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Tunneling Molecular Dynamics in the Light of the Corpuscular-Wave Dualism Theory

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This paper presents the experimental demonstration of the corpuscular-wave dualism theory. The correlation between the de Broglie wavelength related to the thermal motion and the potential barrier width and height is reported. The stochastic jumps of light atoms (hydrogen, deuterium) between two equilibrium sites A and B (identical geometry) occur via different pathways; one pathway is over the barrier (classical dynamics), and the other one is through the barrier (tunneling). On the over-the-barrier pathway, there are no obstacles for the de Broglie waves, and this pathway exists from high to low temperatures up to 0 K because the thermal energy is subjected to the Maxwell distribution and a certain number of particles owns enough energy for the hopping over the barrier. On the tunneling pathway, the particles pass through the barrier, or they are reflected from the barrier. Only particles with the energy lower than barrier heights are able to perform a tunneling hopping. The de Broglie waves related to these energies are longer than the barrier width. The Schrödinger equation is applied to calculate the rate constant of tunneling dynamics. The Maxwell distribution of the thermal energy has been taken into account to calculate the tunneling rate constant. The equations for the total spectral density of complex motion derived earlier by us together with the expression for the tunneling rate constant, derived in the present paper, are used in analysis of the temperature dependence of deuteron spin−lattice relaxation of the ammonium ion in the deuterated analogue of ammonium hexachloroplumbate ($(ND_4)_2PbCl_6$). It has been established that the equation $C_pT_{tun} = E_H$ (thermal energy equals activation energy), where C_p is the molar heat capacity (temperature-dependent, known from literature), determines directly the low temperature T_{tun} at which the de Broglie wavelength, $\lambda_{deBroglie}$, related to the thermal energy, C_pT, is equal to the potential barrier width, L. Above T_{tun}, the $\lambda_{deBroglie}$ wavelength related to the C_pT energy is shorter than the potential barrier width and not able to overcome the barrier. The activation energy E_H equals 7.5 kJ/mol, and therefore, the T_{tun} temperature for deuterons in $((ND_4)_2PbCl_6$ is 55.7 K. The agreement between the potential barrier width following from the simple geometrical calculations ($L = 0.722$ Å) and de Broglie wavelength at T_{tun} ($L = 0.752$ Å) is good. The temperature plots of the deuteron correlation times for $(ND_4)_2PbCl_6$ reveal comparable values of the correlation times of the tunneling, ($\tau^{(T)}$), and over-the-barrier jumps ($\tau^{(H)}$) near 34.8 K. Matsuo, on the basis of the molar heat capacity study, found the first-order phase transition at this temperature.

Introduction

Corpuscular-wave dualism is revealed when the length of the electromagnetic or de Broglie wave comes up to a size comparable to that of the object. Experimental evidence of this phenomenon comes from the diffraction of light, X-rays, electrons, or neutrons as well as the photoelectricity. Well-recognized de Broglie waves are those accompanying the motion of electrons in the electric field (Davisson and Germer experiment). The phenomena of diffraction and interference occur at the de Broglie wavelength comparable with the distances between the atomic planes in the crystal.

The tunneling dynamics seems to be also a proof of the corpuscular-wave dualism. As follows from the Schrödinger equation, the possibility of tunneling dynamics appears when the energy of the particle is lower than the potential barrier height. The kinetic energy of the particle in molecular systems is the thermal energy. The thermal energy causes the stochastic (thermally activated) reorientations of molecules and molecular groups and de Broglie waves related to these motions. As follows from the Schrödinger equation, the de Broglie waves related to the particles in the space of the potential barrier pass through the barrier, or they are reflected from the barrier. However, on the classical pathway (over the barrier), there are no obstacles for the de Broglie waves.

Study of stochastic molecular motions in solids is an important application of the nuclear magnetic relaxation method. Usually, interpretation of the experimentally determined temperature dependence of spin−lattice relaxation time permits identification of molecular motions and determination of the relevant motion parameters, including activation energies and rate constants (correlation times). Recently, theoretical equations for the spectral density of a methyl group motion have been published.[1,2] In this theory, C_3 hindered rotation of a methyl group is considered as a complex motion consisting of jumps

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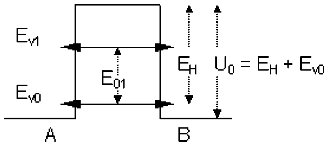

Figure 1. Scheme of the tunneling pathway from the A to B site through a potential barrier; L and U_0 are the barrier width and height, E_{v0} and E_{v1} are energy levels of the vibrational states v0 and v1, and E_H is the activation energy.

over a potential barrier (Arrhenius pathway, classical motion) and tunneling jumps through the potential barrier (tunneling pathway, quantum mechanical type of motion). Tunneling jumps through the barrier and jumps over the barrier cause transport of a mass between the same equilibrium sites, but they are based on different probabilities of occurrence (rate constants).

The purpose of the paper is to present the application of the tunneling rate constant (probability of tunneling, coefficient of the transparency of the potential barrier) according to the Schrödinger equation to analyze the spin−lattice relaxation in a wide temperature regime. The Maxwell distribution of thermal energy will be taken into account in our calculations of the tunneling rate constant. Recently, the tunneling rate constant according to Schrödinger has been proposed in a number of our papers,[1−5] but the problem of the Maxwell distribution of thermal energy has not been considered. We show, on a previously analyzed example[6] of BAC-h6 data,[7] how taking into account the Maxwell distribution changes the theoretical temperature dependences of the T_1.

Our approach to the tunneling and classical dynamics differs from that known from literature. We treat the tunneling and classical hopping as a complex stochastic motion, while these are treated in the literature as a uniform motion, described by a single rate constant. Usually the Müller-Warmuth approach[8,9] is applied to study the molecular dynamics of methyl-bearing solids, and the Skinner and Trommsdorff approach[10] is for hydrogen-bonded tautomers. The single rate constant, proposed in both approaches, is not convincing, which was discussed in our papers.[1−6,11]

The Schrödinger equation applied by us solves several problems. (1) The same expressions for the tunneling rate constant can be used for tunneling hopping of the proton/deuteron in proton transfer and in methyl group hindered rotation. (2) We are able to explain why the tunneling is detectable only at low temperatures up to a certain temperature. (3) It can be shown that the tunneling dynamics of particular atoms begins when the de Broglie wavelength related to the kinetic energy of these atoms (thermal motion) is comparable with the potential barrier width. (4) The over-the-barrier motion can exist up to 0 K because there is no obstacle for the de Broglie waves.

The slower slope on the low-temperature side of the minimum of the $\ln(T_1)$ versus $(1000/T)$ dependence has been observed in a deuterated analogue of ammonium hexachloroplumbate, $(ND_4)_2PbCl_6$.[12] Filipek et al.[12] indicated the tunneling dynamics as an effective mechanism of relaxation below 50 K but did not analyze this mechanism. In the present paper, the data[12] are analyzed in terms of the Schrödinger equation and in the light of the corpuscular-wave dualism.

Reorientation Model

According to the classical mechanics, to overcome a potential barrier, the particles must have a kinetic energy (thermal energy) greater than the height of the barrier (Figure 1). The thermal energy higher than the potential barrier height allows hopping over the barrier. The probability of thermally activated hopping over the potential barrier (rate constant, $k^{(H)}$) is proportional to the barrier height (Arrhenius law); therefore

$$k^{(H)} = k_0^{(H)} \exp(-E_H/RT) \tag{1}$$

where $k_0^{(H)}$ is the preexponential factor, $E_H = V_H - E_{v0}$ is the molar activation energy, V_H and E_{v0} are the potential barrier height and the energy of the ground-state vibrational level for the Avogadro number of particles.

The hopping over the barrier takes place over the entire thermodynamic temperature regime, T, because the thermal energy is subjected to the Maxwell distribution, and a certain number of particles own E_H energy and are able to perform a hopping over the barrier. Zero Kelvin is the final temperature for the probability of classical motion. Moreover, on the Arrhenius pathway, there are no obstacles for the de Broglie waves.

According to quantum mechanics, there is a possibility of passing through a potential barrier by the particles whose kinetic energy is lower than the barrier height. The solution of the Schrödinger equation for the problem of the tunneling motion of particles through the potential barrier explicitly gives the rate constant of tunneling jumps (probability of tunneling, coefficient of transparency of the barrier),[1−5] that is

$$k^{(T)} = k_0^{(T)} e^{-(2L/\hbar)\sqrt{2m(U_0-E)}} \tag{2}$$

where m is mass of the particle, $k_0^{(T)}$ is the preexponential factor, U_0 and L are the height and width of the potential barrier (Figure 1), and E is the energy of the particle.

Equation 2 indicates that the probability of tunneling is greater than zero only when the kinetic energy of the particle, E, is lower than the height of the potential barrier, U_0. Therefore, the tunneling jumps begin at a temperature at which the kinetic energy of the particle becomes equal to that of the potential barrier height, ($E = U_0$). The probability of tunneling increases when $E \rightarrow 0$. The particles are also reflected from the barrier (coefficient of the reflection from the barrier, probability of the reflection). Thus, on the tunneling pathway, the potential barrier is an obstacle for the de Broglie waves related to thermal energies of the particles. However, the energy higher than the potential barrier height allows hopping over the barrier (Arrhenius law).

The energy

$$N_{Av}E = C_p\, T + E_{v0} \tag{3}$$

characterizes the energy of the Avogadro number of particles at the ground-state vibrational level. The C_pT, where C_p is the molar heat capacity and T is temperature in the Kelvin scale, is the thermal energy of the Avogadro number of particles.

The potential barrier height of the Avogadro number of particles equals

$$N_{Av}U_0 = E_H + E_{v0} \tag{4}$$

Thus, eq 2 can be rewritten as

$$k^{(T)} = k_0^{(T)} e^{-B\sqrt{E_H - C_pT}} \tag{5}$$

where

$$B = \frac{2L}{\hbar}\sqrt{\frac{2m}{N_{Av}}} \tag{6}$$

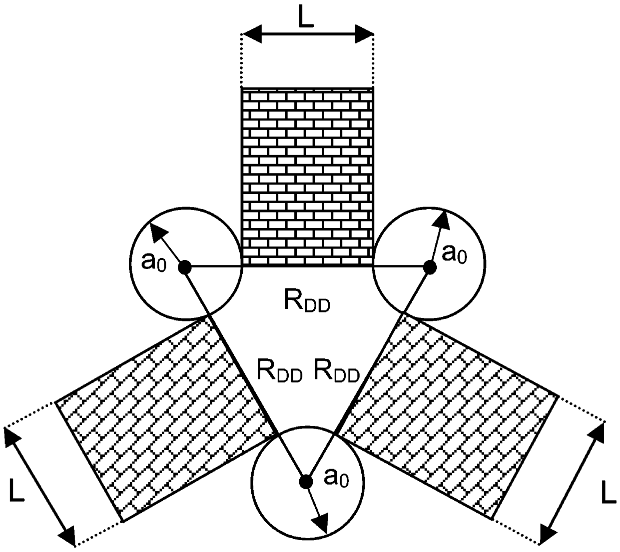

Figure 2. Three deuterons at the distances of $R_{DD} = 1.78$ Å are separated by the barriers of the widths $L = R_{DD} - 2a_0 = 0.722$ Å; $a_0 = 0.529$ Å is the radius of the first orbit of Bohr.

The value of B in eq 6 depends on the mass, m, of the tunneling particle and on the width of the potential barrier, L. The tunneling jumps are expected for the light atoms, H and D, hopping in hydrogen bonds and methyl groups. The mass of the tunneling deuteron is $m = 3.346\ 10^{-27}$ kg.

As follows from the structural data of the deuterated analogue of ammonium hexachloroplumbate, $(ND_4)_2PbCl_6$, three deuterons of the ND_4 group are at the tetrahedron apexes, while the fourth one is along the N−D bond which is the symmetry axis of this molecular group. In such a structure, deuterons undergo hindered rotation, C_3, analogous to that of hydrogen atoms in a methyl group. The fourth deuteron is invisible for this rotation. The distances between deuterons are $R_{DD} = 1.78$ Å. Taking into regard the atomic size (the radius of the first Bohr orbit $a_0 = 0.529$ Å), it is possible to calculate the potential barrier width L, which seems to be simply $L = R_{DD} - 2a_0 = 0.722$ Å (Figure 2), and then, the value of B is $0.144\ (\sqrt{J})^{-1}$.

Equation 5 determines the temperature T_{tun} at which the probability of tunneling becomes nonzero and stays nonzero for temperatures lower than T_{tun}, where

$$T_{tun} = \frac{E_H}{C_p} \tag{7}$$

Despite the thermal energy C_pT reaching the value of E_H at increasing temperature, the thermal energies of some fraction of the molecules are lower than E_H. Therefore, more detailed consideration of the tunneling rate constant requires taking into account the Maxwell's distribution of thermal energies (the expression for the tunneling rate constant which includes the Maxwell distribution of thermal energy is calculated in the Appendix of the present paper)

$$k^{(T)} = f_{0,E_H} k_0^{(T)} e^{-B\sqrt{E_H - E_{0,EH}}} \tag{8}$$

where f_{0,E_H} and E_{0,E_H} are the fraction and the energy of particles with energies from 0 to E_H (only they are capable of tunneling)

$$f_{0,E_H} = \mathrm{erf}\left(\sqrt{\frac{3E_H}{2C_pT}}\right) - \frac{2}{\sqrt{\pi}}\sqrt{\frac{3E_H}{2C_pT}} \exp\left(-\frac{3E_H}{2C_pT}\right) \tag{9}$$

and

$$E_{0,E_H} = C_pT\left[\mathrm{erf}\left(\sqrt{\frac{3E_H}{2C_pT}}\right) - \frac{2}{\sqrt{\pi}}\sqrt{\frac{3E_H}{2C_pT}}\left(\frac{E_H}{C_pT} + 1\right) \exp\left(-\frac{3E_H}{2C_pT}\right)\right] \tag{10}$$

Equation 8 has improved the values of the tunneling rate constant expressed by eq 5 in the temperature regime where $1 < (E_H/C_pT) < 1.5$. As also follows from eq 8, due to Maxwell's distribution, the tunneling rate constant exists in the whole temperature regime but because of the low values of f_{0,E_H}, the tunneling hopping can be negligible above T_{tun}.

The Schrödinger description of the probability of the tunneling jumps is very useful to study the tunneling dynamics of protons and deuterons in the methyl group,[1−3] as well as in the hydrogen bond.[4−6]

The stochastic molecular motions in the ground and first excited vibrational states v0 and v1 do not have the same rates. Therefore, the rate constants $k^{(H)}$ and $k^{(T)}$ for the separate v0 and v1 states have to be defined separately. Assuming that eqs 1 and 5 (or 8) define the $(k^{(H)})_{v0}$ and $(k^{(T)})_{v0}$, the respective rate constant for v1 can be defined as

$$(k^{(H)})_{v1} = k_0^{(H)} \exp[-(E_H - E_{01})/RT] \tag{11}$$

$$(k^{(T)})_{v1} = k'(k^{(T)})_{v0} \tag{12}$$

where $k' \gg 1$. The value of $k' \gg 1$ indicates a greater rate of tunneling in the first excited vibrational state than in the ground state. A value k' of about 30 has been established for the rate $(\tau^{(T)})_{v1}$ of the proton transfer in the hydrogen bond.[13−15]

Spin−Lattice Relaxation of Deuterons in a Methyl Group

The spin−lattice relaxation of a nuclear spin with a quadrupole moment is caused by a stochastic modulation of the electric field gradient at the site of the nucleus caused by molecular motion. The largest tensor components of the deuterons are normally aligned to the X−D distance vector (chemical bond of deuterium). Since the populations of molecules at the vibrational levels obey the Boltzmann distribution (the vibrational relaxation is much faster than T_1 relaxation), the deuteron relaxation rate is given by

$$\frac{1}{(T_1)} = n_{v0}\left(\frac{1}{T_1}\right)_{v0} + n_{v1}\left(\frac{1}{T_1}\right)_{v1} \tag{13}$$

where n_{v0} and n_{v1} are the Boltzmann fractions of molecules in the separate vibrational levels v0 and v1 associated with the average energies E_{v0} and E_{v1} of the ground and first excited vibrational levels.

The fraction n_{v0} of the molecules undergoes motion at the tunneling rate constants of $(k^{(H)})_{v0}$ and $(k^{(T)})_{v0}$, while the fraction n_{v1} undergoes motion at the tunneling rate constants of $(k^{(H)})_{v1}$ and $(k^{(T)})_{v1.}$ Because the population of molecules in the second excited vibrational level is very low, it seems reasonable to take into account only two vibrational levels ($n_{v0} + n_{v1} = 1$ and $n_{v1}/n_{v0} = \exp(-E_{01}/RT)$). Therefore, the values of n_{v0} and n_{v1} are

$$n_{v0} = \frac{\exp(E_{01}/RT)}{\exp(E_{01}/RT) + 1} \tag{14}$$

$$n_{\mathrm{v1}} = \frac{1}{\exp(E_{01}/RT) + 1} \tag{15}$$

The tunnel splitting $\hbar\omega_{\mathrm{T}}^{\mathrm{v}x}$ of each vxth vibrational level is imposed by the symmetry of the methyl group. The spin energy levels in a magnetic field for a purely threefold potential barrier of a CD_3 rotator and for the two lowest vibrational states were calculated by Haupt.[16] In the limit of vibrational energies $E_{\mathrm{v}x} < U_0$, where vx = v0, v1, ..., the vibrational states are degenerated into the states of symmetry A, E_a, and E_b. The A sublevels are split into quartets, while the E levels are split into doublets. The splitting $\hbar\omega_{\mathrm{T}}^{\mathrm{v}x}$ of the vibrational states of the methyl group superimposes the Zeeman splitting of spin levels ω_i in a magnetic field. The C_3 hindered rotation (jumps over the barrier as well as tunneling jumps through the barrier) of methyl deuterons in a triple potential induces the transitions between the spin states. The deuteron spin–lattice relaxation of an isolated CD_3 group is determined only by A ↔ E transitions. The symmetry conserving transitions $E_a \leftrightarrow E_b$ (ω_i and $2\omega_i$) are forbidden by the spin selection rules. Therefore, Haupt[16] has proposed to replace the angular NMR frequencies ω_i and $2\omega_i$ in the well-known BPP formula[17] with $\omega_i \pm \omega_{\mathrm{T}}^{\mathrm{v}x}$ and $2\omega_i \pm \omega_{\mathrm{T}}^{\mathrm{v}x}$, respectively. The numerical factor in the Haupt equation has to be assumed to be twice as small as that in BPP because when $\omega_{\mathrm{T}}^{\mathrm{v}x} = 0$, both theoretical expressions should give identical results. Therefore

$$\left(\frac{1}{T_1}\right)_{\mathrm{v}x} = \frac{9\pi^2}{16}[J^1(\omega_i + \omega_{\mathrm{T}}^{\mathrm{v}x}) + J^1(\omega_i - \omega_{\mathrm{T}}^{\mathrm{v}x}) + J^2(2\omega_i + \omega_{\mathrm{T}}^{\mathrm{v}x}) + J^2(2\omega_i - \omega_{\mathrm{T}}^{\mathrm{v}x})] \tag{16}$$

where

$$J^m(\omega) = \int_{-\infty}^{\infty} \langle F^m(t)F^{m*}(t+\tau)\rangle \exp(-i\omega\tau)\mathrm{d}\tau \tag{17}$$

where m = 1, 2 are the spectral densities of the correlation functions of the fluctuating part of the interaction Hamiltonian. These random functions are

$$F^1(t) = q_{\mathrm{cc}}\sin\vartheta(t)\cos\vartheta(t)\exp[i\varphi(t)] \tag{18}$$

$$F^2(t) = q_{\mathrm{cc}}\sin^2\vartheta(t)\exp[i2\varphi(t)] \tag{19}$$

The $q_{\mathrm{cc}} = <e^2q_{zz}Q/h>$ is the quadrupole coupling constant expressed in hertz. The polar and azimuth angles υ and φ describe the orientation of the electric field gradient, q_{zz}, at the site of the quadrupolar nuclei.

The spectral densities depend on the model of motion. The respective spectral densities, obtained as a result of the Fourier transform of the correlation functions for the model of complex motion of q_{zz} in a triple potential, consisting of jumps over the barrier and incoherent tunneling, have been derived in refs 1 and 18. Inserting the corresponding spectral densities $J^m(\omega)$ (eq 56 in ref 1) into eq 16, one gets

$$\left(\frac{1}{T_1}\right)_{\mathrm{v}x} = \frac{3\pi^2}{20}q_{\mathrm{cc}}^2\sin^2\Theta_3\{\cos^2\Theta_3(f[(\omega_i + \omega_{\mathrm{T}}^{\mathrm{v}x}),(\tau^{(\mathrm{T})})_{\mathrm{v}x}] + f[(\omega_i - \omega_{\mathrm{T}}^{\mathrm{v}x}),(\tau^{(\mathrm{T})})_{\mathrm{v}x}] + f[(\omega_i + \omega_{\mathrm{T}}^{\mathrm{v}x}),(\tau^{(\mathrm{H})})_{\mathrm{v}x}] + f[(\omega_i - \omega_{\mathrm{T}}^{\mathrm{v}x}),(\tau^{(\mathrm{H})})_{\mathrm{v}x}]) + \sin^2\Theta_3(f[(\omega_i + \omega_{\mathrm{T}}^{\mathrm{v}x}),(\tau_i)_{\mathrm{v}x}] + f[(\omega_i - \omega_{\mathrm{T}}^{\mathrm{v}x}),(\tau_i)_{\mathrm{v}x}])\} \tag{20}$$

where

$$\frac{1}{(\tau_i)_{\mathrm{v}x}} = \frac{1}{(\tau^{(\mathrm{T})})_{\mathrm{v}x}} + \frac{1}{(\tau^{(\mathrm{H})})_{\mathrm{v}x}} \tag{21}$$

and

$$f(\omega_i \pm \omega_{\mathrm{T}}, \tau) = \frac{\tau}{1 + (\omega_i \pm \omega_{\mathrm{T}})^2\tau^2} + \frac{4\tau}{1 + (2\omega_i \pm \omega_{\mathrm{T}})^2\tau^2} \tag{22}$$

Here, Θ_3 = 109.4° for the symmetry axis of the electric field gradient (tetrahedral angle of D–C–D in the methyl group).

The correlation time for jumps over the potential barrier (Arrhenius equation) equals

$$(\tau^{(\mathrm{H})})_{\mathrm{v}x} = \frac{1}{3(k^{(\mathrm{H})})_{\mathrm{v}x}} \tag{23}$$

where $(k^{(\mathrm{H})})_{\mathrm{v0}}$ and $(k^{(\mathrm{H})})_{\mathrm{v1}}$ are given by eqs 1 and 11.

The correlation time for tunneling jumps through the potential barrier equals

$$(\tau^{(\mathrm{T})})_{\mathrm{v}x} = \frac{1}{3(k^{(\mathrm{T})})_{\mathrm{v}x}} \tag{24}$$

where $(k^{(\mathrm{T})})_{\mathrm{v0}}$ and $(k^{(\mathrm{T})})_{\mathrm{v1}}$ are given by eqs 8 and 12.

Application of Theory to Experimental Data

The deuteron T_1 was measured at 46 MHz as a function of inverse temperature for a powdered sample of $(ND_4)_2PbCl_6$.[12] Two tunneling frequencies, $\omega_{\mathrm{T}}^{\mathrm{v0}}$, $2\pi \times 0.35$ and $2\pi \times 1$ MHz below the order–disorder phase transition temperature, have been found from the deuteron NMR spectra of $(ND_4)_2PbCl_6$ and attributed to ions in the ordered domains.[12] Such small values of tunnel splitting ($\omega_{\mathrm{T}}^{\mathrm{v0}} < \omega_i$) have an insignificant effect on the T_1 (46 MHz) values.[1,2] Therefore, both eq 16 with $\omega_{\mathrm{T}}^{\mathrm{v0}} \approx 0$ or the well-known BPP equation[17] can be used in the analysis of the deuteron T_1 data for $(ND_4)_2PbCl_6$.

Experimental values are presented in Figure 3 together with the theoretical fit of eqs 13 and 20 with eq 1 and 8 to the data. The fitting parameters q_{cc}, $\tau_0^{(\mathrm{H})}$, $\tau_0^{(\mathrm{T})}$, and E_{H} are listed in Table 1. The value of the quadrupole coupling constant q_{cc} is well estimated from the fitting procedure of T_1 because this parameter determines the value of T_1 at the minimum of the temperature dependence. The temperature dependence of the molar heat capacity, C_{p}, which is necessary for this fit, has been taken from ref 19.

The activation energy E_{H} obtained from the slope of the high-temperature side of the T_1 minimum equals 7.5 kJ/mol. This value of E_{H} and the temperature dependence of thermal energy $C_{\mathrm{p}}T$ indicate the temperature T_{tun} as that at which the value of the thermal energy equals the activation energy ($C_{\mathrm{p}}T_{\mathrm{tun}} = E_{\mathrm{H}}$). The T_{tun} temperature is 55.7 K ($1000/T_{\mathrm{tun}} = 17.95\ \mathrm{K}^{-1}$).

The experimental and theoretical temperature dependencies of the correlation times are presented in Figure 4. The correlation time $(\tau^{(\mathrm{T})})_{\mathrm{v0}}$ (eq 24) is almost a constant value from the low temperatures up to the T_{tun} temperature. Then, with increasing temperatures, a significant increase in the tunneling correlation time values takes place. The characteristic T_{tun} temperature appears in the temperature regime where $(\tau^{(\mathrm{T})})_{\mathrm{v0}} > (\tau^{(\mathrm{H})})_{\mathrm{v0}}$. Therefore, despite the tunneling hopping existence over the entire temperature regime, the low probability of this motion at high temperatures (very long tunneling correlation time, $(\tau^{(\mathrm{T})})_{\mathrm{v0}}$) makes it undetectable. Similarly, the correlation time $(\tau^{(\mathrm{H})})_{\mathrm{v0}}$ characterizing jumps over the barrier (eq 23) follows

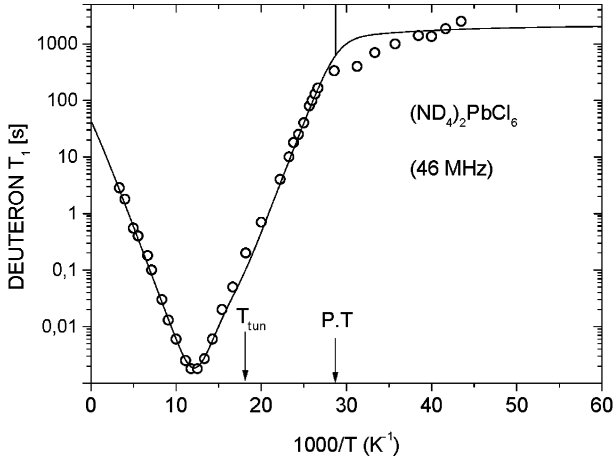

Figure 3. Temperature dependence of the deuteron spin−lattice relaxation time for $(ND_4)_2PbCl_6$ at 46 MHz. The best fit of the experimental data (circles) to eqs 13 and 20 with eqs 1 and 8 is given by the solid line. The arrows show the characteristic temperatures T_{tun} and the phase transition temperature (P. T).

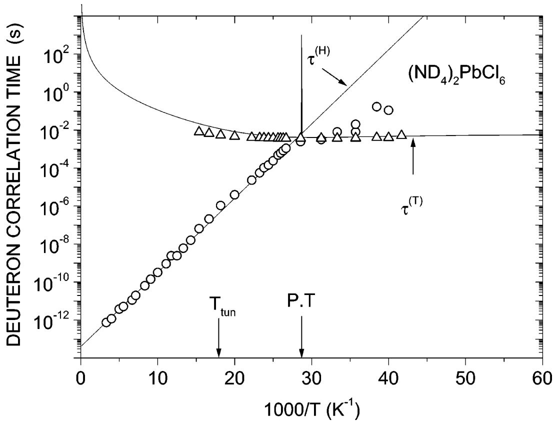

Figure 4. Deuteron correlation times $\tau^{(H)}$ (circles) and $\tau^{(T)}$ (triangles) of $(ND_4)_2PbCl_6$ as a function of 1000/T (K^{-1}). The points and lines refer to the experimental and theoretical correlation times, respectively. The arrows show the characteristic temperatures T_{tun} and the phase transition temperature (P. T).

TABLE 1: The Motional Parameters Obtained from the Fit of the Deuteron T_1 Data to Eqs 13 and 20 with Eqs 1 and 8

	q_{cc} (kHz)	$\tau^{(H)} = 1/(3k_0^{(H)})$ (10^{-14} s)	$\tau^{(T)} = 1/(3k_0^{(T)})$ (10^{-4} s)	E_H (kJ/mol)	T_{tun} (K)
$(ND_4)_2PbCl_6$	145	4	3	7.5	55.7

the Arrhenius dependence in the entire temperature regime, but in low temperatures. this time is so long (much longer than-$(\tau^{(T)})_{v0}$) that this motion does not contribute to the T_1 relaxation.

The less accurate fit of the data in the temperature regime near 1000/$T \sim 30$ K^{-1} can indicate one more mechanism of relaxation. This mechanism could be due to tunnel splitting. In this mechanism, the time-dependent fluctuations of the interaction Hamiltonian do not concern the mass transport between equilibrium sites but the lifetime broadening of spin levels.[8]

In Figures 3 and 4, one sees the T_1 and $(\tau^{(T)})_{v0}$ peaks on the theoretical dependences corresponding to the molar heat capacity C_p peak at 34.8 K (temperature of the first-order transition[19]). There is an interesting feature of the correlation times revealed in the plots in Figure 4, namely, that the phase transition takes place near the temperature at which the experimental correlation times $\tau_3^{(H)}$ and $\tau_3^{(T)}$ have comparable values.

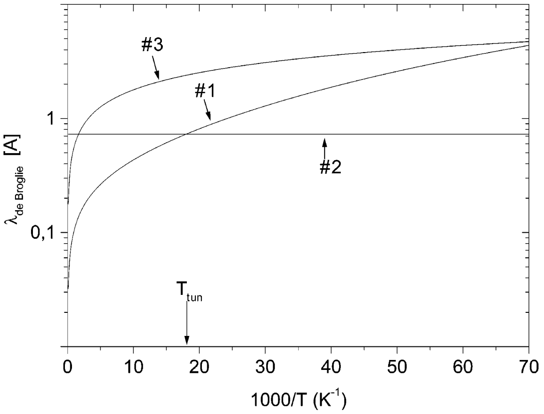

Figure 5. The temperature dependence of the de Broglie wavelength related to the average thermal energy C_pT/N_{Av} (#1) and the particular thermal energy $E_H = (7.5/N_{Av})$ kJ (#2) of the deuteron in $(ND_4)_2PbCl_6$ (#1). Curve #3 represent the $\lambda_{\mathrm{deBroglie}}$ related to the thermal energy (1.5 k_BT) of the deuteron in the ideal gas. The arrow shows the characteristic temperatures T_{tun}.

de Broglie Wave Related to the Thermal Motion of Particles

It has been well-established that the corpuscular-wave dualism is revealed when the lengths of the electromagnetic or de Broglie waves are comparable to or longer than the size of the object onto which the wave is incident.

The de Broglie wavelength is described by the formula

$$\lambda_{\mathrm{deBroglie}} = \frac{h}{\sqrt{2mE_{\mathrm{kin}}}} \tag{25}$$

where $h = 6.63 \times 10^{-34}$ J•s is the Planck's constant, and m and E_{kin} are the mass and kinetic energy of a particle.

In the ideal gas, the kinetic energy (thermal energy) of a particle is described by the equation

$$E_{\mathrm{kin}} = \frac{3}{2}k_BT \tag{26}$$

where k_B =1.38 × 10^{-23} J•K^{-1} is the Boltzmann constant, and T is temperature on the Kelvin scale.

The kinetic energy of a particle in any material equals

$$E_{\mathrm{kin}} = \frac{C_pT}{N_{Av}} \tag{27}$$

where C_p is the molar heat capacity, and $N_{Av} = 6.02 \times 10^{23}$ is the Avogadro number.

As follows from eqs 25−27, the de Broglie wavelength, $\lambda_{\mathrm{deBroglie}}$, related to the thermal motion increases with decreasing temperature. The line #1 in Figure 5 presents the temperature dependence of $\lambda_{\mathrm{deBroglie}}$ related to the thermal energy, C_pT, of a deuteron in the molecule studied, $(ND_4)_2PbCl_6$. This dependence was calculated on the basis of eqs 25 and 27 and the molar heat capacity, C_p, which is temperature-dependent.[19] The de Broglie wavelength corresponding to the particular energy E_H = 7.5 kJ/mol in the Maxwell distribution of thermal energy equals 0.752 Å (#2). The line #1 intersects the line #2 at the temperature T_{tun}, where $C_pT_{\mathrm{tun}} = E_H$, revealing that the de Broglie wavelength related to the thermal energy, C_pT, reaches the value of 0.752 Å at the T_{tun} temperature. This value is close to the value of the barrier width L = 0.722 Å following from the geometrical calculations (Figure 2). Thus, the temperature T_{tun} is the point at which the de Broglie wavelength of the thermal motion becomes comparable to the potential barrier width. Below T_{tun}, the $\lambda_{\mathrm{deBroglie}}$ related to the $C_{\mathrm{p}}T$ energy is longer than the potential barrier width, L, and can pass through the barrier. The longer the wavelength, the higher the probability of tunneling and lower the probability of reflection from the barrier. Above T_{tun}, the $\lambda_{\mathrm{deBroglie}}$ related to the $C_{\mathrm{p}}T$ energy is reflected from the potential barrier.

The line # 3 in Figure 5 was calculated on the basis of eqs 25 and 26. As follow from this figure, the de Broglie wavelength, related to the thermal energy, in the ideal gas (#3) is longer than that in the real substance (#1) at the same temperature.

Other Models of the Tunneling Rate Constant and Total Spectral Density

Our calculations of eq 20 are based on the Woessner[20] and Wallach[21] methods of calculation of the total spectral density for complex motion. Woessner[20] proved that it is not the total correlation time but the total spectral density of a complex motion consisting of a number of independent motions simultaneously modulating the dipolar Hamiltonian, which has to be calculated. The classical and tunneling rate constants in our approach are based on the Arrhenius (eq 1) and Schrödinger (eq 8) equations. These are two different probabilities of jumps; therefore, the temperature dependencies of spectral densities of both types of motion are different.

In contrast to our calculations, the total rate constant, k^{TOTAL}, representing the tunneling and over-the-barrier hopping, is usually approximated by a biexponential dependence whose first term is the Arrhenius-like dependence, and the second describes the deviations from the Arrhenius law. Such an approximation of the spectral density is based on the assumption that at intermediate temperatures, the classical dynamics evolves smoothly into the quantum low-temperature dynamics and that the particle is transferred from the A to B equilibrium site by a single, uniform motional process.

Müller-Warmuth[8,9] introduced the following phenomenological expression for the temperature dependence of total rate constants

$$k^{(\mathrm{TOTAL})} = k_0^{(\mathrm{H})} \exp(-E_{\mathrm{H}}/RT) + k_0^{(\mathrm{T})} \exp(-E_{01}/RT) \quad (28)$$

where $k_0^{(\mathrm{T})}$ is the preexponential factor and $E_{01} = E_{\mathrm{v1}} - E_{\mathrm{v0}}$ is the energy difference between the vibrational states v1 and v0. In the high-temperature limit, the total rate constant, $k^{(\mathrm{TOTAL})}$, invariably corresponds to the classical limit, and at low temperatures, it is governed by the tunneling.

The approximation of $k^{(\mathrm{TOTAL})}$ presented by Limbach et al.[22] assumes also a two-exponential dependence of this value

$$k^{(\mathrm{TOTAL})} = k_{\mathrm{AB}}^{(\mathrm{TOTAL})} + k_{\mathrm{BA}}^{(\mathrm{TOTAL})} \quad (29)$$

where

$$k_{\mathrm{AB}}^{\mathrm{TOTAL}} = k_{01} \exp(-E_1/RT) + k_{02} \exp(-E_2/RT) \quad (30)$$

and

$$k_{\mathrm{BA}}^{\mathrm{TOTAL}} = k_{\mathrm{AB}}^{(\mathrm{TOTAL})}/K_{\mathrm{AB}} \quad (31)$$

where E_1 and E_2 are the average activation energies for the high- and low-temperature motional processes, K_{AB} is the equilibrium constant, and k_{01} and k_{02} are the preexponential factors.

The single $k^{(\mathrm{TOTAL})}$ assumed as a weighted average of the finite time constant, which is evaluated numerically and calculated directly from the exponential proton T_1 temperature dependence, is proposed by Stöckli et al.[23] In this case, the temperature dependence of the correlation time yields the apparent activation energy

$$E_{\mathrm{act}} = \frac{\partial(\ln(1/k^{\mathrm{TOTAL}})}{\partial(1/RT)} \quad (32)$$

The activation energies thus obtained are well below the barrier heights for all compounds studied. This phenomenon according to the authors is the proof of the predominance of tunneling hopping even at high temperatures.

With a view to formulating the smooth transition from tunneling to classical motion, it is assumed by Skinner and Trommsdorff,[10] Heuer and Haeberlen,[24] Meyer and Ernst,[13] and also Horsewill et al.[14,15,25] that

$$k^{(\mathrm{TOTAL})} = k^{(\mathrm{H})} + n_{\mathrm{v0}}(k^{(\mathrm{T})})_{\mathrm{v0}} + n_{\mathrm{v1}}(k^{(\mathrm{T})})_{\mathrm{v1}} \quad (33)$$

where $k^{(\mathrm{H})}$ is given by eq 1. The description of the tunneling rate constant, $(k^{(\mathrm{T})})_{\mathrm{v0}}$, which requires the presence of unequal energy at equilibrium sites A and B, has been given by Skinner and Trommsdorff[10]

$$k^{(\mathrm{T})} = k_0^{(\mathrm{T})} \frac{\exp(\Delta/RT) + 1}{\exp(\Delta/RT) - 1} \quad (34)$$

where Δ is the energy difference between potential energy minima at equilibrium sites; $(k^{(\mathrm{T})})_{\mathrm{v1}} = k'(k^{(\mathrm{T})})_{\mathrm{v0}}$, where $k' \gg 1$. The value of $k' \gg 1$ indicates a faster rate of tunneling hopping in the first excited vibrational state than in the ground state.

All of the above-presented phenomenological approximations of the total rate constant used in the spin−lattice relaxation expressions fit very well with the experimental data because the $k^{(\mathrm{TOTAL})}$ is the best-fit parameter in these approaches. The problems appear only when the same best-fit parameters have to be used for the T_1 temperature dependences at high and low resonance frequencies. It is impossible to obtain an acceptable fit to both the proton T_1 ($\omega_I = 2\pi \times 55.\ 2$ MHz, $\omega_I = 2\pi \times 24.7$ MHz) and $T_{1\rho}$ ($B_1 = 9$ G), obtained for 2,5 DNBA data,[5] by employing eq 33, which is discussed in Figure 5 of ref 5.

In our opinion, the classical and tunneling hopping cannot be treated as a uniform motion described by a single rate constant. Neither the Skinner and Trommsdorff equation nor the Schrödinger equation imply that the particle is transferred from the A to B equilibrium site by a single motional process; therefore, the spectral density for a single motion cannot be correct in describing the wide temperatures dynamics of light atoms as ^{1}H and ^{2}H. That the approach of the spectral density due to classical and tunneling hopping by the total rate constant, k^{TOTAL}, seems to be incorrect has been shown in our papers[1,6] (ref 6, Figure 6 and ref 1, Figure 9).

Summary

The stochastic jumps of light atoms (hydrogen, deuterium) between sites A and B occur by jumps over the barrier (Arrhenius) and by tunneling jumps (Schrödinger). These two stochastic motions, although geometrically identical (transfer of mass from A to B equilibrium sites), are described by two different probabilities and occur via different pathways; one pathway is over the barrier, and the other one is through the barrier.

The two sites A and B can be imagined as two cities separated by a mountain. The way across the mountain leads over the top of the mountain. This way can always be used (0 K is the end of the classical motion), but enough power (thermal energy) has to be available to take this pathway. A decrease in temperature causes a decrease in thermal energy, but the thermal energy is subjected to the Maxwell distribution, and a certain number of particles own enough energy for hopping over the barrier. Another way goes through the tunnel under the mountains, but this way can be used when the gate to the tunnel is opened. The "key which opens the gate to the tunnel pathway" is the de Broglie wave, which is long enough to pass the barrier width. The nature is very gracious for moving atoms, predicts when they do not have enough power to go over the barrier, and opens the gate to the tunnel pathway.

The de Broglie wavelength related to the C_pT energy is equal to the barrier width at the temperature, T_{tun}, where the thermal energy of a particle equals the activation energy ($C_pT_{tun} = E_H$). Below T_{tun} temperature, the de Broglie wavelength, related to the C_pT energy, is longer than the barrier width. This condition is a solution of the Schrödinger's equation and is called the "transparency of barrier". Due to Maxwell's distribution of the thermal energy, the kinetic energies of some particles are lower than the barrier height even at high temperatures, but above T_{tun}, the fraction of molecules with energies lower than E_H is very small. On the tunnel pathway (in the space of the potential barrier), the de Broglie waves related to the thermal motion of particles are also reflected from the barrier (probability of the reflection from the barrier). On the Arrhenius pathway, there are no obstacles for the de Broglie waves. The tunneling motion confirms the corpuscular-wave dualism theory.

Appendix

Equation 5, expressing the tunneling correlation time according to the Schrödinger equation, has been proposed in a number of our papers.[1-5] Despite the fact that the thermal energy $E_{thermal} = C_pT$ reaches the value of E_H with increasing temperature, some fraction of the molecules takes thermal energy lower than E_H. Therefore, more detailed consideration of the tunneling rate constant requires one to take into account the Maxwell's distribution of the thermal energy. In this appendix, we derive the expression for the tunneling rate constant which includes the Maxwell distribution of thermal energy. We also show, on the previously analyzed example T_1 (59.63 MHz) BAC-h6 data,[6] how the allowing of the Maxwell distribution changes the theoretical values of the tunneling rate constant and influences the T_1 temperature fit.

The distribution of kinetic energies, E, of the Avogadro number of atoms or molecules is governed by the Maxwell distribution

$$f(E) = \frac{2}{\sqrt{\pi}}\beta^{3/2}\sqrt{E}\exp(-\beta E) \tag{A1}$$

where

$$\beta = \frac{1}{RT} \tag{A2}$$

for the particles in the ideal gas, where $R = 8.314$ J/K/mol is the gas constant, or

$$\beta = \frac{3}{2C_pT} \tag{A3}$$

for the particles in the real substance.

The area under the Maxwell distribution in the limits of zero to infinity remains the same, giving a value of one

$$\int_0^\infty f(E)\mathrm{d}E = \frac{2}{\sqrt{\pi}}\beta^{3/2}\int_0^\infty \sqrt{E}\exp(-\beta E)\mathrm{d}E = 1 \tag{A4}$$

The fraction of molecules with a the particular energy E_H equals

$$f_{E_H} = \frac{2}{\sqrt{\pi}}(\beta E_H)^{3/2}\exp(-\beta E_H) \tag{A5}$$

The activation energy $E_H = 4.1$ kJ/mol has been determined for BAC-h6 protons.[6,7] The temperature dependence of f_{E_H} calculated from eq A5 is interesting (Figure 6). The fraction of particles with the energy E_H equals zero at low temperatures. This temperature dependence goes through a maximum at the temperature $1000/T_{tun} = 12.7$ K^{-1}. At this temperature, T_{tun}, the thermal energy C_pT equals E_H.

The fraction of atoms with energies from 0 to E_H (only they are capable of tunneling) at a given temperature represents the part of the integral given in eq A4, that is

$$f_{0,E_H} = \int_0^{E_H} f(E)\mathrm{d}E = \mathrm{erf}(\sqrt{\beta E_H}) - \frac{2}{\sqrt{\pi}}\sqrt{\beta E_H}\exp(-\beta E_H) \tag{A6}$$

The $f_{0,E_H} = 1$ at low temperatures and decreases to 0 at high temperatures. This means that all particular energies in the Maxwell distribution of the thermal energy are lower than E_H at low temperatures, and therefore, $f_{0,E_H} = 1$. At higher temperatures, part of the molecules take kinetic energies higher than E_H, and therefore, the fraction of energies in the range of 0 to E_H decreases (Figure 6).

The molar average kinetic energy (thermal energy), $E_{thermal}$, equals (3/2)RT for the ideal gas and C_pT for the real substance. The thermal energy of the Avogadro number of particles equals the field under the $Ef(E)$ function, that is

$$E_{thermal} = \int_0^\infty Ef(E)\mathrm{d}E = \frac{2}{\sqrt{\pi}}\beta^{3/2}\int_0^\infty E^{3/2}\exp(-\beta E)\mathrm{d}E = \frac{3}{2}\beta^{-1} \tag{A7}$$

where β is given by eq A2 or A3.

The thermal energy of the particles in the limit of 0 to E_H energy can be calculated from the equation

$$E_{0,E_H} = \int_0^{E_H} Ef(E)\mathrm{d}E = \frac{3}{2}\beta^{-1}\left[\mathrm{erf}(\sqrt{\beta E_H}) - \frac{2}{\sqrt{\pi}}\sqrt{\beta E_H}\left(1 + \frac{2}{3}\beta E_H\right)\exp(-\beta E_H)\right] \tag{A8}$$

The increasing temperature of the sample BAC-h6 causes an increase in the thermal energy values, C_pT, as shown in Figure 7. The $C_pT = E_H$ at the temperature $1000/T_{tun} = 12.7$ K^{-1}. The temperature dependence of the energy E_{0,E_H} is different than this C_pT. E_{0,E_H} goes through a maximum at the temperature T_{tun} (Figure 7)

As follows from the Schrödinger equation, only the fraction of the molecules of the kinetic energy in the range of 0 to E_H is capable of tunneling jumps. The value of the tunneling rate constant, $k^{(T)}$, can be considered as a sum of the two component parts weighted in the fractions of particles. One of them is the rate constant of the particles of the energies from zero to E_H, while the other is that of the particles of the energies from E_H to infinity. As the particles of the energies higher than E_H do not bring any contribution to the tunneling rate constant

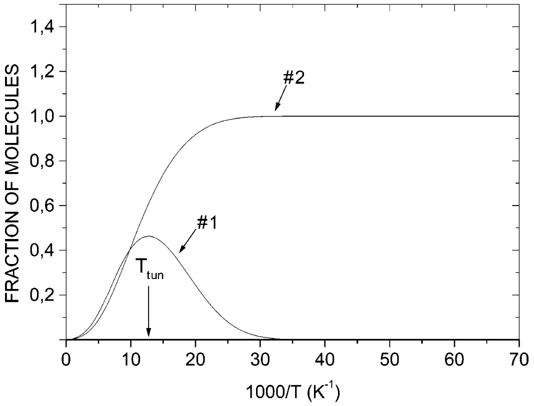

Figure 6. The temperature dependence of the fraction of molecules of the energy $E_H = 4.1$ kJ/mol (eq A5) (#1) and the energy from the range of 0 to 4.1 kJ/mol (eq A6) (#2). The T_{tun} temperature where $C_pT_{tun} = E_H$ is indicated. The values of the molar heat capacity C_p have been taken from ref 26.

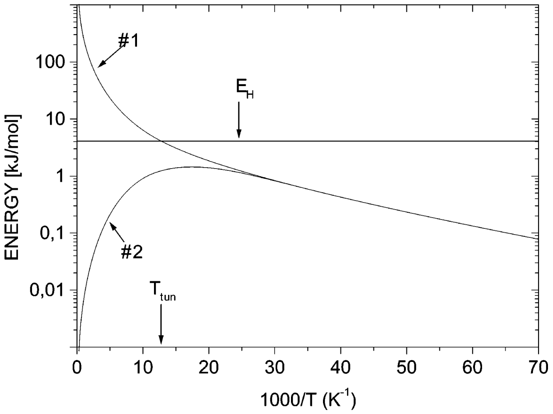

Figure 7. The temperature dependences of the thermal energy, C_pT, for the BAC-h6 sample (eq A7) (#1) and the E_{0,E_H} energy (eq A8) (#2). The activation energy $E_H = 4.1$ kJ/mol and the T_{tun} temperature ($1000/T_{tun} = 12.7$ K^{-1}) are indicated.

(square roots from the negative values do not have the real values), therefore finally

$$k^{(T)} = f_{0,E_H} k_0^{(T)} e^{-B\sqrt{E_H - E_{0,E_H}}} \tag{A9}$$

where f_{0,E_H} and E_{0,E_H} are given by eqs A6 and A8.

Equation A9 gives more accurate values of the rate constant more precisely than eq 5 because in the former, the Maxwell's distribution of the thermal energy has been taken into account. This rate tunneling constant exists over the entire temperature regime, but the low values of f_{0,E_H} (very low number of the molecules able to tunnel at high temperatures) imply that $k^{(T)} \approx 0$ at high temperatures. At low temperatures, $E_{0,E_H} < E_H$ and $f_{0,E_H} \approx 1$.

It seems that in the range from 0 K to the temperature at which $E_H/C_pT) \approx 1.5$, eq A9 can be simplified to the form

$$k^{(T)} = k_0^{(T)} e^{-B\sqrt{E_H}} \tag{A10}$$

Above the T_{tun} temperature ($T_{tun} = E_H/C_p$), the contribution to the spin−lattice relaxation coming from the tunneling stochastic jumps is very small and seems to be negligible.

The theoretical temperature dependence of T_1 (59.63 MHz) for BAC-h6 is given in Figure 8 by the solid line. This fit of the experimental data[7] has been performed on the basis of the same equations as those presented in our previous paper.[6] The only difference is the applied expression for the tunneling rate constant. Equation A9 is used presently, while before, the Skinner and Trommsdorff expression[10] in the restricted temperature range from 0 K to the T_{tun} temperature was applied. It is visible in Figure 8 that the T_1 dependence is continuous and smooth in the entire temperature regime, while before, the sharp change appeared at the temperature T_{tun} (see Figure 3 in the ref 6)

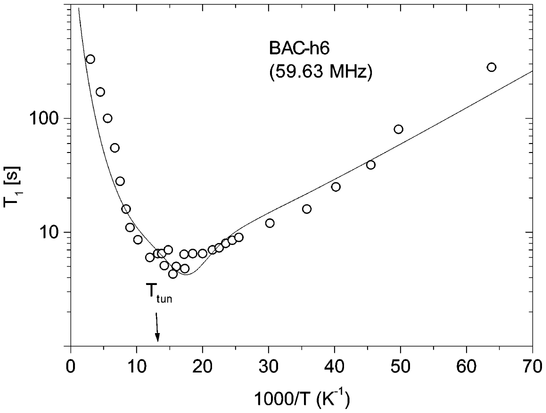

Figure 8. Temperature dependence of the proton T_1 time (59.63 MHz) for a powdered sample of BAC-h6.[7] The solid line represents the best fit of theoretical eqs 11 and 19 from ref 6 with eq A9 from the present paper. The fitting parameters are $E_H = 4.1$ kJ/mol, $\Delta = 0.65$ kJ/mol, $k_0^{(T)} = 1 \times 10^9$ s, $k_0^{(H)} = 8 \times 10^{11}$ s. The temperature dependence of C_p was taken from ref 26.

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