

3P116

Divide and Conquer type Density Functional based Tight Binding Molecular Dynamics (DC-DFTB-MD) Simulation of Proton Transfer in Bulk Water System

(Department of Chemistry and Biochemistry, Waseda University¹, Research Institute for Science and Engineering, Waseda University², Institute for Molecular Science³, JST-CREST⁴, ESICB, Kyoto University⁵) ○Aditya Wibawa Sakti¹, Yoshifumi Nishimura^{2,3}, Hiromi Nakai^{1,2,4,5}

[Introduction] Diffusion of proton in bulk water has attracted long-term attention because it includes not only a simple diffusion process but also a proton transfer via Grotthuss mechanism.^{1,2,3} Experimentally, the Grotthuss shuttling behavior of a proton transfer has been determined by measurement of self-diffusion coefficient of oxygen in hydronium ion.^{2,4,5,6} The behavior of self-diffusion coefficient is usually following the Arrhenius theory while the higher activation barrier of diffusion is observed at low temperature.⁷ In this work, we theoretically study the molecular aspects of the proton transfer at different temperatures.

[Computational Details] We performed molecular dynamic simulations by using divide-and-conquer type density functional based tight-binding method (DC-DFTB-MD).^{8,9,10} The system contains 523 water molecules and one excess proton in $25.924 \times 26.230 \times 25.849$ Å periodic box. Firstly, the system was equilibrated by using Nose-Hoover *NVT* ensemble for 10 ps at 280, 300, 320, and 360 K. Next, 15 ps *NVE* ensemble simulations was performed for production run at each temperature.

In the present research, the diffusion coefficient of proton (D_p) is obtained as the summation of physical diffusion coefficient of water (D_w) and Grotthuss diffusion coefficient (D_G)

$$D_w = \lim_{t \rightarrow \infty} \frac{\langle |r_o(t) - r_o(0)|^2 \rangle}{6t}, \quad D_G = \frac{l^2}{6} r_p, \quad D_p = D_w + D_G = \lim_{t \rightarrow \infty} \frac{\langle |r_o(t) - r_o(0)|^2 \rangle}{6t} + \frac{l^2}{6} r_p \quad (1)$$

where l is the proton hopping length set to 2.5 \AA and $r_o(t)$ is the position vector of oxygen atom at time t . The proton transfer rate r_p was determined from the slope of the following accumulation function

$$h(\delta t) = h(\delta t - 1) + \delta h(\delta t) \quad (2)$$

where $h(0) = 0$ and $\delta h(\delta t)$ is 1, 0, and -1 for forward, no, and backward shuttling, respectively. The activation barrier of diffusion ΔE was evaluated from the logarithm form of the Arrhenius equation,

$$\ln D = \ln D_0 - \frac{\Delta E}{RT} \quad (3)$$

where D is one of D_w , D_G , or D_p , D_0 is pre-exponential factor, R is gas constant, and ΔE is one of ΔE_w , ΔE_G^i , or ΔE_p^i , which describe activation barriers of water, Grotthuss, and proton diffusions, respectively.

[Results and Discussion] Figure 1 shows the time evolution of Eq. (2). The short and long vertical lines indicate the oscillation shuttling and forward jumping behavior in proton transfer, respectively. The obtained r_p of 0.69 ps^{-1} at 300 K is in good agreement with the experimental value ($r_p = 0.67 \text{ ps}^{-1}$).⁴ The low proton transfer rate of 0.11 ps^{-1} at 280 K indicates higher activation barrier of proton transfer due to the frequent forward and backward shuttling. This behavior is caused by very stable special pair interaction between the proton and water molecule, leading to the formation of Eigen complex.

Table 1 shows the calculated diffusion coefficients at 300 K together with previous experimental and theoretical values. This work agrees well the experimental value of D_p . The larger system size and the use of Mulliken charges to identify the hydronium ion seems to improve D_w and D_p from the previous work.

Figure 2 shows the Arrhenius plot of three different diffusion coefficients. The diffusion of water shows a good linear relationship (black) while Grotthuss (red) and proton diffusion (blue) gives a significant deviation at 280 K. It indicates that the mechanism of proton transfer via Grotthuss shuttling is totally different from physical diffusion of water molecule.

The calculated diffusion barriers of water (ΔE_w), Grotthuss ($\Delta E_G^1, \Delta E_G^2$), and proton ($\Delta E_p^1, \Delta E_p^2$) are tabulated in Table 2. The obtained value of ΔE_p^1 (7.76 kJ/mol) is in agreement with the experimental one (10.04 kJ/mol).⁴ The stabilization by hydrogen bonding in Eigen complex is supposed to lead to the higher values of ΔE_G^2 and ΔE_p^2 than ΔE_G^1 and ΔE_p^1 , consistent with the observation in experiment.⁷

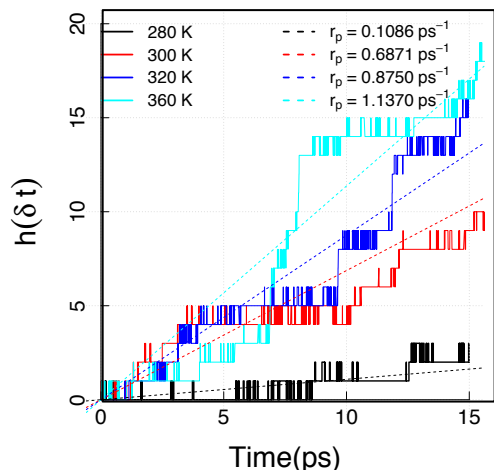


Figure 1. Time course changes of accumulation function $h(\delta t)$.

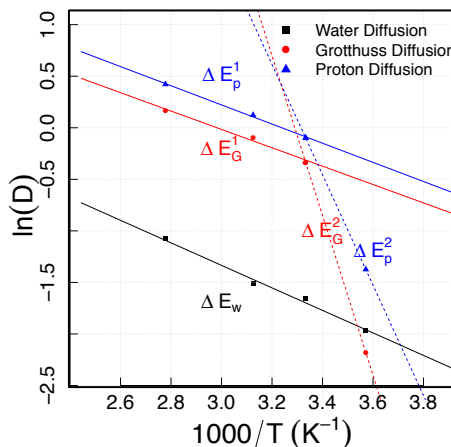


Figure 2. Arrhenius plot for diffusion of water, Grotthuss, and proton.

Table 1. Number of proton and water molecules N , simulation time t , temperature fluctuation in NVE ensemble simulations ΔT , and calculated diffusion coefficients among different theoretical methods at 300 K.

	CPMD ^a	DFTB2 ^a	DFTB3 ^b	DC-DFTB3 (present)	Exp.
$N(H^+)/N(H_2O)$	1/128	1/128	1/128	1/523	
$t(NVT)/t(NVE)$ (ps)	8/35	60/80	100/82	10/15	
ΔT (K)	± 100	± 100	± 100	± 15	
D_w ($\text{\AA}^2/\text{ps}$)	0.10	0.65	0.38	0.19	0.23 ^c
D_G ($\text{\AA}^2/\text{ps}$)				0.72	0.70 ^d
D_p ($\text{\AA}^2/\text{ps}$)	0.33	0.90	0.66	0.91	0.94 ^e
D_p/D_w	3.30	1.38	1.74	4.77	4.09

^a Car-Parrinello MD (CPMD); second order self-consistent charge DFTB (DFTB2) in the Reference 11, ^b DFTB with third-order diagonal term correction (DFTB3) in the Reference 12. ^cReference 5, ^d Reference 2, ^e Reference 6.

Table 2. Activation barrier of diffusion (in kJ/mol) estimated from Eq. (3).

	$T = 300 - 360$ K			$T = 280 - 300$ K	
	ΔE_w	ΔE_G^1	ΔE_p^1	ΔE_G^2	ΔE_p^2
Calc.	8.88	7.41	7.76	64.42	41.52
Exp. ^a			10.04		

^a Reference 4.

[References]

[1] Agmon, N. *Chem. Phys. Lett.*, 1995, **244**, 456-462. [2] Meiboom, S. *J. Chem. Phys.*, 1961, **34**, 375-388. [3] Chen, H., Voth, G.A., Agmon, N. *J. Phys. Chem. B*, 2010, **114**, 333-339. [4] Luz, Z., Meiboom, S. *J. Am. Chem. Soc.*, 1964, **86**, 4768-4769. [5] Mills, R. *J. Phys. Chem.*, 1973, **77**, 685-688. [6] Roberts, N.K., Northey, H.L. *J. Chem. Soc. Faraday Trans.*, 1974, **70**, 253-262. [7] Agmon, N. *J. Phys. Chem.*, 1996, **100**, 1072-1080. [8] Kobayashi, M., Nakai, H. in *Linear-Scaling Techniques in Computational Chemistry and Physics*, Springer, 2011, 97-127. [9] Elstner, M. *J. Phys. Chem. A*, 2007, **111**, 5614-5621. [10] Yang, Y., Yu, H., York, D., Cui, Q., Elstner, M. *J. Phys. Chem. A*, 2007, **111**, 10861-10873. [11] Maupin, C., Aradi, B., Voth, G.A. *J. Phys. Chem. B*, 2010, **114**, 6922-6931. [12] Goyal, P., Elstner, M., Cui, Q. *J. Phys. Chem. B*, 2011, **115**, 6790-6805.