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# Theoretical investigations of proton and hydrogen atom transfer in the condensed phase

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**Abstract. Theoretical studies of the dynamics and kinetics of proton and hydrogen atom transfer processes occupy a special place in the kinetics of chemical reactions. The transition state theory is often inapplicable to these processes due to substantial quantum effects. Different approaches to the description of these reactions are discussed and compared. Calculations for a number of particular condensed-phase reactions involving proton or hydrogen atom transfer are analysed. Data of calculations of potential energy surfaces for the considered systems and the results of experimental kinetic and spectroscopic studies are presented. The bibliography includes 469 references.**

## I. Introduction

Proton transfer (PT) and hydrogen atom transfer (HAT) deserve special consideration in the study of chemical reactions. Due to substantial quantum effects, the transition state (TS) theory — which today forms the basis for investigations of reaction kinetics and mechanisms — is often inapplicable in these cases. The existing numerous theories of PT and HAT are complicated and diverse. This review is an attempt to consider and compare, from a unified standpoint, various approaches to the theoretical description of PT and HAT and to identify the common points and the scopes of applicability of these approaches. Without pretending to an exhaustive consideration, we endeavoured to provide a concerned reader with the main ideas and and trends in the development of the research in this field. More comprehensive formulation of the outlined approaches can be found in the key references.

It should be noted that the difference between PT and HAT is largely conventional. In the limiting case, PT is an ionic heterolytic process in which the influence of the medium is crucial, whereas HAT is a radical homolytic process depending only slightly on the medium. In reality, all types of intermediate situations are encountered and it is difficult to adhere to a consistent terminology. In some cases, the use of a particular term can be contested; however, in our opinion, this discussion does not deserve much attention.

Two factors, namely, tunelling and effect of the medium, restrict the applicability of the TS theory and account for the exceptional position of the PT and HAT processes in the theory of chemical reactions. For consistent treatment of tunnelling, one should consider (or, more precisely, calculate) the quantum-dynamic evolution of the reaction subsystem on a multidimensional potential energy surface (PES). The reaction rate constant is obtained by statistical averaging of the results of this calculation. An adequate allowance for the medium implies that a very large number (hundreds or even thousands) of degrees of freedom for particles surrounding the reaction subsystem should be included in this dynamic investigation. Taking into account simultaneously both factors mentioned above constitutes the essence of the dynamic theory of chemical reactions in the condensed phase as a modern line of research in theoretical chemical physics.

In practice, the stringent requirements outlined above can be markedly released, in particular, by using simplified models for tunnelling transitions and by decreasing the number of additional degrees of freedom interacting with the tunnelling coordinate to tens or even less. Nevertheless, in recent years, record-breaking computations have been carried out (they are described in this review) which attempted to minimise the simplifying assumptions and their consequences. However, real objects (*e.g.*, reactions in enzymes) are so complicated that even these calculations are simplified models.

In any case, the major requirement of explicit inclusion of the tunnelling dynamics into the mechanism of the elementary process remains valid. This feature distinguishes the studies discussed in this review from the numerous studies whose authors attempted to consider the PT and HAT reactions on the basis of the traditional TS theory, *i.e.,* using a quasi-equilibrium statistical rate constant. As the premise, we accepted the statement that interpretation of the kinetics and the mechanism of these reactions based only on the language of the energetic and topographic characteristics of PES such as the height of the potential barrier and the reaction coordinate is inadequate and recedes to the background.

The material presented here is arranged in the following way. First, the main concepts of the PT and HAT dynamics in the condensed phase are considered. They were formulated in the 1970s – 1980s and they are still being developed and refined. This is followed by applications of the theory to calculations of particular systems carried out during the last 10 – 15 years. Many of the publications cited present also original theoretical

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developments; therefore, the subdivision into 'theory' and 'applications' is not fully consistent.

Simpler gas-phase reactions have been investigated much more extensively than reactions in the condensed phase. The relevant studies are not covered systematically but references to earlier reviews and monographs are given. However, since the understanding of the tunnelling dynamics of gas-phase reactions should precede any discussion of tunnelling in the liquid or solid phase or in biological objects, the key studies dealing with the theory of gas-phase PT and HAT are considered as examples.

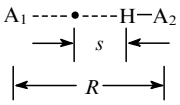
Since we selected studies focused on the dynamics of an elementary process, the quantum-chemical calculations of PES (even the highest-level ones) are not of interest by themselves in this context. A summary of such calculations (the most significant in our opinion) is included as reference data together with experimental results. The experimental works presented in brief represent mainly investigations of the kinetics and mechanisms of PT and HAT by spectroscopy (NMR, UV, IR, radiospectroscopy, *etc.*). These studies provide the factual information necessary for the development and testing of the theoretical models discussed in the review.

## II. Methods for the theoretical description of proton and hydrogen atom transfer

### 1. Potential energy surfaces

#### a. Reaction centre

Let us consider the reaction centre for PT or HAT in a simple two-mode linear model.




(1)

Here $A_1$ and $A_2$ are 'heavy' molecular fragments; their internal structure is not specified in detail now. The centres of gravity of particles $A_1$, $A_2$ and H lie on the same straight line; this type of reaction is called collinear.

The dynamic behaviour of system (1) is fully described by variations of two coordinates, namely, the proton coordinate ($s$) measured from the centre of gravity of the whole complex (1) and the distance ($R$) between the heavy fragments. Figure 1 presents a typical PES $V(s,R)$ in these coordinates and cross-sections $V(s\,|\,R)$ of this surface along the coordinate $s$, which parametrically depend on $R$. For a symmetrical system ($A_1 = A_2$), the cross-sections are symmetrical. As $R$ decreases, the double-well profiles become more gently sloping, which is accompanied by equalisation of the proton (hydrogen atom) bonds with fragments $A_1$ and $A_2$. At the critical point $R_c$, the double-well potential profile turns into a single-well one. This PES topography determines the key characteristics of a PT or HAT reaction. Since one of the two equilibrium configurations of complex (1) is the initial state, either a PES with potential barriers with different heights (if $R_e > R_c$) or a barrierless PES (if $R_e < R_c$) appear, depending on the equilibrium distance $R_e$. In the former case, the initial equilibrium configuration is markedly asymmetrical ($A_1—H\cdots A_2$), while in the latter case, it is nearly symmetrical ($A_1\cdots H\cdots A_2$), even when the fragments $A_1$ and $A_2$ are different. In symmetrical systems, a combination of asymmetrical configurations of the reactants and products gives rise to a symmetrical double-well profile. The position of the top of the barrier, *i.e.*, TS (designated by $R^{\neq}$ in the axis $R$) cannot be smaller than $R_c$ ($R^{\neq} \geqslant R_c$). The $R_e$ and $R_c$ values substantially depend on the nature of fragments $A_1$ and $A_2$, most of all, their terminal atoms, which are linked to the proton or hydrogen atom that is transferred.[1] The distance between the terminal atoms (rather than between the centres of gravity of fragments $A_1$ and $A_2$) is usually taken as the coordinate $R$. For bimolecular reactions of non-polar reactants in the gas phase (for example, C···H···C), the $R_e$ distance is great, $R_e \gg R_c$ (which corresponds to a van der Waals complex) and the barrier is usually

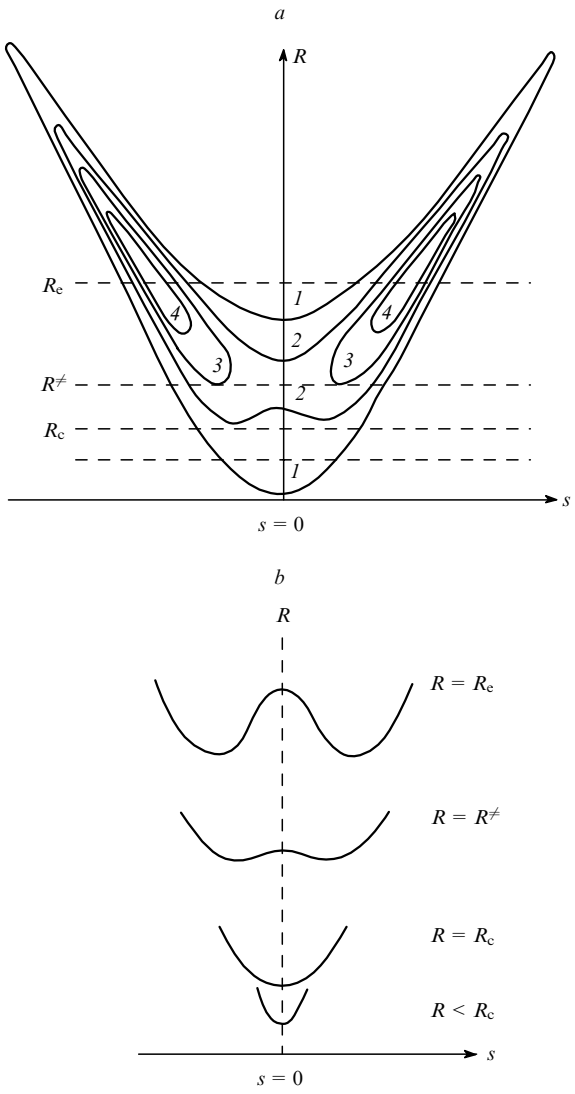



**Figure 1.** Typical symmetrical PES for PT or HAT reaction in the simplest two-mode collinear model;
(*a*) general view of the PES with isoenergy contour lines; closed loops (*1–4*) are isoenergy contour lines in arbitrary units; (*b*) PES cross-sections along the coordinate $s$ for different $R$ values; $R = R_e$ (reactants and products), $R = R^{\neq}$ (transition state) and $R = R_c$ (critical point). In the given case, $R_c < R^{\neq}$. The projections of the cross-sections on the $R, s$ plane are shown by a dashed line in Fig. 1 *a*.

rather high. Conversely, in the case of systems which tend to form strong and medium-strength hydrogen bonds (for example, the O···H···O bonds in the condensed phase), the inequality $R_e < R_c$ usually holds, and the PES is often a single two-dimensional potential well. In this case, one cannot speak about a PT or HAT reaction. Particular examples of different possible situations are presented in Table 1. They mainly refer to electrically neutral systems; charged systems ($FHF^-$, $H_5O_2^+$, *etc.*) with hydrogen bonds normally tend to form single-well PES.[11]

In unimolecular processes, the reaction centre (1) is a fragment of an integrated, more or less rigid molecular structure. The equilibrium distance $R_e$ stipulated by the structure is usually shorter than the $R_e$ value between the reaction centres of the same type in bimolecular reactions. This is due to the fact that the $A_1\cdots H\cdots A_2$ fragment in systems with intramolecular hydrogen bonds is non-linear. A typical example of the latter type is a *cis*-enol form of a β-dicarbonyl compound, for example, malonaldehyde or acetylacetone,[12,13] which are six-membered chelate rings with an intramolecular hydrogen bond. The $R_e$ values for these

**Table 1**. Typical $R_e$ and $R_c$ values in PT and HAT reactions for the $A_1-H\cdots A_2$ reaction sites.

| Fragment | Process | $R_e$ /Å | Determination method | $R_c \approx R^{\neq}$ /Å (see [a]) | Note | Ref. (see [b]) |
|---|---|---|---|---|---|---|
| O–H···O | PT and double PT in a symmetrical double-well potential | 2.64 | X-ray diffraction analysis of the benzoic acid crystal | 2.40 | the O···O distance in the TS for systems with a symmetrical two-well potential | 2, 3 |
| N–H···O | double PT in an asymmetrical double-well potential | 2.95 | X-ray diffraction analysis of the formamide cyclic dimer | 2.55 | the distance in the TS structure [B-LYP/6-311++G(d,p) calculations] | 4, 5 |
| N–H···N | double PT in a symmetrical double-well potential | 2.93 | the calculation (HF/3-21G) for the amidine dimer | 2.53 | the N···N distance in the TS structure for systems with a symmetrical double-well potential | 6, 7 |
| {C–H/C}$^-$ | PT in a symmetrical double-well potential | 3.71 | the calculation [MP2/6-31+G(d,p)] for the $CH_4/CH_3^-$ ion–molecular complex | 2.86 | the C···C distance in the TS structure [MP2/6-31+G(d,p) calculation] | 8 |
| {C–H/C}$^{\bullet}$ | HAT in an asymmetrical double-well potential | 3.35 | spectroscopic and structural data on H abstraction from ethanol by the methyl radical in glasses | 2.68 | the C···C distance in the TS structure of the $CH_3^{\bullet}/CH_3OH$ system (MP2/6-31G calculation) | 9, 10 |

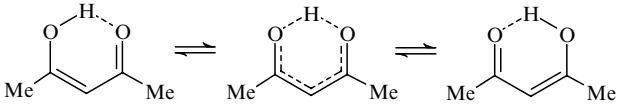
**Note**. Systems with intramolecular PT or HAT were not considered because in this case, the triatomic $A_1-H\cdots A_2$ fragment is essentially non-linear. [a] No direct estimate for the $R_c$ value is known; therefore, the corresponding $R^{\neq}$ values are given, which are close to $R_c$. [b] The $R_e$ value was taken from the first reference and $R_c$ is from the second reference.

systems are much shorter than the corresponding value for the O–H···O fragment presented in Table 1. The rigid structure of the environment ('cage effect') is probably responsible for acceleration of enzymic PT reactions.[14,15] In this case, the structure of the reaction centre is dictated by the architecture of the protein globule of the enzyme, while $R_e$ is sufficiently small to lower the reaction barrier to a plausible value.

Thus, the potential relief depends appreciably on the distance between the chemically non-bonded heavy atoms, which accounts for stringent requirements to the accuracy of quantum-chemical methods used to calculate the PES. Slight errors in the estimation of $R_e$ can change the calculated height of the potential barrier (defined as the difference between the energies of the saddle point and the reactant minimum on the PES) and can appreciably distort the potential relief that controls the reaction event.[16] On the other hand, in constructing semiempirical PES, it is expedient to consider the $R_e$ value as a control parameter whose variation allows one to reproduce a required potential relief.[17]

**b. Rearrangement of the medium and classification of modes**

**Intramolecular and intermolecular relaxation**. In most cases, the simplest two-mode model (1) does not provide an adequate description of PT. As an example, we consider the PT in acetylacetone molecule.




Here $R_e = 2.535$ Å (see Ref. 18). According to the above simplest model, this geometry is expected to produce a single-well symmetrical equilibrium configuration of the O···H···O hydrogen bond. In reality, acetylacetone is an example of a system having a potential barrier, although it is relatively low: $\Delta V^{\neq} = 2.5$ kcal mol$^{-1}$ (see Ref. 19). This 'classical' barrier disappears when the quantum zero-point vibrations of the H atom are taken into account.[19] The tendency for the formation of an asymmetrical structure by the molecule is enhanced by rearrangement of its bond lengths and bond angles around the reaction centre caused by the variation of the proton coordinate $s$ (Table 2). In the literature, this effect is often referred to as 'environment reorganisation'; this term has been borrowed from electron transfer theory. In this particular case, an intramolecular reorganisation is involved.

**Table 2**. Bond lengths (Å) and O···H–O angles (deg) for a fragment of the cyclic acetylacetone structure and the structure corresponding to the TS of the intramolecular PT reaction found by the Möller–Plesset *ab initio* calculations [19] (MP2/D95++**).

| Parameter | Cyclic enol form [a] | TS |
|---|---|---|
| C=C | 1.376 (1.382) | 1.410 |
| C–C | 1.452 (1.430) | 1.410 |
| C–O | 1.338 (1.319) | 1.295 |
| C=O | 1.259 (1.243) | 1.295 |
| O–H | 1.004 (1.049) | 1.201 |
| O···H | 1.626 (1.626) | 1.201 |
| O···O | 2.549 (2.512) | 2.363 |
| O···H–O | 150.6 (137.0) | 159.1 |

[a] The values in parentheses are experimental data.[18]

When the PT process is accompanied by a substantial change in the charge distribution and takes place in a polar solvent, there exists an alternative mechanism for stabilisation of asymmetrical structures due to solvent reorganisation: the solvation shell is adjusted to the charge distributions, which are different for the reactants and the reaction products. This situation is referred to as the 'medium reorganisation'. Proton transfer in electrically neutral systems, for example, in a conjugate acid–base system usually does not occur in the gas phase,[20] but readily proceeds in polar solvents,[21] which is due to medium reorganisation.

It can be seen from the above examples that reorganisation of the surrounding of the reaction centre (both intramolecular reorganisation and that of the environment) includes simultaneous change of many degrees of freedom, *i.e.*, it is a multimodal process.

**Harmonic double-well potential energy surface.** The simplest pattern of multimode reorganisation corresponds to the model harmonic PES formed by two multi-dimensional paraboloids shifted relative to each other. The two-dimensional analogue of this PES is shown in Fig. 2. The reorganising modes $Q$ are

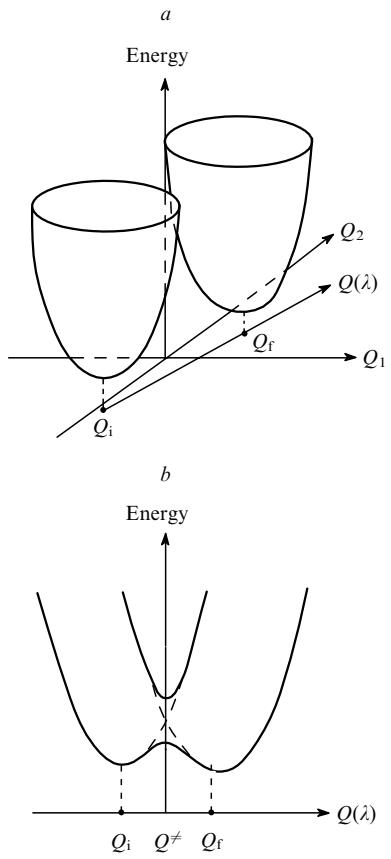



**Figure 2.** Two-dimensional scheme of the reaction transition between two paraboloids;
(*a*) two-dimensional analogue of the model harmonic PES; the paraboloid minima are located at points $Q_i$ and $Q_f$; (*b*) energy profile of the reactive transition (shown by a dashed line in the intersection area of two parabolic potential curves corresponding to the PES cross-section along the straight line $Q_iQ_f$). The continuous lines show splitting of two energy profiles due to anharmonic interactions.

numbered by using subscripts $v = 1,...,N$; for Fig. 2 *a*, $N$ is equal to 2. Their equilibrium positions for the reactants (subscript i) and products (subscript f) will be denoted by $Q_{iv}$ and $Q_{fv}$. The description is simplified if the paraboloids are identical, *i.e.*, the reactants and the products are characterised by identical systems of vibration frequencies and forms of normal vibrations (modes).

Let us denote the vectors with the components $Q_{iv}$ and $Q_{fv}$ by $(Q_i)$ and $(Q_f)$ and then form the vector

$$[Q(\lambda)] = (Q_i) + \lambda[(Q_f) - (Q_i)]; \; 0 \leqslant \lambda \leqslant 1, \tag{2}$$

which describes the change of the modes along the straight line connecting the projections ($Q_i$ and $Q_f$) of the minima of the two paraboloids onto the $Q_1Q_2$ plane (Fig. 2 *a*). Then the parameter $\lambda$ can be considered as the 'reaction coordinate'. If the paraboloids are identical, they intersect along some straight line in the coordinate plane. In this straight line (or in a planar hypersurface if $N > 2$), the PES cross-section passes through a minimum, which is characterised by a set of coordinates: $Q^{\neq} = (Q_1^{\neq}),...,(Q_N^{\neq})$, the point $Q^{\neq}$ lies in straight line (2). The cross-section of the PES along the coordinate (2) is shown in Fig. 2 *b*. At the intersection point of the parabolic potential curves, the reaction coordinate is found as

$$\lambda = \frac{1}{2}\left(1 + \frac{\Delta V}{E_r}\right), \tag{3}$$

where $\Delta V$ is the difference between the energies corresponding to the reactant and product minima

$$\Delta V = V_f - V_i, \tag{4}$$

$E_r$ is the reorganisation energy characterising the energy consumption for transition from the reactant minimum to the product minimum; $E_r$ is an additive relative to the contributions of separate modes characterised by masses $m_v$ and frequencies $\omega_v$:

$$E_r = \sum_v E_{rv}, \qquad E_{rv} = \frac{m_v\omega_v^2}{2}\left(Q_{fv} - Q_{iv}\right)^2. \tag{5}$$

The height of the potential barrier in this PES obeys the Marcus formula

$$\Delta V^{\neq} = \frac{(E_r + \Delta V)^2}{4E_r}. \tag{6}$$

This PES model underlies most of the theories of multimode processes. Although the model is idealised, it can be useful for a qualitative discussion. Real PES are highly anharmonic,[22–24] and the contributions of separate modes to the potential barrier cannot be distinguished unambiguously, as would be the case according to relations (5) and (6). There exist semiempirical interpolation-type analytical formulae, which allow one to describe the anharmonic PES and the free energy surface (FES) for PT in terms of a set of characteristic parameters.[25,26]

**Combination of reorganisation and promoting modes.** It is of interest to analyse how the allowance for reorganisation modes modifies the two-mode model described in Section II.1.a.[27–31] For this purpose, we consider three points, $(Q_i)$, $(Q^{\neq})$ and $(Q_f)$, on the reaction coordinate $Q$. Even for a symmetrical system ($A_1 = A_2$), by fixing $(Q)$ at the points $(Q_i)$ and $(Q_f)$, we obtain asymmetrical potential energy profiles along the proton coordinate $s$ (here we do not consider the dependence on $R$). This is shown schematically in Fig. 3. When $(Q) = (Q^{\neq})$, the $V(s)$ profile is symmetrical or nearly symmetrical even for the systems with dissimilar heavy fragments $A_1$ and $A_2$. As noted above, in a two-mode double-well symmetrical system, the potential barrier is often relatively low and

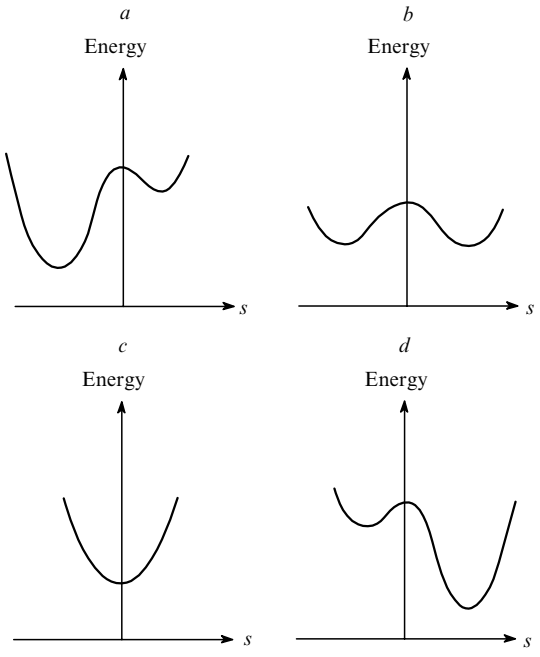



**Figure 3.** Potential curves of the reaction system along the proton coordinate $s$ with allowance for reorganisation modes;
(*a*, *d*) reactant and product regions, respectively; (*b*, *c*) TS region.

transitions between the wells occur rapidly. The asymmetry brought about by the relaxation of reorganisation modes hinders the transitions and thus contributes to fixing of the reactant and product configurations. In the case of bimolecular gas-phase reactions, this fixing is possible even in a two-mode model due to the spatial separation of the reactants and products along the reaction coordinate $R$. In the condensed phase, the reactants and products are in relatively close contact [the $R_e$ distance is about the van der Waals distance in complex (1)]. Therefore, stabilisation of the initial and final states owing to relaxation of the environment modes acquires a crucial role.

In view of the foregoing, the following, frequently used classification of inter- and intramolecular degrees of freedom involved in PT processes can be proposed. First, the proton coordinate $s$ is considered, which is called the reaction mode. Second, those modes are considered that do not change (or almost do not change) in the initial and final states but appreciably change in the TS and thus modify the height of the potential barrier. There modes are called promoting. A typical example is the $R$ coordinate; other promoting modes are discussed below. Finally, some modes change their equilibrium positions on passing from the reactant configuration to the product configuration. They are referred to as reorganisation modes.

Naturally, this classification is not universal. However, it often reflects adequately the essential features of the PT process and is widely used in model considerations. Note that the term 'reaction mode', introduced above for the coordinate $s$ does not necessarily mean the 'reaction coordinate'. For real anharmonic PES, the mode $s$ interacts with other reaction modes and, generally, it is not an independent motion in the region of the TS, as it would be the case for a strictly defined reaction coordinate. The mode $s$ may be identified with the reaction coordinate only in terms of the simplest models; this terminology is often encountered in the literature and below it is used in some cases without special reservations.

In reality, the reaction mode for PT and HAT is always a combination of several simple modes. This is illustrated, in particular, by the following examples. According to the data of femtosecond spectroscopy, the rate of PT for the lower singlet electronically excited state of methyl salicylate, 2-(2′-hydroxyphenyl)benzothiazole and 1,8-dihydroxyanthraquinone is $50-60\ fs^{-1}$ in the gas phase [32–34] and $170\ fs^{-1}$ in aprotic solvents.[35] The reaction coordinate for the PT includes, as a first approximation, the coordinate of the OH stretching vibrations and the coordinate of the O···H···O out-of-plane vibration.[32] The periods of vibration are 13 fs for the OH bond and 190 fs for the O···H···O fragment. These vibration modes interact appreciably with one another, their relative contributions to the reaction mode being dependent on the process conditions. In systems with equivalent initial and final states, PT is manifested as tunnel splitting of the ground vibration state.[36–38] The tunnel splittings have been measured for not only the ground state but for a number of vibrationally excited states for some systems in the lower singlet electronically excited state.[39–42] A sharp increase in the tunnel splitting was observed upon selective excitation of particular low-frequency vibrations.[39,40] In the case of tropolone, this active vibrational mode was the displacement of heavy atoms of the O···H···O fragment,[41] and in the case of azaindole dimer, an intermolecular stretching vibration.[39] Data of *ab initio* calculations of the PES for intra- and intermolecular PT in various systems [22–24,43] confirm the experimental results.

## 2. Dynamics and kinetics

### a. Reactions with a low potential barrier

**Quantisation of the reaction mode.** A key feature of PT reactions is a quantal nature of, at least, one essential mode, namely, the reaction mode $s$. Let $\omega_0$ be the characteristic frequency of the mode $s$ and $\hbar\omega_0/k_BT \gg 1$. In this case, the traditional description of the kinetics using the classical TS theory is inapplicable. Due to this fact, theoretical description of PT is a difficult task. Nevertheless, the classical approach can be used in the modified form if the height of the barrier $\Delta V^{\neq}$ on the PES is sufficiently low for the reactant well to contain only one quantum level with a frequency close to $\omega_0$:

$$\frac{\hbar\omega_0}{\Delta V^{\neq}} \lesssim 1. \tag{7}$$

The quantum motion along $s$ occurs much faster than along other modes ($\omega_0 \gg \omega_i$, where $\omega_i$ are other eigenfrequencies of the system); this allows one to use the double (along both the electronic and proton coordinates) adiabatic approximation. Different modifications of this model with a classical description of the promoting mode $R$ have been discussed.[29–31] The Schrödinger equation for the mode $s$ has the form

$$h_s\varphi_n(s) = \varepsilon_n\varphi_n(s), \tag{8}$$

where $h_s$ is a Hamiltonian,

$$h_s = -\frac{\hbar^2}{2m_0}\frac{\partial^2}{\partial s^2} + V(s|R,Q). \tag{9}$$

Here, $m_0$ is the corresponding mass, and the potential coincides with the full PES $V(s,R,Q)$. The notation of this function in Eqn (9) emphasises that it follows a parametric dependence on the $R,Q$ coordinates of the heavy atoms. The eigenvalues and eigenfunctions in Eqn (8) depend on $R$ and $Q$. In particular, the energies $\varepsilon_n(R,Q)$ are the PES (electron–proton PES) for the coordinates $R,Q$. In the adiabatic limit, it is sufficient to consider the ground state ($n = 1$), *i.e.*, the PES $\varepsilon_1(R,Q)$. In many cases, the motion of heavy atoms in such a potential can be regarded to be classical and described using the TS theory in one or another variant.

A similar approximation is widely used in hydrogen bond spectroscopy.[44,45] It is called the Born–Oppenheimer separation of motions of light and heavy nuclei [46] or the adiabatic separation of vibrational variables.[47] A significant feature of the calculations of the vibrational spectrum of the $A_1-H\cdots A_2$ fragment is the quantum description of the promoting mode $R$.[48–53]

**Evolution of heavy modes.** The specificity of using the double adiabatic approximation lies in the fact that the reaction coordinate $s$, natural for a chemist, is excluded from dynamic consideration. The role of the reaction coordinate is played by one of the reorganisation modes $Q$. For example, for low-barrier PT in polar media, the collective variable $Q = y$, describing the behaviour of the medium, is used as the new reaction coordinate. According to this model, the motion along $y$ determines the reaction dynamics and kinetics. In the simplest case, the mode $R$ is excluded from consideration, and the equation of motion reduces to the diffusion equation for the distribution function $n(y,t)$, which determines the probability density for realisation of various $y$ values, depending on time $t$

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial y^2} - \frac{D}{k_BT}\frac{\partial}{\partial y}\left(n\frac{\partial U_a}{\partial y}\right), \tag{10}$$

where $D$ is the corresponding diffusion coefficient, and the potential profile $U_a(y)$ should be regarded as the cross-section of the electron–proton PES (Fig. 4).† The subscript 'a' means that the potential is adiabatic, *i.e.*, double-well. (Further, an alternative description using diabatic, single-well potentials is also discussed.) The rate constant for PT can be estimated in terms of the Kramers approximation.[54,55]

$$k = A\exp\left(-\frac{\Delta U^{\neq}}{k_BT}\right), \tag{11}$$

† From here on, one-dimensional potential profiles present in the diffusion equations are denoted by the letter $U$.

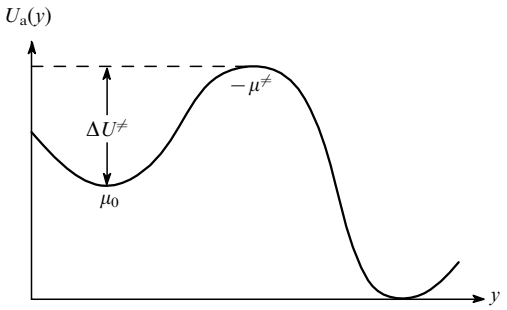



**Figure 4.** Adiabatic potential profile $U_a(y)$ obtained as a cross-section of the electron-proton PES and used in the Kramers equation.

where

$$A = \frac{(\mu_0 \mu^{\neq})^{1/2}}{\pi\gamma},$$

$\Delta U^{\neq}$ is the height of the potential barrier on the electron–proton PES, $\mu_0$ and $-\mu^{\neq}$ are the force constants of the potential $U_a(y)$ in the bottom of the reactant well and on the top of the barrier. The friction coefficient $\gamma$ is related to the diffusion coefficient $D$ by the Einstein relation

$$D = \frac{k_B T}{\gamma}. \tag{12}$$

The Arrhenius dependence (11) with an activation energy equal to the height of the potential barrier is an immutable indication of the classical equilibrium kinetics. In more complex cases, the expression for the pre-exponential factor is modified depending on the particular dynamic model accepted for description of heavy modes instead of the simplest diffusion equation (10). For example, the common one-dimensional Kramers stochastic model proceeds from the Langevin equation

$$m_y \ddot{y} + \gamma \dot{y} + \frac{\partial U_a}{\partial y} = \mathrm{GRF}, \tag{13}$$

where $m_y$ is the mass corresponding to the collective mode of the medium, and GRF stands for the Gaussian random force, which gives rise to fluctuations of the variable $y$ and is responsible for its diffusion motion. If the $\gamma/m_y$ ratio is not very low, Eqn (13) corresponds to the Arrhenius rate constant (11) with the pre-exponential factor

$$A = \left\{ \left[ \left( \frac{\gamma}{2m_y} \right)^2 + (\omega^{\neq})^2 \right]^{1/2} - \frac{\gamma}{2m_y} \right\} \left( \frac{\mu_0}{\mu^{\neq}} \right)^{1/2}, \tag{14}$$

where $\omega^{\neq}$ is a characteristic frequency on the top of the barrier [that is, $i\omega^{\neq}$ is the decay frequency, $m_y(\omega^{\neq})^2 = \mu^{\neq}$]. This well-known Kramers formula provides the pre-exponential factor in Eqn (11) if $\gamma/(2m_y\omega^{\neq}) \gg 1$, *i.e.*, in the limiting case of great friction. Further correction of the dynamic description results in a stochastic equation with a time-dependent friction coefficient (generalised Langevin equation). This equation is applicable to multimodal systems. The rate constant is calculated in terms of the Kramers–Grote–Hynes approximation (KGH).[54–56] This procedure is briefly described in Supplement I. The standard multidimensional TS theory can also be used; with allowance made consistently for the medium modes, it is equivalent to the KGH theory.[54–60] Finally, direct calculation of the reaction rate constant by classical molecular dynamics (MD) is also possible,[61,62] for example, by the reaction flux method.[55]

**Electron–proton PES.**[63–65] A typical electron–proton PES depending on two heavy coordinates, the medium coordinate $y$ and the promoting mode $R$, is shown in Fig. 5. The direction of the reaction coordinate at the saddle point coincides with the direction of the mode $y$. The rate constant can be estimated within the framework of the multi-dimensional KGH theory. Estimation of

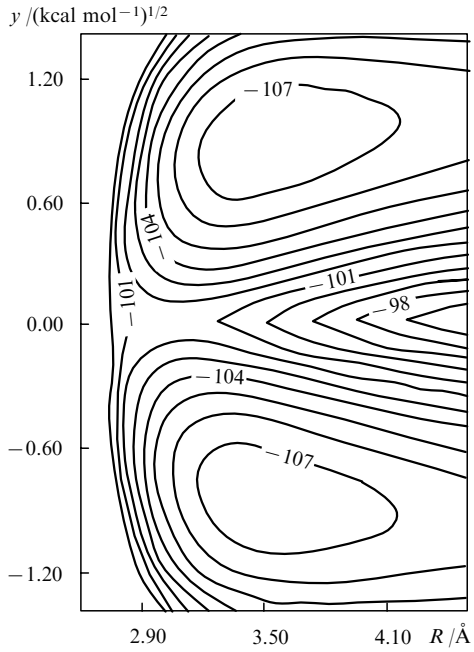



**Figure 5.** Electron-proton PES $\varepsilon_1(y,R)$ for the ground state of the reaction system $ACH_3 + {}^-CH_2A \rightarrow ACH_2^- + CH_3A$; A = $C_6H_5$.[64] Isoenergy contour lines are spaced by 1 kcal mol$^{-1}$. The reactant and product minima correspond to the energy −107.3 kcal mol$^{-1}$.

the rate constant in terms of the stochastic (or the equivalent diffusion) theory requires the knowledge of dynamic characteristics of the solvent collective mode $y$ such as the mass $m_y$, the friction or diffusion coefficient, *etc*. They can be found using semiempirical continuum models of the solvent.[65–69] The most consistent and direct way of calculating these values is based on MD.[61–63]

To conclude, note that the classical description of the promoting mode $R$ accepted in the multidimensional TS theory, KGH theory and classical MD calculations is an approximation which often does not correspond to the real situation.[70–77] The quantum treatment of $R$ is discussed in Section II.4.c.

**b. Proton tunnelling as a non-adiabatic transition**

**Adiabatic and non-adiabatic models of reaction transitions.** Section II.2.a considered the adiabatic PT model. In this context, the term 'adiabatic' means that a double-well potential $V$ appears in the Schrödinger equation (8). It corresponds to the lower electronic adiabatic PES; in more detailed notation,

$$V = V_{a1}(s,R,Q).$$

The next PES $V_{a2}(s,R,Q)$ corresponds to the first electronically excited state of the system. This is a single-well surface, its minimum being close to the top of the barrier of the lower PES, which corresponds to the ground state. The profiles of these two adiabatic PES are shown in Fig. 2 *b* by continuous lines.

In an alternative description, the potentials $V_{a1}$ and $V_{a2}$ are considered as combinations of the potentials $V_{d1}$ and $V_{d2}$, corresponding to single-well surfaces, which are called 'diabatic'. The theory of this transformation was outlined in several publications.[78–81] The diabatic and adiabatic PES are sketched in Fig. 2 *b*. They almost coincide near the minima. The error of the diabatic description is the highest near the TS, *i.e.*, near the barrier top of the lower adiabatic surface or, what is the same, around the intersection of the diabatic surfaces (shown by dashed lines).

Equations (8) and (9) describe the transition from the electronic PES $V_{a1}(s,R,Q)$ to the electron–proton PES $\varepsilon_1(R,Q)$. In the same way, by substituting $V_{a2}(s,R,Q)$ into Hamiltonian (9), one can obtain the electron–proton PES $\varepsilon_2(R,Q)$ for the electron–

proton excited state. Like the initial electronic PES, $\varepsilon_1$ has two wells, while $\varepsilon_2$ has one well. These surfaces are adiabatic, and they can be transformed into two single-well diabatic electron – proton PES, which we designated by $e_1(R,Q)$ and $e_2(R,Q)$. By substituting diabatic electronic potentials, instead of $V$, into Hamiltonian (9), we obtain two diabatic Schrödinger equations similar to Eqn (8). The surfaces $e_1$ and $e_2$ correspond to their eigenvalues. The corresponding eigenfunctions, which we designate by $\chi_1(s)$ and $\chi_2(s)$, are referred to as diabatic states. Unlike adiabatic states $\varphi_n(s)$ ($n = 1,2$) in Eqn (8), these are always localised in their diabatic potential wells. The difference between the lower adiabatic potential and the combination of low-energy fragments of diabatic potentials (which is substantial near the TS) is considered to be responsible for the transitions between the diabatic states $\chi_1$ and $\chi_2$. These transitions, called non-adiabatic, are identified with a PT or HAT process. For reactions with high barriers, splitting of the adiabatic potentials is extremely small (Fig. 6) and the intensity of the transitions is very low.

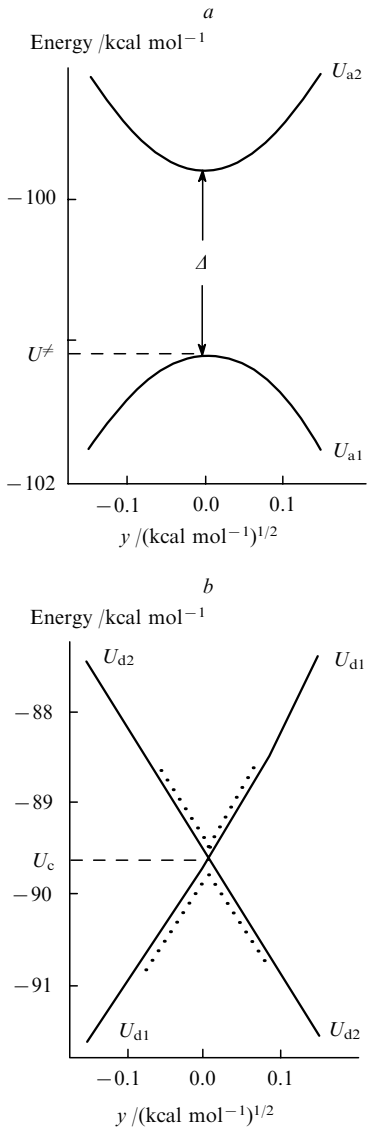



**Figure 6.** Double-well potential profiles for the two limiting mechanisms of PT and HAT reactions; only the TS region is given;
(*a*) adiabatic energy profiles for a low-barrier reaction, see Fig. 5 (A = $C_6H_5$); $U^{\neq}$ is the saddle-point energy for the ground state of the reaction system, $\Delta$ is the splitting of PES in the saddle point; (*b*) diabatic energy profiles for a high-barrier reaction, A = $C_{13}H_9$ (fluorenyl);[65] $U_c$ is the level intersection point; the abscissa $y_0$ of this point is taken to have the coordinate 0.0. The lower and upper broken lines consisting of two diabatic 'rays' can be regarded as two adiabatic potential profiles (shown by dots). The splitting of PES is very small; therefore, $U_c = U^{\neq}$.

**Two-level kinetic equation.** The scenario of a PT reaction described in Section II.2.a corresponds to the situation shown in Fig. 6 *a*. For a low-barrier potential $V_{a1}$, the lower adiabatic level $\varepsilon_1$ is located near the top of the barrier and the next adiabatic level $\varepsilon_2$ is located much higher [$\Delta > 1000$ cm$^{-1}$ (see Ref. 82)], therefore, its population is negligibly low. In this case, it is sufficient to consider the PES $\varepsilon_1(R,Q)$.

The alternative situation shown in Fig. 6 *b* with a high barrier and a clearly defined double-well-potential relief requires a different description. Despite the fact that the proton motion in the wells remains fast, the probability of the inter-well tunnelling transition $P_{12}$ is low: $P_{12} \ll 1$. If it is low enough, the transition between the diabatic states $\chi_1(s)$ and $\chi_2(s)$ becomes the rate-determining step of the process. In the two-level approximation, the localised diabatic wave functions $\chi_1(s)$ and $\chi_2(s)$ are linear combinations of the adiabatic functions $\varphi_1$, $\varphi_2$. The variable $s$ becomes the reaction coordinate, although of the quantum type. It is represented by two diabatic states with the PES $e_1(R,y)$ and $e_2(R,y)$ (we have replaced $Q$ by $y$) and their cross-sections $U_{d1}(y)$ and $U_{d2}(y)$.

The limiting cases illustrated in Fig. 6 correspond to two limiting mechanisms of PT, namely, the classical motion of heavy atoms over the adiabatic surface $\varepsilon_1(R,y)$ with the cross-section $U_{a1}(y)$ and a quantum non-adiabatic transition between the PES $e_1(R,y)$ and $e_2(R,y)$ with the cross-sections $U_{d1}(y)$ and $U_{d2}(y)$. Now we consider the competition between these reaction mechanisms at a qualitative level using a simple one-dimensional model ($Q = y$ is the medium coordinate, and promoting mode $R$ is excluded from consideration). The equations of motion for the populations $n_1(y,t)$ and $n_2(y,t)$ of the diabatic states have the form

$$\frac{\partial n_1}{\partial t} = D\left[\frac{\partial^2 n_1}{\partial y^2} - \frac{1}{k_B T}\frac{\partial}{\partial y}\left(n_1\frac{\partial U_{d1}}{\partial y}\right)\right] + \langle\omega\rangle(n_2 - n_1),$$
$$\frac{\partial n_2}{\partial t} = D\left[\frac{\partial^2 n_2}{\partial y^2} - \frac{1}{k_B T}\frac{\partial}{\partial y}\left(n_2\frac{\partial U_{d2}}{\partial y}\right)\right] + \langle\omega\rangle(n_1 - n_2), \quad (15)$$

where $\langle\omega\rangle$ is the average frequency of interlevel transitions. In the standard theory of non-adiabatic transitions with a linear approximation of the diabatic energy levels (terms) in the region of their intersection (see Fig. 6 *b*), it is usually assumed that [83–87]

$$\langle\omega\rangle = \frac{2\pi V_{12}^2}{\hbar|\Delta F|}\delta(y - y_0), \quad (16)$$

where $V_{12}$ is the matrix element of the interaction between terms; $\Delta F = F_2 - F_1$, where $F_n = -\partial U_{dn}/\partial y$, ($n = 1, 2$) are forces acting on the system at the intersection point $y = y_0$; $\delta(y - y_0)$ designates the Dirac $\delta$-function.

According to this (local) transition model, the expression for the probability of transition between the terms is formally similar to the Landau–Zener approximation [88]

$$P_{12} = \frac{2\pi V_{12}^2}{\hbar|\Delta F|\,\dot{y}}. \quad (17)$$

The value

$$j_{na} = \frac{2\pi V_{12}^2}{\hbar|\Delta F|}\exp\left(-\frac{U_c - U_e}{k_B T}\right) = |\dot{y}|P_{12}\exp\left(-\frac{U_c - U_e}{k_B T}\right) \quad (18)$$

is a non-adiabatic diffusion flux at the point $y_0$,[89] $U_c = U_{d1}(y_0) = U_{d2}(y_0)$, and $U_e$ is the energy in the reactant minimum.

Turning back to the adiabatic description in terms of the diffusion equation (10), we can express an analogous adiabatic flux near the top of the barrier of the lower PES $U_{a1}$ (see Fig. 4). For the case where the barrier $\Delta U^{\neq}$ on the initial electronic PES is

high and the splitting $\Delta$ is small (see Fig. 6 *b*), this potential profile corresponds to a triangular potential barrier (shown by dots). For such PES, the adiabatic flux equals [89]

$$j_a = \frac{D}{k_B T}\frac{|F_1||F_2|}{|F_1|+|F_2|}\exp\left(-\frac{U_c - U_e}{k_B T}\right). \quad (19)$$

A different adiabatic flux corresponds to Kramers' result (11), (14). The difference is due to the fact that the potential shown by dots in Fig 6 *b* has a singularity (cusp) on the top and the potential in Fig. 4 is smooth. Fluxes (18) and (19) are found by solution of diffusion equation (15) in the limiting cases of weak and strong coupling between the levels. In the intermediate kinetic regime, the flux $j$ can be expressed as the ratio of the non-adiabatic to adiabatic fluxes [89]

$$j = \frac{j_{na}}{(1 + j_{na}/j_a)}. \quad (20)$$

The corresponding rate constant is found from Eqn (20) by division by the partition function of the reaction system calculated within the reactant well.

The ratio $j_{na}/j_a$ can be estimated by taking into account the fact that, within the model of non-adiabatic transition with linear intersecting diabatic energy levels,[65, 79–81]

$$V_{12} = \frac{1}{2}\Delta; \quad (21)$$

$$|\Delta F| = |J|\Delta.$$

Here $\Delta$ and $J$ are characteristics of adiabatic levels:

$$\Delta = \varepsilon_2(y_0) - \varepsilon_1(y_0),$$

$$J = \left\langle \varphi_2 \left| \frac{\partial}{\partial R} \right| \varphi_1 \right\rangle_{y_0} = \Delta^{-1} \left\langle \varphi_2 \left| \frac{\partial \varepsilon_1}{\partial y} \right| \varphi_1 \right\rangle_{y_0}, \quad (22)$$

*i.e.*, $\Delta$ is the minimum splitting of the adiabatic levels and $J$ is the measure of their interaction calculated for $y = y_0$. If the signs of the forces $F_1$ and $F_2$ are opposite, then

$$|\Delta F| = |F_2| + |F_1|.$$

Thus,

$$\frac{j_{na}}{j_a} = \frac{2\pi}{\hbar}\frac{\Delta^2}{|F_1||F_2|}\frac{k_B T}{4D} \simeq \frac{2\pi}{\hbar}\frac{k_B T}{DJ^2}. \quad (23)$$

The above approximate equality corresponds to the symmetrical case

$$|F_1| = |F_2| = \frac{1}{2}|F_1 - F_2|.$$

**Competition between adiabatic and non-adiabatic mechanisms of proton transfer.** It follows from Eqns (20)–(23) than the non-adiabatic kinetic mechanism of PT takes place when the splitting of the adiabatic levels is small (in this case, $U_c = U^{\neq}$). Small $\Delta$ values are typical of double-well potential profiles of the ground electronic state with a sharp relief. They give rise to electron–proton profiles with a cusp at the intersection (see Fig. 6 *b*). For these electronic PES, tunnelling is observed, the model of non-adiabatic transitions on the electron–proton PES being a way of describing the tunnelling phenomenon. Equation (23) expresses the relative intensities of the tunnelling (non-adiabatic flux $j_{na}$) and activation (adiabatic flux $j_a$) mechanisms of proton transition. According to (23), they depend on the temperature. At the critical temperature $T = T_c$ where $j_{na}/j_a = 1$, the reaction mechanism switches. Thus, the flux ratio (23) is the key control parameter of the simplest expression for the rate constant taking into account both PT mechanisms.[87]

The inclusion of the promoting mode $R$ substantially complicates the PT description. In this case, the cross-section profile of the reaction PES depends on $R$ (see Fig. 1 *a*): the barrier is relatively low in the TS region ($R = R^{\neq}$); when $R \gg R^{\neq}$, the product and reactant wells become deeper, which disturbs the adiabaticity criterion (7). Hence, according to criterion (23), the transition is either adiabatic (activated, $j_{na}/j_a \gg 1$) or non-adiabatic (tunnelling, $j_{na}/j_a \ll 1$), depending on $R$ and the temperature. In many cases, both mechanisms occur simultaneously on the same PES.[90] If the equilibrium position $R_e$ is close to $R^{\neq}$ and (or) the temperature is relatively high, the reaction dynamics will mainly be classical. In the case of a sharp relief of the PES cross-section along the coordinate $s$ and (or) low temperature, the reaction mainly follows the tunnelling mechanism.

## 3. The principles of description of the tunnelling kinetics

### a. One-dimensional and quasi-one-dimensional tunnelling

**Bimolecular rate constant.** The character of tunnelling transitions is substantially different for the three different types of PES cross-sections $V(s)$ (Fig. 7). In the one-dimensional model of the bimolecular reaction, the states in the reactant and product regions belong to a continuum spectrum (Fig. 7 *a*). In a quasi-classical approximation, the rate constant for this reaction is as follows: [55, 91–94]

$$k(T) = \frac{1}{2\pi\hbar Z(T)}\int_0^\infty \exp\left(-\frac{E}{k_B T}\right) P(E)\mathrm{d}E, \quad (24)$$

where $E$ is the energy referred to the threshold (a minimum in the reactant region) and $P(E)$ is the quasi-classical coefficient for barrier penetration

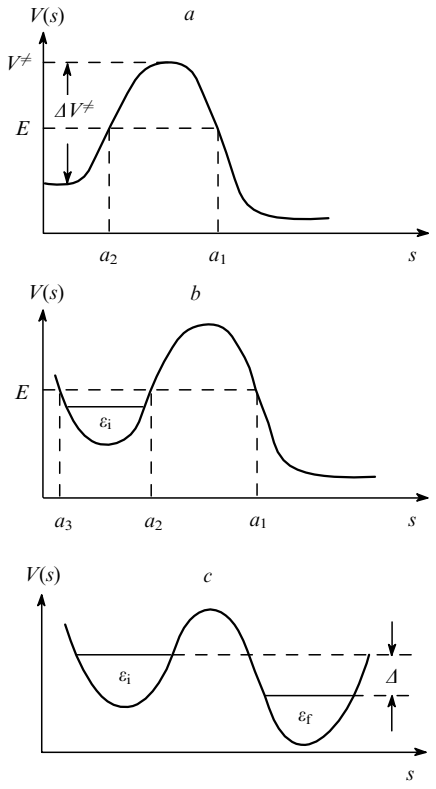



**Figure 7.** Three different types (*a*–*c*) of PES cross-sections $V(s)$ for the one-dimensional reaction scheme.
The turning points $a_2$, $a_1$ bound the classically inaccessible region, while points $a_3$, $a_2$, confine the classically accessible region; $\varepsilon_i$ is the reactant energy level, $\varepsilon_f$ is the product energy level, $\Delta$ is the resonance misfit.

$$P(E) = \frac{1}{1 + \exp[2W(E)]}, \tag{25}$$

$$W(E) = \frac{1}{\hbar}\int_{a_2}^{a_1} \{2m_0[V(s) - E]\}^{1/2} \mathrm{d}s.$$

The turning points $a_1$, $a_2$ depend on the energy $E$ and confine the under-barrier area inaccessible for classical motion. In this case, the partition function $Z(T)$ corresponds to one-dimensional translational motion; as a result, the bimolecular rate constant has the dimensionality (time)$^{-1}$(length)$^{-1}$. In the classical limit, $P(E)$ is replaced by a stepwise function

$$P(E) = \begin{cases} 0, & (E < \Delta V^{\neq}) \\ 1, & (E > \Delta V^{\neq}), \end{cases} \tag{26}$$

where $V^{\neq}$ is the height of the potential barrier. In this case, relation (24) provides the standard result of the one-dimensional classical transition state theory, TST.

$$k_{\mathrm{TST}}(T) = \frac{1}{2\pi\hbar Z(T)} \exp\left(-\frac{\Delta V^{\neq}}{k_{\mathrm{B}}T}\right). \tag{27}$$

Relations (24)–(27) can be recommended for application to real three-dimensional PT processes if a 'one-dimensional' transmission coefficient

$$\kappa = \frac{k(T)}{k_{\mathrm{TST}}(T)} \tag{28}$$

is introduced and used as a correction factor, *i.e.,* the rate constant for a real three-dimensional reaction obtained by the standard TS method is multipled by this factor.

**Decay kinetics of single-well systems.** In the decomposition reaction with a potential profile shown in Fig 7 *b*, the states of reactants are quantised, while those in the product region belong to a continuum spectrum. By designating the energies of the reactant level by $\varepsilon_v$ and the partial decay rates by $(1/\hbar)\Gamma_v$ ($\Gamma_v$ is the width of the level), we obtain the rate constant

$$k(T) = \sum_v \frac{\exp(-\varepsilon_v/k_{\mathrm{B}}T)}{Z(T)} \frac{\Gamma(\varepsilon_v)}{\hbar}. \tag{29}$$

In the quasi-classical approximation,[95]

$$\Gamma(E) = \frac{\hbar\omega(E)}{2\pi} \exp[-2W(E)], \tag{30}$$

where the under-barrier action integral $W(E)$ is defined in the same way as in Eqn (25); however, now $V(s)$ has the form shown in Fig. 7 *b*. The decay frequency $\omega(E)$ is expressed in terms of the action integral $\theta(E)$, which is calculated in the region of classical motion confined by the turning points $a_3$ and $a_2$,

$$\theta(E) = \frac{1}{\hbar}\int_{a_3}^{a_2} \mathrm{d}s\left[2m_0(E - V(s))\right]^{1/2};$$
$$\omega(E) = \frac{\pi}{\hbar(\partial\theta/\partial E)}. \tag{31}$$

When the interaction of the coordinate $s$ with the environment modes is taken into account, these relations are modified in the following way. The interaction makes the levels $\varepsilon_v$ diffuse; in this case, it is expedient to introduce the distribution function $\rho_v(E)$ for a level $v$

$$\int_0^{\infty} \rho_v(E)\mathrm{d}E = 1, \tag{32}$$

and the density of states

$$\rho(E) = \sum_v \rho_v(E). \tag{33}$$

The $N(E)$ value, called the 'cumulative transition probability',[92–94] is defined as follows:

$$N(E) = 2\pi\rho(E)\Gamma(E). \tag{34}$$

Then the expression for rate constant (29) is reduced to the form

$$k(T) = \frac{1}{2\pi\hbar Z(T)} \int_0^{\infty} \exp\left(-\frac{E}{k_{\mathrm{B}}T}\right) N(E)\mathrm{d}E. \tag{35}$$

This expression formally coincides with expression (24) for the rate constant of the bimolecular reaction, the difference being in the interpretation of the partition function. The $Z(T)$ value now includes the states located in the reactant well; taking account of the level broadening due to interaction, it is found as

$$Z(T) = \int_0^{\infty} \exp\left(-\frac{E}{k_{\mathrm{B}}T}\right) \rho(E)\mathrm{d}E. \tag{36}$$

The quasi-classical expression for the cumulative probability (34) is similar to expression (25) [55,92–94]

$$N(E) = \frac{1}{1 + \exp[2W(E)]} \tag{37}$$

with an action integral defined in the under-barrier region (see Fig. 7 *b*). This description of decay processes is almost identical to the quasi-one-dimensional theory of bimolecular reactions. However, a consistent definition of the decay model should take into account the interaction of the reaction centre with its environment not only in the reactant region but also for tunnelling under the barrier.[55,96] The calculation of the action integral is modified by introduction of a non-local potential brought about by the interaction. The corresponding theory [55,96–98] is a quantum generalisation of the classical stochastic scheme based on the Langevin equation (13) for the tunnelling coordinate $s$. The friction coefficient $\gamma$ is a parameter of the interaction intensity; it is present in the final quantum expression for the rate constant.

**The activation and tunnelling mechanisms.** The classical and quantum dynamic effects are manifested in the chemical reaction kinetics as a competition between the activation (classical) and tunnelling (quantum) mechanisms of the reactive transition. This was described above within the framework of a non-adiabatic diffusion model. Now it will be considered using an alternative tunnelling dynamics language.

As in the previous case, in the simplest one-dimensional scheme, there exists a critical temperature $T_{\mathrm{c}}$ (see several studies [55,97–99]) such that the activation mechanism with the Arrhenius temperature dependence of the rate constant predominates above this temperature. At temperatures below $T_{\mathrm{c}}$, the reaction mainly follows a tunnelling mechanism and in the limit $T/T_{\mathrm{c}} \ll 1$, the reaction rate does not depend on the temperature. This low-temperature limit differs from zero when the reactant region is a potential well; it corresponds to transition from the ground vibrational level of the reactants. Systematic analysis of the ratio of the tunnelling and activated transitions is reduced to investigation of the integral over energy in Eqns (24) and (35). The theory can be reformulated using the language of classical dynamics, which describes the motion in the 'inverted' potential $\overline{V}(s)$ [$\overline{V}(s) = -V(s)$] for the total energy $E$.[55,97] In this potential, a cyclic classical trajectory with the period $t(E)$ is formed. The energy corresponding to the highest contribution of the integrand to integral (35) satisfies the equation

$$t(E) = \frac{\hbar}{k_B T}. \tag{38}$$

Its solution determines the energy corresponding to the cyclic trajectory as a function of temperature. This consideration underlies the calculation of integral (35) by the stationary phase method.[97, 100, 101] The temperature-dependent extremal trajectory that satisfies condition (38) is called instanton. There exists a critical temperature above which Eqn (38) has no solution. It can be identified with the above-mentioned $T_c$ value. Then the maximum contribution to the integral is determined by the energy near the top of the barrier, and formula (35) reduces to the result of the TS theory with slight quantum corrections. In the stochastic tunnelling model, which takes into account the interaction with the environment based on the Langevin equation, the Kramers equation for the rate constant, similar to relation (11) but with allowance for (14), is obtained in the classical limit.[102–104] Thus, the relationship between two theories, the non-adiabatic and the tunnelling, is established; the tunnelling probability is determined in the latter case by the value of action on the instanton trajectory. The simplest equation for the critical temperature obtained for a parabolic barrier $V(s)$ with the decay frequency $\omega^{\neq}$ has the form [99, 105]

$$T_c = \frac{\hbar\omega^{\neq}}{2\pi k_B}. \tag{39}$$

**Tunnelling in a double-well potential**. The calculation of tunnelling is complicated on passing to a double-well potential where it is necessary to take account of the quantisation of energy levels in both wells. Transitions between two levels take place only in the presence of interaction between the coordinate $s$ and other degrees of freedom. Even where the levels are in resonance, *i.e.*, very close or coinciding, as in symmetrical systems, the interaction with the environment is required to ensure energy dissipation and destruction of the transition coherence, which are necessary conditions for irreversibility. Only due to these factors, can the system be fixed in the product region and a stationary flux for the two wells can be formed. In asymmetric systems, the interaction with the environment is also necessary in order to compensate for the resonance misfit (*i.e.*, the energy difference between the levels between which the transition takes place) by means of the intermode energy exchange.

Thus, double-well transitions are, in essence, multidimensional even in the case where the PES structure seems to allow the reaction mode to be considered as an independent variable. The intermode interactions, which ensure the energy exchange and phase relaxation (the latter term is equivalent to the term 'coherence desctruction'), can be small within the scale of the energy variation on the PES, but only consistent allowance for these interactions provides the possibility of correct description of the tunnelling dynamics.

### b. Collinear model of simple gas-phase reactions

**Quantum computation scheme.** Let us consider a two-dimensional quantum problem for collinear model (1) of a PT with two coordinates $s$, $R$ and the corresponding reduced masses $m_0$ and $M$. After conversion to a mass-weighted coordinates $s' = s(m_0)^{1/2}$ and $R' = R(M)^{1/2}$, it is expedient to introduce polar coordinates

$$y = \left[(s')^2 + (R')^2\right]^{1/2}, \tag{40}$$

$$\alpha = \arctan\frac{s'}{R'}.$$

The potential energy surface in these coordinates is shown in Fig. 8. The two valleys stretched along $y$ correspond to the translational motion in the asymptotic regions, as we consider a gas-phase bimolecular reaction. This PES is confined within the angle

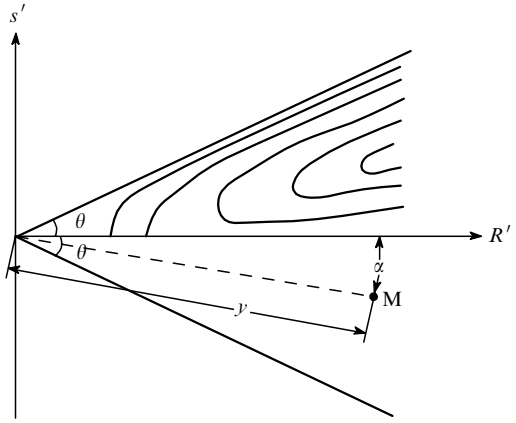



**Figure 8.** Potential energy surface of the gas-phase PT and HAT reaction in the polar coordinates.
The isoenergy contour lines of PES are shown only for the product valley ($\alpha > 0$). The potential energy in the reactant valley ($\alpha < 0$) has the same form. The point M has the polar coordinates $y$, $\alpha$.

$$2\theta = \arctan\left(m_H \frac{m_{A_1} + m_{A_2} + m_H}{m_{A_1} m_{A_2}}\right)^{1/2}, \tag{41}$$

where $m_H$, $m_{A_1}$, $m_{A_2}$ are the masses of the H atom and the heavy fragments $A_1$ and $A_2$, respectively. The reduced masses $m_0$ and $M$ are related to these masses in the usual way. The Hamiltonian for this problem has the form

$$H = -\frac{\hbar^2}{2}\left(\frac{\partial^2}{\partial y^2} + \frac{1}{y}\frac{\partial}{\partial y}\right) + h_\alpha, \tag{42}$$

$$h_\alpha = -\frac{\hbar^2}{2y^2}\frac{\partial^2}{\partial\alpha^2} + V(\alpha|y),$$

where the operator $h_\alpha$ depends parametrically on $y$. When $y$ is constant, variation of the mode $\alpha$ is described by the Schrödinger equation

$$h_\alpha \varphi_n(\alpha|y) = \varepsilon_n(y)\varphi_n(\alpha|y). \tag{43}$$

Equations (42) and (43) are similar to Eqns (8), (9) for the coordinate $s$ and are converted into the latter (to within a mass factor) after the substitution

$$s = y\alpha. \tag{44}$$

As a result of the coordinate scaling performed, the major dynamic feature of PT reactions, *i.e.*, the fact that the ratios

$$\frac{m_H}{m_{A_1}} \ll 1, \frac{m_H}{m_{A_2}} \ll 1$$

are small, is manifested in the PES relief, in particular, the angle $\theta$ becomes a small parameter in this description

$$\theta \ll 1. \tag{45}$$

It can be seen in Fig. 8 that in this case, the reactant and product valleys are nearly parallel, the barrier separating them being narrow. This accounts for the specific features of process dynamics (1), the possibility of tunnelling along the variable $\alpha$ being the most important of them.

In numerical dynamic studies of system (1), the solutions $\varphi_n(\alpha)$ of Eqn (43) are used as the basis functions. The two-dimensional Schrödinger equation (43) is reduced to a set of one-dimensional coupled equations for the motion along the translational coordinate $y$. The solution of this set of equations provides the probabilities $P_{mn}(E)$ of reactive transitions from the reactant valley to the product valley and the probabilities $R_{mn}(E)$ of reflection in the reactant valley. The transition takes place between the states $\varphi_m$ and $\varphi_n$ at a given total energy $E$. The

procedure of such calculations has been well developed [106, 107] and extended to the description of reaction in a real 3D space, which takes into account the interaction of the internal degrees of freedom with the rotational motion.[108] The results of numerical studies are reported in several reviews.[109–112] The potential in Eqn (43) has a complex form. Depending on $y$, it can be either double-well (large $y$) or single-well (small $y$). For non-symmetric reactions, the potential is asymmetric. It should be emphasized that the use of eigenfunctions of the Hamiltonian $h_\alpha$ with this complex potential as the basis functions has a crucial impact on the success of calculations.[106, 107] The convergence of the solution of Eqn (43) with oscillatory basis functions proved to be unsatisfactory.

The results of calculations showed that the reactions in symmetrical systems are adiabatic, *i.e.*,

$$\frac{P_{mn}(E)}{[P_{mm}(E)P_{nn}(E)]^{1/2}} \ll 1. \tag{46}$$

In the case of asymmetric reactions, transitions between the vibrational levels of the reactants $\varepsilon_{im}$ and the products $\varepsilon_{fn}$ characterised by the smallest in magnitude resonance misfits

$$\Delta_{mn} = \varepsilon_{fn} - \varepsilon_{im}$$

sharply predominate. This is a natural consequence of inequality (45). The small parameter $\theta$ is a measure of dynamic interaction between the coordinates $\alpha$ and $y$. Since the interaction is weak, transformation of the resonance defect energy into the energy of translational motion is unlikely and resonance or nearly resonance processes predominate.

**Study of the collinear dynamics at a qualitative level.** When analysing studies of the collinear dynamics at a qualitative level, we restrict ourselves to the discussion of HAT reactions that have rather high potential barriers ($V^{\neq} \geqslant 10$ kcal mol$^{-1}$) and can be expected to proceed in the tunnelling regime even at high temperature ($T \geqslant 300$ K). The early studies of these systems [113, 114] were performed using a multi-dimensional quasi-classical approximation,[115, 116] whose one-dimensional version is considered in Section II.3.a. Extension to multidimensional (two-dimensional, for a collinear reaction) case brings about a procedural difficulty: it is necessary to match the trajectories of a multidimensional classical motion at the boundary of classically allowed (reactant and product valleys) and classically forbidden (under-barrier region) PES sections. A rigorous solution of this problem is extremely unwieldy. It is more convenient to proceed directly from quantum equations of motion which do not face the matching problem.

The quantum interpretation becomes simple for those regions of PES where the cross-sections along the coordinate $\alpha$ have a rather sharp double-well profile. This is not the case in the vicinity of the saddle point, which imposes restrictions on the conditions under which the HAT process can be calculated; it is assumed to proceed in the tunnelling regime, the classical activated transitions being suppressed. In this situation, there exist diabatic states well localised in the reactant $\chi_{im}(\alpha)$ and product $\chi_{fn}(\alpha)$ regions. They can be regarded as eigenfunctions of two different one-dimensional Hamiltonians $h_i$ and $h_f$:

$$\begin{aligned} h_i\chi_{im}(\alpha) &= e_{im}\chi_{im}(\alpha), \\ h_f\chi_{fn}(\alpha) &= e_{fn}\chi_{fn}(\alpha). \end{aligned} \tag{47}$$

Single-well potentials in the Hamiltonians $h_i$ and $h_f$ are distorted with respect to the true double-well profile $V(\alpha|y)$ [see Eqn (42)] in such a way as to ensure localisation of eigenfunctions. In Fig. 9 *a*, the continuous line shows the double-well adiabatic profile $V(\alpha)$ for a given value $y$. The diabatic potentials coincide with it in the region of one of the wells and are continued by dots to the region of the neighbouring well. As noted above, it is legitimate for considering the transitions between two diabatic states closest in energy. Let energies of these states be $e_{im}$ and $e_{fn}$. This corresponds to the two-level model in which the designations can be simplified: $\chi_{im} \to \chi_i$, $e_{im} \to e_i$, $\chi_{fn} \to \chi_f$, $e_{fn} \to e_f$. The solu-

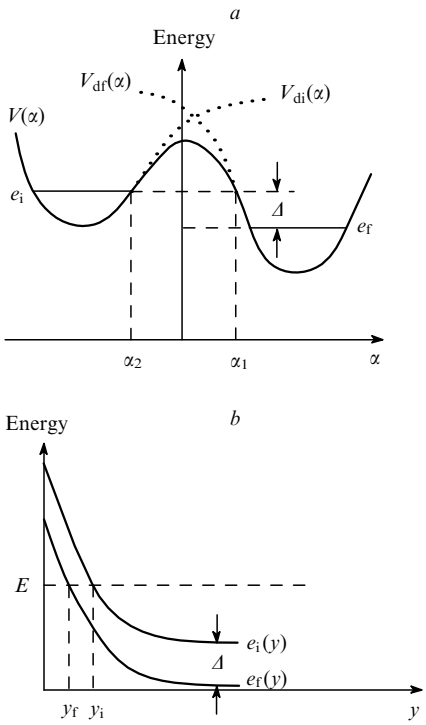



**Figure 9.** Model of a two-dimensional tunnelling transition for the PES shown in Fig. 8 (asymmetric case);
(*a*) adiabatic [$V(\alpha)$] and diabatic [$V_{di}(\alpha)$ and $V_{df}(\alpha)$] energy profiles along the coordinate $\alpha$; (*b*) pattern of the translational motion along the coordinate $y$ in the reactant and product valleys. The difference in the diabatic potentials $e_i(y) - e_f(y) = \Delta$ is constant. The turning points $y_i$, $y_f$ correspond to the energy $E$.

tions of the complete Schrödinger equation (43) designated by $\varphi_n$ are adiabatic states; in the two-level model, they are linear combinations of two functions, $\chi_i$ and $\chi_f$. For symmetrical systems, $e_i = e_f = e$ and adiabatic functions possess definite symmetry properties, one of them being symmetric and the other, antisymmetric

$$\begin{aligned} \varphi_s(\alpha) &= \frac{1}{[2(1+\sigma)]^{1/2}}[\chi_i(\alpha) + \chi_f(\alpha)], \\ \varphi_a(\alpha) &= \frac{1}{[2(1-\sigma)]^{1/2}}[\chi_i(\alpha) - \chi_f(\alpha)], \end{aligned} \tag{48}$$

where $\sigma$ is the overlap integral of diabatic functions.

When the potential $V(\alpha,y)$ is substantially asymmetric, one of the adiabatic functions is mainly composed of function $\chi_i$ with a small portion of function $\chi_f$, while the other, mainly of the function $\chi_f$. Then the adiabatic states are labelled by the same subscripts i and f. In the tunnelling regime, the adiabatic energy levels $\varepsilon_i$, $\varepsilon_f$ differ little from the diabatic energies $e_i$, $e_f$. In this case, the resonance misfit

$$\Delta_{if} = \varepsilon_f - \varepsilon_i \approx e_f - e_i \tag{49}$$

becomes an important dynamic parameter.

Within the framework of the model with two coordinates $\alpha$ and $y$, the potential profiles shown in Fig. 9 *a* depend on $y$. Diabatic levels become the functions of $y$ and their energies play the role of repulsive potentials $e_i(y)$ and $e_f(y)$ in the reactant and product channels, as shown in Fig. 9 *b*. More complex potential profiles along $y$ (with a well near the saddle point) can arise in special cases;[106, 107, 117] however, for reactions with high potential barriers considered here, these situations are unlikely. Each vibrational state of the reaction system or 'reaction channel' (i and f, or s and a for a symmetrical reaction) is matched by its own potential.

Due to the small magnitude of the $\theta$ parameter [see inequality (45)], the interaction of a given pair of closest channels with other channels is negligibly small. This simplification has been suggested by the experience of full multichannel computations. In an approximation that takes into account only transitions between two reactant and product channels closest in energy, we will consider analytical expressions for the probability of reactive transitions for different limiting situations.

In the case of a symmetrical system, channels s and a also split. By solving a one-dimensional Schrödinger equation for the coordinate $y$ for each of them, one can get the following expression for the probability of the reaction transition between the diabatic states i and f:[118]

$$P_{\rm if}(E) = \sin^2(\xi_{\rm s} - \xi_{\rm a}), \tag{50}$$

where $\xi_{\rm s}$ and $\xi_{\rm a}$ are the shifts of scattering phases in the channels s and a. Quasi-classical estimate gives

$$\sin(\xi_{\rm s} - \xi_{\rm a}) \approx \xi_{\rm s} - \xi_{\rm a} \approx \frac{2}{\pi}\int_{y_0}^{\infty} \frac{e_{\rm i}(y)}{p_{\rm i}(y)} \exp[-W_{\rm i}(y)]{\rm d}y. \tag{51}$$

Here

$$e_{\rm i}(y) = e_{\rm f}(y),$$

$p_{\rm i}(y)$ is the momentum for the translational motion along the coordinate $y$

$$p_{\rm i}(y) = \{2[E - e_{\rm i}(y)]\}^{1/2},$$

$W_{\rm i}(y)$ is the under-barrier action integral calculated between the turning points $\alpha_2$ and $\alpha_1$ [the symmetrical variant is considered (see Fig. 9 *a*)].

Expression (51) can be simplified by expanding in a series near the $y_0(E)$ turning point in which $p_{\rm i}(y) = 0$ (see Fig. 9 *b*).[113, 114, 119–121]

In the case of an asymmetric potential profile, the transition probabilities $P_{\rm if}(E)$ can be estimated only in terms of the perturbation theory ('golden rule'), whose applicability is ensured by low values of these probabilities ($P_{\rm if} \ll 1$) and, finally, by the smallness of the PES parameter $\theta$. It is convenient to accept an exponential form of diabatic repulsive potentials in channels i and f (see Fig. 9 *b*):

$$e_{\rm i}(y) = e_0 \exp(-cy),$$
$$e_{\rm f}(y) = e_0 \exp(-cy) + \Delta, \tag{52}$$

where $c$ is the potential parameter, $\Delta = \Delta_{\rm if}$ is the resonance misfit [see Eqn (49)].

For energy $E$, the potentials have turning points $y_{\rm i}(E)$ and $y_{\rm f}(E)$. When the resonance misfit $|\Delta|$ is small, the following expression was obtained:[119–121]

$$P_{\rm if}(E) = P_{\rm sif}(E) \exp\left(-\frac{\Delta^2}{2cF}\right), \tag{53}$$

where $P_{\rm sif}(E)$ is the probability of non-adiabatic transition [see Eqn (50)] for a symmetrical potential profile (see Fig. 9 *a*),

$$F = -\left.\frac{\partial e}{\partial y}\right|_{y_0(E)},$$

$F$ is the force for the average potential

$$e = \frac{1}{2}[e_{\rm i}(y) + e_{\rm f}(y)]$$

at the turning point $y_0(E)$.

Relation (53) is valid when $|\Delta/E| \ll 1$ and some additional conditions are met.

If $|\Delta/E| \gg 1$, a different asymptotic estimate follows [122]

$$P_{\rm if}(E) = \frac{6}{\pi^2 c|\Delta|[(E+\Delta)^{1/2} - E^{1/2}]} \left[\left(\frac{{\rm d}\ln A}{{\rm d}y}\right) A\right]^2 \times$$
$$\times \exp\left\{-\frac{2\pi}{c}[(E+\Delta)^{1/2} - E^{1/2}]\right\}. \tag{54}$$

Here $A = A(y)$ is a matrix element for the transition along the vibrational coordinate (the tunnelling transition amplitude)

$$A(y) = \int \chi_{\rm i}(\alpha|y)\left[H - \frac{1}{2}(e_{\rm i} + e_{\rm f})\right]\chi_{\rm f}(\alpha|y){\rm d}\alpha, \tag{55}$$

where $H$ is a two-dimensional Hamiltonian [see Eqn (42)]. The amplitude $A(y)$ is calculated at the turning point for function $\chi_{\rm i}$. The dependence of the matrix transition element along the translational coordinate $y$ plays an important role in HAT reactions [the probability $P_{\rm if}(E)$ vanishes if this dependence is missing].

Equations (53)–(55) reflect the main features of energy transfer between vibrational and translational degrees of freedom in collinear HAT reactions. The main parameters that determine the probability of transfer include the resonance misfit ($\Delta$), characteristics of adiabatic translational potentials ($c$, $F$), the amplitude of the tunnelling transition, and its dependence on the translational coordinate.

## 4. Tunnelling in a multidimensional double-well potential

### a. Specific features of the reactive transition dynamics in double-well systems

**Continuum spectrum of vibration frequencies.** Up to here, the discussion has been concerned with reactions for which the states of the reactants or the products (or both) have a continuum spectrum of eigenvalues. The reactions in double-well systems where all the energy levels are discrete require a specific approach. They can proceed only due to interactions with the environment, which is assumed to be a macroscopic system and, hence, has a continuum energy spectrum. However, the continuum spectrum of the medium differs from the one-dimensional continuum spectrum inherent in the translational degrees of freedom of the reaction system. The medium can consist of subsystems, each having a discrete energy spectrum: in the simplest case, the medium can be considered as an ensemble ('reservoir') of harmonic oscillators. The continuous nature of the general spectrum of the medium is ensured by the fact that the number of its degrees of freedom is infinite, *i.e.*, we are dealing with a continuum spectrum of vibration frequencies.

The interaction of the reaction mode with the oscillator reservoir having a continuum spectrum of frequencies, as well as the interaction with the translational degree of freedom (see Section II.3.b) ensures transfer of the resonance misfit energy and destruction of the transition coherence — *i.e.*, two conditions needed for a chemical reaction to proceed. As a result of this interaction, the reservoir oscillators rearrange (*i.e.*, change equilibrium positions) and are involved in the reaction. Thus, the chemical reaction in a double-well reaction system is an essentially multimode process that includes rearrangement of the states of the medium with a continuum spectrum of frequencies.

**The simplest pattern of quantum rearrangement.** The theory of quantum rearrangement processes has been developed for a model in which the reaction transition occurs between two multidimensional paraboloids with shifted minima which describe the PES of the reactants and the products (see Fig. 2).[123–129] We restrict ourselves to the case where the normal modes of the reaction system and their frequencies do not change during the transition (a more general theory is extremely cumbersome, although it still can be formulated [123, 127]). The straight line connecting the minima of the paraboloids (see Fig. 2 *a*), *i.e.*, the reaction coordinate, is a linear combination of the normal modes of the reactants and the products. The change in the distance along this straight line is

measured using the scalar parameter $\lambda$ [see Eqn (3)]. Let one normal mode with the frequency $\omega_0$ be quantum

$$\frac{\hbar\omega_0}{k_B T} \gg 1. \tag{56}$$

First, this is the high-frequency proton mode; as in Sections II.1 and II.2, we designate it by $s$. On the harmonic PES that we consider, each mode makes its individual contribution to the height of the potential barrier; the contribution of the mode $s$ equals

$$\Delta V_s^{\neq} = \frac{m_0\omega_0^2}{2}(\lambda^{\neq})^2(s_f - s_i)^2, \tag{57}$$

where $m_0$ is the mass corresponding to this coordinate, $\lambda^{\neq}$ is the value of the reaction coordinate at the point of quasi-intersection of diabatic PES (this is a minimum on their intersection hypersurface),

$$\lambda^{\neq} = \frac{1}{2}\left(1 + \frac{\Delta V}{E_r}\right),$$

$\Delta V = V_f - V_i$ is the energy difference between the minima of the diabatic paraboloids, *i.e.*, the heat of the reaction; $E_r$ is the reorganisation energy, $s_f$ and $s_i$ are the values of the coordinate $s$ at the minima. The other modes $\omega_v$ will be considered classical

$$\frac{\hbar\omega_v}{k_B T} \ll 1. \tag{58}$$

The frequencies $\omega_v$ form continuum spectra. Then one can expect that the reaction rate constant would have the form

$$k = k_s \exp\left(-\frac{\Delta V_1^{\neq}}{k_B T}\right), \tag{59}$$

where $k_s$ is the one-dimensional tunnelling rate constant in a double-well potential profile that corresponds to the PES cross-section along the mode $s$, $\Delta V_1^{\neq}$ is the contribution of classical modes to the height of the potential barrier. It is significant that the partial height of the barrier determined by formula (57) is much smaller than the total value $V^{\neq}$, which is given by the Marcus formula (6) with allowance for (5).

This qualitative discussion has been extended to the case of a larger number of quantum modes.[126–129] The quantum modes that satisfy criterion (56) form altogether the tunnelling pre-exponential factor of the rate constant, which depends only slightly on the temperature. Classical modes are responsible for the Arrhenius exponential factor in which the activation energy is equal to their contributions to the barrier height.

Turning back to the classification of modes introduced in Section II.1.b, one can state that formula (59) reflects the situation where all the rearranging modes $Q_v$ ($v$ = 1, 2...) are classical in conformity with criterion (58). As the temperature decreases, condition (58) starts to be violated for some of these modes. They become quantum modes and form the tunnelling pre-exponential factor, whereas those modes that still remain classical form the ever decreasing reaction barrier. This idealised pattern is valid only for a double-well harmonic potential. In PT reactions, the PES anharmonicity is substantial and the separation of variables throughout the whole path along the reaction coordinate (*i.e.*, along the curve connecting the potential minima *via* the saddle point) is impossible. However, at a qualitative level, the idea of more or less independent contributions of the proton ($s$) and rearrangement ($Q_v$) modes to the potential barrier remains valid.

**Comparison of different ways of description of the reaction transition.** Let us discuss in more detail how the theory formulated in terms of normal modes (non-interacting degrees of freedom)[124–129] can be correlated with the statement according to which one or several reaction modes interact with an ensemble of harmonic oscillators of the medium.[130, 131] We have in view the following. The discrete coordinates of the reaction system are considered oscillatory in each of the two diabatic regions (those of the reactants and the products). In each of these regions, their interaction with the medium oscillators is assumed to be bilinear and is excluded by diagonalisation of the corresponding diabatic oscillatory Hamiltonian. The normal modes thus found are those used in the double-well transition model. The allowance for the interaction results in renormalisation of the initial oscillator frequencies (both discrete and medium oscillators), shift of their equilibrium positions and the change in the form of vibrations. The assumption that normal vibration frequencies and forms are the same in both diabatic regions is actually made for the system of modes resulting from the diagonalisation mentioned above. The oscillator modes of the medium change most appreciably. Their interaction with the reaction system leads to a shift in the equilibrium of the reservoir oscillators, which are different for the reactants and the products.

Thus, the chemical reaction is accompanied by reorganisation of the medium, which is a necessary item of the theory we consider. Two limiting cases are analysed below. In the first case, the promoting mode $R$ is ignored and the reaction dynamics is entirely determined by the medium reorganisation (electron transfer). Conversely, in the second case, the role of the medium is minimised and the main dynamic features of the reaction system are determined by the interaction between the proton ($s$) and promoting ($R$) modes (HAT in non-polar media). The promoting mode is usually assumed to be classical.

**b. Electron transfer as an example of multimode tunnelling**

**Calculation technique.** We will consider multimode transitions between the reactant and product states in which the quantum numbers of oscillators in the reactant well ($im_1, im_2, ...$) are replaced by oscillator quantum numbers in the product well ($fn_1, fn_2, ...$); the first character implies the belonging to either the reactants or the products, while the second one is the number of the level of the corresponding oscillator. To simplify the designations, we replace the set of characters in the parentheses by a single letter ($a$ or $b$) and write down the transition probability per unit time as $T_{ab}$ (it is measured in $s^{-1}$). In a deep tunnelling regime, the probabilities of individual transitions are low. They can be calculated using the perturbation theory (in terms of the golden rule)

$$T_{ab} = \frac{2\pi}{\hbar} A_{ab}^2 \delta(E_b - E_a). \tag{60}$$

Here, $A_{ab}$ is the transition amplitude

$$A_{ab} = \langle\chi_b|H - E_a|\chi_a\rangle, \tag{61}$$

where $\chi_a$ and $\chi_b$ are the wave functions of multimode diabatic states, which are the products of oscillatory functions; $H$ is the total double-well Hamiltonian; $E_a$ and $E_b$ are the energies of diabatic multimode states in the reactant $a$ and product $b$ wells, respectively; they are the sums of energies of the levels $e_{m_1}, e_{m_2}, ...$ and $e_{n_1}, e_{n_2}, ...$ for separate oscillators

$$\begin{aligned} E_a &= e_{m_1} + e_{m_2} + \ldots; \\ E_b &= e_{n_1} + e_{n_2} + \ldots \end{aligned} \tag{62}$$

As in the one-dimensional formulation (see Section II.3.b), $\chi_a$ and $\chi_b$ are not eigenstates of $H$: the oscillatory functions corresponding to them are localised in the reactant and product wells and, hence, they are the eigenfunctions of two different diabatic Hamiltonians, so that the corresponding off-diagonal matrix element $H_{ab}$ does not vanish. According to the perturbation theory, the probabilities $T_{ab}$ are additive, and the resultant thermal rate constant for the reaction equals[99, 124, 125]

$$k = \frac{2\pi}{\hbar}\sum_{a,b}\exp\left(-\frac{E_a}{k_B T}\right)A_{ab}^2\delta(E_b - E_a). \quad (63)$$

In Eqns (60) and (63), the delta-function expresses the energy conservation law for the multimode transition, which is accompanied by the intermode energy exchange. The summation is carried out over all combinations of the oscillatory functions, *i.e.*, multipliers in the multimode product functions $\chi_a$, $\chi_b$. The use of the delta-function provides the possibility of counting all combinations that ensure energy conservation.

Like any other relation containing the delta-function, expression (63) acquires a definite meaning and can be really calculated only if the sums appearing in it contain a continuum frequency spectrum and can be reduced to integrals. Reactions in the condensed phase represent an appropriate object for the application of this calculation procedure. In the harmonic model of the medium, a continuum frequency spectrum is specified using the spectral function $J(\omega)$ (spectral density, see Supplement II).[96, 130–132]

Let us consider the case where there is only one quantum reaction mode (with the frequency $\omega_0$), while the other modes (modes of the medium) are reorganisation modes with a continuum frequency spectrum. Then the function $J(\omega)$ gives the frequency distribution for the intensity of interaction between the reaction mode and the medium modes

$$J(\omega) = \text{const}\,\Delta Q(\omega)\rho(\omega), \quad (64)$$

where $\Delta Q(\omega)$ is the shift of the equilibrium position of the medium reorganisation mode $Q$ with the frequency $\omega$, which is induced by this interaction and can serve as its measure; the function $\rho(\omega)$ characterises the density of oscillator levels with the frequency $\omega$; it is different for different condensed media; the constant in the equation does not depend on $\omega$.

The description of the continuum frequency spectrum by means of the spectral density is considered in more detail in Supplement II.

**Expression for the rate constant**.[124, 125, 127, 131] Now we list once again the key assumptions made in the model of multidimensional tunnelling transition in a medium consisting of a continuum ensemble of harmonic oscillators.

First, the reaction system is described by a single reaction mode $s$ with the frequency $\omega_0$. This is a quantum mode [see criterion (56)] related to the medium modes $Q_v$, which are characterised by frequencies $\omega_v$ and masses $m_v$. All modes of the medium are reorganisation modes. In the continuum limit, $Q_v \to Q(\omega)$. This limiting transition gives rise to the spectral function $J(\omega)$ as a characteristic of the interaction between the reaction mode and the medium.

Second, the tunnelling reaction does not change the frequency spectrum of the medium [*i.e.*, the function $J(\omega)$] or the forms of normal vibrations $Q_v$ [or $Q(\omega)$]. This assumption is not fundamental but it allows one to represent the results of the theory in a rather simple form.

Finally, one special assumption concerning the form of the amplitude of the tunnelling transition is also required

$$A_{ab} = A_0\langle\overline{\chi}_a|\overline{\chi}_b\rangle, \qquad A_0 = \left\langle\chi_i\left|H - \frac{1}{2}(e_i + e_f)\right|\chi_f\right\rangle. \quad (65)$$

Here, the diabatic functions are represented by the products

$$\chi_a = \chi_i\overline{\chi}_a, \quad \chi_b = \chi_f\overline{\chi}_b,$$

where $\chi_i$ and $\chi_f$ are the eigenfunctions for the reaction mode $s$, corresponding to the energies $e_i$ and $e_f$, while $\overline{\chi}_a$ and $\overline{\chi}_b$ are the products of the wave functions of the medium oscillators. The functions $\overline{\chi}_a$ and $\overline{\chi}_b$ correspond to the energies

$$\overline{E}_a = E_a - e_i, \quad \overline{E}_b = E_b - e_f.$$

These relations follow from the energy conservation law. The overlap integral $\langle\overline{\chi}_a|\overline{\chi}_b\rangle$ is equal to the product of the overlap integrals for the shifted oscillators of each of the medium modes; it is called the multidimensional Frank–Condon factor.

Equations (65) represent the Condon approximation according to which the dependence of the matrix element $A_0$ on the oscillatory coordinates is not taken into account. This approximation is justified provided that the frequency $\omega_0$ is much greater than the medium frequencies. In this case, the $A_0$ value is calculated for those medium coordinates that make the greatest contribution to the full transition amplitude.

When these assumptions are taken into account, the reaction rate constant given by relation (63) is transformed in the following way:[127, 133–137]

$$k = \frac{A_0^2}{\hbar^2}\int_{-\infty}^{\infty} C(t)\exp\left(-\frac{it\Delta V}{\hbar}\right)\mathrm{d}t,$$
$$C(t) = \exp\left[-\frac{1}{\pi\hbar}\times\right.$$
$$\left.\times\int_0^{\infty}\frac{J(\omega)}{\omega^2}\,\frac{\mathrm{ch}(\hbar\omega/2k_BT)(1-\cos\omega t) + i\,\mathrm{sh}(\hbar\omega/2k_BT)\sin\omega t}{\mathrm{sh}(\hbar\omega/2k_BT)}\mathrm{d}\omega\right]. \quad (66)$$

Here, $t$ is time; $\Delta V = V_f - V_i$ is the difference between the energies of the diabatic PES at their minima [see Eqn (4)].

Relation (66) is a typical result of the multimode oscillatory perturbation theory. It is widely used in the theory of electron transfer in polar solvents.[127, 129, 133–137] In this case, $s$ is the electron coordinate and the function $J(\omega)$ is proportional to the reorganisation energy of the modes of the medium, *i.e.*, the energy evolved upon the shift of the equilibrium positions of the oscillatory modes. The frequency dependence of $J(\omega)$ is determined by the function $\mathrm{Im}\{\epsilon(\omega)/|\epsilon(\omega)|^2\}$, where $\epsilon(\omega)$ is the frequency-dependent complex dielectric constant, which is the key phenomenological characteristic of the dynamic properties of the dielectric medium. This representation of the spectral density is valid for any reactions with charge redistribution in polar disordered media. The parametrisation of $J(\omega)$ can be quite different for reactions in non-polar media or in molecular crystals (see Supplement II).

Equation (66), which seems to be complicated, holds for a broad range of temperatures including the lowest ones and describes the reorganisation dynamics for both classical and quantum modes of the medium. More precisely, this theory is valid as long as the key expression of the golden rule (60) holds. There is always a lower temperature limit depending on the resonance misfit and on the spectral density,[130, 131] beyond which the steady-state regime (which ensures the existence of exponential decay and the rate constant) is violated and quantum beats appear, *i.e.*, coherent periodic transitions of the reaction system from the reactant well to the product well and back. This lower temperature limit is commonly considered to arise in the extremely low-temperature region.

If all modes of the medium are considered to be classical in conformity with criterion (58), expression (66) is reduced to the usual Arrhenius law (59), which was postulated above relying on intuitive considerations:

$$k = \frac{A_0^2}{\hbar}\left(\frac{\pi}{E_r k_B T}\right)^{1/2}\exp\left[-\frac{(E_r + \Delta V)^2}{4E_r k_B T}\right]. \quad (67)$$

Here, the activation energy coincides with the potential barrier (6).

Thus, in the high-temperature limit, the electron transfer kinetics is mainly determined by three key reaction parameters, namely, the transition amplitude for the reaction mode, the medium reorganisation energy $E_r$, and the heat of the reaction $\Delta V$. The dependence of the rate constant on details of the frequency spectrum of the medium is manifested only in the low-

temperature quantum regime. Various approximations of expression (66) are possible, which are valid in more or less broad temperature ranges.[99, 138–141] One of them is given below.

**c. Hydrogen atom transfer in the liquid and solid phase**

**Reaction model.** The PT and HAT reactions in the condensed phase have been considered in a number of early studies using relation (66).[27–31, 142–147] The proton coordinate was used as the only quantum coordinate $s$. It can be seen from the above consideration that this approximation is inadequate and that the promoting mode $R$ is to be taken into account.[148] The simplest plausible model should explicitly include the modes $s$, $R$ and the medium modes $Q_v$.[30, 148–151] This model is formulated as follows.[99, 148] The interaction of modes $s$ and $R$ is introduced through the dependence of the proton transition amplitude $A_{if}$ on $R$ (recall that this dependence plays a crucial role in the energy exchange in gas-phase hydrogen atom abstraction). A convenient approximation is

$$A_{if}(R) = \bar{A}_0 \exp[-\alpha(R - R_e) - \gamma(R - R_e)^2], \tag{68}$$

where $R_e$ is the equilibrium $R$ value.

The second term in brackets rapidly decreases both for positive and negative values of the $R - R_e$ difference. It is necessary for providing the convergence of the perturbation theory integrals with the continuum spectrum. Then it is sufficient to assume that only the low-frequency mode $R$ interacts with the medium oscillators. The corresponding frequency and mass will be designated by $\omega_R$ and $m_R$. This mode is not a reorganisation mode, *i.e.*, its equilibrium position does not change upon the reaction. Correspondingly, the modes of the medium do not change equilibrium positions and remain exclusively promoting modes. The full expression for the rate constant in this model [99] is cumbersome and unwieldy. A rather simple expression can be obtained by neglecting the squared dependence on $R$ in the exponent in Eqn (68) and taking that $\gamma = 0$. Then

$$k = \frac{\bar{A}_0^2}{\hbar^2} \int_{-\infty}^{\infty} C(t) \exp\left(-\frac{it\Delta V}{\hbar}\right) dt\,,$$

$$C(t) = \exp\left[\frac{(\hbar\alpha)^2}{\pi\hbar} \times \right. \tag{69}$$

$$\left. \times \int_0^{\infty} J(\omega) \frac{\mathrm{ch}(\hbar\omega/2k_BT)\,(1 + \cos\omega t) - i\,\mathrm{sh}(\hbar\omega/2k_BT)\sin\omega t}{\mathrm{sh}(\hbar\omega/2k_BT)}\, d\omega \right].$$

Here the spectral density $J(\omega)$ describes the expansion of the promoting mode $R$ over the normal modes of the full system comprising the reaction subsystem and the medium. In the discrete representation,

$$R - R_e = \sum_v C_v Q_v\,.$$

The methods for the transition to the continual representation that allow one to obtain expressions (66) and (69) are considered in Supplement II.

**Temperature dependence of the rate constant.** One can expect that there exists, at least, one localised normal mode that makes a substantial (perhaps, the major) contribution to the coordinate $R$. Therefore, the expansion

$$J(\omega) = \mathrm{const}\,\delta(\omega - \omega_R) + J_{cont}(\omega), \tag{70}$$

where $\omega_R$ is the frequency of the localised normal mode, can be an appropriate approximation.

The second (continuum) term remains, as usual, a smooth spectral function. Therefore, using relation (70), the factor [99, 148, 152]

$$k \sim \exp\left\{\mathrm{const}\left[\frac{(\hbar\alpha)^2}{\pi\hbar}\,\mathrm{cth}\,\frac{\hbar\omega_R}{2k_BT}\right]\right\}, \tag{71}$$

which determines the temperature dependence of the rate constant in the temperature range where

$$\frac{\hbar\omega_R}{2k_BT} \lesssim 1, \tag{72}$$

can be separated in the rate constant.

This dependence is well fulfilled for photochemical elimination of a hydrogen atom by the singlet excited acridine impurity in the molecular crystal of fluorene (Fig. 10). Condition (72) determines the position of inflection point on the temperature kinetic curve; this is used to determine the resonance frequency $\omega_R$. The value found in this way coincided with the frequency of the promoting mode ($\omega_R = 130\ \mathrm{cm}^{-1}$) found by an independent procedure using the vibrational spectrum of the fluorene crystal.[153, 154]

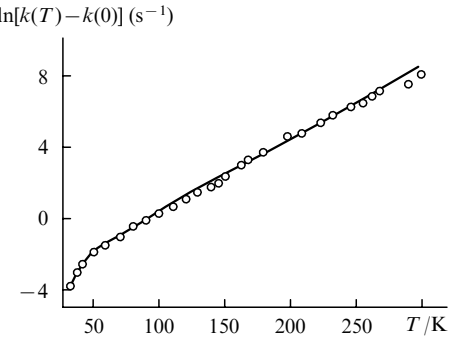



**Figure 10.** Temperature dependence of the rate constant for a photochemical reaction of HAT in a fluorene molecular crystal doped with acridine.
Experimental data are shown by dots.[153] The continuous line was calculated using relation (71) for $\omega_R = 131\ \mathrm{cm}^{-1}$ (see Ref. 152).

The factor (71) can also be distinguished in the equation for the rate constant of the reaction with medium reorganisation [see Eqn (66)]. The correlation (71) cannot be extended to a too broad temperature range. With an increase in temperature, one should take into account the Gaussian exponential component in the transition amplitude (68),[99] which is ignored in expression (69). The corresponding temperature factor for $\hbar\omega_R/k_BT \ll 1$ (when the promoting mode becomes classical) has the form

$$k \sim \exp\left(\frac{1}{2}\,\frac{\alpha^2 l_R^2}{2l_R^2\gamma + \hbar\omega_R/4k_BT}\right), \tag{73}$$

where $l_R$ is the amplitude of zero-point vibrations along the coordinate $R$

$$l_R = \left(\frac{\hbar}{m_R\omega_R}\right)^{1/2}.$$

This factor can be derived using simple quasi-classical consideration.[148] Provided that

$$2l_R^2\gamma \ll \frac{\hbar\omega_R}{4k_BT}$$

this leads to a linear dependence of $\ln k$ on $T$, which was observed in many experiments. As the temperature further increases, the dependence becomes more gentle. The linear section can be clearly seen in Fig. 10. At very low temperatures ($\hbar\omega_R/k_BT \gg 1$), the continuum spectrum component $J(\omega)$ should be taken into account. The factor (71) becomes constant at this temperature. The corresponding temperature dependence, which follows from relation (69), has the form

$$\ln k \sim T^n,$$

the power $n$ ($2 < n < 4$) being determined by the spectral density $J(\omega)$ of the condensed medium.[99, 155] This conclusion, however, is not fully unambiguous due to the presence of a lower temperature limit below which the concept of rate constant becomes invalid in terms of the harmonic oscillatory model of the medium, and the energy exchange proceeds by an anharmonic mechanism.

The above analysis of the temperature dependence of the rate constant is wholly determined by the dynamics of the promoting mode, which interacts with the modes of the continuous spectrum, according to the accepted model [in the derivation of formula (69), it is expanded over normal vibrations of the overall system composed of the promoting mode and the medium coordinates]. The coordinate $R$ does not pass across a potential barrier; therefore, the usual Arrhenius dependence such as (59) is not observed at all. Within the framework of a classical consideration of the coordinate $R$, this dependence could arise only due to the reaction mode $s$, but this is a quantum mode at any temperature that may be of interest and, hence, it does not make a significant contribution to the temperature dependence of the reaction rate.

# III. Calculations for particular systems

## 1. Multidimensional quasi-classical calculations

### a. Problem definition

Quasi-classical calculations are based on the quasi-one-dimensional model of tunnelling (see Section II.3.a). In the space of active coordinates of the reaction system, the reaction path curve connects the regions of reactants and products. Let us consider one-dimensional tunnelling on the energy profile along this curve and calculate the quasi-classical action $W(E)$ [see Eqn (25)] in the region under the potential barrier, which determines the amplitude of the tunnelling transition. Selection of the reaction path is the key problem in this procedure. For a rigorous definition of the problem, the curve should ensure a classical action extremum for motion of the system in the inverted potential (the potential barrier becomes a potential well, and the reactant and product minima become top points of the potential relief). The classical trajectory with specified initial and end points is calculated in the inverted potential. The trajectory depends on the initial and final quantum states between which the transition takes place. Boltzmann averaging of the initial states gives rise to a dependence of the reaction path on temperature. The paths are different for low-temperature (tunnelling predominates) and high-temperature (tunnelling effects are slight) processes; its optimisation ensures a smooth transition between these kinetic regimes. However, in practice, such advanced scheme has never been applied to particular HAT or PT reactions. Actually, calculations are always carried out for a fixed trajectory chosen by some procedure.

The equation for the rate constant in a multidimensional case has the form:[156, 157]

$$k = A \exp[-W(E)].$$

The pre-exponential factor $A$ can be conveniently calculated in a special coordinate system, which is usually referred to the reaction path curve, also called the reference curve. One of the coordinates (the reaction coordinate) is measured as an arc length along the reference curve. A local system of Cartesian transverse coordinates is specified at every point of the reference curve; usually, the coordinates are modelled as harmonic oscillators. In these 'natural reaction coordinates,'[158, 159] the PES is a multidimensional valley stretched along the reaction path and the expression for kinetic energy has a complex form depending on the curvature of the reference curve.[158–161] The corresponding multidimensional Hamiltonian is called the reaction path Hamiltonian.[160] The mimimum potential energy route is normally used as the reference curve: in this curve, the PES cross-sections along the transverse coordinates have minima.[161] This path connects the TS, *i.e.*, the saddle point on the PES, with the reactant and product minima, although the action for transverse coordinates rather than the potential cross-section profile should have a minimum on the reference curve in a consistent theory.[157]

### b. The variational transition state theory

In the variational approach, the standard minimum potential energy route on the PES is chosen as the reaction path (in some cases, insignificant modifications are made).[162–164] The theory remains classical in this respect. The expression for the rate constant derived in terms of the classical TS theory by the variational method is used.[91, 165] The critical point in the reaction coordinate at which the reaction flux is calculated (*i.e.*, the TS) does not coincide with the top of the barrier. According to the variational theory, it is determined by minimising the expression for the rate constant with respect to the position of the TS in the reaction coordinate. At the final stage, a transmission factor (28), determined by tunnelling along a curvilinear reaction trajectory, is introduced to the rate equation.

This method was used to study HAT reactions in the gas phase[166–168] and in solutions[169–172] and PT and hydride ion transfer in enzymes.[173, 174] The calculation of a model collinear reaction (see Section II.3.a) in the presence of 250 solvent (methyl chloride) molecules is notable from the procedural standpoint.[175] The classical minimum energy path was calculated taking into account all degrees of freedom of the system. As noted above, the variational TS theory was implemented to calculate the transmission factor.

It is clear that this approach cannot be extended to the region of low-temperature kinetics.

### c. Low-temperature instanton method

In the low-temperature instanton approach,[176] the reaction path corresponds to a classical action minimum on the under-barrier trajectory in the inverted potential. The start of the trajectory is chosen in the reactant minimum on the real (rather than inverted) PES. This is valid for $T = 0$ K. The classical action is calculated along such trajectory and a correction for the interaction with transverse vibrational degrees of freedom is introduced into the resulting expression (in terms of the perturbation theory).[177–180]

The use of this method is currently restricted to the study of tunnel splittings in the microwave spectra of non-rigid molecules. The calculations of splittings have been carried out for both the ground state and the vibrationally excited states. Systems with intra- and intermolecular hydrogen bonds, namely, malondialdehyde and formic acid dimer, have been considered. Two-proton tunnelling transfer in the porphyrin molecule has been discussed.[181] A study of splittings in the malondialdehyde molecule with 21 degrees of freedom is the utmost achievement in this series of studies.[182]

### d. The model instanton method

The model instanton approach[151] employes the classical reaction path with a classical TS at the PES saddle point. This is an attempt to take into account the influence of all the other (transverse) vibration modes without resorting to the perturbation theory. This is indeed possible for a model two-dimensional PES formed by two paraboloids (see Fig. 2 *a*).[183] Extrapolation of this model to a multidimensional situation gave the equation[184, 185]

$$W = \frac{W_0}{1 + \sum_{\mathrm{s}} \delta_{\mathrm{s}}(T)} + \alpha_{\mathrm{s}} \sum_{\mathrm{a}} \delta_{\mathrm{a}}(T), \qquad (74)$$

where $W$ is the dimensional action, unlike the dimensionless action $(1/\hbar)W$ [see, for example, relation (25)]. The action $W_0$ is calculated along the standard classical reaction path. The transverse degrees of freedom are separated into symmetrical (the subscript s) and antisymmetrical (the subscript a); the symmetry is determined at the point of classical TS. 'Symmetrical' and 'antisymmetrical' are synonyms for 'reorganisation' and 'promoting' modes. The corrections they introduce to the action are additive. The $\delta_{\mathrm{s}}$, $\alpha_{\mathrm{s}}$ and $\delta_{\mathrm{a}}$ values can be explicitly calculated

from a specified multidimensional PES. Expression (74) is an empirical prescription, which provides physically reasonable estimates in some limiting situations. Of interest is the appearance of a typical temperature dependence of the action

$$\delta_s(T) = \delta_s\Big|_{T=0} \operatorname{cth}\frac{\hbar\omega_s}{2k_B T},$$

where $\omega_s$ is the frequency of the corresponding symmetrical vibration. The reaction rate constant is calculated in terms of the standard instanton procedure

$$k(T) = A(T)\exp\left[-\frac{1}{\hbar}W(T)\right]. \tag{75}$$

As in standard instanton methods, the pre-exponential factor is replaced by an effective frequency, which characterises the system vibrations in the reactant potential well.

This method was applied to study the tunnel splittings for intramolecular PT (malondialdehyde,[151] tropolone[186] and 9-hydroxyphenalenone[185]). The rate constants have been calculated for many reactions[187–191] including two-proton transfer in porphins.[185] The temperature dependences of the rate constants and the isotope effects were compared with experimental data.

The tunnel splittings for malondialdehyde have been calculated taking into account all the vibrational degrees of freedom and using various modifications of the instanton method.[192–194]

## 2. Two-state model with the molecular description of the medium

### a. Collective coordinate of the medium

The quantum theory of PT reactions with allowance for two electron–proton states is used fairly often (see Section II.2). A Hamiltonian depending on the variables $s$ (proton coordinate) and $R$ (symmetrical vibration of the $A_1$ and $A_2$ fragments, promoting mode) is written down for a three-particle $A_1\cdots H\cdots A_2$ model system. An ensemble of modes of the medium $Q_v$, which interact with $s$ and $R$, is added to the system. The complete Hamiltonian depends on each of the variables. Quantisation of the coordinate $s$ in the basis set of two diabatic functions $\varphi_n(s|R,Q_v)$, $n = 1, 2$, gives the matrix Hamiltonian

$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}, \quad H_{12} = H_{21}. \tag{76}$$

The diagonal elements are the classical Hamiltonians for two electron–proton states

$$\begin{aligned} H_{11} &= T_R + T_Q + \varepsilon_1(R, Q_v), \\ H_{22} &= T_R + T_Q + \varepsilon_2(R, Q_v), \end{aligned} \tag{77}$$

where $T_R$ and $T_Q$ are the kinetic energies for the mode $R$ and the medium coordinate $Q$; $\varepsilon_1$ and $\varepsilon_2$ are the corresponding FES, which are found by solving the Schrödinger equation for the coordinate $s$

$$h_s\varphi_n(s|R, Q_v) = \varepsilon_n(R, Q)\varphi_n(s|R, Q_v), \quad n = 1, 2. \tag{78}$$

The proton Hamiltonian $h_s$ is specified by Eqn (9). The potential in this case is the full PES in the coordinates $s$, $R$ and $Q_v$, in which $R$ and $Q_v$ are considered as parameters. The corresponding parametric dependence appears in the solution of Eqn (78), *i.e.*, in the eigenvalues $\varepsilon_n$ and eigenfunctions $\varphi_n$.

A remark concerning the designations is pertinent. In the key relations (8), (9) for quantisation of the proton coordinate $s$, the type of representation (either adiabatic or diabatic) is not specified; therefore, the potentials $V(s)$ and the eigenfunctions $\varphi_n(s)$ can be both adiabatic and non-adiabatic. In further consideration in Section II.2, the designation $\varphi_n$ is used for functions of the adiabatic basis, whereas diabatic functions were designated by $\chi_n$. Here, it is more convenient to use the common designation $\varphi_n$ for both diabatic and adiabatic functions.

It should be noted that Hamiltonian (76) can be represented in the form

$$H = \begin{pmatrix} 0 & H_{12} \\ H_{21} & \Delta\varepsilon \end{pmatrix} + H_{11}, \tag{79}$$
$$\Delta\varepsilon = H_{22} - H_{11} = \varepsilon_2(R, Q_v) - \varepsilon_1(R, Q_v).$$

The dynamics and kinetics of the interlevel transition do not depend on the scalar (non-matrix) value $H_{11}$. The matrix element of the transition $H_{12}$ (equal to $H_{21}$) is specified empirically. The energy gap $\Delta\varepsilon$ is the only significant variable; as can be seen from Eqn (79), the dependence on the particle velocity, present in Eqn (77), has disappeared because the classical kinetic energy is the same in the states $\varphi_1$ and $\varphi_2$. The variable $\Delta\varepsilon$ is a typical collective coordinate; calculation procedures with the use of this variable are well developed (numerical modelling by the MD or Monte-Carlo methods). This investigation scheme was first applied by Warshel and coworkers;[195–197] subsequently, various modifications of this scheme were applied by many authors.

### b. Triatomic model of a proton transfer reaction in a model solvent. Calculations by molecular dynamics

A popular investigation object is the PT reaction (acid–base equilibrium) in the molecular complex

$$A-H\cdots B \rightleftharpoons A^-\cdots H-B^+, \tag{80}$$

where PT is accompanied by pronounced polarisation of the heavy fragments A and B. In the calculations described above, the fragment A is represented by phenoxide $C_6H_5O^-$, while the fragment B is the amino group [trimethylamine $N(CH_3)_3$ is a typical example]. The reactants and products in reaction (80), described by the functions $\varphi_n$, which have served as the basis for constructing Hamiltonian (76), have dipole moments $\mu_1 \approx 2$ D (covalent complex) and $\mu_2 \approx (10-15)$ D (ion pair), respectively. The solvent particles are simulated in MD calculations by methyl chloride ($CH_3Cl$, $\mu = 2.15$ D).

The calculation starts with explicit solution of the Schrödinger equation (78) for the diabatic proton states. The single-well diabatic potentials $V(s|R,Q_v)$ appearing in the proton Hamiltonian $h_s$ are modelled empirically by combining the LEPS (London–Eyring–Polanyi–Sato) type schemes for the internal variables $s$, $R$ in the gas-phase reactions[198] with the MD parametrisation of the interactions involving the solvent particles.[63] With respect to the proton coordinate $s$, the functions $V(s|R,Q_v)$ are highly asymmetric single-well potentials (see Fig. 3). With these potentials, Eqn (78) can be solved numerically. This demonstrates the unique advantage of introducing the collective variable $\Delta\varepsilon(R,Q_v)$ [see Eqn (79)]. Equation (78) is solved for a one-dimensional set of values of the coordinate $\Delta\varepsilon$ rather than for the whole set of combinations of $R$ and $Q_v$ (which arise, for example, in a calculation with 256 solvent particles[63]). This gives two diabatic FES, $\varepsilon_1(R,Q_v)$ and $\varepsilon_2(R,Q_v)$, in which the explicit dependence on the medium coordinate is included through $\Delta\varepsilon$. Diagonalisation of the Hamiltonian (79) gives two adiabatic FES

$$E_{1,2} = \frac{1}{2}\left[\varepsilon_1 + \varepsilon_2 \pm (\Delta\varepsilon^2 + 4H_{12}^2)^{1/2}\right]. \tag{81}$$

The free energy surface for the ground adiabatic state $E_1$ is double-well (see Fig. 2 *b*). It is significant that in the TS region, the medium coordinate $\Delta\varepsilon$ is the reaction coordinate: the FES profile along $\Delta\varepsilon$ has a maximum at the saddle point.

The way for calculating the kinetics of reaction (80) is obvious in the adiabatic approximation where the transitions between surfaces $E_1$ and $E_2$ are ignored. In the simplest version, the coordinate $R$ is considered to be classical (the medium coordinates $Q_v$ are always classical in this model). The rate constant is then calculated using a standard MD procedure, namely, the steady-state reaction flux method.[55] It is reduced to the calculation of

$k_{TST}$, *i.e.*, the rate constant in the TS approximation, and the correcting classical transmission factor $\kappa_c$:

$$k = \kappa_c k_{TST}. \tag{82}$$

For determining $\kappa_c$, the correlation functions for the coordinate $\Delta\varepsilon$ and its derivative with respect to time ($\Delta\dot{\varepsilon}$) have to be calculated (by MD methods).[63, 199, 200] When these functions are known, one can also determine the friction kernel in the generalised Langevin equation (see Supplement I) and calculate $\kappa_c$ within the framework of the KGH stochastic theory.[63]

In earlier studies of reaction (80), the promoting mode $R$ was not taken into account.[29, 200–203] The most comprehensive study was carried out for a two-dimensional model ($R$,$\Delta\varepsilon$) with allowance for quantisation of $R$.[63] The transmission factor varied in the range of $0.4 < \kappa_c < 0.8$ depending on the parametrisation. The attempts to take into account the non-adiabatic transitions within the framework of this scheme are not quite consistent.[63, 200] The transition probability for a one-dimensional potential profile along the coordinate $\Delta\varepsilon$ has been calculated by the Landau–Zener method.[88] Then it was averaged with allowance for the statistical distribution of the $\Delta\varepsilon$ values using the MD technique. The choice of parametrisation for the transition matrix element $H_{12}$ is significant at this stage.

**c. Quantum effects**

According to the accepted terminology (see Section II.2.a), reaction (80) has a low barrier. The quantum effects involved are insignificant. Conversely, HAT reactions in systems containing hydrocarbon molecules have high barriers. The quantum transmission factors for them are low ($\kappa_q < 10^{-4}$ or lower [166–168]). The golden rule procedure for their calculation is considered in Sections II.4.a and II.4.c. This line of research was initiated by early studies performed before the mid-1980s.[126, 143, 148] Subsequently, this approach was modified by using advanced computer simulation procedures.[27, 28, 30, 149] However, no calculations of this type for particular systems taking account of quantum effects have been reported so far.

A complete and consistent theory for describing the kinetics of reaction systems with multidimensional double-well FES taking into account the tunnelling and non-adiabatic transitions should cover the two above-mentioned limiting cases and intermediate kinetic regimes. No theory of this type has yet been developed. Some approximate approaches are considered in Section II.2.b. Calculations of the probabilities of non-adiabatic transitions in model one-dimensional multilevel systems are documented.[204–206] In terms of the principles inherent in them, these calculations are related to calculations of two-level systems considered in this Section and to quantum-classical calculations of PT (see below, Section III.4).

## 3. Continuum models of the medium

**a. Definition of the problem in the adiabatic representation**

A two-state model of the reaction subsystem with explicit inclusion of the surrounding solvent particles is considered in Section III.2. An alternative problem formulation is possible on the basis of a continuum description of the medium.[64, 65, 69]

The first stage is to construct the FES for the ground state of the system spanned by the coordinates $s$, $R$, $X$, where $X$ is the collective coordinate of the medium. Its definition was borrowed from the theory of electron transfer.[66, 87, 207, 208] The corresponding Hamiltonian has the form

$$H = T_s + T_R + S + W(s, R, X), \tag{83}$$

where $T_s$ and $T_R$ are the kinetic energies of modes $s$ and $R$; in the general case, these are quantum-mechanical operators; the value $S = X^2/2E_r$ is the self-energy of the polarisation field of the medium. Polarisation is induced by the electric charges of the chemical subsystem, which are calculated by quantum-chemical methods. The reorganisation energy $E_r$ appearing in the expression for the self-energy is the key parameter of the electron transfer theory (see Sections II.1.b and II.4.b); it is calculated within the framework of continuum models of the medium.[209–212] The three-dimensional FES $W(s,R,X)$ is constructed in terms of the semi-empirical scheme combining the quantum-chemical calculation with calculation of the polarisation effects (dependence on $X$) in terms of continuum models.[213, 214] This FES is a double-well surface on which the reaction transition takes place.

The proton coordinate $s$ is excluded at the next stage. The numerical solution of the Schrödinger equation

$$[T_s + W(s,R,X)]\,\varphi_n(s|X,R) = \varepsilon_n(X,R)\,\varphi_n(s|X,R) \tag{84}$$

for different fixed $X$ and $R$ values gives the eigenvalues $\varepsilon_n(X,R)$ and the eigenfunctions $\varphi_n(s|X,R)$; $n = 1, 2$. They correspond to the adiabatic representation, because $W(s,R,X)$ in Eqn (84) is the total potential of a two-level system. (In this respect, this scheme differs from the diabatic one considered in Section III.2.b, although the diabatic definition is also possible in the continuum model of the medium.[215]) Two two-dimensional FES, $\varepsilon_1(X,R)$ and $\varepsilon_2(X,R)$, obtained from Eqn (84) correspond to the ground and excited states of the proton subsystem. The dynamic description of the continuum variable $X$ is performed using stochastic or diffusion models. Two-dimensional and two-level stochastic (or diffusion) equations of motion, whose one-dimensional versions are considered in Section II.2.b and in Supplement I, are found for these surfaces.

**b. Non-adiabatic transitions**

The matrix element which determines non-adiabatic transitions between the levels in the adiabatic representation is an imaginary quantity [65, 69]

$$H_{12} = \frac{\hbar}{i}(\upsilon_R J_R + \upsilon_X J_X), \tag{85}$$

where $\upsilon_R$ and $\upsilon_X$ are the velocities corresponding to the coordinates $R$, $X$

$$J_R = \left\langle \varphi_2 \left| \frac{\partial}{\partial R} \right| \varphi_1 \right\rangle, \qquad J_X = \left\langle \varphi_2 \left| \frac{\partial}{\partial X} \right| \varphi_1 \right\rangle. \tag{86}$$

The intensity of non-adiabatic transitions is determined by the parameter $\xi$

$$\xi = \frac{|\langle H_{12}\rangle_T|}{\varepsilon_2 - \varepsilon_1}, \qquad \langle H_{12}\rangle_T = \hbar\left(\frac{2k_B T}{\pi}\right)^{1/2}\left(\frac{J_R}{\sqrt{m_R}} + \frac{J_X}{\sqrt{m_X}}\right). \tag{87}$$

Here, the averaging $\langle ... \rangle_T$ takes place over the Maxwell velocity distribution; $m_R$ and $m_X$ are the masses corresponding to the coordinates $R$ and $X$ ($m_X$ is estimated on the basis of generalised Langevin equation [64, 69]). The $\xi$ value is calculated at the point where the surfaces $\varepsilon_2$ and $\varepsilon_1$ approach each other most closely and the energy gap $\varepsilon_2 - \varepsilon_1$ is the smallest.

**c. Systems with the C–H···C reaction centre**

The free energy surface $\varepsilon_1(X,R)$ for the ground (proton) state of the reaction system

$$C_6H_5CH_3 + {}^-CH_2{-}C_6H_5 \longrightarrow C_6H_5CH_2^- + CH_3C_6H_5 \tag{88}$$

is shown in Fig. 5. It bears a strong resemblance to a similar double-well FES calculated in the molecular description of the medium.[63] The calculation of reaction (88) showed [64] that $\xi \ll 1$, *i.e.*, the reaction is adiabatic. This is a reaction with a low barrier. If non-adiabatic transitions are neglected, the classical reaction kinetics can be derived using the KGH theory.

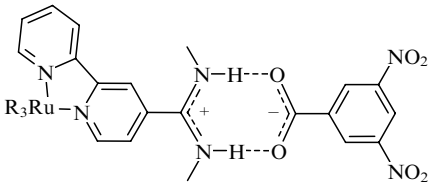
The opposite limiting case is represented by the reaction

$$Flu^- + HFlu \longrightarrow FluH + Flu^-, \tag{89}$$

where FluH is the fluorene molecule. This is a reaction with a high barrier, a very small energy gap $\varepsilon_2 - \varepsilon_1$ and $\xi \gg 1$, which complies with the non-adiabatic kinetics. The quantum transmission factor is estimated as $\kappa_q \approx 10^{-5} - 10^{-7}$ (see Ref. 65). This exceptionally low value corresponds to the deep tunnelling regime and is at variance with the insignificant isotope effect ($k_H/k_D \approx 10$) observed in the experiment. Apparently, this contradiction can be eliminated by noting that two internal coordinates $s$ and $R$ are inadequate for full description of the PES for reaction (89). It is necessary to take into account the dependence of PES on the reorganisation modes describing the change in the environment of the reaction centre. Their role is described in Section II.1.b. In view of this circumstance, it is possible to decrease the effective barrier to tunnelling [216] and to increase the quantum transmission factor by several orders of magnitude.

**d. Coupled electron and proton transfer**

The model described above was developed and applied for interpreting the features of coupled electron and proton transfer.[215, 217–219] This type of process takes place in the system




(90)

where R is 3,3′,4,4′-tetramethyl-2,2′-bipyridine. The synchronous transition of two protons is accompanied by substantial charge redistribution between fragments of system (90). For describing these effects one should circumvent the limitations of the two-level model of the reaction subsystem. A large number (4 or 8 [215, 218]) of electron – proton states corresponding to various basis structures of the valence bond method should be explicitly included into consideration. In the case of $N$ states, a matrix $(N \times N)$ Hamiltonian and $N$ coordinates of the medium $(X_1, ..., X_N)$ appear. Before constructing the matrix Hamiltonian (*i.e.*, before excluding the coordinate $s$), one should proceed from the ground state Hamiltonian, similar to Hamiltonian (83) but depending on all the medium coordinates $X_i$, $i = 1,...,N$. The self-energy $S$ of the medium polarisation field is [208, 209]

$$S = \frac{1}{2}\sum_{i,j}(T^{-1})_{ij}X_iX_j\,, \tag{91}$$

where $T$ is the reorganisation matrix, which is calculated using techniques of the continuum theory of the medium.

When dealing with the given multilevel theory, non-adiabatic transitions between various pairs of basis states arise. They can be classified into transitions with electron transfer and transitions with PT. This calculation procedure has been developed in detail [215, 220] and brought to the calculation of the rate constant in a kinetic regime such that the non-adiabatic electron transfer is treated in the usual way in terms of the golden rule and PT takes place on adiabatic FES without transitions between the FES.[215, 219] The results provided an explanation for some features of the coupled electron and proton transfer for system (90) and other related systems. An alternative interpretation has been proposed in earlier theoretical studies,[221, 222] but they appear less convincing.

**e. Some conclusions**

Little experience in using continuum models of the medium to calculate PT reactions has been accumulated so far. Apart from the studies described above, calculations of bimolecular and intramolecular PT in water should be mentioned.[223, 224] The available material allows one to draw some conclusions concerning the prospects of the continuum method as applied to PT reactions.

First, the use of continuum models greatly facilitates the calculations compared to those done in terms of similar molecular models of the medium.

Second, description of the rearrangement of chemical subsystem in the basis set of two electron-proton states restricts the scope of the method. This is true not only for coupled electron and proton transfer where extension of the basis of quantum states is the key item of the theory.[215, 218, 219] The calculations of FES for usual PT systems revealed characteristic situations in which the limitations of the two-level model result in serious inconsistencies.[69] The two-level approximation equally restricts the validity of calculations with the molecular description of the solvent.

Third, a substantial restriction follows from the usual two-coordinate model of PT, which takes into account only two internal degrees of freedom (coordinates $s$ and $R$) of the reaction subsystem. The reorganisation of modes associated with the change in the close environment of the reaction centre is an important factor for many PT and HAT reactions with a high barrier.[216] It has a crucial influence on the kinetics of HAT reactions; when the changes in these modes are ignored, the tunnelling effect is substantially overestimated.

Fourth, it is necessary to note a serious problem of the continuum theory, which restricts its practical value. The problem lies in the basic concept of the cavity which incorporates the reaction subsystem in the continuum medium. The change in the cavity during the reaction is supposed to induce no substantial energy or dynamic effects. This hypothesis is applicable to intramolecular processes for which the change of the cavity can indeed be considered insignificant. In bimolecular systems with PT and HAT, the cavity changes during the reaction but no procedures for calculation of the concomitant effects are suggested by the continuum model of the medium. This problem does not arise in the case of molecular models of the medium; this forms the strategic advantage of the latter.

Thus, the existing continuum theories of the solvent are barely applicable to a detailed quantitative description of PT and HAT reactions, although they are attractive for a qualitative description due to their simplicity and clarity.

## 4. Numerical modelling of proton transfer reactions by molecular dynamics

**a. Quantum-classical methods**

The use of simplified structural and dynamic models for a reacting subsystem (see Sections III.2 and III.3) restricts the scope of investigation of real chemical objects. In this respect, of interest are attempts at direct computer simulation of PT dynamics based on microscopic (molecular-dynamic) description of the solvent without rigorous constraints on the form of quantum electron – proton states. These approaches consider joint dynamic evolution of quantum and classical degrees of freedom. The number of quantum variables is limited; usually, only a single proton coordinate $s$ is considered. The list of classical variables includes several selected kinetically active coordinates of the reacting subsystem and the coordinates of several hundred of solvent particles. The general strategy for deriving the quantum-classical equations of motion is standard (the main principles are outlined in Sections II.2.a, II.2.b and III.2). The equations of motion along quantum coordinates (the Schrödinger equation for the wave function or the von Neumann equation for the density matrix) involve a parameteric dependence on all the classical variables (*via* the interaction potential).

Further development of this approach includes explicit derivation of the time dependence of the classical variables by MD computation of their evolution. Substituting the resulting multidimensional classical trajectory into the quantum equation of motion, *i.e.*, expressing the parameters of the potential of a quantum variable as functions of time, gives a time-dependent Hamiltonian. It controls the quantum evolution, which is accompanied by transitions between the levels. This non-adiabatic multilevel dynamic set of equations contains, in principle, tunnel-

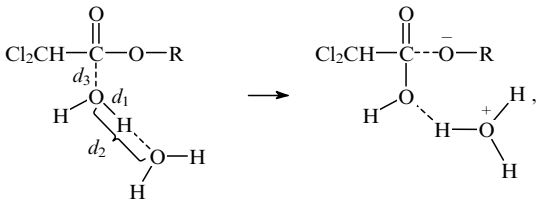
ling effects. The back influence of the quantum subsystem on the classical variables is taken into account using the generalised Helmann – Feynman theorem; the corresponding classical forces are determined by differentiating the electron – proton PES along the classical coordinates. Since the total quantum state is time-dependent, *i.e.*, it contains several stationary adiabatic components with time-dependent coefficients, their contributions are averaged with time-dependent weights.

Thus, a classical MD computation gives non-pairwise multiparticle forces, which are added to the pairwise Lennard-Jones forces acting between the solvent molecules. As a result, one can obtain a closed self-consistent scheme for the calculation of combined dynamic evolution of quantum and classical coordinates adapted for the use of well-developed MD procedures. This is the main advantage of this scheme; however, the scope of its applicability is not entirely clear. The completeness and self-consistency is attained at the expense of several simplifying assumptions having no convincing substantiation. Moreover, no consistent algorithms for the calculation of reaction rate constants (similar to the reaction flux method in usual classical MD [55]) have yet been formulated within the framework of this theory.

**b. Some applications**

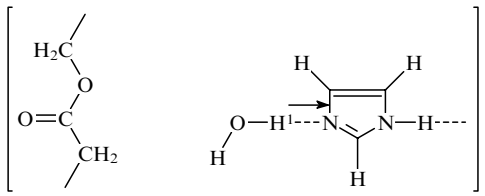
Without further dwelling on the principles of quantum-classical dynamics, we would like to note that there are several versions of its computational implementation, which have been described in reviews.[225, 226] The calculations are rather laborious; most often, they are applied to oversimplified model objects. We restrict our consideration to the studies attempting to apply these procedures to real chemical or even biochemical systems.

**Ester hydrolysis**. Hydrolysis of esters in a neutral aqueous medium has been studied.[227] The reaction complex of a dichloroacetic acid ester includes two water molecules. The following mechanism was postulated:



where R is the methoxyphenyl group. The distances $d_1$ (O – H, quantum variable), $d_2$ and $d_3$ (O···O and C···O, two classical variables) were included in the dynamic calculation, while the other coordinates within the complex were optimised. The PES was calculated by the AM1 semiempirical quantum-chemical method with the addition of the reactive field of the solvent to the electronic Hamiltonian. This system, together with 510 solvent (water) molecules, was included in the MD calculation. For the estimation of the rate constant, the procedure described in Section III.4.a was markedly simplified. A mechanism was postulated according to which the most probable pre-reaction configuration of the complex is formed initially and then fast PT takes place in this configuration. The structure of the pre-reaction configuration was also postulated; its formation was considered as a purely classical equilibrium process (as in the TS theory). The free energy change was calculated by the thermodynamic integration method, standard for MD. A temperature dependence of the rate constant (free activation energy is 10.7 kcal mol$^{-1}$) appears at this stage. The frequency of the quantum transition that contributes to the pre-exponential factor for the PT was then determined by solving the time-dependent Schrödinger equation.[228] The primary result is the value of kinetic H/D isotope effect, equal to 3.9, which is consistent with experimental data.

**Enzymic hydrolysis**.[229, 230] The active site of the catalytic system of an enzyme (phospholipase $A_2$) can be represented in the form



During enzymic hydrolysis, dissociation of water molecules takes place

$$H_2O \longrightarrow OH^- + H^+.$$

As a consequence, the $H^1$ atom moves to the imidazole fragment (shown by an arrow).

The system fragment represented in the picture was calculated by quantum-chemical methods (valence bond method calibrated against the data of *ab initio* calculations using the density functional theory). This fragment was inserted into the remaining part of the enzyme structure, which was calculated by molecular mechanics, while its dynamics was simulated by MD techniques. The coordinate of the $H^1$ proton was assumed to be a quantum one, while the other reaction centre coordinates were taken to be classical and were included in the MD calculation. The combined dynamic calculation of the evolution of the quantum variable and its classical environment was described in Section III.4.a; as has been noted, the reaction rate constant cannot be calculated in this way. Therefore, auxiliary characteristics of the reaction were extracted from the calculation which provided useful information for the understanding of the mechanism of catalysis.

**Tentative conclusions.** It can be seen from the above examples that model-free quantum-classical calculations still cannot be regarded as a routine tool for chemists. However, good prospects of this approach are beyond doubt. Its practical implementation requires higher computational facilities and development of new, more efficient and reliable calculation algorithms.

Note that in all systems studied by this method, the tunnelling effects were insignificant. They were also insignificant in the test calculations for simple systems that preceded the calculations described above {PT reactions in the $[NH_3\cdots H\cdots NH_3]^+$ system,[229, 231] in protonated malonate ion,[228] and in deprotonated water dimer $[H-O-H\cdots OH]^-$ (see Ref. 232) were studied}. The question of the possibility of reliable description of PT kinetics in a deep tunnelling regime in terms of the quantum-classical approach remains open. More promising in this respect is the theory in which the PT or HAT kinetics is considered on the basis of the quantum-mechanical perturbation theory, while the dynamic effect of the medium can be taken into account within the framework of classical MD.[233] This advanced modification of the multimodal harmonic PT theory (see Section II.4) fully takes into account the anharmonic effects and removes restrictions on the shape of diabatic potentials of the reactants and products. However, practical application of this strategy to PT or HAT processes is still unknown.

## IV. Experimental data and summary of calculations of the potential and free energy surfaces

Detailed description of PT and HAT kinetics in the gas phase and condensed media requires determination of the reaction rate constants and the isotope effects over a broad temperature range. These experimental data are, however, available for a small number of reactions, because the temperature range in a particular experiment is often limited due to the destruction of organic molecules and/or crystal melting. In the liquid phase, the temperature variation range is determined by the melting and boiling points of the solvent; in addition, the solubility of many substances sharply decreases with a decrease in temperature. Moreover, the reaction mechanism can change on passing from

one aggregate state to another. For example, many processes involving acids and bases do not proceed in the gas phase but easily occur in polar media;[21] bimolecular HAT reactions which are barrierless in the gas phase are characterised by high barriers in organic crystals,[234,235] and crystal field effects can result in asymmetric double-well PES for systems with symmetrical O–H···O fragments.[236] Therefore, experimental data often cannot be interpreted unambiguously without invoking quantum-chemical calculations. In what follows, the conclusions drawn in experimental works are compared, whenever possible, with the data of calculations. Note in this connection that the applicability of quantum-chemical methods is restricted by many factors: the size of the hydrogen-bonded system (not more than 10 heavy atoms), the occurrence of PT or HAT in electronically excited states and the influence of solvation or crystal environment.

## 1. Gas phase

In descriptions of intramolecular PT in the lower singlet or triplet electronically excited states, the terms of PT and HAT are often used as synonyms. When intra- and intermolecular reactions are considered together and the principles outlined in the Introduction are taken into account, it is expedient to distinguish between these terms. Proton transfer usually involves a step of hydrogen bond formation.[237] The PES for this process is characterised by the presence of a potential well (or two wells), whose depth can exceed the hydrogen bond energy (5–10 kcal mol$^{-1}$). Hydrogen atom transfer is a radical process; therefore only shallow minima can appear on the PES (about $k_BT$).

Let us consider, for example, two exothermic reactions[238] for which the motion in the reactant and product valleys can be considered translational as a first approximation (see Section II.3.b). One of these reactions is HAT involving neutral molecules and radicals

$$F^{\bullet} + HCl \longrightarrow FH + Cl^{\bullet}. \quad (92)$$

The other process is an ion–molecular PT reaction

$$F^- + HCl \longrightarrow FH + Cl^-. \quad (93)$$

The PES profiles for these reactions are essentially dissimilar (Fig. 11). The PES (93) has a deep minimum [$\sim$14 kcal mol$^{-1}$ (see Ref. 238)], which corresponds to the formation of the $FHCl^-$ complex. In addition, reaction (93) involves reactants with closed electronic shells and their electronically excited states lie very high (in $k_BT$ units). The radicals in reaction (92) can exist in different electronic states, $F(^2P_{3/2})$ and $F(^2P_{1/2})$; therefore, correct description of reaction (92) requires that at least two PES be considered.[238]

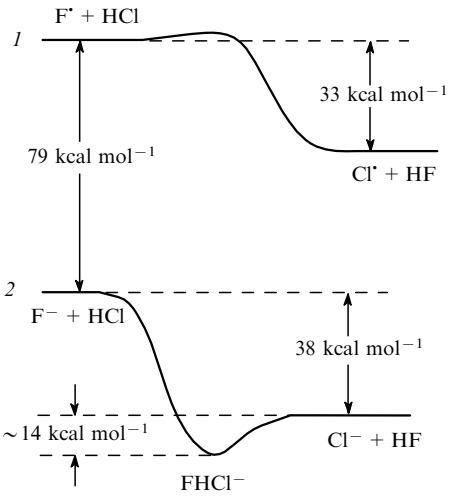



**Figure 11.** PES profiles for two bimolecular gas-phase reactions. (*1*) radical HAT reaction, (*2*) ion–molecular PT reaction.

In the general case, HAT in the gas phase can be represented as follows:

$$Y^{\bullet} + HX \longrightarrow YH + X^{\bullet}, \quad (94)$$

where Y = H, D, F, Cl, O, CN; X = H, D, Cl, Br, I, *etc.*[239,240]

The PT reaction in the gas phase can be described by several schemes:

$$Y^- + HX \longrightarrow YH + X^-, \quad (95)$$

(Y and X are the same as in the previous case[239]);

$$Y + H^+ \longrightarrow YH^+, \quad (96)$$

(Y is water, ammonia, *etc.*[241]);

$$YH^+ + X \longrightarrow Y + XH^+, \quad (97)$$

($YH^+$ is $H_3O^+$, X is methylamine[242]);

$$AH\cdots B \longrightarrow A\cdots HB, \quad (98)$$

(A and B are either heteroatoms incorporated in the same molecule and linked by an intramolecular H-bond or terminal atoms in hydrogen-bonded dimers, trimers, *etc.*);

$$AH + B \longrightarrow A^- + BH^+, \quad (99)$$

(AH and B designate a conjugate acid–base system).

Many HAT reactions [see Eqn (94)] and ion–molecular PT reactions [see Eqns (95)–(97)] are highly exothermic and readily proceed in the gas phase. The intramolecular PT process (98), where A = B (or the synchronous transfer of two protons in dimers with two hydrogen bonds), proceeds in a symmetrical double-well potential and is accompanied by simultaneous rearrangement of the system of double and single bonds. Finally, the gas-phase PT reaction between neutral molecules [see reaction (99)] is endothermic, the equilibrium being often appreciably shifted to the left.[20,21]

A special type of reaction is represented by hydride ion $H^-$ transfer, for example

$$[R^1]^+ + R^2H \longrightarrow R^1H + [R^2]^+, \quad (100)$$

where $[R^1]^+ = C_2H_5^+$, *tert*-$C_4H_9^+$ and so on, and $R^2H$ are hydrocarbons with 4–8 carbon atoms containing at least one quarternary carbon atom.[243]

### a. Intermolecular hydrogen atom transfer

A large number of experimental and theoretical works on the intermolecular HAT in the gas phase have been published.[109–112] The corresponding rate constants and their temperature dependences are systematically summarised and discussed in monographs and reviews.[244–246] It has been noted above that this reaction follows a radical mechanism and that the pre- and post-reaction states in the gas phase have shallow minima on the PES (depths of about $k_BT$). Therefore, the scattering cross-section is a fundamental characteristic of the process and the methods of process investigation are based on the scattering theory, which describes transition from an unbound state of the reactants into an unbound state of the product (see Section II.3.b). An adequate description of HAT dynamics requires that at least two coordinates be taken into account. In the simplest case, these are the lengths of the breaking and forming bonds of the hydrogen atom. Considerable attention has been devoted to the reaction $H_2 + X$, where X = H, D, F, Cl, *etc.*[247–253]

The PES of reaction (92) has a relatively low potential barrier [$\sim$1 kcal mol$^{-1}$ (Ref. 254)].

The scattering in a system comprising three atoms, 'heavy–light–heavy', for example,

$$I^{\bullet} + HI \longrightarrow IH + I^{\bullet}, \quad (101)$$

requires particular attention because many theoretical methods developed to describe this reaction[49,255] are applicable to the

description of intramolecular PT or synchronous transfer of two protons in dimers (98). The main conclusion of the theory is the possibility of formation of the metastable IHI complex in the PES region corresponding to the TS. The complex is of a dynamic nature. The minimum on the PES is not very deep, about 2 kcal $mol^{-1}$ (see Ref. 49). However, calculations show that several levels corresponding to symmetric vibrations of IHI may occur in the potential well.[256] Experimental studies confirmed the existence of a metastable IHI complex.[257, 258]

The bimolecular elimination of a hydrogen atom from methanol and dimethyl ether

$$H^{\bullet} + CH_3X \longrightarrow H_2 + {}^{\bullet}CH_2X,\ X = OCH_3,\ OH \qquad (102)$$

has been studied both in the gas phase and in aqueous solutions. In the gas phase, this exothermic reaction ($\Delta H \sim -10$ kcal $mol^{-1}$) was studied over a broad temperature range (298 to 575 °C).[259] The H/D-isotope effect is very small; the temperature dependence of the rate constant is well described by the Arrhenius equation. Therefore, it was concluded that no tunnelling effects are involved in reaction (102).[259]

**b. Proton transfer in ion – molecular reactions**

Gas-phase PT in ion – molecular reactions of type (95) – (97) have been extensively studied (see reviews [239, 241, 242, 260]). Ion cyclotron resonance, high-pressure mass spectrometry and flowing afterglow technique were used most often in these studies. The principal results of these investigations include elucidation of gas-phase acidity scales,[260–264] basicity and proton affinity scales [242, 264–266] and a detailed description of solvation of the $H_3O^+$ ion in the gas phase.[267]

A large array of kinetic data has been obtained for PT reaction (95) (see Table III in Ref. 239). Depending on the nature of the anion and the 'acid' molecule participating in the reaction, its exothermic effect varies from $-0.68$ to $-2.82$ eV and the rate constant ranges from $1.5 \times 10^{-10}$ to $3.7 \times 10^{-14}$ $cm^3$ $(molecule)^{-1}$ $s^{-1}$. Comparison of the kinetic parameters of this reaction with similar data for HAT reactions [see reaction (94)] shows that, with exothermic effects being similar, the rate constant for PT is two or three orders of magnitude higher than the rate constant for the corresponding HAT reaction, which is due to the presence of a deep minimum on the PES of ion – molecular reactions (see Fig. 11).

**c. Intramolecular proton transfer**

The intramolecular PT and synchronous transfer of two protons in carboxylic acid dimers in the electronic ground state have been studied by radiospectroscopy and vibrational spectroscopy. Symmetrical reactions, *i.e.*, those with equivalent initial and final states, are usually considered. Proton transfer in these reactions shows itself as tunnel splitting of the ground vibrational state. The experimental value of splitting is $\sim 21$ $cm^{-1}$ for malondialdehyde,[37] varies from 1 to 5 $cm^{-1}$ for mixed carboxylic acid dimers,[36] or equals 1 $cm^{-1}$ for tropolone.[38] Due to procedural difficulties, virtually no data on the tunnel splitting for vibrationally excited states are available.[36, 268, 269]

The influence of H/D isotope substitution on the tunnel splitting and on the geometric structure of H-bonded systems has been studied. The tunnel splitting for deuteron was found to be strongly reduced (by an order of magnitude). The equilibrium distance between hydrogen-bonded atoms usually increases by $\sim 0.02$ Å. This is the so-called Ubbelohde effect,[270] whose theoretical interpretation is based on the assumption of strong interaction between the coordinate of the tunnelling particle and low-frequency vibrations of hydrogen-bonded heteroatoms.[3, 78] Theoretical estimates of tunnel splitting are discussed in Sections III.1.c and III.1.d.

Vibration-rotational tunnelling spectroscopy seems to be a promising method for the study of systems with H-bonds in the ground electronic state.[271] However, this method has not yet been applied to PT reactions.

Numerous publications describe the use of spectroscopy to study PT in the lower singlet electronically excited state $S_1$ (see Refs 90 and 272). This is due to fast development of spectral methods with high temporal or space resolution based on the use of frequency-controlled lasers.[42, 273, 274] The studies are usually carried out for large aromatic (pseudo-aromatic) molecules containing one or several functional groups which are linked by an intra- or intermolecular H-bond. The type of PES in the ground electronic state $S_0$ of the H-bond varies from a symmetric or asymmetric double-well surface to a highly asymmetric single-well one. Upon excitation to the $S_1$ state of the $\pi\pi^*$ type, the H-bond is usually retained; however, its potential markedly changes.

For systems with a symmetric double-well PES, the potential barrier separating two minima normally decreases along the effective PT coordinate (9-hydroxyphenalenone, tropolone, benzoic acid dimer), which results in a sharp increase in the tunnel splitting of the ground vibrational state.[40, 275, 276] This is due to substantial shortening of the distance between the atoms linked by the hydrogen bond as a result of electronic excitation and is confirmed by *ab initio* calculations for malondialdehyde and tropolone in the $S_0$ and $S_1$ states.[24, 277, 278]

Electronic excitation of systems with highly asymmetric intramolecular hydrogen bonds often results in an inversion of the H-bond potential.[272] The excitation causes a sharp change in the acid – base properties of the functional groups that form the H-bond.[279] Proton transfer is accompanied by very fast rearrangement of the system of double and single bonds; therefore, the 'classical' keto form is formed in the $S_1$ state, instead of the zwitter-ion.[90] This is confirmed by the data of *ab initio* calculations of *o*-hydroxyacetophenone, 2-(2′-hydrophenyl)benzoimidazole and salicylic acid in the $S_0$ and $S_1$ states.[52, 280, 281] The intramolecular PT in the $S_1$ state usually proceeds in such systems without a barrier [32] and can be regarded as intramolecular vibrational relaxation. This accounts for the very high rate of PT in the $S_1$ state (more than $10^{12}$ $s^{-1}$),[90] typical of systems with hydrogen bonds. The absence of H/D isotope effect for the rate of PT supports the conclusion that the reaction is barrierless. 1,5-Dihydroxyanthraquinone is, apparently, the only system with a highly asymmetric H-bond for which the intramolecular PT was proved to proceed through tunnelling.[282]

Transfer of several protons in various hydrogen-bonded complexes in the $S_0$ state has been studied in a number of theoretical works. Carboxylic acid dimers,[43, 283–286] hydrogen fluoride oligomers,[287] water tetramers,[288] methanol tetramers [289] and mixed dimers[191] have been considered. A synchronous PT mechanism was assumed for the most stable cyclic structures.[290–292] Various dynamic methods were used to calculate the tunnel splittings on the basis of PES determined by *ab initio* calculations. Note that the magnitude of tunnel splitting is very sensitive to calculation details. Slight variations of the PES caused by the use of different basis sets [283] or insignificant modifications of the dynamic calculation procedure [288] can change the resulting value of tunnel splitting by two orders of magnitude. Experimental determination of the tunnel splitting in cyclic molecular complexes by microwave spectroscopy is difficult because of the absence of a permanent dipole moment. It was suggested that synchronous transfer of protons in methanol-based complexes takes place only in cyclic structures with an even number of molecules.[289]

**d. Proton transfer in molecular clusters in the $S_0$ and $S_1$ states**

Proton transfer in isolated 1 : 1 asymmetric complexes with one hydrogen bond in the $S_0$ state is usually not observed in the gas phase.[293–296] In neutral weak acid – base complexes ($FH : NH_3$ and $PhOH : NH_3$), the proton is localised near the 'acid' heteroatom. The potential profile along the proton coordinate corresponding to stretching of the O – H bond is single-well and highly asymmetric.[297, 298] As the strength of the acid increases, the proton moves to the base; the profile remains single-well but becomes

very smooth.[298] The potential energy surface for charged 1 : 1 complexes also has one minimum.[299, 300]

When considering ROH : $X_n$ type clusters where ROH is an 'acid' molecule (phenol, 1-naphthol, *etc.*) and $X_n$ are *n* solvent molecules that interact with the 'acid' (and with each other) through H-bonds, note that most of experimental data correspond to the electronic state $S_1$. Ammonia or water are used most often as solvents. In the case where $X_n = (H_2O)_n$ for *n* from 1 to 21, no PT was detected.[301] For $X_n = (NH_3)_n$, PT does take place in the $S_1$ state when $n = 3$ for 1-naphthol and $n = 5$ for phenol,[301, 302] because ammonia is a stronger base than water. Clusters consisting of several ammonia molecules, for example $(NH_3)_5$, are known to have a fairly high proton affinity.[20] Thus, the PES of phenol or 1-napthol clusters with ammonia in the $S_1$ state can have two minima.

Experimental and theoretical data allow one to draw an important conclusion, namely, there exists a threshold number of solvent (ammonia) molecules starting from which PT is possible[301–308] and an adequate description of the PT dynamics requires explicit consideration of the collective coordinate, which describes synchronous motion of molecules forming the first solvation shell[309, 310] and ensures favourable energy characteristics for the PT process.[311]

## 2. Liquid phase

The structure of the reaction site (and the whole reaction system) in the liquid phase depends on the properties of the solvent (polarity, proton-donor or proton-acceptor characteristics), reactant concentrations, temperature and impurities. Proton or hydrogen atom transfer is accompanied by the rearrangement of the solvation shell of the system,[312–314] which sharply complicates the process description at the molecular level. During the last five decades, enormous experimental material on liquid-phase reactions has been accumulated; however, interpretation of the results is the underbelly of most studies. The key problem is the difficulty of experimental determination of the geometric structures of reaction products in the liquid phase. In many cases, the product structures are postulated in order to bring the experimental data in the correspondence with the model used. The model is usually based on representing the isolated reaction complex as A—H···B or on placing the reaction complex in a cavity surrounded by a dielectric.

Thus, the molecular structure of the solvent and the problems caused by the presence of impurities (traces of water), counter-ion, complexation, *etc.* are usually neglected in the interpretation of experimental data.

### a. Proton transfer between neutral molecules in aprotic solvents

A number of terms are used in the literature to describe the PT in organic aprotic solvents:[315] proton exchange reactions, molecular exchange between H-bonded complexes, ion–molecular PT, and reversible PT in H-bonded complexes. The last-mentioned term appears the most appropriate for describing the PT between neutral molecules [see Eqn (99)]. Phenol and carboxylic acid derivatives are usually considered as acids, and pyridine derivatives, pyridine *N*-oxides and aliphatic amines are taken as bases. Halogen-substituted hydrocarbons and acetonitrile are the most typical solvents.

The proton transfer in H-bonded complexes is accompanied most often by a substantial increase in the dipole moment (to 10 D),[316] pointing to an appreciable change in the geometric and electronic structures of the complex induced by PT. The changes are detected by NMR, IR and UV spectroscopy and by measurement of dielectric properties. It is clear that in a 'strong base–weak acid' system, the equilibrium is shifted almost entirely to the left, while in a 'weak base–strong acid' system, it is shifted to the right. The degree of shifting of equilibrium (99) can be found from a plot where the value

$$\Delta pK_a = pK_a(HB^+) - pK_a(AH),$$

where $pK_a$ (the proton affinity), is laid off along the *x*-axis, while the *y*-coordinate is an observed quantity (the change in the dipole moment,[317] the $^1H$, $^{13}C$ or $^{15}N$ NMR chemical shift,[318] integral intensity of the A—H stretching vibration[319] or the centre of gravity of this band,[320] *etc.*). Usually, this gives an S-shaped curve whose inflection point corresponds to a 50% degree of PT. A feature of these dependences is sharp change in the spectral characteristic over a small range of variation of $\Delta pK_a$. The proton affinity,[320] the enthalpy of formation of the H-bonded complex,[321] or another quantity can be used instead of $\Delta pK_a$. The plots obtained in this case will have a break. A unified theory for explaining these dependences is missing. It was suggested[322] that a mobile equilibrium of the considered type exists in the liquid phase but this hypothesis provoked a lot of debate. According to another publication,[323] only one complex is formed in each case in which the proton shifts from $A^-$ to $B^+$ as the base becomes stronger and the acid becomes weaker. Nevertheless, in some cases, mobile equilibrium still does exist because the dependence under discussion does not have any break in systems without PT.[324]

Equilibrium (99) has been repeatedly studied by UV spectroscopy.[21, 325, 326] It was shown that depending on the dielectric constant of the solvent[327] or the solution pH,[328] different complexes with H-bonds are formed, in particular the $A^-\cdots H-B^+$ complex with the transferred proton. The UV absorption bands of these complexes markedly differ in frequency and intensity.

Most of the studies mentioned above give only qualitative characteristics of PT: the structure with the transferred proton is detected and the degree of PT is estimated. The reported equilibrium constants of the PT process (see, for example Refs 317 and 329) are often phenomenological (*i.e.*, they characterise a complex multistep process whose detailed mechanism is unknown). In the case of relatively weak acids and bases, the following reactions are most probable:[330–333] dimerisation of carboxylic acids or polymerisation of phenols; dissociation of the structure with a transferred proton to give free ions; and self-association of complexes with a transferred proton.

With excess free acid or base, other side reactions can also proceed to give ions like $(BHB)^+$, $(AHA)^-$, *etc.*[334–336] A review of the literature published before 1968 dealing with the secondary processes that accompany PT in solutions can be found in Chapter 8 of the monograph (Ref. 337).

It follows from the foregoing that experimental determination of the rate constant for a PT reaction in the conjugate acid–base system in an aprotic solvent in the $S_0$ state is a rather complicated task. Quantitative estimates of the PT kinetics in aprotic solvents were obtained in a number of the most recent studies.[338, 339] The kinetic H/D-isotope effect in the reaction between 2,4,6-trinitrotoluene and 1,8-diazabicyclo[5.4.0]undec-7-ene in benzonitrile was found to change from 18.3 to 14.5 as the temperature rises from 288 to 308 K.[338] The ratios of the pre-exponential factors ($\sim$2.5) and the difference between the activation energies ($\sim$2.1 kcal mol$^{-1}$) are also reported. In is suggested that these values point to a tunnelling mechanism of PT.

In a study of the PT in the complex of 2,4-dichlorophenol with triethylamine in chloroethane,[339] measurement of the temperature dependence of the chemical shift of the bridging proton made it possible to establish thermodynamic and kinetic characteristics of the PT process. It was concluded that in this case, the FES is almost symmetrical and has two minima. The free activation energy of PT at 195 K is only 8.9 kcal mol$^{-1}$ and the heat of the reaction is 0.2 kcal mol$^{-1}$. The rate constant of the forward PT reaction is 605 s$^{-1}$. The concentration dependences of these values were not studied in this publication;[339] therefore, the assignment of these characteristics to the PT process is not validated. Rather high reactant concentrations were used, 0.2 mol litre$^{-1}$ for phenol and 0.4–0.6 mol litre$^{-1}$ for amine. At these concentrations, dissociation of aggregates with high-molecular masses to give kinetically active components rather than the PT is the rate-determining step of the process.[340]

Subsequently, the occurrence of a competing process, namely, the formation of a complex consisting of two 2,4-dichlorophenol molecules and one triethylamine molecule was discovered.[331]

The PT kinetics in the $S_1$ state has been characterised more comprehensively than that for the $S_0$ state.[341–346] Depending on experimental conditions (temperature and solvent) and the nature of the reactants, the rate of this reaction can be limited by either non-adiabatic transitions or diffusion processes.[347]

The results of some other studies are briefly considered below. Study of H-bonded complexes of 7-hydroxyquinoline and methanol by UV spectroscopy [348] showed that PT takes place in the $S_1$ state of the 1 : 2 complex. The activation energy of this process equals 0.54 kcal mol$^{-1}$. The activation energy of the 'back' PT in the $S_0$ state is 4.2 kcal mol$^{-1}$ in $CH_3OH$ and 5.5 kcal mol$^{-1}$ in $CH_3OD$.

The PT kinetics in the $S_1$ state of 2-(2′-hydroxyphenyl)benzothiazole in aprotic non-polar solvents has been studied by femtosecond spectroscopy.[35, 349, 350] The formation of the keto-form upon PT was confirmed by the appearance of a spectral band corresponding to the N—H stretching vibrations.[349] The characteristic time of the PT is equal to 170 fs.[35] In 2-(2′-hydroxyphenyl)benzothiazole derivatives, the PT time varies from 100 to 200 fs. These times correspond to the motion of a proton with a great vibration amplitude and a frequency varying from 100 to 200 cm$^{-1}$ (see Ref. 350). A similar procedure has been used to estimate the rate constant for the PT in a 1-pyrenol – triethylamine complex using a number of organic solvents.[351] The characteristic time was equal to 1 ps and almost did not depend on the solvent polarity; the replacement of the bridging proton by deuterium also had only a slight influence on the rate constant.[351]

The kinetics of PT in the lower triplet electronically excited state has been studied in a number of publications.[352–355] The keto – enol tautomerism in the lower triplet state of 2-(2′-hydroxyphenyl)benzothiazole in hexane has been investigated.[352] It was found that the observed rate constant for PT almost does not depend on temperature below 70 K. The H/D-isotope effect is 30 at 200 K and more than 100 at 100 K. Proton transfer was concluded to follow a tunnelling mechanism.

Quantum-chemical calculations of the PES of a PT reaction in the $S_1$ state are usually carried out without explicit allowance for the presence of a solvent. High-level *ab initio* calculations [278, 356] are used when considering model photochemical systems, for instance, CIS calculations [357–358] are used for real systems with intramolecular PT (1-hydroxy-2-acetophenone [357]) or double PT (7-azaindole dimer [358, 359]).

A number of kinetic data have been obtained for synchronous transfer of several protons in hydrogen-bonded complexes in the $S_0$ state. Proton exchange in formic acid and methanol clusters in perdeuterated tetrahydrofuran has been studied by NMR spectroscopy.[360] The acid and methanol form 1 : 1 and 2 : 1 hydrogen-bonded complexes in which transfer of two or three protons (deuterons), respectively, takes place. The rate constant was measured in the temperature range from 255 to 335 K. No deviations from the linearity of the Arrhenius plots were found. The activation energy varies from 6.5 to 10 kcal mol$^{-1}$.

The PT reaction in the porphin ion [361] and the double proton transfer in the porphin molecule [362] in various aprotic solvents have also been studied by NMR. In these systems, one or two protons move in a four-well potential. The rate constants for hydrogen, deuterium and tritium transfer were determined over a broad temperature range. The Arrhenius dependence is clearly non-linear. The kinetic H/D-isotope effect equals 93(34) at $T = 240$ K and 16.5(11.4) at $T = 298$ K; the values for the porphin molecule are given in parentheses.

The mechanism of double PT in the formic acid dimer in the $S_1$ state in aprotic solvents has been studied in detail,[363] although there is still no consensus about its nature.

The PT structure and dynamics in the H-complexes of the M—H···H—OR type, where M—H is the $(PMe_3)_2(CO)_2$.(NO)W—H hydride ligand and H—OR is trifluoroacetic acid, have been vigorously studied in the last decade.[364] Low-temperature NMR and IR spectroscopy were used to obtain information on the PT kinetics and the activation barrier depending on the properties of H···H complexes, determined by the nature of the metal, the ligands and the medium (hexane, toluene and dichloroethane).[365, 366]

**b. Proton transfer in protic solvents**

Proton transfer in protic solvents (water, alcohols, *etc.*) requires special consideration because the reaction complex forms additional H-bonds with solvent molecules.[314] This complicates the PT and in some cases, also changes the reaction mechanism. Usually, four types of PT reactions in aqueous solutions are distinguished:[367] neutralisation, protolysis, hydrolysis and PT in a conjugate acid – base system. The first three reactions are complex processes, in which one cannot distinguish the individual characteristics of an elementary PT step. The last-mentioned reaction can be described as follows

$$(AH)\cdot nH_2O + (B)\cdot nH_2O \longrightarrow (A^-)\cdot nH_2O + (HB^+)\cdot nH_2O, \qquad (103)$$

where $n$ is the number of water molecules that interact with reacting molecules through the formation of H-bonds.

A large number of publications has been devoted to so-called abnormally high proton mobility in aqueous solutions. To interpret the obtained data, it is necessary to know the structure of the simplest stable proton hydrate. X-Ray diffraction and neutron diffraction methods as well as NMR provide little information due to the thermal motion of molecules in the liquid. Conclusions about the structure of the simplest proton solvate in aqueous solutions of acids are usually drawn by examining the vibrational spectra. It has been suggested initially that the simplest proton solvate is the hydroxonium ion, $H_3O^+$ (see Ref. 368). Thus, PT in the aqueous medium can be represented as

$$H_2O + H_3O^+ \longrightarrow H_3O^+ + H_2O. \qquad (104)$$

The PT process in water enriched in the $^{17}O$ isotope has been studied by NMR in the temperature range from 288 to 348 °C.[369, 370] The rate constant was found from broadening of the spectral lines. The results were described by the Arrhenius equation in which the rate constant for the PT is

$$k = 6.0 \times 10^{11} \exp\left(-\frac{2.4}{RT}\right) \text{ litre mol}^{-1}\ \text{s}^{-1}.$$

Thus, PT in water has a low activation energy. The lifetime of the simplest proton hydrate is 1 ps. (Most of modern theoretical studies rely on these experimental data; for example, see Ref. 371.) The hydroxonium ion really exists in solid and liquid systems if only one water molecule per acid proton is present.[368] The existence of this ion, whose vibrations are both IR- and Raman-active, in dilute aqueous solutions of acids is not confirmed experimentally.[372, 373]

The IR spectra of all systems containing proton hydrates exhibit continuous intense absorption in the range from 3500 to 800 cm$^{-1}$ (see Ref. 374). Studies devoted to this phenomenon are discussed in several reviews.[45, 375] According to Zundel's model,[376] $H_9O_4^+$ is the most stable ion – molecular species whose vibrations can be observed in the IR spectrum of a solution. In this model, a special role is played by the extremely high polarisability of the hydrogen bond. This feature is postulated for the O—H···O fragment. The origin of the continuous absorption can be explained by assuming strong interaction of the bridging proton with the medium. This model is widely used in many theoretical and experimental works, despite the fact that continuous absorption is observed when the formation of the $H_9O_4^+$ ion is impossible and the solvation effects are minimised (aprotic low-field solvent).[377, 378] Thus, continuous absorption may be due not only to the influence of the medium but also to intrinsic properties of ions with a symmetrical hydrogen bond, the simplest of them being the $H_5O_2^+$ ion.[379]

A particular theory could, in principle, be validated by MD simulation of the IR spectra. However, applicability of MD techniques to the simulation of spectral properties of the proton in aqueous solutions is quite limited. The trajectory length found by so-called *ab initio* MD methods [312] is several picoseconds; this is inadequate for calculating the IR spectrum of the solution.[380] Molecular-dynamic approaches based on the valence bond method either make use of a linear approximation of the system dipole moment [381, 382] or imply calculation of the vibrational spectrum by Fourier transform of the velocity autocorrelator.[383] However, the linear approximation is inapplicable to the description of the dipole moment of the $H_5O_2^+$ ion [379, 384] and the velocity autocorrelator was calculated for the Raman spectrum of this ion.[384]

Experimental data on PT reactions in protic solvents can be found in several reviews.[385, 386] A widely used non-aqueous solvent is methanol, which makes it possible to measure the rate constant for the PT over a broad temperature range, from −97 to 64 °C.[387] The double PT in the $(CH_3)_3NH^+ + CH_3OH + N(CH_3)_3$ system in methanol has been studied by NMR spectroscopy.[388] It was found that the activation energy decreases with an increase in the temperature: from 3.8 kcal $mol^{-1}$ at −97.8 °C to 2.2 kcal $mol^{-1}$ at 25 °C; a tunnelling mechanism for double PT was proposed.

The influence of the solvent on the PT can be taken into account using the variational TS theory (see Section III.1.b), numerical MD or Monte Carlo modelling (see Section III.2.b), models in terms of the continual description of the medium (see Section III.3), or various quantum-classical methods (see Section III.4). Molecular dynamics methods have been successfully used to describe PT in acid – base equilibria [199] and in model systems [231] simulating ionisation of HCl in water [389] and ester hydrolysis.[227] Self-consistent reaction field methods were used to simulate the PT dynamics in systems with strong hydrogen bonds [223] and in amino acids.[224] Combined (hybrid) approaches were used to describe the solvation of the hydroxide ion,[390] to model PT in systems with strong hydrogen bonds [232] and to calculate barriers to the PT reaction in water.[391]

**c. Hydrogen atom transfer in liquids**

A large number of reactions involving HAT take place in liquids. In particular, HAT limits the chain termination during oxidation of organic compounds in the liquid phase.[392] Data on the rate constants for HAT and the influence of the H/D isotope effect on these constants are summarised and discussed in monographs and reviews (see, for example, Refs 393 – 395), although usually it is impossible to draw an unambiguous conclusion on the magnitude of the tunnelling effect on the basis of experimental data because no reliable data on the temperature dependence of the kinetic H/D-isotope effect in HAT are available.

The hydrogen atom transfer in the first step of oxidation of 4*a*,4*b*-dihydrophenanthrene with dioxygen in 2,2,4-trimethylpentane has been studied at $T = 191 – 263$ K.[396] In this case, the Arrhenius plot is essentially non-linear. The experimental H/D-isotope effect is 95 at 242 K.[396] Arrhenius parameters were also found for the bimolecular elimination of a hydrogen atom from methanol in aqueous solutions in the temperature range from 283 to 359 K.[397] The corresponding activation energy amounted to 30 kJ $mol^{-1}$ and the observed rate constant at 25 °C was $2.8 \times 10^6$ litre $mol^{-1}$ $s^{-1}$. Comparison with the data for gas-phase reactions [259] shows that the interaction with the solvent leads to some acceleration of the reaction (∼25%).

A lot of data have been accumulated for intramolecular HAT.[398] In most cases, the experimental values for the kinetic isotope effect do not exceed 3.[398] The intramolecular HAT involved in the isomerisation of aryl radicals with bulky substituents has been characterised in sufficient detail.[399, 400] Isomerisation of 2,4,6-tri-*tert*-butylphenyl into 3,5-di-*tert*-butylneophenyl in cyclopropane has been studied by EPR in the temperature range from 113 to 247 K. It was found that due to steric hindrance, the abstraction of hydrogen from the solvent molecule is virtually impossible. Hydrogen atom transfer proceeds *via* a five-membered cyclic TS. The Arrhenius plot for the transfer of hydrogen and deuterium atoms is highly non-linear. The experimental kinetic H/D-isotope effect varies from 80 at 250 K to 13 000 at 120 K.

Various approaches are used for theoretical investigation of HAT reactions in the liquid phase. The variational TS theory is successfully used to calculate the temperature dependences of the reaction rate constant, H/D-isotope effect, the addition of a hydrogen atom to benzene [401] and elimination of a hydrogen atom from methanol [402] in aqueous solutions. Empirical models for the radical abstraction of hydrogen [403, 404] are used to classify the results of analysis of the experimental rate constants and activation energies for HAT reactions.

**d. Proton transfer in ion – molecular reactions in the liquid medium**

A PT reaction results in highly reactive systems: carbanions, carbocations, carbenes and ylides, *etc*. Therefore, ion – molecular reactions involving PT play an important role in organic chemistry.[405, 406] The rate and equilibrium constants for such reactions are determined by a variety of factors including the spatial and electronic structures of the reactants, their concentrations, the natures of the solvent and the catalyst and so on. Direct approach to the problem of elucidating the structure – reactivity relationship based on quantum chemistry and statistical physics techniques is seldom used for complex organic compounds. As a rule, methods of physical organic chemistry are used.[337, 405 – 407] At this level, the mechanisms of chemical reactions are considered in terms of empirical and semiempirical rules. These rules can be formulated in a quantitative form as linear free energy relationships.[337] Interpretation of the obtained results can be simplified by considering so-called intrinsic barriers (*i.e*., barriers for symmetrical reactions [26]) and the intrinsic rate constants for the PT in ion – molecular reactions.[408, 409] From the kinetic standpoint, this situation occurs in the case where the rates of forward and back reactions are equal, and from the thermodynamic standpoint, where the reaction heat is zero irrespective of temperature and pressure. The use of intrinsic rate constants allows one to separate the thermodynamic effects from purely kinetic effects.

The dependences of the rate constant for PT on the nature of the solvent, the substituents and the strength of the base are studied most often.[410 – 413] In the case of PT in carboxylic acids, this provides detailed characterisation for the relative contributions of the resonance and induction effects and the nature of the solvent to the increase in the CH acidity.[411, 413] For PT reactions involving radical cations, negative activation energies and H/D-isotope effect values smaller than unity are often obtained.[412] This may imply the existence of mechanisms alternative to the direct PT from the radical cation to the base. The H/D-isotope effects in the PT rate constant for the reaction of various methylarene radical cations and pyridine bases in dichloroethane have been estimated.[414] Depending on the structure of the reactants, they vary from 31 to 47. In the studies cited, the rate constants were usually determined at room temperature.

Numerous experimental works have been devoted to the PT from nitroalkanes to anions of various bases.[415] Usually these reactions are studied by spectrophotometry because the anions formed in the reaction exhibit strong absorption bands in the visible region. The PT from 1-nitro-1-(4-nitrophenyl)ethane to the hydroxyl ion has been studied. Aqueous acetonitrile was used as the solvent. The reaction was found to occur in two steps, the PT process taking place in the second step, which follows a unimolecular mechanism (irreversible decomposition of the 'kinetically important' intermediate). The PT kinetics has been studied in detail in the temperature range from 289 to 319 K. The rate constant for the PT (289 K) is 11.5 $s^{-1}$ and the primary isotope effect is 26. As the temperature increases to 319 K, the isotope effect decreases to 16.9. The difference between the activation energies and the ratio of the pre-exponential factors for proton

and deuteron transfer have been estimated.[415] The researchers believe that the obtained data point unambiguously to the tunnelling mechanism of the PT reaction.

**e. Coupled electron and proton transfer**

Coupled electron and proton transfer can occur for the electronically excited states of organic molecules containing two functional groups (for example, 6-hydroxyquinolinone) in aqueous solutions of acids or bases;[416] in donor–acceptor pairs such as $Ru(bipyridine)_3^{2+}$ – 3,5-dinitrobenzene;[417] in ruthenium complexes on a polycrystalline gold electrode;[418] in triads consisting of carotenoid–porphyrin–quinone molecules;[419] in proteins;[420] in photoactive centres of bacteria.[421]

The reaction in question takes place in a complex system which includes an electron and proton acceptor (Ac), several H-bonds and heteroatoms with a free electron pair and a proton donor (H-Dp). Its mechanism includes several successive steps:[422] (*i*) electron transfer on Ac to give a radical anion having a high proton affinity; (*ii*) the formation of a covalent bond between the radical anion $Ac^-$ and the proton; (*iii*) rearrangement of the system of hydrogen bonds resulting in elimination of the proton from the H-Dp donor to give the $Dp^-$ anion; (*iv*) recovery of $Dp^-$ to Dp; (*v*) the reverse rearrangement of hydrogen bonds resulting in the formation of the initial Ac and H-Dp.

The central point of this scheme is a sharp enhancement of the proton-acceptor properties of the molecule (functional group Ac) and the proton-donor properties of the molecule (functional group H-Dp) upon their oxidation. The rate-determining step of the reaction is electron transfer;[417] nevertheless, the rate constant changes when the bridging H atoms are replaced by D in the $Ru(bipyridine)_3^{2+}$ – 3,5-dinitrobenzene donor–acceptor pairs.[417] Experimental value for the H/D-isotope effect in the electron transfer varies from 1.34 to 1.7.[417]

The theory of these reactions is considered in Section III.3.d; the key references to theoretical studies are also given.

**f. Proton and hydrogen atom transfer in biologically active compounds**

Proton, hydrogen atom, and hydride ion transfer underlie a large number of processes which take place in biologically active compounds.

First, proton transfer plays a key role in bioenergetics,[423] which is concerned with the mechanisms of energy conversion in redox processes in living organisms. The modern views in this field are based on the 'chemiosmotic theory,' which implies the presence of an electrochemical potential difference ('proton gradient') in protein complexes[424,425] and in cytochrome *c*-oxidase.[426,427] Proton transfer through membranes takes place against the proton gradient, the thickness of biological membranes being about 40–60 Å.[425]

Second, proton and hydride ion transfer are key steps in one of the most versatile biological oxidation reactions, namely, dehydrogenation of an alcohol to give a ketone or an aldehyde.[428,429] The process is catalysed by dehydrogenase enzymes. These are dimers or tetramers composed of subunits with a molecular mass of 20 000–40 000. The removed hydrogen atoms (or hydride ions, or protons) migrate to hydrogen-transporting coenzymes, for example, nicotinamide adenine nucleotide, *etc*. The mechanism of this process is not entirely clear.[430]

Third, a large number of studies have been devoted to the role of strong (short) hydrogen bonds in enzyme-catalysed reactions.[13] These hydrogen bonds are assumed to stabilise intermediates and/or transition states in the reactions under interest.[14] On the PES of these H-bonds, two wells are separated by a very low barrier ($\sim$2 kcal mol$^{-1}$).[15]

For the first two of the above-mentioned types of process, detailed description of the thermodynamics and kinetics of PT and hydride ion transfer is missing. Therefore, of considerable interest are kinetic studies of HAT in enzymes.[431] Enzyme-catalysed C–H bond cleavage has been studied in detail.[432–433] A specific feature of this reaction is a very high kinetic H/D-isotope effect, which varies from 17 (see Ref. 434) to 56 (see Ref. 432). Hydrogen atom transfer in these systems is a rate-determining step of the complex process of C–H bond oxidation,[434] the rate constant for HAT ranging from several to several hundred reciprocal seconds. Study of the temperature dependence of the rate constants for H and D made it possible to estimate the activation energy, which can reach 24.5 kcal mol$^{-1}$ (see Ref. 433) and the pre-exponential factor. These experimental data suggest that HAT follows a tunnelling mechanism.

Extensive literature is devoted to the theoretical study of PT and HAT reactions in enzymic systems. In order to give a general idea of the methods and approaches used in this, rather specific field, we will mention the results of some most recent studies. Widely used are hybrid approaches[435–437] which combine quantum-chemical calculations of the PES in the models of reaction centres with calculation of the medium effects using MD or molecular mechanics methods. Oxidation of the enzyme cytochrome P450eryF has been studied;[435] proton tunnelling is described as a one-dimensional process (see Section III.1.a). The rate constants for HAT for three model enzymic reactions were calculated in terms of the variational transition state theory;[436] the calculated kinetic H/D-isotope effect is in satisfactory agreement with the experiment. The energy profiles of the PT involved in the hydrolysis of peptide bonds by a model enzyme have been obtained.[437] Phenomenological models have been used to describe the PT through biological membranes.[438]

## 3. Solids

The tunnelling mechanism of PT and HAT reactions in solids has been proved experimentally for a relatively small number of systems. These processes include both intermolecular and intramolecular reactions taking place in molecular crystals and in glasses. The results obtained are analysed in several reviews.[99,157,439–442] The conclusion concerning the tunnelling mechanism of the reactions is based on three facts:

— the temperature dependence of the reaction rate constant $k$ found experimentally deviates from the Arrhenius dependence over a broad temperature range, the Arrhenius dependence (*i.e.*, a linear dependence of $\log k$ on the reciprocal temperature) being observed at relatively high temperatures;

— a large H/D-isotope effect for the PT and HAT rate constants is found;

— the rate constants reach a plateau at relatively low temperatures.

**a. Proton transfer reactions**

The intramolecular PT in the molecular crystals of 9-hydroxyphenalenone derivatives has been studied by IR spectroscopy.[443,444] At 5 K, the IR spectra of 5-bromo- and 5-iodo-9-hydroxyphenalenone exhibit intense bands at 83 and 68 cm$^{-1}$, respectively. These bands disappear when the bridging proton is replaced by deuterium. It was suggested[443,444] that these bands correspond to tunnel splitting of the ground vibrational state in non-deuterated molecules.

The proton transfer in carboxylic acid dimers in the solid state often differs sharply from similar processes in the gas phase or in solutions. The reason is the crystal field effect, resulting in asymmetry of the FES along the PT coordinate for the O–H···O fragment, as opposed to the symmetric FES for the gas phase.[73,74] In the case of a molecular crystal of the benzoic acid dimer, the asymmetry was 35 cm$^{-1}$ (non-deuterated compound) and 108 cm$^{-1}$ (deuterated compound).[236] By passing to crystals doped with dye molecules, the crystal field effects can be minimised.[445] The double proton transfer in the crystals of benzoic acid dimer was studied by optical spectroscopy,[446] NMR[73,74] and quasi-elastic neutron scattering[446,447] over a broad temperature range. A sharp increase in the rate of proton transfer upon excitation of definite low-frequency vibrations has been established experimentally.[73] It was shown that the exper-

imental data (the NMR longitudinal relaxation time) can be adequately interpreted only using at least two-dimensional FES.[74]

Some data on PT dynamics have been obtained by non-elastic neutron scattering for various crystals with intra- and intermolecular hydrogen bonds.[448–454] Alternative models for the N···H···O hydrogen bond, ionic[448,449] and neutral ones,[451,452,454] have been proposed for PT in *N*-methylacetamide crystals (this process is a prototype of PT in peptides). The reasons for choosing these models are not analysed and remain obscure.

**b. Hydrogen atom transfer**

Apparently, a tunnelling mechanism of the HAT reaction in a solid was observed experimentally for the first time by Wang and Williams,[455] who studied the kinetics of hydrogen atom capture by methyl radicals in crystalline methyl isocyanate using EPR in the temperature range from 77 to 125 K. The Arrhenius plot for the corresponding rate constant is non-linear. The observed activation energy for the HAT reaction was 1.4 kcal mol$^{-1}$ at 77 K and increased to 4.5 kcal mol$^{-1}$ at 120 K. The isotope effect at 110 K exceeded 1000. It was impossible to obtain a more precise value, as the rate of abstraction of a deuterium atom was too low in the given temperature range to be measured by EPR. Later, a low-temperature limit of the HAT reaction rate has been found experimentally.[456] Detachment of a hydrogen atom from a methanol molecule (in glasses) by a methyl radical was studied by EPR in the temperature range from 15 to 89 K. At 40 K, a low-temperature plateau was reached. Analogous results have been obtained in a study of hydrogen atom elimination by a methyl radical from acetonitrile,[457] methanol[458] and other molecules.[399,400,459]

A large body of experimental data on the rate constant and H/D isotope effect in the temperature range from 1.4 to 300 K and for pressures from 1 to 30 atm has been obtained for HAT in the fluorene molecular crystals doped with acridine molecules.[153] In the lower triplet electronically excited state of the acridine admixture, the hydrogen atom is detached from the nearest fluorene molecule and passes to the acridine nitrogen atom. A typical feature of this reaction is the presence of several low-frequency (intra- and intermolecular) modes whose excitation accelerates HAT. This conclusion is based on investigation of the Raman spectra of these crystals at different temperatures.[154] For this reaction, calculations of the PES,[460] in particular those with explicit allowance for the crystal environment[216] were published. (The interpretation of the temperature dependence of the rate constant[152] is discussed in Section II.4.c.)

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## V. Supplement I. Generalised Langevin equation

For a stochastic variable $x$ corresponding to an oscillator with the mass $m_x$, the frequency $\omega_x$ and the force constant $\mu_x = m_x\omega_x^2$, the generalised Langevin equation (GLE) is written in the form[55,56,132,461]

$$m_x\ddot{x} + \int_0^t \beta(t-\tau)\dot{x}(\tau)\mathrm{d}\tau + \mu_x x = \mathrm{GRF}, \tag{I.1}$$

where GRF is the Gaussian random force (time-dependent). Due to the presence of the dissipative integral term, the dynamics of the coordinate $x(t)$ at time $t$ is dictated by its preceding evolution during the time period (0, $t$). Such equations are called equations with memory or non-Markov equations. The function $\beta(\tau)$ is called the memory kernel. The regular force $\mu_x x$ is linearised; as a result, Eqn (I.1) describes a harmonic oscillator in a medium. The force linearisation is not obligatory; if the corresponding potential $U(x)$ is not quadratic, the force $(-\partial U/\partial x)$ is used. The generalised Langevin equation with a double-well potential corresponds to the Kramers equation (13) and reduces to the latter if $\beta(t-\tau) = \gamma\,\delta(t-\tau)$. This particular case is called the local or Markovian limit. Equation (I.1) can be written in an alternative form

$$m_x\ddot{x} + \int_0^t \phi(t-\tau)x(\tau)\mathrm{d}\tau + \bar{\mu}_x x = \mathrm{GRF}, \tag{I.2}$$

with a renormalised force constant

$$\bar{\mu}_x = \mu_x + \beta(\tau = 0).$$

The dissipative force in Eqn I.2 depends on the coordinate rather than on the rate. The memory kernels $\beta(\tau)$ and $\phi(\tau)$ are related as follows:

$$\beta(\tau) = \int_\tau^\infty \phi(\tau')\mathrm{d}\tau'. \tag{I.3}$$

Important in the GLE theory is the Fourier – Laplace transform[462,463]

$$\phi(\omega) = \int_0^\infty \exp(i\omega t)\phi(t)\mathrm{d}t = \phi_1(\omega) + i\phi_2(\omega), \tag{I.4}$$

where $\phi(\omega)$ is a complex function, its real $[\phi_1(\omega)]$ and imaginary $[\phi_2(\omega)]$ components being even and odd functions of frequency, respectively.

In the steady-state regime, the average $\bar{x} = \langle x\rangle_T$ value is constant. Here $\langle ...\rangle_T$ means averaging over an equilibrated ensemble with temperature $T$. The correlation function of the coordinate $x$ is the fluctuation thermal average

$$C(t) = \left\langle \left[x(0) - \bar{x}\right]\left[x(t) - \bar{x}\right]\right\rangle_T. \tag{I.5}$$

When $t = 0$, this gives a statistical distribution of the stochastic variable $x$ with the variance $D[x] = C(t = 0)$. The Fourier transform of the function $C(t)$

$$C(\omega) = \int_{-\infty}^\infty \exp(i\omega t)C(t)\mathrm{d}t \tag{I.6}$$

is related to the imaginary part of the Fourier image of the memory kernel by the relation

$$C(\omega) = \hbar\phi_2(\omega)\mathrm{cth}\frac{\hbar\omega}{2k_\mathrm{B}T}. \tag{I.7}$$

This relation is called fluctuation-dissipation theorem (FDT).[132,461–463] Relation (I.7) holds for quantum systems, its range of applicability being wider than that for the classical GLE (I.2). At the classical limit ($\hbar\omega/k_\mathrm{B}T \ll 1$), equation (I.7) assumes the form

$$C(\omega) = \frac{2k_\mathrm{B}T}{\omega}\phi_2(\omega). \tag{I.8}$$

Since the function $C(t)$ can be calculated by molecular dynamics methods, relations (I.7) and (I.8) open up the way to microscopic calculation of the key GLE parameters. According to the KGH theory, in the case of GLE with a double-well potential $U(x)$ having a barrier with the height $U^{\neq}$, the following approximate expression for the reaction rate constant is valid:[55,60,464–469]

$$k_\mathrm{KGH} = \frac{\Omega}{2\pi}\sqrt{\frac{\mu_x}{\mu^{\neq}}}\exp\left[-\frac{U^{\neq}}{k_\mathrm{B}T}\right]. \tag{I.9}$$

Here, $\Omega$ is the decay frequency, which is determined by the characteristic equation

$$-m_x\Omega^2 + \phi(\Omega) + [\mu^{\neq} - \phi(\omega = 0)] = 0,$$
$$\mu^{\neq} = m_x(\omega^{\neq})^2\,, \qquad \text{(I.10)}$$
$$\mu_x = m_x\omega_x^2\,.$$

The function $\phi(\omega)$ is defined in Eqn (I.4); it is real for $\omega = 0$. The values $\mu_x$ and $\mu^{\neq}$ are force constants at the bottom of the reactant well and on the top of the barrier. On the barrier, the force constant is negative and the value $\mu^{\neq}$ is found as its absolute value. In a special case where the memory kernel $\beta(\tau)$ is proportional to the delta-function (Markovian limit), expressions (I.9), (I.10) lead to Eqns (11) and (14) for the rate constant. There exists a multimode generalisation of the KGH theory.[55, 60, 464–469] Its use is mentioned in Section III.3.a.

## VI. Supplement II. Spectral density

In the linear approximation, the collective coordinate of the medium which interacts with the coordinate of the reaction subsystem is the linear combination

$$Q = \sum_v C_v Q_v\,, \qquad \text{(II.1)}$$

where $Q_v$ are modes of the medium corresponding to masses $m_v$ and frequencies $\omega_v$. The spectral density [96, 131]

$$J(\omega) = \frac{\pi}{2}\sum_v \frac{C_v^2}{m_v\omega_v}\delta(\omega - \omega_v). \qquad \text{(II.2)}$$

is associated with the coordinate $Q$.

This formula can be used to calculate the sums over the modes of the medium containing the $C_v^2$ coefficients. It is equivalent to the sum rule:

$$\frac{2}{\tau}\int_0^{\infty} J(\omega)F(\omega)\mathrm{d}\omega = \sum_v \frac{C_v^2}{m_v\omega_v}F(\omega_v), \qquad \text{(II.3)}$$

where $F(\omega)$ is an arbitrary (rather smooth) function. The combination appearing in the right-hand part is often found in applications [see relation (69)]. By using the sum rule, one can pass from the discrete (simpler and more obvious) to a continuum (more convenient for calculations and transformations) description of the medium coordinates.

A different formulation is also useful. Let us consider a 'chemical' variable $x$ which interacts with modes of the medium according to a bilinear law. The interaction potential is

$$h_{x\Omega} = \mathrm{const}\, xQ = x\sum_v \bar{C}_v Q_v\,. \qquad \text{(II.4)}$$

Here, const has the dimensionality of a force constant:

$$\bar{C}_v = \mathrm{const}\, C_v\,.$$

In this case, the spectral density $\bar{J}(\omega)$

$$\bar{J}(\omega) = \frac{\pi}{2}\sum_v \frac{\bar{C}_v^2}{m_v\omega_v}\delta(\omega - \omega_v) = \mathrm{const}^2 J(\omega), \qquad \text{(II.5)}$$

is determined;[96, 131] here, the sum rule is derived from (II.3) by replacing $C_v$ by $\bar{C}_v$ and $J$ by $\bar{J}$.

The function $J(\omega)$ is often specified parametrically. It should disappear ($J = 0$) when $\omega = 0$ and should rapidly decay at frequencies exceeding some critical value, $\omega_\infty$. The typical representation for non-polar media is

$$J(\omega) = J_0\left(\frac{\omega}{\omega_\infty}\right)^n \exp\left(-\frac{\omega}{\omega_\infty}\right). \qquad \text{(II.6)}$$

The power $n$ is usually 1 for processes in disordered media (liquids). In three-dimensional molecular crystals, relation (II.6) corresponds to the Debye type phonon spectrum, $n = 2$. The frequency $\omega_\infty$ cutting the spectrum in the crystal corresponds to the Debye frequency.[462] In a similar representation for $\bar{J}(\omega)$, the constant factor $J_0$ is modified.

The spectral density is closely related to the classical generalised Langevin equation, which describes, in the case of interaction (II.4), the relaxation kinetics for the collective variable $x$. For the GLE in form (I.2), the key result is that

$$\bar{J}(\omega) = -\phi_2(\omega), \qquad \text{(II.7)}$$

where $\phi_2(\omega)$ is the imaginary component of the memory kernel [see Eqn (I.4)]. It allows one to calculate the spectral density for microscopic models of the medium by MD methods because, according to FDT (I.7), (I.8), the function $\phi_2(\omega)$ can be determined from the correlation function $C(t)$ (I.5) available from an MD computation.

## References


1. S Scheiner *Acc. Chem. Res.* **18** 174 (1985)
2. G A Sim, J M Robertson, T H Goodwin *Acta Crystallogr.* **8** 157 (1955)
3. N D Sokolov, M V Vener, V A Savel'ev *J. Mol. Struct.* **177** 93 (1988)
4. E D Stevens *Acta Crystallogr., Sect. B* **34** 544 (1978)
5. J Florian, B G Johnson *J. Phys. Chem.* **99** 5899 (1995)
6. T J Zielinski, R A Poirier *J. Comput. Chem.* **5** 466 (1984)
7. O Knop, K N Rankin, R J Boyd *J. Phys. Chem. A* **105** 6552 (2001)
8. S Gronert *J. Am. Chem. Soc.* **115** 10258 (1993)
9. W Siebrand, T A Wildman, M Z Zgierski *Chem. Phys. Lett.* **98** 108 (1983)
10. H Tachikawa, N Hokari, H Yoshida *J. Phys. Chem.* **97** 10035 (1993)
11. S Scheiner *Hydrogen Bonding. A Theoretical Perspective* (New York: Oxford University Press, 1997) Ch. 6.3
12. J Emsley *Struct. Bonding* **57** 147 (1984)
13. C L Perrin, J B Nielson *Annu. Rev. Phys. Chem.* **48** 511 (1997)
14. C S Cassidy, J Lin, P A Frey *Biochemistry* **36** 4576 (1997)
15. B Schiott, B B Iversen, G K H Madsen, F K Larsen, T C Bruice *Proc. Natl. Acad. Sci. USA* **95** 12799 (1998)
16. M J Frisch, A C Scheiner, H F Schaefer, J S Binkley *J. Chem. Phys.* **82** 4194 (1985)
17. L Jaroszewski, B Lesyng, J J Tanner, J A McCammon *Chem. Phys. Lett.* **175** 282 (1990)
18. A Camerman, D Mastropaolo, N Camerman *J. Am. Chem. Soc.* **105** 1584 (1983)
19. J J Dannenberg, R Rios *J. Phys. Chem.* **98** 6714 (1994)
20. O Cheshnovsky, S Leutwyler *J. Chem. Phys.* **88** 4127 (1988)
21. Th Zeegers-Huyskens, P Huyskens, in *Molecular Interactions* Vol. 2 (Eds H Ratajczak, W J Orville-Thomas) (New York: Wiley, 1981) p. 1
22. T Carrington, W H Miller *J. Chem. Phys.* **84** 4364 (1986)
23. N Shida, P F Barbara, J Almlöf *J. Chem. Phys.* **91** 4061 (1989)
24. M V Vener, S Scheiner, N D Sokolov *J. Chem. Phys.* **101** 9755 (1994)
25. R A Marcus *J. Phys. Chem.* **72** 4249 (1968)
26. P M Kiefer, J T Hynes *J. Phys. Chem. A* **106** 1850 (2002)
27. D Borgis, S Lee, J T Hynes *Chem. Phys. Lett.* **162** 19 (1989)
28. D Borgis, J T Hynes, in *The Enzyme Catalysis Process* (Eds A Cooper, J Houben, L Chien) (New York: Plenum, 1989) p. 293
29. D Borgis, G Tarjus, H Azzouz *J. Chem. Phys.* **97** 1390 (1992)
30. D Borgis, J T Hynes *Chem. Phys.* **170** 315 (1993)
31. A M Kuznetsov, J Ulstrup *Chem. Phys.* **188** 131 (1994)
32. J L Herek, S Pedersen, L Banares, A H Zewail *J. Chem. Phys.* **97** 9046 (1992)
33. S Lochbrunner, A J Wurzer, E Riedle *J. Chem. Phys.* **112** 10699 (2000)
34. S Y Arzhantsev, S Takeuchi, T Tahara *Chem. Phys. Lett.* **330** 83 (2000)
35. F Laermer, T Elsaesser, W Kaiser *Chem. Phys. Lett.* **148** 119 (1988)

36. C C Costain, G P Srivastava *J. Chem. Phys.* **41** 1620 (1964)
37. S L Baughcum, R W Duerst, W F Rowe, Z Smith, E B Wilson *J. Am. Chem. Soc.* **103** 6296 (1981)
38. K Tanaka, H Honjo, T Tanaka, H Kohguchi, Y Ososhima, Y Endo *J. Chem. Phys.* **110** 1969 (1999)
39. K Fuke, K Kaya *J. Phys. Chem.* **93** 614 (1989)
40. H Sekiya, Y Nagashima, Y Nishimura *J. Chem. Phys.* **92** 5761 (1990)
41. H Sekiya, Y Nagashima, T Tsuji, Y Nishimura, A Mori, H Takeshita *J. Phys. Chem.* **95** 10311 (1991)
42. K Nishi, H Sekiya, H Kawakami, A Mori, Y Nishimura *J. Chem. Phys.* **111** 3961 (1999)
43. N Shida, P F Barbara, J Almlöf *J. Chem. Phys.* **94** 3633 (1991)
44. G Zundel, in *The Hydrogen Bond. Recent Developments in Theory and Experiments* Vol. 2 (Eds P Schuster, G Zundel, C Sandorfy) (Amsterdam: North-Holland, 1976) p. 681
45. G Zundel *Adv. Chem. Phys.* **111** 1 (2000)
46. N Rougeau, C Kubash *Chem. Phys. Lett.* **299** 120 (1999)
47. N D Sokolov, V A Savel'ev *Chem. Phys.* **181** 305 (1994)
48. S A Barton, W R Thorson *J. Chem. Phys.* **71** 4263 (1979)
49. J Manz, R Meyer, E Pollak, J Römelt, H H R Schor *Chem. Phys.* **83** 333 (1984)
50. V Spirko, G H F Diercksen, A J Sadlej, M Urban *Chem. Phys. Lett.* **161** 519 (1989)
51. V C Epa, W R Thorson *J. Chem. Phys.* **92** 473 (1990)
52. M V Vener, S Scheiner *J. Phys. Chem.* **99** 642 (1995)
53. A Rabold, R Bauer, G Zundel *J. Phys. Chem.* **99** 1889 (1995)
54. H A Kramers *Physica (Utrecht)* **7** 284 (1940)
55. P Hänggi, P Talkner, M Borcovec *Rev. Mod. Phys.* **62** 251 (1990)
56. R F Grote, G T Hynes *J. Chem. Phys.* **73** 2715 (1980)
57. Yu I Dakhnovskii, A A Ovchinnikov *Khim. Fiz.* **5** 36 (1986) [a]
58. Y I Dakhnovskii, A A Ovchinnikov *Mol. Phys.* **58** 237 (1986)
59. E Pollak *J. Chem. Phys.* **85** 865 (1986)
60. E Pollak, in *Dynamics of Molecules and Chemical Reactions* (Eds R E Wyatt, J Z H Zhang) (New York: Marcel Dekker, 1996) p. 617
61. D Chandler *Introduction to Modern Statistical Mechanics* (New York: Oxford University Press, 1987)
62. J T Hynes, in *Theory of Chemical Reaction Dynamics* Vol. 14 (Ed. M Baer) (Boca Raton, FL: CRC Press, 1985) p. 171
63. A Staib, D Borgis, J T Hynes *J. Chem. Phys.* **102** 2487 (1995)
64. M V Basilevsky, A V Soudackov, M V Vener *Chem. Phys.* **200** 87 (1995)
65. M V Basilevsky, M V Vener, G V Davidovich, A V Soudackov *Chem. Phys.* **208** 267 (1996)
66. D F Calef, P G Wolynnes *J. Phys. Chem.* **87** 3387 (1983)
67. J T Hynes *J. Phys. Chem.* **90** 3701 (1986)
68. I Rips, J Jortner *J. Chem. Phys.* **87** 6513 (1987)
69. M V Vener, I V Rostov, A V Soudackov, M V Basilevsky *Chem. Phys.* **254** 249 (2000)
70. E A Pshenichnov, N D Sokolov *Int. J. Quantum Chem.* **1** 855 (1967)
71. A Sarai *J. Chem. Phys.* **76** 5554 (1982)
72. S Okuyama, D W Oxtoby *J. Chem. Phys.* **88** 2405 (1988)
73. A Stockli, B H Meier, R Keis, R Meyer, R R Ernst *J. Chem. Phys.* **93** 1502 (1990)
74. R Meyer, R R Ernst *J. Chem. Phys.* **93** 5518 (1990)
75. V P Sakun, M V Vener, N D Sokolov *J. Chem. Phys.* **105** 379 (1996)
76. D Antoniou, S D Schwartz *J. Chem. Phys.* **108** 3620 (1998)
77. D Antoniou, S D Schwartz *J. Chem. Phys.* **109** 2287 (1998)
78. E E Nikitin, S Ya Umansky *Theory of Slow Atomic Collisions* (Berlin; Heidelberg: Springer, 1984)
79. F T Smith *Phys. Rev.* **179** 111 (1969)
80. M Desouter-Lecomle, J C Lorquet *J. Chem. Phys.* **66** 4006 (1977)
81. R Cimiraglia, M Persico *Mol. Phys.* **38** 1707 (1979)
82. N D Sokolov, M V Vener, V A Savel'ev *J. Mol. Struct.* **222** 365 (1990)
83. A I Burshtein *Lektsii po Kursu 'Kvantovaya Kinetika'* (Lectures on the Course 'Quantum Kinetics') (Novosibirsk: Novosibirsk State University, 1968) Vol. 2
84. A I Burshtein, B I Yakobson *Khim. Vys. Energ.* **14** 291 (1980) [b]
85. B I Yakobson, A I Burshtein *Chem. Phys.* **49** 385 (1980)
86. A I Burshtein, A V Storozhev *Chem. Phys.* **119** 1 (1988)
87. L D Zusman *Chem. Phys.* **49** 295 (1980)
88. E E Nikitin *Teoriya Elementarnykh Atomno-Molekulyarnykh Protsessov v Gazakh* (The Theory of Elementary Atom – Molecule Processes in Gases) (Moscow: Khimiya, 1970)
89. L D Zusman *Kinet. Katal.* **27** 775 (1986) [c]
90. A Douhal, F Lahmani, A H Zewail *Chem. Phys.* **207** 477 (1996)
91. P Pechukas, in *Dynamics of Molecular Collisions* (Ed. W H Miller) (New York: Plenum, 1976) p. 269
92. W H Miller *Acc. Chem. Res.* **26** 174 (1993)
93. W H Miller *Adv. Chem. Phys.* **101** 853 (1997)
94. W H Miller *J. Phys. Chem. A* **102** 793 (1998)
95. I I Gol'dman, V D Krivchenkov *Sbornik Zadach po Kvantovoi Mekhanike* (Collection of Problems on Quantum Mechanics) (Moscow: Nauka, 1970)
96. A O Caldeira, A Leggett *Ann. Phys. (USA)* **149** 374 (1983)
97. V A Benderskii, D E Makarov, C A Wight *Adv. Chem. Phys.* **88** 1 (1994)
98. P Hänggi, in *Activated Barrier Crossing. Applications in Physics, Chemistry and Biology* (Eds G R Fleming, P Hänggi) (Singapore: World Scientific, 1993) p. 268
99. V I Gol'danskii, L I Trakhtenberg, V N Flerov *Tunnel'nye Yavleniya v Khimicheskoi Fizike* (Tunnelling Phenomena in Chemical Physics) (Moscow: Nauka, 1986)
100. W H Miller *J. Chem. Phys.* **62** 1899 (1975)
101. C G Callan, S Coleman *Phys. Rev. D* **16** 1762 (1977)
102. P G Wolynes *Phys. Rev. Lett.* **47** 968 (1981)
103. H Grabert, U Weiss *Phys. Rev. Lett.* **53** 1787 (1984)
104. Y I Dakhnovskii, A A Ovchinnikov *Phys. Lett. A* **113** 147 (1985)
105. V I Gol'danskii *Dokl. Akad. Nauk SSSR* **124** 1261 (1959) [d]
106. A Kuppermann, J A Kaye, J P Dwyer *Chem. Phys. Lett.* **74** 257 (1980)
107. G Hauke, J Manz, J Römelt *J. Chem. Phys.* **73** 5040 (1980)
108. G C Schatz, A Kuppermann *J. Chem. Phys.* **65** 4668 (1976)
109. R B Bernstein (Ed.) *Atom – Molecule Collision Theory* (New York: Plenum, 1979)
110. T Su, M T Bowers, in *Gas-Phase Ion Chemistry* Vol. 1 (Ed. M T Bowers) (New York: Academic Press, 1979) p. 84
111. D G Truhlar (Ed.) *Potential Energy Surfaces and Dynamics Calculations* (New York: Plenum, 1981)
112. R D Levine, R B Bernstein *Molecular Reaction Dynamics and Chemical Reactivity* (New York: Oxford University Press, 1987)
113. M Y Ovchinnikova *Chem. Phys.* **19** 313 (1977)
114. M Y Ovchinnikova *Chem. Phys.* **36** 85 (1979)
115. T F George, W H Miller *J. Chem. Phys.* **57** 2458 (1972)
116. W H Miller *Adv. Chem. Phys.* **25** 69 (1974)
117. J Manz, R Meyer, J Römelt *Chem. Phys. Lett.* **96** 607 (1983)
118. V K Babamov, R A Marcus *J. Chem. Phys.* **74** 1790 (1981)
119. V K Babamov, V Lopez, R A Marcus *Chem. Phys. Lett.* **101** 507 (1983)
120. V K Babamov, V Lopez, R A Marcus *J. Chem. Phys.* **78** 5621 (1983)
121. V Lopez, V K Babamov, R A Marcus *J. Chem. Phys.* **81** 3962 (1984)
122. M V Basilevsky, G E Chudinov, V M Ryaboy *Chem. Phys.* **104** 281 (1986)
123. R Kubo, I Toyozawa *Prog. Theor. Phys.* **13** 160 (1955)
124. V G Levich, R R Dogonadze *Dokl. Akad. Nauk SSSR* **124** 123 (1959) [d]
125. V G Levich *Adv. Electrochem. Eng.* **4** 249 (1965)
126. R R Dogonadze, A M Kuznetsov *Kinetika Khimicheskikh Reaktsii v Polyarnykh Rastvoritelyakh. Fizicheskaya Khimiya. Kinetika (Itogi Nauki i Tekhniki)* [Kinetics of Chemical Reactions in Polar Solvents. Physical Chemistry. Kinetics (Advances in Science and Engineering Series)] (Moscow: Izd. VINITI, 1973)
127. J Ulstrup *Charge Transfer Processes in Polar Media* (Berlin: Springer, 1979)
128. B Fain *Theory of Rate Processes in Condensed Media* (Berlin: Springer, 1980)
129. A M Kuznetsov, J Ulstrup *Electron Transfer in Chemistry and Biology* (Chichester: Wiley, 1999)
130. A J Leggett, S Chakravarty, A T Dorsey, M P A Fisher, A Gard, W Zwegger *Rev. Mod. Phys.* **59** 1 (1987)
131. U Weiss *Quantum Dissipative Systems. Series in Modern Condensed Matter Physics* Vol. 2 (Singapore: World Scientific, 1999)

132. S Adelman *Adv. Chem. Phys.* **44** 143 (1980)
133. A A Ovchinnikov, M Ya Ovchinnikova *Zh. Eksp. Tekhn. Fiz.* **56** 1278 (1969)
doi 134. J S Bader, R A Kuharski, D Chandler *J. Chem. Phys.* **99** 230 (1990)
doi 135. X Y Song, R A Marcus *J. Chem. Phys.* **99** 7768 (1993)
136. R R Dogonadze, A M Kuznetsov *Elektrokhimiya* **7** 763 (1971) [e]
137. R R Dogonadze, A M Kuznetsov *Phys. Status Solidi B* **53** 439 (1972)
138. R R Dogonadze, E M Itskovich, A M Kuznetsov, M A Vorotyntsev *J. Phys. Chem.* **79** 2827 (1975)
doi 139. R R Dogonadze, A M Kuznetsov, M A Vorotyntsev, M G Zaqaraia *J. Electroanal. Chem.* **75** 315 (1977)
doi 140. J Tang, S H Lin *J. Chem. Phys.* **107** 3485 (1997)
doi 141. G Lang, E Palladino, U Weiss *Chem. Phys.* **244** 111 (1999)
doi 142. R R Dogonadze, A M Kuznetsov, V G Levich *Electrochim. Acta* **13** 1025 (1968)
143. E D German, A M Kuznetsov, R R Dogonadze *J. Chem. Soc., Faraday Trans. 2* **76** 1128 (1980)
144. N Brünische-Olsen, J Ulstrup *J. Chem. Soc., Faraday Trans. 1* **75** 205 (1979)
145. E D German, A M Kuznetsov. *J. Chem. Soc., Faraday Trans. 2* **77** 2203 (1981)
146. A M Kuznetsov *Aspects Electrochem.* **20** 95 (1989)
147. E D German, A M Kuznetsov *Kinetika Zhidkofaznykh Reaktsii Perenosa Zaryada* (Kinetics of Liquid-Phase Charge Transfer) (Moscow: Izd. VINITI, 1990)
doi 148. L I Trakhtenberg, V I Klochikhin, S Ya Pshezetsky *Chem. Phys.* **69** 121 (1982)
doi 149. D Borgis, G T Hynes *J. Phys. Chem.* **100** 1118 (1996)
doi 150. Z K Smedarchina, W Siebrand *Chem. Phys.* **170** 347 (1993)
doi 151. W Siebrand, Z K Smedarchina, M Z Zgierski, A Fernandez-Ramos *Int. Rev. Phys. Chem.* **18** 5 (1999)
doi 152. L I Trakhtenberg, V I Klochikhin *Chem. Phys.* **232** 175 (1998)
153. B Prass, D Stehlik, I Y Chan, L I Trakhtenberg, V L Klochikhin *Ber. Bunsen-Ges. Phys. Chem.* **102** 498 (1998)
doi 154. B Prass, J P Colpa, D Stehlik *Chem. Phys.* **136** 187 (1989)
doi 155. G K Ivanov, M A Kozhushner, L I Trakhtenberg *J. Chem. Phys.* **113** 1992 (2000)
156. D G Truhlar, A D Isaakson, B C Garrett, in *Theory of Chemical Reactions* Vol. 4 (Ed. M Baer) (Boca Raton, FL: CRC Press, 1985)
157. V A Benderskii, D E Makarov, C A Wight *Chemical Dynamics at Low Temperatures* (New York: Wiley, 1994)
158. R A Marcus *J. Chem. Phys.* **45** 4493 (1966)
doi 159. M V Basilevsky *Chem. Phys.* **24** 81 (1977)
160. W H Miller, N C Handy, J E Adams *J. Chem. Phys.* **72** 99 (1980)
161. K Fukui *J. Phys. Chem.* **74** 4161 (1970)
doi 162. D G Truhlar, B C Garrett, S J Klippenstein *J. Phys. Chem.* **100** 12771 (1996)
163. D G Truhlar, B C Garrett *Acc. Chem. Res.* **13** 440 (1980)
doi 164. D G Truhlar, B C Garrett *Annu. Rev. Phys. Chem.* **35** 159 (1984)
165. E Wigner *J. Chem. Phys.* **5** 720 (1937)
166. B C Garrett, D G Truhlar *J. Phys. Chem.* **83** 1079 (1979)
167. B C Garrett, D G Truhlar *J. Chem. Phys.* **81** 309 (1984)
168. B C Garrett, D G Truhlar *J. Phys. Chem.* **95** 10374 (1991)
doi 169. G K Schenter, R P McRae, B C Garrett *J. Chem. Phys.* **97** 9116 (1992)
doi 170. R P McRae, G K Schenter, B C Garrett, G R Hynes, G A Voth, G C Schatz *J. Chem. Phys.* **97** 7392 (1992)
doi 171. R P McRae, B C Garrett *J. Chem. Phys.* **98** 6929 (1993)
doi 172. R P McRae, G K Schenter, B C Garrett *J. Chem. Soc., Faraday Trans.* **93** 997 (1997)
doi 173. C Alhambra, J Gao, J C Corchado, J Villa, D G Truhlar *J. Am. Chem. Soc.* **121** 2253 (1999)
doi 174. C Alhambra, J C Corchado, M L Sanchez, J L Gao, D G Truhlar *J. Am. Chem. Soc.* **122** 8197 (2000)
doi 175. R P McRae, G K Schenter, B C Garrett, Z Svetlicic, D G Truhlar *J. Chem. Phys.* **115** 8460 (2001)
176. V A Benderskii *Izv. Akad. Nauk, Ser. Khim.* **12** 2215 (1999) [f]
doi 177. V A Benderskii, E V Vetoshkin, S Yu Grebenshchikov, L von Laue, H P Trommsdorff *Chem. Phys.* **219** 119 (1997)
doi 178. V A Benderskii, E V Vetoshkin, L von Laue, H P Trommsdorff *Chem. Phys.* **219** 143 (1997)
doi 179. V A Benderskii, E V Vetoshkin, H P Trommsdorff *Chem. Phys.* **234** 153 (1998)
doi 180. V A Benderskii, E V Vetoshkin. *Chem. Phys.* **234** 173 (1998)
181. V A Benderskii, S Y Grebenshchikov, E V Vetoshkin, G V Milnikov, D E Makarov *J. Phys. Chem.* **98** 3300 (1994)
doi 182. V A Benderskii, E V Vetoshkin, I S Irgibaeva, H P Trommsdorff *Chem. Phys.* **262** 393 (2000)
doi 183. V A Benderskii, V I Goldanski, D E Makarov *Chem. Phys.* **154** 407 (1991)
doi 184. A Fernandez-Ramos, Z Smedarchina, M Z Zgierski, W Siebrand *J. Chem. Phys.* **109** 1004 (1998)
doi 185. Z Smedarchina, M Z Zgierski, W Siebrand, P M Kozlowski *J. Chem. Phys.* **109** 1014 (1998)
doi 186. Z Smedarchina, W Siebrand, M Z Zgierski *J. Chem. Phys.* **104** 1203 (1996)
doi 187. W Siebrand, M Z Zgierski, Z Smedarchina *Chem. Phys. Lett.* **279** 377 (1997)
doi 188. Z Smedarchina, W Siebrand, A Fernandez-Ramos, L Gorb, J Leszczynski *J. Chem. Phys.* **112** 566 (2000)
doi 189. A Fernandez-Ramos, Z Smedarchina, M Z Zgierski *J. Chem. Phys.* **113** 2662 (2000)
doi 190. A Fernandez-Ramos, Z Smedarchina, W Siebrand, M Z Zgierski *J. Chem. Phys.* **113** 9714 (2000)
doi 191. A Fernandez-Ramos, Z Smedarchina, J Rodriges-Otero *J. Chem. Phys.* **114** 1567 (2001)
doi 192. H Nakamura, G V Milnikov *J. Chem. Phys.* **115** 6881 (2001)
doi 193. K Yagi, T Taketsugu, K Hirao *J. Chem. Phys.* **115** 10 655 (2001)
doi 194. C S Tautermann, A F Voegele, T Loerting, K R Liedl *J. Chem. Phys.* **117** 1962 (2002)
195. A Warshel *J. Phys. Chem.* **86** 2218 (1982)
doi 196. A Warshel, J K Hwang *J. Chem. Phys.* **84** 4938 (1986)
197. J-K Hwang, G King, S Creighton, A Warshel *J. Am. Chem. Soc.* **110** 5297 (1988)
198. A I Voronin, V I Osherov *Dinamika Molekulyarnykh Reaktsii* (Dynamics of Molecular Reactions) (Moscow: Nauka, 1990)
doi 199. D Borgis, J T Hynes *J. Chem. Phys.* **94** 3619 (1991)
doi 200. H Azzouz, D Borgis *J. Chem. Phys.* **98** 7361 (1993)
doi 201. H Azzouz, D Borgis *J. Mol. Liq.* **61** 17 (1994)
doi 202. D Laria, G Ciccoti, M Ferrario, R Kapral *J. Chem. Phys.* **97** 378 (1992)
doi 203. D Laria, G Ciccoti, M Ferrario, R Kapral *Chem. Phys.* **180** 181 (1994)
doi 204. S Hammes-Schiffer, J C Tully *J. Chem. Phys.* **101** 4657 (1994)
205. S Hammes-Schiffer, J C Tully *J. Phys. Chem.* **99** 5793 (1995)
doi 206. S Hammes-Schiffer *J. Phys. Chem. A* **102** 10 443 (1998)
207. M Ya Ovchinnikova *Khim. Fiz.* **4** 3 (1985) [a]
doi 208. M V Basilevsky, G E Chudinov *Chem. Phys.* **157** 345 (1991)
doi 209. M V Basilevsky, G E Chudinov, M D Newton *Chem. Phys.* **179** 263 (1994)
210. Y-P Liu, M D Newton *J. Phys. Chem.* **99** 12382 (1995)
doi 211. M V Basilevsky, G E Chudinov, I V Rostov, Y-P Liu, M D Newton *J. Mol. Struct. (THEOCHEM)* **371** 191 (1996)
doi 212. M D Newton, I V Rostov, M V Basilevsky *Chem. Phys.* **232** 201 (1998)
213. J Tomasi, M Persico *Chem. Rev.* **24** 2027 (1994)
doi 214. M V Basilevsky, I V Rostov, M D Newton *Chem. Phys.* **232** 189 (1998)
doi 215. A Soudackov, S Hammes-Schiffer *J. Chem. Phys.* **111** 4672 (1999)
doi 216. V A Tikhomirov, A V Soudackov, M V Basilevsky *J. Phys. Chem. A* **105** 3226 (2001)
doi 217. A V Soudackov, S Hammes-Schiffer *Chem. Phys. Lett.* **299** 503 (1999)
doi 218. A Soudackov, S Hammes-Schiffer *J. Am. Chem. Soc.* **121** 10598 (1999)
doi 219. S Hammes-Schiffer *Acc. Chem. Res.* **34** 273 (2001)
doi 220. I Rostov, S Hammes-Schiffer *J. Chem. Phys.* **115** 285 (2001)
doi 221. R I Cukier *J. Phys. Chem.* **100** 15 428 (1996)
doi 222. R I Cukier, D G Nocera *Annu. Rev. Phys. Chem.* **49** 337 (1998)
doi 223. M F Ruiz-Lopez, A Oliva, I Tunón, J Bertrén *J. Phys. Chem. A* **102** 10728 (1998)
doi 224. F R Tornada, E Silla, I Tunón, D Rinaldi, M F Ruiz-Lopez *Theor. Chem. Acc.* **104** 89 (2000)

225. D F Coker, in *Computer Simulation in Chemical Physics* (Eds M P Alen, D S Tildesley) (Boston: Kluwer Academic, 1993) p. 315
226. S Okazaki *Adv. Chem. Phys.* **118** 191 (2001)
227. M F Lensik, J Mavri, H J C Berendsen *J. Comput. Chem.* **20** 886 (1999)
228. J Mavri, H J C Berendsen, W F van Gunsteren *J. Phys. Chem.* **97** 13 469 (1993)
229. P Bala, P Grochowski, B Lesyng, J A McCammon *J. Phys. Chem.* **100** 2535 (1996)
230. P Bala, P Grochowski, B Lesyng, J A McCammon *Ber. Bunsen-Ges. Phys. Chem.* **102** 580 (1998)
231. P Bala, B Lesyng, J A McCammon *Chem. Phys.* **180** 271 (1994)
232. I Tunòn, M T C Martins-Costa, C Millot, M F Ruiz-Lopez *J. Chem. Phys.* **106** 3633 (1997)
233. J S Cao, G A Voth *J. Chem. Phys.* **105** 6856 (1996)
234. T Miyazaki, T Shiba, K Fueki, Y Kamiya *J. Phys. Chem.* **95** 9115 (1991)
235. R Gelabert, M Moreno, J M Lluch *Can. J. Chem.* **75** 1229 (1997)
236. T Agaki, F Imashiro, T Terao, N Hirota, S Hayashi *Chem. Phys. Lett.* **139** 331 (1987)
237. N D Sokolov *Dokl. Akad. Nauk SSSR* **60** 825 (1948) [d]
238. J C Weisshaar, T S Zwier, S R Leone *J. Chem. Phys.* **75** 4873 (1981)
239. V M Bierbaum, G B Ellison, S R Leone, in *Gas-Phase Ion Chemistry* Vol. 3 (Ed. M T Bowers) (New York: Academic Press, 1984) p. 1
240. B D Bean, F Fernandez-Alonso, R N Zare *J. Phys. Chem. A* **105** 2228 (2001)
241. P Kebarle *J. Mass Spectrom.* **32** 922 (1997)
242. D H Aue, M T Bowers, in *Gas-Phase Ion Chemistry* Vol. 2 (Ed. M T Bowers) (New York: Academic Press, 1979) p. 1
243. M Meot-Ner, F H Field *J. Chem. Phys.* **64** 277 (1976)
244. Kh S Bagdasar'yan *Teoriya Radikal'noi Polimerizatsii* (The Theory of Radical Polymerisation) (Moscow: Nauka, 1966)
245. M V Bazilevsky, E A Trosman *Usp. Khim.* **41** 3 (1972) [*Russ. Chem. Rev.* **41** 1 (1972)]
246. V N Kondrat'ev, E E Nikitin, A I Reznikov, S Ya Umanskii *Termicheskie Bimolekulyarnye Reaktsii v Gazakh* (Thermal Bimolecular Reactions in Gases) (Moscow: Nauka, 1976)
247. A A Westenberg, N de Haas *J. Chem. Phys.* **47** 1393 (1967)
248. D N Mitchell, D J Leroy *J. Chem. Phys.* **58** 3449 (1973)
249. A Kupermann, in *Theoretical Chemistry. Theory of Scattering: Papers in Honor of Henry Eyring* Vol. 6, Pt. A (Ed. D Henderson) (New York: Academic Press, 1981) p. 79
250. M V Basilevsky, V M Ryaboy *Adv. Quantum Chem.* **15** 1 (1982)
251. O I Tolstikhin, H Nakamura *J. Chem. Phys.* **108** 8899 (1998)
252. P Honvault, J M Launay *J. Chem. Phys.* **114** 1057 (2001)
253. S Sukiasyan, H D Meyer *J. Phys. Chem. A* **105** 2604 (2001)
254. P F Fennelly, J D Payzant, R S Hemsworth, D K Bohme *J. Chem. Phys.* **60** 5115 (1974)
255. B B Grayce, R T Skodje *J. Chem. Phys.* **95** 7249 (1991)
256. C Kubach, G N Vien, M Richard-Viard *J. Chem. Phys.* **94** 1929 (1991)
257. A Weaver, R B Metz, S E Bradforth, D M Neumark *J. Phys. Chem.* **92** 5558 (1988)
258. I M Waller, T N Kitsopoulos, D M Neumark *J. Phys. Chem.* **94** 2240 (1990)
259. J F Meagher, P Kim, J H Lee, R B Timmons *J. Phys. Chem.* **78** 2650 (1974)
260. J E Bartmess, R T McIver, in *Gas-Phase Ion Chemistry* Vol. 2 (Ed. M T Bowers) (New York: Academic Press, 1979) p. 87
261. J B Cumming, P Kebarle *Can. J. Chem.* **56** 1 (1978)
262. G Caldwell, R Renaeboog, P Kebarle *Can. J. Chem.* **67** 611 (1989)
263. R W Taft, I A Koppel, R D Topson, F Anvia *J. Am. Chem. Soc.* **112** 2047 (1990)
264. M I Kabachnik *Usp. Khim.* **48** 1523 (1979) [*Russ. Chem. Rev.* **48** 814 (1979)]
265. S G Lias, J F Liebman, R D Levin *J. Phys. Chem. Ref. Data Suppl.* **1** 695 (1984)
266. S G Lias, J E Bartmess, J F Liebman, J L Holmes, R D Levin, W G Mallard *J. Phys. Chem. Ref. Data Suppl.* **17** 1 (1988)
267. P Kebarle, S K Searles, A Zolla, J Scarborough, M Arshadi *J. Am. Chem. Soc.* **89** 6393 (1967)
268. F Madeja, M Havenith *J. Chem. Phys.* **117** 7162 (2002)
269. R L Redington, R L Sams *J. Phys. Chem. A* **106** 7494 (2002)
270. I Olovsson, P-G Jönsson, in *The Hydrogen Bond. Recent Developments in Theory and Experiments* Vol. 1 (Eds P Schuster, G Zundel, C Sandorfy) (Amsterdam: North-Holland, 1976) p. 393
271. J D Cruzan, L B Braly, K Liu, M G Brown, J G Loeser, R J Saykally *Science* **271** 59 (1996)
272. P F Barabara, P K Walsh, L E Brus *J. Phys. Chem.* **93** 29 (1989)
273. K Nishi, H Sekiya, T Moshida, T Sugawara, Y Nishimura *J. Chem. Phys.* **112** 5002 (2000)
274. A H Zewail *J. Phys. Chem. A* **104** 5660 (2000)
275. V E Bondybey, R C Haddon, J H English *J. Chem. Phys.* **80** 5432 (1984)
276. K Remmers, W L Meerts, I Ozier *J. Chem. Phys.* **112** 10 890 (2000)
277. J J Paz, M Moreno, J M Lluch *J. Chem. Phys.* **103** 353 (1995)
278. S Scheiner *J. Phys. Chem. A* **104** 5898 (2000)
279. W Klopffer *Adv. Photochem.* **10** 311 (1977)
280. M A Rios, M C Rios *J. Phys. Chem. A* **102** 1560 (1998)
281. A L Sobolewski, W Domcke *Phys. Chem. Chem. Phys.* **1** 3065 (1999)
282. G Smulevich, P Foggi *J. Chem. Phys.* **87** 5657 (1987)
283. Y Kim *J. Am. Chem. Soc.* **118** 1522 (1996)
284. T Loerting, K R Liedl J *Am. Chem. Soc.* **120** 12 595 (1998)
285. H Ushiyama, K Takatsuka *J. Chem. Phys.* **115** 5903 (2001)
286. M V Vener, O Kühn, J E Bowman *Chem. Phys. Lett.* **349** 562 (2001)
287. W Klopper, M Quack, M A Suhm *Mol. Phys.* **94** 105 (1998)
288. T Loerting, K R Liedl, B M Rode *J. Chem. Phys.* **109** 2672 (1998)
289. M V Vener, J Sauer *J. Chem. Phys.* **114** 2623 (2001)
290. J Sauer, A Bleiber *Pol. J. Chem.* **72** 1524 (1998)
291. U Buck, F Huisken *Chem. Rev.* **100** 3863 (2000)
292. M Quack, J Stohner, M A Suhm *J. Mol. Struct.* **599** 381 (2001)
293. A C Legon *Chem. Soc. Rev.* **22** 153 (1993)
294. A Iwasaki, M Fujii, T Watanabe, T Ebata, N Mikami *J. Phys. Chem.* **100** 16063 (1996)
295. M Rospenk, T Zeegers-Huyskens *J. Phys. Chem. A* **101** 8428 (1997)
296. J E Del Bene, M J T Jordan, P M W Gill, A D Buckingham *Mol. Phys.* **92** 429 (1997)
297. M V Vener *Chem. Phys. Lett.* **244** 89 (1995)
298. J E Del Bene, M J T Jordan *J. Chem. Phys.* **108** 3205 (1998)
299. L Ojamäe, I Shavitt, S J Singer *Int. J. Quantum Chem., Quantum Chem. Symp.* **29** 657 (1995)
300. M Y Yi, S Scheiner *Chem. Phys. Lett.* **262** 567 (1996)
301. J A Syage *J. Phys. Chem.* **99** 5772 (1995)
302. S K Kim, J J Breen, D M Willberg, L W Peng, A Heikal, J A Syage, A H Zewail *J. Phys. Chem.* **99** 7421 (1995)
303. W Siebrand, M Z Zgierski, Z K Smedarchina, M Vener, J Kaneti *Chem. Phys. Lett.* **266** 47 (1997)
304. M V Vener, S Iwata *Chem. Phys. Lett.* **292** 87 (1998)
305. C Dedonder-Lardeux, G Gregoire, C Jouvet, S Martrenchard, D Solgani *Chem. Rev.* **100** 4023 (2000)
306. R Knochenmuss *Chem. Phys. Lett.* **311** 439 (1999)
307. W Siebrand, M Z Zgierski *Chem. Phys. Lett.* **320** 153 (2000)
308. A L Sobolewski, W Domcke *J. Phys. Chem. A* **105** 9275 (2001)
309. M F Hineman, G A Bruker, D F Kelly, E R Bernstein *J. Chem. Phys.* **97** 3341 (1992)
310. J A Syage *Faraday Discuss. Chem.* **97** 401 (1994)
311. M V Vener *Chem. Phys.* **233** 77 (1998)
312. M Tuckerman, K Laasonen, M Sprik, M Parrinello *J. Chem. Phys.* **103** 150 (1995)
313. N Agmon *Chem. Phys. Lett.* **244** 456 (1995)
314. V B Kazansky *Top. Catal.* **11/12** 55 (2000)
315. M Szafran *J. Mol. Struct.* **381** 39 (1996)
316. H Ratajczak *J. Phys. Chem.* **76** 3000 (1972)
317. R Nouwen, P Huyskens *J. Mol. Struct.* **16** 459 (1973)
318. E Grech, J Kalenik, L Sobczyk *J. Chem. Soc., Faraday Trans. 1* **75** 1587 (1979)

doi> 319. R Langner, G Zundel *J. Chem. Soc., Faraday Trans.* **94** 1805 (1998)
320. Z Dega-Szafran, A Hrynio, M Szafran *Spectrochim. Acta, Part A* **43** 1553 (1987)
321. S E Odinokov, A A Mashkovsky, A K Dzizenko, V P Glazunov *Spectrosc. Lett.* **8** 157 (1975)
322. G M Barrow *J. Am. Chem. Soc.* **78** 5802 (1956)
323. M M Davis *Acid-Base Behaviour in Aprotic Organic Solvents* (Washington, DC: National Bureau of Standards: 1968)
doi> 324. A V Iogansen *Spectrochim. Acta, Part A* **55** 1585 (1999)
325. P Schuster, G Zundel, C Sandorfy (Eds) *The Hydrogen Bond. Recent Developments in Theory and Experiments* Vols 1 – 3 (Amsterdam: North-Holland, 1976)
326. P L Huyskens, W A P Luck, T Zeegers-Huyskens (Eds) *Intermolecular Forces* (Berlin: Springer, 1991)
doi> 327. H Baba, A Matsuyama, H Kokubun *Spectrochim. Acta, Part A* **25** 1709 (1969)
328. D Guha, A Mandal, R Das, S Mitra, S Mukherjee *Isr. J. Chem.* **39** 375 (1999)
329. H Romanowski, L Sobczyk *J. Phys. Chem.* **79** 2535 (1975)
330. L M Epshtein *Usp. Khim.* **48** 1600 (1979) [*Russ. Chem. Rev.* **48** 854 (1979)]
doi> 331. M Ilczyszyn, H Ratajczak *J. Mol. Liq.* **67** 125 (1995)
doi> 332. S N Smirnov, N S Golubev, G S Denisov, H Benedict, P Schah-Mohammedi, H-H Limbach *J. Am. Chem. Soc.* **118** 4094 (1996)
doi> 333. T Kuc, Z Pavelka, L Sobczyk *Phys. Chem. Chem. Phys.* **2** 211 (2000)
334. P Barczynski, M Szafran *J. Chem. Soc., Faraday Trans.* **90** 2489 (1994)
doi> 335. B Brycki, M Szafran *J. Mol. Liq.* **59** 83 (1994)
336. V V Burdin, I S Kislina, V D Maiorov, S G Sysoeva, N B Librovich *Izv. Akad. Nauk, Ser. Khim.* 48 (1998) [f]
337. L P Hammett *Physical Organic Chemistry* (New York: McGraw-Hill, 1970)
338. N Sugimoto, M Sasaki, J Osugi *Bull. Chem. Soc. Jpn.* **57** 366 (1984)
doi> 339. M Ilczyszyn, H Ratajczak, J A Ladd *Chem. Phys. Lett.* **153** 385 (1988)
340. M Szwarc, A Streitwieser, P C Mowery, in *Ions and Ion Pairs in Organic Reactions* Vol. 2 (Ed. M Szwarc) (New York: Wiley, 1974) p. 151
341. I Yu Martynov, A B Demyashkevich, B M Uzhinov, M G Kuz'min *Usp. Khim.* **46** 3 (1977) [*Russ. Chem. Rev.* **46** 1 (1977)]
342. W M Nau, G Greiner, H Rau, M Olivucci, M A Robb *Ber. Bunsen-Ges. Phys. Chem.* **102** 486 (1998)
343. M Glasbeek *Isr. J. Chem.* **39** 301 (1999)
344. E T J Nibbering, C Chudoba, T Elsaesser *Isr. J. Chem.* **39** 333 (1999)
doi> 345. A Mandal, D Guha, R Das, S Mitra, S Mukherjee *J. Chem. Phys.* **114** 1336 (2001)
doi> 346. L M Tolbert, K M Solntsev *Acc. Chem. Res.* **35** 19 (2002)
doi> 347. B Kohen, J Segal, D Huppert *J. Phys. Chem. A* **106** 7462 (2002)
348. M Itoh, T Adachi, K Tokumura *J. Am. Chem. Soc.* **106** 850 (1984)
doi> 349. T Elsaesser *Chem. Phys. Lett.* **128** 231 (1986)
doi> 350. M Wiechmann, H Port, F Laermer, W Frey, T Elsaesser *Chem. Phys. Lett.* **165** 28 (1990)
351. H Miyasaka, N Mataga, in *Dynamics and Mechanism of Photo-induced Transfer and Related Phenomena* (Eds N Mataga, T Okaba, H Musuhara) (Amsterdam: Elsevier, 1992) p. 155
doi> 352. K H Grellmann, A Mordzinski, A Heinrich *Chem. Phys.* **136** 201 (1989)
doi> 353. S Nagaoka, S Yamamoto, K Mikami *J. Photochem. Photobiol., A* **105** 29 (1997)
doi> 354. B Nickel, P J Walla *Chem. Phys.* **237** 371 (1998)
355. B Nickel, K H Grellmann, J S Stephan, P J Walla *Ber. Bunsen-Ges. Phys. Chem.* **102** 436 (1998)
doi> 356. A L Sobolewski, W Domcke *Chem. Phys.* **259** 181 (2000)
doi> 357. J A Organero, M Moreno, L Santos, J M Lluch, A Douhal *J. Phys. Chem. A* **104** 8424 (2000)
doi> 358. V Guallar, V S Batista, W H Miller *J. Chem. Phys.* **110** 9922 (1999)
doi> 359. M Moreno, A Douhal, J M Lluch, O Castano, L M Frutos *J. Phys. Chem. A* **105** 3887 (2001)
360. D Gerritzen, H-H Limbach *J. Am. Chem. Soc.* **106** 869 (1984)
doi> 361. J Braun, R Schwesinger, P G Williams, H Morimoto, D E Wemmer, H-H Limbach *J. Am. Chem. Soc.* **118** 11 101 (1996)
362. J Braun, M Schlabach, B Wehrle, M Köcher, E Vogel, D E Wemmer, H-H Limbach *J. Am. Chem. Soc.* **116** 6593 (1994)
doi> 363. S Takeuchi, T Tahara *Chem. Phys. Lett.* **347** 108 (2001)
doi> 364. E S Shubina, N V Belkova, A N Frylov, E V Vorontsov, L M Epstein, D G Gusev, M Niedermann, H Berke *J. Am. Chem. Soc.* **118** 1105 (1996)
doi> 365. N V Belkova, E V Bakhmutova, E S Shubina, V I Bakhmutov, M Peruzzini, L M Epstein *Eur. J. Inorg. Chem.* 2163 (2000)
366. L MEpstein, E S Shubina *Coord. Chem. Rev.* **231** 166 (2002)
367. M Eigen, G Ilgenfritz, W Kruse *Chem. Ber.* **98** 1623 (1965)
368. R C Taylor, O L Vidale *J. Am. Chem. Soc.* **78** 5999 (1956)
369. S Meiboom *J. Chem. Phys.* **34** 375 (1961)
370. Z Luz, S Meiboom *J. Am. Chem. Soc.* **86** 4768 (1964)
371. N Agmon *Isr. J. Chem.* **39** 493 (1999)
372. C C Ferriso, D F Hornig *J. Chem. Phys.* **23** 1464 (1955)
373. I Pernoll, U Maier, R Janoschek, G Zundel *J. Chem. Soc., Faraday Trans. 2* **71** 201 (1975)
374. T Ackermann *Discuss. Faraday Soc.* 180 (1957)
doi> 375. V G Yukhnevich, E G Tarakanova, V D Mayorov, N B Librovich *Usp. Khim.* **64** 963 (1995) [*Russ. Chem. Rev.* **64** 901 (1995)]
doi> 376. G Zundel, M Eckert *J. Mol. Struct. (THEOCHEM)* **59** 73 (1989)
377. A A Pankov, V Yu Borovkov, V B Kazanskii *Dokl. Akad. Nauk SSSR* **258** 902 (1981) [d]
378. N S Golubev, G S Denisov, in *Physics of Ionic Solvation* (Ed. R R Dogonadze) (Amsterdam: Elsevier, 1984) p. 42
doi> 379. G V Yukhnevich, E G Tarakanova, V D Mayorov, N B Librovich *J. Mol. Struct.* **265** 237 (1992)
doi> 380. M E Tuckerman, G J Martyna *J. Phys. Chem. B* **104** 159 (2000)
doi> 381. R Vuilleumier, D Borgis *J. Chem. Phys.* **111** 4251 (1999)
doi> 382. J Kim, U W Schmitt, J A Gruetzmacher, G A Voth, N E Scherer *J. Chem. Phys.* **116** 737 (2002)
doi> 383. U W Schmitt, G A Voth *J. Chem. Phys.* **111** 9361 (1999)
doi> 384. M V Vener, O Kühn, J Sauer *J. Chem. Phys.* **114** 240 (2001)
385. E F Caldin, V Gold (Eds) *Proton-Transfer Reactions* (London: Chapman and Hall, 1975)
386. K M Dyumaev, B A Korolev *Usp. Khim.* **49** 2065 (1980) [*Russ. Chem. Rev.* **49** 1021 (1980)]
387. E Grunwald, D Eustace, in *Proton-Transfer Reactions* (Eds E F Caldin, V Gold) (London: Chapman and Hall, 1975) Ch. 4.
388. E Grunwald *J. Phys. Chem.* **86** 1302 (1982)
doi> 389. K Ando, J T Hynes *J. Phys. Chem. B* **101** 10464 (1997)
390. I Tuñòn, D Rinaldi, M F Ruiz-López, J L Rivail *J. Phys. Chem.* **99** 3798 (1995)
doi> 391. M A Lill, M C Hutter, V Helms *J. Phys. Chem. A* **104** 8283 (2000)
doi> 392. E T Denisov *Usp. Khim.* **65** 547 (1996) [*Russ. Chem. Rev.* **65** 505 (1996)]
393. E T Denisov *Konstanty Skorosti Gomoliticheskikh Zhidkofaznykh Reaktsii* (Rate Constants of Homolytic Liquid-Phase Reactions) (Moscow: Nauka, 1971)
394. K J Laider, L F Loucks, in *Comprehensive Chemical Kinetics* Vol. 5 (Eds C H Bamford, C F H Tipper) (Amsterdam: Elsevier, 1972) p. 1
395. G S Eastmond, in *Comprehensive Chemical Kinetics* Vol. 14A (Eds C H Bamford, C F H Tipper) (Amsterdam: Elsevier, 1976) p. 104
396. A Bromberg, K A Muszkat, E Fisher, F S Klein *J. Chem. Soc., Perkin Trans. 2* 588 (1972)
397. S P Mezyk, D M Bartels *J. Phys. Chem.* **98** 10578 (1994)
398. H Kwart *Acc. Chem. Res.* **15** 401 (1982)
399. G Brunton, D Griller, L R C Barclay, K U Ingold *J. Am. Chem. Soc.* **98** 6803 (1976)
400. G Brunton, D Griller, L R C Barclay, K U Ingold *J. Am. Chem. Soc.* **100** 4197 (1978)

401. B C Garret, G K Schenter, in *Structure and Reactivity in Aqueous Solution: Characterization of Chemical and Biological Systems* (Eds C J Cramer, D G Truhlar) (Wachington, DC: American Chemical Society, 1994) p. 122
402. Y Y Chuang, M L Radhakrishnan, P L Fast, C J Cramer, D G Truhlar *J. Phys. Chem. A* **103** 4893 (1999)
403. E T Denisov *Usp. Khim.* **66** 953 (1997) [*Russ. Chem. Rev.* **66** 859 (1997)]
404. I A Romanskii *Zh. Org. Khim.* **36** 1328 (2000) [g]
405. E M Arnett *J. Chem. Educ.* **62** 385 (1985)
406. R W Taft *Prog. Phys. Org. Chem.* **14** 247 (1983)
407. V A Pal'm *Osnovy Kolichestvennoi Teorii Organicheskikh Reaktsii* (Foundations of the Quantitative Theory of Organic Reactions) (Leningrad: Khimiya, 1967)
408. C F Bernasconi *Acc. Chem. Res.* **25** 9 (1992)
409. M Goez, R Heun *Angew. Chem., Int. Ed.* **37** 3052 (1998)
410. J R Murdoch, J A Bryson, D F McMillen, J I Brauman *J. Am. Chem. Soc.* **104** 600 (1982)
411. C F Bernasconi, R L Montanez *J. Org. Chem.* **62** 8162 (1997)
412. V D Parker, Y T Chao, G Zheng *J. Am. Chem. Soc.* **119** 11390 (1997)
413. C F Bernasconi, J A Moreira, L L Huang, K W Kittredge *J. Am. Chem. Soc.* **121** 1674 (1999)
414. V D Parker, Y Zhao, Y Lu, G Zheng *J. Am. Chem. Soc.* **120** 12 720 (1998)
415. Y Zhao, Y Lu, V D Parker *J. Am. Chem. Soc.* **123** 1579 (2001)
416. E Bardez, A Chatelain, B Larrey, B Valeur *J. Phys. Chem.* **98** 2357 (1994)
417. J A Roberts, J P Kirby, D C Nocera *J. Am. Chem. Soc.* **117** 8051 (1995)
418. H Haga, H-G Hong, Y Shiozawa, Y Kawata, H Monjushiro, T Fukuo, R Arakawa *Inorg. Chem.* **39** 4566 (2000)
419. S-C Hung, A N Macpherson, S Lin, P A Liddell, G R Seely, A L Moore, T A Moore, D Gust *J. Am. Chem. Soc.* **117** 1657 (1995)
420. B G Malmstrom *Acc. Chem. Res.* **26** 332 (1993)
421. M S Graige, M L Paddock, J M Bruce, G Feher, M Y Okamura *J. Am. Chem. Soc.* **118** 9005 (1996)
422. M Di Donato, R Borrelli, A Capobianco, G Monaco, R Improta, M Brahimi, A Peluso *Adv. Quantum Chem.* **36** 301 (2000)
423. P Brzezinski *Biochem. Biophys. Acta, Bioenerg.* **1458** 1 (2000)
424. S Brandsburg-Zabary, O Fried, Y Marantz, E Nachliel, M Gutman *Biochem. Biophys. Acta, Bioenerg.* **1458** 120 (2000)
425. J Heberle *Biochem. Biophys. Acta, Bioenerg.* **1458** 135 (2000)
426. H Michel *Biochemistry* **38** 15 129 (1999)
427. M Wikström *Biochemistry* **39** 3515 (2000)
428. J P Klinman *CRC Crit. Rev. Biochem.* **10** 39 (1981)
429. G Pettersson *CRC Crit. Rev. Biochem.* **21** 349 (1987)
430. S Ramaswamy, D H Park, B Plapp *Biochemistry* **38** 13 951 (1999)
431. N S Scrutton, J Basran, M J Sutcliffe *Eur. J. Biochem.* **264** 666 (1999)
432. T Jonsson, M H Glickman, S Sun, J P Klinman *J. Am. Chem. Soc.* **118** 10 319 (1996)
433. J C Nesheim, J D Lipscomb *Biochemistry* **35** 10240 (1996)
434. J Basran, M J Sutcliffe, N S Scrutton *Biochemistry* **38** 3218 (1999)
435. V Guallar, D L Harris, V S Batista, W H Miller *J. Am. Chem. Soc.* **124** 1430 (2002)
436. G Tresadern, J P MsNamara, M Mohr, H Wang, N A Burton, I H Hiller *Chem. Phys. Lett.* **358** 489 (2002)
437. A V Nemukhin, I A Topol, S K Burt *Int. J. Quantum Chem.* **88** 34 (2002)
438. Y Georgievskii, E S Medvedev, O A Stuchebrukhov *J. Chem. Phys.* **116** 1692 (2002)
439. H P Trommsdorff *Adv. Photochem.* **24** 147 (1998)
440. D W Firth, P F Barbara, H P Trommsdorff *Chem. Phys.* **136** 349 (1989)
441. V A Tolkachev *Reactivity of Molecular Solids* (Eds E Boldyreva, V Boldyrev) (Chichester: Wiley, 1999)
442. A B Yaroslavtsev, V Yu Kotov *Izv. Akad. Nauk, Ser. Khim.* 515 (2002) [f]
443. T Matsuo, K Kohno, M Ohama, T Mochida, A Isuoka, T Sugewara *Europhys. Lett.* **47** 36 (1999)
444. T Matsuo, S Baluja, Y Koike, M Ohama, T Mochide, T Sugewara *Chem. Phys. Lett.* **342** 22 (2001)
445. M A Neumann, S Craciun, A Corval, M R Johnson, A J Horsewill, V A Benderskii, H P Trommsdorff *Ber. Bunsen-Ges. Phys. Chem.* **102** 325 (1998)
446. C Rambaud, A Oppenländer, M Pierre, H P Trommsdorff, J C Vial *Chem. Phys.* **136** 355 (1989)
447. A J Horsewill, D F Brougham, R I Jenkinson, C J McGloin, H P Trommsdorff, M R Johnson *Ber. Bunsen-Ges. Phys. Chem.* **102** 317 (1998)
448. G J Kearley, F Fillaux, M H Baron, S Bennington, J Tomkinson *Science* **264** 1285 (1994)
449. F Fillaux *Int. Rev. Phys. Chem.* **19** 553 (2000)
450. F Fillaux, M H Limage, F Romain *Chem. Phys.* **276** 181 (2002)
451. C N Tam, P Bour, J Eckert, F R Trouw *J. Phys. Chem. A* **101** 5877 (1997)
452. M Barthes, H N Bordallo, J Eckert, O Maurus, G de Nunzio, J Leon *J. Phys. Chem. B* **102** 6177 (1998)
453. B S Hudson, J S Tse, M Z Zgierski, S F Parker, D A Braden, C Middleton *Chem. Phys.* **261** 249 (2000)
454. G J Kerley, M R Johnson, M Plazanet, E Suard *J. Chem. Phys.* **115** 2614 (2001)
455. J Wang, F Williams *J. Am. Chem. Soc.* **94** 2930 (1972)
456. R L Hudson, M Shiotany, F Williams *Chem. Phys. Lett.* **48** 193 (1977)
457. E D Sprague *J. Phys. Chem.* **81** 516 (1977)
458. R J LeRoy, H Murai, F Williams *J. Am. Chem. Soc.* **102** 2325 (1980)
459. K Toriyama, K Nunome, M Iwasaki *J. Am. Chem. Soc.* **99** 5823 (1977)
460. L I Trakhtenberg, A A Fokeyev, S P Dolin *Chem. Phys. Lett.* **341** 551 (2001)
461. R Zwanzig *Nonequilibrium Statistical Mechanics* (Oxford: Oxford University Press, 2001)
462. L D Landau, E M Lifshits *Statisticheskaya Fizika* (Statictical Physics) (Moscow: Nauka, 1976) Pt. 1
463. R Kubo, M Toda, N Hashizume *Statistical Physics* Vol. 2 (Berlin: Springer, 1985)
464. J S Langer *Ann. Phys. (USA)* **41** 108 (1967)
465. H A Weidenmüller, J S Zhang *J. Stat. Phys.* **34** 191 (1984)
466. R F Grote, J T Hynes *J. Chem. Phys.* **74** 4465 (1981)
467. R F Grote, J T Hynes *J. Chem. Phys.* **75** 2191 (1981)
468. A Nitzan *Adv. Chem. Phys.* **70** 489 (1988)
469. M V Basilevsky, G E Chudinov *Chem. Phys.* **144** 155 (1990)


[a] — *Chem. Phys. Rep. (Engl. Transl.)*
[b] — *High. Energy Chem. (Engl. Transl.)*
[c] — *Kinet. Catal. (Engl. Transl.)*
[d] — *Dokl. Chem. (Engl. Transl.)*
[e] — *Russ. J. Electrochem. (Engl. Transl.)*
[f] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[g] — *Russ. J. Org. Chem. (Engl. Transl.)*