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# The NMR Signal Shape of Identical Nuclei Exchanging between Two Different Environments*

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The Gutowsky-Holm equation has been transformed into a formula which expresses the signal as a function of dimensionless parameters ($a=2\pi\tau\,|\nu_A-\nu_B|$, $r=1/2\pi T_2\,|\nu_A-\nu_B|$ and $p_B$) and a dimensionless variable ($f=(\nu-\nu_A)/(\nu_B-\nu_A)$). The shape function in this form is convenient for graphic representation and can be easily calculated for a desired combination of the parameters by using a suitable computer. The exchange rate can be determined by searching for a theoretical curve that agrees with the shape of the experimental signal.

When an assembly of identical nuclei are exchanging in a random statistical manner between two environments with different chemical shifts, the signal takes on various shapes, depending on the exchange rate, the fractional populations, and the transverse relaxation times. In this report we shall neglect all coupling, and examine the signal shape observed under these circumstances.

This problem has already been solved mathematically by Gutowsky and Holm for the case where the two transverse relaxation times, $T_{2A}$ and $T_{2B}$, are equal.[1] The equation thus obtained is, however, inconvenient for a general discussion of signal shape because it is formulated in terms of dimensional quantities. The main purpose of the present report is to transform it into a formula which expresses the shape of a signal as a function of dimensionless parameters, and then to discuss its application to the determination of exchange rates.

## Theoretical Consideration

First of all we shall define the dimensionless parameters:

$$a = 2\pi\tau\,|\nu_A-\nu_B| = 2\pi p_B\tau_A\,|\nu_A-\nu_B| = 2\pi p_A\tau_B\,|\nu_A-\nu_B| \tag{1}$$

$$r = 1/2\pi T_2\,|\nu_A-\nu_B| = w/|\nu_A-\nu_B| \tag{2}$$

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[1] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

and a dimensionless variable:

$$f = (\nu_{\mathrm{A}}-\nu)/(\nu_{\mathrm{A}}-\nu_{\mathrm{B}}) = (\nu-\nu_{\mathrm{A}})/(\nu_{\mathrm{B}}-\nu_{\mathrm{A}}) \quad (3)$$

By substituting them into the Gutowsky-Holm equation, we get a general formula:

$$\begin{aligned} v = C\times &[(1+ar)\{-af(f-1)+r(1+ar)\} \\ &+a(f+p_{\mathrm{B}}-1)(f+2arf-ar-p_{\mathrm{B}})] \\ &\div[\{-af(f-1)+r(1+ar)\}^2 \\ &+(f+2arf-ar-p_{\mathrm{B}})^2] \qquad (4) \end{aligned}$$

where $C = -\gamma H_1 M_0/2\pi\,|\nu_{\mathrm{A}}-\nu_{\mathrm{B}}|$

Here $v$ describes the transverse component of the resultant magnetic moment, which is perpendicular to the rotating field, $H_1$, and which is proportional to the absorption intensity. The same symbol, $v$, will be used hereafter to represent the absorption intensity. $C$ is a constant, dependent on the apparatus sensitivity. The other notations, other than $w$, have their usual meanings. The parameter, $r$, is one half of the half-height-width of the A (or B) signal, $w$, divided by the separation between the A and B signals, in the absence of exchange effects and with no overlap of signals.

Equation 4 is convenient for graphic representation because this formula gives the relative intensity as a function of the relative position, $f$, with respect to the signal positions of the A and B states. The shape function can be easily calculated for a desired combination of $a$, $r$, and $p_{\mathrm{B}}$ by using a suitable computer. An IBM-1620 computer performed the calculation in a quarter of an hour. The Fortran program is shown in Table I. In this program, the maximum signal height is made equal to unity by choosing automatically a proper value of $C$.

Table I. Fortran program for Eq. 4

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C        SHAPE FUNCTION
         DIMENSION F(301), V(301)
         READ 1, A, R, PB
         AR=A*R
         AR1=1.+AR
         RAR1=R*AR1
         HIST=0.
         D0 20 I=1, 301
         P=I+99
         F(I)=P/100.-2.
         B=RAR1-A*F(I)*(F(I)-1.)
         C=F(I)+PB-1.
         D=F(I)+2. *AR*F(I)-AR-PB
         V(I)=(AR1*B+A*C*D)/(B*B+D*D)
         IF (V(I)-HIST) 20, 20, 10
   10    HIST=V(I)
   20    CONTINUE
         D0 30 I=1, 301
         V(I)=V(I)/HIST
   30    TYPE 2, F(I), V(I)
    1    FORMAT (E12.8, E12.8, F4.2)
    2    FORMAT (F5.2, 5X, F8.5)
         END
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In several limiting cases, Eq. 4 becomes simpler and is reduced to the familiar relations, 5 to 9.

$$v_{(p_{\mathrm{B}}=0)} = C\times\{r/(r^2+f^2)\} \qquad (5)$$

$$v_{(p_{\mathrm{A}}=0)} = C\times[r/\{r^2+(f-1)^2\}] \qquad (6)$$

$$v_{(a\to\infty)} = C\times[rp_{\mathrm{A}}/(r^2+f^2)+rp_{\mathrm{B}}/\{r^2+(f-1)^2\}] \qquad (7)$$

$$v_{(a=0)} = C\times[r/\{r^2+(f-p_{\mathrm{B}})^2\}] \qquad (8)$$

$$v_{(r\to\infty)}=0 \qquad (9)$$

$$\begin{aligned} v_{(r=0)}&=C\times[ap_{\mathrm{A}}p_{\mathrm{B}}/\{a^2f^2(f-1)^2+(f-p_{\mathrm{B}})^2\}] \\ &=C'\times[1/\{a^2f^2(f-1)^2+(f-p_{\mathrm{B}})^2\}] \end{aligned} \qquad (10)$$

The last equation (10) has previously been derived by the author and presented graphically for many combinations of $a$ and $p_{\mathrm{B}}$.2)

A one-to-one correspondence can be shown to hold between the signal shape (expressed in the relative intensity as a function of $f$) and the set of parameters ($a$, $r$, and $p_{\mathrm{B}}$). One important exception, however, is the case where $r$ equals zero, and where $a$ tends to infinity. In this case, two lines appear, at $f=0$ and at $f=1$. The ratio of their heights varies from $p_{\mathrm{A}}/p_{\mathrm{B}}$ to $p_{\mathrm{A}}^2/p_{\mathrm{B}}^2$, depending on the product of $a$ and $r$, or, in other words, on the ratio of $\tau$ to $T_2$. Both times are infinitely large compared with $1/|\nu_{\mathrm{A}}-\nu_{\mathrm{B}}|$, but their ratio may be finite.

$$v_{(\mathrm{at}\ f=0)}/v_{(\mathrm{at}\ f=1)} = p_{\mathrm{A}}(p_{\mathrm{A}}+ar)/p_{\mathrm{B}}(p_{\mathrm{B}}+ar) \qquad (11)$$

The following two cases may also be considered as rather exceptions. As is shown by Eq. 9, no signal appears for an infinitely large $r$ value, regardless of the values of $a$ and $p_{\mathrm{B}}$. The same Lorentzian curve is obtained for sets of parameters which have $r$'s all equal, $a$'s all different, and $p_{\mathrm{B}}=0$ (or 1). A detailed discussion of these cases seems unnecessary, however, since no information of practical importance could be derived from such a discussion.

The most important application of Eq. 4 is probably to the case where $p_{\mathrm{A}}=p_{\mathrm{B}}=1/2$. Except for the last paragraph, we shall be concerned exclusively with this case in the remainder of this section. Equation 4 can be reduced to Eq. 12, which is symmetrical with respect to $f=1/2$:

$$\begin{aligned} v = C\times&\{a^2rf(f-1)+r(1+ar)^2+a(1+2ar)/4\} \\ &\div\{a^2f^2(f-1)^2+(1+2ar+2a^2r^2)f(f-1) \\ &+r^2(1+ar)^2+(1+2ar)^2/4\} \end{aligned} \qquad (12)$$

The signal shapes have been calculated and presented graphically for all combinations of $a=\infty$, 32, 8, 4, $2\sqrt{2}$, 2, 1.7, $\sqrt{2}$, 1.2, 1, $1/\sqrt{2}$, 1/2,

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2) T. Nakagawa, *Ann. Rept. Shionogi Lab.*, **13**, 60 (1963).

1/4, 1/16, 0 and $r=0$, 1/20, 1/10, 1/5, 1/3, 1/2.[**] Both the life-time, $\tau_A$ $(=\tau_B)$, and the transverse relaxation time, $T_2$, can be determined by searching for a figure that agrees with the shape of the experimental signal.

Provided one of the signal positions of the components, $\nu_A$, or $\nu_B$, is known on the chart by some means, the comparison is easy. The scale of $f$ can be determined from the center of symmetry $(f=1/2)$ and from the position of $\nu_A$ or $\nu_B$ $(f=0$ or $1)$. Because of the one-to-one correspondency, both $a$ and $r$ can be determined unequivocally.

In most cases, however, we cannot scale $f$ by a glance at the chart. Equation 12 has two independent parameters, $a$ and $r$; therefore, it is necessary to use at least two shape parameters in order to compare the experimental and theoretical curves. The ratios of maximum to minimum height, of quarter-height-width to half-height-width, of half-height-width to three-quarter-height-width, etc., may be used as such parameters. A more precise comparison can be achieved by dividing the signal peak into many equal heights, and by comparing the relative widths of the experimental and theoretical curves at corresponding heights.

Provided $a=0$, the signal displays a Lorentzian curve for any $r$ value; the value of $r$ cannot be determined from the signal shape. Even in this case, however, we are able to evaluate $T_2$ from the half-height-width $(T_2=1/2\pi w)$, and deduct $\tau_A$ $(=\tau_B)=0$ from the Lorentzian shape of the signal. The signal position of the components, $\nu_A$ and $\nu_B$, cannot be determined. For $a\neq 0$, there is only one theoretical curve that accurately coincides with the signal obtained experimentally, thus, $a$, $r$, $\nu_A$, and $\nu_B$ can all be determined.

Life-times have frequently been estimated by ignoring the effect of $T_2$. In more rigorous analysis, $T_2$ has been evaluated from the line width at high temperatures, where the signal narrows into a sharp peak. Then the life-time can be evaluated, for example, by comparing the peak separations at a temperature in the transition region and at a temperature sufficiently low to stop the exchange. The temperature independency of $T_2$, $\nu_A$, and $\nu_B$ is assumed in this analysis.

The advantage of the present method is that it is free from these assumptions. At least in principle, $\tau$, $T_2$, $\nu_A$, and $\nu_B$ can be determined uniquely and simultaneously from a single experiment at any temperature in the transition region. The applicability to an actual system depends on the adequacy of the assumption that $T_{2A}=T_{2B}$, and on the accuracy of the apparatus used.

For the case where $T_{2A}\neq T_{2B}$[3)] a more general formula:

$$v=C\times[\{(1+ar_Ap_B+ar_Bp_A)K+a(f+p_B-1)L\}/(K^2+L^2)] \quad (13)$$

where

$$\begin{aligned} K &= (r_Ap_A+r_Bp_B)+a\{r_Ar_B-f(f-1)\} \\ L &= f(1+ar_A+ar_B)-(ar_A+p_B) \\ C &= -\gamma H_1M_0/2\pi\,|\nu_A-\nu_B| \\ a &= 2\pi\tau\,|\nu_A-\nu_B| \\ r_A &= 1/2\pi T_{2A}\,|\nu_A-\nu_B| \\ r_B &= 1/2\pi T_{2B}\,|\nu_A-\nu_B| \\ f &= (\nu-\nu_A)/(\nu_B-\nu_A) \end{aligned}$$

is derived. It is easy to design a program similar to that shown in Table I.

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[**] Duplicates are available on microfilm on request to the author.

[3)] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).