Physical Chemistry

Vibrational stimulation of the coherent tunneling transition in the cyclopentanone molecule

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The tunneling interconversion of the cyclopentanone molecule, which leads to the appearance of tunneling doublets in the microwave spectrum of the system, is studied. The dynamics of interconversion is described by two generalized coordinates, one of which corresponds to bending (non-tunneling promoting mode), while the other of which corresponds to twisting of the molecular plane (tunneling coordinate). The coupling between two coordinates is symmetric. A method for quasi-classical calculation of the wave functions in the tunneling region and of the tunneling splittings of the vibrationally excited states in a two-dimensional potential with symmetric coupling is proposed. The tunneling spectrum of cyclopentanone is calculated. It agrees well with the experimental one, and the tunneling splitting increases by 140 times when the transverse quantum number goes from 0 to 6. The dynamic effect of the vibrationally assisted tunneling is shown to be due to the increase in the width of the tunneling channel with the quantum number of bending mode, as well as to the simultaneous shortening of the tunneling distance. The transition state geometry is found using the wave function at the dividing line of the potential.

Key words: cyclopentanone; microwave spectrum; tunneling splitting; quasi-classical approximation; two-dimensional potential energy surface.

The application in molecular spectroscopy of tunable frequency IR lasers, together with supersonic cooling, allowed not only the spectral resolution to be significantly increased but also investigations of the fine structure of excited vibrational levels[1,2] to be started. The thereby opened possibilities for obtaining quantitative characteristics of great amplitude molecular motions resulted in fast development of the spectroscopy of nonrigid molecules and molecular complexes having at least two equilibrium nuclear configurations, where tunneling transitions (along the tunneling coordinate) produce splittings of vibrational levels. Studies of hydrogen atom transfer, hindered internal rotation, and conformational transitions in many systems (see Ref. 3) have shown that tunneling coordinate x is strongly coupled to non-tunneling (transverse) y_k modes. This means that an investigation of the process of tunneling should be done using multidimensional non-separating potential energy surfaces. The main consequence of a multidimensional tunneling, which was verified by experiment, is that the tunneling splittings $\Delta(n_k)$ depend on the vibrational quantum numbers n_k; an increase in the vibrational series of one mode and a decrease in another make it possible to speak about vibrational stimulation

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and vibrational selectivity of tunneling transitions. In this process, the normal modes strongly coupled to the tunneling coordinate can be approximately considered as non-interacting among themselves. Consequently, a multidimensional potential energy surface (PES) effectively separates itself into sets of two-dimensional surfaces (slices) onto which the tunneling takes place. In principle, the topology of these two-dimensional PES determines the main features of the tunneling spectrum of a multidimensional system, and knowledge of their unique parameters allows one to reconstruct the multidimensional PES. The tunneling splitting $\Delta(n_k)$ characteristics are in fact the only source of information about the potential function $V(x,y_k)$ in regions far from the equilibrium position. Thus, one of the problems in the molecular spectroscopy of nonrigid molecules is the determination of parameters of the two-dimensional potential functions from which the multidimensional PES can be constructed.

Earlier, three model potentials were suggested, different in the symmetry of the coupling between tunneling and non-tunneling modes[4], which may be used for studying the tunneling features in nonrigid molecules with two equilibrium positions[5]: "linear" potential

$$V(x,y) = V_0(x^2-x_0^2)^2 + 0.5\omega_1{}^2y^2 + Cxy, \quad (1)$$

"gated" potential

$$V(x,y) = V_0(x^2-x_0^2)^2 + 0.5\omega_1{}^2y^2 + Cx^2y, \quad (2)$$

"squeezed" potential

$$V(x,y) = V_0(x^2-x_0^2)^2 + 0.5\omega_1{}^2y^2 + Cx^2y^2. \quad (3)$$

The linear coupling (1) produces a shift in equilibrium positions, resulting in an increase in both the tunneling length and the barrier height, resulting in a decrease in the tunneling splitting. With semisymmetrical coupling (2), transverse vibrations decrease the tunneling length and the barrier height, inducing a growth in Δ with an increase in the coupling parameter and the quantum number of transverse vibration. In cases (1, 2) the tunneling trajectory position and the barrier height along it do not depend on n_2. In an entirely symmetrical potential (3) the tunneling trajectory always coincides with the straight line $y = 0$; thus, the dependence of the tunneling splitting on n_2 is not the result of a change in the trajectory shape, but is a purely dynamic effect.

For molecules with one transitional configuration (a single saddle point) the model potentials (1—3) exhaust all possible two-dimensional potential functions. The choice among them can be made based on the measured dependence $\Delta(n_2)$ and the symmetry of the molecule.

The spectrum of systems with simple two-dimensional surfaces like (1—3) is found by numerical diagonalization of a Hamiltonian. Yet the solution of the reverse problem, *i.e.*, inferring the potential from the spectral data, requires knowledge of the analytical dependence of tunneling splittings on model PES parameters. This (necessarily) requires the development of different approaches to the calculation of excited levels in multidimensional systems. The traditional alternative to a numerical solution of the Schrödinger equation is the quasi-classical method; its modern mathematical formulation for multidimensional systems is given by Maslov.[6]

The tunneling splitting of the ground state of a multidimensional system can be found with the "multidimensional instanton method".[7] Here, it is assumed that the tunneling takes place mostly along the extremal classical trajectory in the inverted potential. In terms of the quasi-classical approximation, the extremal trajectory has a "width" corresponding to the trajectories in the vicinity of the extremal one that allows one to talk about a "channel of tunnelings", giving the main component of the wave function in the subbarrier region and accordingly in Δ. The trajectory method of tunneling splitting calculations can be more informative than a direct quantum mechanical calculation because it allows not only the estimation of the splittings but also a conclusion about the geometry of the tunneling interconversion without referring to precise computations. Until the present time no quasi-classical method was developed that is able to calculate the tunneling splittings of vibrationally excited states even in the two-dimensional case. The ultimate importance of the two-dimensional case for quantitative analysis of the vibrational-tunneling spectra of nonrigid molecules mentioned above calls for the development of such an approach for model two-dimensional potentials. Hereafter the possibility of comparing tunneling splittings calculated with quasi-classical wave functions with results of quantum calculations allows one to make an "external" estimate of the precision of the quasi-classical method.

One should bear in mind that usually the tunneling system is linked to the environment (harmonic or anharmonic thermal bath). This situation is typical, for example, in studying the temperature dependence of rotational tunneling, that is, the temperature evolution of the positions and shapes of spectra of inelastic neutron scattering,[8] while observing the transition from coherent tunneling to a thermal activation regime. In this case the "exact" solution of the tunneling problem is hardly possible, and quasi-classical methods proved to be indispensable. The most well studied is the tunneling in one-dimensional systems linearly coupled to a harmonic bath.[9] The method used for solution of integral-differential equations considers all coordinates except one (the reaction coordinate) as a dissipative media. Thus far it has not been directly extended to the two-dimensional case, yet the development of two-dimensional quasi-classical quantization methods may prove to be the first step in this direction.

The microwave spectrum of cyclopentanone[10] shows the interconversion of a five-membered carbon cycle, having in equilibrium a "twist"-configuration. The transition state is planar and corresponds to a barrier height

of 750 cm^{-1}. It has been shown[11] that the movements of five-membered saturated carbon cycles are described by two generalized coordinates, one of which corresponds to a bending and other to a twisting of the molecule plane. The interconversion corresponds to a tunneling along the twisting coordinate x while the transversal vibration corresponds to the non-tunneling bending y. In these coordinates the potential has[10] the form (3). The microwave spectrum has a long transverse series, which distinctly demonstrates the effect of vibrationally assisted tunneling: the tunneling splitting increases by 140 times as the transverse quantum number n_2 grows from 0 to 6. Thus, cyclopentanone is a very convenient object for studying this effect.

In this work a method is suggested for a quasiclassical calculation of the wave functions in a tunneling region and the tunneling splittings of the excited states of the two-dimensional potential (3). The dynamic effect of the vibrationally assisted tunneling is shown to be due to the increase with growth in n_2 of the width of the tunneling channel, as well as to the simultaneous shortening of the effective tunneling distance. The geometry of the transition state has been determined in correspondence with the wave function on the dividing line $x = 0$.

Results and Discussion

A calculation of the tunneling splittings of vibrational levels

The Hamiltonian for the interconversion of cyclopentanone in mass-weighted coordinates has the form:

$$H = V_0\{0.5(\dot{x}^2+\dot{y}^2) + V(x,y)\} \qquad (4)$$

with potential of the type (3):

$$V(x,y) = V_0(x^2-y^2)^2 + 0.5\omega_1^2y^2 + 0.25\alpha y^4 + Cx^2y^2, \quad (5)$$

where the y-vibration is anharmonic, $C > 0$, $V_0x_0^4$ is the barrier height along the coordinate x. The equipotential levels of the potential (5) are presented in Fig. 1. The transversal frequency in the saddle point $x = y = 0$ is less than in the minimum contrary to the case of a negative coupling $C < 0$. The minimum energy path (MEP) is defined by the equation $\mathbf{n}\,\mathrm{grad}V(x,y) = 0$, where $\mathbf{n}$ is the normal to the trajectory unit vector. Because of the symmetry of the coupling with respect to both coordinates, it is a straight line along the coordinate x, independent of the magnitude of coupling.

As was mentioned earlier, up to now the generalization of the "instanton" method to excited states has not been performed, so approximate methods of reducing a two-dimensional potential into an effective one-dimensional one are used (see, for example Refs. 12—14). If the transversal frequency is much higher than the longitudinal one, an effective vibrationally adiabatic potential with fixed transversal quantum number n_2 can be introduced:[12]

$$V_{va}(y,n_2) = V(0,y) + \frac{\hbar\tilde{\omega}(y)}{2}(2n_2 + 1) \ , \qquad (6)$$

where the renormalized longitudinal frequency $\tilde{\omega}(x) = (\omega_1^2 + 2Cx^2)^{1/2}$. Then the splitting of the level with energy $E_{n_1n_2}$ is defined by the usual one-dimensional expression:

$$\Delta_{va} = \frac{2\hbar}{\tau_{n_1n_2}}\exp(-W_{n_1n_2}/\hbar) \ , \qquad (7)$$

where n_1 is the longitudinal quantum number; a shortened action $W_{n_1n_2}$ and a classical oscillating period are calculated for the potential (6).

In the reverse case of a slow transverse mode an approximation of a fast tunneling[14,15] can be used.

The wave function can be presented in the form

$$\Psi(x,y) = \Psi_1(x(y = \mathrm{const})) \cdot \Psi_2(y)$$

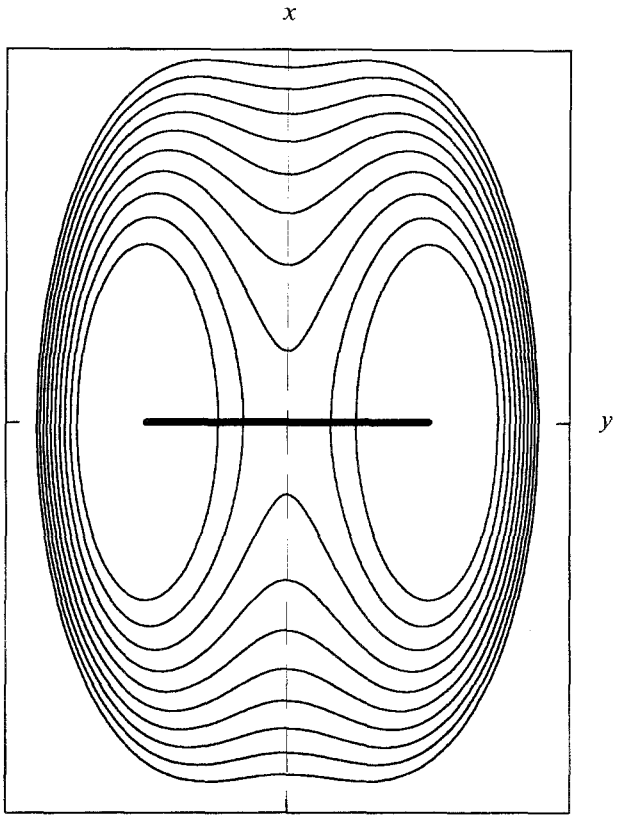

Fig. 1. The equipotential levels of the potential (5). The tunneling one-dimensional trajectory $y = 0$ does not depend on the transversal quantum number.

in the same manner as is done in the Born—Oppenheimer approximation for a fast (Ψ_1) and a slow (Ψ_2) subsystem. By inserting this wave function in the Schrödinger equation, one obtains for the tunneling splitting

$$\Delta_s = \int |\Psi_{n_2}(y)|^2 \Delta_{1D}(y;n_1)dx, \qquad (8)$$

where $\Psi_{n_2}(y)$ is the wave function of a slow movement in a potential defined by solution of the Schrödinger equation for the fast subsystem. A comparison with exact values Δ_{exact}, obtained by a diagonalization of the Hamiltonian (4), shows (Table 1) that although for low-lying levels ($n_2 = 0, 1, 2$), these methods give results close to Δ_{exact}, for higher levels $n_1 = 0$, $n_2 \geq 4$) the approximate methods underestimate Δ by 3—10 times. As has been shown,[14] this discrepancy is due to the fact that both approximations underestimate the amplitude of the wave function on the dividing straight line $x = 0$. A straightforward quasi-classical solution of the problem meets serious mathematical difficulties owing to the complex form of a Lagrange finite field in a classically accessible region.[16] In this work we replace the function in the vicinity of a potential minima with an effective variational function of a simple form, which enables a unique definition of a quasi-classical wave function in a classically forbidden region and a determination of the tunneling splittings.

The tunneling splitting of the $E_{n_1n_2}$ level in the quasi-classical approximation is

$$\Delta_{n_1n_2} = 2\hbar^2 \frac{\int \Psi(x,y) \frac{\partial}{\partial x} \Psi(x,y)|_{x=0} dy}{\iint \Psi(x,y)\Psi^*(x,y)dxdy} \quad . \qquad (9)$$

This expression is a straightforward generalization in the two-dimensional case of the Lifshits[17] formula for one-dimensional splitting. Here $\Psi(x,y)$ is the quasi-classical wave function of the (n_1, n_2) level in the zero barrier permeability approximation. The crucial difficulty in calculations[6] is the impossibility of constructing a quasi-classical wave function in the entire x—y region. This makes it necessary to distinguish the subbarrier region on the x—y plane where the unique solution of the quasi-classical equations is specifically sought; then the problem is reduced to matching of the wave function obtained in a classically accessible region. Since the integral in the numerator of expression (9) is calculated over the dividing straight line $x = 0$, it is enough for evaluation of $\Delta_{n_1n_2}$ to calculate the "tail" of the wave function in an subbarrier region, where $\Psi(x,y)$ in quasi-classical approximation has the form:

$$\Psi(x,y) = \exp(-\frac{1}{\hbar}\{W_1(x,y) + \hbar W_2(x,y)\}) \quad , \qquad (10)$$

and $W_{1,2}$ obeys, respectively, the Hamilton—Jacobi and transport equations:

$$\frac{1}{2}(\nabla W_1)^2 - V(x,y) = -E_1 \quad , \qquad (11)$$

$$(\nabla W_1)(\nabla W_2) - \frac{1}{2}\nabla^2 W_1 + (E_{n_1n_2} - E_1)/\hbar = 0 \quad . \qquad (12)$$

The equations written in this form have an arbitrary separation energy parameter of E_1 that does not change the precision of the quasi-classical solution. Eqs. (11), (12) are solved by the method of characteristics that are the classical trajectories in an inverted potential $-V(x,y)$. Boundary conditions should be imposed on some curve $x = x^*(\gamma)$, $y = y^*(\gamma)$, defining the initial Lagrange finite field $W_1(\gamma)$ and thus making the solution $W_{1,2}$ be uniquely defined in some region of the x,y plane (see Ref. 6). In accordance with the general ideology of multidimensional quasi-classical approximation, the tunneling splitting Δ is defined by $\Psi(x,y)$ with a quasi-classical precision in the vicinity of an extremal trajectory, providing a minimum of the Euclidean action W_1. From the symmetry of the potential it follows that the only such trajectory is the tunneling trajectory $y = 0$ and the boundary conditions for Eqs. (11), (12) should be symmetrical with respect to the x axis. It is convenient, accordingly, to choose $x^*(\gamma)$, $y^*(\gamma)$, and $W_1(\gamma)$, conforming to the conditions $x^*(\gamma) = x^*(-\gamma)$, $y^*(\gamma) = -y^*(-\gamma)$, $W_1(\gamma) = W_1(-\gamma)$. We have chosen earlier[14] the curves $x^*(\gamma)$, $y^*(\gamma)$ coinciding with the caustic for various quasi-classical levels. It has been shown that the choice of the initial moment on the tangent to the caustic enables one to match wave functions in different regions divided by the caustic.

Note that, having in the Hamilton—Jacobi equation a free parameter E_1, we can choose a convenient form of the curve $x^*(\gamma)$, $y^*(\gamma)$. Let us substitute the wave function in the vicinity of the minimum by some function $\Psi(x)\Phi(y)$ that can be found, for example, using the variational principle.[17] The corresponding self-consistent equations can be written in the form

Table 1. The tunneling splittings for the cyclopentanone molecule $n_1 = 0$ series*

n_1, n_2	$\Delta_{exact}\times10^3$	$\Delta_{va}\times10^3$	$\Delta_s\times10^3$	$\Delta_{q.cl}\times10^3$
0, 0	1.05	0.99	1.03	1.09
0, 1	1.56	1.50	1.61	2.54
0, 2	3.36	2.27	2.75	5.30
0, 3	8.02	3.40	4.6	13.1
0, 4	20.1	5.03	7.63	28.9
0, 5	52.2	7.08	12.7	63.0
0, 6	140.0	10.4	22.1	135.1

* $\Delta_{q.cl}$ and Δ_{exact} correspond to the formula (20) and the precise quantum mechanical calculation. The tunneling splittings Δ_{va} and Δ_s, obtained by approximate methods,[14] are presented for comparison.

$$[-\frac{\hbar^2}{2}\frac{\partial^2}{\partial x^2} + V_0(x^2-x_0^2)^2+Cx^2<\Phi|y^2|\Phi>-(E-E_y)]\Psi(x) = 0\ , \quad (13)$$

$$[\frac{\hbar^2}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}\omega_1'^2y^2+Cy^2<\Psi|x^2|\Psi>-(E-E_x)]\Phi(y) = 0\ , \quad (14)$$

where $\omega_1'^2 = \omega_1^2+\frac{1}{2}\alpha<\Phi|y^2|\Phi>$,

$$E_y = <\Phi|-\frac{\hbar^2}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}\tilde{\omega}_1^2y^2|\Phi>,$$

$$E_x = <\Psi|-\frac{\hbar^2}{2}\frac{\partial^2}{\partial x^2} + V_0(x^2-x_0^2|\Psi>.$$

Below we restrict ourselves to consideration of the levels with $n_1 = 0$. In this case $\Psi(x)$ is the wave.function of the ground state in the potential

$$V_0(x^2-\tilde{x}_0^2)^2, \quad (15)$$

and $\Phi_{n_2}(y)$ corresponds to the harmonic oscillator's n_2th level of frequency $\tilde{\omega}_1^2$. The state $(0,n_2)$ has energy

$$E_{n_2} \equiv \hbar\tilde{\omega}_1(n_2+1/2) + \hbar(2V_0\tilde{x}_0^2)^{1/2} + V_0(x_0^4-\tilde{x}_0^4)-2V_0\tilde{x}_0(x_0^2-\tilde{x}_0^2),$$

where the renormalized parameters $\tilde{x}_0$ and $\tilde{\omega}_1$ obey the following system of algebraic equations:

$$\tilde{\omega}_1^2 = \omega_1^2+\frac{\hbar\alpha}{2\tilde{\omega}_1}(n_2 + 1/2) + 2C\tilde{x}_0^2\ , \quad (16)$$

$$\tilde{x}_0^2 = x_0^2-\frac{C\hbar}{2V_0\tilde{\omega}_1}(n_2 + 1/2)\ . \quad (17)$$

A quasi-classical approximation for $\Psi(x)$ is not applicable in the vicinity of the point

$$x_1(n_2) \equiv \pm(\tilde{x}_0^2-\hbar^{1/2}\tilde{x}_0^{1/2}(2/V_0)^{1/4})^{1/2},$$

where the classical moment becomes zero. In order to match the subbarrier quasi-classical wave function with $\Psi(x)\Phi(y)$, it is necessary to set $x^*(\gamma) = x_1(n_2)$, $y^*(\gamma) = \gamma$, and choose E_1 equal to $\hbar(2V_0\tilde{x}_0^2)^{1/2}$ *i.e.*, the energy of the ground state in the potential (15). Note also the change in the "one-dimensional" part of the potential

$$\Delta V(x) \equiv V_0(x^2-x_0^2)^2-V_0(x^2-\tilde{x}_0^2)^2 = O(\hbar).$$

Consequently, one can change x_0^2 in the Hamiltonian—Jacobi equation to the renormalized value $\tilde{x}_0^2$ by adding to Eq. (12) an additional element $\Delta V(x)/\hbar$. The method of solution of Eqs. (11), (12) in an subbarrier region has been described by us earlier,[14] and here we present only the main results.

Under the parametrization chosen by us, the extremum trajectory corresponds to $\gamma = 0$, and the Cauchy problem for the characteristic

$$\mathbf{R}(t,\gamma) = (x(t,\gamma),\ y(t,\gamma))$$

can be written in the form

$$\ddot{\mathbf{R}}(t,\gamma) = \nabla\tilde{V}(\mathbf{R}(t,\gamma)), \quad (18a)$$

$$\mathbf{R}(0,\gamma) = (x_1(n_2),\ \gamma), \quad (18b)$$

$$\left.\frac{\partial x}{\partial t}\right|_{t=0} = 0\ , \quad (18c)$$

$$H(\dot{\mathbf{R}},\mathbf{R}) = E_1, \quad (18d)$$

where $\tilde{V}$ differs from $V(x,y)$ (5) by the change of x_0 to the renormalized value of $\tilde{x}_0$. In the approximation of small fluctuations (ASF)[14] the solution W_1 of Eq. (11) has the form

$$W_1(\mathbf{R}(t,\gamma)) = W_1^0(\mathbf{R}(t,\gamma = 0) + \frac{1}{2}\frac{\dot{y}(t,\gamma)}{y(t,\gamma)}y^2(t,\gamma), \quad (19)$$

where $W_1^0(\mathbf{R}(t,\gamma = 0))$ is the action along the one-dimensional classical trajectory $x(t)$, starting from the point $x_1(n_2)$, and transversal fluctuations $y(t,\gamma)$ obey the equation

$$\ddot{y}(t,\gamma) = \tilde{V}''_{yy}(\mathbf{R}(t,\gamma = 0)\cdot y(t,\gamma).$$

In accordance with the boundary condition the variables (t,γ) perform a one-to-one mapping into (x,y); because the relation $\frac{\dot{y}(t,\gamma)}{y(t,\gamma)}$ in the ASF does not depend on γ and the solution of (11) in variables (x,y) can be written as

$$W_1(x,y) = W(x) + A(x)y^2/2, \quad (19a)$$

where $W(x)$ is the one-dimensional action in the potential (15), $A(x) = \frac{\dot{y}(t(x))}{y(t(x))}$ (the expression for $A(x)$ can also be obtained by inserting (19a) into Eq. (11) and omitting members $\propto y^4$), and $t(x)$ is the time of the movement along the extremum trajectory.

By inserting expression (19) into the transport equation (12), one obtains that in an approximation of small deviations the solution $W_2(x,y)$ has the form

$$W_2(x,y) = \frac{1}{2}\ln(p(x)) - n_2\ln(y) + (n_2+1/2)\int_0^{t(x)}[(A(x(\tau))-\tilde{\omega}_1)+\frac{C}{\tilde{\omega}_1}(\tilde{x}_0^2-x^2(\tau))]d\tau\ . \quad (19b)$$

Expressions (19a,b) solve the problem of calculating $\Psi(x,y)$ and, therefore, Δ:

$$\Delta_{0,n_2} = B_{n_2}\Delta_{1D}(n_2) , \qquad (20)$$

$$B_{n_2} = \left|\frac{\tilde{\omega}_1}{A(t_0)}\right|^{n_2+1/2} \exp(2n_2+1)\int_0^{t_0}[(\tilde{\omega}_1 - A(x(t))) - \frac{C}{\tilde{\omega}_1}(\tilde{x}_0^2 - x^2(\tau))]d\tau.$$

Here $\Delta_{1D}(n_2)$ is the one-dimensional splitting in the potential $\bar{V}(x)$, whose dependence on the transversal quantum number is coupled to the shift of the minimum position of the effective potential $\bar{V}(x)$, and t_0 is the time of the motion to the dividing line on the extremum trajectory $x(t)$. The expression for the tunneling splitting (20) is the product of the longitudinal part $\Delta_{1D}(n_2)$, calculated along the tunneling trajectory, and the prefactor, determined by transversal fluctuations. Note that for an extremum trajectory one can take[18] the trajectory starting from the minimum of the potential $(\tilde{x}_0,0)$. In that case[19]

$$x(t) = \tilde{x}_0\tanh(\omega_0 t/2),$$

$$\Delta_{1D}(n_2) = \frac{\hbar\omega_0}{\pi}[2\pi\frac{\omega_0^3}{V_0}]^{1/2}\exp(-\omega_0^3/12V_0),$$

$$\omega_0 = (8V_0\tilde{x}_0^2)^{1/2}$$

and integration over time in formula (20) should be done from $-\infty$ to 0.

For small values of the coupling constant C the transversal prefactor B_{n_2} can be written in a more compact form. In this case

$$\int_{-\infty}^{0}[(\tilde{\omega}_1 - A(x(\tau))) - \frac{C}{\tilde{\omega}}(\tilde{x}_0^2 - x^2(\tau))]d\tau \cong \frac{2C^2\tilde{x}_0^4}{3\omega_0\tilde{\omega}_1^3},$$

$$B_{n_2} = \left|\frac{\tilde{\omega}_1}{A(t_0)}\right|^{n_2+1/2} \exp\frac{2C^2\tilde{x}_0^4}{3\omega_0\tilde{\omega}_1^3}(2n_2+1) . \qquad (21)$$

The results of calculations of the tunneling splittings for the cyclopentanone molecule using the formula (20) in the series $n_1 = 0$, $n_2 = 0$ to 6 agree well with the results of an exact diagonalization of the Hamiltonian (1) (see Table 1). Thus, an increase in the tunneling splitting with transverse quantum number of the symmetry coupled transverse mode is due to two factors. The first is the "width of the tunneling channel", which shows itself in the growth of B_{n_2} with an increase in the quantum number of the transverse vibration. This effect is caused by the fact that for $C > 0$ the transverse frequency on the dividing straight line is less than in the potential minimum. The second cause is the effective shortening of the tunneling length because of the positive symmetrical coupling ($x_0 > \tilde{x}_0$).

The approach suggested enables one not only to calculate the tunneling splittings but also to evaluate the quasi-classical wave function (10), obtained with the help of formulas (19a,b), with an exact, calculated numerical diagonalization of the Hamiltonian, that is, to directly estimate the precision of the quasi-classical method, and, in particular, the approximation of small fluctuations related to it. The comparison can be done on the dividing straight line $x = 0$, since this region of the wave function particularly determines Δ. The results of the calculations are presented in Fig. 2. One can see a reasonable agreement of the wave function amplitudes for different levels n_2. At the same time, the width of quasi-classical wave functions is somewhat less than the exact ones, and the discrepancy tends to grow with an increase in the quantum number n_2, which indicates a crudeness of the ASF for higher vibrationally excited states.

Knowledge of the wave functions on the dividing straight line enables one to elucidate the geometry of the cyclopentanone molecule in the transition state. As one can see from Fig. 2, in the ground state the transition state configuration is planar, in agreement with the conclusion made earlier.[10] In excited states the wave function acquires two maxima, symmetrically situated about the x axis. The distance between them grows simultaneously to n_2 and the corresponding configuration becomes bent. The bending angle achieves 35° for $n_2 = 6$, and in this case the interconversion of higher vibrationally excited states of cyclopentanone is closer to the pseudorotation characteristic of cyclopentane and its derivatives.[20]

* * *

The importance of an analysis of the two-dimensional tunneling in interpretating the spectra of nonrigid molecules was mentioned earlier. Yet a study of spectral line shapes may require a departure from the approximation of non-interacting transversal modes and consideration of tunneling on N-dimensional non-splitting PES. Upon increase in the number N of coupled vibrations, it is very difficult to obtain precise quantum dynamics or energetic spectrum of a polyatomic molecule because a very large number of basis functions is needed; this number grow exponentially[21] with an increase in N. At the same time the quasi-classical methods look more efficient, because they require solution of classical equations of motion only, which actually imposes no restrictions on the system size. The procedure suggested in this work can be easily generalized in the case of several interacting non-tunneling coordinates, because if an extremum subbarrier trajectory is known, one can always introduce curvilinear coordinates orthogonal to it (a similar numerical procedure is well developed in the modern theory of transition states[22]). In these coordinates the Hamilton—Jacobi equation transforms itself into expression (19) and variables in the transport equation uncouple in the ASF. Consequently, the tunneling splitting has the form (20) and transversal prefactors for each coordinate are multiplied. These problems, as well as calculations of the spectra of molecules described by the potential functions (1) and (2), will be considered in subsequent publications.

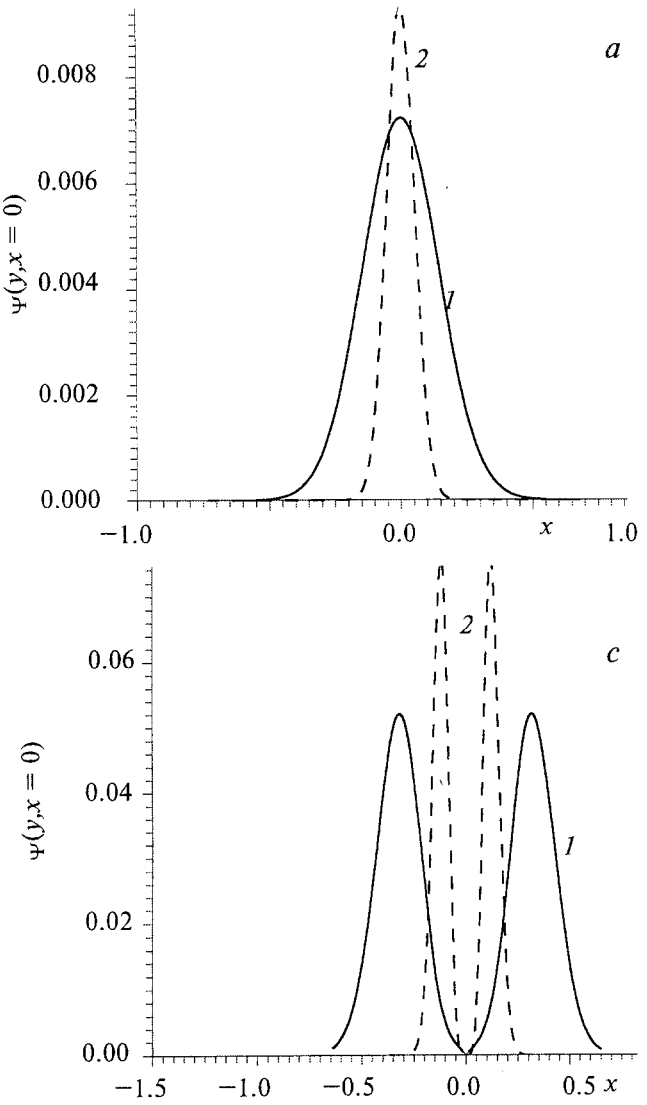

Fig. 2. The wave function on the dividing straight line $x = 0$. Solid line (*1*) corresponds to the exact calculation, dotted line (*2*) represents quasi-classical wave function (10) for $n_1 = 0$, $n_2 = 0$ (*a*); $n_1 = 0$, $n_2 = 2$ (*b*); $n_1 = 0$, $n_2 = 4$ (*c*) levels.

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