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Transition from Nuclear Tunneling to Activated Rate Processes in Condensed Phases

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We utilize the theory of nonradiative, nonadiabatic, multiphonon processes in a dense medium to derive an explicit expression for the transition of the rate constant from low-temperature nuclear tunneling to an Arrhenius-type activated rate expression.

Electron-transfer (ET) and atom- or molecule-transfer (AT) processes play a central role in a variety of biological systems. Notable examples are the primary events of photosynthesis,¹ the primary photochemical processes in some visual pigments,² and the reversible uptake of oxygen and carbon monoxide by myoglobin and hemoglobin.³ The dynamics of all these processes are characterized by some general features exhibiting an Arrhenius-type temperature dependence of the unimolecular rate constant W at high temperatures, while at low temperatures W does not vanish but rather remains finite and temperature independent. The constant low-temperature rate reflects zero-point energy effects⁴ and manifests a nuclear tunneling phenomena.⁵ The modern theory of nonadiabatic multiphonon radiationless processes was recently successfully applied for the elucidation of the general features of a variety of such nonadiabatic electron-transfer⁶ and group-transfer⁷ processes, which can be explored from a unified point of view. It is of some methodological and practical importance to determine the transition temperature T_0 from low-temperature nuclear tunneling to the high-temperature activated region without dwelling on elaborate numerical calculations. Goldanskii⁸ expressed the low-temperature rate in terms of the Gamow tunneling formula⁹ $W = \nu_0 \exp(-\delta(\mu E_A)^{1/2}d/\hbar)$, where ν_0 is a characteristic frequency, $\delta = (2)^{1/2}$ is a numerical constant, μ is a characteristic nuclear mass, E_A is the barrier height, while d is the barrier width. Comparing the low-temperature rate with the activated rate $W \propto \exp(-E_A/k_B T)$ and disregarding preexponential terms, Goldanskii concluded that the two rates are equal at the temperature $k_B T_0 = \hbar E_A^{1/2}/\delta\mu^{1/2}d$. Goldanskii's result rests on firm theoretical grounds in view of the equivalence between the Gamow exponential tunneling factor and the Franck-Condon vibrational nuclear overlap factor.¹⁰ It would be useful to provide an alternative and more transparent expression for $k_B T_0$ on the basis of the modern theory of nonadiabatic multiphonon processes, which is the subject matter of the present note. The results are useful for the analysis of the primary ET events in photosynthesis. We consider a nonadiabatic multiphonon ET or AT process occurring between two nuclear potential surfaces which are both characterized by the frequency ω ; the horizontal (reduced) displacement of their minima is Δ , while the vertical displacement between the minima representing the energy gap is ΔE . The electron vibration coupling strength is $S = \Delta^2/2$, while the

medium reorganization energy is $E_S = S\hbar\omega$. This oversimplified description of the nuclear distortions in terms of an (average) single-mode approximation is adequate and sufficiently accurate for our purposes. The residual coupling V which induced the process corresponds to a two-center, one-electron, transfer integral for ET processes or a spin-orbit coupling for nonadiabatic AT processes. The rate takes the well-known form⁵

$$W = A \exp[-S(2\bar{\nu} + 1)] I_p \{ 2S[\bar{\nu}(\bar{\nu} + 1)]^{1/2} [(\bar{\nu} + 1)/\bar{\nu}]^{p/2} \} \quad (1)$$

$$A = 2\pi |V|^2 / \hbar^2 \omega \quad (1a)$$

$$p = |\Delta E| / \hbar \omega \quad (1b)$$

$$\bar{\nu} = [\exp(\hbar\omega/k_B T) - 1]^{-1} \quad (1c)$$

Here $I_p\{\}$ is the modified Bessel function of order p , the parameter p , eq 1b, represents the normalized energy gap, while the temperature dependence is incorporated in the Bose factor, eq 1c. Equation 1 contains distinct separate contributions from the electronic term appearing in A , eq 1a, and the thermally averaged nuclear Franck-Condon vibrational overlap factor. The rate expression exhibits a continuous transition from the low-temperature nuclear tunneling expression

$$W = A \exp(-S) S^p / p! \quad (2)$$

characterized by a Poissonian nuclear overlap to a high-temperature activated rate expression

$$W = A(\hbar\omega/4\pi S k_B T)^{1/2} \exp(-E_A/k_B T) \quad (3)$$

where the activation energy E_A is given by the quadratic function

$$E_A = (S\hbar\omega + \Delta E)^2 / (4S\hbar\omega) \quad (4)$$

The low-temperature limit, eq 2, holds for $\hbar\omega \gg k_B T$, while the high-temperature situation, eq 4, prevails for $k_B T \gg \hbar\omega$. A more precise and useful estimate of the transition temperature T_0 can be obtained for exoergic processes ($\Delta E < 0$) by recasting the low-temperature rate, eq 2, in the energy gap form¹¹

$$W = [A/(2\pi p)^{1/2}] \exp(-S - \gamma p) \quad (2a)$$

$$\gamma = \ln(p/S) - 1$$

which just rests on the application of the Stirling approximation. For exoergic processes the activation energy, eq 4, is $E_A = \hbar\omega(p - S)^2/4S$. Looking now for the temperature T_0 at which eq 2a and 3 are equal, this is obtained from the transcendental equation

$$-\frac{(p - S)^2 \hbar\omega}{4Sk_B T_0} + (S + \gamma p) + \frac{1}{2} \ln \left(\frac{\hbar\omega p}{2Sk_B T_0} \right) = 0 \quad (5)$$

The first-order solution, which is valid for $p \neq S$, is given by

$$k_B T_0 = \frac{\hbar\omega(p - S)^2}{4S \left[S + \gamma p + \frac{1}{2} \ln \left[\frac{2p(S + \gamma p)}{(p - S)^2} \right] \right]} \quad (6)$$

The following limit cases are of interest:

(1) Strong coupling case: $S \gg 1$ and $S \gg p$ when, according to eq 6, $k_B T_0 \approx \hbar\omega/4$.

(2) Weak coupling case: $S \approx 1$ and $S \ll p$. Now eq 6 yields $k_B T_0 \approx \hbar\omega p/4S\gamma$.

(3) Activationless processes. In the special case $p = S$ we have $E_A = 0$. The rate exhibits a negative apparent activation energy, as at high temperatures $W \propto 1/T^{1/2}$ according to eq 3. Equation 6 is then inapplicable. A cursory examination of eq 5 reveals that now $\gamma = -1$, whereupon there is no solution to this equation for a finite T as, in this case, no transition to an activated range will be exhibited.

To provide some physical insight into the nature of these results and to make contact between the present analysis and Goldanskii's original work,⁸ we shall recast the low-temperature rate, eq 2a, for an exoergic process in the alternative form¹⁰

$$W = [A/(2\pi p)^{1/2}] \exp(p - S) \exp[-(1 + \gamma)p] \quad (7)$$

Neglecting the contribution of the second exponential in eq 7 and setting¹⁰ $|S - p| = (4SE_A/\hbar\omega)^{1/2} = (2\mu E_A)^{1/2}(d/\hbar)$ results in the Gamow tunneling formula. Utilizing a similar approximate relation in eq 6, where logarithmic contributions are neglected, we obtain for the transition temperature $k_B T_0 \approx \hbar\omega|S - p|/4S$. This latter result provides an adequate picture for the strong and weak coupling situations (1) and (2) but is inapplicable, of course, for activationless processes.

The new general expression for the transition temperature are useful for a rough but reliable estimate of the relevant molecular parameters in systems which reveal a "transition" from nuclear tunneling to activated rate. More important, these relations can be utilized for general analysis of some experimental data for some ET processes in biological systems which reveal a temperature-independent rate over the range 4–300 K.¹ A notable example involves electron transfer from bacteriopheophytin (BPH) to ubiquinone 10 (Q): (BPH)⁻Q → (BPH)Q⁻ in the primary steps of bacterial photosynthesis.¹ This chemical process is characterized by a half-lifetime of $\tau = 150$ ps,^{1d} which is constant over the temperature range 4–300 K.^{1d} Attempting to interpret this process as nuclear tunneling over a finite barrier, we have to utilize eq 1 and 2 with $\Delta E < 0$ and $E_A > 0$. According to eq 6 the characteristic phonon frequency will be $\hbar\omega \geq 1000$ cm⁻¹. This frequency is considerably higher than what is expected for molecular frequencies of the ligand-ring modes in porphyrins. For example, the characteristic frequency for the oxidation of cytochrome c in chromatium is $\hbar\omega \approx 500$ cm⁻¹. We can thus assert that the ET process (BPH)⁻Q → (BPH)Q⁻ cannot be interpreted in terms of low-temperature nuclear tunneling over a finite barrier, but it rather corresponds to an activationless ET process,¹² where the nuclear potential surfaces of the initial and final states intersect at the minimum of the initial state potential surface.

References and Notes

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