Theor Chim Acta (1985) 68, 351-362

THEORETICA CHIMICA ACTA

Two-dimensional model of intramolecular hydrogen bond

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(Received January 9, revised July 15/Accepted July 26, 1985)

One- and two-dimensional vibrational problems were solved to determine the states of *H* and *D* in the intramolecular hydrogen bond of malonic dialdehyde. Within the one-dimensional approach the model potential (barrier height 51 kJ/mol) satisfied with the *IR* and microwave spectroscopy data. For the two-dimensional problem an approach to evaluation of eigenvalues with high accuracy based on the Ritz method was developed. Within the two-dimensional approximation the barrier height was taken to be 57 kJ/mol. An introduction of the second dimension was found to give rise to the vibrational non-adiabatic effects.

Key words: Intramolecular hydrogen bond — Numerical methods — Eigenvalue problem — Malonic dialdehyde

1. Introduction

Quantum-mechanical tunnelling is known to play an important role in hydrogen atom or proton transfer encountered in many chemical and biological processes [1, 2]. In computing rate constants for chemical reactions tunnelling is most often introduced by using the Wigner type tunnel corrections [3], whereby only the probability of tunnelling through the one-dimensional barrier is computed. The latter is given by the potential $V(s)$ along the minimal reaction energy path. This approach was applied to studying hydrogen bonds (*h.b.*) in malonic dialdehyde (MDA) [4, 5, 6, 7] which is one of the most convenient model compounds [8] to investigate intramolecular hydrogen bonds.

From the theoretical viewpoint, Miller [9] and Marcus-Coltrin [10] corrections considering the influence of the transverse vibrational modes on the motion along the reaction coordinate proved to be more accurate methods to treat the tunneling effect. In [9] and [10], two main approximations were used, namely first, the vibrational adiabaticity (the vibrational quantum number n of the mode ν of reactants was assumed to remain unchanged along the reaction coordinate), and secondly, the quasi-classical approximation for calculating the tunnelling probabilities.

It should be noted, however, that the former approximation proved good only when the motion along the reaction coordinate is much slower than the vibrational motion. Two main sources were stated [11] to give rise to the vibrational-nonadiabatic effects. They are (1) the variation of frequencies of transverse modes along the reaction coordinate; (2) curvilinear effects, e.g. a sharp change of the reaction coordinate direction.

As was demonstrated by Brickmann and Zimmermann, in numerical computations of H atom states in the model double-well *h.b.* potentials, the quasi-classical approximation can lead to high errors [12].

The approach developed to avoid these approximations is the system-bath decomposition of the reaction-path Hamiltonian [13]. The reaction coordinate is assumed to be coupled strongly to a few of the transverse vibrational modes, and more weakly to the remaining ones. Thus, the complete polyatomic molecular system can be divided into a "system" (the reaction coordinate and the strongly coupled modes) and a "bath" (the weakly coupled modes). The problem for a "system" can be solved accurately: while the effects of "bath" modes are considered by approximate methods (e.g. perturbational or statistical).

To solve the problems dealing with the intramolecular proton transfer within the framework of the approach discussed above we have composed a program for the numerical solution of the one-particle Schroedinger equation with the two-dimensional potential.

This paper describes the technique for solving the two-dimensional one-particle Schroedinger equation and compares the two models of *h.b.* in MDA considering the motion of proton and deuteron in one- and two-dimensional adiabatic potentials.

2. Numerical solution of the two-dimensional problem

2.1. *Initial equation*

Consider the Schroedinger equation for a two-dimensional motion of a particle of mass m with potential energy V. The function V represents a surface with a number of wells separated by barriers. All the wells are in a relative proximity to the origin of a certain coordinate system. With the increasing range from the origin the function V either grows or approximates to the limit value V_∞. Our interests are focused on those states of a particle for which its energy, from the viewpoint of the classical mechanics, is insufficient to overcome a barrier, so that a particle is localized inside a potential well.

In those particular cases when potential energy minima are arranged around the origin in a certain way, the symmetry of the problem invites the use of the polar coordinates. In the atomic units the Schroedinger equation takes the form:

$$\left(-\frac{d^2}{dr^2}-\frac{1d^2}{r_2 d\varphi^2}+mV(r,\varphi)\right)U(r,\varphi)=m\lambda U(r,\varphi) \tag{1}$$

with the boundary conditions:

$$U(0,\varphi)=U(\infty,\varphi)=0 \tag{2a}$$

$$U(r,\varphi)=U(r,\varphi+2\pi). \tag{2b}$$

In order to simplify the solution of this problem the minimum potential energy path (the reaction path) is suggested to be a circle with $r=r_0$. Furthermore, let $V(r,\varphi)$ satisfy the condition:

$$\frac{d^2V(r_0,\varphi)}{dr^2}\gg\frac{1}{r_0^2}\frac{d^2V(r_0,\varphi)}{d\varphi^2}.$$

If we denote r as x and φ as y, the simplified Schroedinger equation will take the form:

$$\left(-\frac{d^2}{dx^2}-\frac{1}{x_0^2}\frac{d^2}{dy^2}+mV(x,y)\right)U(x,y)=m\lambda U(x,y). \tag{3}$$

Since the function $U(x,y)$ rapidly vanishes in the classically inaccessible domain, one is in a position to neglect all its values for x not belonging to a certain interval. Bearing this in mind one can substitute the approximate boundary condition:

$$U(x_{\min},y)=U(x_{\max},y)=0 \tag{4}$$

for the strict one (2a).

Apparently, with x_0^2 set equal to the unity Eq. (3) will equally fit the particular case of a particle in a double-well potential. Therefore the boundary condition (2b) is reduced to:

$$U(x,y_{\min})=U(x,y_{\max})=0. \tag{5}$$

2.2. *The algorithm of solving model equation (3)*

So, we have to solve Eq. (3) either with boundary conditions (4) and (2b) or with (4) and (5). Let us apply the Ritz method, and expand U as:

$$U(x,y)=\sum_{i=1}^{N_x}\sum_{j=1}^{N_y}U_{ij}X_i(x)Y_j(y)$$

Y are always trigonometric functions and X, depending on the boundary conditions, are either trigonometric functions or the eigenfunctions of harmonic oscillators. The bases are assumed to be orthonormal. The coefficients U_{ij} can be determined by solving the following eigenvalue problem:

$$\sum_{kl} A_{ijkl} U_{kl} = \lambda U_{ij} \tag{6}$$

where the elements of the matrix A are:

$$A_{ijkl} = \int_{x_{\min}}^{x_{\max}} \int_{y_{\min}}^{y_{\max}} X_i(x) Y_j(y) H X_k(x) Y_l(y)\, dx\, dy. \tag{7}$$

Here

$$H = -\frac{d^2}{dx^2} - \frac{d^2}{x_0^2\, dy^2} + V(x, y). \tag{8}$$

Since we must determine only a few of the lowest eigenvectors and corresponding eigenvalues of the matrix A, we use the modified Davidson method [14], whereby we can avoid explicit calculation of all matrix elements.

Suppose we are to calculate K of the lowest eigenvalues and eigenvectors of the matrix A. The vectors $U^i (i = 1, \ldots, K)$ are determined by iterations. At every step the vectors U are expanded with respect to the vectors of the intermediate basis e^i:

$$U^i = \sum_{j=1}^{L} S_{ji} e^j.$$

In the coordinate representation e^i is expanded as follows:

$$e^i(x, y) = \sum_{k,l} e^i_{kl} X_k(x) Y_l(t) \qquad \sum_i e^i_{kl} = 1.$$

Initialization of the process includes the formation of the vectors e^i by means of diagonalization of the matrix A^1 which is a restriction of A onto the smaller basis consisting of M_x of the function $X(x)$ and M_y of $Y(y)$.

Analysis of the nature of convergence within the Davidson's method along with the numerical computations prompted us to use for A_{jj} the matrix A^0, constructed in accordance with the following rules:

$$A^0_{ijkl} = A_{ijkl} \quad \text{if } i,\ k \leq M_x \text{ and } j,\ l \leq M_y$$

$$A^0_{ijkl} = A_{ijkl}\, \delta_{ik}\, \delta_{jl} \quad \text{for } i > M_x \text{ or } j > M_y.$$

The choice of the numbers M_x and M_y was determined by the fact that their increase ensues on speeding up the convergence. On the other hand, the matrix A^0 containing a nondiagonal block of the order $M_x \cdot M_y$ must be diagonalized once that requires $M_x^3 \cdot M_y^3$ of operations. Besides, to multiply a vector by the matrix $(A^0 - \lambda)^{-1}$ we need $M_x^2 \cdot M_y^2$ operations more in each iteration. The modification of the method which we used here enables us to lower significantly a number of iterations compared to the Davidson's method.

While solving the model problems with $N_x = 20$ and $N_y = 70$ we succeeded by the choice of $M_x = 8$ and $M_y = 25$ in the greater than 10 times decrease of the error of determination of an eigenvalue.

The multiplication of a vector by the matrix A was performed using the Gaussian quadratures for polynomial bases and the trapezoidal rules for trigonometric ones. The maximum accuracy was observed when the number of gridpoints of quadrature is roughly equal to the number of basis functions. Taking into account that in the coordinate representation the differential term of the operator H is rather simple and the potential term is diagonal the left multiple of a vector by the matrix A can be calculated by only $2(N_x^2 \cdot N_y + N_x \cdot N_y^2)$ of multiplications and additions.

Consider an accuracy of eigenvalues obtained by this method. The arithmetic problem can be solved with the highest accuracy, so the crux is actually the convergence of the expansion of the function to be found in the terms of the chosen basis. In the basis of the weighted algebraic polynomials or trigonometric functions the convergence is determined by the smoothness of the expanded function. We will treat the convergence for the following exemplifying problem:

$$-U''_{xx} + p(x)U = \lambda U$$

$$U(A) = U(B) = 0.$$

Solutions of this problem obviously have limited derivatives of $K+2$ order, where K is the highest order of limited derivative of the function $p(x)$. An expansion of p over the properly chosen basis converges in such a way that the residual term has $N^{-(K+2)}$ order of magnitude, N being the number of basis functions. If the function $p(x)$ and an eigenvalue λ correlate in a way that the function U and it's derivatives are fairly small in the neighborhood of the points A and B, the expansion of U in the terms of the trigonometric basis converges with approximately the same rate as the expansion in the terms of algebraic polynomials, since the function under consideration can be treated as periodic with the period $B-A$. The estimate of the convergence can be obtained through integration by parts of the rule for Fourier coefficients. In practice, calculations with trigonometric basis are more convenient than with polynomials. Smallness of the functions and their derivatives can be easily ensured by means of quasi-classical formulas. The same formulas stand for the choice of new points A', B' when A and B are infinite. It's noteworthy that the one-dimensional problem requires from 20 up to 80 of the basis functions, while 1400 of them must be involved in the solution of the two-dimensional problem. Meanwhile in view of their much slower convergence an application of routine finite-difference methods would require a significantly greater number of parameters to approximate the functions.

Gridpoints and all Gaussian quadratures are conveniently calculated by a modified Harris method [15] which reduces the problem to diagonalizing the matrix of the product of an operator and an independent variable in an orthogonal polynomial basis.

3. A comparison of the accurate solution of the two-dimensional vibrational problem and the approximate solution obtained by the reaction coordinate method

Consider the model Schroedinger equation (for simplicity written for $m=1$):

$$\left(-\frac{d^2}{dx^2}+\alpha(y)x^2-\frac{1}{x_0^2}\cdot\frac{d^2}{dy^2}+f(y)\right)U=\lambda U \tag{9}$$

with the boundary conditions:

$$U(0,y)=U(\infty,y)=0$$
$$U(x,y)=U(x,y+2\pi).$$

Here $f(y)$ and $\alpha(y)$ are assumed to be 2π-periodic functions, the reaction path is directed along the y-axis. Eq. (9) gives an approximate description of the motion in a narrow deep valley. To analyse its solutions we introduce the following set of functions defining the vibrations along the x-axis, i.e. perpendicular to the reaction coordinate:

$$Q_i(x,y)=N_iH_i(\sqrt[4]{\alpha(y)}\cdot x)\exp\{-\sqrt{\alpha(y)}\cdot x^2/2\}$$

where N_i are the normalization coefficients, $Q_i(x,y)$ being the eigenfunctions of the problem:

$$\left(-\frac{d^2}{dx^2}+\alpha(y)x^2\right)Q_n(x,y)=\varepsilon_nQ_n(x,y)$$
$$\varepsilon_n=\sqrt{\alpha(y)}\cdot(2n+1).$$

The function U can be expanded as:

$$U(x,y)=\sum_i\varphi_i(y)Q_i(x,y) \tag{10}$$

Upon substituting (10), (9) becomes:

$$\left(-\frac{1}{x_0^2}\frac{d^2}{dy^2}+f(y)+\varepsilon_i-\lambda_i\right)\varphi_i$$
$$=A_{i,-2}\varphi_{i-4}+A_{i,-1}\varphi_{i-2}+A_{i,0}\varphi_i+A_{i,1}\varphi_{i+2}+A_{i,2}\varphi_{i+4}.$$

The coefficients A are expressed through $\alpha'(y)/\alpha(y)$ and $\alpha''(y)/\alpha(y)$ ratios. Clearly, in a particular case of $\alpha(y)$ being a constant, the latter equation can be split.

Suppose that the coefficients A are sufficiently small to solve the problem by means of the perturbation technique. The most interesting case is that of the ground state of the transverse vibrational mode. Zeroth-order eigenvalues λ_i and eigenfunctions φ_i are given by the equation:

$$\left(-\frac{1}{x_0^2}\cdot\frac{d^2}{dy^2}+f(y)+\sqrt{\alpha(y)}\right)\varphi_i(y)=\lambda_i\varphi_i(y).$$

This equation occurs within the reaction coordinate approach. Representation of α as $\beta \cdot \alpha_0(y)$ enables us to estimate the fall-off rate of functions φ_i which appears to be $1/\sqrt{\beta}$ for large β. Hence, for narrow valleys where the variation of curvature is much smaller than its value, the reaction coordinate method might be expected to be fairly accurate. However, its applicability limits can be tested only in numerical calculations.

4. A comparison of the one- and two-dimensional problems

The potential energy profile for hydrogen bond (*h.b.*) in MDA along the reaction coordinate was taken from the *ab initio* MO-LCAO-SCF calculations [17]. An approximation to this potential function was sought as a polynomial of degree 8 (the separation between the potential minima was taken to be 0.65 Å in accordance with the microwave experiment on MDA [18]):

$$G(x) = L(a_0 + a_2x^2 + a_4x^4 + a_6x^6 + a_8x^8) \tag{11}$$

with the empirical parameter L estimated from the condition of equality of tunnel splittings obtained by the model double-well calculations and their experimental values for the ground state of O—H bond stretching vibration in MDA assigned to the tunnelling of H or D. This condition is satisfied for the barrier height $G(0)$ equal to 51 kJ/mol in a good agreement with the estimates obtained by the *ab initio* SCF calculations [8, 17, 19]. The calculated tunnel splittings for the barrier height were $\Delta E_0(H) = 22.1\ \mathrm{cm}^{-1}$, $\Delta E_0(D) = 0.95\ \mathrm{cm}^{-1}$. It's noteworthy that the energies of the transition from the ground vibrational state to the lower sublevel of the first excited state as 2420 cm^{-1} for H and 2190 cm^{-1} for D, in a satisfactory agreement with the experiment [20].

As was found for MDA [4] the frequencies of only two of the transverse in-plane modes undergo a significant change if the motion along the reaction coordinate is taken into consideration. One of them, the O—H bond in-plane bending mode

Table 1. The vibrational frequencies for acetylacetone (A) and dimeric formic acid (B) pertaining to COH, COD fragments

	Frequencies, cm^{-1}	
Mode	A [20]	B [21]
$\nu(\mathrm{OH})_{\mathrm{stretching}}$	2750	2688
$\nu(\mathrm{OH})_{\mathrm{bending\ in\text{-}plane}}$	1460[a], 1400[b]	1415
$\nu(\mathrm{OH})_{\mathrm{bending\ out\text{-}of\text{-}plane}}$	957	917
$\nu(\mathrm{OD})_{\mathrm{stretching}}$	2020	2068
$\nu(\mathrm{OD})_{\mathrm{b.i.\text{-}p.}}$	1076[a], 1080[b]	1250
$\nu(\mathrm{OD})_{\mathrm{b.o.\text{-}o.\text{-}p.}}$	707	678
$\nu(\mathrm{O\text{-}H\cdots O})_{\mathrm{b.i.\text{-}p.}}$	-	137.1
$\nu(\mathrm{O\text{-}D\cdots O})_{\mathrm{b,i.\text{-}p.}}$	-	130.0

[a] From [22]
[b] From [23]

was treated within the two-dimensional model. The plots for the normal and dideuterated forms of MDA were assumed to be closely similar.

Vibrational frequencies at the minimum of the potential function and in the transition state were taken from the vibrational spectra of the close analogue of MDA, acetylacetone, and the dimer of formic acid. We can use the Raman frequencies for the latter because the vibrational frequencies pertaining to COH (COD) fragments are virtually close to those for acetylacetone (see Table 1). Thus, the frequencies of the in-plane bending mode of the O–H (O–D) bond at the potential function minima were taken to be 1400 cm^{-1} and 1080 cm^{-1}, respectively, meanwhile in the transition state these values were taken to be 137 cm^{-1} and 130 cm^{-1}; the latter estimates are based on the Raman spectra of the dimeric formic acid [21].

Thus, the model two-dimensional potential functions of *h.b.* in MDA were chosen as:

$$G(x, y) = G(x) + \frac{m}{2}\left(\frac{\nu(x)}{\hbar}\right)^2 \cdot y^2 \tag{12a}$$

$$G(x, y) = G(x) + \frac{m}{2}\left(\frac{\nu_0}{\hbar}\right)^2 \cdot y^2 \tag{12b}$$

where

$$\nu_0 = \begin{cases} 1400 \text{ cm}^{-1} \text{ (for hydrogen)} \\ 1080 \text{ cm}^{-1} \text{ (for deuterium).} \end{cases}$$

The plots of the potential surfaces (12a) and (12b) are represented in Figs. 1a, b.

A series of computations performed with potential energy function (12a) demonstrated that the tunnel splitting for the ground vibrational state approximated the experimental values for the barrier height $G(0, 0)$ equal to 57 kJ/mol and amounted to: $\Delta E_{00}(\mathrm{H}) = 21.4$ cm^{-1} and $\Delta E_{00}(\mathrm{D}) = 0.79$ cm^{-1}, the energy being quantized along the reaction coordinate (first number) and the transverse vibration (second number).

Several words should be said about the details of the computations. Total 800 functions of trigonometric basis were obtained as products of 40 functions representing the motion along the reaction coordinate and 20 functions-perpendicular to it. An average number of iterations per eigenvalue to be required for convergence was 10–12: the convergence criterium being 10^{-6} cm^{-1}.

In order to evaluate the changes introduced by the transverse mode $\nu(x)$ we solved the problems on H and D states in the one-dimensional potential function (11) with $G(0) = 57$ kJ/mol, and in the two-dimensional models (12a) and (12b) with the same height of $G(0, 0)$. The energy levels of H and D states and the tunnel splittings in the three model potential functions introduced above are sketched in Figs. 2 and 3.

Solving the problems with (12a) yields markedly enlarged values of the tunnel splitting and the reduced separation between those levels that correlated with

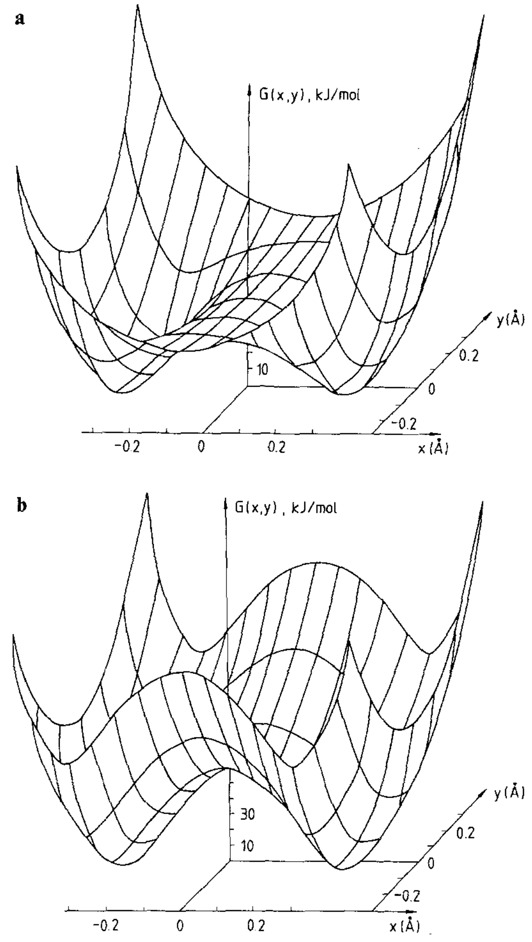

Fig. 1. The plots of model two-dimensional potential functions with $G(0, 0) = 57$ kJ/mol: **a)** potential function (12a), **b)** potential function (12b)

one and the same vibrational state along the reaction coordinate. The tunnel splitting values obtained by the exact solution of the two-dimensional vibrational problem with the potential function (12a) are compared with those obtained by the reaction coordinate method (consult Table 2). The dependence of the in-plane

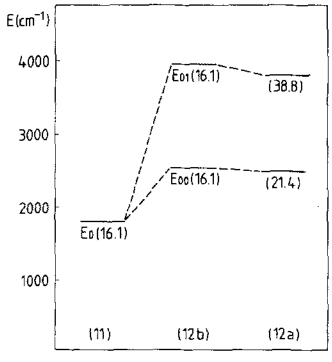

Fig. 2. Energy levels for the states of H (in parentheses the tunnel splittings are given) in the one-dimensional potential the (11) and in the two-dimensional potentials (12b), (12a) with barrier height 4760 cm^{-1} (57 kJ/mol)

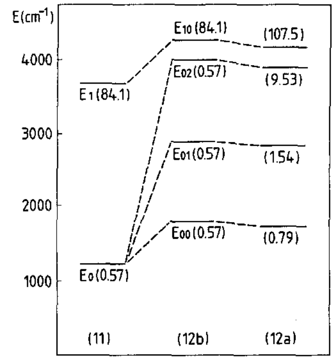

Fig. 3. Energy levels for the states of D (in parentheses the tunnel splittings are given) in the one-dimensional potential the (11) and in the two-dimensional potentials (12b), (12a) with barrier height 4760 cm^{-1} (57 kJ/mol)

Table 2. Comparison of tunnel splittings obtained by the straightforward solution of two-dimensional vibrational problem with the potential function (12a) (A) with those obtained by the reaction coordinate method (B). The notations of energy levels are introduced in Fig. 2.3. Barrier height 57 kJ/mol

	Tunnel splittings, cm^{-1}		$\frac{(B)-(A)}{(A)} \cdot 100\%$
	Method A	Method B	
$\Delta E_{00}(\mathrm{H})$	21.4	24.2	12.9
$\Delta E_{01}(\mathrm{H})$	38.8	57.1	47.3
$\Delta E_{00}(\mathrm{D})$	0.79	0.95	17.9
$\Delta E_{10}(\mathrm{D})$	107.5	115.9	7.9
$\Delta E_{01}(\mathrm{D})$	1.54	2.60	68.8
$\Delta E_{02}(\mathrm{D})$	9.53	8.09	−14.9
$\Delta E_{00}(\mathrm{T})$[a]	0.065	0.068	4.6
$\Delta E_{10}(\mathrm{T})$	13.0	15.1	16.2
$\Delta E_{01}(\mathrm{T})$	0.177	0.181	2.3
$\Delta E_{02}(\mathrm{T})$	3.23	0.53	−83.6
$\Delta E_{03}(\mathrm{T})$	33.4	32.5	−2.7

[a] In the case of tritium the following values were taken for the frequencies of the transverse mode: 850 cm^{-1} at the minimum of the potential curve, 127 cm^{-1} in the transition state

bending mode frequency on the reaction coordinate results in vibrational nonadiabaticity that is supposed to account for the discrepancies between the solutions. This effect becomes very significant once an excitation of the vibrations perpendicular to the reaction coordinate is concerned.

5. Conclusive remarks

The exact solution of the two-dimensional problem made it possible to define the role of vibrational-nonadiabatic effects. Here we treated only those effects arising from the dependence between the frequencies of transverse modes and the reaction coordinate. We have demonstrated that the magnitudes of the vibrational-nonadiabatic corrections, are, in general, the most significant ones for the excited levels.

The in-plane bending mode of O–H bond in MDA as well as the O···O mode (skeletal deformation) were shown [4] to be coupled strongly to the reaction coordinate. Thus, the "system" of the MDA molecule necessarily includes three degrees of freedom. However, considerable difficulties which one must overcome while accurately solving the three-dimensional problem elicited a deep interest in estimating the errors arising from the neglect of one of strongly coupled modes.

The large magnitude of the frequency of the transverse mode at the potential energy minimum enables one to consider only those energy levels that correspond to the ground state of the transverse vibration (throughout the paper denoted as E_{K0}). As follows from the results of the present work, the reaction coordinate method gives fairly accurate values of the tunneling probabilities not only for E_{00} level, but also for the excited level E_{10} (relative difference not exceeding 20%). Naturally, their evaluation by the reaction coordinate method is by far less difficult than the exact solution of the two-dimensional problem. Therefore, our results provide a basis for the exclusion of the O–H bending mode from the "system" in calculating the tunneling probabilities.

A comparison of the one- and two-dimensional problems has shown that in cases when other than E_{K0} levels can be ignored, the one-dimensional approximation can be successfully used for estimating tunneling probabilities and barrier heights.

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