

# $^1\text{H}$ and $^2\text{H}$ NMR Relaxation in Hydrogen-Bonded Solids Due to a Complex Motion: Classical Jumps over a Barrier and Incoherent Tunneling

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**Equations for the temperature dependence of proton and deuterium spin–lattice relaxation rates and second moments due to a complex motion consisting of classical jumps over a potential barrier and quantum mechanical tunneling through the barrier have been derived. Asymmetric double and triple potential wells are considered. These equations have been employed to analyze proton spin–lattice relaxation data for solid naphthazarin in the laboratory and rotating frames as a function of temperature. It is shown that tunneling plays an important role in the proton transfer dynamics of this compound.** © 1998 Academic Press

**Key Words:** spin–lattice relaxation; hydrogen bond dynamics; tunneling; complex motions; naphthazarin B.

## INTRODUCTION

Systems in which a hydrogen atom undergoes an exchange motion within a hydrogen bond in a solid have been the topic of a number of research papers. This simple chemical process, which results in an equilibrium dynamical disorder between tautomers in solids, is of great importance in many chemical and biological processes (1). For example, the structure of crystalline naphthazarin is dynamically disordered and involves a tautomeric equilibrium which is fast at room temperature. The polymorphs of naphthazarin have been studied extensively by using infrared, Raman,  $^{13}\text{C}$  NMR, and neutron and X-ray diffraction methods (2–10). Two equivalent tautomeric forms, corresponding to the structures in which the two hydroxyl groups are on the same ring (Fig. 1a), have been found. The transfer of the two protons seems to be a two-step process through an intermediate species in which the two hydroxyls are on different rings (Fig. 1b) or as a one-step two-proton transfer proceeding through the centrosymmetric species (Fig. 1c) (4). However, theoretical calculations (2, 10) show that the interconversion of the two minimum energy tautomers has one absolute maximum and two saddle points. The absolute maximum corresponds to structure D (Fig. 1c) in which the two hydrogen-bonded protons are equidistant from the oxygens.

Therefore, these solids have double potential minima with equilibrium configurations A, B, and double (C, C' configurations) or single (D configuration) potential maxima, as shown in Fig. 1. Hydrogen-bonded naphthazarins are particularly suitable for detailed investigations of the energetics and dynamics associated with the proton transfer process. Reynhardt (11) measured proton spin–lattice relaxation times of the B and C modifications of naphthazarin (5, 9) as a function of temperature. A relaxation model in which the proton jumps between two potential minima in the vicinity of adjacent quinonoid and hydroxyl oxygens failed to account for the observed temperature dependence of the relaxation times. A model in which the proton jumps over the barrier between three potential minima yielded better agreement between calculated and measured relaxation times, but the result was not convincing.

TTAA is another example of a material which exhibits dynamic disorder of hydrogen atoms in the two N–H · · · N hydrogen bonds of the molecule. The four tautomeric forms correspond to the structures 1, 2, 3, and 4, as shown in Fig. 2 (12). These tautomers correspond to unequal potential minima, the population of tautomer 4 being almost zero. Therefore, the situation can be described by a triple potential well with equilibrium configurations 1, 2, and 3. The minimum corresponding to configuration 1 is the deepest, while the other two minima are of almost equal depth (13). The relaxation results for this molecule have not been published yet.

Techniques in nuclear magnetic resonance (NMR) have been employed to study the dynamics of hydrogen-bonded atoms and the shape of the potential wells in the solid state (11–36). In the simplest case the proton spin–lattice relaxation time is determined by homonuclear dipolar interactions and, according to the well-established theory, the motional spectrum of the hydrogen atom is sampled at the proton Larmor frequency  $\omega_I$  and at  $2\omega_I$ . If heteronuclear I–S interactions are present, extra terms are introduced into the spectral density function which determines  $T_1$ . Consequently,

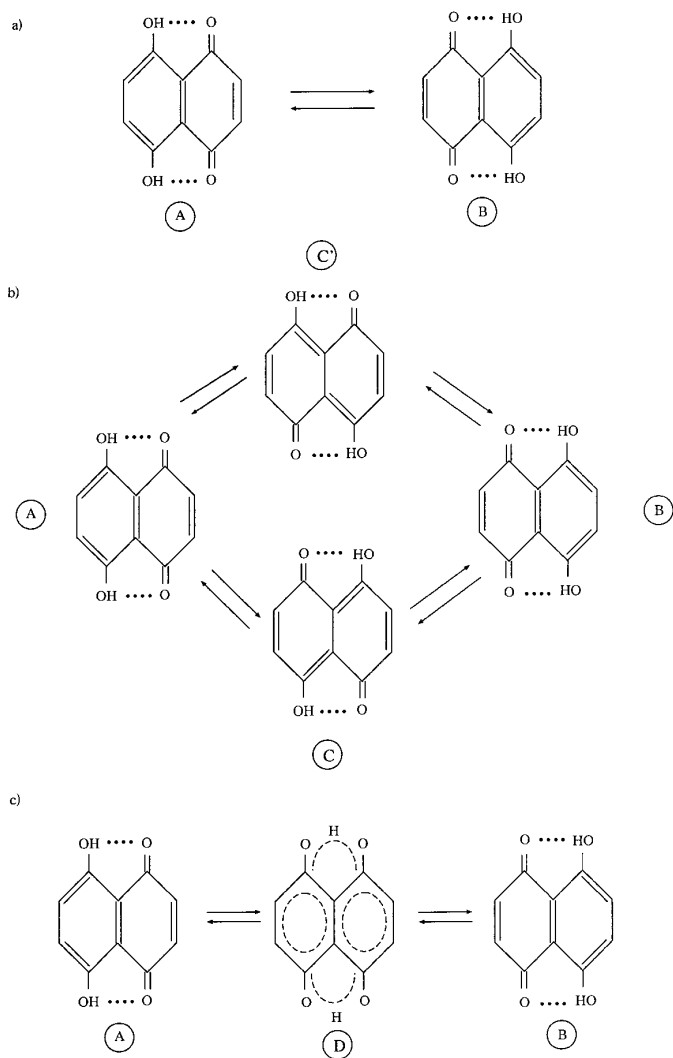


FIG. 1. The tautomerism of naphthazarin (see Refs. 2–10).

the motional spectrum of the hydrogen nuclei is sampled at frequencies of both the proton and the second nucleus (37–39). The spin–lattice relaxation of a nuclear spin which has a quadrupole moment is dominated by the motionally induced modulation of the electric field gradient at the site of the nucleus. For deuterons the field gradient tensor is along the  $^2\text{H}-X$  bond direction ( $X$  is the atom bonded to the deuteron), which simplifies the analysis of the data. The deuteron relaxation monitors the dynamics of the  $^2\text{H}-X$  bond in the sample (40–42). In most cases the  $\ln T_1$  versus  $1/T$  curves associated with the proton transfer dynamics are not symmetric, the slopes on the high-temperature side of the minima being much steeper than those on the low-temperature side (11, 14, 15, 19, 20, 29, 34, 35). Such spin–lattice relaxation behavior cannot be interpreted in terms of a classical jump motion over the barrier in an asymmetric potential well. For classical jumps the slope on the low-temperature

side is higher than the slope on the high-temperature side. Meier *et al.* (14) and Nagaoka *et al.* (15) suggested that quantum mechanical tunneling played an important role in the proton transfer dynamics. Recently Skinner and Trommsdorff (19) developed a theory taking into account phonon-assisted tunneling through the potential barrier and hopping over the barrier. Their model accommodates the asymmetric nature of the double minimum potential. It is assumed that the Zeeman splitting is much smaller than the other energy differences involving tunnel splittings. If the value of the tunnel splitting is comparable with that of the Zeeman splitting, the transitions between the tunneling levels should be taken into account in the relaxation equation.

In this paper the equations for the temperature dependence of the polycrystalline proton and deuteron spin–lattice relaxation rates and second moment of the NMR line, in the presence of a complex motion consisting of jumps over the barrier and tunneling motion in asymmetrical double and triple potential wells, are derived. It is assumed that both motions are described in terms of individual correlation functions and spectral densities. The correlation function of this complex motion is considered to be the product of the correlation functions of the individual motions. Possible ways of distinguishing between the activation parameters of tunneling and jumps over the barrier are discussed.

The observed deviations from classical behavior, as revealed by the lower slope on the low-temperature side of the minimum of the  $\ln T_1$  versus  $1/T$  curve (11), suggest

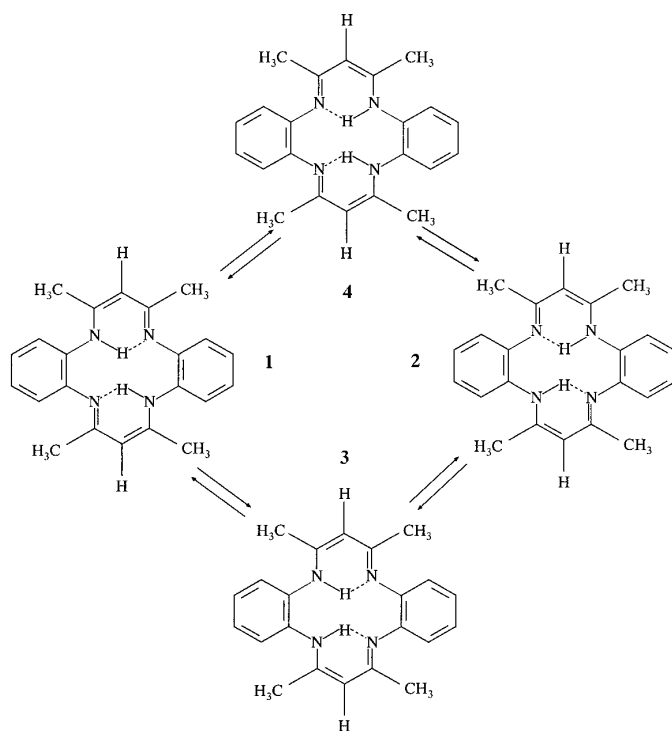


FIG. 2. The tautomerism of TTA (see Ref. 13).

that naphthazarin has the potential for displaying quantum mechanical incoherent tunneling. Therefore, we have decided to reanalyze the published data (11), taking into account quantum mechanical tunneling.

### REORIENTATION MODEL

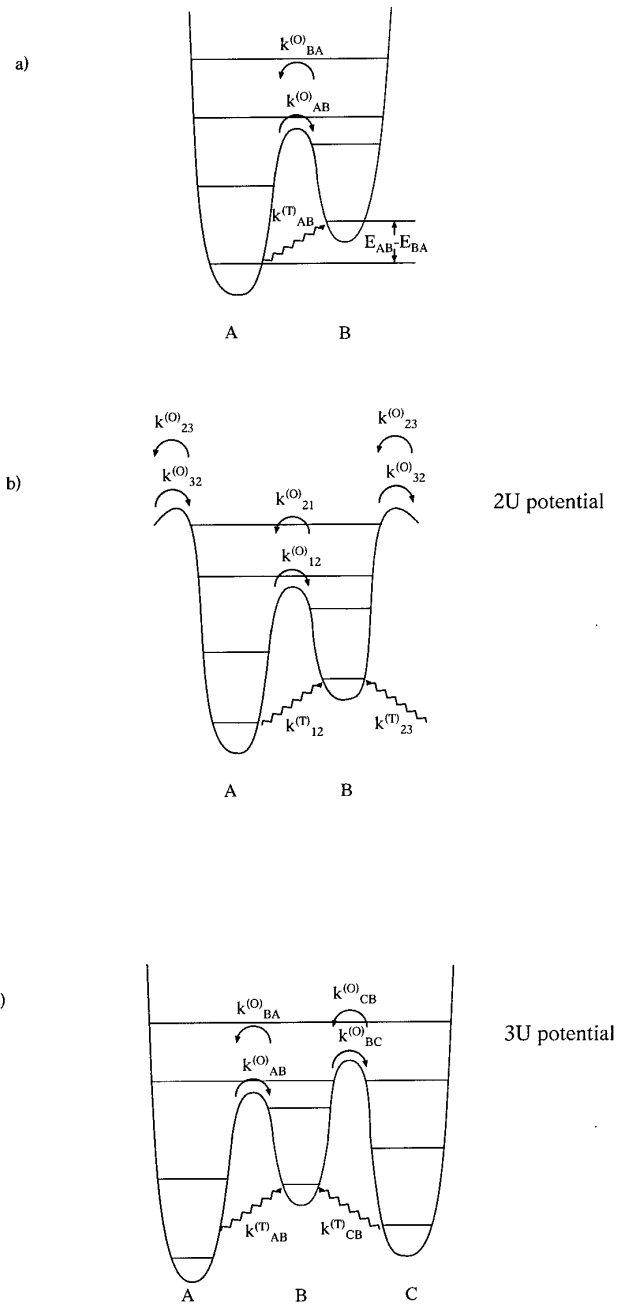
The dynamics of the interconversion between the two tautomeric forms  $A$  and  $B$  is governed by the rate constants  $k_{AB}$  and  $k_{BA}$  for the forward and reverse crossing of the potential barrier, respectively (Fig. 3a). In hydrogen-bonded solids the effect of neighboring molecules is to break the symmetry of the potential well, resulting in an asymmetric potential well with  $k_{AB} \neq k_{BA}$ . Debye (43) and Hoffman (44, 45) proposed a model for jumps in a potential well to explain the phenomenon of dielectric relaxation in solids. This model can also be applied in the case of NMR relaxation. In the Debye model the reorientation between the minima of a potential well is described in terms of thermally activated stochastic jumps over potential barriers. The rate constants obey Arrhenius' law, viz.,

$$\begin{aligned} k_{AB}^{(O)} &= k_{AB}^0 \exp\left(-\frac{E_{AB}}{RT}\right) \\ k_{BA}^{(O)} &= k_{BA}^0 \exp\left(-\frac{E_{BA}}{RT}\right), \end{aligned} \quad [1]$$

where  $E_{AB}$  and  $E_{BA}$  are the heights of the potential barrier. Usually the preexponential factors  $k_{AB}^0$  and  $k_{BA}^0$  are in the range  $10^{11}$ – $10^{12}$  s $^{-1}$  (11–36).

For asymmetric potential wells coherent as well as incoherent tunneling can occur at low temperatures, but for symmetric potential wells the tunneling is always incoherent (46). Usually only one pair of tunneling levels is assumed, but in reality there may be a number of vibrational levels of the  $A$  and  $B$  sites which happen to coincide with each other and which are split by the tunneling interactions. The average over all possible transitions should be taken in the calculations and the weighted average of the tunneling activation energy should be used. Nagaoka *et al.* (15) proposed that the spin–lattice relaxation is induced by the transitions between the ground state levels (there is no splitting of the ground state of the  $A$  configuration due to the asymmetry of the potential well) and first excited levels. Activation energies are required to make transitions between the ground states of the  $A(B)$  sites and the tunneling levels. The activation energies for these transitions are expected to be small. Nagaoka *et al.* (15) proposed the following rate constants for low-temperature activated tunneling,

$$k_{AB}^{(T)} = k_a^{(T)} \exp\left(-\frac{E_T}{RT}\right), \quad [2]$$



**FIG. 3.** Shapes of potential wells considered in the text.  $k_{xy}^{(O)}$ , where  $x, y = A, B, C, 1, 2, 3$ , are rate constants for jumps over the barrier, while  $k_{xy}^{(T)}$  are rate constants for tunneling.

where  $E_T$  ( $> (E_{AB} - E_{BA})$ ) is the activation energy for tunneling from the lower to the upper state. By detailed balance the down rate is

$$k_{BA}^{(T)} = k_0^{(T)} \exp\left(-\frac{E_T - \Delta E}{RT}\right), \quad [3]$$

where  $\Delta E = (E_{AB} - E_{BA})$ .

Skinner and Trommsdorff (19) pointed out that at low temperatures the rate constant should become temperature independent, corresponding to direct phonon-assisted tunneling (spontaneous phonon emission) from the upper state to the lower state. In this case Eqs. [2] and [3] would rather be given by

$$k_{BA}^{(T)} = k_0^{(T)}$$

$$k_{AB}^{(T)} = k_0^{(T)} \exp\left(-\frac{\Delta E}{RT}\right). \quad [4]$$

Skinner and Trommsdorff (19) developed a theory for hydrogen bond dynamics which accommodates the asymmetric nature of a double potential well. The dynamics between the two minima is governed by the rate constants  $k_{AB}$  and  $k_{BA}$  for the forward and reverse motions, respectively. At low temperatures the motion is dominated by phonon-assisted tunneling, and if  $E_{AB} > E_{BA}$ , the tunneling rate constants are given by

$$k_{AB}^{(T)} = k_0^{(T)} \frac{1}{[\exp((E_{AB} - E_{BA})/RT)] - 1}$$

$$k_{BA}^{(T)} = k_0^{(T)} \frac{\exp((E_{AB} - E_{BA})/RT)}{[\exp((E_{AB} - E_{BA})/RT) - 1]}. \quad [5]$$

In this model the tunneling relaxation between localized states occurs by one-phonon emission or absorption. Alternatively, at high temperatures the proton transfer dynamics follows the Arrhenius law. Usually the preexponential factor  $k_0^{(T)}$  is of the order of  $10^8 - 10^7 \text{ s}^{-1}$  (19–21).

### SPIN-LATTICE RELAXATION RATES

In the weak-collision limit the spin-lattice relaxation rates of a spin pair in the laboratory and rotating frames for the standard type of spin interactions, such as the direct dipole-dipole interaction, are given by (37–39)

$$\frac{1}{T_1} = \frac{3}{2} I(I+1) \gamma_I^4 \hbar^2 [J^{(1)}(\omega_I) + J^{(2)}(2\omega_I)] \quad [6]$$

$$\frac{1}{T_{1\rho}} = \frac{3}{2} I(I+1) \gamma_I^4 \hbar^2$$

$$\times \left[ \frac{1}{4} J^{(0)}(2\omega_1) + \frac{5}{2} J^{(1)}(2\omega_I) + \frac{1}{4} J^{(2)}(2\omega_I) \right], \quad [7]$$

respectively, for homonuclear dipolar interactions and by

$$\frac{1}{(T_1)_I} = S(S+1) \gamma_I^2 \gamma_S^2 \hbar^2$$

$$\times \left[ \frac{1}{12} J^{(0)}(\omega_I - \omega_S) + \frac{3}{2} J^{(1)}(\omega_I) \right. \\ \left. + \frac{3}{4} J^{(2)}(\omega_I + \omega_S) \right] \quad [8]$$

$$\frac{1}{(T_{1\rho})_I} = S(S+1) \gamma_I^2 \gamma_S^2 \hbar^2$$

$$\times \left[ \frac{1}{3} J^{(0)}(\omega_1) + 3J^{(1)}(\omega_S) \right. \\ \left. + \frac{1}{12} J^{(0)}(\omega_I - \omega_S) + \frac{3}{2} J^{(1)}(\omega_I) \right. \\ \left. + \frac{3}{4} J^{(2)}(\omega_I + \omega_S) \right] \quad [9]$$

for heteronuclear dipolar interactions.  $\gamma_I$  is the gyromagnetic ratio of the resonant spins.

The angular NMR frequencies in the laboratory frame are  $\omega_I$  and  $\omega_S$ , while  $\omega_1$  is the frequency of the rotating magnetic field and

$$J^{(m)}(\omega) = \int_{-\infty}^{+\infty} \langle F^m(t) F^{m*}(t+\tau) \rangle \exp(-i\omega\tau) d\tau \quad [10]$$

are the spectral densities of the correlation functions of the fluctuating part of the interaction Hamiltonian. These random functions are

$$F^0(t) = R(t)(1 - 3 \cos^2[\vartheta(t)]) \quad [11]$$

$$F^1(t) = R(t) \sin[\vartheta(t)] \cos[\vartheta(t)] \exp[i\varphi(t)] \quad [12]$$

$$F^2(t) = R(t) \sin^2[\vartheta(t)] \exp[2i\varphi(t)]. \quad [13]$$

Here  $R(t) = R_{ik}^{-3}(t)$ , where  $R_{ik}$  is the internuclear distance, and  $\vartheta$  and  $\varphi$  are the polar and azimuthal angles, respectively, describing the orientation of the internuclear vector in the laboratory frame with the  $z$  axis in the direction of the external magnetic field  $B_0$ . Thermal motions or quantum tunneling motions in the physical system cause  $R(t)$ ,  $\vartheta(t)$ , and  $\varphi(t)$  to be time dependent.

The spin-lattice relaxation of a nuclear spin with a quadrupole moment is dominated by the motionally induced modulation of the electric field gradient at the site of the nucleus. The spin-lattice relaxation of a nucleus with spin  $I = 1$ , which experiences quadrupolar relaxation resulting from the interaction of the nuclear quadrupole moment with an axially

symmetric electric field gradient, can be expressed as (40, 42)

$$\frac{1}{T_1} = \frac{9}{8} \pi^2 [J^{(1)}(\omega_I) + J^{(2)}(2\omega_I)]. \quad [14]$$

In this case the spectral densities  $J^m(\omega)$  (Eq. [10]) refer to the orientation function of the symmetry axis of the electric field gradient. The quantity  $R(t)$  in Eqs. [11] to [13] equals  $C_{\text{QF}} = \langle e^2 q_{22} Q/h \rangle$ , which is the quadrupole coupling constant expressed in hertz. The polar and azimuthal angles  $\vartheta$  and  $\varphi$  describe the orientation of  $C_{\text{QF}}$ .

## SECOND MOMENT OF AN NMR LINE

It has been demonstrated (47) that best fits of equations for the temperature dependence of the second moment of an NMR line in the presence of a complex molecular motion to the experimental second moment data yield the same information obtained from spin-lattice relaxation time measurements as a function of temperature. The equation for the dipolar second moment,  $M_2$ , of an NMR line was derived by Van Vleck (48) and extended by Powels and Gutowsky (49), who showed that if the correlation function of a given reorientation is known, the second moment of the NMR line for a system of two homonuclear spins can be written as

$$M_2 = \frac{3}{4} \gamma_I^2 \hbar^2 I(I+1) \int_{-\delta\nu}^{+\delta\nu} J^{(0)}(\omega) d\nu \quad [15]$$

and for a system of two heteronuclear spins as

$$M_{2(I)} = \frac{1}{2} \gamma_I \gamma_S \hbar^2 S(S+1) \int_{-\delta\nu}^{+\delta\nu} J^{(0)}(\omega) d\nu, \quad [16]$$

where  $\delta\nu$  is the linewidth,  $\omega = 2\pi\nu = \gamma\sqrt{M_2}$ , and  $J^0(\omega)$  is the spectral density (Eq. [10]) of the correlation function of the random function  $F^0(t)$  given by Eq. [11].

## CORRELATION FUNCTIONS FOR A UNIAXIAL REORIENTATION

### A. 2U Potential (Fig. 3b)

The autocorrelation function for a double minimum potential well in a polycrystalline sample involves only one correlation time  $\tau_c$  and can be written as (50–54)

$$\langle F^m(t) F^{m*}(t+\tau) \rangle = Z_m \left[ C_1 + C_2 \exp\left(-\frac{|\tau|}{\tau_2}\right) \right], \quad [17]$$

where  $Z_m = 4/5, 2/15$ , or  $8/15$  for  $m = 0, 1, 2$ , respectively, and

$$1/\tau_2 = k_{12} + k_{21} + k_{23} + k_{32}. \quad [18]$$

$k_{12}, k_{21}, k_{23}$ , and  $k_{32}$  are rate constants, as shown in Fig. 3b. Also

$$\begin{aligned} C_1 &= \frac{K_{AB}}{(1 + K_{AB})^2} \\ &\times [K_{AB}^{-1} R(A)R(A) + K_{AB} R(B)R(B) \\ &\quad + R(A)R(B) \times (3 \cos^2 \theta_{AB} - 1)] \quad [19] \\ C_2 &= \frac{K_{AB}}{(1 + K_{AB})^2} \\ &\times [R(A)R(A) + R(B)R(B) \\ &\quad - R(A)R(B)(3 \cos^2 \theta_{AB} - 1)], \quad [20] \end{aligned}$$

where  $R(A)$  and  $R(B)$  are the discrete values of  $R_{ik}$  or  $C_{\text{QF}}$  at the  $A$  and  $B$  sites and the equilibrium constants  $K_{AB}$  are given by

$$\begin{aligned} K_{AB} &= \frac{k_{12}}{k_{21}} \\ &= \frac{k_{23}}{k_{32}}. \quad [21] \end{aligned}$$

### B. 3U Potential (Fig. 3c)

After spatial averaging for a polycrystalline sample, the autocorrelation function for the unperiodical and unequal triple minimum potential (Fig. 3c) contains two correlation times, characterizing the two modes of reorientation (44, 45, 52, 53, 55, 56), viz.,

$$\begin{aligned} &\langle F^m(t) F^{m*}(t+\tau) \rangle \\ &= Z_m \left[ C_1 + C_2 \exp\left(-\frac{|\tau|}{\tau_{31}}\right) + C_3 \exp\left(-\frac{|\tau|}{\tau_{32}}\right) \right], \quad [22] \end{aligned}$$

where  $Z_m = 4/5, 2/15$ , or  $8/15$  for  $m = 0, 1, 2$ , respectively.

The correlation times  $\tau_{31}$  and  $\tau_{32}$  and the factors  $C_1, C_2$ , and  $C_3$  can be obtained by solving the following set of differential equations which describes the time dependence of the populations  $P_A, P_B$ , and  $P_C$  of the relaxation vectors at the separate sites (52):

$$\frac{dP_A}{dt} = -(k_{AB} + k_{AC})P_A + k_{BA}P_B + k_{CA}P_C \quad [23]$$

$$\frac{dP_B}{dt} = k_{AB}P_A - (k_{BA} + k_{BC})P_B + k_{CB}P_C \quad [24]$$

$$\frac{dP_C}{dt} = k_{AC}P_A + k_{BC}P_B - (k_{CB} + k_{CA})P_C. \quad [25]$$

For very high barriers  $E_{AC}$  and  $E_{CA}$ ,  $k_{AC} = k_{CA} = 0$ . The correlation times are

$$1/\tau_{31} = -\lambda_2 \quad [26]$$

$$1/\tau_{32} = -\lambda_3, \quad [27]$$

where  $\lambda_2$  and  $\lambda_3$  are the eigenvalues of the matrix

$$\begin{vmatrix} (a_{11} - \lambda) & a_{12} & a_{13} \\ a_{21} & (a_{22} - \lambda) & a_{23} \\ a_{31} & a_{32} & (a_{33} - \lambda) \end{vmatrix} \\ = \begin{vmatrix} (-k_{AB} - k_{AC} - \lambda) & k_{BA} & 0 \\ k_{AB} & (-k_{BA} - k_{BC} - \lambda) & k_{CB} \\ 0 & k_{BC} & (-k_{CA} - k_{CB} - \lambda) \end{vmatrix} \quad [28]$$

and

$$\lambda_1 = 0 \quad [29]$$

$$\lambda_2 = \frac{-(J + Q)}{2} \quad [30]$$

$$\lambda_3 = \frac{-(J - Q)}{2} \quad [31]$$

$$J = k_{AB} + k_{BA} + k_{CB} + k_{BC} + k_{AC} + k_{CA} \quad [32]$$

$$Q = [J^2 - 4(k_{AB} \cdot k_{BC} + k_{CB} \cdot k_{BA} + k_{AB} \cdot k_{CB} \\ + k_{BA} \cdot k_{AC} + k_{CA} \cdot k_{AB} + k_{CA} \cdot k_{BA} \\ + k_{BC} \cdot k_{CA} + k_{AC} \cdot k_{CB} + k_{BC} \cdot k_{AC})]^{1/2} \quad [33]$$

$$C_1 = C_1^{(1)}P_A S_1 + C_1^{(2)}P_B S_2 + C_1^{(3)}P_C S_3 \quad [34]$$

$$C_2 = C_2^{(1)}P_A S_1 + C_2^{(2)}P_B S_2 + C_2^{(3)}P_C S_3 \quad [35]$$

$$C_3 = C_3^{(1)}P_A S_1 + C_3^{(2)}P_B S_2 + C_3^{(3)}P_C S_3. \quad [36]$$

Also

$$S_1 = \chi_1^{(1)}R(A)R(A) + \frac{1}{2}\chi_2^{(1)}R(A)R(B)(3 \cos^2\theta_{AB} - 1) \\ + \frac{1}{2}\chi_3^{(1)}R(A)R(C)(3 \cos^2\theta_{AC} - 1) \quad [37]$$

$$S_2 = \frac{1}{2}\chi_1^{(2)}R(A)R(B)(3 \cos^2\theta_{AB} - 1) + \chi_2^{(2)}R(B)R(B) \\ + \frac{1}{2}\chi_3^{(2)}R(B)R(C)(3 \cos^2\theta_{BC} - 1) \quad [38]$$

$$S_3 = \frac{1}{2}\chi_1^{(3)}R(A)R(C)(3 \cos^2\theta_{AC} - 1) \\ + \frac{1}{2}\chi_2^{(3)}R(B)R(C)(3 \cos^2\theta_{BC} - 1) \\ + \chi_3^{(3)}R(C)R(C), \quad [39]$$

where  $R(A)$ ,  $R(B)$ , and  $R(C)$  are the discrete values of  $R_{ik}^{-3}$  or  $C_{QF}$ , with

$$\chi_1^{(n)} = 1 \quad [40]$$

$$\chi_2^{(n)} = \frac{\begin{vmatrix} -(a_{11} - \lambda_n) & a_{13} \\ -a_{21} & a_{23} \end{vmatrix}}{\begin{vmatrix} a_{12} & a_{13} \\ (a_{22} - \lambda_n) & a_{23} \end{vmatrix}} \quad [41]$$

$$\chi_3^{(n)} = \frac{\begin{vmatrix} a_{12} & -(a_{11} - \lambda_1) \\ (a_{22} - \lambda_1) & -a_{21} \end{vmatrix}}{\begin{vmatrix} a_{12} & a_{13} \\ (a_{22} - \lambda_n) & a_{23} \end{vmatrix}}. \quad [42]$$

Here  $n = 1, 2, 3$  and

$$C_1^{(1)} = \frac{\begin{vmatrix} 1 & \chi_2^{(1)} & \chi_3^{(1)} \\ 0 & \chi_2^{(2)} & \chi_3^{(2)} \\ 0 & \chi_2^{(3)} & \chi_3^{(3)} \end{vmatrix}}{W} \quad [43]$$

$$C_1^{(2)} = \frac{\begin{vmatrix} \chi_1^{(1)} & 1 & \chi_3^{(1)} \\ \chi_1^{(2)} & 0 & \chi_3^{(2)} \\ \chi_1^{(3)} & 0 & \chi_3^{(3)} \end{vmatrix}}{W} \quad [44]$$

$$C_1^{(3)} = \frac{\begin{vmatrix} \chi_1^{(1)} & \chi_2^{(1)} & 1 \\ \chi_1^{(2)} & \chi_2^{(2)} & 0 \\ \chi_1^{(3)} & \chi_2^{(3)} & 0 \end{vmatrix}}{W} \quad [45]$$

$$C_2^{(1)} = \frac{\begin{vmatrix} 0 & \chi_2^{(1)} & \chi_3^{(1)} \\ 1 & \chi_2^{(2)} & \chi_3^{(2)} \\ 0 & \chi_2^{(3)} & \chi_3^{(3)} \end{vmatrix}}{W} \quad [46]$$

$$C_2^{(2)} = \frac{\begin{vmatrix} \chi_1^{(1)} & 0 & \chi_3^{(1)} \\ \chi_1^{(2)} & 1 & \chi_3^{(2)} \\ \chi_1^{(3)} & 0 & \chi_3^{(3)} \end{vmatrix}}{W} \quad [47]$$

$$C_2^{(3)} = \frac{\begin{vmatrix} \chi_1^{(1)} & \chi_2^{(1)} & 0 \\ \chi_1^{(2)} & \chi_2^{(2)} & 1 \\ \chi_1^{(3)} & \chi_2^{(3)} & 0 \end{vmatrix}}{W} \quad [48]$$

$$C_3^{(1)} = \frac{\begin{vmatrix} 0 & \chi_2^{(1)} & \chi_3^{(1)} \\ 0 & \chi_2^{(2)} & \chi_3^{(2)} \\ 1 & \chi_2^{(3)} & \chi_3^{(3)} \end{vmatrix}}{W} \quad [49]$$

$$C_3^{(2)} = \frac{\begin{vmatrix} \chi_1^{(1)} & 0 & \chi_3^{(1)} \\ \chi_1^{(2)} & 0 & \chi_3^{(2)} \\ \chi_1^{(3)} & 1 & \chi_3^{(3)} \end{vmatrix}}{W} \quad [50]$$

$$C_3^{(3)} = \frac{\begin{vmatrix} \chi_1^{(1)} & \chi_2^{(1)} & 0 \\ \chi_1^{(2)} & \chi_2^{(2)} & 0 \\ \chi_1^{(3)} & \chi_2^{(3)} & 1 \end{vmatrix}}{W}, \quad [51]$$

where

$$W = \begin{vmatrix} \chi_1^{(1)} & \chi_2^{(1)} & \chi_3^{(1)} \\ \chi_1^{(2)} & \chi_2^{(2)} & \chi_3^{(2)} \\ \chi_1^{(3)} & \chi_2^{(3)} & \chi_3^{(3)} \end{vmatrix}. \quad [52]$$

At a given time  $t$  the molecules are statistically distributed among the three possible sites with probabilities  $P_A$ ,  $P_B$ , and  $P_C$ . These probabilities are

$$P_A = \frac{1}{K_{AB} + K_{AC} + 1} \quad [53]$$

$$P_B = \frac{1}{K_{AB}^{-1} + K_{BC} + 1} \quad [54]$$

$$P_C = \frac{1}{K_{AC}^{-1} + K_{BC}^{-1} + 1}, \quad [55]$$

where  $K_{AB} = k_{AB}/k_{BA}$ ,  $K_{BC} = k_{BC}/k_{CA}$ , and  $K_{AC} = K_{AB} \times K_{BC}$ .

### CORRELATION FUNCTIONS FOR COMPLEX MOTION CONSISTING OF TUNNELING AND JUMPS OVER THE BARRIER

We assume that jumps over the barrier and tunneling through the barrier are two independent reorientations. The geometries of both motions are the same, but the rate constants  $k_{xy}$ , where  $x, y \equiv A, B, C$ , are different and each motion has its own spectral density. Woessner (57) proved that if the random function for two independent reorientations can be written as a product of the functions, which are time dependent due to the separate reorientation, the correlation function for the complex motion is also a product of two correlation functions, that is

$$F^m(t) = f_1^m(t)f_2^m(t) \quad [56]$$

$$\begin{aligned} \langle F^m(t)F^{m*}(t + \tau) \rangle \\ = \langle f_1^m(t)f_1^{m*}(t + \tau) \rangle \langle f_2^m(t)f_2^{m*}(t + \tau) \rangle. \end{aligned} \quad [57]$$

Dunn and McDowell (58) and Latanowicz and Reynhardt (47, 59) developed a theory for a complex motion of molecular groups in solids. With a view to expressing the  $F^m(t)$  functions given in Eqs. [11] to [13] as products of two functions  $f_1^m(t)$  and  $f_2^m(t)$ , we write

$$f_1^0(t) = R(t)(1 - 3 \cos^2\vartheta(t)) \quad [58]$$

$$f_2^0(t) = r(t) \quad [59]$$

$$f_1^1(t) = R(t) \sin \vartheta(t) \cos \vartheta(t) \exp[i\phi(t)] \quad [60]$$

$$f_2^1(t) = r(t) \quad [61]$$

$$f_1^2(t) = R(t) \sin^2\vartheta(t) \exp[-2i\phi(t)] \quad [62]$$

$$f_2^2(t) = r(t), \quad [63]$$

where  $R(t) = R_{ik}^{-3}(t)$  or  $R(t) = C_{QF}(t)$  and  $r(t) = 1$ . The  $r$  value can also be time dependent if, for example, the proton pair distance changes due to the jumping or tunneling along the hydrogen bond of one proton. Assume that the time dependence of  $f_1^m(t)$  is due to thermally activated jumps over the barrier and that the time dependence of  $f_2^m(t)$  is due to tunneling.

#### A. 2U Potential

Recently Meyer and Ernst (60) calculated the spectral densities for a tunneling motion. Skinner and Trommsdorff (19) employed the Look and Lowe double inequivalent site model (50) and jump probabilities given by Eqs. [2] to [5] to calculate these values. In the Look and Lowe model it is assumed that the time for a jump between two potential minima is shorter than the lifetime at the equilibrium site. Therefore, the correlation functions for jumps over the barrier and tunneling in the 2U potential (Fig. 3b) follow from Eqs. [17] and [58] to [63],

$$\langle f_1^m(t)f_1^{m*}(t + \tau) \rangle = Z_m [C_1^{(O)} + C_2^{(O)}] \exp\left(-\frac{|\tau|}{\tau_2^{(O)}}\right), \quad [64]$$

$$\langle f_2^m(t)f_2^{m*}(t + \tau) \rangle = C_1^{(T)} + C_2^{(T)} \exp\left(-\frac{|\tau|}{\tau_2^{(T)}}\right), \quad [65]$$

where the correlation times for jumps over the barrier and tunneling are

$$\frac{1}{\tau_2^{(O)}} = k_{12}^{(O)} + k_{21}^{(O)} + k_{23}^{(O)} + k_{32}^{(O)} \quad [66]$$

$$\frac{1}{\tau_2^{(T)}} = k_{12}^{(T)} + k_{21}^{(T)} + k_{23}^{(T)} + k_{32}^{(T)}. \quad [67]$$

$k_{12}^{(O)}, k_{21}^{(O)}, k_{23}^{(O)}, k_{32}^{(O)}$  and  $k_{12}^{(T)}, k_{21}^{(T)}, k_{23}^{(T)}, k_{32}^{(T)}$  are rate constants for jumps over the barrier and tunneling, respectively, with

$$\begin{aligned} C_1^{(O)} &= \frac{K_{AB}^{(O)}}{(K_{AB}^{(O)} + 1)^2} \\ &\times [K_{AB}^{(O)-1}R(A)R(A) + K_{AB}^{(O)}R(B)R(B) \\ &+ R(A)R(B)(3 \cos^2\theta_{AB} - 1)] \end{aligned} \quad [68]$$

$$C_2^{(O)} = \frac{K_{AB}^{(O)}}{(K_{AB}^{(O)} + 1)^2} \times [R(A)R(A) + R(B)R(B) - R(A)R(B)(3 \cos^2 \theta_{AB} - 1)] \quad [69]$$

$$C_1^{(T)} = \frac{K_{AB}^{(T)}}{(K_{AB}^{(T)} + 1)^2} \times [(K_{AB}^{(T)-1} r(A)r(A) + K_{AB}^{(T)} r(B)r(B) + r(A)r(B)(3 \cos^2 \theta_{AB} - 1)] \quad [70]$$

$$C_2^{(T)} = \frac{K_{AB}^{(T)}}{(K_{AB}^{(T)} + 1)^2} \times [r(A)r(A) + r(B)r(B) - r(A)r(B)(3 \cos^2 \theta_{AB} - 1)]. \quad [71]$$

The equilibrium constants  $K_{AB}^{(O)}$  and  $K_{AB}^{(T)}$  are

$$K_{AB}^{(O)} = \frac{k_{12}^{(O)}}{k_{21}^{(O)}} = \frac{k_{23}^{(O)}}{k_{32}^{(O)}} \quad [72]$$

$$K_{AB}^{(T)} = \frac{k_{12}^{(T)}}{k_{21}^{(T)}} = \frac{k_{23}^{(T)}}{k_{32}^{(T)}}. \quad [73]$$

$R(A)$  and  $R(B)$  are the values of the functions  $R_{ik}^{-3}$  or  $C_{QF}$ .  $r(A)$  and  $r(B)$  are the values of the function  $r(t) = 1$  at the  $A$  and  $B$  sites. If  $R(B) \neq R(A)$ ,  $r(A) = 1$  and  $r(B) = R(B)/R(A)$ . Therefore, the correlation functions of a complex motion consisting of tunneling and jumps over the barrier are

$$\begin{aligned} \langle F^m(t) F^{m*}(t + \tau) \rangle &= Z_m \left[ C_1^{(O)} + C_2^{(O)} \exp\left(-\frac{|\tau|}{\tau_2^{(O)}}\right) \right] \\ &\times \left[ C_1^{(T)} + C_2^{(T)} \exp\left(-\frac{|\tau|}{\tau_2^{(T)}}\right) \right] \\ &= Z_m \left[ C_1 + C_2 \exp\left(-\frac{|\tau|}{\tau_2^{(T)}}\right) \right. \\ &\quad \left. + C_3 \exp\left(-\frac{|\tau|}{\tau_2^{(O)}}\right) \right. \\ &\quad \left. + C_4 \exp\left(-\frac{|\tau|}{\tau_2^i}\right) \right], \quad [74] \end{aligned}$$

where

$$C_1 = C_1^{(O)} C_1^{(T)} \quad [75]$$

$$C_2 = C_1^{(O)} C_2^{(T)} \quad [76]$$

$$C_3 = C_1^{(T)} C_2^{(O)} \quad [77]$$

$$C_4 = C_2^{(O)} C_2^{(T)} \quad [78]$$

and

$$\frac{1}{\tau_2^i} = \frac{1}{\tau_2^{(O)}} + \frac{1}{\tau_2^{(T)}}. \quad [79]$$

The spectral density for this complex motion is

$$J^m(\omega) = Z_m \left[ C_2 \frac{2\tau_2^T}{1 + (\omega\tau_2^T)^2} + C_3 \frac{2\tau_2^O}{1 + (\omega\tau_2^O)^2} + C_4 \frac{2\tau_2^i}{1 + (\omega\tau_2^i)^2} \right]. \quad [80]$$

The equilibrium constants  $K_{AB}^{(O)}$  and  $K_{AB}^{(T)}$  are

$$K_{AB}^{(O)} = \frac{k_{12}^{(O)}}{k_{21}^{(O)}} = \frac{k_{23}^{(O)}}{k_{32}^{(O)}} \quad [72]$$

$$K_{AB}^{(T)} = \frac{k_{12}^{(T)}}{k_{21}^{(T)}} = \frac{k_{23}^{(T)}}{k_{32}^{(T)}}. \quad [73]$$

$R(A)$  and  $R(B)$  are the values of the functions  $R_{ik}^{-3}$  or  $C_{QF}$ .  $r(A)$  and  $r(B)$  are the values of the function  $r(t) = 1$  at the  $A$  and  $B$  sites. If  $R(B) \neq R(A)$ ,  $r(A) = 1$  and  $r(B) = R(B)/R(A)$ . Therefore, the correlation functions of a complex motion consisting of tunneling and jumps over the barrier are

$$\begin{aligned} \langle F^m(t) F^{m*}(t + \tau) \rangle &= Z_m \left[ C_1^{(O)} + C_2^{(O)} \exp\left(-\frac{|\tau|}{\tau_2^{(O)}}\right) \right] \\ &\times \left[ C_1^{(T)} + C_2^{(T)} \exp\left(-\frac{|\tau|}{\tau_2^{(T)}}\right) \right] \\ &= Z_m \left[ C_1 + C_2 \exp\left(-\frac{|\tau|}{\tau_2^{(T)}}\right) \right. \\ &\quad \left. + C_3 \exp\left(-\frac{|\tau|}{\tau_2^{(O)}}\right) \right. \\ &\quad \left. + C_4 \exp\left(-\frac{|\tau|}{\tau_2^i}\right) \right], \quad [74] \end{aligned}$$

where

$$C_1 = C_1^{(O)} C_1^{(T)} \quad [75]$$

$$C_2 = C_1^{(O)} C_2^{(T)} \quad [76]$$

Using this spectral density, the relaxation rates due to jumps over the barrier and tunneling in an inequivalent double potential well are given by

$$\frac{1}{T_{1(1\rho)}} = C [C_2 f(\tau_2^{(T)}) + C_3 f(\tau_2^{(O)}) + C_4 f(\tau_2^i)], \quad [81]$$

where

$$C = \frac{3}{10} \gamma_i^4 \hbar^2 \quad [82]$$

for homonuclear dipolar  $1/T_1$  and  $1/T_{1\rho}$  with spin =  $\frac{1}{2}$ ,

$$C = \frac{2}{15} S(S+1) \gamma_I^2 \gamma_S^2 \quad [83]$$

for heteronuclear dipolar  $1/T_1$  and  $1/T_{1\rho}$ , and

$$C = \frac{3}{10} \pi^2 \quad [84]$$

for deuteron  $1/T_1$ . Also

$$f(\tau) = \frac{\tau}{1 + \omega_I^2 \tau^2} + \frac{4\tau}{1 + 4\omega_I^2 \tau^2} \quad [85]$$

for a homonuclear dipolar and deuteron  $1/T_1$ ,

$$f(\tau) = \frac{3}{2} \frac{\tau}{1 + 4\omega_I^2 \tau^2} + \frac{5}{2} \frac{\tau}{1 + \omega_I^2 \tau^2} + \frac{4\tau}{1 + 4\omega_I^2 \tau^2} \quad [86]$$



for a homonuclear dipolar  $1/T_{1\rho}$ ,

$$f(\tau) = \frac{\tau}{1 + (\omega_I - \omega_S)^2 \tau^2} + \frac{3\tau}{1 + \omega_I^2 \tau^2} + \frac{6\tau}{1 + (\omega_I + \omega_S)^2 \tau^2} \quad [87]$$

for a heteronuclear dipolar  $1/T_1$ , and

$$f(\tau) = \frac{4\tau}{1 + \omega_I^2 \tau^2} + \frac{6\tau}{1 + \omega_S^2 \tau^2} + \frac{\tau}{1 + (\omega_I - \omega_S)^2 \tau^2} + \frac{3\tau}{1 + \omega_I^2 \tau^2} + \frac{6\tau}{1 + (\omega_I + \omega_S)^2 \tau^2} \quad [88]$$

for a heteronuclear dipolar  $1/T_{1\rho}$ .

The spectral density given by Eq. [80] can be substituted into Eqs. [15] and [16] to obtain

$$M_2 = \frac{3}{2} \gamma^{-2} C \left[ C_1 + C_2 \frac{2}{\pi} \tan^{-1}(\gamma_I \tau_2^{(T)} \sqrt{M_2}) + C_3 \frac{2}{\pi} \tan^{-1}(\gamma_I \tau_2^{(O)} \sqrt{M_2}) \times C_4 \frac{2}{\pi} \tan^{-1}(\gamma_I \tau_2^{i} \sqrt{M_2}) \right], \quad [89]$$

where  $C_2$ ,  $C_3$ ,  $C_4$ ,  $\tau_2^{(O)}$ ,  $\tau_2^{(T)}$ , and  $\tau_2^i$  are given by Eqs. [75] to [78], [66], [67], and [79]. The  $C$ 's are given by Eq. [82] or [83].

The temperature dependence of  $T_1$  for a complex motion (jumps over the barrier and tunneling through the barrier) of an interproton vector  $R_{ik}$  ( $=1.6 \text{ \AA}$ ), between two sites of unequal energy (Fig. 3a), is illustrated in Figs. 4a–4d. The temperature dependence for the separate reorientations (jumps over the barrier and tunneling) is also shown in these figures. At low temperatures the relaxation rates are dominated by the tunneling motion and a flat  $T_1$  temperature dependence is observed. At higher temperatures the  $T_1$  minimum due to the complex motion differs from the temperature dependence of  $T_1$  due to jumps over the barrier (solid lines in Figs. 4a–4d). Usually it is assumed that both motions, tunneling and jumps over the barrier, contribute to the total rate constants (19, 28, 34, 35, 60–62):

$$k_{AB}^{\text{total}} = k_{AB}^{(O)} + k_{AB}^{(T)} \quad [90]$$

$$k_{BA}^{\text{total}} = k_{BA}^{(O)} + k_{BA}^{(T)}. \quad [91]$$

This is the case if both motions contributing to the complex motion have correlation functions which decrease to zero:

$$\langle F^m(t) F^m(t + \tau) \rangle^{(O)} = Z_m C_2^{(O)} \exp\left(-\frac{|\tau|}{\tau_2^{(O)}}\right) \quad [92]$$

$$\langle F^m(t) F^m(t + \tau) \rangle^{(T)} = C_2^{(T)} \exp\left(-\frac{|\tau|}{\tau_2^{(T)}}\right). \quad [93]$$

However, as can be seen from Eqs. [64] and [65], the correlation functions decrease to  $Z_m C_2^{(O)}$  and  $C_2^{(T)}$ , respectively. However, if we assume in Eq. [18] that  $k_{23} = k_{32} = 0$  and, therefore,  $\tau_2 = \tau_2^{\text{total}} = (k_{12}^{(O)} + k_{21}^{(O)} + k_{12}^{(T)} + k_{21}^{(T)})^{-1}$  and substitute Eq. [18] into Eqs. [6], [10], and [17], we obtain the equation given by Skinner and Trommsdorff (19) ( $R(A) = R(B) = R_{ik}^{-3}$ ):

$$\frac{1}{T_1} = \frac{9}{10} \gamma_I^4 \hbar^2 \frac{K_{AB}}{(1 + K_{AB})^2} R_{ik}^{-3} \sin^2 \theta \times \left[ \frac{\tau_2^{\text{total}}}{1 + \omega_I^2 (\tau_2^{\text{total}})^2} + 4 \frac{\tau_2^{\text{total}}}{1 + 4\omega_I^2 (\tau_2^{\text{total}})^2} \right]. \quad [94]$$

As can be seen from Figs. 4b and 4d, the temperature dependence of  $T_1$ , given by Eq. [94], differs from that given by Eq. [81] for the same motional parameters. The most prominent difference is between Fig. 4a and Fig. 4b, where  $K_0^{(T)} = 5 \times 10^8 \text{ s}^{-1}$ . For  $K_0^{(T)} = 5 \times 10^7 \text{ s}^{-1}$  (Figs. 4c and 4d) the difference is less prominent. It is also clear that at temperatures below room temperature the difference between the temperature dependence of  $T_1$  according to the Skinner–Trommsdorff (Eq. [5]) and Nagaoka (Eq. [4]) models is negligible.

The temperature dependence of the second moment for a complex motion consisting of jumps over the barrier ( $k_0^{(O)} = 2 \times 10^{12} \text{ s}^{-1}$ ) and tunneling ( $k_0^{(T)} = 2 \times 10^{12} \text{ s}^{-1}$ ) of an interproton vector  $R_{ik}$  ( $=1.6 \text{ \AA}$ ) between two sites of unequal energy (Fig. 3a) is illustrated in Fig. 5. The temperature dependencies of the separate motions are also shown in these figures.

Using the Skinner–Trommsdorff tunneling rate constant (Eq. [5]), it is clear that different calculations of the correlation function result in temperature dependencies of the second moment which differ dramatically. The method proposed by Woessner (57) (Eq. [57]) leads to separate reductions for tunneling at low temperatures and hopping over the barrier at high temperatures. The magnitudes of the reductions depend on the geometry of the motion. These reductions appear when the linewidth  $\delta\nu$  ( $2\pi\delta\nu = \gamma\sqrt{M_2}$ ), expressed in frequency units, is comparable with the frequency of the relevant molecular motion. On the other hand, the assumption of the total rate constant (Eqs. [90] and [91]) results in only one reduction at a frequency  $\nu = 1/2\pi\tau_2^{\text{total}}$ , which is comparable with the linewidth. The circles in Fig. 5 coincide with the solid line, which shows the temperature dependence of the second moment for tunneling

only. Therefore, information about the composite motions is lost in the case of a complex motion.

### B. 3U Potential

The correlation functions of the two motions in the 3U potential (Fig. 3c) are given by Eq. [22] and, therefore, the correlation function for a complex motion (tunneling motion and jumps over the barrier) can be written as a product of the two correlation functions

$$C_6 = C_2^{(O)} \cdot C_2^{(T)} \quad [105]$$

$$C_7 = C_2^{(O)} \cdot C_3^{(T)} \quad [106]$$

$$C_8 = C_3^{(O)} \cdot C_2^{(T)} \quad [107]$$

$$C_9 = C_3^{(O)} \cdot C_3^{(T)}. \quad [108]$$

$C_1^{(O)}$ ,  $C_2^{(O)}$ ,  $C_3^{(O)}$  and  $C_1^{(T)}$ ,  $C_2^{(T)}$ , and  $C_3^{(T)}$  are given by Eqs. [34] to [36] with  $S_1$ ,  $S_2$ , and  $S_3$  given by Eqs. [37] to [39] for jumps over the barrier and

$$\begin{aligned} \langle F^m(t)F^{m*}(t + \tau) \rangle &= Z_m \left[ C_1^{(O)} + C_2^{(O)} \exp\left(-\frac{|\tau|}{\tau_{31}^{(O)}}\right) + C_3^{(O)} \exp\left(-\frac{|\tau|}{\tau_{32}^{(O)}}\right) \right] \\ &\quad \times \left[ C_1^{(T)} + C_2^{(T)} \exp\left(-\frac{|\tau|}{\tau_{31}^{(T)}}\right) + C_3^{(T)} \exp\left(-\frac{|\tau|}{\tau_{32}^{(T)}}\right) \right] \\ &= C_1 + C_2 \exp\left(-\frac{|\tau|}{\tau_{31}}\right) + C_3 \exp\left(-\frac{|\tau|}{\tau_{32}}\right) + C_4 \exp\left(-\frac{|\tau|}{\tau_{31}}\right) + C_5 \exp\left(-\frac{|\tau|}{\tau_{32}}\right) \\ &\quad + C_6 \exp\left(-\frac{|\tau|}{\tau_{i1}}\right) + C_7 \exp\left(-\frac{|\tau|}{\tau_{i2}}\right) + C_8 \exp\left(-\frac{|\tau|}{\tau_{i3}}\right) + C_9 \exp\left(-\frac{|\tau|}{\tau_{i4}}\right), \quad [95] \end{aligned}$$

where

$$1/\tau_{i1} = \frac{1}{\tau_{31}^{(O)}} + \frac{1}{\tau_{31}^{(T)}} \quad [96]$$

$$1/\tau_{i2} = \frac{1}{\tau_{31}^{(O)}} + \frac{1}{\tau_{32}^{(T)}} \quad [97]$$

$$1/\tau_{i3} = \frac{1}{\tau_{32}^{(O)}} + \frac{1}{\tau_{31}^{(T)}} \quad [98]$$

$$1/\tau_{i4} = \frac{1}{\tau_{32}^{(O)}} + \frac{1}{\tau_{32}^{(T)}}. \quad [99]$$

The values of  $\tau_{31}^{(O)}$ ,  $\tau_{32}^{(O)}$ ,  $\tau_{31}^{(T)}$ , and  $\tau_{32}^{(T)}$  are given by Eqs. [26] and [27], respectively.  $k_{AB}$ ,  $k_{BA}$ ,  $k_{CB}$ , and  $k_{BC}$  for tunneling and jumps over the barrier are given by Eqs. [1] to [5].

$$C_1 = C_1^{(O)} \cdot C_1^{(T)} \quad [100]$$

$$C_2 = C_1^{(O)} \cdot C_2^{(T)} \quad [101]$$

$$C_3 = C_1^{(O)} \cdot C_3^{(T)} \quad [102]$$

$$C_4 = C_1^{(T)} \cdot C_2^{(O)} \quad [103]$$

$$C_5 = C_1^{(T)} \cdot C_3^{(O)} \quad [104]$$

$$S_1 = \chi_1^{(1)} r(A)r(A) + \frac{1}{2}\chi_2^{(1)} r(A)r(B)(3 \cos^2\theta_{AB} - 1) + \frac{1}{2}\chi_3^{(1)} r(A)r(C)(3 \cos^2\theta_{AC} - 1) \quad [109]$$

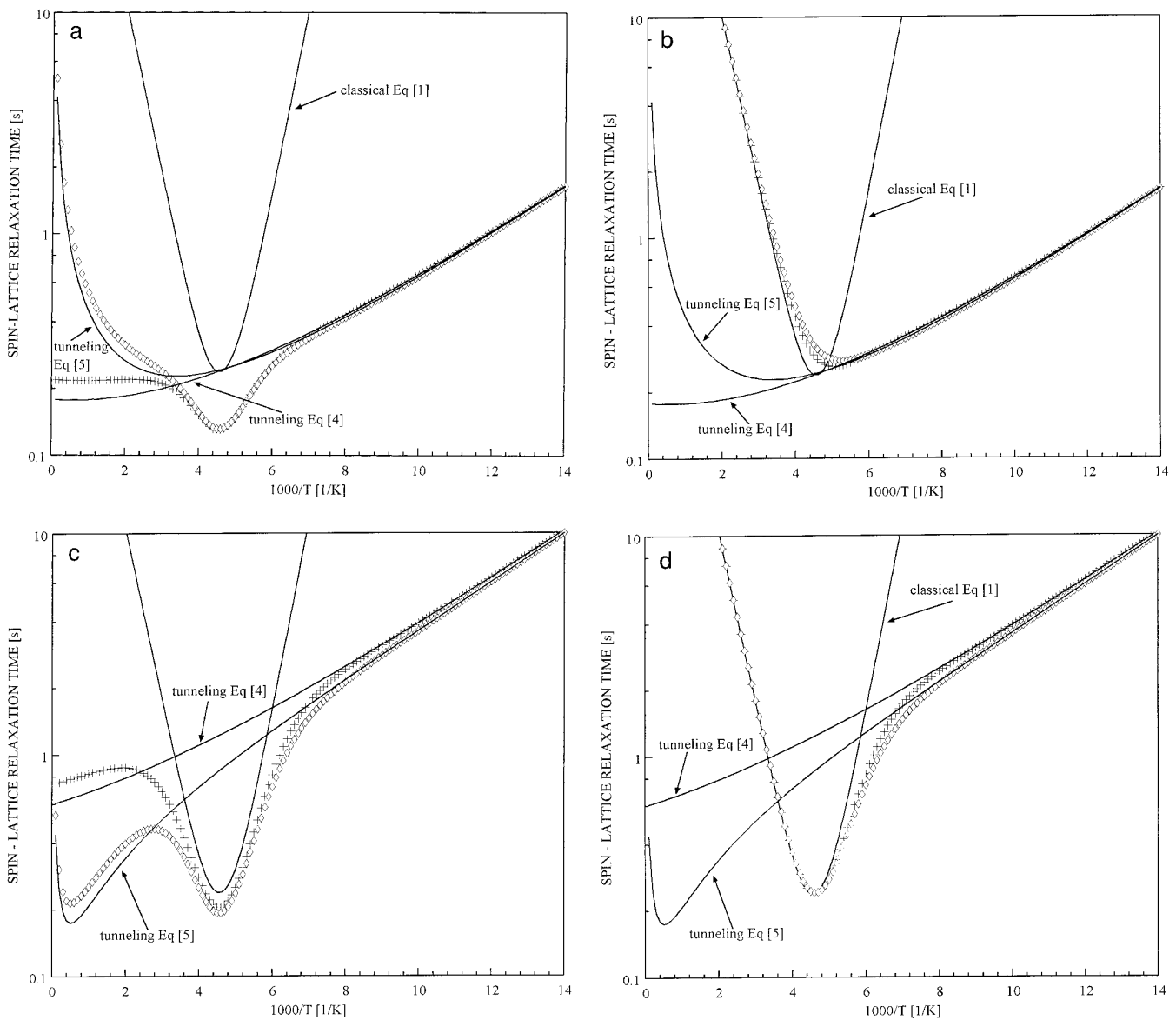
$$S_2 = \chi_2^{(2)} r(B)r(B) + \frac{1}{2}\chi_1^{(2)} r(A)r(B)(3 \cos^2\theta_{AB} - 1) + \frac{1}{2}\chi_3^{(2)} r(B)r(C)(3 \cos^2\theta_{BC} - 1) \quad [110]$$

$$S_3 = \chi_3^{(3)} r(C)r(C) + \frac{1}{2}\chi_2^{(3)} r(B)r(C)(3 \cos^2\theta_{BC} - 1) + \frac{1}{2}\chi_1^{(3)} r(A)r(C)(3 \cos^2\theta_{AC} - 1) \quad [111]$$

for tunneling with  $\chi_m^n$  given by Eqs. [40] to [42] and tunneling rate constants  $k_{AB}^{(T)}$ ,  $k_{AC}^{(T)}$ , and  $k_{BC}^{(T)}$  given by Eqs. [2] to [5]. If the internuclear distances change during the tunneling motion,  $r(B) = R(B)/R(A)$  and  $r(C) = R(C)/R(A)$ .

It seems that the proper approach is to treat the separate motions as a complex motion. The spectral density for the complex motion is

$$\begin{aligned} J^m(\omega) &= C_2 \frac{2\tau_{31}^{(T)}}{1 + \omega^2\tau_{31}^{(T)}} + C_3 \frac{2\tau_{32}^{(T)}}{1 + \omega^2\tau_{32}^{(T)}} + C_4 \frac{2\tau_{31}^{(O)}}{1 + \omega^2\tau_{31}^{(O)}} \\ &\quad + C_5 \frac{2\tau_{32}^{(O)}}{1 + \omega^2\tau_{32}^{(O)}} + C_6 \frac{2\tau_{i1}}{1 + \omega^2\tau_{i1}} \\ &\quad + C_7 \frac{2\tau_{i2}}{1 + \omega^2\tau_{i2}} + C_8 \frac{2\tau_{i3}}{1 + \omega^2\tau_{i3}}. \quad [112] \end{aligned}$$



**FIG. 4.** The temperature dependence of  $T_1$  (75 MHz) for  $R_{ik}$  ( $=1.6 \text{ \AA}$ ) hopping over the barrier ( $k_0^{(0)} = 2 \times 10^{12} \text{ s}^{-1}$ ) and tunneling through the barrier ((a, b)  $k_0^{(T)} = 5 \times 10^8 \text{ s}^{-1}$ ; (c, d)  $k_0^{(T)} = 5 \times 10^7 \text{ s}^{-1}$ ) in a double potential well (Fig. 3a) for tunneling rates given by Eq. [5] (diamonds) and Eq. [4] (crosses). Sites are displaced by  $\theta = 30^\circ$ . (a, c) Both motions are components of a complex motion (Eq. [81]). (b, d) Motion is described by a single correlation function with a common rate constant (Eqs. [90] to [94]). Other values are  $E_{AB} = 16.8 \text{ kJ/mol}$  and  $E_{BA} = 14.7 \text{ kJ/mol}$ . Solid lines represent relaxation times for separate reorientations—jumps over the barrier and tunneling.

Using these spectral densities, the relaxation rates and second moment of an NMR line, due to jumps over the barrier and tunneling in a inequivalent triple potential well, are found to be

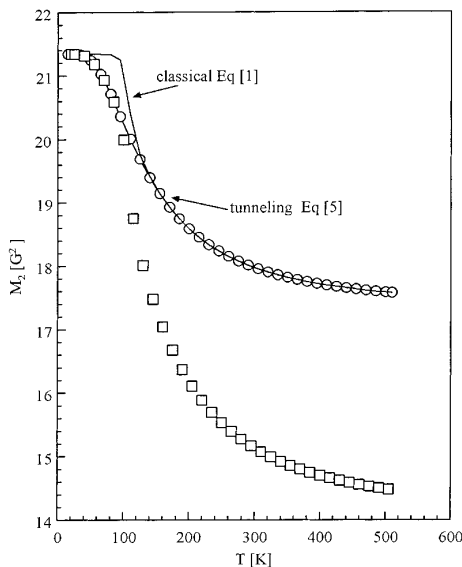
$$\frac{1}{T_{1(1\rho)}} = C[C_2 f(\tau_{31}^{(T)}) + C_3 f(\tau_{32}^{(T)}) + C_4 f(\tau_{31}^{(O)}) + C_5 f(\tau_{32}^{(O)}) + C_6 f(\tau_{i1}) + C_7 f(\tau_{i2}) + C_8 f(\tau_{i3}) + C_9 f(\tau_{i4})], \quad [113]$$

$$M_2 = \frac{3}{2} \gamma^{-2} C \left[ C_1 + C_2 \frac{2}{\pi} \tan^{-1}(\gamma_N \sqrt{M_2} \tau_{31}^{(T)}) + C_3 \frac{2}{\pi} \tan^{-1}(\gamma_N \sqrt{M_2} \tau_{32}^{(T)}) + C_4 \frac{2}{\pi} \tan^{-1}(\gamma_N \sqrt{M_2} \tau_{31}^{(O)}) + C_5 \frac{2}{\pi} \tan^{-1}(\gamma_N \sqrt{M_2} \tau_{32}^{(O)}) \right]$$

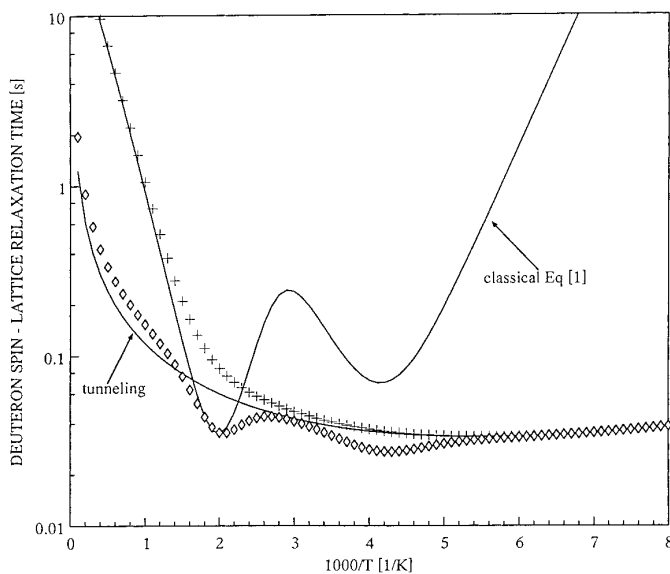
$$\begin{aligned}
& + C_6 \frac{2}{\pi} \tan^{-1}(\gamma_I \sqrt{M_2} \tau_{i1}^{(T)}) \\
& + C_7 \frac{2}{\pi} \tan^{-1}(\gamma_I \sqrt{M_2} \tau_{i2}) \\
& + C_8 \frac{2}{\pi} \tan^{-1}(\gamma_I \sqrt{M_2} \tau_{i3}) \\
& + C_9 \frac{2}{\pi} \tan^{-1}(\gamma_I \sqrt{M_2} \tau_{i4}) \Big], \quad [114]
\end{aligned}$$

where  $C$  and  $f(\tau)$  are given by Eqs. [82] to [88] and  $P_A$ ,  $P_B$ , and  $P_C$  are given by Eqs. [53] to [55].

The temperature dependence of the deuteron  $T_1$  for a complex motion of the axially symmetric field gradient tensor (taking  $q_{zz}$  to be along the chemical bond directions with  $C_{QF} = 150$  kHz) involved in a complex motion (jumps over the barrier and tunneling) between three inequivalent sites, as shown in Fig. 3c with  $E_{AB} - E_{BA} = 2.1$  kJ/mol and  $E_{CB} - E_{BC} = 0.8$  kJ/mol, is illustrated in Fig. 6. The separate temperature dependencies for jumps over the barrier and tunneling are also shown in this figure. For such a triple potential well a splitting of the  $T_1$  minimum is observed for jumps over the barrier (53, 59).



**FIG. 5.** Temperature dependence of the second moment of the NMR line ( $R_{ik} = 1.6$  Å) for hopping over the barrier ( $k_0^{(O)} = 2 \times 10^{12}$  s $^{-1}$ ) and tunneling ( $k_0^{(T)} = 5 \times 10^8$  s $^{-1}$ ) in a double potential well (Fig. 3a) for tunneling rates given by Eq. [5]. Sites are displaced by  $\theta = 30^\circ$ . (Squares) Both motions are components of a complex motion. (Circles) Motion is described by a single correlation function with a common rate constant. Other values are  $E_{AB} = 16.8$  kJ/mol and  $E_{BA} = 14.7$  kJ/mol. Solid lines represent second moments for separate reorientations—jumps over the barrier and tunneling.



**FIG. 6.** The temperature dependence of deuteron  $T_1$  (46 MHz) ( $C_{QF} = 150$  kHz) for jumping over the barrier ( $k_0^{(O)} = 2 \times 10^{12}$  s $^{-1}$ ) and tunneling through the barrier ( $k_0^{(T)} = 2 \times 10^8$  s $^{-1}$ ) in a triple potential well for tunneling rates given by Eq. [5]. Sites are displaced by  $\theta_{AB} = \theta_{BC} = 30^\circ$ . (Squares) Both motions are components of a complex motion (Eq. [113]). (Crosses) Motion is described by a single correlation function with total rate constants  $k_{xy}$ , where  $x, y = A, B, C$  (Eqs. [90] and [91]). Other values are  $E_{AB} = 35.6$  kJ/mol,  $E_{BA} = 33.5$  kJ/mol,  $E_{BC} = 15$  kJ/mol, and  $E_{CB} = 16.8$  kJ/mol.  $E_{AC} = E_{CA} \rightarrow \infty$ . Solid lines represent relaxation times for separate reorientations—jumps over the barrier and tunneling.

The low-temperature relaxation rates are dominated by tunneling, while the higher temperature minimum of  $T_1$  exhibits a different temperature dependence for different ways of treating the motions. Tunneling with a very low activation energy ( $E_{AB} - E_{BA} = 2.1$  kJ/mol and  $E_{AC} - E_{CA} = 0.8$  kJ/mol) contributes to  $T_1$  over the entire temperature range.

#### APPLICATION OF THEORY TO EXPERIMENTAL DATA FOR NAPHTHAZARIN B

The experimental temperature dependencies of  $T_1$  (200 and 75 MHz) and  $T_{1\rho}$  ( $H_1$  values of 9.8, 14, and 25 G) are displayed in Fig. 7 for polycrystalline naphthazarin B. At each frequency one relaxation time minimum was observed as a function of temperature. At high temperatures  $T_{1\rho}$  decreases with increasing temperature, but a minimum was not reached.

Since the dynamic equilibrium between the  $A$  and  $B$  tautomers (Fig. 1a) includes configurations  $C$  and  $C'$  (Fig. 1b), which correspond to energy maxima, the  $2U$  potential well (Fig. 3b) was assumed and Eq. [81] was employed to ana-

lyze the data in the temperature range of the observed minima. The angles  $\theta_{ikAB}$  and interatomic distances  $R_{ikA}$  and  $R_{ikB}$  were calculated for the separate  $ik$  spin pairs (5). Since each proton of the naphthazarin molecule interacts with five nearest neighbor protons, the addition of interactions was assumed and the average value of the relaxation rate calculated. The mechanism responsible for the decrease of  $T_{1\rho}$  at high temperatures could be due to the breaking of hydrogen bonds and the additional motional freedom associated with it. However, since the  $T_{1\rho}$  minimum was not observed, this motion cannot be identified. The temperature dependencies of the relaxation rates over the entire temperature range are therefore given by

$$\frac{1}{T_{1(1\rho)}} = \frac{1}{6} \sum_{i=1}^n \sum_{k=1}^n \left( \frac{1}{T_{1(1\rho)ik}} \right) + Cf(\tau_c), \quad [115]$$

where  $1/T_{1ik}$  and  $1/T_{1\rho ik}$  are given by Eq. [81] with  $\tau_2^{(T)}$ ,  $\tau_2^{(O)}$ , and  $f(\tau_c)$  given by Eqs. [5], [1], and [85], respectively.  $C$  is the relaxation constant and

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{RT}\right), \quad [116]$$

where  $\tau_c$  is the correlation time and  $E_a$  is the activation energy. Best simultaneous fits to all the data are shown in Fig. 7. The parameters thus obtained are listed in Table 1.

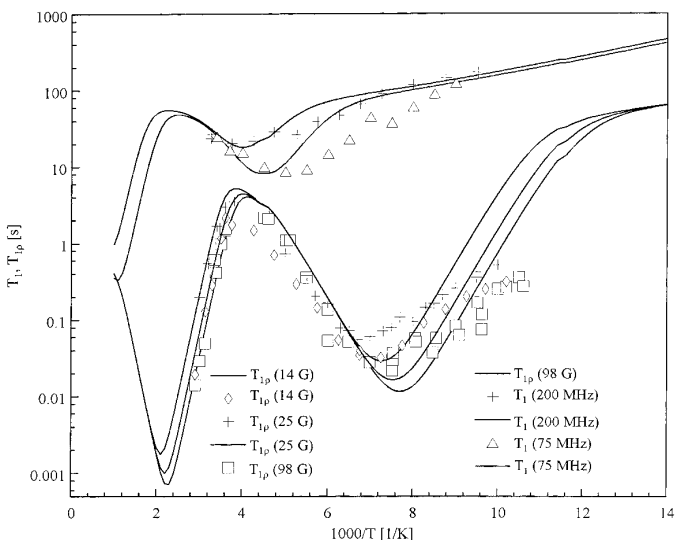


FIG. 7. Proton spin-lattice relaxation times as a function of inverse temperature for naphthazarin B. Solid lines represent the best fit of Eq. [81] to the data ( $1 \text{ G} = 10^{-4} \text{ T}$ ).

TABLE 1  
Motional Parameters for Proton Transfer in the Hydrogen Bond in Naphthazarin B

Parameter	Value
$k_0^{(O)}$ ( $\text{s}^{-1}$ )	$2 \times 10^{12}$
$k_0^{(T)}$ ( $\text{s}^{-1}$ )	$5 \times 10^8$
$\tau_0$ (s)	$2 \times 10^{-12}$
$E_{12}$ (kJ/mol)	19.3
$E_{21}$ (kJ/mol)	16.8
$E_{23}$ (kJ/mol)	15.9
$E_a$ (kJ/mol)	50

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