Reviews

Quantum theory of molecular rearrangements

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A universal approach to description of quantum dynamics of nonrigid molecules and molecular complexes is outlined. The method includes reconstruction of the potential energy surface using data of quantum-chemical calculations of the geometry and eigenfrequencies for the ground and transition states followed by solution of the multidimensional dynamical problem with the semiclassical approximation. The approach is based on the path integral technique and can be used for calculations of frequencies of interconfigurational tunneling transitions in the ground and lowest excited states of molecules with several stable configurations and for determination of decay probabilities for the same states of metastable systems.

Key words: potential energy surface, tunneling, semiclassical approach, molecular rearrangement, unimolecular reaction.

Introduction

Any chemical reaction can be considered as a rearrangement of the reactive complex, which transfers a stable configuration on the potential energy surface (PES) in the reactant valley into a stable configuration in the product valley. The strategic goal of modern quantum chemical dynamics is to develop a universal formalism for the description of chemical reactions proceeding at initial energies E that are lower than the height $V^{\#}$ of the barrier dividing these valleys, *i.e.*, to establish regularities relating the probabilities of tunneling transitions to peculiarities of the PES structure. In this definition we emphasize the distinction between the quantum chemical dynamics and classical dynamics, which deals with thermally activated reactions proceeding at initial energies that are higher than the barrier height ($E \geq V^{\#}$) and corresponding to strong vibrational excitation of the reactants. Since for polyatomic systems the density of vibrational states increases in proportion to the factorial of the vibrational quantum number, in the energy range corresponding to classical reaction transitions (in the vicinity of $V^{\#}$) the energy spectrum becomes so dense that even relatively weak nonlinear interactions (*e.g.*, cross-anharmonicity) provide stochastic behavior of the states, *i.e.*, transition from regular to stochastic motion.[1,2] This transition substantiates the use of statistical theories (*e.g.*, the transition state theory and the Russel—Ramsperger—Kassel—Marcus (RRKM) theory[3,4]) in classical chemical dynamics. At the same time, at low initial energies, *i.e.*, in the region of a discrete spectrum of vibrational states with "good" quantum numbers, the motion remains regular.

A thermally activated regime of chemical reaction is changed by a tunneling regime at temperatures below the characteristic crossover temperature T_c.[5] In the vicinity of T_c, the temperature dependence of the rate constant shows a bend and the Arrhenius law is no longer valid. At temperatures below T_c the major contribution to the rate constant comes from low-energy

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states; therefore the region of regular motion is of prime interest for quantum dynamics. Because of distinctions between the states dominating in classical and quantum dynamics, spectroscopic investigations of nonrigid molecules, whose rearrangements reproduce almost all types of transformations occurring in chemical reactions, have a crucial advantage over studies of reactive complexes. In the latter case, available information on the dynamics of the systems studied is restricted to the dependence of the rate constants on the energy (or temperature) only. At the same time, rearrangements of nonrigid molecules and molecular complexes are characterized by a set of tunneling frequencies (tunneling matrix elements) for different vibrational states which are measured by high-resolution molecular spectroscopy[6] and make it possible to perform much more sophisticated tests for the validity of the theory than chemical kinetics data. The development of different methods of vibration-tunneling spectroscopy, including laser spectroscopy of supersonic cooling,[7] NMR spectroscopy, and inelastic neutron scattering[8] (see also review[6]), made it possible to study a wide variety of molecular rearrangements and stimulated the progress of quantum chemical dynamics in the last decade. The state-of-the-art in this new area of theoretical chemistry is determined not only by the quest to create a more universal theory of chemical reactions than the transition state theory, but also by the search for new methods of increasing their selectivity, which, apparently, is associated with selective activation of only those degrees of freedom which participate in the reaction. This can be done in the case of mode specific excitation of the reactive complex[9,10]; however, the above-mentioned mixing of higher vibrational states prevents such an activation. It is possible to reduce this undesirable effect by passing to low energies and temperatures, *i.e.*, to the region where nonmixed vibrational states dominate. It should be emphasized that the mode specific reactions form a basis for the development of new efficient methods for isotope separation.

Most theoretical studies on quantum chemical dynamics are carried out following two main investigation lines, namely, introduction of quantum corrections into statistical theories[11,12] and consideration of quantum transitions in a discrete spectrum of vibrational states.[6] If the known approaches are mostly used in the former case, the progress of the latter investigational line is associated with the development of new methods for quantitative description of multidimensional tunneling. In this connection, mention may be made of the reaction path Hamiltonian approach,[13,14] in which a specific trajectory is introduced in the spirit of the transition state theory and the narrow vicinity of this trajectory makes the major contribution to the transition probability. If the vibrationally adiabatic approximation is valid (the frequencies of transverse vibrations with respect to the reaction path are higher than the characteristic frequency of longitudinal motion), the multidimensional problem can be reduced to the one-dimensional one in which the motion occurs along the reaction path in the effective potential and the width of the reaction channel is determined by the reaction coordinate dependent amplitudes of transverse vibrations. Later, improved two-dimensional models[14,15] based on the Feynman path integrals technique[16] were proposed. Nevertheless, it was impossible to study tunneling dynamics of polyatomic molecules without artificial reduction of the number of degrees of freedom. Recently,[17—21] a universal semiclassical approach, free from this limitation, was suggested. In this work we briefly outline this approach in order to sum up the previously reported results in a form suitable for calculating particular systems.

Classical and tunneling extreme trajectories

The probability of a thermally activated overcoming of a barrier is determined by its height $V^{\#}$ only, so the reaction path coincides with the minimum energy path (MEP) and passes through a saddle point on the surface dividing the reactant and product valleys (Fig. 1). The width of the classical reaction channel is determined by the amplitudes of thermal transverse vibrations about the MEP, which are equal to $(k_B T/m)^{1/2}$, where k_B is the Boltzmann constant and m is the reduced mass. The same path characterizes the tunneling reaction in the vibrationally adiabatic limit at $T < T_c$ where the channel width becomes equal to the zero-point amplitude $(\hbar/m\omega)^{1/2}$, where ω is the frequency of vibration. In the Feynman picture of quantum mechanics[22] the probabilities of different quantum trajectories are determined by the minimum action principle and, hence, are dependent not only on $V^{\#}$, but also on the path length. For low-frequency transverse vibrations the extreme tunneling trajectory (ETT) does not coincide with the MEP; the higher the barrier, the shorter the ETT. These "cutting corner" trajectories[23] (see Fig. 1) have been studied in detail in the low-frequency limit, which is opposite to the adiabatic limit.[24—26] The shape of the ETT at arbitrary longitudinal/transverse vibration frequency ratios has been considered previously.[17—21] The passage from adiabatic trajectories approaching the MEP to corner-cutting trajectories with decreasing frequency of transverse vibration is illustrated in Fig. 2. In the path integrals formalism the tunneling path is defined as a zero-energy ETT satisfying the minimum action principle in the classically forbidden region of the potential barrier. It was shown[27—29] that such an ETT can be found from the solution of the classical equations of motion in imaginary time and with an "upside-down" barrier. This requires such a transformation of the phase space that the coordinates (X) remain real, whereas the conjugate momenta (p) become imaginary, so the potential and energy change their signs:

$$t \to -\mathrm{i}t, \quad X \to X, \quad p \to \mathrm{i}p, \quad V \to -V, \quad E \to -E, \qquad (1)$$

where t is time.

Relationships (1) show that, in contrast to the motion in the classically accepted region with real momenta, the motion in the potential barrier is instantaneous on the real time scale. For this reason, the ETT defined above was called instanton. A review concerning applications of the instanton approach to quantum chemical dynamics was reported.[6] Two stable configurations correspond to global maxima of "upside-down" PES, the system occupies one of them, passes to the other maximum, and returns back (Fig. 3). Since the direct and reverse transitions are separated by an arbitrary time interval, the ETT consists of a "kink—antikink" pair. An ETT called "bounce," which includes a portion from the top to the wall and back, corresponds to decay of a metastable state. If a double-well potential becomes asymmetric, the kink—antikink pair is transformed into a bounce.[30] The instanton approach is semiclassical in the sence that it uses expansion in terms of small semiclassical parameter γ^{-1}, which is equal to the ratio of the zero-point energy to the barrier height

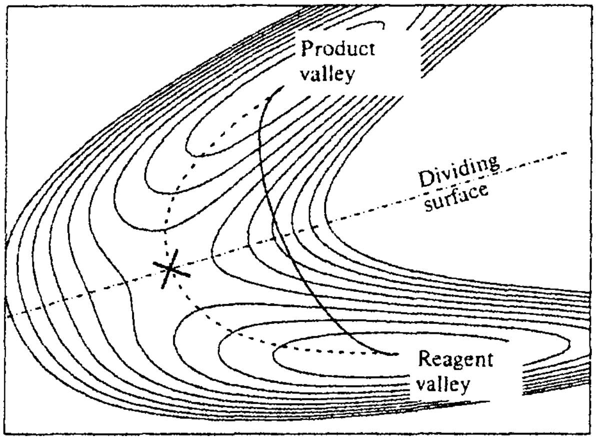

Fig. 1. Equipotential plot of two-dimensional cut of the PES with two equivalent configurations. The MEP connecting the PES minima and passing through the saddle point on the PES is shown by a dashed line; the corner-cutting tunneling trajectory is shown by a solid line. The saddle point is shown by a cross.

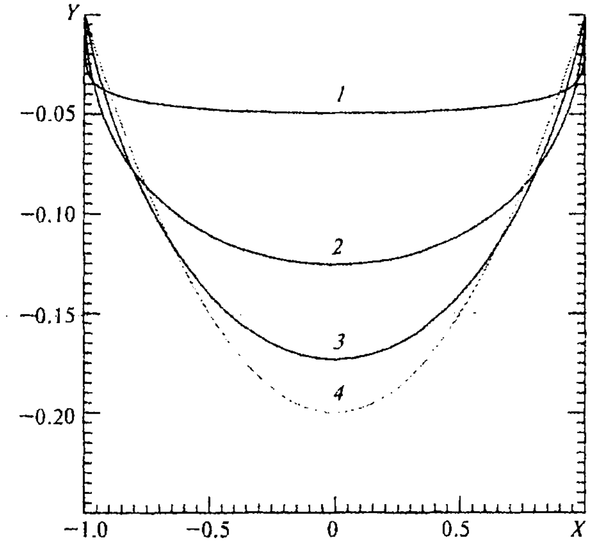

Fig. 2. Change in the shape of 2D tunneling trajectory depending on the transverse vibration frequency ω. The transverse/longitudinal vibration frequency ratio is 0.15 (*1*), 0.6 (*2*), and 1.5 (*3*). Curve *4* is the MEP.

$$\gamma = m\Omega a^2/(2\hbar) = \zeta V^{\#}/(\hbar\Omega), \tag{2}$$

where $2a$ is the distance between the PES minima (the transfer length), Ω and m are the frequency and mass of longitudinal vibration at the PES minimum, respectively, and ζ is the shape factor of the barrier. The semiclassical action on the instanton (W) has the form

$$W = \int_{-T/2}^{T/2} [0.5m(\mathrm{d}s/\mathrm{d}t)^2 + V(s)]\mathrm{d}t = \int_{-a}^{a} \sqrt{2mV(s)}\,\mathrm{d}s \tag{3}$$

(where T is the period of vibration and s is the distance along the ETT) and determines the exponent of the semiclassical wave function (Ψ). The dependence of Ψ on vibrational quantum numbers is included in the prefactor A, which is determined by root-mean-square fluctuations about the ETT for the ground-state function:

$$\Psi_{n,\{n_k\}} = A_{n,\{n_k\}}\exp(-W/\hbar). \tag{4}$$

where n and n_k are the vibrational quantum numbers. Though the expansion in powers of γ^{-1} used in the instanton approach is equivalent to the expansion in $\hbar$ in conventional semiclassical approximation (see, *e.g.*, Ref. 31), the distinctions are that (1) the ETT has zero energy (see Eq. (3)) and (2) no motion in the classically acceptable regions is considered in the instanton approach and, hence, there are no turning points at which the solutions for the accepted and forbidden regions are to be matched. Such an approach is substantiated by the fact that an asymptotically smooth transformation of the semiclassical wave function (4) into the product of the functions of harmonic oscillators, corresponding to normal vibrations, occurs at the PES minima.[16,17,32] The method of calculations of prefactors for excited states of longitudinal and transverse vibrations[18] with quantum numbers (n, $\{n_k\}$) is based on the solution of the semiclassical Hamilton—Jacobi equations (HJE)

$$\left(\frac{\partial W}{\partial X}\right)^2 + \sum_k\left(\frac{\partial W}{\partial Y_k}\right)^2 = V(X, \{Y_k\}) \tag{5}$$

and the transport equation (TE)

$$\frac{\partial W}{\partial X}\frac{\partial A_{n,\{n_k\}}}{\partial X} + \sum_k \frac{\partial W}{\partial Y_k}\frac{\partial A_{n,\{n_k\}}}{\partial Y_k} - {} - 0.5\left(\frac{\partial^2 W}{\partial X^2} + \sum_k \frac{\partial^2 W}{\partial Y_k^2}\right)A_{n,\{n_k\}} = E_{n,\{n_k\}}A_{n,\{n_k\}}. \tag{6}$$

In accord with the main idea of the instanton approach, the energy eigenvalue $E_{n,\{nk\}}$ (the value of the order of $\hbar$, *i.e.*, of γ^{-1}) is transported from the HJE into the TE. Solutions of these equations are found as expansions in power series of coupling coefficients between the longitudinal and transverse coordinates. The instanton approach has the advantage over conventional semiclassical approximation that it is possible to circumvent the up-to-date unsolved problem of matching the solutions in the multidimensional case where isolated turning points become caustic surfaces (see above). The known methods for calculations of complex-time trajectories in regions bound by caustic surfaces and their continuations[33—35] can be applied to 2D problems only and their complexity is comparable with quantum calculations. At the same time, real ETT used in the instanton approach require only a system of differential equations of motion to be solved. For model PES of general form,[18,21] first-order (with respect to the coupling coefficients) solutions can be obtained analytically. It should also be noted that the whole set of excited vibrational states is characterized by a common ETT and that the action along the ETT is independent of vibrational quantum numbers. The choice of the wave functions (4) in the form of a product of the exponent, which is independent of (n, $\{n_k\}$), and the prefactor $A_{n,\{n_k\}}$ corresponds to the wave functions, which (in the weak coupling limit) are equal to the product of the functions of normal vibrations.

Symmetry of low-energy PES

Low-energy PES are expansions in a power series of internal coordinates, which include the 1D potential for angular tunneling coordinate ϕ (in some instances it becomes the rectilinear coordinate X) and a set of small-amplitude transverse vibrations $\{Y_k\}$ coupled with the ϕ coordinate. The equilibrium positions and frequencies of $\{Y_k\}$ vibrations are dependent on ϕ. The choice of such PES is due to the existence of well-defined lowest levels of normal vibrations in the classically accepted regions near the PES minima. The system of equations of motion is integrable and classical trajectories belong to the surfaces of undestroyed tori in the phase space.[1,2] The wave functions of these regular states are characterized by a set of "good" vibrational quantum numbers and exponentially decrease in the classically forbidden region. Since for typical molecular rearrangements the barrier between stable configurations is much lower than the dissociation threshold, the phase space region corresponding to irregular classical trajectories is well separated from the region of quantum transitions between the low-energy states and it is possible to use the PES with small anharmonicity of transverse vibrations, *i.e.*, to operate in the weak coupling limit.

If the geometry of the transition state is chosen as a reference system, the manifold of the configurations along the MEP is characterized by a set of internal coordinates $\delta_\alpha(\phi)$ for which the tunneling coordinate ϕ is a parameter. Let us introduce intrinsic coordinates, *i.e.*, changes in the bond lengths and bond angles with respect to the reference system, in the form

$$\delta_\alpha = \delta_\alpha{}^0 + f_\alpha(\phi), \tag{7}$$

where $f_\alpha(\phi)$ is the displacement of the equilibrium position for the αth coordinate along the MEP and $\delta_\alpha{}^0$ is the displacement with respect to the MEP point at a given value of ϕ. Generalized small-amplitude coordinates Y_k are chosen as linear combinations of δ_α, corresponding to the symmetry of the nonrigid molecule:

$$Y_k = \sum_\alpha c_{k_\alpha}\delta_\alpha. \tag{8}$$

Substituting Eq. (7) into Eq. (8), we get expressions analogous to Eq. (7):

$$Y_k = Y_k^0 + F_k(\varphi), \tag{9}$$

where Y_k can be chosen as independent variables and $F_k(\phi)$ are the displacements of the equilibrium positions for Y_k-vibrations with respect to the reference system for which $F_k(0) = 0$. Thus, the set of internal coordinates includes the large-amplitude coordinate ϕ and $3N - 7$ transverse coordinates Y_k. Let us expand the potential energy of transverse vibrations in a power series of Y_k. Since the standard configuration corresponds to a stationary point on the PES, the linear term of the expansion is equal to zero. The set of Y_k coordinates belongs to irreducible representations of the symmetry group of a nonrigid molecule[36] and, in the harmonic approxima-

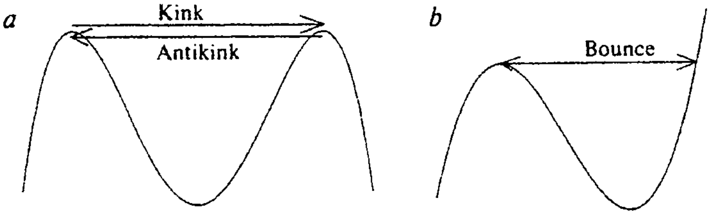

Fig. 3. Trajectories of classical motion in the upside-down barrier: the kink—antikink pair in a symmetric double-well potential (*a*); bounce in a decay potential (*b*).

tion, the potential energy of transverse vibrations $V(\{Y_k\})$ has the form

$$V(\{Y_k\}) = 0.5\sum_k \omega_k^2 Y_k^2 + 0.5\sum_k \omega_k^2 F_k^2(\phi) + \sum_k \omega_k^2 F_k(\phi) Y_k. \quad (10)$$

The first term in expression (10) describes uncoupled vibrations, the second term renormalizes the 1D potential for the tunneling coordinate, and the third term defines couplings between the tunneling and transverse coordinates. By expanding the $F_k(\phi)$ functions into a Fourier series (or into a power series for the rectilinear X coordinate) and restricting ourselves to the lowest nonzero terms it is possible to distinguish only a limited number of types of ϕY-coupling. The corresponding two-dimensional PES are shown in Fig. 4. Since the low-energy PES is characterized by small cross-anharmonicity, these two-dimensional cuts are structural elements of the multidimensional PES. The linear XY-coupling (L) is responsible for the displacement of the PES minima along the Y axis, so the ETT and MEP become longer than the one-dimensional path in a separable (with zero coupling) potential. Owing to the path elongation, the linear coupling increases the action and suppresses tunneling. On the contrary, the gated X^2Y coupling (G) causes no shifts of the minima; however, it is responsible for the displacement of the transition state, lowering the height of the potential barrier, and, thus, for increasing the tunneling probability. In the case of squeezed X^2Y^2 coupling (Sq) the one-dimensional path remains unchanged; however, the transverse frequency becomes X-dependent. There exist five types of coupling for the angular tunneling coordinate with a period of $2\pi/l$

$$\text{Sh} - Y\sin(l\phi);\quad \text{Bre} - Y\cos(l\phi);\quad \text{Asq} - Y^2\cos(l\phi);$$
$$\text{Hl} - Y\sin(0.5l\phi);\quad \text{Hga} - Y\cos(0.5l\phi). \quad (11)$$

The corresponding 2D cuts of the PES are shown in Fig. 5.

From formula (10) it follows that the approximation of noninteracting transverse vibrations corresponds to harmonic vibrations. The third- and fourth-order anharmonicities produce Sq-couplings and ϕ-dependent couplings between transverse coordinates of the type

$$Y_k Y_{k'} \sum_{k''} \gamma_{kk'k''} F_{k''}(\phi) = R_{kk'}(\phi) Y_k Y_{k'}. \quad (12)$$

Neglecting small proper anharmonicity of transverse vibrations, the PES can be represented in the form

$$V(\phi, \{Y_k\}) = V_0(\phi) + 0.5\sum_k (\omega_k^2 + R_k^S(\phi)) Y_k^2 + \sum_k R_k^{L(G)}(\phi) Y_k + \sum_{kk'} R_{kk'}(\phi) Y_k Y_{k'}, \quad (13)$$

where $R_k^{L(G)}(\phi) = \omega_k^2 F_k(\phi)$. The advantage of the PES representation in the form (13) is the possibility of establishing the type of coupling using symmetry properties of normal vibrations of the nonrigid molecule.[19] A set of "feasible" symmetry operations corresponding to displacement along the MEP forms the isodynamic group

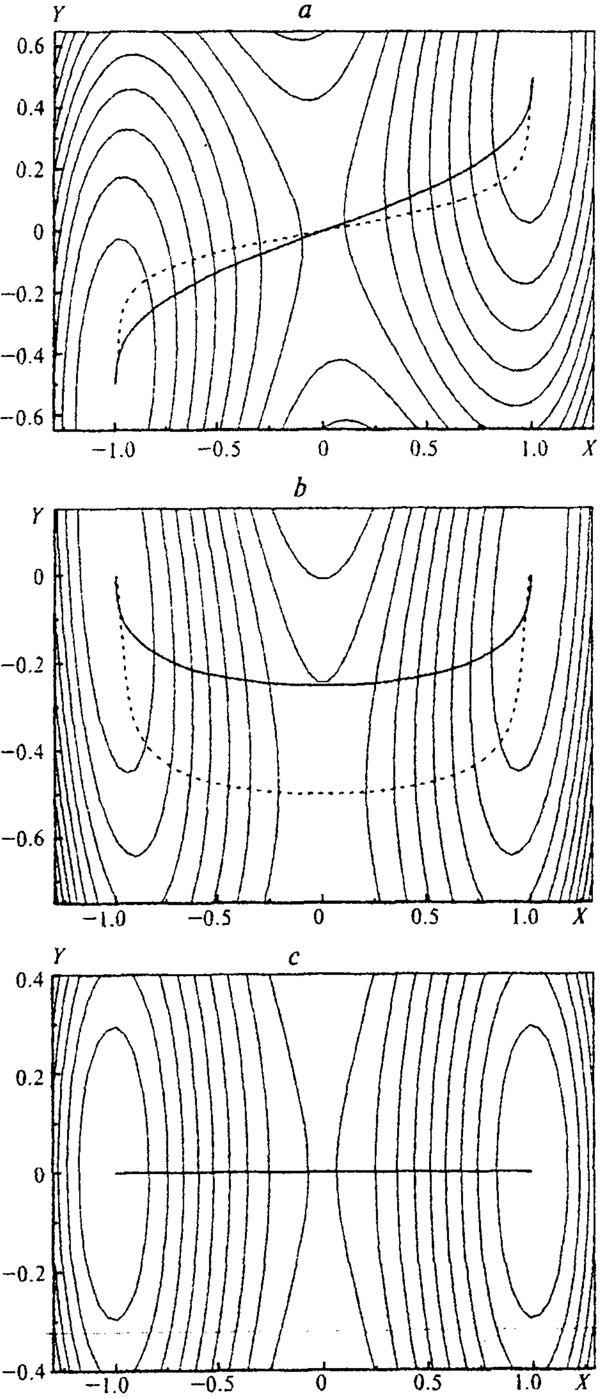

Fig. 4. Two-dimensional PESs with different symmetries of coupling between the rectilinear tunneling and transverse coordinates: L, $V = V_0(X) + 0.5\omega^2(Y - C/\omega^2X)^2$ (*a*); G, $V = V_0(X) + C(1 - X^2)Y + 0.5\omega^2Y^2$ (*b*); and Sq, $V = V_0(X) + CX^2Y^2 + 0.5\omega^2Y^2$ (*c*). $V_0(X)$ is the 1D potential. The ETT and MEP are shown by solid and dashed lines, respectively.

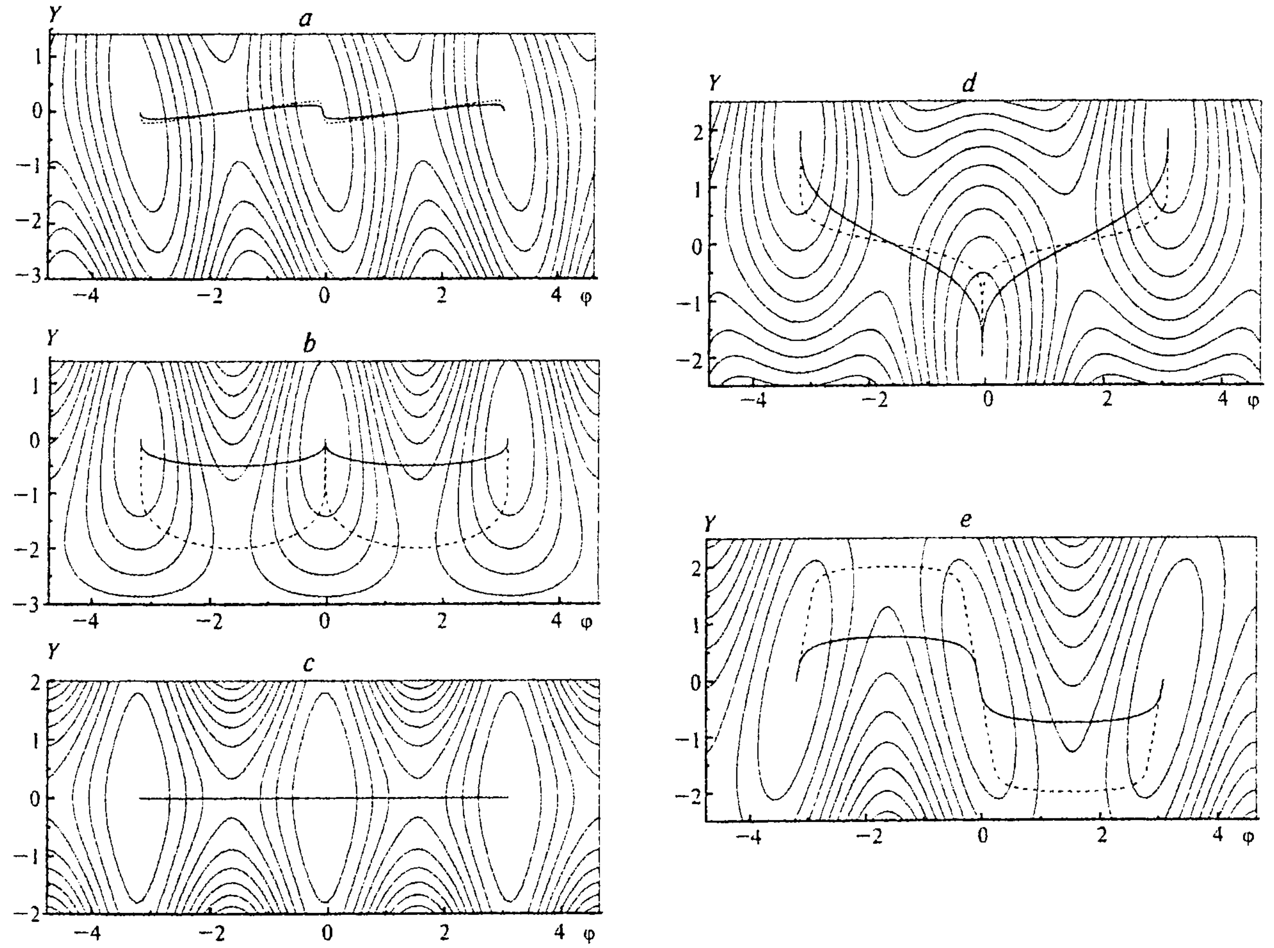

Fig. 5. Two-dimensional PESs with different symmetries of coupling between periodic tunneling and transverse coordinates: Sh (*a*), Bre (*b*), Asq (*c*), Hl (*d*), and Hga (*e*). The ETT and MEP are shown by solid and dashed lines, respectively.

G, which includes (i) the point group G^p for an arbitrary ϕ value and (ii) the internal group G^1, which transforms one stable configuration into another one, as subgroups[36—38]:

$$G = G^p \otimes G^1,$$

where the symbol $\otimes$ denotes the semi-direct product. The type of coupling is established using the correlation diagram relating the irreducible representations of the point symmetry groups for the ground ($G^p{}_0$) and transition ($G^p{}_\#$) states *via* the irreducible representations of the isodynamic group. The $G^p{}_\#$ point group always contains the $O_\#$ operation, which transforms one stable configuration into another one, the ϕ coordinate being antisymmetric with respect to $O_\#$. If $O_\#$ is a mirror in plane $\sigma_\#$, the latter coincides with the dividing surface of the PES where the transition state is situated. If the $G^p{}_0$ group contains no symmetry operations absent in $G^p{}_\#$ (*i.e.*, if $G^p{}_0$ and (E, $O_\#$) are subgroups of $G^p{}_\#$), antisymmetric transverse vibrations belonging to the same representation in the $G^p{}_0$ group as ϕ are coupled linearly, because the characters of all operations except for $O_\#$ coincide in this representation. If symmetric vibrations and ϕ belong to the same representation in $G^p{}_0$ but to different representations in $G^p{}_\#$, the coupling is of the gated-type. If Y and ϕ belong to different representations in both the $G^p{}_0$ and $G^p{}_\#$ groups, the coupling is totally symmetric. This simplest case corresponds to the linear tunneling coordinate and, *e.g.*, to a proton transfer. The corresponding correlation diagrams are shown in Fig. 6, *a*. For the elements absent in $G^p{}_\#$ to appear in the $G^p{}_0$ group, the internal group G^1 must contain a C_l symmetry axis of an order higher than 2, which lies in the $\sigma_\#$ plane and transforms this plane into the corresponding element of $G^p{}_0$. Hence it follows that the tunneling coordinate should be an angular coordinate with a period of $2\pi/l$ ($l > 2$), while the isodynamic group should contain degenerate irreducible representations (one of them is symmetric, whereas the other is antisymmetric with respect to $\sigma_\#$) correlating with different irreducible representations of $G^p{}_0$ and $G^p{}_\#$. If there is only the MEP for the nonrigid molecule, the tunneling coordinate belongs to the nondegenerate antisymmetric repre-

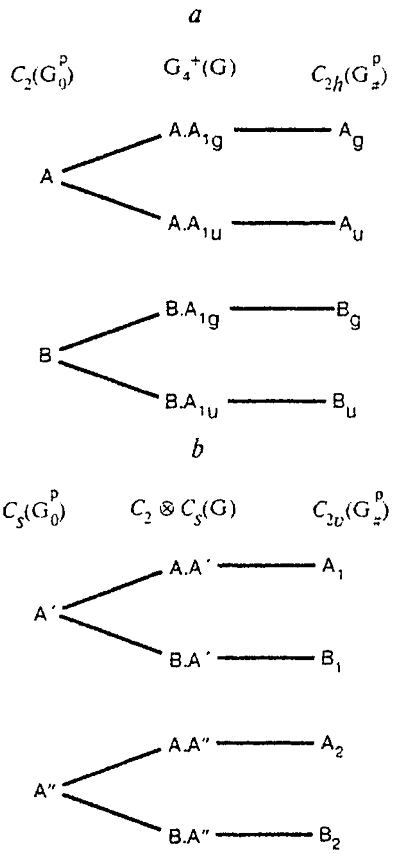

Fig. 6. Correlation diagrams of irreducible representations for the H_2O_2 molecule $C_2(G^P{}_0)-C_2\otimes C_{2h}-C_{2h}(G^P{}_\#)$ (*a*) and the hydroxyoxalate ion $C_s(G^P{}_0)-C_2\otimes C_s-C_s(G^P{}_\#)$ (*b*).

sentation of the isodynamic group. The diagram for $l = 3$ is shown in Fig. 6, *b*. Types of coupling for different nonrigid molecules were described previously.[19] Since the (ϕ, $\{Y_k\}$) coordinates are not normal modes of the ground state, kinematic couplings arise between them in addition to potential couplings, and the kinetic energy operator[20] depends on ϕ.

Determination of the PES parameters from the data of quantum-chemical calculations

The following parameters are determined in standard quantum-chemical calculations of the equilibrium geometry, frequencies, and eigenvectors of normal vibrations of a nonrigid N-atomic molecule in the ground and transition states:

(1) the barrier height in the transition state ($V^\#$);

(2) 3-vectors of atomic positions $\boldsymbol{a}_\alpha{}^\#$ and $\boldsymbol{a}_\alpha{}^0$, $\alpha = 1, ..., N$ in three-dimensional Cartesian frames, which are different for the transition ($E^\#$) and ground (E^0) states;

(3) $2(3N - 6)$ eigenfrequencies and $2(3N - 6)$ effective masses of normal vibrations for the transition ($\Omega_k{}^\#$, $m_k{}^\#$) and ground ($\Omega_k{}^0$, $m_k{}^0$) state, $k = 1, ..., 3N - 6$;

(4) $3N\times(3N - 6)$-matrices $s^\#$ (and s^0), which relate the $\boldsymbol{d}_{\alpha i}{}^\#$ ($\boldsymbol{d}_{\alpha i}{}^0$) displacements ($i = 1, 2, 3$) in the $E^\#(E^0)$ frame to the $\boldsymbol{Q}_k{}^0$ ($\boldsymbol{Q}_k{}^\#$) eigenvectors in the respective $(3N - 6)$-dimensional spaces of normal vibrations

$$s_{k\alpha i} = \partial Q_k/\partial \boldsymbol{d}_{\alpha i}, \qquad Q^\# = s^\# \boldsymbol{d}^\#, \qquad Q^0 = s^0 \boldsymbol{d}^0. \tag{14}$$

Transformation of the E^0 frame into the $E^\#$ frame is performed using the Eckart conditions, according to which the molecular geometry (its internal deformation) is independent of both displacements of the center of mass $\boldsymbol{R}^0$ and rotation of the entire molecule given by the rotation matrix $U(\chi^0,\theta^0,\varphi^0)$. The Eckart conditions separate six external coordinates (projections of the 3-vector $\boldsymbol{R}^0$ and three angles of rotation χ^0, θ^0, and φ^0) and define the position vectors and Cartesian displacements in the ground and transition states in the same frame for the $E^\#$ state

$$\begin{aligned} \tilde{\boldsymbol{a}}^0_{\alpha i} &= \boldsymbol{R}_i^0(\phi) + U(\chi^0, \theta^0, \varphi^0)\,\boldsymbol{a}^0_{\alpha i}, \\ \boldsymbol{d}^\#_{\alpha i} &= U(\chi^0, \theta^0, \varphi^0)\,\boldsymbol{d}^0_{\alpha i}. \end{aligned} \tag{15}$$

Eqs. (14) and (15) define the $(3N - 6)\times(3N - 6)$ transformation matrix of normal coordinates

$$Q^\# = SQ^0, \qquad S = s^\# U(s^0)^{-1}. \tag{16}$$

Eqs. (15) and (16) are analogous to those used in the standard FG-formalism, which describes small-amplitude vibrations of polyatomic molecules with the only stable configuration.[39]

The type of ϕY-coupling uniquely determines the forms of the $R_{kk'}(\phi)$ functions in potential (13) and those of kinematic ϕY- and YY'-couplings.[19,20] For such a Hamiltonian of the nonrigid molecule, the frequency of ϕ-vibrations at the PES minimum, $(3N - 7)$ frequencies of transverse Y-vibrations (ω_k), $(3N - 7)$ coefficients of ϕY-couplings, and $(3N - 6)(3N - 7)/2$ coefficients of both Sq- and YY'-couplings should be determined.

The potential function $V(\phi, Y)$ and the classical kinetic energy $T(P_\phi, P_Y)$ become quadratic forms of coordinates ($\phi - \phi^\#$, $\{Y - Y^\#\}$) and ($\phi - \phi^0$, $\{Y - Y^0\}$) and their conjugate momenta ($P_\phi{}^\#$, $\{P_Y{}^\#\}$) and ($P_\phi{}^0$, $\{P_Y{}^0\}$) in the vicinity of stationary points $\phi = \phi^\#$ and $\phi = \phi^0$, respectively. Let us introduce the $(3N - 6)\times(3N - 6)$-matrices of transformation of these coordinates into normal ones

$$Q^\# = P^\#[(\phi - \phi^\#), \{Y - Y^\#\}],\ Q^0 = P^0[(\phi - \phi^0), \{Y - Y^0\}], \tag{17}$$

where the $(3N - 6)$-dimensional vectors ($\phi - \phi^\#$, $\{Y - Y^\#\}$) and ($\phi - \phi^0$, $\{Y - Y^0\}$) are equal because they differ in origin only. From Eqs. (16) and (17) it follows that

$$Q^\# = P^\#(P^0)^{-1}Q^0, \qquad S = P^\#(P^0)^{-1}. \tag{18}$$

The problem of determining the elements of the $P^\#$ and P^0 matrices and the above-listed parameters of the Hamiltonian is inverse to the eigenvalue problem for normal vibrations. Since V and T are diagonal in the $Q^\#$ and Q^0

coordinates, diagonalization of these pairs of quadratic forms provides a set of equations for determination of the PES parameters. It is convenient to choose an intrinsic coordinate corresponding to the change in the geometry element (the bond length, bond angle, dihedral angle, *etc.*) as ϕ coordinate. After choosing the large-amplitude coordinate it is possible to introduce the $U_0(\phi^{\#} - \phi^0)$ operation, which changes the position vectors after replacing $\phi^{\#}$ by ϕ^0 at fixed equilibrium positions for all transverse coordinates. Taking into account that the Cartesian frame transformation satisfies the Eckart conditions, let us perform a transformation analogous to transformation (15)

$$\begin{aligned}\tilde{\boldsymbol{a}}^0_{\alpha i}(\phi^{\#} - \phi^0) &= \boldsymbol{R}_i(\phi^{\#} - \phi^0) + \\ &+ U(\chi(\phi^{\#} - \phi^0), \theta(\phi^{\#} - \phi^0), \varphi(\phi^{\#} - \phi^0))U_0(\phi^{\#} - \phi^0)\boldsymbol{a}_{\alpha i}(\phi^0). \quad (19)\end{aligned}$$

Introduction of a deformed transition state whose geometry differs from the equilibrium geometry owing to ϕY-couplings only makes it possible to determine the coupling parameters by comparing the geometries and eigenvectors of normal vibrations for two rigid configurations of the transition state, corresponding to equilibrium positions of transverse coordinates at $\phi = \phi^{\#}$ and at $\phi = \phi^0$.

$$\Delta_{\alpha i}(\phi^{\#} - \phi^0) = \tilde{\boldsymbol{a}}_{\alpha i}(\phi^{\#} - \phi^0) - \boldsymbol{a}^{\#}_{\alpha i}$$

The large-amplitude coordinate and external coordinates are excluded by applying the U_0 operation and using the Eckart conditions, respectively, analogously to the case of rigid molecules. Previously,[20] it was shown that the above-listed data of quantum-chemical calculations make it possible to find the set of Y-coordinates if (1) the kinematic matrix $G^{\#}$ is a unit matrix for all types of vibrations; (2) the force constant matrix $F^{\#}$ is a diagonal supermatrix whose blocks correspond to the vibrations of different symmetry; (3) the blocks of the $F^{\#}$ matrix, corresponding to the G-, Sq-, Bre-, Asq-, and Hga-vibrations, are diagonal, while the frequencies and eigenvectors of these vibrations coincide with $\Omega_k^{\#}$ and $Q_k^{\#}$, respectively; (4) the blocks of the $F^{\#}$ matrix, corresponding to the ϕ-, L-, Sh-, and Hl-vibrations, contain off-diagonal elements equal to the coefficients of ϕY-couplings; and (5) the off-diagonal elements of YY'-couplings in the $F^{\#}$ matrix are equal to zero. These conditions follow from the shapes of the two-dimensional cuts (see Figs. 4 and 5) and take into account that the coordinates belonging to the same irreducible representation of the isodynamic group can be chosen to be mutually orthogonal. From Eqs. (17) and (18) we get

$$G^0 = (P^0)^{-1}(\tilde{P}^0)^{-1} = S(P^{\#})^{-1}(\tilde{P}^{\#})^{-1}\tilde{S} = S\tilde{S}, \quad (20)$$

where $\tilde{P}^0$ and $\tilde{S}$ are transposed matrices.

Changes in the geometry can be expressed in units of the zero-point amplitudes $[\hbar/(m_k\omega_k)]^{1/2}$. Transformations (14) and (18) make it possible to find changes in Y-coordinates in the ground state with respect to the transition state

$$\Delta Y_k(\phi^{\#} - \phi^0) = \sum_{k'\alpha i} P^{\#}_{kk'} S^{\#}_{k'\alpha i} \frac{\Delta_{\alpha i}}{\delta_k}. \quad (21)$$

The ΔY_k values are related to the coupling constants $C_k = \omega_k^2 \Delta Y_k$, thus determining $3N - 7$ coefficients for all types of coupling (11) except for Sh-coupling, for which $\Delta Y_k = 0$ and the C_k values are found from the solution of the secular equation. From the fact that the PES (13) includes the potential barrier it follows that the C_k coefficients satisfy the following inequality:

$$\sum_k (C_k/\omega_k)^2 < 1, \quad (22)$$

which makes it possible to solve the PES reconstruction problem perturbatively.[40]

Tunneling splittings in vibrational spectra of nonrigid molecules

If a nonrigid molecule has m stable configurations, vibrational levels become m-fold degenerate. Tunneling transitions remove degeneracy, thus causing splittings of vibration bands. If the splittings are small as compared with the frequencies, the energy eigenvalues for a bistable molecule ($m = 2$) are determined by

$$\begin{vmatrix} E_n^{\mathrm{L}} - E & H_{nn} \\ H_{nn} & E_n^{\mathrm{R}} - E \end{vmatrix} = 0, \quad (23)$$

where $E_n{}^{\mathrm{L}}$ and $E_n{}^{\mathrm{R}}$ are the energies of isolated left and right configurations, respectively, and the tunneling matrix element H_{nn} is calculated using the Lifshitz—Herring formula[31,41] as the probability flow through the dividing surface

$$H_{nn} = \frac{\hbar^2}{2m}\int \mathrm{d}\{Y_k\}\left(\Psi_n^{\mathrm{R}}\nabla\Psi_n^{\mathrm{R}} - \Psi_n^{\mathrm{L}}\nabla\Psi_n^{\mathrm{L}}\right)\Big|_{\phi=0}, \quad (24)$$

where $\Psi_n{}^{\mathrm{L}}$ and $\Psi_n{}^{\mathrm{R}}$ are the wave functions of isolated left and right states, respectively. The semiclassical wave functions (4) can be determined from the solution of Eqs. (5) and (6) up to normalizing factors, which, according to the basic idea of the instanton approach, can be found using the asymptotically smooth transformation of functions (4) into the product of the functions of harmonic oscillators near the potential minima.[32,42] Such a normalization of semiclassical functions makes it possible to find the H_{nn} values using Eq. (24), thus completely describing vibration-tunneling spectra of nonrigid molecules.

Since going along the tunneling coordinate is accompanied by displacements along transverse coordinates, the H_{nn} matrix element can be represented as the product of a one-dimensional matrix element along the tunneling coordinate and the Franck—Condon factor (FC)

$$H_{nn} = H^0_{nn}\,\mathrm{FC}. \tag{25}$$

Calculations of the $H^0{}_{nn}$ values are simplified by choosing simple one-dimensional potentials. For bistable molecules the double-well potential is often approximated by the so-called X^4-potential

$$V(X) = 0.125m\Omega^2a_0{}^2(1 - X^2)^2 = 0.25\gamma\hbar\Omega(1 - X^2)^2, \tag{26}$$

which depends on the parameters a_0 and Ω, which allow one to fit the shape of the one-dimensional barrier. If $\hbar\Omega$ is chosen as the energy unit, the potential and action are measured in the units of the semiclassical parameter γ defined by Eq. (2). For the potential given by expression (26) the tunneling matrix element is

$$H^0_{nn} = \hbar\Omega 2^{4n+2}\gamma^{n+1/2}/(\sqrt{2\pi}\, n!). \tag{27}$$

The following equations can be derived for hindered internal rotation about the l-fold axis in the one-dimensional potential:

$$V_0(\phi) = I\Omega^2[1 - \cos(l\phi)]/l^2 = \gamma\hbar\Omega[1 - \cos(l\phi)]/2l, \tag{28}$$

$$H^0_{nn} = [\hbar\Omega 2^{4n+2}(\gamma/l)^{n+1/2}/(\sqrt{2\pi}\, n!)]\exp(-4\gamma/l). \tag{29}$$

Eqs. (27) and (29) are the leading terms of the expansion of tunneling matrix elements in powers of the semiclassical parameter γ. If necessary, corrections of the order of γ^{-1} can also be calculated.[17] At $\gamma \geq 10$, they do not exceed 10 to 20%. The advantage of the potentials given by formulas (26) and (28) is that the kink is respectively described by simple analytical expressions

$$X = \mathrm{th}(\Omega t), \qquad \cos(l\phi) = \mathrm{th}(0.5l\Omega t). \tag{30}$$

Asymmetric molecules with inequivalent configurations are described by more complicated one-dimensional potentials (see, *e.g.*, Ref. 43).

The exponent of the Franck—Condon factor, which is due to the deviation of the action along the ETT from the one-dimensional one, was studied in detail when solving the problem of dissipative tunneling in the double-well potentials linearly coupled with a set of harmonic oscillators.[44—46] The basic idea of Feynman formalism[22] is to exclude harmonic variables, which are found as functions of X at other moments of time by integrating the equations of motion

$$Y_k(t) = -\frac{C_k}{2\omega_k^2}\int\limits_{-\infty}^{\infty}\exp(-\omega_k|t - t'|)X(t')\mathrm{d}t'. \tag{31}$$

Substituting Eqs. (30) into Eq. (31), we get a set of $Y_k(t)$ coordinates which, in combination with $X(t)$, defines the first-order ETT in parametric form. Since the solutions of the equations of motion for Y_k are found as expansions in the series of odd powers of coupling parameters, the ETT given by Eq. (31) deviates from the true ETT by terms proportional to higher degrees of C_k. The series for $X(t)$ and $Y_k(t)$ in powers of C_k/ω_k converge rapidly and monotonically, so the deviations of the first-order ETT from the true one do not exceed 5—10% even for active transverse vibrations (with largest C_k/ω_k values equal to 0.5).[17—20]

The contribution to the semiclassical action due to linear XY-coupling has the form[6]

$$\delta W = \sum_k \frac{C_k^2}{4\omega_k^3}\int\limits_{-\infty}^{\infty}\exp(-\omega_k|t - t'|)\,\dot{X}(t)\,\dot{X}(t')\mathrm{d}t\mathrm{d}t'. \tag{32}$$

Previously,[17,47] it was shown that similar contribution of G-coupled vibrations is described by the sum of the same integrals and differs from Eq. (32) by the $-\omega_k{}^{-2}$ factor. Variations of the transverse frequencies along the ETT introduce a correction to the action[17] of the order of γ^{-1}. In the harmonic approximation, the contributions are additive. Using the perturbative instanton approach (PIA), it is easy to find analytical expressions for the second-order action by substituting Eqs. (30) into integral (32). The effect of the transverse vibration anharmonicity and ϕ-dependent YY'-interactions is, as a rule, insignificant.[19] At $\omega_k < \Omega$, the contribution of the kth transverse vibration to the action increases proportionally to ω_k and reaches a maximum value of $\pm 2(C_k/\omega_k)^2/3$ for L- and G-vibrations at $\omega_k >> \Omega$, so that active high-frequency vibrations make the major contribution to δW.

The transverse prefactor for the ground state differs only slightly from unity due to changes in the transverse frequencies along the ETT.[17,48] Mixing of (n, n_k) and $(n', n_k - 1)$ states $(n' = n + 1, n + 2, \ldots)$ due to XY-coupling causes a substantial increase in the prefactor for excited vibrational states.[18] Though the coefficients of the "pure' states with $n' > n$ in the mixed wave functions $\Psi_{n,\{nk\}}$ are small (of the order of C_k/ω_k), their contribution to H_{nn} appears to be large because of appreciable increase in the tunneling splitting with increasing n, as follows from Eqs. (27) and (29). According to the first-order perturbation theory, the mixing coefficients are inversely proportional to the energy difference between the mixing (n, n_k) and $(n', n_k - 1)$ states, so the tunneling splitting of the level of the kth excited transverse vibration increases by several orders of magnitude in the regions of the Fermi resonance between this vibration and the longitudinal vibration. The resonance-type frequency dependence of the splitting is shown in Fig. 7. For the asymmetric double-well PES, the Fermi resonance can occur between the closely lying levels with any quantum numbers of the longitudinal vibration. For the periodic PES characteristic of internal rotations, additional selection rules exist, namely, $n - n' = \pm 1, \pm 3, \ldots$ for L- and Hga-couplings and $n - n' = \pm 2, \pm 4, \ldots$ for Bre- and Hl-couplings.

For asymmetric double-well potentials with the difference A between the minima, the energy difference between a pair of the closest-lying levels is given by

$$E_{1(2)} = 0.5\left(E_n^0 + E_{n'}^0\right) \mp \sqrt{0.25\left(E_n^0 - E_{n'}^0\right)^2 + H_{nn'}^2}\,, \tag{33}$$

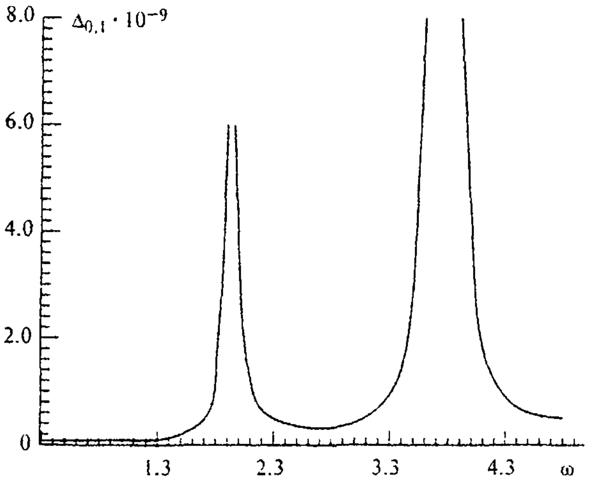

Fig. 7. Dependence of tunneling splitting of the (0, 1) level on the frequency of transverse vibration in the potential with gated coupling. $C/\omega = 0.04$; $\gamma = 20$.

where $E_n{}^0$ and $E_{n'}{}^0$ are the energies of the *n*th and *n*'th levels for isolated wells. From relationship (33) it follows that a large tunneling effect is expected in the vicinity of several types of resonances. In the regions of longitudinal resonances, where $E_n{}^0 - E_{n'}{}^0 \approx \hbar\Omega$, the tunneling matrix element $H_{nn'}$ is $H_{nn'} \approx \sqrt{H^0_{nn}H^0_{n'n'}}$. At $E_n{}^0 - E_{n'}{}^0 \approx \hbar\omega_k$, the tunneling matrix element corresponds to a transition with absorption or emission of $\hbar\omega_k$ quanta. For this process, called vibrationally assisted tunneling,[49] the $H_{nn'}$ matrix element is proportional to $C_k{}^2$.[50] At $E_n{}^0 - E_{n'}{}^0 \approx \hbar(\Omega - \omega_k)$, tunneling is associated with the Raman process of absorption and emission of the quanta of longitudinal and transverse vibrations.[50,51]

Quantum decay of metastable states

The theory of unimolecular dissociation reactions is based on the solution of the model problem of decay of metastable states separated from isoenergetic states of a continuous spectrum by a potential barrier (see, *e.g.*, Refs. 3 and 4). At energies lying close to the barrier height $V^{\#}$, the spectrum becomes so dense that the cross-anharmonicity of vibrations mixes the states with different quantum numbers, thus transforming them into ergodic states[52] for which the decay probability is independent of the energy distribution over vibrations and is determined by their total energy only. Stochastic behavior of polyatomic vibrational systems at high energies ($E > V^{\#}$) permits use of the statistical RRKM model[3,4] in the theory of unimolecular decay. This model postulates the existence of fast vibrational exchange to maintain the statistical equilibrium in the course of the decay. In statistical models, decay of states with energies lower than $V^{\#}$ is taken into account by introducing tunneling corrections equal to the transparency of the one-dimensional barrier along the reaction path. At sufficiently high barriers, such a description is obviously inapplicable to the low-energy states characterized by the set of "good" quantum numbers for the longitudinal (n) and transverse $\{n_k\}$ vibrations for which the decay rate is related to the small imaginary part of the eigenvalues

$$E_{n,\{n_k\}} = E^0_{n,\{n_k\}} - 0.5i\Gamma(n, \{n_k\}). \qquad (34)$$

The existence of two types of states (regular and ergodic ones) can be demonstrated, *e.g.*, by calculating the spectrum of the model two-dimensional Henon—Heiles potential,[1,53] in which, at a barrier height of 1/6, regular states lie at energies lower than 1/10.

The theory of multidimensional metastable state decay is closely related to the problem of mode specific chemical reactions. Single-channel decay selectivity arises only from violation of the equilibrium between the levels upon optical pumping of one of them and is considered beyond the initial assumptions of statistical models.[10,52—54] In multichannel reactions,[55—57] the relative probabilities of channels also become dependent on the quantum numbers (n, $\{n_k\}$). Obviously, the mode specificity must increase with decreasing rate of vibrational exchange to reach a maximum in the molecules with separable longitudinal and transverse motions. In this case the excitation of transverse vibrations has no effect on the decay rate, whereas excitation of the longitudinal vibration causes exponential increase in the decay rate. Coupling between the vibrations must weaken the dependence of the decay rate on (n, $\{n_k\}$), especially in the regions of Fermi resonances. Whereas considerable progress in studying the decay of ergodic states has been achieved due to going beyond the scope of statistical models,[55—57] the decay of low-energy states was studied only recently using the PIA.[50,58] The PES includes the one-dimensional decay potential of the form

$$V(X) = 0.5X^2(1 - X) \qquad (35)$$

and the set of linearly coupled transverse vibrations

$$\Gamma_n = \sqrt{2/\pi}\,\frac{2^{6n+3}\gamma^{n+1/2}}{n!}\,e^{-16\gamma/15}. \qquad (36)$$

For the ground state, Eq. (36) is reduced to a relation derived[59] (see also Refs. 6 and 43) from analysis of the eigenfrequencies of small fluctuations about the ETT

$$\Gamma_0 = \omega_0\sqrt{\frac{60W^*}{\pi\hbar}}e^{-2W^*/\hbar} = \omega_0\sqrt{\frac{32\gamma}{\pi}}e^{-16\gamma/15}, \qquad (37)$$

where W^* is the action between the turning points. The ETT in potential (35) is called bounce

$$X(t) = \mathrm{ch}^{-2}(0.5t). \qquad (38)$$

It approaches the minimum at $t \to -\infty$ and $t \to +\infty$ and reaches the point $X = 1$ at $t = 0$ (see Fig. 3), which doubles the action as compared to that on the kink. The transverse displacement of the bounce, proportional to C/ω, is described by the equation

$$\ddot{Y} = \omega^2(Y - CX/\omega^2) \tag{39}$$

and has the form

$$Y(X) = 4CX\int_0^{\infty} e^{-2\omega Z}\,\frac{\mathrm{sh}(Z)\mathrm{ch}(Z)}{1 + X\mathrm{sh}^2(Z)}\,\mathrm{d}Z. \tag{40}$$

The action is calculated using the following expressions for $X(t)$ and $Y(t)$:

$$W^* = \frac{8}{15} + \frac{4}{3}\frac{C^2}{\omega^2} - 16C^2\omega\int_0^{\infty} e^{-2\omega Z}\,(Z\mathrm{cth}(Z) - 1)\mathrm{d}Z. \tag{41}$$

Eq. (39) shows that linear coupling decreases the decay rate, thus elongating the tunneling trajectory as compared to the 1D trajectory. The ETT is shortened and the correction to the action decreases as the frequency of the transverse vibration increases. In the adiabatic limit, the correction to the action vanishes. The $W^*(\omega)$ value monotonically decreases as the frequency increases and reaches a value corresponding to the 1D bounce. The contribution of low-frequency transverse vibrations to the action is due to the deviation of the trajectory from the adiabatic one.

As follows from relations (40) and (41), the first-order bounce and the second-order action on this bounce are described by universal functions of frequency, which are independent of the coupling constants (Fig. 8). This essentially simplifies analysis of multidimensional quantum dynamics. According to the Fermi golden rule, the decay rate is proportional to the square of the tunneling matrix element, so the Lifshitz—Herring formula (24) can be rewritten as follows

$$\Gamma_{n,\{n_k\}} = \Gamma^0_{n,\{n_k\}} + $$
$$+ \sum_{n',\{n'_k\}} C_k^2\left|\left\langle n,\{n_k\}\right|V_{\mathrm{int}}\left|n',\{n'_k\}\right\rangle\right|^2\left(E_{n,\{n_k\}} - E_{n',\{n'_k\}}\right)^{-2}\Gamma^0_{n',\{n'_k\}}, \tag{42}$$

where $\Gamma^0_{n,\{n_k\}}$ are the decay rates of the "pure" $(n, \{n_k\})$ states with "good" quantum numbers and V_{int} is the operator of the interaction between these states.[18] Relationship (42) can be called the generalized Lifshitz—Herring formula, which takes into account the mixing of different states due to the coupling between the longitudinal and transverse coordinates. Using the selection rule for the V_{int} matrix elements $(n'_1 = n_1 \pm 1)$, we exclude the terms with $n'_1 = n_1$ from the sum in expression (42), so for the $(0, \ldots, 1_k, \ldots)$ state it has the form

$$\frac{C_k^2}{\omega_k^2}\left[\frac{\omega_k}{\left(1 - \omega_k^2\right)^2}\Gamma^0_{10} + \frac{2\omega_k^3}{\gamma\left(1 + \omega_k\right)^2\left(4 - \omega_k^2\right)^2}\Gamma^0_{20} + \right.$$
$$\left. + \frac{3\omega_k^3}{\gamma^2\left(1 + \omega_k\right)^2\left(2 + \omega_k\right)^2\left(9 - \omega_k^2\right)^2}\Gamma^0_{30} + \ldots\right], \tag{43}$$

As can be seen, even at small coupling parameters the Γ_{01} value increases by several orders of magnitude as compared with Γ^0_{00}. The resonance type of Eq. (43) shows that the decay rates of the $(0, n_1)$ states must appreciably increase near the Fermi resonances. This result obtained in the framework of the PIA confirms the results of quantum calculations (Fig. 9). The widths of the resonances increase as the coupling coefficients increase, thus decreasing the mode specificity. The latter also decreases as the vibrational quantum numbers increase. The decay rates of the lowest excited states of different vibrations can differ by several orders of magnitude, which provides the possibility for mode specific photochemical reactions initiated by optical pumping of the corresponding vibrational levels to proceed. This mechanism is much more selective than the multiphoton dissociation[60] inducing the decay of the ergodic states with energies lying near the dissociation threshold. The possibility of isotope separation in mode specific reactions is due to the changes in the vibrational

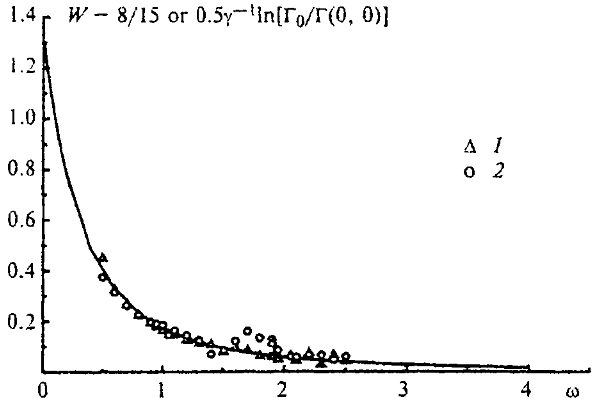

Fig. 8. The action $W - 8/15$ (solid line) and correction to the action $0.5\gamma^{-1}\ln(\Gamma_0/\Gamma(0, 0))$ as functions of the frequency of transverse vibration (ω). Obtained from exact calculations for $C/\omega = 0.1$ (*1*) and 0.25 (*2*).

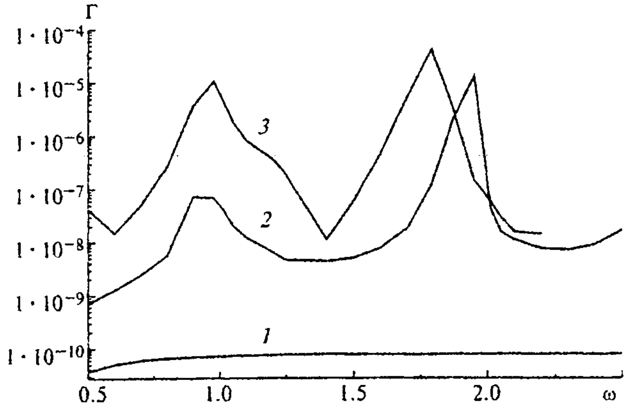

Fig. 9. Dependence of decay rate for (0, 0), (0, 1), and (0, 2) states (curves *1*, *2*, and *3*, respectively) on the frequency of transverse vibration (ω). $C/\omega = 0.1$.

frequencies upon isotope substitution. If the frequency difference between the isotopomers exceeds the widths of the (01) vibrational bands, monochromatic optical pumping excites only one isotopomer, thus providing the selectivity of further excitation up to the dissociation threshold. Tunneling decay of the state with $n_k = 1$ characterizes both the optical selectivity and the mode specificity of the chemical reaction.

* * *

The PIA allows one to quantitatively describe the dynamics of molecular rearrangements without using simplified models with a reduced number of degrees of freedom for the two most typical manifestations of tunneling, namely, for tunneling splittings in the vibrational spectra and for the decay of metastable compounds. In the former case we deal with coherent transitions between the stable configurations. They are characterized by the tunneling frequency, so the concept of the rate constant is inapplicable for their description. For initiating tunneling chemical conversions, it is necessary to consider the processes of coherency destruction,[6,61,62] associated with collisions of molecules or with their interaction with the medium. Phenomenologically, these processes are taken into account by introducing the characteristic correlation time τ_c or the friction coefficient $\eta = m/\tau_c$.[6,44,45,63] At $\tau_c\Delta_n/\hbar << 1$, the rate constant of incoherent tunneling transition from the initial state with tunneling splitting Δ_n is described by the relationship

$$K_n = 0.25\Delta_n^2\tau_c. \qquad (44)$$

The overall rate constant is determined by statistical averaging of partial constants K_n over the initial energy distribution. However, such an interpretation of tunneling chemical reactions excludes a broad intermediate region of weak chaos (incomplete loss of coherency) from consideration. It would be more correct to say that at present the quantum theory allows one to calculate the rate constant rather than to explain from where it is originated.

The PIA formalism describes the dynamics of proton transfer in the molecules with intramolecular hydrogen bonds (*e.g.*, in malonaldehyde[17,19,64] and tropolone[64] molecules and in formic acid dimer[17,19]), internal rotations about the C_2 or C_3 axes (H_2O_2,[20] HNO_3,[65] and MeOH [19] molecules), inversion,[66] and interconversion.[48] Studies of two-proton tunneling transfer in the porphyrin molecule[67,68] have led to generalization of the PIA for the molecules with two tunneling coordinates. As was emphasized in the Introduction, limitations of this approach are due not only to the weak coupling condition (22), but also to the absence of overlapping Fermi resonances, which are characteristic of higher excited vibrational states.

References

1. G. M. Zaslavskii, *Stokhastichnost' dinamicheskikh sistem* [*Stochasticity of Dynamic Systems*], Nauka, Moscow, 1984 (in Russian).
2. M. C. Gutzwiller, *Chaos in Classical and Quantum Mechanics*, Springer, Berlin, 1990.
3. H. Eyring, S. H. Lin, and S. M. Lin, *Basic Chemical Kinetics*, Wiley Interscience, New York, 1983.
4. W. Forst, *Theory of Unimolecular Reactions*, Academic Press, New York, 1973.
5. V. I. Gol'danskii, *Dokl. Akad. Nauk SSSR*, 1959, **124**, 1261; **127**, 1037 [*Dokl. Chem.*, 1959, **124**; **127** (Engl. Transl.)].
6. V. A. Benderskii, D. E. Makarov, and C. A. Wight, *Chemical Dynamics at Low Temperatures*, Wiley Interscience, New York, 1994.
7. R. J. Saykally and G. A. Blake, *Science*, 1993, **259**, 1570.
8. W. Press, *Single Particle Rotations in Molecular Crystals*, *Springer Trends in Modern Physics*, Springer, Berlin, 1981, **92**.
9. S. A. Rice, in *Advances in Laser Chemistry*, Ed. A. H. Zewail, Springer, Berlin, 1978, 2.
10. B. A. Waite and W. H. Miller, *J. Chem. Phys.*, 1980, **73**, 3713.
11. G. Voth, *Adv. Chem. Phys.*, 1996, **93**, 135.
12. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN 94*, Revision C. 4, Gaussian, Inc., Pittsburgh (PA), 1995.
13. W. H. Miller, *J. Phys. Chem.*, 1979, **83**, 960.
14. W. H. Miller, N. C. Handy, and J. E. Adams, *J. Chem. Phys.*, 1980, **72**, 99.
15. V. A. Benderskii, V. I. Goldanskii, and D. E. Makarov, *Chem. Phys.*, 1991, **154**, 407; 1992, **159**, 29.
16. V. A. Benderskii, V. I. Goldanskii, and D. E. Makarov, *Phys. Repts.*, 1993, **233**, 195.
17. V. A. Benderskii, E. V. Vetoshkin, S. Yu. Grebenshchikov, L. von Laue, and H.-P. Trommsdorff, *Chem. Phys.*, 1997, **219**, 119.
18. V. A. Benderskii, E. V. Vetoshkin, L. von Laue, and H.-P. Trommsdorff, *Chem. Phys.*, 1997, **219**, 143.
19. V. A. Benderskii, E. V. Vetoshkin, and H.-P. Trommsdorff, *Chem. Phys.*, 1998, **234**, 153.
20. V. A. Benderskii and E. V. Vetoshkin, *Chem. Phys.*, 1998, **234**, 173.
21. V. A. Benderskii and E. V. Vetoshkin, *Zh. Fiz. Khim.*, 1997, **71**, 1985; 1998, **72**, 50; 469; 2035; 2196; 2202 [*Russ. J. Phys. Chem.*, 1997, **71**; 1998, **72** (Engl. Transl.)].
22. R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals*, McGraw-Hill, New York, 1965.
23. M. Ya. Ovchinnikova, *Chem. Phys.*, 1979, **36**, 15.
24. V. A. Benderskii, V. I. Goldanskii, and A. A. Ovchinnikov, *Chem. Phys. Lett.*, 1980, **73**, 492.
25. V. K. Babamov and R. A. Marcus, *J. Chem. Phys.*, 1981, **74**, 1790.

26. V. K. Babamov, V. Lopez, and R. A. Marcus, *J. Chem. Phys.*, 1983, **78**, 5621.
27. C. G. Callan and S. Coleman, *Phys. Rev., D*, 1977, **16**, 1762.
28. S. Coleman, *Aspects of Symmetry*, Cambridge Univ. Press, Cambridge, 1985.
29. A. M. Polyakov, *Nucl. Phys., B*, 1977, **121**, 429.
30. A. Lapides and E. Motolla, *Nucl. Phys., B*, 1982, **203**, 58.
31. L. D. Landau and E. M. Lifshits, *Quantum Mechanics*, Pergamon, Elmsford, New York, 1981.
32. A. Schmid, *Ann. Phys.*, 1986, **170**, 333.
33. V. P. Maslow and M. V. Fedoryuk, *Semiclassical Approximation in Quantum Mechanics*, Reidel, Dordrecht, 1981.
34. M. Wilkinson, *Physica, D*, 1986, **21**, 341; 1987, **27**, 201.
35. S. Takada and H. Nakamura, *J. Chem. Phys.*, 1994, **100**, 98; 1995, **102**, 3977.
36. G. C. Ezra, *Symmetry Properties of Molecules, Lecture Notes in Chemistry*, Springer, Berlin, 1982, **28**.
37. H. C. Longuet-Higgins, *Mol. Phys.*, 1963, **6**, 445.
38. S. L. Altmann, *Proc. Roy. Soc.* (*London*), 1967, **A298**, 184.
39. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955.
40. V. A. Benderskii, E. V. Vetoshkin, and H.-P. Trommsdorff, *Zh. Fiz. Khim.*, 2000, **73**, in press [*Russ. J. Phys. Chem.*, 2000, in press (Engl. Transl.)].
41. C. Herring, *Rev. Mod. Phys.*, 1962, **34**, 341.
42. V. A. Benderskii, S. Yu. Grebenshchikov, and G. V. Milnikov, *Chem. Phys.*, 1994, **188**, 19.
43. H. Dekker, *Physica, A*, 1987, **146**, 375, 387, 396; 1988, **154**, 61.
44. A. J. Leggett, S. Chakravarty, T. Dorsey, P. M. Fischer, A. Garg, and M. Zwerger, *Rev. Mod. Phys.*, 1987, **59**, 1.
45. H. Grabert, P. Schramm, and G.-L. Ingold, *Phys. Repts.*, 1988, **168**, 115.
46. H. Dekker, *Physica, A*, 1991, **175**, 485; **178**, 264; **178**, 289.
47. V. A. Benderskii, E. V. Vetoshkin, L. von Laue, and H.-P. Trommsdorff, *Zh. Fiz. Khim.*, 1998, **72**, 469 [*Russ. J. Phys. Chem.*, 1998, **72** (Engl. Transl.)].
48. V. A. Benderskii, S. Yu. Grebenshchikov, and G. M. Milnikov, *Chem. Phys.*, 1995, **194**, 281; **198**, 19.
49. J. L. Skinner and H.-P. Trommsdorff, *J. Chem. Phys.*, 1988, **89**, 897.
50. V. A. Benderskii, E. V. Vetoshkin, and H.-P. Trommsdorff, *Chem. Phys.*, 1999, **244**, 293.
51. R. Silbey and H.-P. Trommsdorff, *Chem. Phys. Lett.*, 1990, **165**, 540.
52. R. Shinke, *Photodissociation Dynamics*, Cambridge Univ. Press, Cambridge, 1993.
53. B. A. Waite and W. H. Miller, *J. Chem. Phys.*, 1981, **74**, 3910.
54. B. A. Waite, S. K. Gray, and W. H. Miller, *J. Chem. Phys.*, 1983, **78**, 259.
55. W. F. Polik, C. B. Moore, and W. H. Miller, *J. Chem. Phys.*, 1988, **89**, 3584.
56. W. H. Miller, R. Hernandez, C. B. Moore, and W. F. Polik, *J. Chem. Phys.*, 1990, **93**, 5657.
57. R. Hernandez, W. H. Miller, C. B. Moore, and W. F. Polik, *J. Chem. Phys.*, 1993, **99**, 950.
58. V. A. Benderskii, E. V. Vetoshkin, and I. R. Medvedev, *Chem. Phys.*, 2000, in press.
59. A. Caldeira and A. J. Leggett, *Ann. Phys.*, 1983, **149**, 374.
60. V. S. Letokhov and B. Mur, *Kvantovaya Elektronika* [*Quantum Electronics*], 1976, **3**, 248, 485 (in Russian).
61. E. E. Nikitin and N. N. Korst, *Teor. Eksp. Khim.* [*Theor. Exp. Chem.*], 1965, **1**, 5 (in Russian).
62. M. Simmonius, *Phys. Rev. Lett.*, 1978, **26**, 980.
63. Yu. I. Dakhnovski and A. A. Ovchinnikov, *Phys. Lett. A*, 1985, **113**, 147.
64. Z. Smedarchina, W. Siebrand, and M. Z. Zgierski, *J. Chem. Phys.*, 1995, **103**, 5326; **104**, 1203.
65. V. A. Benderskii, E. V. Vetoshkin, and H.-P. Trommsdorff, *Chem. Phys.*, 1999, **244**, 173.
66. Z. Smedarchina, W. Siebrand, M. Z. Zgierski, and F. Zerbetto, *J. Chem. Phys.*, 1995, **102**, 7024.
67. V. A. Benderskii, V. I. Goldanskii, and D. E. Makarov, *Chem. Phys. Lett.*, 1991, **186**, 94.
68. V. A. Benderskii, S. Yu. Grebenshchikov, D. E. Makarov, and G. V. Milnikov, *J. Phys. Chem.*, 1994, **98**, 3300.

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