THEORY OF PROTON-TRANSFER PROCESSES IN A POLAR MEDIUM

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In considering processes of charge transfer in polar media resulting from strong interaction between the charge and optical phonons of the medium (polarization) almost the only effective method of describing the system as a whole, i.e., in terms of electron+phonons and the nuclei provided by the media (reagents), is in practice the Born-Oppenheimer approximation (BOA) for the separation of electron and nuclear motions [1-3]. The way in which the problem is usually stated involves the isolation from the complete Hamiltonian of a system of interactions V_i and V_j, which leads to transfer (or redistribution) of charge, i.e., the separation of the initial (i) and final (f) channels of the process. The use of the BOA in each channel enables channel electron terms to be constructed, i.e., $U_i(q)$ and $U_f(q)$ (terms of the zero approximation), which include a diagonal (with respect to the state of the appropriate channel) part of the interaction V_i or V_f. Charge transfer corresponds to transitions between the terms U_i and U_f, which is achieved because of the presence of nondiagonal matrix elements (electron exchange integrals) $\langle f \mid V_i \mid i \rangle$ and $\langle i \mid V_f \mid f \rangle$.

The problem of describing the probability of transition W_{if} for an arbitrary type of vibrational spectrum of a system in the initial and final states, in the presence of interchange of the normal coordinates has been solved for small values of the electron exchange integral (nonadiabatic transitions) [1, 2]. The calculations for large values of $\langle i \mid {}_{if} \mid f \rangle$ (adiabatic transition) have so far been carried out only for the case where the vibration frequency and the systems of normal coordinates in the initial and final states are the same and the vibrational spectrum as a whole satisfies the condition [3, 4]

$$\hbar\omega_k \ll kT. \tag{1}$$

In this case it is possible to show that the problem formally reduces to a description of the probability of transition between two effective unidimensional terms, characterized by the frequency ω_{eff}.

A class of processes will be considered in which, as a result of charge transfer, changes occur not only in the state of the electrons and the low frequency [in the sense of Eq. (1)] phonons but also in the state of the high frequency, local vibration

$$\hbar\omega_p \gg kT \tag{2}$$

in the absence of interchange of the normal coordinates, using as an example the transfer of a proton between two molecules in solution at a fixed distance from each other (or between two crystal lattice sites). For simplicity it is assumed that both molecules and the protons are located on a straight line and only the motion of the proton along its chemical bonds in the molecule is allowed for (linear complex model). The charged proton reacts strongly with the optical phonons. Allowing for the large difference between the vibration frequency of the proton ω_p and the frequencies of the phonons ω_k, the BOA is also used to describe the state of the proton in the initial and final channels, but the motion of the proton is separated from the remaining vibrational system (double adiabatic approximation). This enables the electron–proton channel terms $U_i^{ep}(q)$ and $U_f^{ep}(q)$ to be introduced (Fig. 1). (In Fig. 1 the effective unidimensional terms of the phonon subsystem are represented schematically.) The transition of the system from the initial state to the final state corresponds to a transition between these terms, which is brought about because of

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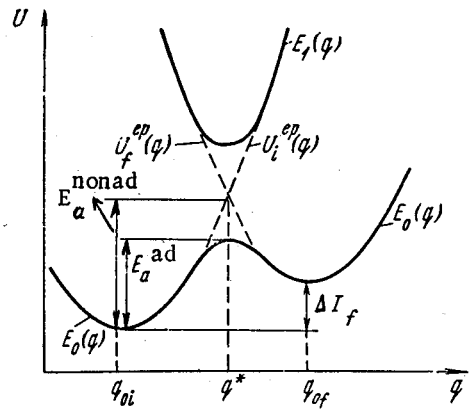

Fig. 1

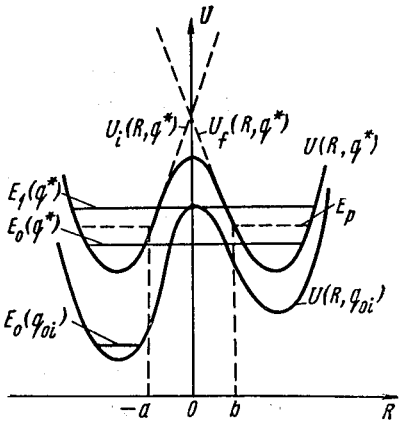

Fig. 2

the presence of a nondiagonal matrix element V_{ep}, which represents the exchange integral from the energy of interaction both with respect to electrons and protons for the initial and final wave functions. Moreover, for excessively high values (in module) of the thermal effect of the ΔI_f process (Fig. 1) (normal region), for a completely nonadiabatic transition it is possible to limit the consideration to the terms $U_i^{ep}(q)$ and $U_f^{ep}(q)$, corresponding to nonexcited initial and final vibrational states of the proton (two-level approximation) [2].

The expression for the probability of completely nonadiabatic transitions (of both electrons and protons) can be obtained within the framework of the first order of excitation theory with respect to V_{ep}, i.e.,

$$W_{if} = \frac{\omega_{\text{eff}}}{2\pi} \cdot \varkappa_{ep} \cdot e^{-E_a^{\text{nonad}}/kT},$$
$$\varkappa_{ep} = |V_{ep}|^2 \cdot \left(\hbar^2 \omega_{\text{eff}}^2 kTE_r \frac{\pi^{-3}}{4}\right)^{-1/2} \equiv \frac{2|V_{ep}|^2}{V_{\text{crit}}^2}, \tag{3}$$

where the activation energy E_a^{nonad} is determinded by the point of intersection of the terms $U_i^{ep}(q)$ and $U_f^{ep}(q)$ (Fig. 1). In this calculation the following conditions must be fulfilled:

$$2\pi |\langle i|V_i|f\rangle|^2 / \hbar |v_p| \cdot |F_i^p - F_f^p| \ll 1; \qquad \varkappa_{ep} \equiv 2|V_{ep}|^2 / V_{\text{crit}}{}^2 \ll 1, \tag{4}$$

where $F_i^p = \partial U_i / \partial R$ and $F_f^p = \partial U_f / dR$ represent the slopes of the electron terms $U_i(R;q^*)$ and $U_f(R; q^*)$ for the initial and final state (for values of the normal coordinates of the phonons corresponding to the saddle point at the intersection of the electron–proton terms $U_i^{ep}(q^*) = U_f^{ep}(q^*)$ (Fig. 1) at their intersection point, $|v_p| = (\partial [U_i(0;q^*) - E_p]/m_p)^{1/2}$, and E_p is the energy of the main vibrational state of the proton in the reaction channels.*

The exchange integral V_{ep} in the quasiclassical approximation can be approximated by the equation

$$|V_{ep}| \sim |\langle i|V_i|f\rangle| \exp(-\sigma_{\text{nonad}}/2), \tag{5}$$

where

$$\sigma_{\text{nonad}} = \frac{2}{\hbar}\int_{-a}^{0} dR \sqrt{2m_p [U_i(R; q^*) - E_p]} + \frac{2}{\hbar}\int_{0}^{b} dR \sqrt{2m_p [U_f(R; q^*) - E_p]}, \tag{6}$$

where the coefficient of proportionality depends on the form of the terms.

At large values of the electron exchange integral $|\langle i|V_i|f\rangle|$, a condition which is the opposite of the first inequality in (4) can be shown to be fulfilled, whereas a condition of the type $\varkappa_{ep} \ll 1.0$ can also apply. This case corresponds to the situation where the electrons have time to adjust adiabatically to the change in state of the proton, whereas the process as a whole is nonadiabatic, since the proton does not have time to adjust adiabatically to the change in state of the phonons of the medium.

*The condition such as the first inequality in (4) was obtained in [9] for unidimensional linear terms.

Using this as a starting point, in order to find the probability of the proton transition W_{if}, it is convenient at first to consider the basic adiabatic electron term U(R, q) of the accurate Hamiltonian (with allowance for the nonadiabatic part of the interactions of V_i and V_f). The splitting up of this term corresponding to various fixed values of q is shown schematically in Fig. 2. Allowing for the slowness of the phonon subsystem (q), it is possible to find the energy levels of the proton $E_0(q)$, and $E_1(q)$, . . . in the potential well [U(r; q) (Fig. 2), i.e., the electron–proton terms (Fig. 1). In order to calculate W_{if}, the two-level approximation often used in collision theory is used below. (For criteria as to the applicability of this approximation in problems of the type under consideration, see [7].) In this case it is possible to restrict consideration to the ground $E_0(q)$ and the first excited $E_1(q)$ levels of the proton at the potential U(R; q). Figure 1 gives a qualitative picture of the relation between these quantities and q.

In posing the problem of calculating the probability of a proton transition from one molecule to another, account must be taken of the fact that because of interaction of the proton with phonons, the configuration of the potential well U(R; q) for the proton depends on the values of the normal coordinates of the phonons $\{q_k\}$. For values of q_k close to q_{k0}^{i}, the minimum of the left-hand potential well is located significantly lower than that of the right-hand potential well (Fig. 2), so that the wave function $\Phi_0(R; q)$ for the ground state of the proton, which is an inherent function of the complete Hamiltonian for the nuclei less the kinetic energy of the phonons, corresponds to localization of the proton close to the first molecule (Fig. 2). On changing the coordinates of the phonons q_k the minimum of the left-hand potential well is raised relative to the minimum of the right-hand potential well. Moreover, the two lower energy levels $E_0(q)$ and $E_1(q)$ converge at the potential U(R; q), so that at $\{q_k = q_k^*\}$ the difference $E_1 - E_0$ passes through a minimum, while the minimum distance between these levels $\Delta E_{ad} = \min (E_1 - E_0)$ determines the magnitude of the "splitting" of the corresponding electron–proton terms $E_0(q)$ and $E_1(q)$ (Fig. 1). With further change in the coordinates q_k the distance between the energy levels E_0 and E_1 again increases, and the minimum of the right-hand potential well falls below the minimum of the left-hand potential well. For values of the coordinates q_k close to q_{k0}^{f}, the wave function for the ground state of the proton $\Phi_0(R; q)$ corresponds to localization of the proton in the second molecule. Accordingly, the problem of calculating the probability of proton transfer reduces to describing the probability that when the system passes through a region close to the point $\{q_k^*\}$ it remains at the lower electron–proton term $E_0(q)$. The probability of such a transition depends essentially on the magnitude of the "splitting" ΔE_{ad} of the electron–proton terms $E_0(q)$ and $E_1(q)$ [8, 9].

If ΔE_{ad} is small, so that the condition

$$\varkappa_{ep}^{ad} = 2\pi(\Delta E_{ad}/2)^2/\hbar v_T|\bar{F}_i - \bar{F}_j| \equiv (\Delta E_{ad}/2)^2(\hbar^2\omega_{eff}^2 kTE_r/4\pi^3)^{-1/2} \ll 1 \tag{7}$$

is fulfilled, the equation for the probability of a transition takes the form [5]

$$W_{if} = \frac{\omega_{eff}}{2\pi}\varkappa_{ep}^{ad}\exp(-\tilde{E}_a^{nonad}/kT), \tag{8}$$

Equation (8) differs from (3) in that $\varkappa_{ep}$ has been replaced by $\varkappa_{ep}^{ad}$. The activation energy E_a^{nonad} is in this case determined by the point of intersection of the electron–proton terms $\tilde{U}_i^{ep}(q)$ and $\tilde{U}_f^{ep}(q)$, which are introduced in accordance with the relations

$$E_{0,1}(q) = {}^1/_2\{[\tilde{U}_i^{ep}(q) + \tilde{U}_f^{ep}(q)] \mp \sqrt{[\tilde{U}_i^{ep}(q) - \tilde{U}_f^{ep}(q)]^2 + (\Delta E_{ad})^2}\}, \tag{9}$$

where the minus sign applies to the term $E_0(q)$ and the plus sign refers to the term $E_1(q)$. The quantities $\bar{F}_i = \partial\tilde{U}_i^{ep}/\partial q$ and $\bar{F}_f = \partial\tilde{U}_f^{ep}/\partial q$ represent the slopes of the terms $\tilde{U}_i^{ep}(q)$ and $\tilde{U}_f^{ep}(q)$ at their point of intersection.

The "splitting" ΔE_{ad} may be small, in spite of the large value of the electron exchange integral, so that the probability of tunneling of a proton from one potential well into another (Fig. 2) is small. In the quasiclassical approximation ΔE_{ad} may be approximated by an expression of the type

$$\Delta E_{ad} \sim \hbar\omega_p \exp(-\sigma_{ad}/2); \quad \sigma_{ad} = \frac{2}{\hbar}\int dR\sqrt{2m_p[U(R; q^*) - E_0(q^*)]}, \tag{10}$$

where the proportionality factor depends on the form of the potential well U(R; q*). Accordingly, even at large values of the electron exchange integrals the process as a whole can exhibit an essentially nonadiabatic character, which is associated with the passage of heavy particles below the potential barrier.

Finally, if ΔE_{ad} is sufficiently large, so that a condition which is the opposite of (7) is fulfilled, i.e., the proton also has time to adjust adiabatically to the changes in state of the phonons (completely adiabatic transition), the equation for the probability of transition then takes the form [5]

$$W_{if} = \frac{\omega_{eff}}{2\pi} \exp\left(-E_a^{ad}/kT\right). \tag{11}$$

Equation (11) differs from (8) in that the term $\varkappa_{ep}^{ad}$, which defines the probability of readjustment of the state of the proton on the passage of the phonon subsystem through the region of intersection of the terms $\tilde{U}_i^{ep}(q)$ and $\tilde{U}_f^{ep}(q)$ has been replaced by unity. Moreover, the activation energy E_a^{ad} is now determined by the saddle point on the electron–proton term $E_0(q)$.

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