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Analytical Functions for the Proton Transfer in the $H_5O_2^+$ Complex Immersed in a Solvent (Water, 1-Octanol)

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The analytical functions for the energy barrier of the proton transfer in $H_5O_2^+$ complex have been fitted by nonlinear regression from *ab initio* quantum mechanical calculations for the complex in gas phase and solvent phase (water, 1-octanol) simulated using the PCM approach. The best fitted function describing the proton transfer energy for any distance R between H_3O^+ and H_2O and for any proton position is of the form $E(R,r) = E(R/2)Erfc(z)$, where $Erfc(z)$ is the complementary error function, $z = [(r - 0.5R)/c]^2$, R is the $O(H_3O^+)$–$O(H_2O)$ distance, r is the space position of proton relative to $R/2$ and c a constant determined by regression for each proton transfer at a given R distance. The fitted functions are: $E(R/2) = [a + b/(R/2)]^2$ which is the highest potential energy value for the proton situated at $R/2$ and $c = a + b\ln(R/2)$. The energy barriers for the solvent phase are higher than those for the gas phase, because of the solute–solvent interactions considered by PCM. The energy barrier for the 1-octanol phase is somewhat lower than that for water phase, most likely due to the amphipathic character of the 1-octanol. The energy potential values for the proton transfer in solvent can be expressed as a sum of two terms corresponding to the gas phase and to solvent effects contributions.

Key words: proton transfer, Zundel complex, PCM, potential energy barrier, *Erfc*, octanol, GAMESS

The search for potential models designed to describe the intramolecular energy surface in $H_5O_2^+$ as well as the proton transfer between H_3O^+ and H_2O subunits was already reported [1]. Such potential models are useful to understand the proton transfer taking place through a hydrogen bond in aqueous solution [2,3] or in biological systems [4]. Another way to describe the proton transfer between H_3O^+ and H_2O is to find accurate analytical functions for the potential energy barrier. A number of different functions has been tested and fitted using *ab initio* quantum mechanical calculations for gas phase rigid geometries [5].

The aim of this paper is to obtain accurate analytical functions for the potential energy barrier of the proton transfer reaction

$$H_3O^+ + H_2O \Leftrightarrow H_5O_2^+ \text{ (Zundel Complex)} \rightarrow H_2O + H_3O^+$$

using *ab initio* quantum mechanical calculations for two cases, where the Zundel complex is embedded in a solvent (water and 1-octanol). The two solvents are

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particularly important, because water is the usual solvent in chemical and biological systems and 1-octanol represents the best surrogate to simulate the biological membranes [6–7]. This kind of functions may supply valuable information regarding the proton transfer in the Zundel complex for any proton position during the proton transfer and for any distance between H_2O and H_3O^+ subunits. Such empirical functions are also useful on one hand to describe the route of the proton between H_3O^+ ion and adjacent water molecules and on the other hand to examine the influence produced by the solvent on the proton transfer process.

RESULTS AND DISCUSSION

Ab initio quantum mechanical calculations have been performed for $O(H_3O^+)$–$O(H_2O)$ distances within 2.0–4.0 Å values, using the controlled modeling with flexible geometries, where the molecular structures are optimized except the $O(H_3O^+)$–$O(H_2O)$ distance and the proton position in space, which are maintained fixed during each calculation.

Instead of the microscopic models, where the solvent is represented by a limited number of molecules around the solute, we used the Polarizable Continuum Medium (PCM) [8,9], where the solvent is treated as a structureless and continuous medium with the properties of the real solvent (dielectric constant, radius, molar volume, surface tension). For the Zundel complex $H_5O_2^+$, the energetically favoured structure seems to be that geometry, where the O–H bonds in water and hydronium ion are contained in almost perpendicular planes (Figure 1).

Ab initio mechanical calculations were performed using the GAMESS code (RHF, 6-31G**, PCM) [10]. The AO's basis set 6-31G** has been preferred, because it leads to realistic molecular geometries for the hydronium ion and for the water molecule.

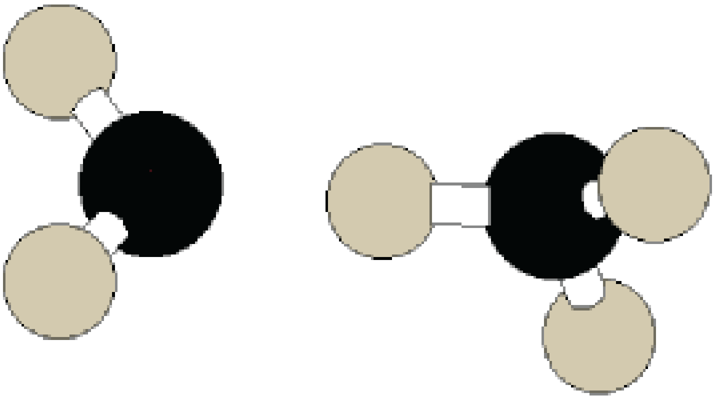

Figure 1. Stereo-view of the Zundel complex ($H_5O_2^+$).

The calculations were done for $H_5O_2^+$ in the gas phase and for $H_5O_2^+$ embedded in a solvent (water and 1-octanol). PCM parameters for water are contained in the GAMESS program. For the solvent 1-octanol the following parameters have been used: dielectric constant = 10.3 [6,7,11,12]; solvent radius = 3.250 Å [11]; molar volume = 160 [7]; surface tension coefficient = 27.1 [13]. Results are summarized in Table 1 for some proton positions between $O(H_3O^+)$–$O(H_2O)$, for which the proton is co-linear with the two oxygen atoms.

Table 1. Potential energy values for the proton transfer in $H_5O_2^+$ (Kcal/mol) for gas (MP = 0; 4) and solvent phases.

H_3O^+–H_2O (Å)	O(hydronium)–H(proton) (Å)	MP = 4	MP = 0	Water phase	1-octanol phase
2.523	1.114	0.000	0.000	0.000	0.000
	1.165	0.293	0.943	1.082	1.071
	1.214	0.627	1.657	1.858	1.850
	1.259	0.711	1.965	2.056	2.050
	1.264	0.711	1.865	2.056	2.050
	1.310	0.629	1.657	1.858	1.850
	1.359	0.293	0.943	1.082	1.071
	1.410	0.000	0.000	0.000	0.000
3.000	1.003	0.000	0.000	0.000	0.000
	1.209	7.411	11.290	13.812	13.592
	1.410	16.526	23.318	26.488	26.182
	1.497	17.030	24.109	27.380	27.138
	1.511	17.030	24.109	27.380	27.138
	1.600	16.526	23.318	26.488	26.182
	1.801	7.411	11.290	13.812	13.592
	2.003	0.000	0.000	0.000	0.000
3.500	0.997	0.000	0.000	0.000	0.000
	1.249	15.178	20.097	22.708	22.349
	1.575	39.198	48.422	53.732	53.210
	1.750	43.095	53.085	58.991	58.429
	1.929	39.198	48.422	53.732	53.210
	2.251	15.178	20.097	22.708	22.349
	2.500	0.000	0.000	0.000	0.000
4.000	0.986	0.000	0.000	0.000	0.000
	1.357	29.600	36.435	39.976	39.709
	1.672	59.820	69.464	76.004	75.513
	2.010	74.470	85.313	92.517	91.819
	2.053	74.470	85.313	92.517	91.819
	2.369	59.820	69.464	76.004	75.513
	2.667	29.600	36.435	39.976	39.709
	3.005	0.000	0.000	0.000	0.000

As may be seen in Table 1, the maximum values of barrier energy correspond to those cases, where the proton is located in the middle between the two oxygen atoms. For the gas phase situation, the potential energy values without Møller-Plesset corrections (MP = 0) for the electron correlation are much higher than those, where the corrections up to the fourth-order term are considered (MP = 4). The energy barrier maximum values for the last case MP = 4, where the Møller-Plesset corrections up to the fourth term are considered, agree with those in literature [5].

Because the PCM-GAMESS procedure does not allow the Møller-Plesset corrections for the electron correlation, the changes in the barrier energy values caused by the solvent will be related to the gas phase situation (MP = 0). As may be seen below, there exists the possibility to add the solvent effects obtained with PCM approach to the energy barrier for the gas phase, where the electron correlation has been taken into account (MP = 4).

The search for the analytical expression was performed using the regression techniques and testing numerous analytical functions used in spectroscopy, statistics and electronics for the shape of the absorption bands and signals. We found for all cases considered in Table 1, that the best function, which approximates the shape of potential energy values for the proton transfer, is the complementary error function (*Erfc*)

$$E(R,r) = E\left(\frac{R}{2}\right) Erfc(z) \tag{1}$$

where $z = [(r - 0.5R)/c]^2$, R is the $O(H_3O^+)$–$O(H_2O)$ distance and r the space position of proton relative to $R/2$. The fitted function has been found by least squares regression, using the quantum calculation results summarized in Table 1. As may be seen in Table 2, the function given by (1) reproduces quite well the results contained in Table 1, as suggested by the square of the regression coefficient R^2 close to unity.

Table 2. Regression results for $E(R,r) = E(R/2)Erfc(z)$, $z = [(r - 0.5R)/c]^2$.

H_3O^+–H_2O (Å)	phase	E(*R*/2) (kcal/mol)	*c*	R^2
2.523	Gas (MP = 4)	0.729	0.124445876	0.9942
	Gas (MP = 0)	1.914	0.132277201	0.9849
	Water	2.126	0.133808835	0.9809
	1-octanol	2.177	0.133543943	0.9815
3.000	Gas (MP = 4)	17.351	0.393343445	0.9982
	Gas (MP = 0)	24.509	0.405305836	0.9977
	Water	27.842	0.417563115	0.9960
	1-octanol	27.546	0.416466876	0.9963
3.500	Gas (MP = 4)	43.308	0.610043730	0.9982
	Gas (MP = 0)	53.357	0.623496681	0.9969
	Water	59.225	0.626832127	0.9965
	1-octanol	58.645	0.625630152	0.9967
4.000	Gas (MP = 4)	74.730	0.831124042	0.9969
	Gas (MP = 0)	85.822	0.850410604	0.9951
	Water	93.330	0.853805515	0.9947
	1-octanol	92.643	0.854012624	0.9947

In Table 2, the expression $E(R/2)$ from the equation (1) represents the highest potential energy value of the proton transfer, in this case for the proton situated in the middle of the $O(H_3O^+)$–$O(H_2O)$ distance. The general formulas for $E(R/2)$ and the c constant function of $O(H_3O^+)$–$O(H_2O)$ distance R, may be found by regression using the data contained in Table 2.

The analytical function for the energy barrier *E(R/2)*, found for the values given in Table 2, is of the type $E(R/2) = \left[a + \frac{b}{(R/2)}\right]^2$, where *a* and *b* coefficients assume the following values:

gas phase (MP = 0) $a = 22.15212846$; $b = -51.9070542$; $R^2 = 0.9998$
gas phase (MP = 4) $a = 21.83630166$; $b = -53.2155071$; $R^2 = 0.9996$
water phase $a = 22.81482010$; $b = -52.9319537$; $R^2 = 0.9996$
1-octanol phase $a = 22.76133950$; $b = -52.8654575$; $R^2 = 0.9996$

For the coefficient *c* in (1), the best fitted simple function using the *c* values given in Table 2 appears to be of the form $c = a + b\ln(R/2)$, where the coefficients *a* and *b* assume the following values:

gas phase (MP = 0) $a = -0.22338134$; $b = 1.528099339$; $R^2 = 0.9995$
gas phase (MP = 4) $a = -0.22534319$; $b = 1.504328792$; $R^2 = 0.9997$
water phase $a = -0.21771218$; $b = 1.527049698$; $R^2 = 0.9991$
1-octanol-phase $a = -0.21862732$; $b = 1.527739428$; $R^2 = 0.9991$

As may be seen above, the fitted functions for *E(R/2)* and *c* reproduce satisfactorily the data given in Table 2, as shown by the square of the regression coefficient R^2 close to unity.

The complementary error function can be calculated using approximate formulas (Abramowitz M., Stegun J.A., "Handbook of Mathematical Functions", National Bureau of Standards, Applied Mathematics Series, 55, 1964), or the *erfc.c* subroutine (1986–92 Numerical Recipes software). In this subroutine, the complementary error function is approximated as $Erfc(z) = t \cdot \exp(s)$, the exponent "s" and the pre-exponential term "t" being functions of the parameter $z = [(r - 0.5R)/c]^2$ as defined in expression (1):

$$s = -z^2 - 1.26551223 + t(1.00002368 + t(0.37409196 + t(0.09678418 + \\ t(-0.18628806 + t(0.27886807 + t(-0.82215223 + 0.17087277t)))))))$$

and $t = 1/(1 + 0.5z)$.

The potential energy barriers corresponding to the proton-transfer, where the proton is co-linear with the two oxygen atoms of H_3O^+ and H_2O units, are illustrated in Figure 2.

As may be seen in Figure 2, the energy barriers for the proton transfer in the case of the solvent phase (water, 1-octanol) are higher than that of the gase phase (MP = 0 or MP = 4). Solvent effects on the proton transfer energy barriers reported in [14,15] usually lead to an moderate increase of the barrier height. The difference between solvent (water, 1-octanol) phase and gase-phase (MP = 0 and MP = 4) is certainly due to the various solute–solvent interactions considered by the PCM model [8–9,11].

The higher potential energy barrier of the proton transfer corresponds to the case, where $H_5O_2^+$ is embedded in water as solvent (Figure 2, curve 1). The solute–solvent interactions seem to be less intense for the 1-octanol phase (Figure 2, curve 2), most

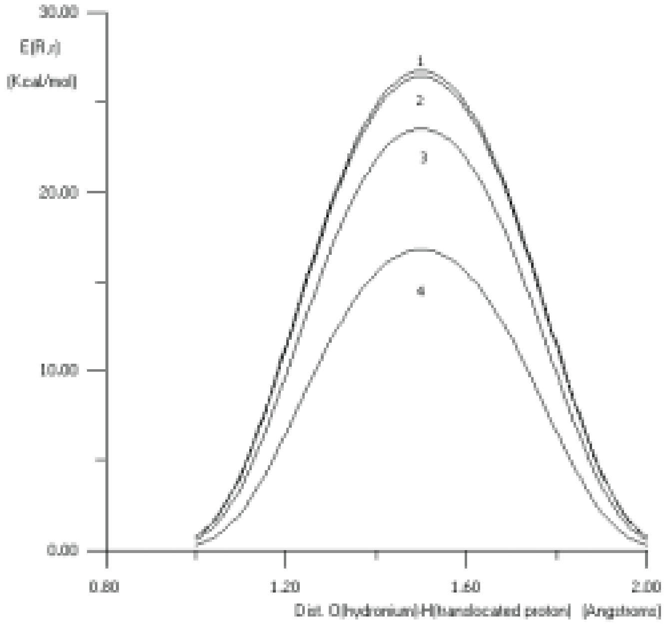

Figure 2. Energy barrier for the proton transfer in $H_5O_2^+$ (O–O distance of 3 Å): 1. water; 2. 1-octanol; 3. gas (MP = 0); 4. gas (MP = 4).

likely due to the amphipathic character of this solvent. Indeed, 1-octanol exhibits both a hydrophilic character due to the presence of the OH– group but also a hydrophobic character of the long hydrocarbon tail. This character (amphipathic) of 1-octanol may be the cause of discrimination between the energy barrier for the aqueous and 1-octanol phases, as may be seen in Figure 2 (curves 1 and 2).

Since the shape of the potential energy barrier for the gas phase (MP = 0 and MP = 4) and solvent phase (water, 1-octanol) is described by the same expression (1), we shall try in the following, to see if the solvent effects calculated by PCM-GAMESS approach without Møller-Plesset corrections (MP = 0) could be added to the gas phase energy barrier found for the level MP = 4. We may obtain in this way more reliable energy barrier shapes for the proton transfer using the PCM approach. Fortunately, this possibility is allowed by the obvious fact that the *Erfc*(*z)* function in (1) is almost the same for both gas and solvent phases, inasmuch the only parameter *c* involved in $z = [(r - 0.5R)/c]^2$ assumes close values for all phases here considered (see Table 2, column 4). This result allow us to add the contributions of the solute–solvent interactions calculated using PCM approximation to the gas phase calculations, where the Møller-Plesset corrections for the electron correlations are considered (*e.g*. MP = 4). This solvent effects contribution $\Delta E(R/2)$ should be equal to the difference between the results obtained with PCM approximation (solvent phase, MP = 0) and the results derived for gas phase without Møller-Plesset corrections (gas phase, MP = 0):

$$\Delta E(R/2) = E(R/2)(\text{solvent phase, MP} = 0) - E(R/2)(\text{gas phase, MP} = 0) \quad (2)$$

The energy potential values for the proton transfer in solvent can accordingly be expressed as a sum of two terms

$$E(R,r) \approx [E(R/2) + \Delta E(R/2)]Erfc(z) \quad (3)$$

where $E(R/2)$ represents the gas phase (MP = 4) maximum energy barrier and $\Delta E(R/2)$ represents the energy contribution due to the solute–solvent interactions, calculated in the frame of PCM model (equation 2).

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