Chemical Physics

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Citation: J. Chem. Phys. **94**, 4809 (1991); doi: 10.1063/1.460565 View online: http://dx.doi.org/10.1063/1.460565 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v94/i7 Published by the American Institute of Physics.

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## Hydrogen tunneling in condensed media

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(Received 13 November 1990; accepted 21 December 1990)

A microscopic description for reactions in condensed media involving hydrogen tunneling, valid over a large temperature range, is presented. The tunneling system, represented by a pseudospin (S = 1/2), reaches equilibrium when coupled to its environment, modeled by a collection of harmonic oscillators that behave like a heat bath. The environment includes both modes of the lattice (or solvent) and those molecular vibrations which play an active role in the tunneling process. Analytical expressions for the reaction rate are given in various regimes.

## I. INTRODUCTION

Recent experiments have determined relaxation parameters associated with hydrogen transfer reactions in condensed media over a wide range of temperatures.<sup>1-4</sup> The systems which have been studied occur in two tautomeric forms, which we shall designate as L and R, respectively. The interconversion between these tautomers implies a change in the position of one or more hydrogen atoms, and the rearrangement of single and multiple bonds in the molecule. Examples of this type of molecule are tropolone and malonaldehyde (see Fig. 1).

The rate constant for this class of reactions presents a very complex temperature dependence. A qualitative explanation for the results can be given as follows: At very low temperatures, tunneling relaxation occurs through one phonon emission or absorption. As temperature increases, multiphonon processes become more important, and eventually lead to a semiclassical regime in which the rate constant shows the characteristic features of an activated process. The high temperature regime has been experimentally probed by nuclear magnetic resonance (NMR)<sup>2</sup> and inelastic neutron scattering;<sup>3</sup> recently, novel optical techniques have been applied to access the lower temperature region.<sup>4</sup>

The rich variety of behavior displayed by this kind of system makes it very difficult to put forth a comprehensive theoretical description valid in all the various regimes. Hence most of the theoretical models that have been considered in the past focused on rather specific limits and are inapplicable otherwise. It shall be our aim to propose a model which is general enough to cover most of the situations encountered in experiments, and yet remain analytically tractable.

### **II. MODEL HAMILTONIAN**

There are two aspects in the problem which are of particular interest from a theoretical standpoint: The effects of the coupling of the system to its environment, and the multidimensional character of the tunneling.

The effects of the environment are included in a standard fashion, within the framework of relaxation theory.<sup>5-7</sup> The second problem has been dealt with by Carrington *et al.*<sup>8</sup> and Shida *et al.*<sup>9</sup> by means of a multidimensional reaction surface description, in which the dynamics along the large amplitude modes (e.g., the two C–H bond lengths in the case of malonaldehyde in Ref. 8) are treated accurately. A locally harmonic approximation is then made for the remainder of the modes (small amplitude motion, treated adiabatically). In this manner, the dimensionality of the problem is reduced, rendering the numerical calculations feasible. Our approach to this aspect of the problem is rather different. We shall assume that the tunneling process is basically unidimensional, for an appropriately chosen tunneling coordinate. Coupled molecular vibrations shall be handled in a perturbative fashion, on the same footing as the lattice (or the solvent) is treated in relaxation theory. Hence in our model, the environment comprises both modes of the lattice and those molecular vibrations which substantially modify the dynamics along the tunneling mode. We suggest that in this fashion, the main features of multidimensional tunneling will be properly captured.

The motion along the tunneling coordinate  $\xi$  takes place in a bistable potential (Fig. 2). We shall consider the general case of an asymmetric double well, where the asymmetry is due either to differences in the structure of the two tautomers or induced by the crystal field. Instead of treating the whole problem, we shall restrict our analysis to the subspace spanned by the two lowest eigenstates of  $H_s$ . The suitable restrictions for this approximation to remain valid are:  $V_0 \gg \omega_{\pm} \gg 2\Delta_0$  and  $\kappa_B T \ll \omega_{\pm}$ , where  $V_0$  is the barrier height,  $\omega_{\pm}$  the vibrational frequencies at the bottom of the wells and  $2\Delta_0$  the difference in energy between the lowest two levels [i.e., the splitting in the absence of tunneling (see Fig. 2)]. Obviously, our treatment will not reproduce the features of an activated process with an activation energy equal to the classical barrier. The system Hamiltonian is thus truncated to that of a pseudospin with  $S = \frac{1}{2}$ . In a localized basis  $\{|L>, |R>\}$ , the Hamiltonian is

$$H_s = -\Delta_0 \sigma_z + J \sigma_x, \tag{1}$$

where J is the tunneling matrix element and the standard definition for the Pauli matrices  $\{\sigma_i\}_{i=x,y,z}$  is used. The lattice (solvent) shall be modeled by a collection of harmonic



FIG. 1. Tautomerization reaction for malonaldehyde.

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$$\omega_{\pm} = \left(\frac{d^2 V}{d\xi^2}\right)_{\xi=\pm\xi_0}$$

FIG. 2. Double well potential for the tunneling motion.

oscillators, with infinite heat capacity (it behaves as a heat bath) and a continuous spectrum (which ensures relaxation to equilibrium of the isolated lattice). The main effect of the lattice on the system is to induce fluctuations in the asymmetry of the double well, without substantially modifying the tunneling matrix element. If we assume these fluctuations to be linear in the lattice oscillator coordinates, the Hamiltonian for the supersystem (tunneling system plus environment) is

$$H = -\Delta_0 \sigma_z + J \sigma_x + \frac{1}{2} \sum_{i=1}^{N} (p_i^2 + \omega_i^2 q_i^2) + \sum_{i=1}^{N} f_i q_i \sigma_z,$$
(2)

known in the literature as the spin-boson Hamiltonian.<sup>10</sup> We note that the term in  $\sigma_y$  is not present, as it would break time reversal symmetry. In the case of a symmetric double well ( $\Delta_0 = 0$ ), the Hamiltonian must be symmetric with respect to spatial parity. This implies that  $f_i$  must vanish for those modes of the bath which are symmetric with respect to the parity operator of the bath.

Finally, we have to modify Eq. (2) in order to include the effect of strongly coupled local vibrations. For the sake of concreteness, we shall consider one particular vibrational coordinate Q assumed to induce fluctuations in both the tunneling matrix element and the asymmetry of the system. As an example, consider the following case:

The tunneling coordinate is 
$$\xi$$
, and the molecular vibration  
which has been singled out is  $Q$ . We remark that the width  
(and possibly the height) of the barrier depends on the value  
of  $Q$ , the O-O distance (Fig. 3). Assuming that the change  
of the width of the barrier is linear in  $Q$ , the change of the  
splitting  $J$  should be exponential<sup>11</sup>

$$J(Q) = C_0 e^{\gamma Q} \quad \gamma < 0,$$

where the origin for Q has been chosen to be  $Q_e$ , the equilibrium O-O distance. This Q dependence should be valid for not too high temperatures ( $\langle Q^2 \rangle \ll Q_e^2$ , where  $\langle \cdots \rangle$  is a thermal average, as described later in the paper). The final expression for the Hamiltonian is

$$H = -\Delta_0 \sigma_z + C_0 e^{\gamma Q} \sigma_x + \frac{1}{2} \sum_{i=1}^{N+1} (p_i^2 + \omega_i^2 q_i^2) + \sum_{i=1}^{N+1} f_i q_i \sigma_z, \qquad (3)$$

where the (N+1)th mode is the Q oscillator  $(P = p_{N+1}, f = f_{N+1}, \text{ and } \omega = \omega_{N+1})$ . In the case  $\Delta_0 = 0$ , we must also have f = 0, as Q is symmetric with respect to parity. A Hamiltonian of this form has been previously considered by Borgis *et al.*<sup>11</sup> in the same context. However, throughout their treatment, the solvent is described by a single collective coordinate, and their calculations are restricted to limiting cases in which only the short time dynamics of the solvent are relevant. This should be appropriate for a high temperature regime with respect to the solvent  $(\beta \omega_c \leq 1, \text{ where } \beta = 1/\kappa_B T \text{ and } \omega_c \text{ is a suitable cutoff for the solvent frequencies}), and in the limit of adiabatic solvent <math>(\omega_c \rightarrow 0)$ . Furthermore, the perturbation chosen in their pa-



FIG. 3. Dependence of the barrier width with the molecular vibration Q.

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per has a nonzero thermal average and could give rise to divergences (due to the presence of secular terms in the perturbation expansion) in the rate constant for the symmetric case, in particular at low temperatures. Our treatment provides an explicit model for the solvent, which is adequate both in the low and high temperature regimes. Special care shall be taken in choosing a perturbation which possesses a zero thermal average, thus avoiding spurious divergences.

#### **III. DYNAMICS**

### A. General

The rest of the paper will be devoted to the study of the dynamics generated by the Hamiltonian derived in the previous section:

$$H = -\Delta_0 \sigma_z + C_0 e^{\gamma Q} \sigma_x + \frac{1}{2} \sum_{i=1}^{N+1} (p_i^2 + \omega_i^2 q_i^2) + \sum_{i=1}^{N+1} f_i q_i \sigma_z + \sum_{i=1}^{N+1} \frac{f_i^2}{2\omega_i^2}, \qquad (4)$$

where the last term (a shift in the energy origin) has been included for convenience. There are several ways of dividing this Hamiltonian into an integrable part  $H_0$  and a perturbation V. The criteria we shall use in order to choose a partition are:

(1) The dynamics generated by  $H_0$  should be close to those generated by the full Hamiltonian.

(2) Assuming that  $\lambda$  is a unitless parameter measuring the strength of the perturbation, the characteristic relaxation time for the system coupled to its environment is  $\tau_R \sim \lambda^{-2}$ . The environment, as included in  $H_0$ , should have a characteristic relaxation time  $\tau_b \ll \tau_R$ .<sup>6</sup>

Both of the conditions are fulfilled by the choice

$$H_{0} = -\Delta_{0}\sigma_{z} + \frac{1}{2}\sum_{i=1}^{N+1} (p_{i}^{2} + \omega_{i}^{2}q_{i}^{2}) + \sum_{i=1}^{N+1} f_{i}q_{i}\sigma_{z} + \sum_{i=1}^{N+1} \frac{f_{i}^{2}}{2\omega_{i}^{2}},$$
(5)

$$V = C_0 e^{\gamma Q} \sigma_x \tag{6}$$

provided that  $C_0$  is sufficiently small.

Performing on H the unitary transformation that diagonalizes  $H_0$ ,

$$U = \exp\left\{i\sum_{j=1}^{N+1}\frac{f_jp_j}{\omega_j^2}\sigma_z\right\},\,$$

the following expression is obtained:

The thermal average of an observable O is defined as

$$\langle O \rangle \equiv \frac{Tr_b (Oe^{-\beta H_b})}{Tr_b (e^{-\beta H_b})}.$$

Adding and subtracting the thermal average of  $\tilde{V}$ ,

$$\begin{split} \langle \widetilde{V} \rangle &= C_0 \exp\left\{\frac{\gamma^2}{4\omega} \xi(\omega)\right\} \exp\left\{-\sum_{i=1}^{N+1} \frac{f_i^2}{\omega_i^3} \xi(\dot{\omega}_i)\right\},\\ \xi(\omega_i) &= \coth\frac{\beta\omega_i}{2}, \end{split}$$

we obtain

$$\begin{split} \widetilde{H} &= \widetilde{H}_0 + \Delta \widetilde{H}, \\ \widetilde{H}_0 &= -\Delta_0 \sigma_z + \langle \widetilde{V} \rangle \sigma_x + H_b, \\ \Delta \widetilde{H} &= (\widetilde{V} - \langle \widetilde{V} \rangle) \sigma_x. \end{split}$$
(8)

The physical picture emerging from this choice of zeroth order Hamiltonian is that of a particle tunneling together with a phonon cloud. This representation was first introduced by Holstein<sup>12</sup> in the theory of electron transport in solids; in that context, the dressed tunneling pseudoparticle is called *small polaron*. It should be an adequate description whenever  $\tilde{V}$  has small fluctuations around its thermal average  $\langle \tilde{V} \rangle$ , and the dressing time, or characteristic time in which the bath modes undergo a displacement in order to adjust themselves to the instantaneous state of the system, is short compared to the time scale of the system relaxation.

We remark that in the original representation the tunneling matrix element is given by  $J = \langle C_0 e^{\gamma Q} \rangle = C_0 \exp\{(\gamma^2/4\omega)\xi(\omega)\}$ , whereas after the small polaron transformation, this quantity has a different magnitude:  $\tilde{J} = J \exp\{-\sum_{i=1}^{N+1} (2f_i^2/\omega_i^3)\xi(\omega_i)\}$ ; the renormalization factor  $\exp\{-\sum_{i=1}^{N+1} (2f_i^2/\omega_i^3)\xi(\omega_i)\}$  represents the thermal average of the overlap between oscillator wave functions displaced by  $\pm (f_i/\omega_i)$ , respectively (i.e., it is a Frank-Condon factor).

It shall be convenient for the following discussion to make a particular choice for the lattice and the interaction. The form of the spectral function  $\mathcal{T}(w) = \sum_{j=1}^{N} (f_j^2/\omega_j) \delta(w - \omega_j)$  which shall be considered is the following:

$$\mathcal{T}(w) = \frac{\eta}{w_c^2} w^3 e^{-w/w_c} \tag{9}$$

corresponding to a collection of acoustic modes in a threedimensional solid, with a coupling f(w) proportional to w(deformation potential approximation);  $\eta$  represents a unitless parameter measuring the strength of the coupling, and  $w_c \sim 10^2$  cm<sup>-1</sup> is an appropriate cutoff frequency for the bath in molecular solids. The frequency of the Q mode can take values ranging from  $\sim 10$  cm<sup>-1</sup> (torsional modes) to  $\sim 10^3$  cm<sup>-1</sup> (optical modes).

It shall also be useful to define several quantities related to the bath and the interaction:  $E_Q = 2f^2/\omega^2$  represents the difference in energy between the  $|L\rangle$  and  $|R\rangle$  states of the system arising from the displacement of the Q oscillator. The analogous quantity for the lattice modes is defined as  $E_l = \sum_{i=1}^{N} E_{q_i} = \sum_{i=1}^{N} (2f_i^2/\omega_j^2) = 4\eta w_c$ . Finally,  $E_{\gamma} = \gamma^2/2$ , and  $E_{\text{total}} = E_Q + E_l + E_{\gamma}$  (see Fig. 4).

Assuming that a second order perturbation description is appropriate, the population relaxation rate in the localized basis is<sup>7</sup>

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 $\Delta_{0} = 0$ 





FIG. 4. (a) Adiabatic potential curves for the *i*th mode of the environment (symmetric case). (b) Adiabatic potential curves for the *i*th mode of the environment (asymmetric case).

$$K_{R-L} = \int_{-\infty}^{\infty} \left[ \langle \widetilde{V}_{LR}(t) \widetilde{V}_{RL} \rangle - \langle \widetilde{V} \rangle^2 \right] e^{i w_{LR} t} dt. \quad (10)$$

This expression shall be evaluated in the limit that the asymmetry  $2\Delta_0 > 0$  is smaller than both the cutoff frequency for the solvent  $w_c$ , and the frequency of the molecular vibration  $\omega$ . In particular, for our model

$$\widetilde{V}_{LR} = C_0 e^{-\gamma f/\omega^2} e^{\gamma Q} \exp\left\{-2i \sum_{i=1}^{N+1} \frac{f_i}{\omega_i^2} p_i\right\}$$
$$\widetilde{V}_{RL} = C_0 e^{\gamma f/\omega^2} e^{\gamma Q} \exp\left\{2i \sum_{i=1}^{N+1} \frac{f_i}{\omega_i^2} p_i\right\};$$

therefore the rate is

$$K_{R-L} = \int_{-\infty}^{\infty} C_0^2 \left[ \left\langle e^{\gamma Q(t)} \exp\left\{ -2i \sum_{i=1}^{N+1} \frac{f_i}{\omega_i^2} p_i(t) \right\} \right. \\ \left. \times e^{\gamma Q} \exp\left\{ 2i \sum_{i=1}^{N+1} \frac{f_i}{\omega_i^2} p_i \right\} \right\rangle - \left\langle \widetilde{V} \right\rangle^2 \right] e^{-2i\Delta_0 t} dt.$$

$$(11)$$

Note that the term

$$\langle \tilde{V} \rangle^2 = C_0^2 \left\langle e^{\gamma Q} \exp\left\{-2i \sum_{i=1}^{N+1} \frac{f_i}{\omega_i^2} p_i\right\}\right\rangle$$
$$\times \left\langle e^{\gamma Q} \exp\left\{2i \sum_{i=1}^{N+1} \frac{f_i}{\omega_i^2} p_i\right\}\right\rangle$$

is being subtracted from the integrand. It ensures that the integral of the time correlation function, which defines the rate, is convergent and therefore provides a meaningful expression for the rate: For  $t \gg \tau_b$ , the characteristic relaxation time of the bath, the time correlation function factorizes and the integrand goes to zero.

The expression above can be readily evaluated to yield

$$K_{R-L} = C_0^2 \exp\left\{\frac{\gamma^2}{2\omega}\xi(\omega) - \sum_{i=1}^{N+1} 2\frac{f_i^2}{w_i^3}\xi(\omega_i)\right\}$$
$$\times \int_{-\infty}^{\infty} dt \, e^{-2i\Delta_0 t} \left[\exp\left\{\frac{\gamma^2}{2\omega}[\xi(\omega)\cos\omega t - i\sin\omega t]\right]$$
$$- 2\frac{f\gamma}{\omega^2}[\cos\omega t - i\xi(\omega)\sin\omega t]$$
$$+ \sum_{j=1}^{N+1} \frac{2f_j^2}{\omega_j^3}[\xi(\omega_j)\cos\omega_j t - i\sin\omega_j t]\right\} - 1 \left].$$
(12)

Making a change of variable  $\tau = t + i(\beta/2)$ , and deforming the contour to the real axis:

$$K_{R-L} = C_0^2 \exp\left\{\frac{\gamma^2}{2\omega}\xi(\omega) - \sum_{i=1}^{N+1} 2\frac{f_i^2}{\omega_i^3}\xi(\omega_i) - \beta\Delta_0\right\}$$
$$\times \int_{-\infty}^{\infty} d\tau \, e^{-2i\Delta_0\tau}$$
$$\times \left[\exp\left\{\frac{\gamma^2}{2\omega}\frac{\cos\omega\tau}{\sinh(\beta\omega/2)} + i\frac{2f\gamma}{\omega^2}\frac{\sin\omega\tau}{\sinh(\beta\omega/2)} + \sum_{j=1}^{N+1} \frac{2f_j^2}{\omega_j^3}\frac{\cos\omega_j\tau}{\sinh(\beta\omega_j/2)}\right\} - 1\right]. \tag{13}$$

In the derivation of this expression, we have assumed that

$$\lim_{t \to \infty} \int_{\pm t}^{\pm t + i(\beta/2)} d\tau [\text{integrand of Eq. (13)}] = 0.$$

This is true for the modes  $\{i = 1,...,N\}$ , due to the fact that they belong to an acoustic branch with an associated dispersion  $\Delta w \sim w_c$ . The *Q* oscillator has no dispersion associated with it. Consequently, the time correlation functions of this mode do *not* factorize at any time, leading to divergences in their time integrals when the limits of integration are extended to infinity. This can be avoided by allowing some dispersion in this mode. Grover and Silbey<sup>13</sup> propose several alternatives: Assuming that the main dispersion occurs in the frequencies, with  $\gamma(w)$  and  $N(w) = (e^{\beta w} - 1)^{-1}$  re-

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maining approximately constant, in Eq. (13),  $e^{i\omega t}$  is replaced by  $e^{i\omega t}A(t)$ , with the definition  $A(t) = \int_{-\infty}^{\infty} dw' \rho(w') e^{iw' t}$ , where  $\rho(w')$  is the shape of the dispersion in Q centered at  $\omega$ . Various forms of  $\rho(w)$  give different decays as described in Table I. In an equivalent fashion, we could have introduced an imaginary component for the frequency, whose origin can be assigned to interactions with other modes. If  $\Delta$  is the phonon bandwidth (in the order of several cm<sup>-1</sup>), for times  $t \ge \Delta^{-1}$  (of the order of 100 ps), the integrand in Eq. (13) has decayed to zero and the rate is well defined. Although we are not going to include dispersion explicitly in all of our calculations, we should bear in mind that it is essential for the convergence of the expressions we are using.

We remark that in Ref. 11, the solvent time-correlation functions show a Gaussian decay (which automatically ensures the convergence of their expression for the rate), instead of factorizing in the manner exhibited in this paper. This is due to the fact that only the short time solvent dynamics are taken into account.

#### B. Limiting case: $\beta W_c \ll 1$

At high temperatures for the bath  $(\beta w_c \leq 1)$ , using the form given by Eq. (9) for the spectral function  $\mathcal{T}(w)$ , we find

$$K_{R-L} = C_0^2 \exp\left\{\left(\frac{\gamma^2}{2\omega} - 2\frac{f^2}{\omega^3}\right)\xi(\omega) - \frac{4\eta}{\beta w_c} - \beta \Delta_0\right\}$$
$$\times \int_{-\infty}^{\infty} d\tau \, e^{-2i\Delta_0\tau} \left[\exp\left\{\left(\frac{\gamma^2}{2\omega} + \frac{2f^2}{\omega^3}\right)\right\}$$
$$\times \frac{\cos\omega\tau}{\sinh(\beta\omega/2)} + i\frac{2f\gamma}{\omega^2}\frac{\sin\omega\tau}{\sinh(\beta\omega/2)}$$
$$+ \frac{4\eta}{\beta w_c}\frac{1}{1 + \tau^2 w_c^2}\right] - 1\right]. \tag{14}$$

For the cases of strong and moderate coupling  $[\eta \sim \mathcal{O}(1)]$ , the condition  $4\eta/\beta w_c \ge 1$  allows the possibility of evaluating the integral in Eq. (14) by the method of stationary phase. Expanding the exponent to second order in  $\tau$ , around the saddle point  $\tau = 0$ , and evaluating the resulting Gaussian integral, the following result is obtained:

$$K_{R-L} = C_0^2 \left( \frac{\pi}{\gamma^2 \omega/4 \sinh(\beta \omega/2) + \Sigma [f_j^2/\omega_j \sinh(\beta \omega_j/2)]} \right)^{1/2} \exp\left\{ \frac{\gamma^2}{2\omega} \frac{1 + \cosh(\beta \omega/2)}{\sinh(\beta \omega/2)} + \sum_{j=1}^{N+1} \frac{2f_j^2}{\omega_j^3} \frac{1 - \cosh(\beta \omega_j/2)}{\sinh(\beta \omega_j/2)} - \beta \Delta_0 \right\} \exp\left\{ -\frac{1}{4} \frac{[2\Delta_0 - 2f\gamma/\sinh(\beta \omega/2)]^2}{\omega\gamma^2/4 \sinh(\beta \omega/2) + \Sigma [f_j^2/\omega_j \sinh(\beta \omega_j/2)]} \right\}.$$
 (15)

This expression can be simplified for the different temperature regimes with respect to the Q vibration.

#### 1. $\beta \omega \ll 1$ (high temperature limit for the Q mode)

$$K_{R+L} = (C_0 e^{-2(\gamma f/\omega)})^2 \exp\left\{\frac{4E_{\gamma}}{\beta\omega^2} + \beta \frac{E_{\gamma}}{2}\right\} \left(\frac{\pi\beta}{E_{\text{total}}}\right)^{1/2} \\ \times \exp\left\{-\frac{\beta}{4E_{\text{total}}} \left(2\Delta_0 + E_{\text{total}} - 4\frac{f\gamma}{\beta\omega}\right)^2\right\}.$$
(16)

Note that in the expression above, the tunneling matrix element has been evaluated at  $Q = -f/\omega^2$ , which corresponds to the displacement of the Q mode when the system is fixed in the localized state |L>. The temperature dependence resembles that of an activated process, with an activation energy which is temperature dependent

$$E_{a} = \frac{\left[2\Delta_{0} + E_{\text{tot}} - 4(f\gamma/\beta\omega)\right]^{2}}{4E_{\text{tot}}} - \frac{4E_{\gamma}}{\beta^{2}\omega^{2}} - \frac{E_{\gamma}}{2}.$$

In the symmetric case  $(\Delta_0 = 0, f = 0)E_a = (E_l - E_{\gamma})/4$ -  $(4E_{\gamma}/\beta^2\omega^2)$ .

## 2. $\beta \omega \gg 1$ (low temperature limit for the Q mode)

$$K_{R-L} = C_0^2 e^{(E_r - E_Q)/\omega} \left(\frac{\pi\beta}{E_l}\right)^{1/2} \exp\left\{-\beta \frac{(2\Delta_0 + E_l)^2}{4E_l}\right\}.$$
(17)

The splitting is now evaluated at Q = 0, due to the fact that the Q mode is frozen in its ground state. Its effect simply amounts to a redefinition of the tunneling matrix element, which becomes  $\tilde{C}_0 = C_0 e^{(E_\gamma - E_Q)/2\omega}$ . The behavior is truly activated, with an apparent barrier of  $E_a$  $= (2\Delta_0 + E_1)^2/4E_1$  for the asymmetric case, and  $E_a$  $= E_1/4$  for the symmetric one. Note that, in both cases  $E_a$  is just the reorganization energy due to the displacement of the lattice oscillators (the energy of the crossing point of the two adiabatic curves in Fig. 4).

In case of extremely weak coupling, where we still assume  $\beta \omega_c \ll 1$ , but  $4\eta / \beta \omega_c \ll 1$  the expression for the rate is

$$K_{R-L} = C_0^2 \exp\left\{ \left( \frac{\gamma^2}{2\omega} - 2\frac{f^2}{\omega^3} \right) \xi(\omega) - \frac{4\eta}{\beta w_c} - \beta \Delta_0 \right\} \\ \times \int_{-\infty}^{\infty} d\tau \, e^{-2i\Delta_0 \tau} \\ \times \left[ \exp\left\{ \frac{\gamma^2}{2\omega} + \frac{2f^2}{\omega^2} \frac{\cos \omega \tau}{\sinh(\beta \omega/2)} \right. \\ \left. + i \frac{2f\gamma}{\omega^2} \frac{\sin \omega \tau}{\sinh(\beta \omega/2)} \right] \\ \times \left( 1 + \frac{4\eta}{\beta w_c} \frac{1}{1 + \tau^2 w_c^2} + \mathcal{O}(\eta^2) \right) - 1 \right].$$
(18)

In the low temperature limit for the *Q* oscillation ( $\beta \omega \ge 1$ ):

$$K_{R-L} = C_0^2 \frac{4\eta\pi}{\beta w_c^2} e^{(E_{\gamma} - E_Q)/\omega} \times \exp\left\{-\beta \Delta_0 - \frac{4\eta}{\beta w_c} - 2\frac{|\Delta_0|}{w_c}\right\},$$
(19)

TABLE I. Models for the dispersion in the Q mode and the resulting decay functions (from Ref. 13).

	ρ(w)	A(t)
Lorentzian	$\frac{\Delta}{\pi} \frac{1}{\Delta^2 + w^2}$	$e^{-\Delta[t]}$
Gaussian	$\frac{1}{\Delta \pi^{1/2}} e^{-w^2/\Delta^2}$	$e^{-\Delta^2 t^2/4}$
Optical	$w(k) = \omega_0 + \Delta \cos k$	$J_0(\Delta t)$

which gives rise to a linear T dependence for the rate (since the terms in the exponent do not have a significative contribution in this region).

## C. Limiting case: $\beta w_c \ge 1$

For low temperature with respect to the lattice  $(\beta w_c \ge 1)$ , two extreme behaviors are encountered:

(1) In the high temperature limit for the Q vibration the condition  $1/\sinh(\beta\omega/2) \sim 2/\beta\omega \ge 1$  provides a large parameter, which suggests the possibility of evaluating the integral by the stationary phase method. The integral is going to be dominated by contributions in the vicinity of the saddle points given by the equation

$$e^{i\omega t_s} = \left| \frac{\gamma \omega - 2f}{\gamma \omega + 2f} \right| \tag{20}$$

provided that  $E_{\gamma} - E_Q$  is not too small. Note that, unless a dispersion is assumed for the Q mode, there is an infinite number of such saddle points, each giving the same finite contribution. The rate would thus diverge. If the dispersion in Q has been included, only  $\mathscr{O}(\omega/\pi\Delta)$  points contribute. We shall assume a dispersion such that the decay function is a step function  $\theta(\Delta|t| - 1)$  (i.e., each of the  $\omega/\pi\Delta$  points yields the same contribution). With this assumption, the result is

$$K_{R-L} = \frac{\omega}{\pi\Delta} C_0^2 \frac{\pi\beta}{|E_{\gamma} - E_Q|} \\ \times \exp\left\{4\mu \frac{E_{\gamma} - E_Q}{\beta\omega^2} - 2\eta - \beta\Delta_0\right\} \\ \times \left|\frac{\gamma\omega - 2f}{\gamma\omega + 2f}\right|^{2\Delta\omega'\omega} \exp\left\{-\beta \frac{\Delta_0^2}{|E_{\gamma} - E_Q|}\right\}$$
(21)

where  $\mu = 1$  for  $E_{\gamma} - E_Q > 0$  and  $\mu = 0$  for  $E_{\gamma} - E_Q < 0$ . This formula is also valid in the limit of high temperature for both the lattice and the molecular vibration, and extremely weak coupling  $(\beta w_c \leq 1, \beta \omega \leq 1, 4\eta / \beta w_c \leq 1)$ , with the substitution of  $2\eta$  by  $4\eta / \beta w_c$  in the expression above.

(2) In the low temperature region  $(\beta\omega \ge 1 \text{ and } \beta w_c \ge 1)$ we can expand the integrand in Eq. (13) disentangling the contributions from one-phonon, two-phonon processes, etc. If the calculation is restricted to one-phonon processes (taking into account that these are not possible for the Q vibration) the result derived by Skinner and Trommsdorff<sup>14</sup> obtains. The calculation is valid for the limit in which  $2\Delta_0\beta \ge 1$ , but has failed to explain the temperature dependence of the rate constant in the opposite regime for at least one experimental situation: measurements in benzoic acid dimers with small asymmetries, at low temperature.<sup>4</sup> An explanation of the unusual temperature dependence (the rate increased as  $\sim T^4$  between 1–5 K) was attempted by Silbey and Trommsdorff, <sup>15</sup> who stressed the role of two-phonon processes (which are assumed to be dominant over the one-phonon contribution) and of an experimentally observed local mode. We shall therefore explicitly calculate the contributions of up to two vibrational quanta. There are four contributions which shall be considered separately:

$$K_{R-L} = K_{1P} + K_{2P} + K_R + K_{QP}.$$
 (22)

The contribution from one phonon emission or absorption (depending on the sign of  $\Delta_0$ ,

$$K_{1P} = \widetilde{C}_0^2 e^{-2\eta} \frac{4\pi\eta}{\omega_c^2} \frac{\Delta_0 e^{-\beta\Delta_0}}{\sinh\beta\Delta_0} e^{-2|\Delta_0|/\omega_c},$$

which has an activated behavior at low temperature  $(E_a = 2\Delta_0 \text{ if } \Delta_0 > 0, \text{ or } E_a = 0 \text{ if } \Delta_0 < 0)$ , and increases linearly with T in the opposite limit,  $2\Delta_0 \beta \leq 1$ . There are several processes involving two quanta:

(a) two-phonon emission/absorption

$$K_{2P} = \tilde{C}_{0}^{2} e^{-2\eta} e^{-\beta \Delta_{0}} \frac{2\pi \eta^{2}}{w_{c}^{4}} e^{-2|\Delta_{0}|/w_{c}}$$

$$\times \int_{0}^{2|\Delta_{0}|} dw \frac{w(2|\Delta_{0}|-w)}{\sinh(\beta w/2)\sinh(\beta (2|\Delta_{0}|-w)/2)}.$$
In the limit 2A  $\beta \neq 1$  it leads to a  $T^{2}$  dependence.

In the limit  $2\Delta_0 \beta \ll 1$ , it leads to a  $T^2$  dependence

$$K_{2P} = \widetilde{C}_{0}^{2} e^{-2\eta} e^{-\beta \Delta_{0}} \frac{16\pi \eta^{2}}{\beta^{2} w_{c}^{4}} |\Delta_{0}| e^{-2|\Delta_{0}|/w_{c}}.$$

(b) Two-phonon Raman processes

$$K_R = \widetilde{C}_0^2 e^{-2\eta} e^{-\beta \Delta_0} \frac{4\pi \eta^2}{w_c^4} e^{-2|\Delta_0|/w_c}$$

$$\times \int_0^\infty dw \, \frac{w(2|\Delta_0|+w)}{\sinh(\beta w/2)\sinh(\beta(2|\Delta_0|+w)/2)} \, e^{-2w/w_c}.$$
A  $T^3$  behavior obtains for  $2 \wedge \beta \not < 1$ :

A T<sup>3</sup> behavior obtains for  $2 \Delta_0 \beta \ll 1$ 

$$K_{R} = \tilde{C}_{0}^{2} e^{-2\eta} e^{-\beta \Delta_{0}} \frac{16\pi^{3}\eta^{2}}{3\beta^{3}w_{c}^{4}} e^{-2|\Delta_{0}|/w_{c}}$$

which is closer to the experimental measurements  $K \sim T^4$  than the usual  $T^7$  dependence.

(c) Raman processes involving one phonon and one quantum of the Q vibration

$$\begin{split} K_{PQ} &= \widetilde{C}_{0}^{2} e^{-2\eta} e^{-\beta \Delta_{0}} \frac{\eta \pi}{w_{c}^{2}} \\ &\times \left( \frac{\left(\sqrt{E_{\gamma}} + \sqrt{E_{Q}}\right)^{2}}{\omega} \frac{(\omega + 2\Delta_{0})}{\sinh(\beta(\omega + 2\Delta_{0})/2)} e^{-2\Delta_{0}/w_{c}} \right. \\ &+ \frac{\left(\sqrt{E_{\gamma}} - \sqrt{E_{Q}}\right)^{2}}{\omega} \frac{(\omega - 2\Delta_{0})}{\sinh(\beta(\omega - 2\Delta_{0})/2)} e^{2\Delta_{0}/w_{c}} \right) \\ &\times \frac{e^{-\omega/w_{c}}}{\sinh(\beta\omega/2)}. \end{split}$$

## **IV. CONCLUSIONS**

The goal of the present investigation has been to develop a microscopic treatment for hydrogen transfer reactions in condensed media, in the limit that these occur through tunneling without vibrational activation. The description we have presented is a minimal one, in the sense that we have tried to characterize the reaction by the least possible number of microscopic parameters, and a simple model Hamiltonian:

The isolated reactants and products are represented by the two lowest lying states of a double well potential, with the assumption that the barrier between the wells is very large. In this fashion, the isolated system is characterized by  $2\Delta_0$ , the difference in energy between reactants and products in the absence of tunneling, and J, the tunneling matrix element. Note that this model does not allow excitations within each of the wells.

The lattice (solvent) is assumed to be a collection of independent harmonic oscillators (i.e., a boson field) and is characterized by the spectral function  $\mathcal{T}(w)$ . In this paper we have chosen a particular form for the spectral function corresponding to an acoustic phonon branch in a Debye solid. However, an entirely analogous analysis can be carried out within the same framework for other boson fields (optical phonons, radiation, local phonons, and so on) provided that their spectrum is continuous.

Finally, modes of a different nature than those of the lattice (e.g., molecular vibrations) have been included explicitly.

From this model Hamiltonian we have *derived* the relevant reaction rate making use of the principles of relaxation theory and avoiding the use of phenomenological assumptions as much as possible. This scheme requires that we make a felicitous choice for a (separable) zeroth order Hamiltonian and a perturbation. A convenient perturbation term with zero thermal average is identified after performing a unitary transformation that shifts the equilibrium position of the oscillators. Another important point is the way in which those special modes which cannot be included in the lattice (solvent) are treated: Instead of including explicitly the effects of multidimensional tunneling, we have assumed that there is a single tunneling coordinate; the dynamics along the tunneling mode are affected by the dynamics along the other modes, the effect of which is included in the form of a perturbative analysis. This picture should be valid if the renormalized tunneling coordinate is weakly coupled to the rest of the vibrations; hence the weakness of this coupling should be a necessary criterion to make a suitable choice for the tunneling mode.

Despite its simplicity, our model is sophisticated enough to reproduce the diverse experimental results: At low temperatures, the rate constant has a rather complex temperature dependence and reflects the various elementary processes that are involved in the reaction (one-phonon, two-phonon processes, etc.). The high temperature region is closer to a statistical limit in which the Gaussian approximation is valid; the rate constant presents the features of an activated process, with a barrier which almost in all cases has a direct physical interpretation. A summary of these results is given in Table II. We have also been able to confirm some results of previous investigations, which were made with less detailed models and asystematic approximations.

It is our hope that this paper will serve as the basis for the study of systems of greater complexity, and as a clarification of the experimental situation, which may appear confusing due to the lack of knowledge of the relevant microscopic parameters.

TABLE II. Summary of the results obtained in this paper.

T for lattice	Coupling strength	T for local vibration	Method of evaluation	Expression for the rate	Remarks
	Strong/moderate	High $T$ $(\beta \omega \ll 1)$	Stationary phase. Saddle point provided by solvent.	(16)	Activated process. Temperature dependent activation energy.
	$(4\eta/\beta\omega_c \gg 1)$	Low T	Stationary phase.		
High T		( <i>β</i> ω≥1)	Saddle point provided by solvent	(17)	Activated process. Activation energy is temperature independent.
(βω <b>∢</b> 1)					
	weak	High T (βω ≪1)	Stationary phase. Several saddle points provided by the local vibration	(21), substi- tuting $4\eta/\beta\omega_c$ for $2\eta$	Complex temperature dependence.
	$(4\eta/\beta\omega_{c} \ll 1)$	Low T	Taylor expansion		Linear temperature dependence.
		$(\beta \omega \gg 1)$	in $4\eta/\beta\omega_c$	(19)	
Low T (βω, ≥1)	weak/moderate	High T $(\beta \omega \ll 1)$	Stationary phase. Several saddle points provided by the local vibration.	(21)	Complex temperature dependence. This expression for the rate is only valid for the limit $E_{\gamma} \neq E_Q$ .
		Low T $(\beta \omega \gg 1)$	Taylor expansion of expression (15)	(22)	The reaction proceeds by several mechanisms: 1 phonon/2 phonon absorption (or emission for exothermic reactions), Raman processes involving the lattice only or both lattice and local vibration, etc.

## ACKNOWLEDGMENT

This research was supported in part by the National Science Foundation (Grant No. CHE-8703460).

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