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Predictions of rate constants and estimates for tunneling splittings of concerted proton transfer in small cyclic water clusters

Thomas Loerting, Klaus R. Liedl,[a] and Bernd M. Rode
Department of Theoretical Chemistry, Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

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We present transfer rates for the concerted hydrogen exchange in cyclic water clusters $(H_2O)_n$ ($n=3,4$) based on *ab initio* hypersurfaces. The studied hydrogen exchange involves bond breaking and forming and is in contrast to flipping motions of ''free'' hydrogen atoms in a ''chemical'' reaction. The rates are calculated for gas-phase systems using canonical, variational transition state theory. Multidimensional tunneling corrections are included assuming both a small and a large reaction path curvature. Hybrid density functional theory [B3LYP/6-31+$G(d)$] was used to evaluate the potential energy hypersurface with interpolated corrections of second order perturbation theory [MP2/6-311++$G(3pd,3df)$] at the three stationary points for both systems. Large curvature tunneling corrections are included in dual-level direct *ab initio* dynamics for the cyclic tri- and tetramer of water. The ridge of the reaction swath serves as an estimate for the tunneling probability of various straight-line corner cutting paths. Our results suggest that the investigated species interconvert on a time scale of seconds. The ground-state tunneling splitting is proportional to the square root of the transition probability at the energy of the minima, which is available from the calculation of tunneling corrections. The associated tunneling splittings are estimated to be between 10^{-4} and 10^{-5} cm^{-1}, which is close to the experimental resolution limit. © *1998 American Institute of Physics.* [S0021-9606(98)00431-0]

I. INTRODUCTION

Neutral, cyclic water clusters $(H_2O)_n$ are important molecular species for the understanding of the condensation process and the nature of hydrogen bonded networks.[1–4] For $(H_2O)_3$ the global minimum was identified as a chiral (i.e., C_1) ring structure having nonlinear hydrogen bonds between the oxygens at various levels of theory.[5] Each oxygen acts as hydrogen acceptor and donor at the same time. Other cyclic, chainlike, pyramidal or otherwise clustered structures are a few kcal/mol higher in energy.[6–8] For $(H_2O)_4$ the achiral (i.e., S_4) ring structure with solely donor/acceptor oxygen atoms is found to be the global minimum. The one of the pentamer is still cyclic, but for oligomers with six or more water monomers, a cagelike structure becomes slightly favorable due to a relatively low zero-point energy.[4,9–11] These findings have been confirmed both theoretically[12,13] and experimentally.[8,14–16] The transition states to the concerted exchange of bridging hydrogens have higher symmetry, as the hydrogen atoms are exactly in the middle of the shortened OO distances, i.e., C_s symmetry for the trimer and D_{2d} for the tetramer.[12] Zero-point effects, monomer interaction-, dissociation- and binding-energies as well as many-body decompositions and investigations of possible reaction mechanisms have been the topic of several studies.[9,17–23] Experimentally observed tunneling splitting patterns and spectral intensities were assigned to different rearrangement pathways between different extrema and categorized as ''feasible'' or ''not feasible'' by Wales and Walsh.[24–26] For the trimer two mechanisms are identified unambiguously by saddles of Hessian index one.[27,28] The most important one for the characterization of the spectra is the low-barrier ''flipping'' motion of a single hydrogen outside a hydrogen bridge. The barrier to this low-frequency (i.e., 87.1 cm^{-1})[29] out-of-plane bending motion was estimated to be <1 kcal/mol.[28,30] Vibrational excitations were assigned to three torsional motions by Klopper *et al.* both in experiments and calculations.[31–34] The motion with the second lowest barrier is the so-called ''double flip,'' which is effectively a rotation of a single water molecule in the cluster around its own C_2 axis.[35,36] It is also known as ''bifurcation'' (sometimes ''donor'') tunneling, as it involves a transition state (TS), in which one water molecule acts as a double acceptor and another one as double donor. This mechanism leads to the quartet fine structure of the far infrared (FIR) spectra.[29,35] Rigid body diffusion Monte Carlo (RBDMC) calculations with correlated sampling of energy differences between states of different symmetry yield splittings in $(H_2O)_3$ of 22 ± 3 cm^{-1} for the ''flipping'' and 0.017 ± 0.004 cm^{-1} for the ''bifurcation'' tunneling.[37,38] Other pathways like ''C_2 rotation+double flip'' or donor-acceptor exchange mechanisms also involve higher barrier motions. Hence the tunneling splittings linked to these motions reach or even fall short of the experimental threshhold of about 1 MHz (3×10^{-5} cm^{-1}).

This study focuses on the pathway suspected by Pugliano and Saykally[7] to be feasible in the water trimer, namely the concerted proton exchange, which connects ''clockwise'' and ''counterclockwise'' enantiomers via a single saddle. This one involves the breaking and rebuilding

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[a] Author to whom correspondence should be addressed.

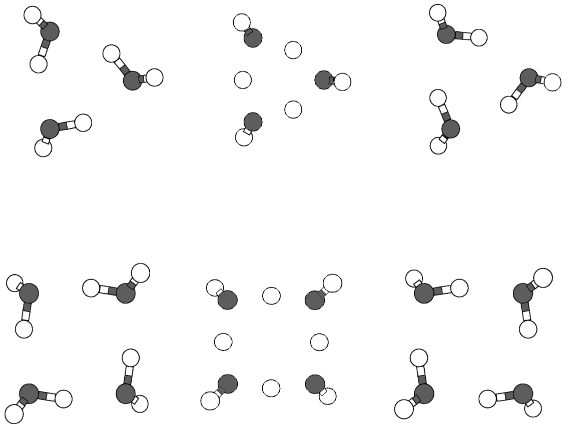

FIG. 1. Stationary points for the concerted exchange process of hydrogen atoms in cyclic oligomers of water calculated using B3LYP/6-31+$G(d)$. On the left and right side the minima are shown. The compacter transition structures can be found in the middle.

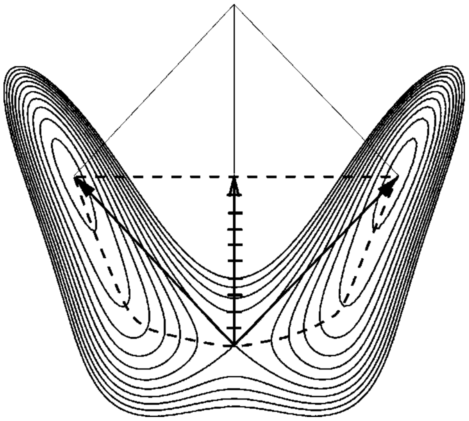

FIG. 2. Simplified, qualitative two-dimensional PES showing the vector from the transition state (in the middle) to the first minimum (top left), the transition state to the second minimum (top right), and the ''ridge vector'' of the reaction swath with ten points on it, where single-point energies were calculated. On the contour plot abscissa and ordinate represent symmetric OH stretching and OO stretching, respectively. The dashed line consists of two parts and is the frame for the swath. The lower part of the line corresponds to the intrinsic reaction coordinate (MEP). The upper part corresponds to the outermost straight LCG3 path.

of covalent bonds. All previously discussed motions only involve rotational motion of single water molecules, and hence no intermolecular hydrogen transfer (i.e., chemical reaction) occurs. Gregory *et al.*[37] concluded from their RB-DMC approach that this isomery is not feasible and that the permutation-inversion (PI) group for the water trimer is of order G_{48} and not G_{96}, i.e., it exists as two sets of 48 minima, which do not interconvert on a chemical timescale. Judging from FIR measurements, Pugliano and Saykally[7] concluded that these tunneling motions are occuring as indicated by the resolution of the quartet structure in the deuterated trimer.

In this work, rate constants and estimates for the ground-state tunneling splittings of the concerted neutral motion are presented using a dual-level *ab initio* hypersurface for both clusters, whose stationary points are depicted in Fig. 1. Rate constants obtained by a transition state theory (TST) treatment have been presented with the inclusion of small curvature tunneling effects (SCT)[12,39] both for the tri- and tetramer and large curvature tunneling (LCT) corrections relying on a rather unsatisfactory standard PM3 description for the trimer only.[12] In another study[40] we have used a specially parametrized PM3 hypersurface to obtain LCT reaction rate constants for the concerted hydrogen exchange reaction in isoelectronic cyclic oligomers of hydrogen fluoride. A reliable inclusion of LCT paths for water clusters is still missing in the literature and is therefore the main subject of the present work.

II. METHODS AND CALCULATIONS

A. Dynamics

Reaction rate constants k were obtained using the TST[41] equations implemented in POLYRATE7.2.[42] The exact theory and equations and further references are found in several reviews.[43–50] In particular, a canonical ensemble and a variational approach were used to obtain a rate constant k^{CVT} (CVT=canonical variational theory) minimized with respect to barrier recrossings (i.e., recrossings through hypersurface dividing reactants from products). The minimum energy path (MEP) was calculated as the steepest-descent path in mass-scaled coordinates starting from the optimized TS in both the reactant's and product's direction.[51–56] A scaling mass of $\mu=1$ amu was used throughout. Quantum effects on the reaction coordinate motion, i.e., nonclassical reflection and tunneling, were estimated from semiclassical[57–63] transition probabilities. Small curvature tunneling corrections (SCT) were included by means of the centrifugal dominant small curvature semiclassical adiabatic ground state method (CD-SCSAG), where the atoms are thought to follow the path of classical turning points on the concave side of the MEP, which is shorter than the MEP itself. The quantum state along this reaction coordinate is conserved (''adiabatic approximation'').[64] This kind of movement involves large-amplitude motions of all atoms and hence the associated reduced mass can reach values as high as the mass of oxygen atoms, which lowers the probability for tunneling drastically. Large curvature tunneling corrections (LCT) are included by means of the large curvature ground state approximation, version 3 (LCG3),[45,65] which assumes that the atoms take straight-line paths between points of equal kinetic energy on the MEP in the educt and product region. The correction for tunneling is evaluated by calculating a Maxwell–Boltzmann integral over all transition probabilities from one side of the potential to the other. These probabilities depend on the potential along the paths crossing the reaction swath (cf. Fig. 2) and are expressed by means of the imaginary action integral (θ-integral).[47] Direct corner cutting implies a change of the quantum state (''sudden approximation'')[66] and involves mainly motions of hydrogen atoms. Hence the reduced mass stays near 1 amu along the whole path, making tunneling a highly probable event. This approach is thought to be superior to the SCT approximation, if the reaction coordinate is highly bent as for the transfer of a light atom between two heavy ones. From the angle between the gradient at the minimum on the MEP and the ''imaginary'' mode of the TS one finds that the skew-angle is about 20° for the trimer and slightly more for the tetramer of water. For such small angles direct corner cutting paths provide a significant shortening of the distance compared to the MEP. It is evident that the incorporation of the ''sudden approximation'' (LCT tunneling) is necessary to describe the physical behavior of the systems unless the barrier is very much higher along the direct corner cutting path compared to the MEP. The barrier along the LCT paths can be extracted directly from the ridge of the reaction swath. To our knowledge there is no study available based on the ''sudden approximation'' and on an *ab initio* PES. It is further new in the literature that tunneling probabilities are directly related to special features of the potential hypersurface.

One can estimate the order of magnitude of the zero-point tunneling splitting Δ_0 from the data of a variational transition state theory (VTST) calculation. The equilibrium frequency of the reaction coordinate ω_0 and the ground state transmission probability P^Q at zero kinetic energy, i.e., ground state of the minima, can be utilized for this purpose:

$$\Delta_0=\left(\frac{\omega_0}{\pi}\right)\times\sqrt{P^Q}.$$

This zero-level tunneling splitting is related to the low-temperature limit of the tunneling correction. It is hence temperature independent and can be compared directly with molecular beam experiments, which involve measuring pure transitions between two well-defined quantum states. The zero-point splittings obtained in this manner are in good agreement with results obtained from instanton theory[67,68] for hydrogen transfer between oxygen atoms.[69] The zero-point as well as mode-specific splittings obtained from instanton theory are in excellent agreement with spectroscopic data for hydrogen and deuterium transfer in malonaldehyde, indoline, and tropolone.[70–72]

B. Ridge of the reaction swath

A sophisticated calculation of reaction dynamics critically depends on a reliable description of the PES in a wide region. At least the harmonic expansion of three stationary points and some points on the MEP from the TS to both minima should be described very well for a reliable inclusion of corner cutting effects for reactions with small curvature.[47,73] Newer approaches try to circumvent the explicit evaluation of the MEP.[74,75] The inclusion of direct corner cutting effects for ''largely curved'' reactions further relies on the description of the so-called reaction swath.[76] For the simplified picture of two normal-modes the reaction swath is within the area enclosed by the dashed line in Fig. 2.

The ridge of the reaction swath is the path connecting the TS and the position *exactly* between the two minima.[40] It lies completely within the hyperplane dividing educts from products. For the determination of the direction of the ridge of the reaction swath a geometrical description of both minima in the basis of the normal modes of the TS is useful (cf. Fig. 2). The result of this transformation is the displacement along each normal-mode direction (i.e., $3n-6$ coefficients) that is needed to reach one minimum starting from the TS. These rotation-free[77] coefficients are independent of the potential between the stationary points. The important normal modes for the description of the reaction path can be identified with the aid of the magnitude of these coefficients easily. By comparing the signs of corresponding coefficients (of same absolute magnitude) of both (symmetrically placed) minima one can distinguish whether movement along certain normal modes determines if the system will be trapped in the ''educt'' or the ''product'' minimum (opposite signs) or not (same signs). The coefficient corresponding to the normal mode with negative force constant (i.e., the ''imaginary'' frequency) always has opposite signs. It is, therefore, an indicator in which direction the reaction is proceeding. When following only the vibrations with same sign of coefficients one stays *exactly* in the middle. The potential there shows the barrier height for a certain orthonormal LCT path. Hence one can give a crude estimate of the transition probability from the ridge's height and shape and by comparing the ridge of different systems even for the overall LCT tunneling correction.

C. Dual-level hypersurfaces

The information for three stationary points for each system was obtained from a MP2/6-311++$G(3pd,3df)$ description of a previous work.[12] The description between these extrema is based on the much cheaper B3LYP/6-31+$G(d)$ method.[78] These data were smoothly fitted to the more expensive points depending on the distance from the stationary points according to the logarithm of ratios.[79] The moment of inertia determinant, the energy of the reaction, the energy barrier, and the frequencies were interpolated by different functional forms,[73,80–85] which ensure a correct weighting of the results in a manner that no steps and kinks are produced. In order to avoid artefacts it is important for all interpolation procedures that the information from the methods are comparable. The lower level [B3LYP/6-31+$G(d)$] used here is in surprisingly good agreement with the higher level results [MP2/6-311++$G(3pd,3df)$], as can be seen from Tables I and II. Especially the barrier height is nearly identical. Bond distances deviate only by about 0.02 Å and bond angles by about 1°. The imaginary frequencies are within an error of 0.5%, the total zero-point energy is 0.7% lower for the TS and 1.2% for the minima. Even directly used (i.e., not interpolated) properties such as the eigenvectors of the Hessian are reproduced very well. The PES generated in this way is referred to as MP2/6-311++$G(3pd,3df)$///B3LYP/6-31+$G(d)$ or shorthand MP2///B3LYP. Two synonyms for triple-slash (///) dynamics are variational transition state theory with interpolated corrections (VTST-IC) and dual-level direct dynamics (DLDD).[83,85,86] The use of *ab initio* lower levels was performed by using the program GAUSSRATE7.4.1,[87] which provides an interface between GAUSSIAN94[88] and POLYRATE7.2.[42]

III. TRIMER

A. Strategy

A full *ab initio* calculation of reaction dynamics is time consuming: a single Hessian calculation can take hours or

TABLE I. Water trimer. Energies in kcal/mol, frequencies in cm^{-1}, bond lengths in Å, and angles in degrees. H_b corresponds to a ‘‘bridged’’ and H_f to a ‘‘free’’ hydrogen atom.

	MP2/6-311++$G(3pd,3df)$		B3LYP/6-31+$G(d)$	
	Minimum	TS	Minimum	TS
Zero-point energy	46.16	42.08	45.91	41.57
Imaginary frequency	···	1832.7i	···	1841.8i
OO distance	2.791–2.798	2.312–2.370	2.767–2.776	2.386–2.387
H_bO distance	0.971–0.972	1.213–1.215	0.984–0.985	1.228
H_fO distance	0.958–0.959	0.960	0.968–0.969	0.970
Angle (H_bOO)	18.5–19.9	12.3–12.5	19.8–21.6	13.6–14.2
Angle (H_bOH_f)	105.2–105.4	111.6–112.6	106.5–106.8	112.0–113.3
Barrier	26.99		26.99	

more, and obtaining a converged reaction rate constant requires several Hessians, several gradients, and a large number of energy calculations. In order to reduce the number of *ab initio* calculations for the dynamics, we tested the convergency behavior of the reaction rate constants by a specially parametrized semiempirical hypersurface. (In contrast to a recently reported semiempirical hypersurface for hydrogen fluoride oligiomers,[40] the one for water oligomers did not fulfill all of our quality criteria for calculation of reaction rate constants and therefore will not be discussed in detail here.) As a starting point we used the stabilized Euler integration procedure to obtain the MEP with a first step in the direction of the normal mode having the negative force constant.[89,90] Using the much cheaper semiempirical method as a lower level, we performed a run with a very small step size of 5×10^{-4} Bohrs for the gradient grid. The path calculation was stopped when the potential reached the value of the minimum structure, which is referenced as the ‘‘zero of energy.’’ Harmonic vibrational frequencies were computed in steps of 0.01 Bohr for the Hessian grid along the whole reaction path and connected according to maximal overlap[12,91,92] of the corresponding normal modes. Frequencies that became ‘‘imaginary’’ along the path were interpolated directly with the IVTST-0[83] method to gain continuous vibrational adiabatic ground state potentials V_a^G.

The number of single-point energy, gradient, and Hessian calculations could be reduced in a series of tests to gradient grid spacings of 0.05 Bohr and of 0.15 Bohr for Hessian recalculations, i.e., one normal-mode analysis at each third gradient point, and comparable results for k^{CVT} and κ(SCT) were achieved. The minimization of the number of energy points (i.e., quadrature points) needed to converge κ(LCT) led to a reduction from originally 120 and 40 to 20 and 9 points, for the Boltzmann-and the θ-integral, respectively. The difference in κ(LCT) is less than 1% in these two cases. The uncertainty in these results mainly stems from the uncertainty in the barrier height at high temperatures (above 200 K) and the uncertainty in the tunneling correction at low temperatures (below 150 K), where the correction factors can become as large as 10^{50}. At higher temperatures the tunneling correction factors are found near one (i.e., no correction) and hardly contribute to the error. Our goal was to predict reaction rate constants down to 100 K. It was not necessary to calculate the whole reaction path to obtain converged rate constants. Choosing the path length by ensuring that all important tunneling paths are on the available grid was enough for this purpose. According to the knowledge gained from the specially parametrized semiempirical hypersurface we used the dual-level *ab initio* hypersurface and calculated 22 Hessian and 66 equally spaced gradient points up to a distance of 3.3 Bohrs away from the saddle point.

B. Discussion of results

The resulting potentials and frequencies are given in Figs. 3 and 4 and are in very good agreement with a previous study.[12] From the normal-mode basis transformation needed for the ridge of the reaction swath we found that mainly three vibrations are relevant for the proton transfer. These are the symmetric OO and OH stretchings and the rocking of the

TABLE II. Water tetramer. Energies in kcal/mol, frequencies in cm^{-1}, bond lengths in Å, and angles in degrees. H_b corresponds to a ‘‘bridged’’ and H_f to a ‘‘free’’ hydrogen atom.

	MP2/6−311++$G(3pd,3df)$		B3LYP/6−31+$G(d)$	
	Minimum	TS	Minimum	TS
Zero-point energy	62.72	56.35	62.25	55.87
Imaginary frequency	···	1674.9i	···	1672.8i
OO distance	2.731	2.396	2.735	2.419
H_bO distance	0.979	1.203	0.992	1.216
H_fO distance	0.958	0.959	0.969	0.970
Angle (H_bOO)	7.8	5.4	8.3	6.0
Angle (H_bOH_f)	105.3	110.7	106.4	110.7
Barrier	23.29		23.20	

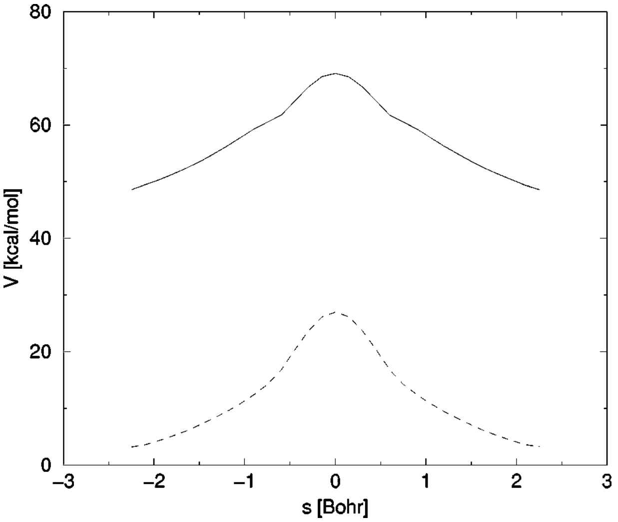

FIG. 3. Water trimer. Adiabatic ground-state potential (solid) and potential along the minimum energy path (dashed).

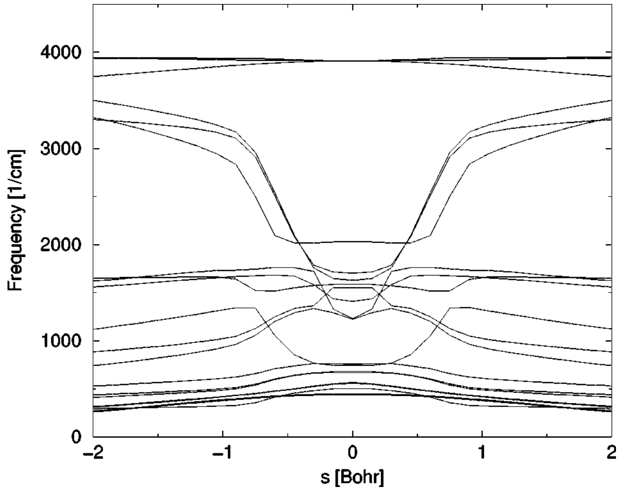

FIG. 4. Water trimer. Frequencies along the minimum energy path (MP2///B3LYP).

free hydrogens. At B3LYP/6-31$+G(d)$ their coefficients are 0.93, 0.80, and 0.69, respectively. All other coefficients are lower than 0.15, most of them near 0.00. They are very similar to a set of coefficients resulting from MP2/6-311$++G(3pd,3df)$ calculations (i.e., deviating less than ±0.03). These numbers, especially the one for the OO stretching, are a measure for the width of the barrier. Figure 5 shows the results for the rate constants and the potential on the ridge of the reaction swath. Our calculated reaction rate constant is in disagreement with the one calculated by Garrett and Melius.[39] They found a reaction rate constant $k(\mathrm{SCT},300\ \mathrm{K})\approx 10^{-14}\ \mathrm{s}^{-1}$. Although their barrier obtained with BAC-MP4 (29.1 kcal/mol) is only slightly higher, their rate constants are lower by more than ten orders of magnitude. Our CVT rate constant without tunneling corrections is already as high as $k^{\mathrm{CVT}}=4.5\times 10^{-6}\ \mathrm{s}^{-1}$ at 300 K. The potential on the ridge is of harmonic shape, which is a hint that deviations from straight paths do not lead to a considerable increase in rate constants, as a reduction in the barrier height is necessarily accompanied by a longer tunneling distance. We assume that a time consuming search for the path with the least action lying between the LCG3 and CD-SCSAG path[52,93] is not necessary because there are no obvious paths considerably lower in action than the LCG3 path. This is in agreement with conclusions of Guo *et al.* in a recent study.[94] If the ridge was steep and anharmonic, the system would presumably prefer a longer path rather than the straight LCG3 path because the action is considerably reduced due to the much lower potential difference.

The ridge finally reaches a total height of 43.1 kcal/mol. Compared to the similarily shaped potential for the trimer of hydrogen fluoride,[40] this point is higher by 30%. The energy gap to the minimum for the exchange in $(H_2O)_3$ is higher by 44% than in $(HF)_3$. This indicates that the overall shape of the PES is very similar for both systems with the exception of a scaling factor linearily dependent on the distance to the TS. The same scaling factors can be used for movement along the MEP and along the ridge. Hence the differences between SCT and LCT results should be similar in both sys-

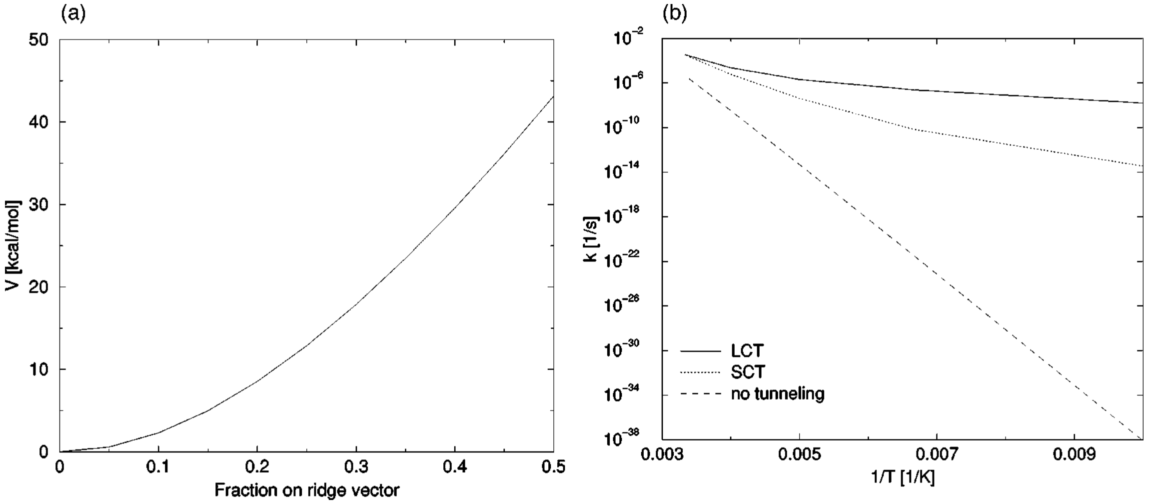

FIG. 5. Water trimer. Ridge of the reaction swath (a) and reaction rate constants for dual-level *ab initio* (MP2///B3LYP) dynamics without tunneling correction (pure CVT), in the small (SCT), and large (LCT) curvature limit (b).

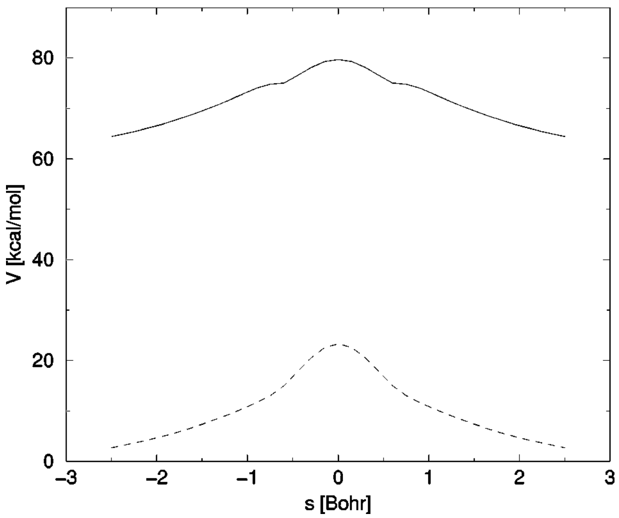

FIG. 6. Water tetramer. Adiabatic ground-state potential (solid) and potential along the minimum energy path (dashed).

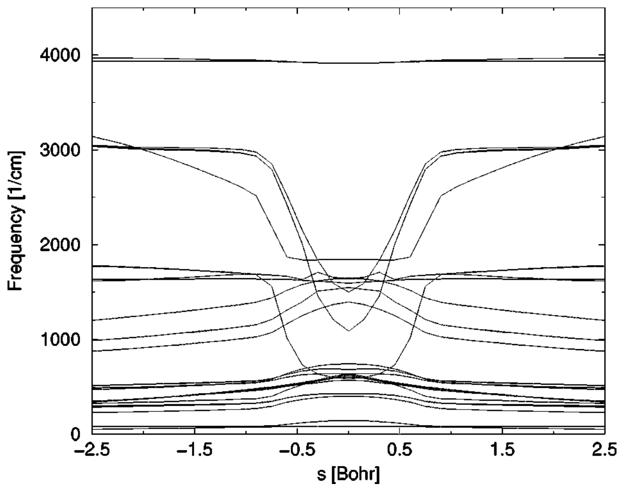

FIG. 7. Water tetramer. Frequencies along the minimum energy path (MP2///B3LYP).

tems. At 100 K one actually finds that the LCT rate constant is higher by five orders of magnitude than the SCT constant for both $(HF)_3$ and $(H_2O)_3$. At about 250 K the LCT and SCT constants approach each other for both systems. The energy of the most probable LCT path at 300 K is 56 kcal/mol, which is midway between the bottom and the top of V_a^G, and shows that the major part of the reaction takes place by tunneling.

The larger tunneling splitting $\Delta_0(\mathrm{LCT})=1.9\times10^{-5}$ cm^{-1} compared to $\Delta_0(\mathrm{SCT})=8.2\times10^{-8}\mathrm{cm}^{-1}$ demonstrates clearly that the main tunneling mechanism for the transfer is in the sudden limit.

IV. TETRAMER

A. Strategy

In contrast to the trimer the run with the Euler integrator was problematic for obtaining the tetramer's concerted hydrogen exchange MEP. In the region where the potential on the intrinsic reaction coordinate flattens out, the frequencies start to oscillate around their equilibrium value, which is a well-known problem of the Euler algorithm.[95] Instead of changing the parameters for the stabilization step, we decided to use the Page–McIver integrator[95] which uses the local quadratic approximation instead of the local linear one, i.e., the eigenvectors of the Hessian are directly used to calculate the MEP. In a similar analysis to the one with the cyclic trimer at the semiempirical level we found out that the same strategy (with the exception of the different integrator) can be applied to the tetramer. It is likely that even slightly larger step sizes can be used to obtain similar results.

B. Discussion of results

Potentials and frequencies for this run are depicted in Figs. 6 and 7. There is again a high consistency with a previous study.[12] Even the slight bend in V_a^G arising from the strong increase in the OH-stretching normal modes can be found at the same position. The normal-mode basis transfor-

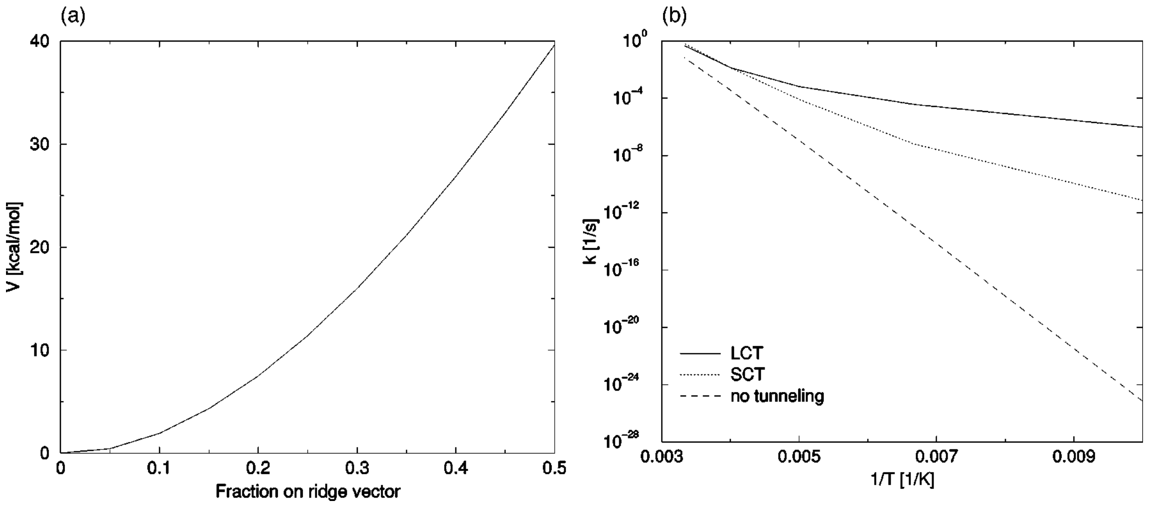

FIG. 8. Water tetramer. Ridge of the reaction swath (a) and reaction rate constants for dual-level *ab initio* (MP2///B3LYP) dynamics without tunneling correction (pure CVT), in the small (SCT) and large (LCT) curvature limit (b).

mation yields 7 nonzero and 23 zero coefficients for the vibrations. The three most important frequencies are again the OO stretching, the ''imaginary'' OH stretching, and the rocking of the free hydrogens. Their coefficients are 1.05, 0.79, and 0.46, respectively, at B3LYP level of theory. These numbers are similar to the trimer's coefficients and hence the barrier width is similar for both systems. Compared to the ridge of the reaction swath of $(HF)_4$ for the analogous reaction the final point is higher by 80%. The classical barrier height is only higher by 80%, too, although the distance from the TS to the minimum is much larger than to the final point on the ridge. This shows that a higher scaling factor is appropriate for a movement on the ridge than for a movement on the MEP. That is, the ridge for the tetrameric water cluster is steeper and the corresponding increase in rate constants in going from SCT to LCT should be lower for $(H_2O)_4$ than for $(HF)_4$. Indeed, at 300 K the increase is more than an order of magnitude for $(HF)_4$, but no increase can be found for $(H_2O)_4$. The calculated zero-point tunneling splittings are $\Delta_0(\mathrm{LCT})=1.9\times10^{-4}\ \mathrm{cm}^{-1}$ and $\Delta_0(\mathrm{SCT})=2.2\times10^{-7}\ \mathrm{cm}^{-1}$. Compared to the trimer these splittings are an order of magnitude larger. Considering the lower barrier for the tetramer at a similar width this is no surprise. The value of $\Delta_0(\mathrm{LCT})$ is near to the experimental resolution limit but larger than tunneling splittings measured for deuterated water clusters.[8] The main mechanism can be explained again by large curvature tunneling, as can be seen from the higher corrections to $k(\mathrm{CVT})$ at low temperatures. Figure 8 shows that the exchange takes place about once per second at 300 K.

V. CONCLUSIONS

This study provides rate constants and estimates of the ground-state tunneling splittings of the concerted exchange reaction in the cyclic tri- and tetramer of water. It is the first time that the ''sudden approximation'' (LCG3) is used to obtain tunneling correction factors to the canonical variational transition state theory rate constants for a pure *ab initio* (dual-level) hypersurface. Below room temperature the rate constants in this approximation are considerably higher than in the ''adiabatic approximation'' (CD-SCSAG) throughout. Our estimated tunneling splittings of about $10^{-4}-10^{-5}\ \mathrm{cm}^{-1}$ indicate that the splittings could be resolvable by FIR spectroscopy for these systems. We find rate constants $k(300\ \mathrm{K,LCT})=3.4\times10^{-4}\ \mathrm{s}^{-1}$ and $k(300\ \mathrm{K,LCT})=0.44\ \mathrm{s}^{-1}$ and tunneling correction factors $\kappa(100\ \mathrm{K,LCT})=2.0\times10^{30}$ and $\kappa(100\ \mathrm{K,LCT})=1.3\times10^{19}$ for tri- and tetramer, respectively. On the basis of this investigation we tend to the opinion that the concerted clockwise–counterclockwise isomery is feasible by direct corner cutting tunneling in small cyclic water clusters. It can be conjectured about a possible relevance of this kind of motion for hydrogen transfer in condensed systems of water.

ACKNOWLEDGMENT

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