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Environmental influence on intramolecular electron-vibration transitions

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Abstract. A path integral method is used to calculate the rate of intramolecular electron-vibration transitions taking into account the influence of the environment as the source of random Gaussian forces for vibrational degrees of freedom. The evaluation of the generating function for the rates of multiquantum transitions is reduced to the solution of some integral equations with the kernels dependent on the random force correlation function. For the Markovian Gaussian random process the exact expression for the generating function is obtained. The manifestation of the dynamical modulation effects of the surroundings fluctuations on tunnel and thermostimulated transitions is investigated.

Radiationless charge transfer transitions in molecular systems interacting with the environment (polar solvent, etc) are of great importance for a wide class of chemical and biochemical processes. Therefore the problem is treated intensively with unremitting interest [1-7]. The environment essentially influences the character of intramolecular electron transitions, their rates, temperature dependence, etc. The best studied model of electron transfer takes account of the interaction of the electron with the dipolar molecules of the polar solvent only. In this model the role of the environment reveals a temporal modulation of electron transition frequencies by Gaussian random processes. If the solvent is described by the Debye-type spectrum of dielectric losses, the above-mentioned Gaussian random process is also the Markovian one. Its correlation function behaves as $\exp(-|t|/\tau_c)$ where τ_c is the correlation time of random forces by which the environment affects the electron. For a sufficiently small perturbation value causing the quantum transition its rate may be obtained by the golden rule and averaging over all possible realisations of random forces. The latter procedure is reduced to averaging some linear-exponential functional and can be easily performed for a Gaussian process. As far as the intramolecular transitions in the presence of a solvent are concerned, the strong interaction between an electron and molecular vibrations is of great importance. Here one of the main channels of the solvent influence on the electron transfer is the indirect electron-solvent coupling through the solvent modification of intramolecular vibration dynamics [8-10].

An important aspect of this modification was considered in [8] by treating the environment as a source of the friction forces for quantum molecular vibrations. In this context the problem of intramolecular transition is similar to the problem of a quantum particle tunnelling in the presence of dissipation. The latter has been actively investigated recently in connection with the study of tunnelling in the Josephson junction [11].

The aim of the present paper is to consider another aspect of the problem. The intramolecular electron-vibration radiationless transitions may be interpreted as an

activation going over (high-temperature regime) or tunnelling through (low-temperature regime) the potential barriers by molecule nuclei. We shall investigate the role of environment as a stochastic modulator of the potential barrier's heights and widths by means of variation of equilibrium nuclei positions in different electronic states and energy gaps between the adiabatic energy surfaces.

The principles of quantum tunnelling in the presence of external time-dependent fields are well elaborated (see [12-15]). The main features of this process reveal themselves also in intramolecular nuclear tunnelling considered here.

In the simplest model used below for describing the solvent dynamic modulation effects on the electron-vibration transition, the generating function for the transition probability will be presented by averaging some exponential-quadratic-type functional of random forces with a symmetric time-translation-invariant kernel. For the Gaussian-Markovian type of random process representing the influence of the environment, the averaging will be executed exactly by direct evaluation of the path integral over all realisations of random forces.

Let us model the energy spectrum of the molecular electron-vibration system in the absence of solvent by two parabolic adiabatic terms $U_{1,2}(q)$ with the same curvature but shifted equilibrium positions (q is the vibration coordinate). The polar solvent action is modelled by the existence of some classical random force affecting the nuclei. For quantum transitions accompanied by charge transfer, the force is, generally speaking, dependent on the electronic state. For the sake of simplicity we shall take this into account in the final state 2 only. The model Hamiltonian for this two-channel electron-vibration system may be presented in a matrix form:

$$\begin{aligned}
 H &= H^d + H^{nd} \\
 H^d &= \begin{bmatrix} H_1 & 0 \\ 0 & H_2 \end{bmatrix} & H^{nd} &= \begin{bmatrix} 0 & M \\ M & 0 \end{bmatrix} \\
 H_{1,2} &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} + U_{1,2}(q) \\
 U_1(q) &= \frac{m\omega^2 q^2}{2} \\
 U_2(q) &= \hbar\omega_0 + \frac{m\omega^2 q^2}{2} - [m\omega^2 q_s + f(t)]q.
 \end{aligned}$$

Here m and ω are the reduced mass and the frequency of nuclei vibration, $\hbar\omega_0 = U_2(0)$ and q_s is the distance between the $U_{1,2}(q)$ minima in the absence of solvent. The force $f(t)$ is the Gaussian-Markovian random process with the correlation function.

$$B(t_1, t_2) = B_0 \exp[-\gamma|t_1 - t_2|] \quad \gamma = 1/\tau_c. \quad (1)$$

The matrix element M of the non-diagonal perturbation producing $1 \rightarrow 2$ transition is assumed to be constant. With the use of the interaction representation the system density matrix $\hat{\rho}$ obeys

$$\begin{aligned}
 \hat{\sigma} &= S^{-1} \hat{\rho} S & i\hbar \frac{dS}{dt} &= H^d S \\
 S(t_3, t_1) &= S(t_3, t_2) S(t_2, t_1) \\
 S(t, t) &= 1.
 \end{aligned}$$

The equation for the non-diagonal matrix element σ_{21} which determines the rate of quantum transition is given by

$$\begin{aligned} i\hbar \frac{d\sigma_{21}}{dt} &= \tilde{H}_{21}^{\text{nd}} \sigma_{11} - \sigma_{22} \tilde{H}_{21}^{\text{nd}} \\ \tilde{H}_{21}^{\text{nd}} &= S_{22}^{-1} S_{11} M. \end{aligned} \quad (2)$$

As is easily shown

$$S_{22}(t, t') = S_{11}(t, t') \exp[-i\omega_0(t-t')] \hat{T} \exp\left(-\frac{i}{\hbar} \int_{t'}^t V(t'') dt''\right)$$

$$V(t) = -q(t)[m\omega^2 q_s + f(t)]$$

$$q(t) = \exp\left(-\frac{i}{\hbar} H_1 t\right) q \exp\left(\frac{i}{\hbar} H_1 t\right)$$

where the \hat{T} operator provides chronological ordering.

Let us assume here that the perturbation causing the transition is weak enough so that the populations of the 1, 2 states are not greatly deviated from their equilibrium values:

$$\begin{aligned} \sigma_{22} &\ll \sigma_{11} \\ \sigma_{11} &\simeq \rho_{11}^0 = \frac{1}{Z} \exp\left(-\frac{H_1}{T}\right) \quad Z = \text{Sp} \left\{ \exp\left(-\frac{H_1}{T}\right) \right\} \end{aligned} \quad (3)$$

where T is the temperature.

The rate of the 1 \rightarrow 2 transition is given by

$$W_{12} = \langle\langle \dot{\rho}_{22} \rangle\rangle \quad (4)$$

where the inner brackets denote the quantum statistical average (trace over vibration quantum states in term 1 $\langle \dots \rangle = \text{Sp} \{ \dots \rho_{11}^0 \}$). The outer brackets mean the average over all realisations of the random process $f(t)$. With the use of (2), (3) and (4) we obtain

$$W_{12} = \frac{2M^2}{\hbar^2} \text{Re} \int_{t_0}^t \langle\langle S_{22}(t, t') S_{11}(t', t) \rangle\rangle dt' \quad (5)$$

where t_0 is the moment of perturbation 'switch on', $t - t_0 \rightarrow \infty$. The stationarity of the $f(t)$ process provides the integrand dependence in (5) on $t - t'$ only. Using the $t - t_0 \rightarrow \infty$ limit one can obtain

$$W_{12} = \frac{2M^2}{\hbar^2} \text{Re} \int_0^\infty e^{-i\omega_0 t} \mathcal{F}(t) dt \quad (6)$$

$$\mathcal{F}(t) = \langle\langle \hat{T} \exp\left(-\frac{i}{\hbar} \int_0^t V(t') dt'\right) \rangle\rangle. \quad (7)$$

The quantum-statistical average in (7) is evaluated exactly by means of standard methods of multiquantum electron-vibration transition theory (see [16])

$$\begin{aligned}\mathcal{T}(t) &= \langle \phi([f(t)]) \rangle \\ \phi[f(t)] &= \exp\left(-\frac{1}{2} \int_0^t \int_0^t [1 + \eta(t_1)] G(t_1, t_2) [1 + \eta(t_2)] dt_1 dt_2\right) \\ G(t_1, t_2) &= \frac{1}{2} a \omega^2 [(\bar{n} + 1) \exp(-i\omega|t_1 - t_2|) + \bar{n} \exp(i\omega|t_1 - t_2|)] \\ \bar{n} &= \left[\exp\left(\frac{\hbar\omega}{T}\right) - 1 \right]^{-1} \quad \eta(t) = \frac{f(t)}{m\omega^2 q_s} \quad a = \frac{m\omega q_s^2}{\hbar}.\end{aligned}\tag{8}$$

It is convenient to average the exponential-quadratic functional $\phi([f(t)])$ in (8) by presenting $\mathcal{T}(t)$ in the form of a path integral:

$$\mathcal{T}(t) = \frac{\int D\eta \exp\{-\frac{1}{2}\eta(G + F^{-1})\eta - \eta\xi\}}{\int D\eta \exp\{-\frac{1}{2}\eta F^{-1}\eta\}} \exp(\frac{1}{2}a\varphi)\tag{9}$$

where

$$\begin{aligned}\xi(t_1) &= \int_{t_0}^t G(t_1, t') dt' \\ F^{-1}(t_1, t_2|t) &= m^2 \omega^4 q_s^2 B^{-1}(t_1, t_2|t) \\ \int_0^t B^{-1}(t_1, t'|t) B(t', t_2) dt' &= \delta(t_1 - t_2) \\ \varphi(t) &= -\frac{1}{a} \int_0^t \int_0^t G(t_1, t_2) dt_1 dt_2 = i\omega t + (\bar{n} + 1) e^{-i\omega t} + \bar{n} e^{i\omega t} - (2\bar{n} + 1).\end{aligned}$$

Here $B^{-1}(t_1, t_2|t)$ is the kernel of the integral operator inverse to $B(t_1, t_2)$ on the finite interval $(0, t)$ (symbol t separated by a vertical line represents the parametric dependence of the kernel on t). The products of functions ($\alpha\beta$), operators (AB), functions and operators ($\alpha A, A\alpha$) present in (9) mean the following:

$$\begin{aligned}\alpha\beta &= \int_0^t \alpha(t')\beta(t') dt' \\ AB &= \int_0^t A(t_1, t')B(t', t_2) dt' \\ \alpha A &= \int_0^t \alpha(t')A(t', t_2) dt' \\ A\alpha &= \int_0^t A(t_1, t')\alpha(t') dt'.\end{aligned}\tag{10}$$

Let us now carry out the procedure of functional shift $\eta = \Omega + \bar{\eta}$ for the path integral in the numerator of (9) in order to eliminate the terms linear in $\bar{\eta}$ from the exponent. The corresponding function Ω has to satisfy

$$\begin{aligned}\Omega &= -L\xi \quad L = (1 + FG)^{-1}F \\ F &= (F^{-1})^{-1} = \frac{1}{am\hbar\omega^3} B.\end{aligned}$$

The quantity $L(t_1, t_2|t)$ obeys the equation

$$L(t_1, t_2|t) = F(t_1, t_2|t) - \int_0^t \int_0^t F(t_1, t'|t) G(t', t'') L(t'', t_2|t) dt' dt''.$$

After performing the shift operation the remaining integration over $\bar{\eta}$ is straightforward due to the Gaussian character of the integral:

$$\mathcal{T}(t) = \frac{1}{\sqrt{\det|1+FG|}} \exp\left(\frac{\alpha\varphi}{2} + \frac{1}{2}\xi L\xi\right). \quad (11)$$

It is easily seen that

$$\psi = \frac{1}{2}\xi L\xi = \frac{1}{2} \int_0^t \int_0^t Q(t_1, t_2|t) dt_1 dt_2 \quad (12)$$

where the quantity $Q = GLG$ satisfies the following integral equation (in symbolic notation):

$$Q = GFG - GFQ. \quad (13)$$

The value of $\det|1+FG|$ may be calculated using the well known formula

$$\det|1+FG| = \exp\{\text{Sp} \ln(1+FG)\}$$

resulting in

$$\frac{d}{dt} \ln \det|1+FG| = \frac{d}{dt} \text{Sp}\{FG - \frac{1}{2}FGFG + \frac{1}{3}FGFGFG - \dots\}. \quad (14)$$

By straightforward differentiation of the sum in (14) one arrives at the expression

$$\frac{d}{dt} \ln \det|1+FG| = 2R(t, t|t) \quad (15)$$

where the quantity $R = (1+FG)^{-1}FG$ obeys the following integral equation:

$$R = FG - FGR. \quad (16)$$

Since $\det|1+FG| = 1$ at $t = 0$ equation (15) leads to

$$\det|1+FG| = \exp\left(2 \int_0^t R(t', t'|t') dt'\right). \quad (17)$$

The expressions (11), (12) and (17) provide the general solution for the generating function $\mathcal{T}(t)$ through the solutions of integral equations (13) and (16). For the correlation function $B(t_1, t_2)$ determined by (1) the latter solutions may be obtained in an explicit form by reducing the integral equations (13) and (16) to differential ones ($x = \omega t_1, y = \omega t_2$):

$$\frac{d^4 R}{dx^4} + (1 - \kappa^2) \frac{d^2 R}{dx^2} + \kappa(2ib - \kappa)R = 2ib\kappa\omega\delta(x - y) \quad (18)$$

$$\frac{d^4 Q}{dx^4} + (1 - \kappa^2) \frac{d^2 Q}{dx^2} + \kappa(2ib - \kappa)Q = 2ib\kappa G(x, y) \quad (19)$$

$$\kappa = \gamma/\omega \quad b = B_0/m\hbar\omega^3.$$

The partial solutions of these inhomogeneous differential equations may be chosen in the form

$$R_p(x, y|t) = \frac{ibx\omega}{S_1^2 - S_2^2} \left(\frac{1}{S_1} e^{-S_1|x-y|} - \frac{1}{S_2} e^{-S_2|x-y|} \right) \quad (20)$$

$$Q_p(x, y|t) = \frac{ia\omega^2}{2(S_1^2 - S_2^2)} \left[\frac{S_2^2 - 1}{S_1} e^{-S_1|x-y|} - \frac{S_1^2 - 1}{S_2} e^{-S_2|x-y|} \right] + G(x, y)$$

$$S_{1,2} = \left\{ \frac{1}{2} [(\kappa^2 - 1) \mp ((\kappa^2 + 1)^2 - 8ibx\kappa)^{1/2}] \right\}^{1/2}. \quad (21)$$

The solutions of (13) and (16) can be found as a sum of partial solutions (20) and (21) and the linear combinations of the solutions of homogeneous equations corresponding to (18) and (19):

$$R(x, y|t) = R_p(x, y|t) + k_1 e^{S_1 x} + \bar{k}_1 e^{-S_1 x} + k_2 e^{S_2 x} + \bar{k}_2 e^{-S_2 x} \quad (22)$$

$$Q(x, y|t) = Q_p(x, y|t) + A_1 e^{S_1(x+y)} + \bar{A}_1 e^{-S_1(x+y)} + A_2 e^{S_2(x+y)} + \bar{A}_2 e^{-S_2(x+y)}$$

$$+ B_1 [e^{S_1(x-y)} + e^{-S_1(x-y)}] + B_2 [e^{S_2(x-y)} + e^{-S_2(x-y)}]$$

$$+ C [e^{S_1 x + S_2 y} + e^{S_2 x + S_1 y}] + \bar{C} [e^{-S_1 x - S_2 y} + e^{-S_2 x - S_1 y}]$$

$$+ E [e^{S_1 x - S_2 y} + e^{-S_2 x + S_1 y}] + \bar{E} [e^{-S_1 x + S_2 y} + e^{S_2 x - S_1 y}]. \quad (23)$$

The substitution of (22) and (23) in (13), (16) yields the system of linear algebraic equations for $k_{1,2}$, $\bar{k}_{1,2}$, $A_{1,2}$, $\bar{A}_{1,2}$, $B_{1,2}$, C , \bar{C} , E , \bar{E} .

The system has been solved in a conventional way but the obtained expressions are not presented here because of their lengthy form. The system determinant $\mathcal{D}(t)$ is given by

$$\mathcal{D}(t) = (\bar{n} + 1)^2 e^{-i\omega t} \left\{ \left[e^{\frac{1}{2}(S_1 + S_2)\omega t} \left(\frac{S_1 + \kappa}{S_2 - i} - \frac{S_2 + \kappa}{S_1 - i} \right) + e^{-\frac{1}{2}(S_1 + S_2)\omega t} \left(\frac{S_1 - \kappa}{S_2 + i} - \frac{S_2 - \kappa}{S_1 + i} \right) \right]^2 \right.$$

$$\left. - \left[e^{\frac{1}{2}(S_1 - S_2)\omega t} \left(\frac{S_1 + \kappa}{S_2 + i} - \frac{S_2 - \kappa}{S_1 - i} \right) + e^{-\frac{1}{2}(S_1 - S_2)\omega t} \left(\frac{S_1 - \kappa}{S_2 - i} - \frac{S_2 + \kappa}{S_1 + i} \right) \right]^2 \right\}$$

$$- \bar{n}^2 e^{i\omega t} \left\{ \left[e^{\frac{1}{2}(S_1 + S_2)\omega t} \left(\frac{S_1 + \kappa}{S_2 + i} - \frac{S_2 + \kappa}{S_1 + i} \right) + e^{-\frac{1}{2}(S_1 + S_2)\omega t} \left(\frac{S_1 - \kappa}{S_2 - i} - \frac{S_2 - \kappa}{S_1 - i} \right) \right]^2 \right.$$

$$\left. - \left[e^{\frac{1}{2}(S_1 - S_2)\omega t} \left(\frac{S_1 + \kappa}{S_2 - i} - \frac{S_2 - \kappa}{S_1 + i} \right) + e^{-\frac{1}{2}(S_1 - S_2)\omega t} \left(\frac{S_1 - \kappa}{S_2 + i} - \frac{S_2 + \kappa}{S_1 - i} \right) \right]^2 \right\}$$

$$- \frac{8\bar{n}(\bar{n} + 1)(S_1^2 - S_2^2)}{(S_1^2 + 1)(S_2^2 + 1)} [S_2(S_1 + \kappa)^2 e^{S_1\omega t} - S_2(S_1 - \kappa)^2 e^{-S_1\omega t}$$

$$- S_1(S_2 + \kappa)^2 e^{S_2\omega t} + S_1(S_2 - \kappa)^2 e^{-S_2\omega t}]. \quad (24)$$

Using (22) and (24) one can verify that

$$R(t, t|t) = \frac{1}{2} \left[\frac{d}{dt} \ln \mathcal{D}(t) - \gamma \right].$$

Thus, in accordance with (17) the explicit form for $\det|1 + FG|$ is

$$\det|1 + FG| = \frac{\mathcal{D}(t)}{\mathcal{D}(0)} e^{-\gamma t}. \quad (25)$$

The above consideration completely resolves the problem of evaluating the generating function $\mathcal{T}(t)$ in terms of elementary functions. The further calculations of the transition rates for various relations among the dimensionless parameters a , b , κ can be easily performed by the computer-generated Fourier transformation (6).

For illustration of the qualitative features of W_{12} dependence on parameters a , b , and κ let us present some asymptotic estimates.

In the limit of extremely low $f(t)$ fluctuations (quasistatic limit, $b/\kappa \gg 1$) the general expression for $\mathcal{T}(t)$ is reduced to

$$\mathcal{T}(t) = \frac{1}{\sqrt{1-b\varphi(t)}} \exp\left(\frac{(a/2)\varphi(t)}{1-b\varphi(t)}\right). \quad (26)$$

After substituting (26) into (6) the W_{12} estimate can be done by the saddle-point method. For high enough values of temperature and of heat release constant

$$\begin{aligned} \hbar\omega a\bar{n}^2 \gg \Delta & \quad \Delta = \hbar\omega \frac{p_0^2}{2a} & \quad p_0 = \frac{|\omega_0|}{\omega} \gg 1 \\ \bar{n} \gg 1 & \quad a \geq 1 \end{aligned} \quad (27)$$

and for the b magnitude satisfying

$$b \ll \frac{a^2\bar{n}}{p_0^2} \quad b = \max\left(\frac{a}{6\bar{n}p_0}, \frac{1}{12\bar{n}}\right)$$

we get the following estimate:

$$W_{12} \sim \exp\left(-\frac{\Delta^*}{T}\right) \quad \Delta^* = \Delta\left(1 - \frac{2\alpha\Delta}{a}\right). \quad (28)$$

Here Δ is the activation energy for the $1 \rightarrow 2$ transition, $\omega_0 < 0$ (i.e. the process of radiationless de-excitation is considered). While deriving (28) we took into account that the intensity of chaotic force is proportional to the temperature: $b = \alpha T$. Thus the interaction of the molecule with the surroundings leads to an activation energy decrease providing the exponential growth of transition rate. Figure 1 shows the activation energy (Δ^*) dependence on the intensity of fluctuations (b), numerically obtained by the use of (6) and (26). This numerical result confirms the above-mentioned tendency of Δ^* to decrease.

For the case of low temperature ($\bar{n} \ll 1$) and small b values one can get the following asymptotic expression:

$$W_{12} \sim W_{12}^0 \exp\left\{\frac{ab}{2} \left[\frac{2p_0}{a} - \ln\left(\frac{2p_0}{a} + 1\right) \right]^2\right\} \quad (29)$$

where W_{12}^0 is the temperature-independent rate of tunnel transition in the absence of external fields. Thus, the interaction with the surroundings leads to an exponential increase in the tunnelling probability and causes strong temperature dependence of the transition rate ($b \sim T$). It is worth mentioning that the enhancement of transition probability is due to random force fluctuations optimal for tunnelling by providing the decrease in barrier widths and heights. The statistical weight of optimal fluctuations rises with temperature and causes the enhancement of transition probability. In figure 2(a) numerical results are plotted for the rate of tunnel radiationless transition against

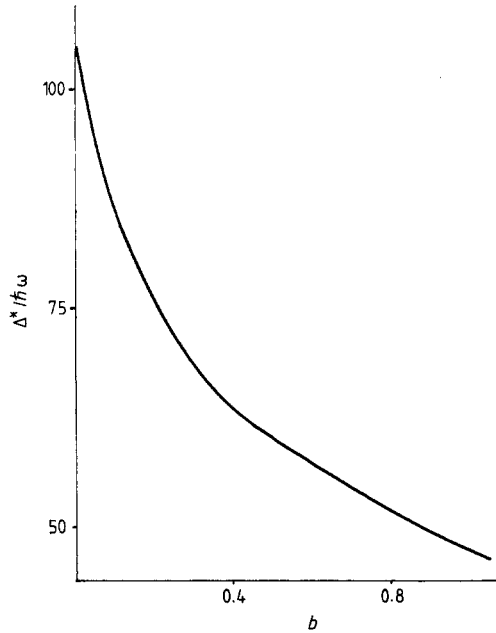


Figure 1. The activation energy Δ^* of thermostimulated radiationless transition as a function of the intensity of the random force (parameter b) in the quasistatic limit; ($\gamma/\omega = 0$), $p_0 = 50$, $a = 10$, $\bar{n} = 30$.

the intensity of random forces for a wide range of variations of the parameter b . The sharp enhancement of the rate value against the b is clearly seen.

The expression (26) may be presented in the form

$$\mathcal{T}(t) = \frac{1}{\sqrt{2\pi B_0}} \int_{-\infty}^{\infty} \exp\left(-\frac{f^2}{2B_0}\right) \mathcal{T}_0[a(f), t] df$$

$$\mathcal{T}_0[a(f), t] = \exp\left\{\frac{1}{2}a(f)g(t)\right\}$$

$$a(f) = a\left(1 + \frac{f}{m\omega^2 q_s}\right)^2.$$

The value $\mathcal{T}_0[a(f), t]$ represents the well known generating function for multiquantum radiationless transitions [16] corresponding to a fixed value of the heat release constant $a(f) = m\omega q_s^2(f)/\hbar$. Here $q_s(f) = q_s + f/m\omega^2$ is the relative displacement of adiabatic potential minima along the q coordinate in the presence of a constant force f . Hence

$$W_{12} = \frac{1}{\sqrt{2\pi B_0}} \int_{-\infty}^{\infty} \exp\left(-\frac{f^2}{2B_0}\right) W_{12}^0(f) df.$$

Thus the W_{12} value is presented as an average of the well known expression $W_{12}^0(f)$ for transition probability in the displaced parabola model (see e.g. [16]). The averaging is performed by means of the Gaussian distribution for all possible realisations of random force value. This interpretation is, of course, the direct consequence of the quasistatic limit ($\kappa \rightarrow 0$) used in (26).

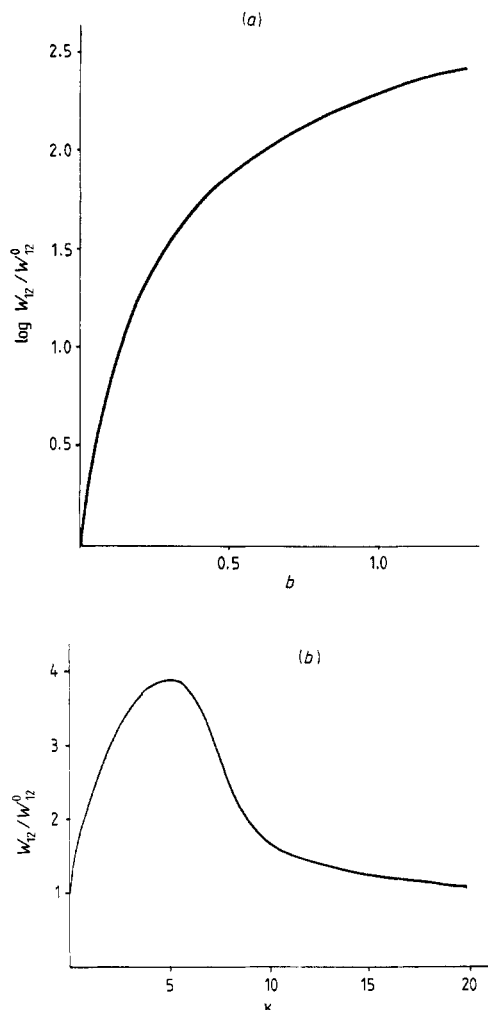


Figure 2. The probability of tunnel radiationless transition as a function of (a) parameter b , ($\kappa = 0$), (b) spectral width κ , ($b = 0.02$); $W_{12}^0 = W_{12}$ ($b = 0$), $p_0 = 8$, $a = 2$.

Let us now consider the opposite limit $b/\kappa \ll 1$, $\kappa \gg 1$, corresponding to very fast environment fluctuations. Using (12), (25) and retaining only the leading terms in b/κ we obtain

$$\begin{aligned}
 (\det|1 + FG|)^{-1/2} &\approx \exp\left(-\frac{b}{2\kappa} (2\bar{n} + 1)\omega t\right) \\
 \psi(t) &\approx -\frac{ab}{2\kappa} \vartheta_1(t)\omega t - i\frac{ab}{2\kappa} \vartheta_2(t) \\
 \vartheta_1(t) &= 2 + e^{i\omega t}[\bar{n} - (\bar{n} + 1)e^{-i\omega t}]^2 \\
 \vartheta_2(t) &= [(\bar{n} + 1)e^{-i\omega t} - \bar{n}]\{4(e^{i\omega t} - 1) - \frac{1}{2}[(\bar{n} + 1)e^{-i\omega t} - \bar{n}](e^{2i\omega t} - 1)\}.
 \end{aligned} \tag{30}$$

In accordance with (30) when $\max(ab/\kappa, b/\kappa) \ll 1$ the environment slightly affects the molecule quantum transitions. Let us consider the intermediate situation, when $b/\kappa \ll 1$, but $a \gg 1$ so that $ab/\kappa \approx 1$. Using the Fourier transform of $\exp[(a/2)\varphi(t)]$ we find

from (6), (11) and (30) that

$$W_{12} = \frac{2M^2}{\hbar^2\omega} \sum_{n=-\infty}^{\infty} Z_{n_0-n}(a, \bar{n}) g\left(p_0 + \frac{a}{2} - n_0 + n\right) \quad (31)$$

$$Z_n(a, \bar{n}) = \exp\left[-\frac{a}{2}(2\bar{n}+1)\right] I_n(a\sqrt{\bar{n}(\bar{n}+1)}) \exp\left(n\frac{\hbar\omega}{2T}\right)$$

$$g(x) = \operatorname{Re} \int_0^{\infty} \exp[ix\tau - \Gamma\tau + \psi(\tau)] d\tau \quad \tau = \omega t. \quad (32)$$

Here $I_n(x)$ is the modified Bessel function, $n_0 = [p_0 + (a/2)]$ is the integer part of $p_0 + (a/2)$ and Γ is the phenomenologically introduced phase relaxation width of the electron transition, expressed in ω units. This relaxation provides the convergence of the integral in (32) when $b/\kappa = 0$. Using the integration by parts in (32) it is easy to obtain the following asymptotic estimate for $x \gg 1$:

$$g(x) \sim \frac{3(2\bar{n}+1)^2 ab}{2\kappa x^4} \quad \frac{3(2\bar{n}+1)ab}{2\kappa x^2} \gg \Gamma.$$

In the absence of the molecule vibration interaction with the surroundings, and for $\Gamma \ll 1$, the leading contribution in (31) is given by the $n = 0$ term

$$W_{12}^0 = \frac{2M^2}{\hbar^2\omega} \frac{1}{(p_0 + (a/2) - n_0)^2 + \Gamma^2} Z_{n_0}(a, \bar{n}).$$

If, however, the value of ab/κ is not too small the terms corresponding to $n = 1, 2, \dots$ turns out to be significant. This is due to the fact that in spite of the slight power-type $g(p_0 + (a/2) - n_0 + n)$ decrease with n the value of Z_{n_0-n} increases exponentially both for high temperature ($\bar{n} \gg 1$), when

$$Z_{n_0-n} \sim \left(\frac{\hbar\omega}{2\pi a T}\right)^{1/2} \exp\left(-\frac{\hbar\omega}{T} \frac{(p_0 - n)^2}{2a}\right)$$

and for low temperature ($\bar{n} \ll 1$), when

$$Z_{n_0-n} \sim \frac{1}{\sqrt{2\pi(n_0 - n)}} \left(\frac{a}{2(n_0 - n)}\right)^{n_0-n} \exp(n_0 - n - \frac{1}{2}a) \quad n_0 - n \gg 1.$$

The simple estimate for W_{12} can be obtained by retaining in (30) only the term with $n = p_0$, which does not contain any exponential smallness ($W_{12} \gg W_{12}^0$):

$$W_{12} \sim \frac{6ab}{\kappa p_0^4 (2\pi)^{1/2}} \left(\frac{T}{\hbar\omega}\right)^{3/2} \quad \bar{n} \gg 1$$

$$W_{12} \sim \frac{3b}{2p_0^4 \kappa} \sqrt{\frac{a}{\pi}} \quad \bar{n} \ll 1.$$

Thus the action of quickly fluctuating surroundings on the molecule vibrational degree of freedom causes again, as in the quasistatic limit, the exponential enhancement of the electron-vibration transition probability and leads to the barrierless character of the transition process. We notice that the rate enlargement with the fluctuation spectrum broadening is provided by non-isoenergetic transitions between the vibration levels of adiabatic terms 1 and 2 induced by far-Fourier components of random forces. However, the molecular nuclei cannot follow the very fast fluctuations, so the environmental influence decreases for $b/\kappa \rightarrow 0$. Thus the W_{12} dependence on κ is a non-monotonous one.

Figure 2(b) presents the numerically obtained W_{12} dependence against γ for a wide range of γ , which confirms the above-mentioned qualitative features.

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