Rotational hopping model and decoherence

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The notion of classical reorientational jumps, which is frequently employed in the analysis of spin-lattice relaxation or inelastic neutron scattering of symmetric molecular groups, is considered within the framework of Feynman-Vernon influence functional theory. It is shown that the validity of the model requires disappearance of certain interference cross terms between amplitudes for transitions among different minima of the hindering potential. In particular, it is demonstrated that within the model discussed, the classical reorientational jump approximation becomes valid when coupling between the XH_3 motion and the bulk librational optical phonons is sufficiently strong. [S0163-1829(99)11729-6]

I. INTRODUCTION

The rotational hopping or jump model[1] has been used extensively in semiclassical calculations of spin-lattice relaxation[2,3] and inelastic neutron scattering[1,4] of XH_3 and XH_4 type molecules or molecular groups embedded in solid lattices. To simplify the discussion, let us restrict ourselves to hindered uniaxial rotational motion of XH_3-type molecular groups in solids (of which the methyl group is probably the most important example) as representative of systems which are believed to exhibit tunneling at low temperatures and classical rotational hopping at high temperatures. The rotational hopping is understood, in this particular case, as follows: each group can assume only three angular orientations about its symmetry axis, which are equally spaced, and it jumps from one orientation to another with a temperature-dependent probability per unit time. This, however, is not consistent with the form of spin-rotational wave functions,[1,5] where a strict correlation between spin and rotational components imposed by Pauli principle precludes orientational localization of the group. As we will show below, the model is nevertheless applicable, provided the interference between amplitudes for transitions among different pairs of minima of the hindering potential is suppressed. It turns out that the mechanism which bridges the gap between the low-temperature tunneling regime and high-temperature rotational hopping is, in our opinion, decoherence as formulated by Zurek.[6–10] To state it briefly, decoherence is a dynamical effect due to the interaction between the quantum system and its environment. It destroys quantum interferences, at least for all practical purposes[11] and allows one to associate probabilities with certain suitably chosen classes of Feynman paths. Needless to say, the mathematical formalism to be employed is the Feynman-Vernon theory of influence functionals.[12] However, to prevent personal preferences from being magnified into general guidelines, we should add that, quite generally, the relaxation processes associated with rotational motion of CH_3 groups in solids can be discussed also very efficiently by using standard wave mechanics and time-ordered cumulants.[13] This approach, for example, provides a systematic procedure for computations to be carried to arbitrary order in rotational-phonon interaction. In the lowest order, an equation of motion for the reduced density matrix can thus be obtained, which is equivalent to the Redfield equation.[14,15] Nevertheless, we believe that it is Feynman path-integral formulation which enables one to see interference effects very clearly and where methyl dynamics lends itself naturally to space-time visualization.

II. FORMULATION OF THE PROBLEM

To be quite specific, we consider a single XH_3-type molecular group undergoing hindered rotational motion around its symmetry axis. We shall also assume that an external dc magnetic field is applied along a fixed direction in space, chosen as the z axis of the laboratory fixed coordinate system. The sole purpose of introducing the magnetic field is to mimic a typical NMR situation and its presence in no way affects the conclusions regarding the rotational hopping model. The density matrix describing the dynamics of the group and its environment is written as

$$\rho(t) = e^{-(i/\hbar)H_z t} U(t,0)\rho(0)U^+(t,0)e^{(i/\hbar)H_z t}, \quad (1)$$

where H_Z is the Zeeman Hamiltonian representing the interaction between the proton spins and the external magnetic field (the proton dipole-dipole interaction is not considered, since it is not important for the present calculation). The time evolution operator $U(t,0)$, which causes the entanglement of the XH_3 rotational states with the states of the environment, is determined via the Feynman path-integral method[16] by the Lagrangian[17]

$$L = \frac{1}{2}I\dot{\chi}^2 - V(\chi) - \sum_j Ic_j\dot{\chi}\dot{q}_j - \sum_j f_j(\chi)Q_j$$

$$+ \frac{1}{2}\sum_j J(\dot{q}_j^2 - \Omega_j^2 q_j^2) + \frac{1}{2}\sum_j m(\dot{Q}_j^2 - \omega_j^2 Q_j^2)$$

$$- \sum_j f_j^2(\chi)/2m\omega_j^2 + \sum_j I^2 c_j^2\dot{\chi}^2/2J. \quad (2)$$

$\rho(0)$ in Eq. (1) represents the initial density matrix, while the meanings of the symbols in Eq. (2) are the following: χ is the rotation angle of the group around its symmetry axis, $\dot{\chi}$

$\equiv d\chi/dt$, $V(\chi) = V(\chi \pm 2\pi/3)$ is the threefold hindering potential, and I is the moment of inertia of the group. Moreover, the environment with which the XH_3 group is interacting is modeled by two distinct sets of harmonic oscillators, the so-called librational and translational phonons[17] denoted by $\{q\}$ and $\{Q\}$, respectively. The corresponding coupling strengths are $\{c\}$ and $\{f\}$, with the additional condition $f_j(\chi) = f_j(\chi \pm 2\pi/3)$, imposed by the symmetry properties of the XH_3 molecular group. The constants J and m have a dimension of moment of inertia and mass, respectively. The last two terms in Eq. (2) are the counterterms taking care of the potential and moment of inertia renormalization.

Since we are interested only in the behavior of the XH_3 groups we introduce, following Feynman and Vernon,[12] the reduced density matrix $\rho_R(t)$ obtained from Eq. (1) by tracing the latter with respect to the oscillator coordinates $\{q,Q\}$. The matrix elements of $\rho_R(t)$ are most conveniently expressed in the basis determined by

$$(H_Z + H_R)|n\,vM\rangle = [E_z(vM) + E_r(n\,v)]|n\,vM\rangle, \quad (3)$$

where $H_R = -(\hbar^2/2I)d^2/d\chi^2 + V(\chi)$ is the rotational Hamiltonian of a single XH_3 group subject to a hindering potential $V(\chi)$. $n = 0,1,2,...,$ is the torsional or librational quantum number, $v \in A, E_a, E_b$ denotes the irreducible representations of the C_3 symmetry group, and M is the magnetic quantum number. For a given n the rotational energy levels form a degenerate doublet of E symmetry and a singlet of A symmetry. The rotational component of the total wave function in the coordinate representation, $\langle \chi|n\,v\rangle = \Psi_n^{(v)}(\chi)$, satisfying $\psi_n^{(v)}(\chi + 2\pi) = \psi_n^{(v)}(\chi)$, may be written for not too large values of n as[5]

$$\psi_n^{(v)}(\chi) \cong \frac{1}{\sqrt{3}} \sum_j \varepsilon^{sj} H^{(n)}(\chi - j2\pi/3), \quad j = 0, \pm 1. \quad (4)$$

$H^{(n)}(\chi - j2\pi/3)$ are the harmonic oscillator functions centered at the minima of $V(\chi)$, and the symmetry label A corresponds to $s = 0$, while E_a and E_b correspond to $s = \pm 1$, respectively.

It is usually assumed that the initial density matrix $\rho(0)$ factors into $\rho_R(0) \cdot \rho_{osc}(0)$ where, in addition, $\rho_{osc}(0)$ is taken to represent the ensemble of oscillators in thermal equilibrium. Next, the matrix elements of the reduced density matrix in the above basis are calculated using the Feynman path-integral method. The result is

$$\langle M\,vn|\rho_R(t)|n'\,v'\,M'\rangle = e^{-i/\hbar[E_z(vM) - E_z(v'M')]t} \sum_m \sum_{m'} \int_{-\pi}^{\pi} \cdots \int_{-\pi}^{\pi} d\chi_1 d\chi_2 d\chi_1' d\chi_2' \psi_n^{(v)*}(\chi_2) \psi_m^{(v)}(\chi_1) \psi_{m'}^{(v')*}(\chi_1') \psi_{n'}^{(v')}(\chi_2')$$

$$\times \langle M\,vm|\rho_R(0)|m'\,v'\,M'\rangle \sum_{N=-\infty}^{\infty} \sum_{N'=-\infty}^{\infty} K_{N,N'}(\chi_2, \chi_2', t; \chi_1, \chi_1', 0), \quad (5)$$

where the propagators $K_{N,N'}$ are defined as

$$K_{N,N'}(\chi_2, \chi_2', t; \chi_1, \chi_1', 0) = \int_{\chi_1}^{\chi_2 + 2\pi N} D\tilde{\chi} \int_{\chi_1'}^{\chi_2' + 2\pi N'} D\tilde{\chi}' A[\tilde{\chi}] A^*[\tilde{\chi}'] e^{(i/\hbar)\Phi[\tilde{\chi}, \tilde{\chi}']}, \quad (6)$$

and $-\pi \leq \chi_1, \chi_1', \chi_2, \chi_2' \leq \pi$. $A[\tilde{\chi}] = e^{i/\hbar(S_0)[\tilde{\chi}]}$, with

$$S_0[\tilde{\chi}] = \int_0^t dt' [\tfrac{1}{2} I\dot{\tilde{\chi}}^2 - \tfrac{1}{2} V_3(1 - \cos 3\tilde{\chi})],$$

is the amplitude for the XH_3 system following the path $\tilde{\chi}(\tau)$ in the absence of the environment such that $\tilde{\chi}(0) = \chi_1$ and $\tilde{\chi}(t) = \chi_2 + 2\pi N$. N is the winding number of the path,[12,18] while $\tilde{\chi}$ runs from $-\infty$ to $+\infty$. The rotation angle $\chi \in [-\pi, \pi]$ is related to $\tilde{\chi}$ by $\chi = \tilde{\chi}(\text{modulo } 2\pi)$. Finally, the influence functional is

$$\Phi[\tilde{\chi}, \tilde{\chi}'] = i \int_0^t dt' \int_0^{t'} dt'' f^{(-)}(\tilde{\chi}(t')) L_Q'(t' - t'') f^{(-)}(\tilde{\chi}(t'')) - \frac{1}{2} I \int_0^t dt' \int_0^{t'} dt'' f^{(-)}(\tilde{\chi}(t')) \Gamma_Q(t' - t'') \dot{f}^{(+)}(\tilde{\chi}(t''))$$

$$- \frac{1}{2} I f^{(+)}(\tilde{\chi}(0)) \int_0^t dt' \Gamma_Q(t') f^{(-)}(\tilde{\chi}(t')) + i \int_0^t dt' \int_0^{t'} dt'' \tilde{\delta}(t') L_q'(t' - t'') \tilde{\delta}(t'')$$

$$- I \int_0^t dt' \int_0^{t'} dt'' \tilde{\delta}(t') \Gamma_q(t' - t'') \dot{\tilde{\eta}}(t'') + I\tilde{\delta}(t) \int_0^t dt' \Gamma_q(t - t')[\tilde{\eta}(t') - \tilde{\eta}(0)] - i\tilde{\delta}(0) \int_0^t dt' \tilde{\delta}(t') B_2(t')$$

$$- i\tilde{\delta}(t) \int_0^t dt' \tilde{\delta}(t') B_2(t - t') + \frac{i\hbar}{4\pi^2} W(\beta)[\tilde{\delta}^2(0) + \tilde{\delta}^2(t)] - i\tilde{\delta}(0)\tilde{\delta}(t) B_1(t). \quad (7)$$

The quantities introduced in Eq. (7) are the following: $f^{(\pm)}(\tilde{\chi}(\tau)) \equiv f(\tilde{\chi}(\tau)) \pm f(\tilde{\chi}'(\tau))$, $\tilde{\delta}(\tau) \equiv \tilde{\chi}(\tau) - \tilde{\chi}'(\tau)$, and $\tilde{\eta}(\tau) \equiv [\tilde{\chi}(\tau) + \tilde{\chi}'(\tau)]/2$. Moreover,

$$L(t) \equiv L'(t) + iL''(t)$$

$$= \frac{1}{\pi} \int_0^\infty d\omega J(\omega)[\coth(\beta\hbar\omega/2)\cos\omega t - i\sin\omega t],$$

$$(8a)$$

$$L''(t) = (I/2)d\Gamma(t)/dt, \qquad (8b)$$

$$J_Q(\omega) = (\pi/2)\sum_j (\lambda_j^2/m\omega_j)\delta(\omega - \omega_j), \qquad (8c)$$

$$J_q(\omega) = (\pi/2)\sum_j (I^2 c_j^2 \Omega_j^3/J)\delta(\omega - \Omega_j), \qquad (8d)$$

$$B_1(t) = \frac{1}{\pi}\int_0^\infty d\omega \frac{J_q(\omega)}{\omega^2}\coth(\beta\hbar\omega/2)\cos\omega t, \qquad (8e)$$

$$B_2(t) = -dB_1(t)/dt. \qquad (8f)$$

We have also set $f_j(\chi) = \lambda_j f(\chi)$, where $f(\chi)$ is a dimensionless function of order 1, and $e^{-W(\beta)}$, with $W(\beta) = (2\pi^2/\hbar)B_1(0)$, is the familiar Debye-Waller factor associated with the librational or $\{q\}$ modes. $\beta = 1/k_B T$, k_B is the Boltzmann constant, and T is the temperature of the oscillator heat bath.

III. ORIENTATIONALLY LOCALIZED STATES AND TRANSITION PROBABILITIES

The eigenstates of the Zeeman-rotational Hamiltonian as defined by Eq. (3) are usually written as products of properly symmetrized spin and rotational components.[1,5] In order to investigate the orientational transitions of the $X\mathrm{H}_3$ group, as commonly envisaged whenever the rotational hopping model is used, we construct the ''orientationally localized'' states by forming linear combinations of the three symmetry spe-

cies corresponding to given values of the torsional and magnetic quantum numbers n and M. Moreover, to simplify the calculation, we shall restrict ourselves to values of n such that the pocket-state approximation (4) is applicable, and write (for each n there are 2^3 distinct states)

$$\langle\chi|\Psi_1^{(n)}\rangle = \frac{1}{\sqrt{3}}[H^{(n)}(\chi - 2\pi/3)$$

$$+ H^{(n)}(\chi) + H^{(n)}(\chi + 2\pi/3)]\alpha\alpha\alpha\rangle, \quad (9a)$$

$$\langle\chi|\Psi_2^{(n)}\rangle = \frac{1}{\sqrt{3}}[H^{(n)}(\chi - 2\pi/3)|\alpha\beta\alpha\rangle + H^{(n)}(\chi)|\alpha\alpha\beta\rangle$$

$$+ H^{(n)}(\chi + 2\pi/3)|\beta\alpha\alpha\rangle], \qquad (9b)$$

$\langle\chi|\Psi_3^{(n)}\rangle, \langle\chi|\Psi_4^{(n)}\rangle$ are obtained from Eq. (9b) by cyclic permutations of the proton-spin labels α and β, which correspond to the spin projections $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively, along the direction of the external dc magnetic field. $\langle\chi|\Psi_i^{(n)}\rangle$, $i = 5,...,8$ follow from Eqs. (9a) and (9b) by replacing α's with β's and vice versa. Among the states defined by Eqs. (9), only those corresponding to $M = \pm\frac{1}{2}$ can be assigned some sort of orientation, characterized by the location of the spin-down or spin-up corner of the equilateral triangle formed by the protons of the $X\mathrm{H}_3$ group. For small torsional quantum numbers n, the three equilibrium orientations corresponding to these states are separated by $2\pi/3$.

To bring out the nature of the rotational transitions let us assume that the initial density matrix is given as $\rho_R(0) = \sum_{j=1}^8 P_j(0)|\Psi_j^{(n)}\rangle\langle\Psi_j^{(n)}|$. Next, let us inquire what is the probability, $P_i(t) = \mathrm{Tr}\{|\Psi_i^{(n)}\rangle\langle\Psi_i^{(n)}|\rho_R(t)\}$, for the group to be in the state $|\Psi_i^{(n)}\rangle$ at time t (we consider only transitions which do not change n). Using Eqs. (4), (5), and (9) and the expressions given in Refs. 1 or 5 for the symmetrized spin components which multiply Eq. (4), we obtain

$$P_i(t) = \sum_{j=1}^8 A_{i,j}(t)P_j(0), \qquad (10)$$

where the matrix A has the form

$$A = \begin{bmatrix} A_{1,1} & & & & & & & \\ & A_{2,2} & A_{2,3} & A_{2,4} & & & & \\ & A_{2,4} & A_{2,2} & A_{2,3} & & & & \\ & A_{2,3} & A_{2,4} & A_{2,2} & & & & \\ & & & & A_{2,2} & A_{2,3} & A_{2,4} & \\ & & & & A_{2,4} & A_{2,2} & A_{2,3} & \\ & & & & A_{2,3} & A_{2,4} & A_{2,2} & \\ & & & & & & & A_{1,1} \end{bmatrix}. \qquad (11)$$

$$A_{1,1}(t) = \frac{1}{9}\sum_{p_i,p_i' = 0,\pm 1} K(p_2 2\pi/3, p_2' 2\pi/3, t; p_1 2\pi/3, p_1' 2\pi/3, 0), \qquad (11a)$$

$$A_{2,2}(t) = \frac{1}{9}\sum_{p,p' = 0,\pm 1} K(p 2\pi/3, p' 2\pi/3, t; p 2\pi/3, p' 2\pi/3, 0), \qquad (11b)$$

$$A_{2,3}(t) = \frac{1}{9} \sum_{p,p'=0,\pm 1} K(p2\pi/3, p'2\pi/3, t; (p-1)2\pi/3, (p'-1)2\pi/3, 0), \tag{11c}$$

$$A_{2,4}(t) = \frac{1}{9} \sum_{p,p'=0,\pm 1} K(p2\pi/3, p'2\pi/3, t; (p+1)2\pi/3, (p'+1)2\pi/3, 0), \tag{11d}$$

and, whenever $-4\pi/3$ or $+4\pi/3$ occurs in Eq. (11c) or Eq. (11d), it has to be replaced by $+2\pi/3$ or $-2\pi/3$, respectively. We have also introduced the so-called coarse-grained propagators

$$K(p_2 2\pi/3, p_2' 2\pi/3, t; p_1 2\pi/3, p_1' 2\pi/3, 0) = \sum_{N,N'} \int_{-\pi}^{\pi} \cdots \int_{-\pi}^{\pi} d\chi_1 d\chi_2 d\chi_1' d\chi_2' H^{(n)}(\chi_2 - p_2 2\pi/3) H^{(n)}(\chi_1 - p_1 2\pi/3) H^{(n)}$$

$$\times (\chi_2' - p_2' 2\pi/3) H^{(n)}(\chi_1' - p_1' 2\pi/3) K_{N,N'}(\chi_2, \chi_2', t; \chi_1, \chi_1', 0). \tag{12}$$

It is clear that such designation is meaningful only for small values of n, when the torsional oscillator states are fairly well localized at the minima of the hindering potential $V(\chi)$. Furthermore, since the environment is assumed to be in thermal equilibrium, the equality $A_{2,3} = A_{2,4}$, should hold.

IV. DISCUSSION OF THE RESULTS AND CONCLUSIONS

Let us assume that initially the XH_3 group is in the state $\langle\chi|\Psi_3^{(n)}\rangle$, i.e., $P_3(0) = 1$. Then it follows from Eq. (10) that the probability $P_2(t)$ for the group to be in the state $\langle\chi|\Psi_2^{(n)}\rangle$ at time t equals $A_{2,3}(t)$. Now, it is evident from Eq. (11c) that, in general, this transition cannot be interpreted as being due to orientational jumps of the group from one equilibrium orientation to another. Namely, the terms in Eq. (11c) with $p \neq p'$ are the familiar interference cross terms. (Incidentally, the transitions among the states, $\langle\chi|\Psi_i^{(n)}\rangle$, $i = 2,3,4$, for example, represent a situation analogous to the one which would occur in a triple slit experiment. The three alternative paths are, in the present case, fixed by the spin components of the total wave function). The interference is especially pronounced in the case of an isolated $(\lambda_j, c_j \to 0)XH_3$ group in a threefold hindering potential. In the low-temperature limit, when only the $H^{(0)}(\chi)$ state needs to be considered, the dilute-instanton-gas approximation yields for Eq. (12),[17,19]

$$K_0(p_2 2\pi/3, p_2' 2\pi/3, t; p_1 2\pi/3, p_1' 2\pi/3, 0) = \tfrac{1}{9}\{1 + 4\cos[(p_2 - p_1)2\pi/3]\cos[(p_2' - p_1')2\pi/3]$$

$$+ 2e^{-i\omega_T^{(0)}t}\cos[(p_2 - p_1)2\pi/3] + 2e^{i\omega_T^{(0)}t}\cos[(p_2' - p_1')2\pi/3]\}, \tag{13}$$

where $\omega_T^{(0)} = 6\omega_c(S_0/2\pi\hbar)^{1/2}e^{-S_0/\hbar}$ is the tunneling frequency corresponding to the E-A splitting of the ground-state manifold $\psi_0^{(v)}(\chi)$. $\omega_c = \sqrt{(9V_3/2I)}$ is the classical torsional or librational frequency, while $S_0 = 8I\omega_c/9$ is the instanton (anti-instanton) action associated with the imaginary-time solution connecting two neighboring minima of the hindering potential.

In general, however, this interference is suppressed due to the presence of the Debye-Waller-like factor $e^{-(W(\beta)/4\pi^2)[\tilde{\delta}^2(0) + \tilde{\delta}^2(t)]}$ in Eq. (7). $\tilde{\delta}(0) = \chi_1 - \chi_1'$, $\tilde{\delta}(t) = \chi_2 - \chi_2' + 2\pi(N - N')$ and, in particular, for the terms in Eq. (11c) corresponding to $p \neq p'$, $\chi_1 - \chi_1'$, $\chi_2 - \chi_2' \cong \pm 2\pi/3$. Specifically, if $W(\beta)$ is sufficiently large, the interference cross terms in Eq. (11c) are completely suppressed. Therefore, just the terms with $p = p'$ survive in Eq. (11c) and, moreover, only the paths with $N = N'$ will contribute substantially to the path integrals in Eq. (12). Thus,

$$A_{2,3} \cong (1/9) \sum_{p=0,\pm 1} K(p2\pi/3, p2\pi/3, t; (p-1)2\pi/3, (p-1)2\pi/3, 0),$$

understood in the coarse-grained sense referred to in connection with Eq. (12), represents a sum of probabilities $K(p2\pi/3,p2\pi/3,t;(p-1)2\pi/3,(p-1)2\pi/3,0)$, corresponding to orientational jumps between neighboring minima of the hindering potential. This is then the content of the rotational hopping or jump model.[1] We also note, by inspecting Eq. (12), that there is a probability for orientational jump associated with each winding number N separately. For a given N, on the other hand, we have to add the amplitudes for all Feynman paths starting at one minimum of the potential and ending at the adjacent one.

The degree of interference suppression depends, of course, on the magnitude of

$$W(\beta)=(2\pi/\hbar)\int_0^\infty d\omega(J_q(\omega)/\omega^2)\coth(\beta\hbar\omega/2),$$

where $J_q(\omega)$ is given by Eq. (8d). In order to make an estimate for $W(\beta)$ we shall assume that the librational spectrum is similar to the spectrum of optical phonons, namely, the librational frequencies $\Omega(\mathbf{k})$ [we made a replacement $\Omega_j\rightarrow\Omega(\mathbf{k})$, where $-\pi\leq k\leq\pi$ is a dimensionless wave number) form a narrow band around ω_c.[20] The width of the librational band is, in this model, due to electrostatic octupole-octupole interaction $g_{TT}V_3$ between neighboring $X\mathrm{H}_3$ groups. V_3 is the height of the hindering potential and g_{TT} is a dimensionless torsion-torsion coupling constant. The corresponding width of the librational band is then roughly equal to $g_{TT}\omega_c$. Consequently, at low temperatures such that $k_BT\ll\hbar\omega_c$, we obtain $W(\beta)\cong2\pi g_{TT}J_q(\omega_c)/\hbar\omega_c$. Using also Eq. (8d) we can finally write $W(\beta)\cong(g_{TT}/16\pi)\times(I/J)(\hbar\omega_c/(\hbar^2/2I))\langle c^2(\mathbf{k})\rangle_{\omega_c}$, where the rotational constant $\hbar^2/2I$ equals 0.65 meV in the case of CH_3 groups, for example. The last factor $\langle c^2(\mathbf{k})\rangle_{\omega_c}=\int_{\Omega(\mathbf{k})=\omega_c}dS_\mathbf{k}c^2(\mathbf{k})/|\nabla\Omega(\mathbf{k})/\omega_c|$ is some sort of a weighted average of the coupling constant $c(\mathbf{k})$ over the constant frequency surface $\Omega(\mathbf{k})=\omega_c$, in $\mathbf{k}$ space. In the case of electrostatic octupole-octupole interactions it is fairly reasonable to assume that $g_{TT}\approx0.1$. To get an estimate, we set $J\approx I$, and considering the range of hindering potentials, $50<V_3/(\hbar^2/2I)<100$ $[20<\hbar\omega_c/(\hbar^2/2I)<30]$, we obtain $W(\beta)\cong0.1\langle c^2(\mathbf{k})\rangle_{\omega_c}$. Unfortunately, not much information of interest regarding the lattice dynamics in molecular crystals is available. We do know, however, that quantum coherence effects are observed up to temperatures high compared to typical tunneling splittings, which are on the order of a few μeV. Thus, we suspect that in most lattices $\langle c^2(\mathbf{k})\rangle_{\omega_c}$ is rather small and, consequently, the Debye-Waller factor is ineffective in suppressing the interference at temperatures $k_BT\ll\hbar\omega_c$. On the other hand, at higher temperatures the $\coth(\beta\hbar\omega/2)$ factor in the expression for $W(\beta)$ can be large enough for decoherence to become effective, resulting in the appearance of classical reorientational jumping.[4]

We therefore conclude that the onset of rotational hopping motion, at least in the model considered, is primarily due to the velocity-dependent interaction, $Ic_j\dot\chi\dot q_j$, of the $X\mathrm{H}_3$ group with librational phonons. The extent of the suppression of the interference cross terms, which is required for the validity of the model, depends on the magnitude of the Debye-Waller factor which, in turn, is determined by the spectral density of the librational modes and temperature. Consequently, in most molecular crystals at temperatures such that $k_BT\ll(\hbar^2/2I)\sqrt{9V_3/(\hbar^2/2I)}$, the rotational motion of the $X\mathrm{H}_3$ groups cannot be interpreted consistently as reorientational jumps. This is in agreement with the experimental results pertaining to rotational tunneling of methyl groups, for example, that the effect is observable at temperatures much higher than the tunneling splitting themselves.[21] On the other hand, at higher temperatures when $W(\beta)\gg1$, the rotational motion may be considered, at least for all practical purposes, as classical reorientational jumping of the molecular group from one equilibrium orientation to another.

The role of the remaining terms of the influence functional (7) is not crucial for the hopping model, and moreover, they were already discussed briefly in Ref. 17. Let us only mention that coupling to translational phonons via the three-fold symmetric coupling term $f_j(\chi)Q_j$ is not very effective in suppressing interference between different Feynman paths.[17]

Last but not least, we should also acknowledge a considerable effort that has been devoted in the past to a wide range of problems concerning methyl dynamics in solids[22–25] and references cited therein. In spite of some difference between various authors on specific points, a fairly coherent picture about the motion of methyl groups has emerged. However, the rather important issue, namely, the consistency of classical hopping, whenever this notion is applicable, with Pauli principle has not been clarified. We believe that decoherence as a mechanism for suppressing interference as defined above, which occurs whenever one is dealing with orientationally delocalized (3) or partially localized states (9),[23,24] achieves this goal.

But, is such an extension of a description of a physical system into the classical domain, when a satisfactory quantum-mechanical prediction is available, still necessary or, is it still useful, especially, since ''nature isn't classical, dammit...,'' as Feynman once said.[26] To be quite precise, by imaging classical hopping of methyl groups we are assigning even more classicality to the system as is usually done in the case of simple ''measured'' systems, where classical behavior is approximated by appropriate coarse graining of their description (passage of a nuclear particle through a bubble chamber).[27] In the world of everyday experience such an extension is certainly mandatory. Here quantum mechanics has to account for the classical trajectories of the planets, for example, whether or not any ''observer'' is looking at them.[27] This is achieved, at least in some schemes,[27] by environment-induced decoherence in the sense discussed above (apparently even scattering by cosmic background photons is sufficient[10]). On the other hand, when one is dealing with a genuinely microscopic system, such as a methyl group embedded in a solid lattice, there seems to be no compelling reason for invoking classical notions, apart from the fact that they appeal to our common-sense intuition. On more general terms, however, it is, of course, gratifying to find out that decoherence could be effective also on a microscopic scale.

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