Semiclassical Calculations of Tunneling Splitting in Hydrogen Peroxide and Its Deuterated Isotopomers[†]

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Torsional tunneling splittings for the ground and selected vibrationally excited states of HOOH, HOOD, and DOOD are calculated using a semiclassical tunneling approach. The approach incorporates tunneling calculations into quasiclassical trajectory simulations and is thus practical for large systems. Comparisons with the experimental and quantum results show that the mode selectivity and isotope effects are generally reproduced in the semiclassical calculations. The causes for the quantitative discrepancies between the quantum and semiclassical calculations are discussed.

I. Introduction

This is a continuation of our efforts to study tunneling effects in polyatomic molecules by using the semiclassical approach[1,2] that incorporates tunneling calculations into classical trajectory simulations. The gist of the approach is to propagate classical trajectories to determine turning points and then compute tunneling probabilities at turning points along some predefined tunneling direction. The energy level splitting or rate constant can be obtained by averaging the results over an ensemble of trajectories representing the specified state. The approach is practical for large systems where quantum-mechanical solutions are not feasible. Since the full-dimensional classical dynamics are explicitly treated, it also provides insight into the effects of intramolecular dynamics on tunneling.

We have applied the method to compute tunneling splittings in large polyatomic systems. The calculated ground-state splittings in several isotopomers of malonaldehyde[3] and methyl-substituted malonaldehyde[4] agree with the experimental values within a factor of 2, indicating that the method may be accurate for treating tunneling in large systems at low energies. However, because of the uncertainty in the accuracy of the potential energy surface (PES), direct comparisons with quantum calculations on the same PES should provide better assessment of the method. Thus, it is useful to study smaller molecules for which quantum results are available.

The main focus of the present work is to further investigate various aspects of this semiclassical approach and to test its accuracy. We apply the method to hydrogen peroxide (HOOH), which has been used as a prototype system for studying spectroscopic and kinetic properties of small polyatomic molecules. The potential along the torsional angle is of double-well form, and there are available experimental values for the tunneling splittings of the ground and selected vibrational excited states. It is found that the splitting strongly depends on the excitation site; some modes promote tunneling, some suppress it, and some do not affect it. This demonstrates the importance of properly treating the intramolecular couplings. Thus, the system provides a good case for testing the method. Although the molecule has been extensively studied both experimentally and theoretically,[5] until only very recently have high quality multidimensional quantum-mechanical calculations become available due to the advance in quantum chemistry and computational power. Kuhn et al.[6] have developed an accurate six-dimensional analytical potential for the electronic ground state of HOOH based on extensive high-level ab initio calculations. Luckhaus[7] and Chen et al.[8] have performed 6D calculations on this potential and obtained vibrational energy levels. Thus, there are available quantum results for comparison.

II. Computational Methods

A. Initial Conditions. We wish to compute tunneling splittings of vibrational states. To represent a given quantum state semiclassically, two sampling methods for selecting the initial conditions were used: the quasiclassical normal-mode and local-mode samplings.[9]

The normal-mode sampling was used for all the states considered here except the OH overtone states. In the normal-mode sampling, initial normal-mode coordinates Q_i and P_i are chosen from the quantized torus of the harmonic Hamiltonian expressed in action-angle variables

$$Q_i = \sqrt{(2n_i+1)\hbar/m\omega_i}\,\sin\phi_i$$
$$P_i = \sqrt{(2n_i+1)\hbar m\omega_i}\,\cos\phi_i \qquad (1)$$

with n_i being the quantum numbers, and the angle variables ϕ_i chosen randomly in the interval (0, 2π). The normal-mode coordinates are then transformed to the Cartesian coordinates, after which the coordinates are scaled so that the total energy equals the eigenvalue of the specified state.

Obviously, for anharmonic systems the normal-mode sampling is an approximation, and the produced initial state is not equivalent to the corresponding quantum one. We have calculated tunneling splittings for a two-dimensional system by employing the normal-mode and the more rigorous adiabatic switching samplings,[10,11] and the results are very close to each other.[12] We have also employed normal-mode sampling in computing the ground-state splittings of several polyatomic molecules, and the results agree well with the experimental values.[3,4] These studies suggest that the approximate normal-mode sampling is generally valid for practical applications of

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the semiclassical approach, especially for the low energy states where anharmonicity is relatively small.

The local-mode sampling was used for selecting the initial conditions for the OH stretch overtone states. Since the molecule has a two-fold classical local mode degeneracy, the corresponding pair of quantum states can be written as

$$|\nu_{\mathrm{OH}},\nu_{\mathrm{OH'}} >^{\pm} = 2^{-1/2}(|\nu_{\mathrm{OH}},\nu_{\mathrm{OH'}} > \pm|\nu_{\mathrm{OH'}},\nu_{\mathrm{OH}} >) \qquad (2)$$

with ν_{OH} quanta in one OH bond and $\nu_{\mathrm{OH'}}$ in the other. The splitting of the two energy levels decreases with increasing energy due to the anharmonic detuning of the two oscillators, leading to the local mode effect.[13] These effects are most easily observed in the $|\nu, 0\rangle^{\pm}$ states (i.e., all quanta in one bond) of X−H bonds where anharmonicity is large and interbond coupling is weak. If the energy difference of the two eigenstates of eq 2 is small, the torsional splittings of the two states should be close to each other. In addition, the two zeroth-order states $|\nu_{\mathrm{OH}},\nu_{\mathrm{OH'}}\rangle$ and $|\nu_{\mathrm{OH'}},\nu_{\mathrm{OH}}\rangle$ should also be good approximations to the eigenstates. We thus compute the torsional tunneling splitting by selecting the initial conditions representing the $|\nu_{\mathrm{OH}}, 0\rangle$ states. The sampling method described in ref 9 for a Morse oscillator was employed for the excited OH bond, and the normal-mode sampling for the unexcited one.

B. Semiclassical Treatment of Tunneling Splittings. The semiclassical approach for computing the level splitting via classical trajectory calculations has been described previously.[1−3] It is formulated based on the WKB expression for tunneling splitting in a one-dimensional potential

$$\Delta E = 2\hbar\nu \exp(-S_{\mathrm{c}}/\hbar) \qquad (3)$$

where ν is the oscillating frequency at energy E, and S_{c} is the classical action integral in the barrier region between the two turning points $x_<$ and $x_>$

$$S_{\mathrm{c}} = \int_{x<}^{x>} \sqrt{2m[V(x) - E]}\,\mathrm{d}x \qquad (4)$$

Using this one-dimensional WKB expression, one approximates the splitting for a multidimensional system by[1]

$$\Delta E = 2\hbar \frac{\mathrm{d}}{\mathrm{d}t} < A(t) > \qquad (5)$$

where the brackets imply an average over an ensemble of trajectories representing the given state and $A(t)$ is accumulated along a classical trajectory

$$A(t) = \sum_i h(t - t_{\mathrm{i}}) \exp(-S_{\mathrm{i}}/\hbar) \qquad (6)$$

Here $h(t - t_{\mathrm{i}})$ is the step function, t_{i} are the times that a trajectory is at the turning points, and S_{i} are the action integrals.

The basic procedures of this semiclassical method are as follows. A trajectory is initialized in one of the wells using the method described in section IIA and propagated classically. Each time a turning point in the predefined tunneling direction is encountered, an action integral S_{i} is computed, which contributes to the accumulated tunneling amplitude factor $A(t)$ of eq 6. $<A(t)>$ is obtained by summing contributions from all the turning points along a trajectory and then averaging over the ensemble of trajectories representing the specified state. Typical plots of $<A(t)>$ are shown in Figure 1 for the ground states of HOOH (panel a) and DOOD (panel b). The level splitting is then derived from eq 5 by obtaining the slope from the least-squares fit of $<A(t)>$.

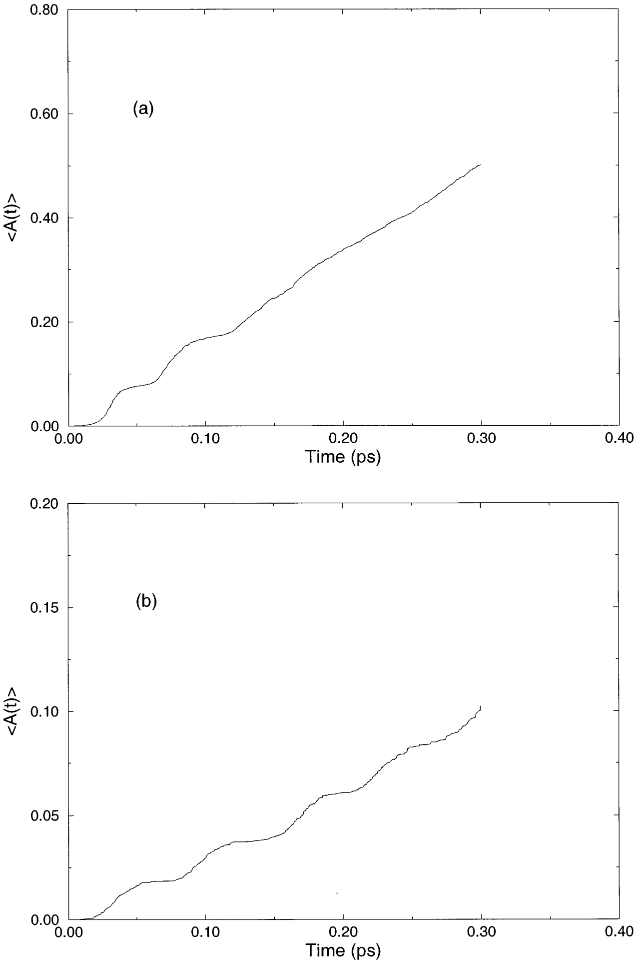

Figure 1. Typical plots of tunneling amplitude factor $A(t)$. Results are for (a) the ground state of HOOH and (b) the ground state of DOOD.

Since the motion of the reaction coordinate is slower than that of the other degrees of freedom, it is an adiabatic case. In the adiabatic limit (i.e., the zero-curvature limit), the Hamiltonian can be reduced to a one-dimensional form[14]

$$H = \frac{p_{\mathrm{s}}^2}{2\mu_{\mathrm{s}}} + V(s) \qquad (7)$$

with an effective potential $V(s)$ including the vibrational energies in the transverse modes

$$V(s) = V_0(s) + \sum_i \left(n_{\mathrm{i}} + \frac{1}{2}\right)\hbar\omega_{\mathrm{i}}(s) \qquad (8)$$

where s is the reaction coordinate, $V_0(s)$ is the potential along s, and $\omega_{\mathrm{i}}(s)$ are the frequencies of transverse modes along s. Note that the harmonic approximation for the transverse modes is implied in eq 8. The tunneling calculation is then reduced to a one-dimensional problem, and the tunneling path is just the minimum energy path. Thus, an ensemble of trajectories starting with the same quantum number but different vibrational phases should stop at the same turning point and have the same tunneling probability. However, the vibrational adiabaticity does not strictly hold for any reaction. The semiclassical method based on the classical trajectory approach takes care of this vibrational nonadiabaticity in an approximate yet natural way. The full-dimensional trajectories are propagated to determine the distribution of the turning points. The action integral for

TABLE 1: Tunneling Splittings of the Ground State and Vibrationally Excited States with One Mode at the First Quantum Level

state	energy	expt[a]	QM[a]	this work
HOOH				
ground state	0	11.4	11.0	18.1
torsion	319	116	119	110
OO stretch	856	12.0	11.0	19.2
antisym bend	1247	20.6	20.8	27.6
sym bend	1395	3.09	6.10	15.7
antisym OH	3609	8.18	7.32	12.8
sym OH	3620	8.15	7.58	18.1
HOOD				
ground state	0	5.8	5.60	13.7
torsion	277		82.5	85.9
OO stretch	854		5.94	14.3
antisym bend	969		7.69	17.5
sym bend	1342		15.9	28.4
antisym OH/OD	2670		3.98	11.7
DOOD				
ground state	0	1.88	1.86	3.6
torsion	235	42.3	43.7	63.6
OO stretch	853		1.78	3.9
antisym bend	926		4.50	9.8
sym bend	1027		1.63	3.9
antisym OD	2662		1.23	2.6
sym OD	2673		6.34	5.4

[a] Results are taken from ref 8.

each individual turning point can be obtained by using the one-dimensional potential of eq 8, with the reaction coordinate s being the torsional angle τ in this case. In this work, for the sake of simplicity, a further approximation is employed in computing the action integral; that is, the total potential, instead of $V(\tau)$, has been used with the transverse degrees of freedom held fixed. Using energy conservation along the tunneling path (the torsional coordinate τ) and the fact that $p_\tau = 0$ at a turning point, the action integral is approximated by

$$S = 2\int_{\tau_<}^{0} p_\tau \, \mathrm{d}\tau = 2\int_{\tau_<}^{0} \sqrt{2G_{\tau\tau}^{-1}(V - V|_{\tau=\tau_<})}\, \mathrm{d}\tau \qquad (9)$$

where $G_{\tau\tau}$ is the G-matrix element for torsional angle and V is the total potential along τ. Since the cis barrier (7.56 kcal/mol) is 6.5 kcal/mol higher than the trans barrier (1.03 kcal/mol), tunneling through only the trans barrier was considered.

Note that the action integral is obtained by performing the integration from the turning point to the top of the barrier and then multiplying it by two. This is because the two potential wells are mirror images of each other and thus the positions of all the atoms have to be symmetrically reflected in passing from one well to the other in computing the action integral.

III. Results and Discussion

We have computed the energy level splittings for selected vibrational states of HOOH, HOOD, and DOOD. The calculations were carried out on the six-dimensional global potential energy surface developed by Kuhn et al.[6] Ensembles of 1000−2000 trajectories were used for each specified state. The trajectories were integrated in a lab-fixed Cartesian coordinate system with a fixed step size of 0.03 fs, and were followed up to 0.3 ps. The total angular momentum is zero in all cases.

The calculated tunneling splittings for the ground state and excited states with one mode at the first quantum level ($n = 1$) are given in Table 1 together with the experimental and quantum-mechanical values taken from ref 8. The initial conditions were selected by quasiclassical normal-mode sampling as described in section IIA. For most of the states, the agreement between the semiclassical and quantum calculations is within a factor of 2. Compared to the ground state splitting, some modes enhance tunneling, some suppress it, and some do not affect it. Not surprisingly, direct excitation of the torsional mode results in a drastic increase in the splitting. Excitation of the OO stretch has essentially no effect, indicating that the OO stretch is weakly coupled to the torsional mode. The effects of excitations of the bending and OH/OD stretching modes are not as simple. For HOOH and DOOD, the antisymmetric bend promotes tunneling while the symmetric bend suppresses tunneling, whereas both modes promote tunneling for HOOD. Excitation of the antisymmetric OH/OD stretch gives rise to lower splitting for all three species, whereas excitations of the symmetric OH and OD stretches have the opposite effects—one suppresses while the other enhances tunneling. The result of the antisymmetric OD stretch excitation of DOOD has been attributed to the mode coupling and state mixing.[15] We note that only absolute values of the splittings are listed in Table 1 because the semiclassical method is unable to account for the sign difference. It is clear that the trends of the mode selectivity and isotope effects are generally well described by the semiclassical method.

The quantitative difference between the semiclassical and quantum results seems to stem in a large part from the errors introduced in computing the ground state splitting, since many of the semiclassical values are shifted by the difference between the quantum-mechanical and semiclassical ground-state splittings. These errors are likely resulted from the intrinsic semiclassical WKB approximation as well as the approximate procedures in computing the action integral. In addition, the normal-mode sampling becomes less valid with increasing anharmonicity and coupling. For instance, it is likely that the initial sampling does not properly account for the couplings between the OH stretch and the reaction coordinate, resulting in the less accurate splitting for the symmetric OH stretch excitation.

The classical propagation introduces another source of errors that usually accumulates with time. In addition, the quasiclassical normal-mode sampling yields nonstationary initial states that will decay with time. Thus, short run times are often used in semiclassical calculations. At low energies where anharmonicity is small, these errors should also be relatively small. It seems that for all the excited states listed in Table 1 with the exception of the torsional one, the states remain fairly stationary within the run time. When the torsional mode is excited, the energy flows out of the torsional coordinate after a short time, and the decay curve levels off after the initial period. In this case, only the initial portion of the curve was used to obtain the splitting, and the error introduced by choosing the cutoff time is nontrivial to assess and is generally far greater than the statistical error of sampling size.

We have also calculated tunneling splittings for selected OH overtone states $|\nu_{\mathrm{OH}},0\rangle$ up to $\nu_{\mathrm{OH}} = 5$. Since the anharmonicity increases with the increase of OH bond energy, the normal-mode sampling is less valid here. On the other hand, it is known that the OH stretch in HOOH is a good local mode at high excitations, thus the local-mode sampling described in section IIA was used here. The results are given in Table 2 along with the quantum-mechanical and experimental values. One has to keep in mind when making comparisons that for each quantum number, the experimental value is the tunneling splitting of just one state of the overtone pair, the quantum result is for the pair (the difference in the splittings for the two states is small though

TABLE 2: Tunneling Splittings of Selected OH Overtone States

(ν_{OH},$\nu_{OH'}$)	expt[a]	QM[a]	this work
(0,0)	11.4	10.6 (11.0)[b]	18.1
(1,0)	8.1	7.6	14.6
(2,0)	6.2	4.5	12.6
(3,0)	4.0	2.7	12.2
(5,0)		0.7	8.8

[a] Values are taken from ref 7. [b] The ground-state splitting given in parentheses is the quantum value taken from ref 8.

and thus not listed here), and the semiclassical calculation was performed for the zeroth-order state with only one OH bond excited. Theoretically, these values should converge for high excitation states where the local-mode effects are strong but are somewhat different at low energies. The semiclassical values reproduce the trend of the experimental and quantum results; the splitting decreases with increasing levels of the OH stretch excitation, but they show a consistent overestimation. Because of the close agreement between experiments and quantum calculations performed on an adiabatic surface, the decrease in the splitting with increasing OH bond excitation can be attributed to the increase of the effective torsional barrier. Since the local-mode sampling is a good approximation here, especially for high overtone states, it seems that the error in the semiclassical splitting comes from the approximations involved in evaluating the action integral. The results would likely be improved if the transverse frequencies $\omega_i(\tau)$ are computed and the effective potential of eq 8 is employed in computing the action integral. For lower energy states, such as the first excited state, the inaccuracy in the local-mode sampling may also be significant.

IV. Summary

Hydrogen peroxide presents an interesting case because of the mode-selective tunneling splittings due to the strong intramolecular couplings. It is found that, depending on the excitation site, vibrational excitations promote, suppress, or do not affect tunneling. This clearly demonstrates the multidimensional nature of the tunneling process in HOOH. Since the semiclassical method employs quasiclassical trajectory simulations to determine the turning points, it also provides a good case for testing the accuracy of the quasiclassical trajectory approach as well as the semiclassical method.

Our calculated level splittings for the ground and selected vibrationally excited states of HOOH generally agree with the trends of the experimental and quantum results. Compared with the ground-state splitting, excitation of the OO stretch essentially has no effect on the splitting. Excitation of the antisymmetric OOH bend increases the splitting, while excitation of the symmetric bend reduces the splitting. The increase in the OH stretch excitation leads to monotonic decrease in the splitting. The isotope effects have also been generally reproduced in our calculations of HOOD and DOOD. These results again demonstrate the applicability of this classical-trajectory-based semiclassical approach.

There are three major causes for the quantitative difference between the semiclassical and quantum results. One is the intrinsic error in the semiclassical WKB approximation, which seems to be the major error in the ground state splitting. Another comes from the normal-mode sampling, which becomes less valid with increasing anharmonicity. The third one lies in the approximations used in computing the action integral, which may be largely responsible for the overestimation of the splittings for the OH overtone states.

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