Electronic Supplementary Information: A Structure-Dynamics Relationship Enables Prediction of the Water Hydrogen Bond Exchange Activation Energy from Experimental Data

Zeke A. Piskulich,[1,2,a)] Damien Laage,[3,b)] and Ward H. Thompson[1,c)]

[1)] *Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA*

[2)] *Current Address: Department of Chemistry, Boston University, Boston, MA, 02215, USA.*

[3)] *PASTEUR, Département de Chimie, École Normale Supérieure, PSL University, Sorbonne Université, CNRS, Paris, 75005, France*

[a)]Electronic mail: piskulichz@gmail.com

[b)]Electronic mail: damien.laage@ens.psl.eu

[c)]Electronic mail: wthompson@ku.edu

ACTIVATION ENERGY DATA

In Table S1 the activation energies of each water model calculated in our previous work[1] are reproduced. Activation energies were calculated using 50,000 20 ps trajectories and uncertainties represent 95% confidence intervals from block averaging using 5 blocks. For full details see Ref. 1.

TABLE S1: Activation energies published in our previous work.[1]

Model	$E_{a,0}$	$E_{a,2}$	$E_{a,D}$
SPC/E	3.09_4	3.54_5	3.61_9
SPC/Fw	3.27_6	3.69_9	3.80_{10}
TIP3P	2.71_5	2.98_7	3.26_8
TIP3P/Fw	3.38_6	3.79_5	4.04_8
OPC3	3.26_6	3.71_5	3.84_7
E3B2	4.11_6	4.69_{10}	4.73_9
E3B3	4.03_2	4.55_8	4.59_{11}
TIP4P/2005	3.63_5	4.12_8	4.10_5
TIP4P/Ew	3.52_6	3.98_{10}	4.03_9

FITS OF $E_{a,X}$ VS $\Delta\Delta H$

In Table S2 the values of the fitting parameters as well as the R^2 goodness-of-fit indicators for the data included in Figures 4a and 4b are provided. Uncertainties in the fits are 95% confidence intervals obtained from block averaging.

FURTHER TESTS OF THE PREDICTED JUMP ACTIVATION ENERGY

Here, we carry out a consistency check the structure-dynamics relationships used to obtain the estimated value of the jump activation energy ($E_{a,0}$ = 3.43 kcal/mol) from the radial distribution functions (RDFs) measured by Skinner *et al.*,[2] Specifically, we use experimental values of $E_{a,2}$ and $E_{a,D}$ in reverse to estimate $\Delta\Delta H$ and then use these values with the correlations presented in the main text and Table S2 to estimate the jump activation energy.

TABLE S2: Linear fitting parameters and R^2 goodness of fit indicators for the fits shown in Figure 4a and 4b of the main text.

	$\Delta\Delta H$			-T$\Delta\Delta S$		
Model	$b_{H,X}$	$m_{H,X}$	R^2	$b_{S,X}$	$m_{S,X}$	R^2
τ_0	0.82_{13}	0.88_6	0.957	1.66_8	-0.97_{13}	0.887
τ_2	0.83_{15}	1.03_6	0.944	1.82_9	-1.13_{15}	0.868
D	1.36_{15}	0.89_5	0.916	2.21_9	-0.97_{13}	0.842

Beginning with the value of the OH reorientation time activation energy of $E_{a,2} = 4.1 \pm 0.5$ kcal/mol obtained by Petersen *et al.*,[3] we find $\Delta\Delta H_{PTB} = 3.17 \pm 0.53$ kcal/mol in good agreement with the $\Delta\Delta H_{expt} = 2.97$ kcal/mol from the RDFs of Skinner *et al.*[3] Proceeding similarly with the Nicodemus *et al.* result of $E_{a,2} = 3.7 \pm 0.5$ kcal/mol yields $\Delta\Delta H_{NCST} = 2.79 \pm 0.53$ kcal/mol, which is also in agreement within error.[4]

We can do the same for the median value, $E_{a,D} = 4.4$ kcal/mol of the reported diffusion activation energies,[5–8] to obtain $\Delta\Delta H_D = 3.42 \pm 0.62$ kcal/mol. While this is larger than the other estimates, it is still in agreement with $\Delta\Delta H_{expt}$ within error bars.

These three values ($\Delta\Delta H_{PTB}$, $\Delta\Delta H_{NCST}$, and $\Delta\Delta H_D$) may then be used to evaluate the jump activation energy. We find values of $E_{a,0} = 3.61 \pm 0.56$ and 3.27 ± 0.55 kcal/mol based on the $E_{a,2}$ measurements of Petersen *et al.* and Nicodemus *et al.*, respectively, and 3.83 ± 0.63 kcal/mol from the average of the measured $E_{a,D}$ results. The jump activation energy of 3.43 kcal/mol derived from the temperature-dependent RDFs of Skinner *et al.* is in agreement with all of these results, indicating the internal consistency of the correlation approach.

It is interesting to consider the same procedure for the water models. For simplicity we focus on the TIP4P/2005 case, which has the advantage that it has good overall agreement with measured activation energies.[1] Considering the $E_{a,2}$ and $E_{a,D}$ values for TIP4P/2005 water obtained in Ref. 1 and given in Table S1, we obtain from the structure-dynamics relationships values of $\Delta\Delta H^{\ddagger}$ of 3.19 and 3.09 kcal/mol, respectively. These are in good agreement with the directly calculated value of 3.25 kcal/mol (Table 1 of the main text). Using these values within the jump time relationship gives estimates for $E_{a,0}$ of 3.63 kcal/mol from the reorientation value and 3.54 kcal/mol from the diffusion result. These are in

excellent agreement with the directly calculated value of $E_{a,0} = 3.63$ kcal/mol, illustrating the consistency of the derived structure-dynamics relationships.

I. SCRIPTS AVAILABLE

We have made the scripts used to generate each result for this work available at the following DOI: 10.5281/zenodo.4064098. A document that includes the activation energies calculated from each model from our previous work can also be found there.

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