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Symmetry and Tunneling in Proton Transfer Reactions. Proton Exchange between Methyloxonium Ion and Methyl Alcohol, Methyl Alcohol and Methoxide Ion, Hydronium Ion and Water, and Water and Hydroxyl Ion

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Abstract: A method previously developed to describe the motion of the proton in a double minimum potential is extended to tunneling times in various symmetric and asymmetric profiles. In asymmetric cases tunneling through the barrier is found only when the energy difference between the ground state of the proton and the top of the barrier ($E - V_0$) is less than the indeterminacy expected from the Heisenberg principle, indicating that the nonclassical behavior of the proton is due to the impossibility of determining whether the energy level is above or below the barrier. In the case of symmetric profiles with finite barriers and interminimal distances, proton tunneling will always occur. A theoretical expression is derived for the transmission coefficient g, which leads to values of g much larger than the values predicted by the WKB method. The possibility of tunneling in the proton exchange between methyloxonium ion and methyl alcohol, methyl alcohol and methoxide ion, hydronium ion and water, and water and hydroxyl ion is investigated by ab initio calculations on the proton transfer in the above systems. At experimental distances and for conformations with a symmetric profile, tunneling frequencies are found to be of the order of 10^{12} to 10^{13} s^{-1} for the four systems considered. These tunneling frequencies are consistent with the experimental values for ice but they are much larger than the experimental values of the other systems. The discrepancy is ascribed to small perturbations which destroy the symmetry of the profile. The rotation of relevant groups is used as an example of this effect. The rate of exchange of the proton between the two wells is determined by the frequency with which the profile attains symmetry.

Introduction

In a previous publication[1] a method was proposed to describe the motion of the proton in a double minimum potential. The potential was represented as the sum of a parabola and a Gaussian. The symmetry of the potential depended on the coincidence of the minimum of the parabola and the maximum of the Gaussian. The eigenstates of the system in this potential were calculated by the variational method using as a basis set the eigenfunctions of the harmonic oscillator centered in the minimum of the parabola. At time $t = 0$, the proton is confined to one of the wells. The state function of the proton $\Psi(x, t)$ at time t is calculated by means of

$$\Psi(x, t) = \int G(x, \xi, t, t_0)\, \Psi_0(\xi, t_0)\, d\xi \qquad (1)$$

where $\Psi_0(x, t)$ is the wave function representing the initial state and $G(x, \xi, t, t_0)$ is the propagation kernel given by

$$G(x, \xi, t, t_0) = \sum \Phi_k^*(\xi)\, \Phi_k(x) \exp\left(-\frac{i}{n} E_k(t - t_0)\right) \qquad (2)$$

$\Phi_k(x)$ and E_k are the stationary eigenfunctions and eigenvalues of the double minimum potential. Substitution of eq 2 into eq 1 gives

$$\Psi(x, t) = \sum \Phi_k(x) \exp\left(-\frac{i}{n} E_k(t - t_0)\right) \times \int \Phi_k^*(\xi)\, \Psi_0(\xi, t_0)\, d\xi \qquad (3)$$

The integral in eq 3 represents the coefficients C_k of the expansion of the wave function of the initial state in terms of the stationary states. These coefficients depend on the particular choice of initial state. Once this has been selected, the energy and the expectation value of the proton's position as a function of time are totally determined. The expectation value of the energy is

$$\langle E \rangle = \sum_k C_k^* C_k E_k$$

which is, as expected, time independent. The expectation value

Table I. Logarithms of Tunneling Time τ and Transmission Coefficient $g = \tau^{-1}\nu_0^{-1}$ in Terms of the Difference between the Energies of the Ground State and the Top of the Barrier $(E - V_0)$, the Interminimal Distance D and the Distance between the Inner Turning Points, δx[a]

	E, kcal/mol	D, au	$E - V_0$, au × 10^3	δx, au	$\delta x(E - V_0)^{1/2}$, au	$\ln(\tau)$	$-\ln(\tau\nu_0)$	$\ln(\tau\nu_0)/\delta x(E - V_0)^{1/2}$	$\ln\tau$ WKB	δE × 10^3
1	1	0.7			0.001 95	−30.6969	0.5956	−305.53		5.7
2	2	0.7			0.010 51	−30.6458	1.1085	−105.45		7.0
3	5	0.7	2.4868	0.281	0.013 97	−30.5926	1.3188	−94.39	−30.58	7.8
4	5	0.9	3.386	0.426	0.024 82	−29.7907	1.9260	−77.61	−29.36	3.2
5	10	0.7	6.930	0.341	0.028 43	−30.2419	2.1619	−76.04	−29.70	7.5
6	6	0.9	4.393	0.445	0.029 48	−29.6606	2.1892	−74.25	−29.04	3.2
7	7	0.9	5.415	0.460	0.033 85	−29.5289	2.4278	−71.73	−28.74	3.1
8	8	0.9	6.457	0.473	0.037 97	−29.3988	2.6472	−69.72	−28.43	3
9	9	0.9	7.552	0.484	0.042 06	−29.2646	2.8596	−68.00	−28.12	3
10	10	0.9	8.676	0.494	0.046 03	−29.1306	3.0620	−66.52	−27.81	3.1
11	5	1.3	4.929	0.763	0.053 54	−27.9608	3.3587	−62.74	−26.23	0.5
12	30	0.7	29.670	0.426	0.073 44	−28.6930	4.4106	−60.06	−26.11	7.7
13	10	1.3	11.392	0.850	0.097 69	−26.6380	5.0836	−52.04	−23.08	0.6
14	20	1.3	25.300	0.929	0.147 84	−24.5052	7.5860	−51.31	−18.03	0.6
15	44	0.9	55.805	0.647	0.152 79	−25.0567	7.8107	−51.12	−18.33	1.4
16	59	0.9	76.890	0.667	0.184 91	−23.8236	9.1930	−49.72	−15.42	1.4
17	30	1.3	39.740	0.970	0.193 42	−22.7572	9.5445	−49.34	−13.90	0.6

[a] WKB values are included for comparison (last column).

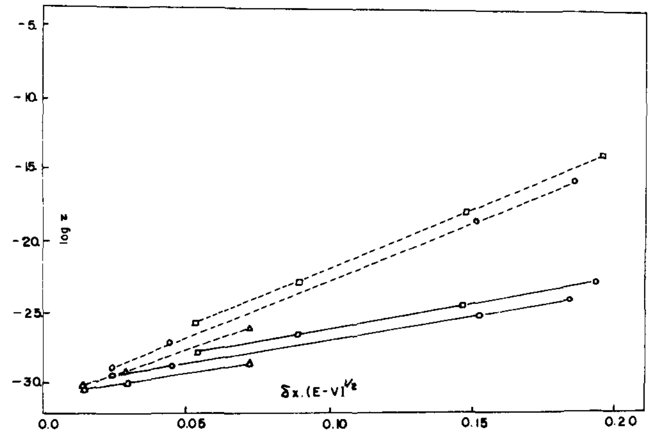

Figure 1. Plot of the logarithm of the tunneling time vs. $\delta x(E - V)^{1/2}$.

of the proton's position is given by

$$\langle x\rangle = \sum_k C_k{}^2\langle\Phi_k|x|\Phi_k\rangle + 2\sum_k\sum_{l<k} C_k{}^*C_l\langle\Phi_k|x|\Phi_l\rangle\cos\omega_{kl}t \quad (4)$$

The time dependent part of the expectation value of the proton's position is contained in the double sum of eq 4. This double sum will vanish if all the coefficients C_k except one are zero. This occurs when the initial state chosen is one of the eigenstates of the Hamiltonian. While the eigenstates are uniquely determined, the initial state is arbitrary and the proper selection should be consistent with the manner in which the system is to be studied. This is particularly important when an attempt is made to correlate quantum mechanical concepts with molecular mechanisms proposed by chemists. In a proton transfer reaction the proton is thought to be bound initially to a proton donor from where it moves toward the proton acceptor. This suggests that the wave function chosen to represent the initial state of the proton should be confined to the well representing the donor.

If the profile that represents the proton transfer is symmetric, the two wells will be indistinguishable and the eigenfunctions will extend over both wells, reflecting the symmetry of the Hamiltonian. The choice of any initial state confining the proton to one of the symmetrical wells will result in the oscillation of the expectation value of the proton's position between the two wells with the proton leaking through the classically forbidden barrier. This tunneling will occur for all finite barriers and finite interminimal distances.

When the profile is asymmetric, each of the eigenstates of the double minimum will be confined to one well except for energy levels near the top of the barrier for which the eigenfunction will extend beyond the barrier into the other well. Farther below the top of the barrier, it is possible to choose an initial state, confined to one well, which is so close to one of the eigenstates that one coefficient approximately equals unity while a few others may be very small; the expectation value of the proton's position will then remain within the well where it was placed initially. Leaking to the other well is expected only if the energy level is close to the top of the barrier.

The above considerations seem to indicate that the process of proton tunneling in symmetric and asymmetric double minimum potentials may be due to different principles.

Symmetric Potentials

The expectation value of the proton's position as a function of time was calculated by the method proposed before[1] for symmetric double minimum potentials with various barriers E and interminimal distances D. From these calculations, tunneling times were found and the results compared with those obtained from the difference between the gerade and ungerade energy level pair. Both methods gave the same result. Tunneling times were also calculated by using the formula

$$\tau^{-1} = \nu_0 g = \nu_0\exp(-95.141\delta x(E - V_0)^{1/2}) \quad (5)$$

suggested by Löwdin[2] and obtained by using the WKB method. τ is the tunneling time, ν_0 the frequency the proton would have if it were confined to the isolated initial well, g the transmission coefficient, δx the distance in atomic units between the two inner turning points, and $(E - V_0)$ the difference in atomic units between the energy level V_0 and the top of the barrier. The results of the calculations are presented in Table I.

The plot of the logarithm of the tunneling time vs. $\delta x(E - V_0)^{1/2}$ is presented in Figure 1. The graph gives the linear plot expected for results obtained from eq 5. Each straight line corresponds to a different intercept because it has a different value of ν_0. To reduce all the results of eq 5 to a single plot, the

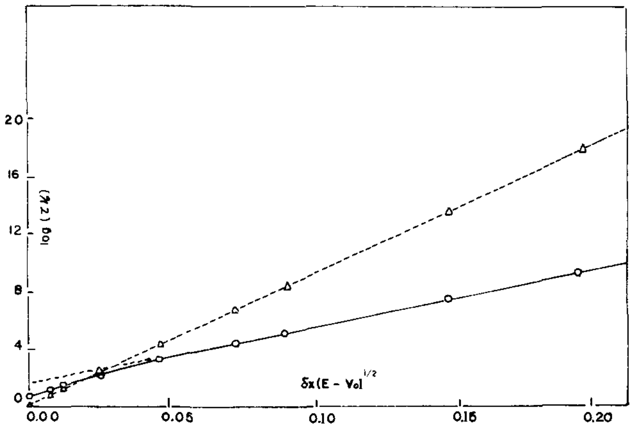

Figure 2. Plot of the logarithm of $\tau\nu_0$ vs. $\delta x(E - V_0)^{1/2}$.

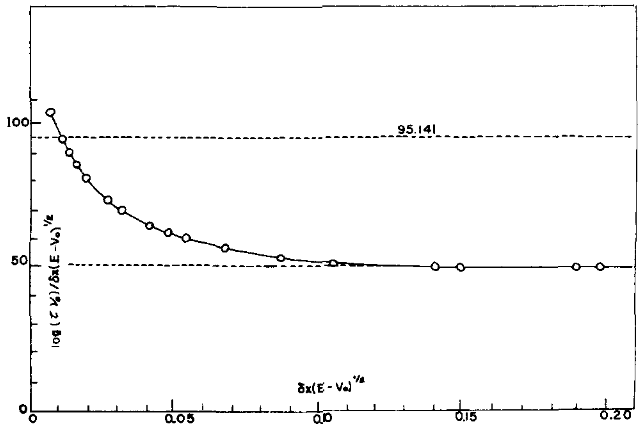

Figure 3. Plot of the ratio of the logarithm of $(\tau\nu_0)$ vs. $\delta x(E - V_0)^{1/2}$.

logarithm of $\tau\nu_0$ is plotted vs. $\delta x(E - V_0)^{1/2}$. This plot produces a straight line passing through the origin with a slope of 95.141 for results obtained with eq 5. With the present method, the results also are reduced to a single plot but they do not produce a straight line; however, for large values of the abscissa, the plot is linear but the slope is 50.0, not 95.141 (Figure 3). It should be noticed that $(\tau\nu_0)^{-1}$ is g, the transmission coefficient. In the case of a proton in a double minimum potential this coefficient could be defined as the ratio between the frequency of oscillation of the proton between the two wells and the frequency the proton would have if it were confined to the initial isolated well. Figure 2 shows that both methods give transmission coefficients of the same order of magnitude for small values of $E - V_0$ which correspond to energy levels close to the top of the barrier; however, for large values of the abscissa, the transmission coefficients are larger, by several orders of magnitude, than those obtained using the semiclassical WKB method.

Asymmetric Case

A similar study was carried out for double minimum potentials with the asymmetry increasing by variation of the parameter ϵ_0 in the equation

$$V = V_0 + a_2x^2 + \nu_0 \exp(-\alpha(x - \epsilon_0)^2) \qquad (6)$$

from zero in the symmetric case until the asymmetry was such that the proton failed to emerge in the second well. For small values of H, the energy difference between the minima, the value of ϵ_0s is given by

$$\epsilon_0 = H/2a_2D$$

The method of calculating tunneling times from the gerade–ungerade doublet cannot be used here as the gerade–ungerade doublet ceases to exist. The expectation value of the proton's position as a function of time however may be used for finding the frequency with which and the distance to which it penetrates into the second well. Actually it is more convenient to calculate the fraction of time the expectation value of the proton's position is in the second well and this gives a criterion for the extent to which tunneling occurs.

Calculations were performed with various values of the barrier E. For each value of E, ϵ_0 was varied from zero until the proton failed to emerge in the second well. Such results are reported in Table II.

It is clear that for small energy barriers, of the order of 5 kcal/mol or less, where the value of $E - V_0$ is small, the proton emerges in the second well even though the double minimum potential is not nearly symmetric; however, at larger values of E the proton failed to emerge into the second well even for small values of H. The fact that once again the behavior of the system changes as one goes from small values of $(E - V_0)$ to larger values suggests that the very smallness of $(E - V_0)$ must be taken into account for any explanation of tunneling, be the double minimum potential symmetric or asymmetric.

Table II. Values of the Ground State Energy, V_0, Energy Difference between the Ground State and the Top of the Barrier $(E - V_0)$, Energy Difference between the Two Minima, H, Together with the Values of δE, the Energy Indeterminacy and the Extent of Tunneling as Reflected by the Fraction of Time the Proton is in the Second Well

	E, kcal/mol	E, au × 10^3	V_0, au 10^3	$E - V_0$, au × 10^3	H, au × 10^3	δE × 10^3	Time in second well, %
1	4.90	7.82	5.75	2.07	0.18	2.1	0.364
2	4.73	7.55	5.54	2.01	0.73	2.2	0.290
3	4.68	7.46	5.48	1.98	0.90	2.2	0.206
4	4.62	7.37	5.43	1.94	1.09	2.3	0.134
5	5.02	8.00	4.61	3.39	−0.18	3.0	0.314
6	5.18	8.27	4.82	3.45	−0.72	2.8	0.208
7	5.25	8.37	4.87	3.50	−0.91	2.7	0.066
8	5.40	8.63	4.90	3.73	−1.27	2.6	0.000
9	7.57	12.08	6.14	5.94	−0.27	3.0	0.270
10	7.75	12.36	6.31	6.05	−0.82	2.8	0.000
11	7.93	12.64	6.42	6.22	−1.37	2.7	0.000
12	9.88	15.76	7.80	7.96	0.37	2.7	0.142
13	9.79	15.58	7.71	7.87	0.73	2.8	0.000
14	10.11	16.12	7.42	8.70	−0.37	3.0	0.144
15	10.12	16.14	7.43	8.71	−0.37	3.0	0.138
16	10.23	16.32	7.51	8.81	−0.73	3.0	0.000

In order to determine if nonclassical behavior can occur one needs to know (a) how close can the energy level be to the top of the barrier before it is uncertain whether it is above or below; (b) how large must the difference between the wells be before it is certain that the system is asymmetric. To be significant, these energy differences should be larger than the energy indeterminacies given by the Heisenberg principle.

The energy indeterminacy can be calculated by means of the expression

$$\delta\epsilon = \{\langle\Psi|\mathcal{H}^2|\Psi\rangle - \langle\Psi|\mathcal{H}|\Psi\rangle^2\}^{1/2} \tag{7}$$

In terms of the eigenvalues E_k and the coefficients of expansion C_k of the initial state eq 7 becomes:

$$\delta\epsilon = \left\{\sum_k C_k{}^*C_kE_k{}^2 - \left(\sum_l C_l{}^*C_lE_l\right)^2\right\}^{1/2}$$

which after some manipulation gives

$$\delta\epsilon = \left\{\sum_k \sum_{l<k} C_k{}^2C_l{}^2(E_k - E_l)^2\right\}^{1/2} \tag{8}$$

If the initial state is one of the stationary states, only one of the C_k will be different from zero and $\delta\epsilon = 0$. This means that the precise determination of the energy depends on the possibility of selecting the initial state as one of the stationary states. Such selection is possible for states localized in one of the wells, e.g., in asymmetric cases for states far below the top of the barrier. In symmetric cases such selection is impossible.

In cases where the initial state could be represented by the contribution of only two of the stationary states eq 8 becomes

$$\delta\epsilon = C_1C_2(E_2 - E_1)$$

or

$$\delta\epsilon = (1/2)\sin 2\theta(E_2 - E_1) \tag{9}$$

where $\theta = \arctan(C_1/C_2)$. It follows from eq 9 that $\delta\epsilon$ will have a maximum when $\theta = \pi/4$, which corresponds to the symmetric case. The energy difference $E_2 - E_1$ will correspond to the difference between the gerade-ungerade pair. One sees from eq 9 that the energy indeterminacy is always less than $(E_u - E_g)$ so that when the whole pair is below the top of the barrier, the energy of the initial state can significantly be placed below the barrier.

In cases where the initial state requires a large contribution from several of the eigenstates of the double minimum, eq 9 must be applied.

For symmetric cases the values of δE are given in the last column of Table I. The results show that tunneling occurs even when the indeterminacy $\delta\epsilon$ is much smaller than $E - V_0$.

For asymmetric cases the value of the energy indeterminacy is presented in the sixth column in Table II. For the first four runs, where the value of $E - V_0$ is less than the indeterminacy of the energy, the proton always emerges in the second well, but the extent of tunneling decreases as the value of H increases. In runs 5 to 8, where the value of $E - V_0$ is slightly larger than the indeterminacy of the energy, the proton fails to tunnel when H is larger than 1×10^{-3} au. In runs 9 to 16, where the value of $E - V_0$ is significantly larger than the indeterminacy of the energy, a value of H equal to or larger than 0.7×10^{-3} au suppresses tunneling. The above results show that proton tunneling in symmetric and asymmetric double minimum potentials has a different explanation. In asymmetric cases of profiles with energy barriers of less than 5 kcal/mol tunneling is a direct consequence of the Heisenberg principle. In symmetric cases tunneling is found to exist always except when the barrier or interminimal distance is infinite; it is due to the fact that the wells are indistinguishable.

In nearly symmetric cases with barriers greater than 5 kcal/mol, tunneling will occur only if the energy difference, H, is very small; under those conditions the system cannot be described with certainty as asymmetric.

This effect may be particularly important in symmetric proton transfer profiles with energy barriers larger than 5 kcal/mol, as a very small change in either the donor or the acceptor may destroy the symmetry of the profile and the indistinguishability of the two wells.

This destruction of symmetry, by a very small perturbation, which suppresses tunneling may be observed in the proton exchange between the hydronium ion and water, between methanol and the methoxide ion, and between the methyloxonium ion and methanol.

In the case of the hydronium ion and water the symmetry may be altered by changing the orientation of the donor or acceptor with regard to the neighboring water molecules to which they are hydrogen bonded. In the case of the exchange in the methyl alcohol species this effect may be caused, among other possibilities, by rotation of a methyl group.

The kinetic aspects of these exchanges have been studied experimentally[3] by determining the broadening or collapsing of the spin-spin coupling of the hydroxyl proton with the hydrogens in the methyl group. The rate constants have been found to be $8.8 \times 10^{10}\ \mathrm{s}^{-1}$ for the proton exchange between the methyloxonium ion and methanol and $1.85 \times 10^{10}\ \mathrm{s}^{-1}$ for the exchange between methanol and the methoxide ion. The proton exchange between a hydronium ion and a water molecule and a hydroxyl ion was studied by Eigen and De Maeyer.[4]

If the proton transfer is the rate-determining step, these fast rates of exchange suggest that either the energy barrier is very small or quantum mechanical tunneling occurs.

The first step to clarify the mechanism of proton transfer in these systems should be the determination of the potential energy profile for the proton as it moves from the donor site to the acceptor site. Except for the transferring proton, the positions of all the atoms are fixed for all of the profiles. For each position of the intervening proton, ab initio calculations were made to determine the energy of the electronic Hamiltonian. This energy as a function of the proton's position gives the desired profile. The form of this profile will depend on the separation and relative orientation of the donor and the acceptor. For small distances, the function will have a single minimum. As the distance increases, the second derivative at the minimum decreases until it becomes zero. Further increase of the distance between the donor and the acceptor will produce a double minimum potential.

The profiles studied in this work correspond to systems for which the experimental value of the proton exchange is known. These systems are the following: hydronium ion-water (I); water-hydroxyl ion (II); methyl alcohol-methoxide ion (III); methyloxonium ion-methyl alcohol (IV); and the proton exchange between two hydrogen bonded water dimers (V).

$$\mathrm{H_3O^+ + H_2O \rightarrow H_2O + H_3O^+} \tag{I}$$

$$\mathrm{H_2O + OH^- \rightarrow OH^- + H_2O} \tag{II}$$

$$\mathrm{CH_3OH + OCH_3{}^- \rightarrow CH_3O^- + HOCH_3} \tag{III}$$

$$\mathrm{CH_3OH_2{}^+ + HOCH_3 \rightarrow CH_3OH + H_2OCH_3{}^+} \tag{IV}$$

$$\mathrm{H_2O \cdot OH_3{}^+ + H_2O \cdot H_2O \rightarrow H_2O \cdot H_2O + H_3O \cdot H_2O^+} \tag{V}$$

At interoxygen distances for which the above systems do not possess a double minimum, and when the energy barrier for the double minimum potential is below or close to the first vibrational energy level of the proton, the rate of exchange is expected to be fast, of the order of near-infrared frequencies; however, if the barrier is definitely above the first vibrational

Table III. Results of ab-Initio Calculations for $(H_2O\text{-}H\text{-}OH_2)^+$ Ions[a]

2.90		2.80		2.76	
A	B	A	B	A	B
0.0000	0.033 774	0.0000	0.023 241	0.0000	0.019 351
0.1000	0.031 703	0.1000	0.021 332	0.0500	0.018 884
0.2000	0.027 040	0.2000	0.016 355	0.1000	0.017 533
0.3000	0.018 605	0.3000	0.010 757	0.1500	0.015 457
0.4000	0.013 016	0.3500	0.009 110	0.2000	0.012 927
0.4286	*0.012 567*	*0.3681*	*0.008 928*	0.2500	0.010 349
0.4500	0.012 783	0.4000	0.009 372	0.3000	0.008 289
0.5000	0.015 773			*0.3415*	*0.007 514*
				0.3500	0.007 515
				0.4000	

2.70		2.50		2.4198	
A	B	A	B	A	B
0.0000	0.0139 57	0.0000	0.001 503	0.0000	0.000 000
0.1000	0.0123 12	0.1000	0.000 879	0.0349	−0.000 012
0.2000	0.0083 93	0.1500	0.000 526	*0.0599*	*−0.000 021*
0.2500	0.0065 04	*0.1510*	*0.000 524*	0.0849	0.000 008
0.3000	0.0054 96	0.2000	0.000 851	0.1099	0.000 125
0.3030	*0.0054 82*	0.3000	0.007 379	0.1599	0.000 930
0.4000	0.0101 02				

2.40		2.30	
A	B	A	B
0.0000	0.000 048	0.0000	0.003 412
0.0500	0.000 076	0.0500	0.003 747
		0.1000	0.004 951
		0.1500	0.007 642
		0.2000	0.012 891

[a] All energies are referred to E_0, the energy of the configuration at the saddle point, with the hydrogen at the center of the 2.4198-Å long O-O bond; $E_0 = -152.152\,877$ au. For each O-O distance the value of the hydrogen position with minimum energy is italicized. The number at the head of each set is the oxygen-oxygen distance in Å. Columns A are distances of H to the center of the O-O bond in Å. Columns B are the energies in atomic units.

energy level, only tunneling can account for the observed rate of exchange.

Method of Computation of the Electronic Energy

The ab initio molecular orbital method was used to calculate the energy for the various geometries and the various positions of the intervening proton, using contracted Gaussian type orbitals as basis set. The program developed by Hehre and Pople[6] was initially used to obtain the main features of the different potential energy surfaces and profiles. However, it was found, in agreement with Newton and Ehrenson,[8] who performed calculations on similar systems, that the minimal basis set with three Gaussians gave profiles with energy barriers lower than needed to predict tunneling times in agreement with experiment. To obtain more reliable profiles an extended basis set introduced by Ditchfield, Hehre, and Pople[7,8] was used. This basis set, known as the 4-31G set, consists of two functions for each valence orbital: three contracted Gaussians represent the inner function while a single Gaussian represents the outer function. The inner shell orbital is given by a contraction of four Gaussians. To represent the molecular environment better, the exponents obtained from the free atoms are multiplied by the following scale factors: 1.0 for the inner orbitals of carbon and oxygen, 0.99 and 0.98 for the two 2sp orbitals in oxygen, 1.0 and 1.04 for the 2sp orbitals in carbon, and 1.20 and 1.15 for the orbitals in hydrogen.

Calculated Energy Profiles

The first profile studied corresponds to the proton exchange between two water molecules ($H_5O_2^+$). The energies for various geometries at different interoxygen distances have been reported by several authors.[7,9,11] The bond angles used here are the bond angles found in ice. The proton is moved from the donor to the acceptor along the line connecting the two oxygen atoms which makes an angle of 109.47° with all the other OH bonds. This geometry is shown in Figure 4A. Table III gives the energy as a function of the distance of the proton from the center of the O–O distance at several interoxygen positions. The minimum energy of the hydrated ion $H_5O_2^+$ occurs at an interoxygen distance of 2.4198 Å with the proton at a distance of ±0.060 Å from the center. This indicates that the potential energy surface for this transfer has a saddle point; however, the energy barrier is too small to be significant. At the interoxygen distance of 2.76 Å, which corresponds to the experimental distance in ice, the barrier is 0.01184 atomic units and the interminimal distance is 0.6830 Å. The barrier and the interminimal distance increase rapidly as the interoxygen distance is increased. Rotation of one of the water molecules around the O–H–O line will not alter the symmetry of the profile although it will increase the value of the barrier. According to the results obtained previously,[1,5] the proton will oscillate between the two wells of the double minimum potential with frequencies that will depend on the interminimal distance and the energy barrier. At an interoxygen distance of 2.76 Å the rate of exchange will be 1.4 × 10^{12} s^{-1} while at 2.90 Å this rate will be 0.4 × 10^{12} s^{-1}. The former rate agrees with the rate of proton exchange in ice; however, it is two orders of magnitude larger than in liquid water.

Table IV. Results of ab-Initio Calculations for $(HO-H-OH)^-$ Ions[a]

2.90		2.80		2.76	
A	B	A	B	A	B
0.0000	0.033792	0.0000	0.022893	0.0000	0.018914
0.3500	0.014173	0.3500	0.007636	0.1000	0.017034
0.4000	0.011484	*0.3782*	*0.007234*	0.2000	0.012200
0.4373	*0.010666*	0.4000	0.007443	0.2500	0.009418
0.4500	0.010713	0.4500	0.010288	0.3000	0.007078
0.5000	0.013073			*0.3500*	*0.005935*
				0.4000	0.007013

2.70		2.50		2.4278	
A	B	A	B	A	B
0.0000	0.013450	0.0000	0.001229	0.0000	0.000000
0.1000	0.011739	0.1000	0.000517	0.0639	−0.000090
0.2000	0.007583	0.1500	0.000470	*0.0876*	*−0.000119*
0.2500	0.005481	*0.1632*	*−0.000004*	0.1139	−0.000075
0.3000	0.004184	0.2000	0.000193		
0.3129	0.004084	0.3000	0.006147		
0.3500	0.004597				
0.4000	0.007945				

2.40		2.30	
A	B	A	B
0.0000	0.000129	0.0000	0.003984
0.0832	*0.000128*	0.1000	0.005405
0.0500	0.000133	0.2000	0.012985
0.1000	0.000294		
0.1500	0.001066		

[a] All energies are referred to E_0, the energy of the configuration at the saddle point, with H at the center of the 2.4278 Å long O-O bond; $E_0 = -151.201\ 427$ au. For each O-O distance the value of the hydrogen position with minimum energy is italicized. The number above each set indicates the oxygen-oxygen distance in Å. Columns A are distances of H to the center of the O-O bond in Å. Columns B are the energies in atomic units.

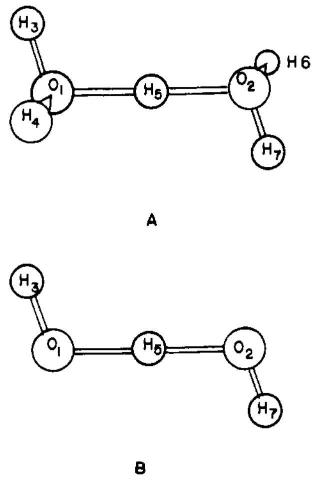

Figure 4. (A) Geometry used to calculate the proton transfer from the hydronium ion to a water molecule. The atoms H(3), O(1), H(5), O(2), and H(7) are in a plane. The angles H(4)-O(1)-H(3), H(4)-O(1)-H(5), and H(7)-O(2)-H(6) are 109.47°; O(1)-H(5)-O(2) is 180°. All the O-H bonds are 0.99 Å except O(1)-H(5) and H(5)-O(2) which are variable and listed in Table I. (B) Geometry used for the transfer between the water molecule and the hydroxyl ion. The atoms are in the same position as in Figure 1A except that atoms H(4) and H(6) are missing.

A similar study was carried out for the exchange between a water molecule and a hydroxyl ion ($H_3O_2^-$). The geometry used is presented in Figure 4B. Table IV gives the energies for various positions of the proton at various interoxygen distances. The surface obtained is similar to the one for hydronium ion and water. The minimum energy occurs at the interoxygen distance of 2.4278 Å with the proton at ±0.0876 Å from the center. The energy barrier is 0.000119 au, very small to be significant. At 2.76 Å, the experimental interoxygen distance in ice, the barrier is 0.0128 au (8.13 kcal/mol) and the interminimal distance 0.700 Å. At this interoxygen distance, the rate of exchange is $1.2 \times 10^{12}\ s^{-1}$. At an interoxygen distance of 2.90 Å the barrier and interminimal distance are 0.02313 au (14.50 kcal/mol) and 0.8746 Å, respectively, with a rate of exchange of $0.02 \times 10^{12}\ s^{-1}$. Again, at the experimental distance, the rate obtained is of the order of magnitude of the proton transfer in ice but about two orders of magnitude faster than the rate of exchange in water.

For the proton between methyl alcohol and the methoxide ion $(CH_3CO)_2H^-$ the conformation of minimum energy was first selected. The geometry is depicted in Figure 5, structure A. Table V shows the energies for various positions of the intervening proton at several interoxygen distances. The surface obtained is similar to the surfaces obtained before. The structure with minimum energy corresponds to an interoxygen distance of 2.4194 Å with the hydrogen at ±0.1097 Å from the center. The energy barrier is 0.000 293 au, very small to be significant. At 2.70 Å, the experimental interoxygen distance in methyl alcohol, the barrier is 0.011 233 au (7.04 kcal/mol) with an interminimal distance of 0.655 Å and a rate of exchange of $1.63 \times 10^{12}\ s^{-1}$, about two orders of magnitude larger than the experimental value.

Several additional geometries were studied in order to determine the effect of the different orientations of the donor and

Table V. Results of ab-Initio Calculations for $(H_3COHO\text{-}CH_3)^-$ Ions with Structure A[a]

2.90		2.76		2.70	
A	B	A	B	A	B
0.0000	0.034586	0.0000	0.019720	0.0000	0.014201
0.4000	0.010008	0.0500	0.019187	0.2500	0.005041
0.4447	0.008790	0.1000	0.017638	0.3000	0.003291
0.4500	*0.008783*	0.1500	0.015234	*0.3275*	*0.002968*
0.5000	0.010673	0.2000	0.012246	0.3500	0.003207
		0.2800	0.007328		
		0.3300	0.005144		
		0.3625	*0.004589*		
		0.3800	0.004701		
		0.4300	0.007228		
2.60		2.50		2.44	
A	B	A	B	A	B
0.0000	0.006562	0.0000	0.001523	0.0000	0.000136
0.2000	0.001804	0.1500	0.000187	0.0700	−0.000143
0.2500	0.000804	*0.1835*	*−0.000453*	0.1200	−0.000434
0.2576	*0.000760*	0.2000	−0.000426	*0.1248*	*−0.000447*
0.3000	0.001338	0.2500	0.000734	0.1700	−0.000237
2.4194		2.40		2.34	
A	B	A	B	A	B
0.0000	0.000000	0.0000	0.000048	0.0000	0.001395
0.0597	−0.000147	0.0500	−0.000014	0.1700	0.004459
0.1002	−0.000287	*0.0782*	*−0.000057*		
0.1097	*−0.000297*	0.1000	−0.000046	2.30	
0.1597	−0.000039	0.1500	0.000415		
0.2097	0.001684			0.0000	0.003437
				0.0075	0.003437
				0.0500	0.003672
				0.1000	0.004580

[a] All energies are referred to E_0, the energy of the configuration at the saddle point, with H at the center of the 2.4194-Å long interoxygen bond. $E_0 = -229.088\ 704$ au. For each interoxygen distance the hydrogen position at the minimum is italicized. The number above each set indicates the interoxygen distance in Å. Columns A give the distance of the H from the center of the O-O bond in Å. Columns B are the energies in atomic units.

acceptor species on the rate of proton exchange. These conformations were selected in order to provide geometries that will produce symmetric profiles with larger energy barriers, or nonsymmetric profiles. Figure 5 shows the geometry of structure B which results from the rotation of the methyl group on the right through an angle of 60° about the C–O bond. Table VI shows the value of the energy at the two minima at interoxygen distances of 2.76 and 2.70 Å. The rotation of the methyl group eliminates the symmetry of the profile. The energy difference between the two minima is 4.054×10^{-4} au at 2.76 Å (Table VIII) with a barrier of 14.93×10^{-3} au. At the experimental interoxygen distance of 2.70 Å the energy difference between the minima is 2.022×10^{-4} au with an energy barrier of 11.33×10^{-3} au. In neither of these two asymmetric profiles does the proton emerge in the other well. This indicates that for this conformation removal of the symmetry of the profile by rotation of the methyl group eliminates tunneling.

The other geometries studied are as follows: in Figure 6, structures C and D and in Figure 7 structure E. Table VI gives the energy of these structures as a function of the interoxygen distance, the distance of the intervening proton from the center of the O(2)–O(3) bond and the rotation angles θ_1, θ_2, and θ_3 about the C(1)–O(2), O(2)–O(3), and O(3)–C(4) bonds. All these rotations are with reference to structure A. Structure A is seen to be the structure of minimum energy and the structure for which the energy barrier is a minimum. Structures C, D, and E all produce a symmetric profile for the proton transfer. As the profiles are symmetric, the small increase in energy barrier does not change significantly the rate of proton exchange. It is clear then that the only conformational change which will significantly decrease or eliminate tunneling will be the rotation around the C–O bond of the methyl group.

Two conformations were selected for a study of the proton transfer from the methyloxonium ion to methyl alcohol. The structures are shown in Figure 8. In structure A, the methyl groups are oriented so as to produce a symmetric profile, while structure B is obtained from structure A by rotation of the methyl group on the right through an angle of 60° about the O(3)–C(4) bond. Table VII gives the energy as a function of the distance of the intervening proton from the center, at the interoxygen distances of 2.70 and 2.76 Å, for the structures A and B. Structure A shows an energy barrier of 0.013 73 au (8.61 kcal/mol) and an interminimal distance of 0.7114 Å at an interoxygen distance of 2.76 Å; an energy barrier of 0.010 04 au (6.29 kcal/mol) and an interminimal distance of 0.632 Å are found for the experimental interoxygen distance of 2.70 Å. The rates of exchange for these two distances are 6.57×10^{11} and 2.36×10^{12} s^{-1}, respectively (Table VIII). Rotation of the methyl group on the right through 60° eliminates the symmetry. The energy difference between the minima is 2.950×10^{-4} au at 2.76 Å and 2.599×10^{-4} au at 2.70 Å. This structure does not show tunneling.

Table VI. Results of ab-Initio Calculations for $(CH_3OHOCH_3)^-$ Ions with Configurations Resulting from Selected Rotations in the Symmetric Structure with Minimum Energy (Structure A, Figure 3)[a]

Structure	D(O-O)	θ_1	θ_2	θ_3	x	E
B	2.76	0	0	60	−0.3625	0.005 172
	2.76	0	0	60	0.3625	0.004 419
	2.70	0	0	60	−0.3275	0.003 498
	2.70	0	0	60	0.3275	0.002 827
C	2.70	0	180	0	0.0000	0.017 158
	2.70	0	180	0	0.3000	0.005 893
	2.70	0	180	0	0.3279	0.005 723
	2.70	0	180	0	0.3500	0.005 726
	2.70	0	180	0	0.4000	0.006 462
D	2.70	60	180	60	0.0000	0.014 913
	2.70	60	180	60	0.3000	0.003 746
	2.70	60	180	60	0.3274	0.003 391
	2.70	60	180	60	0.3500	0.003 605
	2.70	60	180	60	0.4000	0.006 365
E	2.70	60	0	60	0.0000	0.022 427
	2.70	60	0	60	0.3000	0.010 490
	2.70	60	0	60	0.3310	0.010 005
	2.70	60	0	60	0.3500	0.010 138
	2.70	60	0	60	0.4000	0.012 689

[a] The reference level for the energies is the same as in Table IV. Angle θ_1 gives the rotation about the C(1)-O(2) bond; angle θ_2, the rotation about the O(2)-O(3) bond and angle θ_3, the rotation about the O(3)-C(4) bond. Except in structure B the profiles are symmetric.

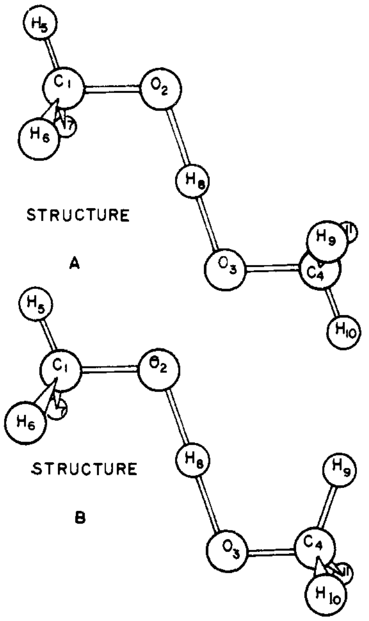

Figure 5. Geometry used to calculate the profile for the proton exchange between two methoxide ions. The atoms H(5), C(1), O(2), H(8), O(3), and C(4) are in a plane. In the same plane are H(10) in structure A and H(9) in structure B. The distances C(1)-O(2) and C(4)-O(3) are 1.43 Å. All C-H bonds are 0.99 Å. The distances O(2)-H(8) and O(3)-H(8) are variable and given in Table IV for structure A and in Table IX for structure B. The angles C(1)-O(2)-H(8) and C(4)-O(3)-H(8) are 105.0°. The remaining angles are 109.47° except for O(2)-H(8)-O(3) which is 180°. Structure B is obtained from structure A by rotating the methyl group on the right 60° about the C(4)-O(3) bond.

The above results indicate that the proton exchange between the methyloxonium ion and methyl alcohol and between methyl alcohol and the methoxide ion is calculated to be about two orders of magnitude faster than the value found experimentally when the structures involved produce symmetric profiles. Rotation of methyl groups resulting in asymmetric profiles eliminates tunneling.

In order to investigate the reason for the difference between experimental and calculated values in water, the profile for the transfer between a singly hydrated hydronium ion ($H_2O\cdot H_3O^+$) and two hydrogen bonded water molecules ($H_2O\cdot H_2O$) was calculated. The geometries are shown in Figure 9. Structure A produces a symmetric profile, while structure B, obtained by rotation through 180° about the O(3)-O(4) bond, produces an asymmetric profile. The value of the energy as a function of the distance from the center of the intervening proton is shown in Table IX for the symmetric profile at the

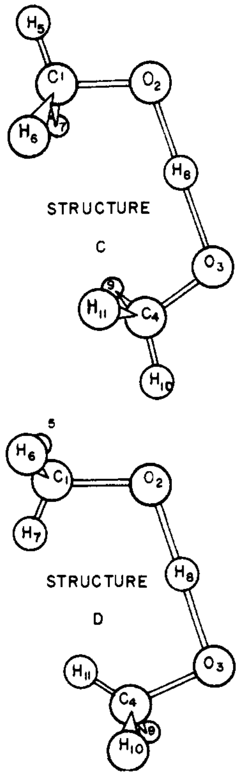

Figure 6. Structure used to calculate the proton exchange between two methoxide ions. Structure C is obtained from structure A by rotating the methoxy group on the right through 180° about the O(3)-H(8) bond. Structure D is obtained from C by rotating both methyl groups through 60° about the C-O bonds. The variable distances O(2)-H(8) and H(8)-O(3) are given in Table IX.

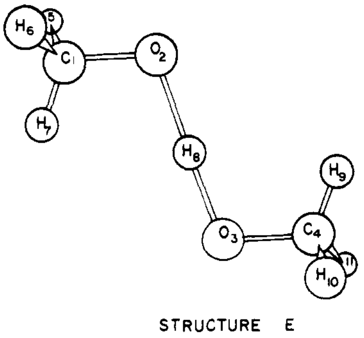

Figure 7. Structure used to calculate the proton exchange between two methoxide ions. Structure E is obtained from structure A by rotating both methyl groups 60° about the C-O bonds. The variable distances O(2)-H(8) and H(8)-O(3) are given in Table IX.

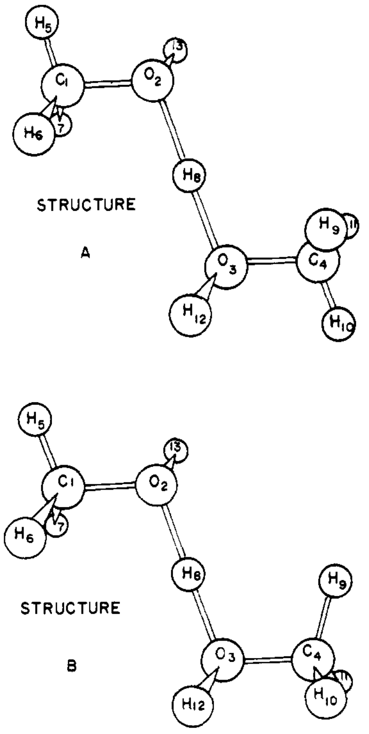

Figure 8. Structure used to calculate the proton exchange between two methyl alcohol molecules. Structure A in this figure is obtained from the structure A given in Figure 3 by adding H(13) below the principal plane and H(12) above the principal plane. Structure B is obtained from structure A by rotating the methyl group on the right through 60° about the bond C(4)-O(3).

experimental interoxygen distance of 2.76 Å. An energy barrier of 0.012 12 (7.6 kcal/mol) at an interminimal distance of 0.6868 Å was found. With these values, the rate of proton exchange is found to be 1.075×10^{12} s^{-1}. For the asymmetric profile, structure B, the energy difference between the two minima was found to be 13.56×10^{-4} au with a barrier of 11.445×10^{-3} au. This profile does not exhibit tunneling.

Conclusion

The results just presented indicate that the behavior of the intervening proton in the systems $(CH_3O)_2H^-$ and $(CH_3OH)_2H^+$ depends on the relative orientation of the two methyl groups. If the conformation is such that the profile for the transfer is symmetric, the two wells will be indistinguishable, the proton will be delocalized and the eigenfunctions will extend over both wells reflecting the symmetry of the profile. The initial assignment of the proton to the donor site implies the use of an initial state that localizes the proton in one of the

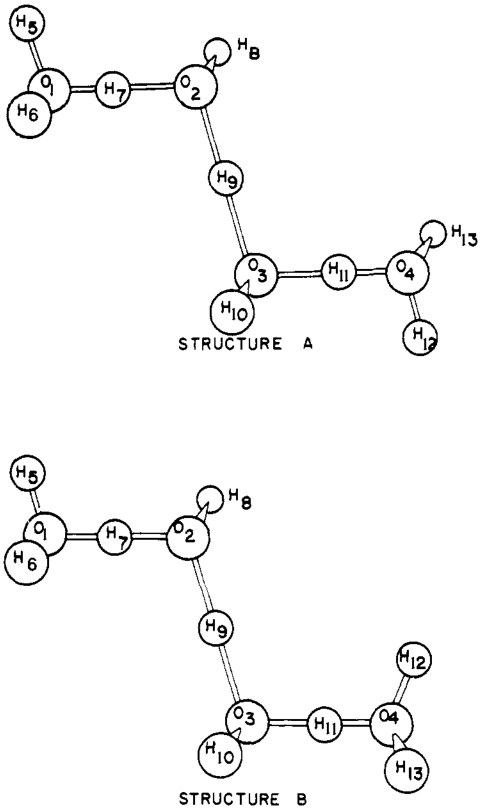

Figure 9. Geometry used to calculate the proton exchange between two water molecule dimers. The atoms H(5), O(1), H(7), O(2), H(9), O(3), H(11), O(4), and H(12) are in a plane. H(6) and H(10) are above the plane in both structures. H(8) is under the plane in both structures. All bond angles are 109.47° except O(2)-H(9)-O(3), O(1)-H(7)-O(2), and O(3)-H(11)-O(4) which are 180°. The bond distances H(5)-O(1), H(6)-O(1), H(7)-O(2), H(8)-O(2), H(10)-O(3), H(11)-O(3), H(12)-O(4), and H(13)-O(4) are 0.99 Å. The bond distances O(1)-O(2) and O(3)-O(4) are 2.76 Å. The bond distances O(2)-H(9) and H(9)-O(3) are variable and given in Table III. Structure B is obtained from structure A by a 180° rotation about the O(3)-O(4) bond.

Table VII. Results of ab-Initio Calculations for $((CH_3OH)H(HOCH_3))^{+a}$

Structure	D(O-O)	x	E
A	2.76	0.0000	0.021 279
		0.0500	0.020 769
		0.1000	0.019 290
		0.2000	0.014 193
		0.2500	0.011 268
		0.2750	0.009 935
		0.3000	0.008 802
		0.3250	0.007 973
		0.3500	0.007 567
		0.3557	0.007 547
		0.3750	0.007 719
A	2.70	0.0000	0.015 601
		0.2500	0.007 122
		0.3000	0.005 696
		0.3160	0.005 556
		0.3500	0.007 122
B	2.76	−0.3557	0.009 545
		0.3557	0.009 839
B	2.70	−0.3160	0.007 570
		0.3160	0.007 830

[a] The energies are referred to the saddle point obtained at interoxygen distances of 2.400 Å with the hydrogen in the center; $E_0 = -230.054\ 906$ au, x is the distance in atomic units from the center.

Table VIII. Parameters of Energy Profiles and Corresponding Tunneling Times[a]

Species	Structure	D(O-O)	D	$10^4 H$	$10^3 E$	a_2	V_0	α	$x_0(10^4)$	Tunneling times
$[(MeO)_2H]^-$	A	2.76	0.7250	0	15.13	0.0678	0.0903	1.563	0.0	2.353(−12)
		2.70	0.6550	0	11.23	0.1342	0.1969	1.000	0.0	0.611(−12)
	B	2.76	0.7250	4.054	14.93	0.0678	0.0903	1.563	40.54	NT
		2.70	0.6550	2.022	11.13	0.1342	0.1969	1.000	20.22	NT
$[(MeOH)_2H]^+$	A	2.76	0.7114	0	13.73	0.1151	0.1808	1.000	0.0	1.52(−12)
		2.70	0.6220	0	10.05	0.1398	0.1997	1.000	0.0	4.23(−13)
	B	2.76	0.7114	2.950	13.58	0.1151	0.1808	1.000	9.540	NT
		2.70	0.6220	2.599	9.92	0.1398	0.1997	1.000	7.786	NT
$[(H_2O{\cdot}H_2O)_2H]^+$	A	2.76	0.6868	0.0	12.123	0.1182	0.1801	1.000	0.0	9.301(−13)
	B	2.76	0.6868	13.56	11.445	0.1182	0.1801	1.000	44.19	NT

[a] D(O-O) is the distance between oxygen atoms in Å; D is the distance between minima. H is the energy difference between the minima in atomic units, E is the height of the barrier. a_2, V_a, α, and x_0 are the parameters of the function describing the profile. The tunneling times are in reciprocal seconds. NT signifies no tunneling, and this is seen to be the case whenever the profile is not symmetric (H does not equal zero).

Table IX. Results of ab-Initio Calculations for $(H_2O\text{-}H_2O\text{-}H\text{-}OH_2\text{-}OH_2)^+$ Ions[a]

Symmetric conformation	
A	B
0.0000	0.012 123
0.2900	0.001 960
0.3400	0.000 018
0.3434	*0.000 000*
0.3900	0.000 911
Conformation obtained by rotating one of the terminal OH_2 groups 180° around the O-O internuclear axis	
A	B
0.3434	0.004 774
−0.3434	0.003 418

[a] All energies are referred to E_0, the energy of the configuration with H at the position of minimum energy when O-O is 2.76 Å. $E_0 = -304.029\ 492$ au. All O-O distances are 2.76 Å. Columns A are distances of H to the center of the O-O bond in Å. Columns B are the energies in atomic units.

wells. The initial state cannot be an eigenstate of the system and the expectation value of the proton's position will oscillate between the two wells, leaking through the classically forbidden region, as shown in the previous publication.[5]

If the relative positions of the methyl groups are such that the symmetry of the transfer profile is removed, the proton will be localized and the eigenfunctions will be confined to either well except for eigenstates with energies close to the top of the barrier.

The initial assignment of the proton to one of the wells will not, in this case, produce the oscillation of the proton between the two wells. The methyl groups of the species $(CH_3O)_2H^-$ and $(CH_3OH)_2H^+$ rotate around the C-O bond with frequencies of the order of 10^{10} s^{-1}. This frequency is two or three orders of magnitude smaller than the frequency of oscillation of the proton between the donor and the acceptor in the symmetric profile. This separation between the two frequencies justifies the independent study of the two motions.

The above considerations suggest the following mechanism for the proton transfer: the proton is bound initially to the donor site in the intermediates $(CH_3O)_2H^-$ and $(CH_3OH)_2H^+$. The methyl group rotates with a frequency of the order of 10^{10} s^{-1}. This frequency of rotation will produce a symmetric profile around 10^{10} times per second. Every time the profile is symmetric the proton will leak through the barrier at the rate of 10^{12} to 10^{13} s^{-1}. This means that the rate-determining step in the process is the rotation of the methyl group.

The rate-determining step in water should be the transfer between two clusters of water molecules. A pair of simple clusters of two hydrogen bonded water molecules is shown in Figure 9, structures A and B. Here again, if the orientation of the water molecules in the system produces a symmetric profile, the proton will oscillate between the donor and acceptor sites with frequencies of the order of 10^{13} s^{-1}. However, if the transfer profile is not symmetric as shown in structure B, Figure 9, the proton will be confined to the donor site.

What we may observe in liquid water, where the rate of exchange is 1×10^{10} for $H_3O^+ + H_2O$ and 5×10^9 for $H_2O + OH^-$ [12] is the frequency with which clusters in their motion relative to one another produce a symmetric profile. In ice, where water molecules are highly structured, the geometry is such that the profile is symmetric and the calculated rate of exchange 10^{13} to 10^{14} [12] s^{-1} is in agreement with the experimental value.

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