

Temperature dependence of the rate constants of cryochemical reactions

G. K. Ivanov,^a M. A. Kozhushner,^a and L. I. Trakhtenberg^{b*}

^aN. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.

Fax: +7 (095) 938 2156. E-mail: kozhush@center.chph.ras.ru

^bState Scientific Center of the Russian Federation "L. Ya. Karpov Physico-Chemical Research Institute,"
10 ul. Vorontsovo Pole, 103064 Moscow, Russian Federation.

Fax: +7 (095) 975 2450. E-mail: trakh@cc.nifhi.ac.ru

The temperature dependence of the reaction rate constant for tunneling transfer of an atomic particle in solid near absolute zero was studied. Different mechanisms describing the temperature dependence were considered: reorganization of the medium, modulation of parameters of the potential barrier, and under-barrier friction. It was established that for the rate constant (K) at low temperatures the equation $\ln K = \ln K_0 + C_4 T^4 + C_5 T^5 + C_6 T^6 + C_8 T^8$ is valid. Experimental data were compared with the theory. A good agreement is achieved when the quantum nature of the hydrogen crystal is applied under the assumption of a predominant role of reorganization of the medium.

Key words: tunneling transition, reorganization of medium, modulation of potential barrier parameters, under-barrier friction, Green function.

Many chemical reactions occurring at helium temperatures have been a subject of study in recent years. Prominent among these are reactions involving transfer of the H atom, which usually proceed *via* the tunneling mechanism. This is indicated by an anomalously high isotope effect and the finite low-temperature limit of chemical reactions. The detailed review and analysis of experimental and theoretical results have previously been reported.^{1,2}

Analyzing the temperature dependence of the rate constants of solid state reactions, three main temperature intervals can be distinguished.^{1–4} In the low-temperature interval, both the particle transfer and the motion of the molecular environment are quantized. In this interval, the temperature dependence of the rate constant is determined by the type of intermolecular vibrations of reagents. In the case of the local mode, the dependence has the form of a low-temperature plateau, and when the phonon continuous spectrum prevails, the logarithm of the rate constant is proportional to the temperature in a sufficiently high power (from the fourth to eighth power, see, *e.g.*, Ref. 5). The next region corresponds to classical intermolecular motions and quantized particle transfer. In this interval, the logarithm of the rate constant is proportional to the temperature. Finally, in the region of sufficiently high temperatures, both intermolecular vibrations and particle transfer show classical behavior. In this region, the temperature dependence of the rate constant is determined by the Arrhenius equation.

Two main approaches to the description of solid state tunneling reactions can be distinguished: (a) analytical method based on the modified theory of nonradiative transitions^{1,4–9} and (b) numerical method of computer simulation of the dynamics of tunneling transition based on the calculation of energy for the system moving along imaginary trajectories (see, *e.g.*, Ref. 10 and literature cited in monographs^{2,10}). As a rule, exact data on the reaction system (the multidimensional potential energy surface, quantum numbers of the final state) are unavailable; therefore, analytical approaches that allow one to present experimental results qualitatively are used for the description of the regularities of chemical reactions. In some cases, the theory can be compared with experimental data.^{1–3,5}

In the low-temperature tunneling pathways, reaction routes deviate from the classical passways. A particle "cuts an angle" and tunnels through a higher, but narrower potential barrier rather than surmount the barrier.¹¹ Using this mechanism, one can describe^{1–3,5} experimental data on the temperature dependence of the rate constants of reactions with H atom transfer between heavy reagents.^{12–16}

The pattern of the temperature dependence of the rate constant depends on the specific features of reorganization of the medium, under-barrier friction, and nonadiabatic effects, which are also manifested at temperatures close to absolute zero. These temperature dependences have recently been observed in several experimental works (see Ref. 17 and literature cited herein).

in which solid state reactions of H atoms (deuterium) in molecular hydrogen (deuterium) were studied. The formation of atoms occurred during γ -irradiation of H_2 , HD, and D_2 crystals. In particular, the temperature dependence of the rate constant of the reaction



was studied in the 2.6–6.5 K interval.¹⁷

This work applies the methods of the theory of nonradiative transitions^{1,5–7} to the detailed analysis of the role of long-wave phonons in tunneling transfer reactions at helium temperatures. We attempted to determine the characteristic temperature dependences of the rate constants of solid state reactions (K) in this region. Although investigation of the kinetics of chemical reactions with hydrogen transfer near absolute zero was a subject of many studies,^{13,18–22} the temperature dependence of the rate constant has been obtained only in one work¹⁷ and, hence, it is of interest to compare our calculated data with the results of that work.

Method of calculation of the transition amplitude

Effects of various factors on the K value can be taken into account on the basis of the general theory of tunneling transitions in the multi-particle system. The method of determination of the amplitude of tunneling transition of one of the particles in the multi-particle system based on using the Lippmann–Schwinger equation has previously been developed.^{6,7,23}

Considering tunneling of heavy particles, one can use the adiabatic approximation that is fulfilled under the conditions that all transitions of heavy particles occur in the same electron state. The following inequality is the necessary condition of validity of the adiabatic approximation:

$$A_{fi}/\Delta \ll 1, \quad (1)$$

where A_{fi} is the amplitude of multi-particle tunneling transition from state i to state f , and Δ is the lowest difference between two adiabatic terms of the system. Since A_{fi} contains an exponentially low factor related to tunneling of one of the atoms, condition (1) is almost always fulfilled. The Hamiltonian of the system is written as follows:

$$\hat{H} = -\frac{1}{2} \sum_n \frac{1}{M_n} \Delta_n \pm U(\{r\}) \quad (2)$$

The atomic system of units is used hereinafter; summation is performed over all particles involved in the transition, M_n is the mass of the n th particle, Δ_n is the Laplacian over coordinates of the n th particle, and $U(\{r\})$ is the multidimensional adiabatic potential energy, where $\{r\}$ means the set of all coordinates of the system. The initial (i) and final (f) states are determined by two local minima on the multidimensional surface of the potential energy. The initial ψ_i and final ψ_f wave

functions can be considered with a high accuracy to be functions of the harmonic oscillator corresponding to normal coordinates q_i , q_f through which deviations $\{r-r_i\}$ and $\{r-r_f\}$ of natural coordinates from the equilibrium positions r_i and r_f , respectively, are expressed. The energy $E > \varepsilon$, where ε is the energy of the full system, which is retained in the transition, can be defined in such a fashion so that in the region of coordinates $\{r\}$, determined by the inequality $U(\{r\}) < E$, the known oscillator functions of normal coordinates sufficiently exactly approximate the initial and final wave functions. Let us name these regions $L_i(E)$ and $L_f(E)$.

The equation for the amplitude of transition A_{fi} has the following form^{6,7,23}:

$$A_{fi} = \int_{L_i(E)} d\{r\} \int_{L_f(E)} d\{r'\} \cdot \langle \psi_f(\{r'\}; \varepsilon) | U(\{r\}) - E | \times \\ \times G_V(\{r\}, \{r'\}; \varepsilon) \cdot [U(\{r\}) - E] \psi_i(\{r\}; \varepsilon). \quad (3)$$

Here G_V is the multidimensional Green function at the ε energy for the H_V Hamiltonian

$$H_V = -\frac{1}{2} \sum_n \frac{1}{M_n} \Delta_n + V(\{r\}), \quad (4)$$

where

$$V(\{r\}) = \begin{cases} U(\{r\}) & \{r\} \in L_i(E), L_f(E) \\ E & \{r\} \in L_i(E), L_f(E) \end{cases} \quad (5)$$

Some "randomness" in choosing E does not result in an ambiguous determination of A_{fi} . This follows from the fact that a change in the E value also implies the redetermination of the V potential and thus, the division of the full Hamiltonian into the "zero" part H_V and the "interaction" ($U(\{r\}) - E$) changes. However, the Lippmann–Schwinger equation, on the basis of which Eq. (3) was obtained, is invariant relative to this division.

Thus, the calculation of the amplitude of transition is entirely reduced to the determination of the Green function $G_V(\{r\}, \{r'\}; \varepsilon)$ and further quadratures. Note that according to the definition of $V(\{r\})$ in Eq. (5) and the fact that $\varepsilon < E$, the Green function "lies" entirely in the under-barrier region. As has been shown,²⁴ if the classical trajectory connecting points $\{r\}$ and $\{r'\}$ lies completely in the above- or under-barrier region, there is a sufficiently simple calculation algorithm for the determination of the quasi-classic Green function, which was used in the calculation program described earlier.²⁵ The inequality

$$\sqrt{2m(V - \varepsilon)} \cdot l_t \gg 1, \quad (6)$$

which determines the applicability of the quasi-classical approximation (here l_t is the characteristic length of the trajectory along the tunneling coordinate; m is the mass of the tunneling particle), is valid for pronounced tunneling transitions. Therefore, the Green function in the

amplitude of Eq. (3) can be calculated, and the determination of the amplitude is reduced to quadratures.

Equation (3) together with definitions (4) and (5) has a clear physical meaning. The amplitude of the tunneling transition A_{fi} from the known in the L_i region initial state ψ_i to the fixed in the L_f region final state ψ_f is reduced to the standard form:

$$A_{fi} = \langle \psi_f | \hat{U} | \psi_i \rangle, \quad (7)$$

where the effective interaction U is determined by the equality:

$$\hat{U} = [U(\{r\}) - E] \cdot G_V(\{r_i\}, \{r'\}; \varepsilon) [U(\{r'\}) - E]. \quad (8)$$

The Green function G_V is determined by the value of the V potential in the "tunneling" region. Thus, the interaction resulting in the transition according to formulas (7) and (8) was not chosen arbitrarily. The U operator is similar to the known Bardin operator in the model of one-particle tunneling.

The method proposed imposes no limitations on the shape of the barrier $U(\{r\})$, the dimensionality of the system in which the tunneling transition occurs, and the energies of the initial and final states. The latter can be any initial and final states of the system of oscillators, i.e., the method can be used for calculations of "state to state" transitions. Note that the widely used "instanton" method¹⁰ deals only with the ground states of oscillators and a sufficiently restricted class of analytical equations for the shape of the potential barrier.

The multi-particle tunneling transition is reduced, in the majority of cases, to the tunneling transition of only one particle (H or D atom), which is not necessarily one-dimensional over the tunneling coordinate r_t . Over coordinates of other particles $\{r_{nt}\}$, the characteristic regions in the initial (L_i) and final (L_f) states overlap. The characteristic height of the tunneling barrier \bar{U} is much higher, as a rule, than the energy ΔE transmitted into "non-tunneling" degrees of freedom. When the following inequality is fulfilled:

$$\sqrt{2m\bar{U}} \cdot l_t \ll \bar{U} / \Delta E \quad (9)$$

(where l_t is the tunneling distance), adiabatic uncoupling of tunneling and non-tunneling coordinates is possible, and the equation for the Green function can be written in the form

$$G_V(\{r_t\}, \{r'\}; \varepsilon_t) \equiv \delta(\{r_{nt}\} - \{r'_{nt}\}) \cdot G(r_t, r'_t, \{r_{nt}\}; \varepsilon_t), \quad (10)$$

$$\delta(\{r_{nt}\} - \{r'_{nt}\}) = \prod_m \delta(r_m - r'_m),$$

where index m passes through all non-tunneling (nt) coordinates.

The Green function $G(r_t, r'_t, \{r_{nt}\}; \varepsilon_t)$ over tunneling variables depends on the ensemble of non-tunneling variables $\{r_{nt}\}$ and energy ε_t as on the parameters; ε_t is

the effective energy of a non-tunneling particle that depends on the energy exchange in centers 1 and 2.⁶ However, in many calculations, it is accepted to be $\varepsilon_t = 1/2(E_1 + E_2)$ (E_1 and E_2 are the bonding energies of the tunneling particle in centers 1 and 2, respectively) and independent of the temperature and parameters of the medium. The effects related to the temperature dependence of ε_t are outside the framework of the adiabatic approximation and will not be considered in this work. Inequality (9) is a condition of the so-called double adiabatic approximation,¹ according to which non-tunneling atoms move much more slowly than the tunneling atom, i.e., the tunneling transition occurs at stationary nuclei (see formula (10)). Then the integration is performed over the coordinates of non-tunneling atoms (a slow subsystem):

$$A_{fi} = \int d\{r_{nt}\} \cdot \int d r_t d r'_t \psi_f(\{r_{nt}\}, r_t) U_f(\{r_{nt}\}, r_t) \times \\ \times G_V(r_t, r'_t; \{r_{nt}\}; \varepsilon_t) \cdot U_i(\{r_{nt}\}, r'_t) \psi_i(\{r_{nt}\}, r'_t). \quad (11)$$

It is often the case when the tunneling $\{r_t\}$ and non-tunneling $\{r_{nt}\}$ degrees of freedom are divided in the initial and final states that

$$\psi_{i,f}(\{r\}) \equiv \psi_{i,f}(\{r_{nt}\}) \cdot \psi_{i,f}(\{r_t\}). \quad (12)$$

Then Eq. (11) for the amplitude A_{fi} can be written in a more compact form:

$$A_{fi} = \langle \psi_f(\{r_{nt}\}) | A_{ad}(\{r_{nt}\}) | \psi_i(\{r_{nt}\}) \rangle, \quad (13)$$

where $A_{ad}(\{r_{nt}\})$ is the amplitude of the adiabatic tunneling transition at a fixed position of the coordinates of the "heavy" (non-tunneling) subsystem $\{r_{nt}\}$, which can be presented in the following form:

$$A_{ad}(\{r_{nt}\}) = \int d r_t d r'_t \langle \psi(\{r_t\}) | U_f(\{r_{nt}\}, r_t) \times \\ \times G_V(r_t, r'_t; \{r_{nt}\}; \varepsilon_t) \cdot U_i(\{r_{nt}\}, r'_t) \psi_i(r'_t) \rangle. \quad (14)$$

Due to a low value of the tunneling amplitude A_{fi} and the quasi-continuous spectrum of the system because of the participation of many non-tunneling variables, the K rate constant of the tunneling transition is determined by the Fermi "gold rule":

$$K = 2\pi A_V \sum_f |A_{fi}|^2 \delta(\varepsilon_f - \varepsilon_i). \quad (15)$$

Equations (3), (14), and (15) are the basis for the determination of the temperature dependence of the rate constant of tunneling transitions in the condensed matter. At low temperatures, the transition occurs mainly from the ground state φ_i of the quantum tunneling system. According to Eqs. (13) and (15), the temperature dependence in the low-temperature limit is completely determined by the low-energy states of the heavy subsystem (medium) on which the amplitude of transition A_{fi} depends. For averaging the equilibrium initial states of the heavy subsystem are used.

Mechanisms of the temperature dependence

The tunneling transition is accompanied, as a rule, by the rearrangement of the slow nuclear subsystem, which is manifested in the difference of wave functions ψ_i and ψ_f in Eq. (13). This rearrangement and related energy of reorganization of the medium result in a strong temperature dependence of the transition rate constant.

In addition, the probability of the tunneling transition strongly depends on the barrier parameters, which can vary substantially during intermolecular vibrations, resulting in a change in the distance between the reagents. The tunneling transition occurs most probably when two reagents approach within the shortest distance. This specific feature of the dynamics of the tunneling transition has previously been considered.⁵ It has been shown that intermolecular motions give an anomalously strong temperature dependence of the rate constant, and this provides a good agreement between the theory and experiment of the tunneling H atom transfer between two heavy particles.

The next specific feature of the process is that a particle moving in the under-barrier region experiences the effect of surrounding atoms (under-barrier friction). The number of atoms active in this respect is usually low. The continual models that describe under-barrier friction are summarized in the review.²⁶ To find a temperature dependence of the tunneling transition near absolute zero and related to the under-barrier friction, one should know how the interaction of phonons with a particle resulting in a change in the energy of this tunneling particle depends on the frequency of a phonon. For this purpose, it is necessary to consider the true Hamiltonian rather than the model for the system in which the length of the tunneling path l_i is comparable with the lattice constant d . Such a consideration will be made below.

The study performed is based on the successive analysis of three (distinguished above) mechanisms of the process.

1. Rearrangement of the slow vibrational subsystem during the transition of a tunneling particle from center 1 to the under-barrier region and from the under-barrier region to center 2.

2. Interaction of a tunneling particle with vibrations in centers 1 and 2, which changes the shape of the potential barrier and the tunneling transfer length.

3. Energy exchange of a tunneling particle with phonons in the under-barrier region (under-barrier friction).

In the general case, all these mechanisms are manifested simultaneously. However, as a rule, one of them is predominant. Then the correlation of different mechanisms can be ignored with good accuracy. Therefore, they can be considered individually, and in the analysis of mechanisms 1 and 2, the results of the previous studies can be used.^{5,7}

A portion of energy evolved in reaction (1) can be transmitted to rotational degrees of freedom of molecules localized in centers 1 and 2, because hydrogen molecules rotate freely in sites of the lattice of the crystalline matrix.²⁷ Since the temperature dependence is also determined by the initial distribution over rotational levels, and the value of a rotational quantum (~ 60 K) exceeds by an order of magnitude the temperature range under consideration, the rotational system does not contribute to the character of the temperature dependence of the rate constant of solid state reactions. Its influence lies only in the redistribution of the energy transmitted to the rotational and vibrational degrees of freedom of the crystal. The slow vibrational (phonon) subsystem, which will be considered hereinafter, exerts the main effect on the character of the low-temperature dependence of K.

First mechanism takes into account the distortion of the phonon subsystem during transfer of a particle. A light particle, removed from one localized state to another, results in the rearrangement of the slow nuclear subsystem, which is expressed as a change in the positions of the centers of vibrations of the nuclei and (in the general case) their frequencies.

Neglecting the dependence of $A_{ad}(\{r_{nt}\})$ in Eq. (13) on coordinates $\{r_{nt}\}$, we can reduce the analysis of the role of this mechanism to the calculation of the Franck—Condon factors^{28,29} that are determined by overlapping integrals of wave functions in the initial and final states of the system:

$$a_{fi}^v = \langle \chi_v^f(\xi_v) | \chi_v^i(\xi_v - \delta_v) \rangle. \quad (16)$$

Here δ_v are the changes in the position of the center of vibration at the $i \rightarrow f$ transition (the changes in the frequencies are neglected, as usual), and $\chi_v^{f,i}$ are the final and initial vibrational wave functions.

For a large energy release, this transition can be characterized by the $p^2/2M$ magnitude (M is the effective mass), which coincides, in the unimodal case, with the energy of the vertical transition in the corresponding parabolic potentials (here p is the effective transmitted momentum).

The strongest dependence of the rate constants of the reactions under consideration on the temperature T originates under the conditions of a strong interaction of a tunneling particle with a heavy subsystem. In this case, the temperature dependence of K is determined by the probability of transfer of the ε_{ph} energy to phonons of the lattice:

$$K \approx \exp[-(\varepsilon_{ph} - P)^2/\beta]. \quad (17)$$

Equation (17) is the generalization of the known Marcus formula³⁰ to the region of thermal energies, comparable with energies of phonons in the crystal. Note that the Gaussian approximation of type (17) in the theory of radiative and nonradiative transitions with a large energy release was developed by independent

methods in various areas of physics.³⁰⁻³² Here the P value (energy of reorganization of the medium) is temperature-independent, and the β function tends to a constant value at $T \rightarrow 0$ and is proportional to the temperature ($\beta \sim T$) at $kT \gg \omega_D$ (ω_D is the Debye frequency).

The temperature dependence of the rate constant of the process is mainly determined by the β function in Eq. (17), which has the following form for the considered mechanism of the medium effect:

$$\beta = \int \frac{p^2(\omega)}{M\omega} \omega^2 f(\omega) \coth \frac{\omega}{2T} d\omega. \quad (18)$$

Here $f(\omega)$ is the spectrum of vibrations (in the case of the Debye spectrum $f(\omega) = 3\omega^2/\omega_D^3$). The energy of reorganization of the medium in Eq. (17) is determined as follows:

$$P = \int \frac{p^2(\omega)}{2M} f(\omega) d\omega. \quad (19)$$

Let us divide the region of integration over ω in Eq. (18) into two intervals, $0-2T$ and $2T-\omega_D$, accepting $\coth(\omega/2T) = 2T/\omega$ in the 1st interval and $\coth(\omega/2T) = 1$ in the 2nd interval. This procedure is approximate, but at this stage of study it is satisfactory, because the exact calculation can result only in some refinement of the coefficients in the expansion of β with respect to powers T .

The $p(\omega)$ values in Eqs. (18) and (19), characterizing the efficiency of vibrational transition in the ν mode with the ω frequency, can be determined from the correlation

$$\{M\omega^2 \delta_\nu^2(\omega)\}/2 = p^2(\omega)/2M, \quad (20)$$

which gives

$$p(\omega) = M\omega \delta_\nu(\omega). \quad (21)$$

The form of the $\delta_\nu(\omega)$ function, which determines the displacement of vibrational centers in the initial and final states, is unknown. It can be obtained only after detailed calculation of the multi-dimensional surface of the potential energy $U(\{r\})$.

Therefore, we consider three particular cases:

1) $\delta_\nu(\omega) = \delta_0 = \text{const}$, i.e., displacements are the same for all modes, then $p \sim M\omega$ and

$$\beta_1^{(1)} = \beta_1^{(1)}(0)[1 + (64/5)(T/\omega_D)^6], \quad (22)$$

where $\beta_1^{(1)}(0) = (1/2)M\omega_D^3 \delta_0^2$, and the energy of reorganization of the medium

$$P_1^{(1)} = (3/5)M\omega_D^3 \delta_0^2.$$

where the lower index at β and P designates the mechanism, and the upper index designates different particular cases of the dependence of δ_ν on ω ;

2) $\delta_\nu(\omega)\sqrt{M\omega} = x = \text{const}$, i.e., the displacements in units of zero vibrations for each mode are the same; here $p \sim \sqrt{\omega}$ and

$$\beta_1^{(2)} = \beta_1^{(2)}(0)[1 + 8(T/\omega_D)^5], \quad (23)$$

where $\beta_1^{(2)}(0) = (3/5)c^2\omega_D^2$, and $P_1^{(2)} = (3/8)c^2\omega_D$;

3) $\delta_\nu(\omega) = \tau\omega$, where $\tau = \text{const}$.

This version is the most probable at very low frequencies, because the centers localized at points R_1, R_2 participate in long-wave vibrations of the crystal, and the distinction of their action on the surrounding centers is expressed by the factor

$$\varphi(\mathbf{q}) = (1/4\pi) \int e^{i\mathbf{q}\mathbf{R}_2} - e^{i\mathbf{q}\mathbf{R}_1} d\Omega \quad (24)$$

(\mathbf{q} is the wave vector of a phonon), which can be included in integrands (18) and (19) for β and P . Then

$$\beta_1^{(3)} = \beta_1^{(3)}(0)[1 + (256/7)(T/\omega_D)^8],$$

where $\beta_1^{(3)}(0) = (3/8)M\tau^2\omega_D^5$. In this case, $P_1^{(2)} = (3/14)M\tau^2\omega_D^4$.

For the cases considered above, the temperature dependence of K is the following:

$$\begin{aligned} K_1^{(1)} &\sim \exp[-Q_1^{(1)} + (64/5)Q_1^{(1)}(T/\omega_D)^6], \\ K_1^{(2)} &\sim \exp[-Q_1^{(2)} + 8Q_1^{(2)}(T/\omega_D)^5], \\ K_1^{(3)} &\sim \exp[-Q_1^{(3)} + (256/7)Q_1^{(3)}(T/\omega_D)^8], \end{aligned} \quad (25)$$

where the $Q_1^{(S)}$ values are determined by the equation

$$Q_1^{(S)} = (\varepsilon_{ph} - P_1^S)^2/\beta_1^S(0).$$

Second mechanism reflects the influence of modulations of the potential barrier due to vibrations of the reagents.⁵ In this case, the temperature dependence of the rate constant is related to the temperature effect on the amplitude of intermolecular vibrations and energy transfer ε_{ph} ($\varepsilon_{ph} \gg \omega$) to the phonon subsystem. The dependence can be described by the equation

$$K_2 \sim e^{D(T)} \exp[-(\varepsilon_{ph} - P_2)^2/\beta_2(T)], \quad (26)$$

which differs from Eq. (17) by the appearance of the additional factor $e^{D(T)}$ in Eq. (26) that depends exponentially on the temperature

$$P_2 = \int \frac{p^2}{2M\omega} f(\omega) \varphi(q) d\omega, \quad (27)$$

$$D_2(T) = \int \frac{p^2}{M\omega} f(\omega) \varphi(q) \coth \frac{\omega}{2T} d\omega, \quad (28)$$

$$\beta_2^{(T)} = \int \frac{p^2}{M\omega} \omega^2 f(\omega) \varphi(q) \coth \frac{\omega}{2T} d\omega, \quad (29)$$

and the p value is directly related to the derivative of the action function S with respect to the R distance between the reagents.

The $\varphi(q)$ function is given by Eq. (24) and takes into account the fact that both centers between which a particle tunnels participate in the same long-wave vibrations of the medium (as in case 3 for the first mechanism). In particular, the vibrations at the angle

$\theta = \arccos(\mathbf{qR}/qR) \neq 0$ to the \mathbf{R} vector in modulations of the barrier shape are presented less efficiently than the vibrations along the \mathbf{R} vector.

In the case of the motion of reagents 1 and 2 correlated in the $\omega_D \gg T$ frequency region ($\varphi(q) \sim \omega^2$), the temperature dependence of the rate constant has the form

$$K_2 \sim \exp[-Q_2 + (64/5)Q_2(T/\omega_D^6)] \exp[D_2 + d_2(T/\omega_D)^4], \quad (30)$$

$$d_2 = (16/3)D_2(0), \quad Q_2 = (\varepsilon_{ph} - P_2)^2/\beta_2(0),$$

where $D_2(0)$, $\beta_2(0)$ are given by Eqs. (28) and (29) at $T = 0$.

Third mechanism of a weak under-barrier friction under adiabatic conditions can be considered as follows. A particle that moves in the under-barrier region undergoes the influence of surrounding atoms. Their vibrations result in modulations of the potential barrier that is overcome by the tunneling particle and, hence, in the energy exchange with this particle. For consideration, it is sufficient to determine the effective momentum transmitted to the phonon system due to the interaction with one of the atoms in the under-barrier region. For this purpose, we may introduce the $V(\mathbf{r}, \mathbf{r}_i)$ interaction with this atom that determines the barrier shape and its modulations $\Delta V = \nabla_p V(\mathbf{r}, \mathbf{r}_i)(\mathbf{r}_i - \mathbf{r}_i^0)$ due to vibrations. Here \mathbf{r} is the radius-vector of a tunneling atom, $\rho = \mathbf{r}_i - \mathbf{r}_i^0$, \mathbf{r}_i is the position of the atom in the under-barrier region, and \mathbf{r}_i^0 is its equilibrium position.

Let us expand the adiabatic action $S(\mathbf{r}, \mathbf{r}_i^0)$ into the tunneling trajectory over the ΔV value; assuming that $V(\mathbf{r}, \mathbf{r}_i)$ depends on the distance between the tunneling particle and the disturbing atom i :

$$S(\mathbf{r}, \mathbf{r}_i) = S_0 + \frac{(\mathbf{r}_i - \mathbf{r}_i^0)\mathbf{z}}{z} \int \frac{1}{v(z)} \frac{dV}{d\rho} \frac{z}{\rho} dz.$$

Integration was performed along the trajectory \mathbf{z} of the tunneling particle, which is assumed to be linear, and $v(z)$ is the "rate" of the particle in the under-barrier region.

Let us present the arbitrary displacement of atom i in the form of a superposition of normal vibrations of the crystal and introduce the momentum \mathbf{p}_q , which is instantly transmitted during the tunneling transition to the mode with the wave vector \mathbf{q} .

Here it is necessary to take into account that the atom which is present in the near-barrier region and induces changes in the barrier shape participates in the same long-wave vibrations as the medium in which the tunneling particle moves. This condition appears in the form of the cofactor $f(\mathbf{q}, \rho) = |1 - e(i\mathbf{q} \cdot \mathbf{p})|$ in the integrand for the effective momentum

$$\mathbf{p}_q = \int \frac{dV}{d\rho} \frac{\mathbf{z}}{\rho v(z)} |e(i\mathbf{q} \cdot \mathbf{p})| dz. \quad (31)$$

It can easily be shown that in this case, the temperature dependence of the K value is described by Eq. (26), although the values are defined differently:

$$P_3 = \frac{1}{4\pi} \int \frac{p_q^2}{2M\omega} f(\omega) d\Omega_q d\omega,$$

$$D_3(T) = \frac{1}{4\pi} \int \frac{p_q^2}{M\omega} f(\omega) \coth \frac{\omega}{2T} d\omega d\Omega_q, \quad (32)$$

$$\beta_3(T) = \frac{1}{4\pi} \int \frac{p_q^2}{M\omega} \omega^2 f(\omega) \coth \frac{\omega}{2T} d\omega d\Omega_q.$$

It can be seen that the dependences on the ω frequencies (at $\omega \ll \omega_D$), which are in integrands (32), are the same as those in Eqs. (27)–(29). Therefore, the characteristic temperature dependences of K obtained in this work are similar to those for the second mechanism.

The consideration performed is appropriate under the condition

$$\frac{\omega_D l_t}{\bar{v}} \ll 1, \quad (33)$$

where l_t is the length of the tunneling path, and \bar{v} is the average "rate" of the particle in the under-barrier region.

Note that similar temperature dependences are also obtained when effects of the nonadiabatic bond in motions of the light (tunneling) particle are taken into account.

Mechanism of establishing the temperature dependence of K by calculation from experimental data¹⁷

Let us analyze the temperature dependence of the rate constant (I) using the results obtained. According to the data presented above (three mechanisms), the temperature dependence of $\ln K$ in the general case can be presented in the following form:

$$\ln K = \ln K_0 + C_4 T^4 + C_5 T^5 + C_6 T^6 + C_8 T^8, \quad (34)$$

where the equations for the coefficients C_s ($s = 4, 5, 6$, and 8) are given in Eqs. (25), (30), and (32). Since the temperature dependence of T^6 can be a result of different statistically independent mechanisms, the C_6 coefficient is determined by the sum of contributions from these mechanisms.

An exact calculation of the dynamics of the irradiated hydrogen crystal, in which reaction (I) occurs, would allow one to determine the coefficients in Eq. (34) and, comparing dependence (34) with the experimental one, some mechanism could be preferred. Since currently it is impossible to perform these calculations, this problem can be solved using the values of the coefficients in Eq. (34) and physically substantiated values of the parameters of the experimental system. All coefficients in Eq. (34) are functions of parameters ε , P ,

and $\beta(0)$ and depend strongly on ω_D (see formulas (25), (30), and (32)).

First of all let us estimate the effective value of the ω_D frequency that should be inserted into these equations. The hydrogen crystal belongs to the class of the so-called quantum crystals in which the amplitude of zero vibrations of molecules is comparable with the distance a accessible for motion (a is the difference between the intermolecular distance and double van der Waals radius of the molecule).²⁷ Anharmonism of intermolecular vibrations is already manifested at very low frequencies. For these crystals, it is not allowed to use a linear approximation of the frequency spectrum for obtaining the Debye frequency

$$\omega_D \approx (2\alpha\pi/d) \cdot c, \quad (35)$$

where c is the sound velocity in the crystal, and d is the lattice constant. For HD crystals, Eq. (35) gives $\omega_D \approx 80$ K. In fact, the exact law of vibration dispersion of vibrations in the hydrogen crystal is unknown. To find the effective frequency ω_D in formulas (25), (30), and (32), let us perform the following analysis.

In the simplified model of the hydrogen crystal, only the repulsive forces involved in the intermolecular interaction can be considered as the zero approximation, and attraction can be considered as a distortion. As shown below, for the unidimensional model of the crystal consisting of repulsing balls, the spectrum of excitations has the Fermi character and does not resemble at all the Bose phonon spectrum. If we neglect the possibility of the statistically improbable transition of these balls from one chain into another in the three-dimensional model of the crystal, the spectrum of the three-dimensional crystal of repulsing balls also has the Fermi character. The collective phonon Bose branch of the spectrum appears only due to the existing attraction, and the ω_D value, which has a sense of the maximum photon energy, should approximately be determined by the average value of interparticle attraction U_{att} . Knowing this value,²⁷ we can easily determine that $\omega_D \approx 15$ –30 K.

According to Eqs. (25)–(30), the general form of the temperature-dependent terms in the equations for $\ln K$ can be given as

$$(\ln K)_s \sim A_s(\epsilon_{\text{ph}} - P_s)^2 \cdot (T/\omega_D)^{n_s}/P_s \cdot \omega_D,$$

where s corresponds to the mechanisms considered above, n_s is the power of the temperature dependence following from this mechanism, and A_s is the numerical factor. From the definition of P_s , we have

$$P_s \sim M\omega_D^2\delta^2,$$

where δ is the effective displacement of centers of vibrations. At $\omega_D \approx 20$ K and $\delta \sim 1$ Å, we obtain $P_s \approx 30$ K. Then the factor in Eq. (34) is $(\epsilon_{\text{ph}} - P_s)^2/P_s \approx \epsilon_{\text{ph}}^2/P_s \approx 10^3$ K.

The thermal effect of reaction (I), related to the difference of zero vibrations of HD and D₂ molecules, is

500 K. However, it should be kept in mind that a portion of this energy, as mentioned above, can be transformed into vibrational degrees of freedom of molecules involved in the reactions. Rotational transitions can compensate a significant fraction of the energy defect. At the same time, due to the fact that a possible change in the rotational energy is quantified with a very large increment (the energy of the first rotational level is ~ 60 K, and with an increase in the number of the level the value of the rotational quantum increases), it is improbable that the excitation of rotational degrees of freedom exactly compensates the energy defect of the reaction. Therefore, the energy transmitted into the phonon subsystem is sufficiently high (in this case, it is ~ 300 –350 K). Note that the Gaussian approximation

$$\epsilon_{\text{ph}}, P \gg \omega_D,$$

which underlies the equation derived above, is valid precisely under these conditions. As follows from the estimations presented above, this inequality is fulfilled sufficiently well.

We accomplished three physically substantiated variants of fitting the coefficients in formula (34) to the experimental temperature dependence¹⁷:

$$1) \ln K = \ln K_0 + C_4 T^4 + C_6 T^6,$$

$$2) \ln K = \ln K_0 + C_6 T^6 + C_8 T^8,$$

$$3) \ln K = \ln K_0 + C_4 T^4 + C_8 T^8.$$

Variant 1) corresponds to the combined manifestation of the barrier modulation (see formula (30)) and rearrangement of the phonon subsystem in case 1 (see formula (25)). Variant 2) is attributed to the first mechanism corresponding to the rearrangement of the vibrational subsystem with combined manifestation of cases 1 and 3. Finally, variant 3) is a combination of the second and third mechanisms.

The following values of the parameters were obtained by fitting:

$$1) \ln K_0 = 1.6832, C_4 = 0, C_6 = 5 \cdot 10^{-5};$$

$$2) \ln K_0 = 1.2647, C_6 = 2 \cdot 10^{-5}, C_8 = 8.245 \cdot 10^{-7};$$

$$3) \ln K_0 = 1.24944, C_4 = 3.3 \cdot 10^{-4}, C_8 = 1.097 \cdot 10^{-6}.$$

To determine which of the mechanisms best fits the experimental temperature dependence, let us calculate the C_4 , C_6 , and C_8 coefficients according to formulas (25), (30), and (32), assuming $\epsilon_{\text{ph}} = 300$ K, $P \approx 30$ K, and $\omega_D \approx 20$ K.

Accepting $C_4 \approx 3 \cdot 10^{-4}$ (variant 3)), we obtain (see formula (30)) the value of the parameter $S' \ll 1$, i.e., the contribution from the barrier modulations to the temperature dependence is negligible. This also corresponds to variant 1) where $C_4 \approx 0$. In general, a strong experimental temperature dependence of the rate constant requires high powers of T in the exponent. The results of fitting show that the lowest value of the power

is six. Therefore, we do not consider case 2 from the first mechanism. The C_6 values in variants 1) and 2) are close by an order of magnitude and satisfactorily described by formula (25) at the above presented values of the P and ω_D parameters. Variant 2) is inappropriate, because the ratio of coefficients $C_6/C_8 \approx 2.5 \cdot 10^{-3}$ can be provided, according to the estimations by formula (25), only at a very low value $\omega_D \approx 6-7$ K. Of variants 1) and 3), the first one can be considered preferable, because in it the value $C_6 = 5 \cdot 10^{-5}$ is obtained according to formula (25) at $\omega_D = 20$ K, $\Delta E = 300$ K, and $P = 30$ K, and in variant 3), to obtain $C_8 \approx 10^{-6}$, the lower values $\omega_D \approx 15$ K and the higher values $P \approx 3 \cdot 10^4$ K should be used. Note that this minor difference in the accepted ω_D values gives a coefficient of 5.6 in the exponent due to the high power ω_D .

Thus, it can be stated that a strong temperature dependence of the rate constant at helium temperatures is determined by the rearrangement of the crystalline phonon subsystem due to the tunneling reaction, with the dependence of δ_v on ω_D corresponding to case 1 in the *first* mechanism.

Results and Discussion

The strong temperature dependence of $\ln K$ can be explained by two factors: a very strong temperature dependence of the population of the initial states (the continuous energy spectrum of degrees of freedom participating in the transition) and a very strong (exponential) dependence of the rate constant of the transition on the energy of the initial state. Both these requirements are fulfilled if modes that determine the temperature dependence are low-frequency phonon modes with a continuous spectrum and a power series ($\sim T^3$) for the temperature dependence of the number of initial states, and the rate constants of the transition are determined by the probability of changing the energy in a set of these modes during the rearrangement of the subsystem related to the transition. This rate constant is determined by the Frank-Condon factors, which can depend exponentially on the energy of the initial state. In addition, it is necessary that the energy release to the phonon modes should be sufficiently high, $\varepsilon_{ph} \gg \omega_D$.

We can see that for the description of the experiment $\omega_D \approx 20$ K should be accepted, and this is precisely the ω_D value which follows from the qualitative consideration of the vibrational spectrum in the hydrogen crystal.

When the value $\omega_D \approx 80$ K proposed in the literature²⁷ is introduced into the C_4 , C_6 , and C_8 coefficients as the approximation of the linear law of dispersion to the value of the wave vectors $2\pi/d$ (see formula (35)), we obtain for the rate constant a plateau down to temperatures ≤ 80 K, which strongly contradicts the experiment.¹⁷

It is intriguing that case (1) from the *first* mechanism is preferable for the dependence of δ_v on ω ($\delta_v = \text{const}$). In fact, the correlation $\delta_v \sim \omega$ is valid for long-

wave vibrations, but it is true in the general case only for small displacements of δ_v or, in other words, for a sufficiently rigid crystal. Due to softness of the hydrogen crystal, the linear size L of the deformation region of the crystal near the internodal atom is high ($L \gg d$). For all phonons with the wave vector q , such as

$$qL \geq 1/\pi, \quad (36)$$

δ_v is independent of q . For $\hbar\omega = 2\pi\hbar cq \geq T_0 = 3$ K (the temperature dependence of the rate constant has previously been studied¹⁷ at $T \geq 3$ K), inequality (36) gives $L \geq 1/q = 2\pi\hbar c/T_0 \sim 5d$. This value seems reasonable for the linear size of the deformation region. In the region of lower temperatures where longer-wave phonons are significant, inequality (36) is distorted, and case 3), $\delta \sim \omega$, is preferable. However, in this temperature region the C_8 value is so low that the true low-temperature plateau should be observed for the rate constant.

At $T \leq \omega_D \approx 20$ K, inhibition of an increase in $\ln K$ with temperature increase should be expected, but the temperature of melting of the crystal falls in this temperature region. However, it is of interest to continue experiments to $T \rightarrow T_{pl}$.

Let us consider a one-dimensional chain of N mutually repulsing structureless particles with mass m . The Hamiltonian of the system can be written in the form:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \frac{d^2}{dx_i^2} + U_1(x_1) + U_N(x_N) + \sum_{p=1}^{N-1} U(x_{p+1} - x_p). \quad (1)$$

$$\text{Here } U(x_{n+1} - x_n) = \begin{cases} 0 & x_{n+1} - x_n > a \\ \infty & x_{n+1} - x_n = -x_p = a, \end{cases} \quad (2)$$

where a is the linear size of the particle,

$$U_1(x_1) = \begin{cases} 0 & x_1 > 0 \\ \infty & x_1 = 0, \end{cases} \quad U_N(x_N) = \begin{cases} 0 & x_N < L \\ \infty & x_N = L, \end{cases} \quad (3)$$

where L is the chain length.

Evidently, according to Eqs. (2) and (3), the multidimensional space in which the system is considered is the interior of the N -dimensional polyhedron in which $0 \leq x_1 \leq x_2 \leq x_3 \leq x_N \leq L$.

Based on (1), (2), and (3), we establish that the full wave function of the system $\psi_N(x_1, \dots, x_N)$ possesses the following boundary conditions:

$$\psi_N = 0 \quad \left[\begin{array}{l} x_1 = 0 \\ x_{p+1} = x_p + d \\ x_N = L \end{array} \right], \quad p = 1, \dots, N-1. \quad (4)$$

The general form of ψ_N that satisfies the Schrödinger equation with Hamiltonian (I) and boundary conditions (4) is the Slater determinant built on the functions of free motion

$$\psi_n = \sin\left(n \cdot \frac{\pi}{L} \tilde{x}_p\right), \quad (5)$$

$$\tilde{x}_p = x_p - (p-1) \cdot d, \quad \tilde{L} = L(N-1)d, \quad (6)$$

$$\psi_N = \sqrt{\frac{2^N}{N!}} \begin{vmatrix} \sin\left(n_1 \frac{\pi}{\tilde{L}} \tilde{x}_1\right) & \dots & \sin\left(n_N \frac{\pi}{\tilde{L}} \tilde{x}_1\right) \\ \sin\left(n_1 \frac{\pi}{\tilde{L}} \tilde{x}_2\right) & \dots & \sin\left(n_N \frac{\pi}{\tilde{L}} \tilde{x}_2\right) \\ \vdots & & \vdots \\ \sin\left(n_1 \frac{\pi}{\tilde{L}} \tilde{x}_N\right) & \dots & \sin\left(n_N \frac{\pi}{\tilde{L}} \tilde{x}_N\right) \end{vmatrix}. \quad (7)$$

It can be readily understood that the boundary conditions are met at the boundaries of the section due to the form of functions (5), and during contact of the particles, $\tilde{x}_{n+1} = \tilde{x}_n$, due to the equality of two rows of determinant (7). It can be seen that only at $n_1 \neq n_2 \neq \dots \neq n_N$ do the wave functions differ from zero, i.e., only one condition of absolute collision of particles ((3), (4)) results in the Fermi wave function and Fermi spectrum.

Thus, for the energy of the system we have:

$$E_{n_1, \dots, n_N} = \sum_{i=1}^N \frac{\hbar^2}{2m} \cdot \left(\frac{\pi}{\tilde{L}}\right)^2 \cdot n_i^2, \quad (8)$$

$$n_1 \neq n_2 \neq \dots \neq n_N,$$

and the Fermi energy is given by

$$E_F = \frac{1}{3} \frac{\hbar^2}{2m} \cdot \left(\frac{\pi}{\tilde{L}}\right)^2 \cdot N^3 = 1/3 \varepsilon_N,$$

$$\varepsilon = \pi^2/r^2,$$

where $l = d - 2a$, where $d = l/N$ is the period of the one-dimensional lattice.

The authors thank V. L. Klochikhin for help in numerical simulation of the experimental curve.

The work was financially supported by the Russian Foundation for Basic Research (Project Nos. 99-03-32139, 99-03-33277, and 99-03-32119).

References

1. V. I. Goldanskii, L. I. Trakhtenberg, and V. N. Fleurov, *Tunnelling Phenomena in Chemical Physics*, Gordon and Breach Science Publ., New York, 1989.
2. E. I. Grigoriev and L. I. Trakhtenberg, *Radiation-Chemical Processes in Solid Phase: Theory and Application*, CRC Press, New York—London—Tokyo, 1996.
3. L. I. Trakhtenberg, *Khim. Fiz.*, 1995, **14**, 96 [*Chem. Phys. Reports*, 1995, **14**, 1177 (Engl. Transl.)].
4. V. L. Klochikhin, S. Ya. Pshezhetskii, and L. I. Trakhtenberg, *Dokl. Akad. Nauk SSSR*, 1978, **239**, 324 [*Dokl. Chem.*, 1978, **239**, 127 (Engl. Transl.)].
5. L. I. Trakhtenberg, V. L. Klochikhin, and S. Ya. Pshezhetskii, *Chem. Phys.*, 1982, **69**, 121.
6. G. K. Ivanov and M. A. Kozhushner, *Fizika Tverdogo Tela* [*Solid State Physics*], 1978, **20**, 9 (in Russian).
7. G. K. Ivanov and M. A. Kozhushner, *Khim. Fiz.*, 1983, **2**, 10396 [*Chem. Phys. Reports*, 1983, **2** (Engl. Transl.)].
8. W. Ziebrand, T. A. Wildman, and M. Z. Zgierskii, *Chem. Phys. Lett.*, 1983, **98**, 108.
9. L. Lavtchieva and Z. Smedarchina, *Chem. Phys. Lett.*, 1991, **184**, 545.
10. V. A. Benderskii, D. E. Makarov, and C. A. Wight, *Chemical Dynamics at Low Temperatures*, J. Wiley and Sons, New York, 1994.
11. H. S. Jonston and D. Rapp, *J. Am. Chem. Soc.*, 1961, **83**, 1.
12. R. L. Hudson, M. Shiotany, and F. Williams, *Chem. Phys. Lett.*, 1977, **48**, 193.
13. K. Toriyama, K. Nunome, and M. Iwasaki, *J. Am. Chem. Soc.*, 1977, **99**, 5823.
14. R. J. Le Roy, H. Murai, and F. Williams, *J. Am. Chem. Soc.*, 1980, **102**, 2325.
15. B. Prass, J. P. Colpa, and D. Stehlik, *J. Chem. Phys.*, 1988, **88**, 191.
16. B. Prass, J. P. Colpa, and D. Stehlik, *Chem. Phys.*, 1989, **136**, 187.
17. T. Kumada, K. Komaguchi, Y. Aratono, and T. Miyazaki, *Chem. Phys. Lett.*, 1996, **261**, 463.
18. K. Toriyama, K. Nunome, M. Iwasaki, M. K. Fukuya, and H. Mujto, *J. Phys. Chem.*, 1977, **81**, 1410.
19. H. Y. Wong and J. E. Willard, *J. Phys. Chem.*, 1979, **83**, 2585.
20. E. B. Gordon, A. A. Pel'menev, O. F. Pugachev, and V. V. Klimenko, *Pis'ma v Zh. Eksp. Teor. Fiz.*, 1983, **37**, 237 [*JETP Lett.*, 1983, **37** (Engl. Transl.)].
21. A. V. Ivliev, A. S. Iskovskii, and A. Ya. Katunin, *Pis'ma v Zh. Eksp. Teor. Fiz.*, 1983, **38**, 317 [*JETP Lett.*, 1983, **38**, 379 (Engl. Transl.)].
22. I. Y. Chan, N. M. Wong, and D. Stehlik, *Chem. Phys. Lett.*, 1994, **219**, 187.
23. G. K. Ivanov and M. A. Kozhushner, *Chem. Phys.*, 1993, **170**, 302.
24. R. Balian and C. Bloch, *Ann. Phys.*, 1971, **63**, 592.
25. K. Ya. Burshtein, G. K. Ivanov, M. A. Kozhushner, and V. S. Posvyanskii, *Zh. Eksp. Teor. Fiz.*, 1996, **109**, 63 [*JETP*, 1996, **82**, 32 (Engl. Transl.)].
26. P. Hanggi, P. Talkner, and M. Borkovec, *Rev. Mod. Phys.*, 1990, **62**, 251.
27. F. Silvera, *Rev. Mod. Phys.*, 1980, **52**, 393.
28. C. I. Pekar and M. F. Deigen, *Zh. Eksp. Teor. Fiz.* [*Sov. J. Exp. Theor. Phys.*], 1948, **18**, 481 (in Russian).
29. H. Kun and A. Rhys, *Proc. Roy. Soc.*, 1950, **204**, 406.
30. R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966; 1959, **26**, 867.
31. S. M. Pekar and M. A. Krivoglaз, *Tr. In-ta Fiziki Akad. Nauk UkrSSR* [*Works of Institute of Physics, Ukrainian Academy of Sciences*], 1953, **4**, 37 (in Russian).
32. G. K. Ivanov, *Zh. Eksp. Teor. Fiz.* [*Sov. J. Exp. Theor. Phys.*], 1963, **44**, 573 (in Russian).

Received March 5, 1999