices and in the presence of

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(18) To obtain a physically meaningful description it may be necessary to include other than just the spin variables in this interaction representation.

(19) A. G. Redfield, *IBM J. Res. Develop.*, **1**, 19 (1957); *Advan. Magnetic Resonance*, **1**, 1 (1965).

(20) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

Matrix I

$$
\begin{array}{c|cccccc}
 & \begin{matrix}[12]^1\\([24]^1)\end{matrix} & \begin{matrix}[13]^1\\([34]^1)\end{matrix} & \begin{matrix}[12]^2\\([24]^2)\end{matrix} & \begin{matrix}[13]^2\\([34]^2)\end{matrix} & \begin{matrix}[12]^3\\([24]^3)\end{matrix} & \begin{matrix}[13]^3\\([34]^3)\end{matrix} \\
\hline
\begin{matrix}[12]^1\\([24]^1)\end{matrix} & \begin{matrix}2\pi i[\nu_2^1 \underset{(+)}{-} (J_1/2) - \nu]\\ - (1/T_2) - K_{12} - K_{13}\end{matrix} & \underset{(-)}{+} i\pi J_1 & K_{21} & 0 & K_{31} & 0 \\
\begin{matrix}[13]^1\\([34]^1)\end{matrix} & \underset{(-)}{+} i\pi J_1 & \begin{matrix}2\pi i[\nu_1^1 \underset{(+)}{-} (J_1/2) - \nu]\\ - (1/T_2) - K_{12} - K_{13}\end{matrix} & 0 & K_{21} & 0 & K_{31} \\
\begin{matrix}[12]^2\\([24]^2)\end{matrix} & K_{12} & 0 & \begin{matrix}2\pi i[\nu_2^2 \underset{(+)}{-} (J_2/2) - \nu]\\ - (1/T_2) - K_{21} - K_{23}\end{matrix} & \underset{(-)}{+} i\pi J_2 & K_{32} & 0 \\
\begin{matrix}[13]^2\\([34]^2)\end{matrix} & 0 & K_{12} & \underset{(-)}{+} i\pi J_2 & \begin{matrix}2\pi i[\nu_1^2 \underset{(+)}{-} (J_2/2) - \nu]\\ - (1/T_2) - K_{21} - K_{23}\end{matrix} & 0 & K_{32} \\
\begin{matrix}[12]^3\\([24]^3)\end{matrix} & K_{13} & 0 & K_{23} & 0 & \begin{matrix}2\pi i[\nu_2^3 \underset{(+)}{-} (J_3/2) - \nu]\\ - (1/T_2) - K_{31} - K_{32}\end{matrix} & \underset{(-)}{+} i\pi J_3 \\
\begin{matrix}[13]^3\\([34]^3)\end{matrix} & 0 & K_{13} & 0 & K_{23} & \underset{(-)}{+} i\pi J_3 & \begin{matrix}2\pi i[\nu_1^3 \underset{(+)}{-} (J_3/2) - \nu]\\ - (1/T_2) - K_{31} - K_{32}\end{matrix}
\end{array}
$$

equivalence and symmetry, an additional factoring ensues. It is important to note, however, that these projections do not eliminate all zeros in $\mathbf{I}^-$ and $\boldsymbol{\sigma}$; they still contain vanishing elements corresponding to the well-known "combination transitions."

Matrix Formalism

In matrix notation the line-shape equation reads

$$G' = \mathbf{I}^-\mathbf{M}_0{}^{-1}\boldsymbol{\sigma} \qquad (18)$$

Apart from the multiplications of the arrays on the right-hand side of eq 18, the only problem faced in practical applications of the theory is the inversion of the complex non-Hermitian matrix $\mathbf{M}_0$, and to this end it suffices to invert the subblocks of $\mathbf{M}_0$ separately. To be specific, we shall treat as an example a two-proton system exchanging between three different chemical environments, characterized by chemical shifts $\nu_1{}^k$ and $\nu_2{}^k$, coupling constants J_k, and populations p_k. Such a situation would for instance be realized in the internal rotation of an asymmetric tetrasubstituted ethane. We shall for simplicity assume that the relaxation operator $\mathcal{R}$ is diagonal in the representation of the spin product basis functions and that all its elements are identical. Such a simplification would apply to cases for which the relaxation behavior of the system may approximately be described by a single transverse relaxation time T_2 as assumed in Bloch's[6] phenomenological equations. In practice one would include a term T_2' to account for field-inhomogeneity broadening and consider $T_2{}^{\text{eff}} = T_2T_2'/(T_2 + T_2')$ as an effective transverse relaxation time. It is clear that such a simple treatment must for instance break down in the presence of specific intramolecular dipole–dipole relaxation mechanism, especially if such mechanisms cause line broadening comparable to or in excess of field-inhomogeneity effects. The two subblocks of the contracted $\mathbf{M}_0$ matrix $[\mathbf{M}_0 = \text{diag}(\mathbf{M}_0{}^-,\mathbf{M}_0{}^+)]$ become that shown as Matrix I. Since there are no combination lines for a two-proton system, all elements of the $\mathbf{I}^-$ row vector are equal to 1 and the $\boldsymbol{\sigma}$ column vector is represented by

$$\begin{aligned}\boldsymbol{\sigma} &= C\{p_1,p_1,p_2,p_2,p_3,p_3,p_1,p_1,p_2,p_2,p_3,p_3\} \qquad (19)\\ &= C\mathbf{P}\end{aligned}$$

Although eq 18 could be used directly for practical line-shape calculations, the inversion of a complex non-Hermitian matrix for each point of the spectrum would be very time consuming. A more efficient computational procedure is obtained as follows.

The complex non-Hermitian and in general nonsymmetrical matrix $\mathbf{M}_0$ can always be reduced to (upper or lower) Jordan canonical form[21] by a similarity transformation

$$\mathbf{U}^{-1}\mathbf{M}_0\mathbf{U} = \mathbf{D} \qquad (20)$$

The transformed matrix $\mathbf{D}$ will be diagonal if $\mathbf{M}_0$ has no nonlinear elementary divisors.[21] The elementary divisors will automatically be linear if all eigenvalues of $\mathbf{M}_0$ are distinct. We shall henceforth assume without proof that for the practical applications with which we are concerned in this paper $\mathbf{M}_0$ can be diagonalized even if there

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(21) J. H. Wilkinson, "The Algebraic Eigenvalue Problem," Clarendon Press, Oxford, 1965.

are degeneracies. We believe this assumption to be a reasonable one on physical grounds. It is in fact borne out by experience; in a variety of numerical calculations of exchange-broadened nmr spectra we have never come across an $\mathbf{M}_0$ matrix that could not be diagonalized.[22] If we decompose $\mathbf{M}_0$ as

$$\mathbf{M}_0 = \mathbf{B} - 2\pi i\nu\mathbf{E} \qquad (21)$$

where **B** is independent of the radiofrequency and **E** is the unit matrix, we see that the same transformation matrix **U** occurring in eq 20 will also diagonalize **B**

$$\mathbf{U}^{-1}\mathbf{B}\mathbf{U} = \mathbf{\Lambda} \qquad (22)$$

since **B** and **E** commute. We therefore obtain

$$\begin{aligned}\mathbf{U}^{-1}\mathbf{M}_0\mathbf{U} &= \mathbf{U}^{-1}\mathbf{B}\mathbf{U} - 2\pi i\nu\mathbf{U}^{-1}\mathbf{E}\mathbf{U} \qquad (23)\\ &= \mathbf{\Lambda} - 2\pi i\nu\mathbf{E} = \mathbf{D}\end{aligned}$$

and

$$\mathbf{M}_0^{-1} = \mathbf{U}\mathbf{D}^{-1}\mathbf{U}^{-1} = \mathbf{U}(\mathbf{\Lambda} - 2\pi i\nu\mathbf{E})^{-1}\mathbf{U}^{-1} \qquad (24)$$

After the eigenvalues and the right and left eigenvectors of **B** have been found, the inversion of $\mathbf{M}_0$ reduces to the trivial problem of inverting the diagonal matrix $\mathbf{D} = \mathbf{\Lambda} - 2\pi i\nu\mathbf{E}$ and to a matrix multiplication. Substitution of eq 24 in eq 18 yields

$$G' = C\mathbf{I}^{-1}\mathbf{U}(\mathbf{\Lambda} - 2\pi i\nu\mathbf{E})^{-1}\mathbf{U}^{-1}\mathbf{P} \qquad (25)$$

Denoting the elements of $\mathbf{U}^{-1}$ by U' and defining a "spectral vector" **Q** by elements

$$Q_\mu = (\Lambda_\mu - 2\pi i\nu)^{-1} \qquad (26)$$

eq 25 may be written

$$G' = C\, \Sigma_\lambda\, I_\lambda^-\, \Sigma_\mu\, U_{\lambda\mu} Q_\mu\, \Sigma_\nu\, U'_{\mu\nu} P_\nu \qquad (27)$$

If we define a "shape vector" **S** by elements

$$S_\mu = \Sigma_{\lambda\nu} I^-{}_\lambda U_{\lambda\mu} U'{}_{\mu\nu} P_\nu \qquad (28)$$

eq 27 becomes

$$G' = C\, \Sigma_\mu\, Q_\mu S_\mu \qquad (29)$$

The absorption line shape is then proportional to the negative real part of the scalar product of the vectors **Q** and **S**

$$Y = -C\,\mathrm{Re}(\mathbf{Q}\cdot\mathbf{S}) \qquad (30)$$

Computer Program

The equations of the preceding section have been programmed in FORTRAN IV for a 65K UNIVAC 1107 computer equipped with a CALCOMP plotter. The input to this program (called DNMR) consists of the chemical shifts, coupling constants, populations, rate constants, the effective transverse relaxation time, and the scaling parameters for the desired plot. The program is completely general, but is limited at the present time to a maximum of 112 lines. No scratch tapes are required. A subroutine BASIS generates the spin-product basis functions for a specified number of coupled spin 1/2 nuclei, and

Table I. Nonnegligible Elements of the Shape Vector **S** and of the Radiofrequency-Independent Part of the Spectral Vector **Q** (Eigenvalues Λ_μ) for an Exchanging Three-Proton System[a]

$\mathrm{Re}(\Lambda_\mu)$	$\mathrm{Im}(\Lambda_\mu)$	$\mathrm{Re}(S_\mu)$	$\mathrm{Im}(S_\mu)$
	$K = 0\ \mathrm{sec}^{-1}$		
−1.250	31.4	0.101	0.000
−1.250	43.1	0.185	0.000
−1.250	98.9	1.104	0.000
−1.250	110.6	1.210	0.000
−1.250	120.7	1.490	0.000
−1.250	164.5	2.222	0.000
−1.250	188.2	0.915	0.000
−1.250	232.0	0.769	0.000
−1.250	245.4	1.583	0.000
−1.250	323.0	0.981	0.000
−1.250	334.7	0.429	0.000
−1.250	366.9	0.231	0.000
−1.250	378.6	0.593	0.000
−1.250	456.1	0.184	0.000
	$K = 0.1\ \mathrm{sec}^{-1}$		
−1.386	31.4	0.101	0.000
−1.415	43.1	0.184	0.001
−1.281	98.9	1.104	0.001
−1.299	110.6	1.210	0.000
−1.287	120.7	1.490	0.001
−1.277	164.5	2.222	−0.001
−1.389	188.2	0.915	−0.001
−1.396	232.0	0.769	0.006
−1.379	245.4	1.583	−0.007
−1.280	323.0	0.981	−0.001
−1.300	334.7	0.429	−0.001
−1.324	366.9	0.231	0.001
−1.258	378.6	0.593	0.000
−1.395	456.1	0.184	−0.001
	$K = 10\ \mathrm{sec}^{-1}$		
−14.919	31.6	0.088	0.050
−17.837	43.5	0.172	0.061
−4.289	99.4	1.123	0.118
−6.089	111.1	1.244	0.001
−4.846	120.3	1.476	0.129
−3.875	164.2	2.234	−0.053
−15.252	188.0	0.889	−0.056
−15.982	233.5	0.581	0.742
−14.046	244.2	1.760	−0.802
−4.209	322.7	0.988	−0.062
−6.064	335.1	0.422	−0.129
−8.741	366.2	0.249	0.064
−2.038	378.5	0.594	−0.008
−15.793	455.6	0.177	−0.055
	$K = 100\ \mathrm{sec}^{-1}$		
−13.290	111.6	1.591	0.087
−7.067	112.2	1.619	0.166
−22.401	139.5	2.344	0.927
−9.141	151.3	2.413	0.050
−154.869	241.7	0.452	−0.048
−11.912	307.3	1.324	−0.179
−8.141	337.9	0.122	−0.154
−46.010	345.4	1.578	−0.796
−6.971	374.9	0.633	−0.059
	$K = 10{,}000\ \mathrm{sec}^{-1}$		
−1.313	114.3	1.635	0.001
−1.496	117.6	1.713	0.004
−1.345	147.4	2.287	0.002
−1.477	149.4	2.364	0.008
−1.383	301.4	1.365	−0.001
−1.873	331.4	1.004	−0.059
−1.408	336.5	0.919	0.047
−1.433	366.3	0.713	−0.002

[a] With chemical shifts $\nu_1 = 19.6$ Hz, $\nu_2 = 22.9$ Hz, $\nu_3 = 52.7$ Hz, coupling constants $J_{12} = 12.3$ Hz, $J_{13} = 7.3$ Hz, $J_{23} = -17.7$ Hz, and an effective transverse relaxation time $T_2 = 0.8$ sec. Protons 1 and 2 undergo mutual exchange characterized by first-order rate constants K.

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(22) This is not to say that such cases could never occur. It is in fact not difficult to artificially construct simple cases where the procedure would lead to a nondiagonalizable matrix, and in practical computations it may happen accidentally for special parameter combinations. It is one of the features of our computer program to detect and reject such accidents. The calculation has then to be repeated with a slightly different parameter set.

HAMILT assembles the Hamiltonian submatrices. The vectors $\mathbf{I}^-$ and $\mathbf{P}$ and some auxiliary index arrays are computed in PRJECT. The submatrices of $\mathbf{B}$ are assembled in TRAMAT and diagonalized individually by a package of routines called CDIAG, COMEIG, COMAT, and NVRT. In the first three of these the eigenvalues and right eigenvectors (*i.e.*, the matrix $\mathbf{U}$) are found by an iterative inverse power deflation algorithm. NVRT inverts $\mathbf{U}$ to produce the left eigenvectors (*i.e.*, the matrix $\mathbf{U}^{-1}$).[23] The results are accumulated in the shape vector $\mathbf{S}$ and the radiofrequency-independent part of the spectral vector $\mathbf{Q}$. Finally, in subroutine SPECT, a sufficient number of points is computed by eq 30, and the coordinates are transferred to magnetic tape. This tape then serves as input device for the CALCOMP XY plotter.[24]

Due to the simplicity of eq 30, the final stage in the computation requires very little computer time. The number of points to be calculated therefore presents no economical limitation. The time-limiting factor of the program is the diagonalization of the $\mathbf{B}$ submatrices. A computation of about 3500 points for a three-spin system exchanging between two chemical environments takes about 3 min on the UNIVAC 1107. The computer time increases steeply with increasing size of the $\mathbf{B}$ submatrices.[25] It is therefore desirable to take maximum advantage of symmetry and magnetic equivalence. We plan to report on the incorporation of such features into the theory in a future publication.

Example

As an example we shall here reproduce the results for a three-proton system with chemical shifts $\nu_1 = 19.6$ Hz, $\nu_2 = 22.9$ Hz, $\nu_3 = 52.7$ Hz and coupling constants $J_{12} = 12.3$ Hz, $J_{13} = 7.3$ Hz, $J_{23} = -17.7$ Hz in which protons 1 and 2 undergo mutual exchange. The system was assumed to be characterized by a single effective transverse relaxation time of 0.8 sec. For a number of different rate constants Table I lists the elements of the shape vector and the radiofrequency-independent elements of the spectral vector (*i.e.*, the eigenvalues Λ_μ of $\mathbf{B}$) that make a nonnegligible contribution to the absorption line-shape function. It can be seen that for no exchange ($K_{12} = K_{21} = K = 0$) the imaginary elements of $\mathbf{S}$ are zero and the real elements of $\mathbf{\Lambda}$ are constant and equal to $-1/T_2$. This is a consequence of the fact that in this particular case the real and imaginary parts of $\mathbf{B}$ commute. The imaginary part of $\mathbf{\Lambda}$ contains the line positions in radians/sec and the real part of the shape vector the intensities of the corresponding absorption peaks. The absorption spectrum consists of a superposition of Lorentzian lines characterized by widths at half-height of $(\pi T_2)^{-1}$ Hz. For finite rate constants the real and

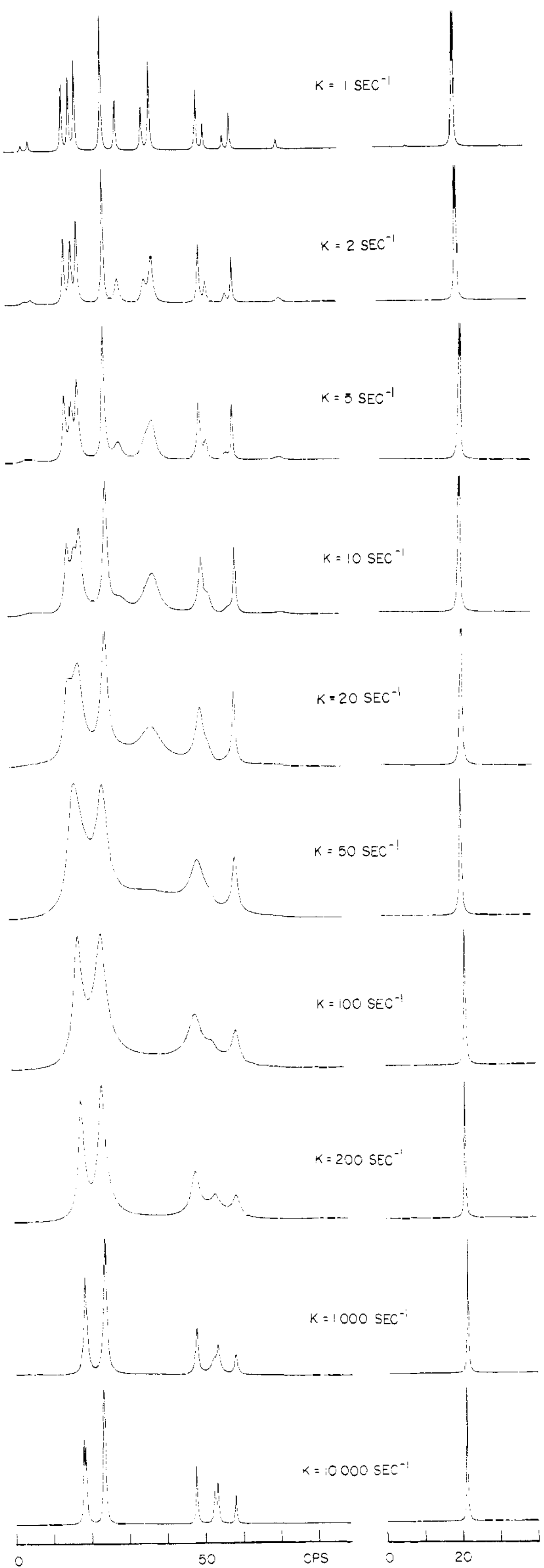

Figure 1. Right part: Nmr line shapes for an exchanging AB system with $\nu_A = 19.6$ Hz, $\nu_B = 22.9$ Hz, $J_{AB} = 12.3$ Hz, $T_2 = 0.8$ sec, and rate constants K. Left part: Nmr line shapes for an exchanging ABC system with $\nu_A = 19.6$ Hz, $\nu_B = 22.9$ Hz, $\nu_C = 52.7$ Hz, $J_{AB} = 12.3$ Hz, $J_{AC} = 7.3$ Hz, $J_{BC} = -17.7$ Hz, and $T_2 = 0.8$ sec. Nuclei A and B undergo mutual exchange characterized by rate constants K.

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(23) CDIAG, COMEIG, COMAT, and NVRT are modified versions of routines developed by the Homewood Computing Center of Johns Hopkins University. I am indebted to Professors A. Allerhand and R. L. Vold for sending me copies of these routines.

(24) Copies of the source program will become available through the Quantum Chemistry Program Exchange at Indiana University, Bloomington, Ind.

(25) When this paper was in preparation I learned that Professor R. G. Gordon (Harvard University) has independently been involved in similar studies. From what Professor Gordon tells me I conclude that his matrix diagonalization routines must be considerably more efficient than the ones I have been using so far. I wish to thank Professor Gordon for informing me about his work prior to publication; R. G. Gordon and R. P. McGinnis, *J. Chem. Phys.*, **49**, 2455 (1968).

imaginary parts of **B** do not commute and the situation therefore becomes more complicated. A simple approximate physical interpretation is, however, still possible. Roughly speaking, the imaginary part of $\mathbf{\Lambda}$ determines the positions of the lines, the real part of $\mathbf{\Lambda}$ their broadness, the real part of **S** their intensity, and the imaginary part of **S** their deviation from Lorentzian shape. Table I shows that the absolute values of the real elements of $\mathbf{\Lambda}$ and the imaginary elements of **S** go through maxima as the rate constants vary from zero to infinity, as we should expect. For infinitely fast exchange the absorption spectrum is again represented by a superposition of Lorentzian lines with widths at half-height of $(\pi T_2)^{-1}$ Hz. Some exchange-broadened absorption spectra are plotted in Figure 1. For comparison, Figure 1 also reproduces the line shapes of a two-proton system derived from the tightly coupled ABC system by omission of the nonexchanging nucleus.

Conclusion

It is instructive to compare the exchange-broadened nmr absorption line shapes of the AB system depicted in the right part of Figure 1 with the corresponding line shapes of the ABC system in which the C nucleus couples with A and B but does not by itself participate in the intramolecular exchange process. Due to the small chemical shift difference between the A and B nuclei and the comparatively large coupling constant J_{AB}, the AB spectra change very little over the whole range of rates. This is especially true when the spectrum has degenerated into a single line. Since the experimental curves are complicated by noise and depend critically on field-inhomogeneity effects, it may become exceedingly difficult to obtain reliable numbers for the rate constants by attempting to fit the computed on the measured AB line shapes. Although this situation is improved somewhat in cases where the AB shift difference is not quite as small as in our example, the spectra still collapse eventually into a single line on increase of the exchange rate. The most pronounced changes in the line shape are observed in the vicinity of the coalescence point, whereas the sensitivity by which the spectra respond to changes in the rate constants decreases rapidly toward both the slow- and fast-exchange limit. It is a well-recognized feature[26] of dynamic studies by nmr spectroscopy that whereas quite reliable rate constants may be obtained by computer-fitting calculated on experimental line shapes in the neighborhood of the coalescence point, the precision of the rate data outside this range is much lower and systematic errors are likely to make an increasingly important contribution. It is therefore not surprising that activation parameters computed from such rate measurements have in the past frequently exhibited such a wide scatter as to render many of them almost worthless for purposes of comparison. The ABC spectra reproduced in the left parts of Figure 1 contain a great deal more information than the corresponding AB line shapes. One might say that a whole series of "coalescence points" is being observed for different values of K. In complex spectra such as these the sensitivity of the nmr line-shape method is obviously more evenly distributed over the accessible range of rate constants, and it seems therefore not unreasonable to expect a higher precision and accuracy for the computed activation parameters. Because of mathematical difficulties it has so far been the general tendency of the experimentalists working in this field to pick very simple spin systems for dynamic studies or to artificially simplify more complex cases by selective deuteration or specific fluorine labeling. It can be seen that this is in fact not always desirable. Rather one should make an attempt to choose moderately complex spin systems and especially spin systems that do *not* collapse into a single resonance line in the fast-exchange limit. We are presently embarking on such studies and hope to report on results in future publications.

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[26] Reference 2 gives a general discussion of these aspects.