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NMR line shape in the regime where the chemical exchange time τ_e approaches the motional correlation time τ_c

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A theory for the nuclear-magnetic-resonance (NMR) absorption of chemically interacting species is derived which is valid when the correlation time τ_c for the molecular motion—which gives rise to NMR relaxation—is less than τ_e, the chemical exchange time. The previous theory is valid only if τ_c were much less than τ_e. This latter theory assumed that the relaxation was defined using the usual Fermi Golden Rule form where the time integration is from zero to infinity. When τ_c begins to approach τ_e, it becomes necessary to replace the $0-\infty$ time integration by a 0–t time integration where t is the time of the next exchange collision. This modification of the previous theory leads to a correction to the previous theory for which the lowest-order term goes as τ_c/τ_e.

In the calculation of nuclear-magnetic-resonance line shapes in liquids, two sorts of relaxation processes must be considered. One arises as the result of translation and rotation of the molecule with a time scale τ_c and the other results from chemical exchange process which occur in a time scale τ_e. Relaxation arising from τ_c processes form the basis of the Bloch equations[1] and were first theoretically evaluated by Wangsness and Bloch[2] and by Bloembergen, Purcell, and Pound.[3] The relaxation arising from exchange processes was first introduced by Gutowsky, McCall, and Schlicter.[4] They assumed that the chemical exchange collisions were separated, random events between which the molecule's nuclear-spin behavior was determined by the Bloch equation.

As shown by Wangsness and Bloch[2] and later generalized by Bloch[5] and Redfield[6] the τ_c processes can be represented by the density-matrix equation

$$\dot{\rho}_A=-i(H_{RA},\rho_A)+R_A\rho_A\,, \tag{1}$$

written in the coordinate system R rotating at the frequency ω of the applied rf field. Here

$$H_{RA}=H_A^0+H_{rf}\,, \tag{2}$$

$$H_{RA}^0=\sum_i(\omega_{0i}-\omega)I_i^z+\sum_{i>j}J_{ij}\vec{I}_i\cdot\vec{I}_j\,, \tag{3}$$

$$H_{rf}=\omega_1\sum I_i^x\,, \tag{4}$$

$$H_{sb}=\sum_\alpha I^\alpha B^\alpha\,, \tag{5}$$

where H_{sb} is the spin-bath interaction with I^α a spin variable and B^α a bath variable. I^α is defined to satisfy the relation

$$e^{i\omega\alpha\tau}I^\alpha e^{-i\omega\alpha\tau}=e^{i\omega\alpha}I^\alpha\,. \tag{6}$$

The relaxation operator R_A is given as

$$R_A\rho_A=-\tfrac{1}{2}\sum_\alpha\int_{-\infty}^{+\infty}d\tau\, e^{i\omega\alpha\tau}C_\alpha(\tau)\times[I^\alpha,e^{-iH_{RA}\tau}[I^{-\alpha},\rho_A-\rho_A^0]e^{iH_{RA}\tau}]\,, \tag{7}$$

where ρ_A^0 is the density-matrix operator at equilibrium and $C_\alpha(\tau)$ are correlation functions of the bath variables B^α and have the approximate form

$$C_\alpha(\tau)=C_\alpha(0)e^{-|\tau|/\tau_c}\,. \tag{8}$$

The effect of exchange is introduced by noting that if the average lifetime of molecule A is τ_{eA} then the exchange averaged value of ρ_A is given as[6,7]

$$\bar{\rho}_A(t)=\int_{-\infty}^{t}\frac{e^{-(t-t_0)/\tau eA}}{\tau_{eA}}\bar{\rho}_A(t,t_0)\,dt_0\,, \tag{9}$$

where

$$\bar{\rho}_A(t,t_0)=e^{(t-t_0)(L_A+R_A)}\bar{\rho}_{A_{\rm col}}(t_0) \tag{10}$$

is the solution of Eq. (1), where

$$L_A\rho_A=-i(H_A,\rho_A) \tag{11}$$

and $\bar{\rho}_{A_{\rm col}}(t_0)$ is the value of $\bar{\rho}_A$ at time $t=t_0$ as the result of an exchange collision.

Differentiating Eq. (9) with respect to t one obtains

$$\dot{\bar{\rho}}(t)=-i[H_{RA},\bar{\rho}_A(t)]+R_A\bar{\rho}_A(t)-(1/\tau_{eA})[\rho_A(t)-\rho_{A_{\rm col}}(t)]\,. \tag{12}$$

In Ref. 7 it is shown how for a wide variety of exchange processes, $\rho_{A_{\rm col}}$ is defined in terms of the density-matrix elements of the other molecules involved in the exchange collision. Equation (12) represents[7] the general theory for chemical-exchange-modified NMR for the regime where

$$\tau_c\ll\tau_e\,. \tag{13}$$

If one requires only that

$$\tau_c < \tau_e \, , \tag{14}$$

then the limits on the time integration given in Eq. (6) ($\pm\infty$), which follows from the assumption that $\tau_c \ll \tau_e$, must be replaced by

$$R'_A \rho_A = -\tfrac{1}{2}\int_{-t}^{+t} \cdots \, d\tau \, , \tag{15}$$

where t is the elapsed time after the last exchange collision. For the case of extreme narrowing ($\tau_c \omega_{0A} \ll 1$), Eq. (15) can be evaluated as

$$R'_A \rho_A = (1 - e^{-t/\tau_c}) R_A \rho_A \, . \tag{16}$$

The result where $\tau_{cA}\omega_{0A} \ll 1$ is not valid is exhibited in the Appendix. Replacing $R_A \rho_A$ by $R'_A \rho_A$ in Eq. (1) one obtains the replacement for Eq. (10) as

$$\bar{\rho}_A(t, t_0) = \exp[(t - t_0)(L_A + R_A) - \tau_{cA} R_A e^{-(t-t_0)/\tau_{cA}}]\, \bar{\rho}_{A_{\mathrm{col}}}(t_0) \tag{17}$$

and Eq. (12) becomes

$$\dot{\bar{\rho}}_A(t) = -i[H_{RA}, \bar{\rho}_A] + R_A \bar{\rho}_A - (1/\tau_{eA})(\bar{\rho}_A - \rho_{A_{\mathrm{col}}}) + R_A \int_{-\infty}^{t} \frac{e^{-(t-t_0)/\tau_{eA}} e^{-(t-t_0)/\tau_{cA}} \bar{\rho}_A(t, t_0)\, dt_0}{\tau_{eA}} \, . \tag{18}$$

Recognizing that $\bar{\rho}_A(t, t_0)$ varies slowly relative to τ_{eA} and τ_c, Eq. (18) can be approximated as

$$\dot{\bar{\rho}}_A \simeq -i[H_{RA}, \bar{\rho}_A] + R_A \bar{\rho}_A - (1/\tau_{eA})(\bar{\rho}_A - \rho_{A_{\mathrm{col}}}) + (\tau_{cA}/\tau_{eA}) R_A \bar{\rho}_{A_{\mathrm{col}}} \, . \tag{19}$$

The effect of the last term in Eq. (19) can be made clear by investigating the exchange of two spin-$\frac{1}{2}$ species with resonant frequencies ω_{0A} and ω_{0B} and chemical exchange rates τ_{eA} and τ_{eB}. The well-known low-power-coupled density-matrix equations for this problem derived from Eq. (12) are

$$\begin{bmatrix} i(\omega_{0A} - \omega) - \dfrac{1}{T_{2A}} - \dfrac{1}{\tau_{eA}} & \dfrac{1}{\tau_{eA}} \\[2ex] \dfrac{1}{\tau_{eB}} & i(\omega_{0B} - \omega) - \dfrac{1}{T_{2B}} - \dfrac{1}{\tau_{eB}} \end{bmatrix} \begin{bmatrix} \bar{\rho}^{A}_{\alpha,\beta} \\[2ex] \bar{\rho}^{B}_{\alpha,\beta} \end{bmatrix} = \begin{bmatrix} C_0 \\[2ex] C_0 \end{bmatrix} , \tag{20}$$

where $C_0 \sim H_0/kT$. The coupled density-matrix equations for the same problem derived from Eq. (19) are

$$\begin{bmatrix} i(\omega_{0A} - \omega) - \dfrac{1}{T_{2A}} - \dfrac{1}{\tau_{eA}} & \dfrac{1}{\tau_{eA}} - \dfrac{\tau_{cA}}{\tau_{eA} T_{2A}} \\[2ex] \dfrac{1}{\tau_{eB}} - \dfrac{\tau_{cB}}{\tau_{eB} T_{2B}} & i(\omega_{0B} - \omega) - \dfrac{1}{T_{2B}} - \dfrac{1}{\tau_{eB}} \end{bmatrix} \begin{bmatrix} \bar{\rho}^{A}_{\alpha,\beta} \\[2ex] \bar{\rho}^{B}_{\alpha,\beta} \end{bmatrix} = \begin{bmatrix} C_0 \\[2ex] C_0 \end{bmatrix} . \tag{21}$$

A more interpretive comparison can be made by defining

$$\begin{aligned} \frac{1}{\tau'_{eA}} &= \frac{1}{\tau_{eA}} - \frac{\tau_{cA}}{\tau_{eA} T_{2A}} = \frac{1}{\tau_{eA}}\left(1 - \frac{\tau_{cA}}{T_{2A}}\right) , \\ \frac{1}{\tau'_{eB}} &= \frac{1}{\tau_{eB}} - \frac{\tau_{cB}}{\tau_{eB} T_{2B}} = \frac{1}{\tau_{eB}}\left(1 - \frac{\tau_{cB}}{T_{2B}}\right) , \\ \frac{1}{T'_{2A}} &= \frac{1}{T_{2A}} + \frac{\tau_{cA}}{\tau_{eA} T_{2A}} = \frac{1}{T_{2A}}\left(1 + \frac{\tau_{cA}}{\tau_{eA}}\right) , \\ \frac{1}{T'_{2B}} &= \frac{1}{T_{2B}} + \frac{\tau_{cB}}{\tau_{eB} T_{2B}} = \frac{1}{T_{2B}}\left(1 + \frac{\tau_{cB}}{\tau_{eB}}\right) , \end{aligned} \tag{22}$$

which permits Eq. (21) to be written in form comparable to Eq. (20) as

$$\begin{bmatrix} i(\omega_{0A} - \omega) - \dfrac{1}{T'_{2A}} - \dfrac{1}{\tau'_{eA}} & \dfrac{1}{\tau'_{eA}} \\[2ex] \dfrac{1}{\tau'_{eB}} & i(\omega_{0B} - \omega) - \dfrac{1}{T'_{2B}} - \dfrac{1}{\tau'_{eB}} \end{bmatrix} \begin{bmatrix} \bar{\rho}^{A}_{\alpha,\beta} \\[2ex] \bar{\rho}^{B}_{\alpha,\beta} \end{bmatrix} = \begin{bmatrix} C_0 \\[2ex] C_0 \end{bmatrix} . \tag{23}$$

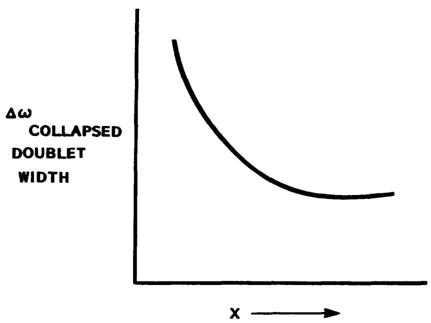

FIG. 1. $\Delta\omega_{\text{collapsed doublet}} = A + B/x + Cx$, where $x = \tau_e^{-1}$, $A = 1/T_2$, $B = \frac{1}{2}\delta^2$, $C = (1/T_2)\tau_c$, $\Delta\omega_{\text{min, collapsed doublet}} = A + 2(BC)^{1/2}$, $x_{\text{min}} = \sqrt{B/C}$.

Given a spin perturbation of strength $\delta\omega$ a relaxation operator can only be defined when

$$\delta\omega\,\tau_c \ll 1 \tag{24}$$

for which $1/T_2$ will be approximately given[8] as

$$1/T_2 \simeq (\delta\omega)(\delta\omega\,\tau_c)\ , \tag{25}$$

or

$$\tau_c/T_2 \simeq (\delta\omega\,\tau_c)^2\ . \tag{26}$$

This shows that within the relaxation operator theory, $\tau_c/T_2 \ll 1$ and thus in the renormalization of T'_{2A} and τ'_{eA} given in Eq. (22) the "fast exchange" correction can be removed in τ'_{eA} but must be kept in T'_{2A}.

Using Eq. (21) or Eq. (23) one can easily derive the linewidth of the collapsed doublet, which for equal spin concentrations ($\tau_{eA} = \tau_{eB}$), equal values for T_2, and

$$\delta\tau_e \ll 1\ , \tag{27}$$

$$2\delta = \omega_{0A} - \omega_{0B}\ , \tag{28}$$

is given as

$$\frac{1}{T_2} + \frac{1}{2}\tau_e\delta^2 + \cdots \left.\begin{matrix}\tau_e\delta \ll 1\ , \\ \tau_c/\tau_e \ll 1\ ,\end{matrix}\right. \tag{29}$$

as obtained from Eq. (20) and

$$\frac{1}{T_2} + \frac{1}{T_2}\frac{\tau_c}{\tau_e} + \frac{1}{2}\tau_e\delta^2 + \cdots \left.\begin{matrix}\tau_e\delta \ll 1 \\ \tau_c/\tau_e < 1\end{matrix}\right. \tag{30}$$

as obtained from Eq. (23).

A curious result of Eq. (30) is that if we were able to keep (T_2, τ_c) fixed and only vary τ_e, the collapsed doublet width as a function of $x = 1/\tau_e$ would schematically appear as shown in Fig. 1.

CONCLUSION

A theory is derived which enables the NMR line shapes of exchanging species in the liquid state to be analyzed under conditions where the previous theory which assumed $\tau_c \ll \tau_e$ is no longer valid. The theory is completely general and makes no assumption as to the form of the relaxation process. The evaluated expression given in Eq. (19) does however, make use of the assumption that the correlation function for molecular motion is exponential.

A number of authors[9] have previously considered line shapes under conditions where $\tau_c \ll \tau_e$ is no longer valid but have limited themselves to describing a totally collapsed line; i.e., the two coupled equations given in Eqs. (21) and (23) would be replaced by a single equation with a redefined T_2. A more important limitation of the previous theories is that they obscure the meaning of the condition $\tau_c < \tau_e$ which is encompassed in the time-dependent limits on the definition of R' [see Eq. (15)]. This type of relaxation coupling may have application in other types of problems.

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