Electronic Supporting Information

Concerted Transfer of Multiple Protons in Acid-Water Clusters: $[(HCl)(H_2O)]_2$ and $[(HF)(H_2O)]_4$

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Abstract: Molecular dynamics simulations using directly ab initio potentials are carried out for the ionically-bonded clusters: $[(Cl^{-})(H_{3}O^{+})]_{2}$ and $[(F^{-})(H_{3}O^{+})]_{4}$, to explore their transitions to the hydrogenbonded $[(HCl)(H_{2}O)]_{2}$ and $[(HF)(H_{2}O)]_{4}$ structures during the first picosecond of simulation. Both the ionic and the H-bonded structures that are formed are highly symmetric. It is found that proton transfers are concerted in all trajectories for $[(Cl^{-})(H_{3}O^{+})]_{2}$. For $[(F^{-})(H_{3}O^{+})]_{4}$, the fully concerted mechanism is dominant but partially concerted transfers of two or three protons at the same time also occur. The concerted mechanism also holds for the reverse process of ionization of neutral acid molecules. It is suggested that the high symmetry of the ionic and the H-bonded structures plays a role in the preference for concerted transfers. Possible implications of the results for proton transfers in other systems are discussed.

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 $[(F^{-})(H_{3}O^{+})]_{4} \rightarrow (symmetric)[(HF)(H_{2}O)]$

1. Transition state of the reaction $[(Cl^{-})(H_{3}O^{+})]_{2} \rightarrow (symmetric)[(HCl)(H_{2}O)]_{2}$

The geometry of the computed transition state (B3LYP-D3, 6-311G**) of this reaction is presented in Figure S1. It has an imaginary frequency of -364.9 cm^{-1} . As mentioned in the main article, it is only 0.03eV higher in energy than the ionic isomer, and 0.08eV higher in energy than the symmetric H-bonded isomer. The distances between the atoms are presented in Table S2. Distances between each of the two transferred protons (H(2) and H(9)) and the other atoms in the system are marked in color. It can be seen that atoms that are symmetric with regard to the protons being transferred share the same distance from the protons (marked in the same color).



Figure S1. The geometry of the computed transition state of the reaction $[(Cl^{-})(H_3O^{+})]_2 \rightarrow (symmetric)[(HCl)(H_2O)]_2$, including partial-charges on the chlorine and oxygen atoms.

	Cl(1)	H (2)	O (3)	H (4)	H (5)	H (6)	O (7)	H (8)	H (9)
H (2)	1.57								
O (3)	2.77	1.19							
H (4)	3.23	1.77	0.96						
H (5)	3.15	1.76	1	1.59					
H (6)	2	2.6	3.41	3.96	3.17				
O (7)	2.98	3.33	3.91	4.47	3.42	1			
H (8)	3.41	3.86	4.47	5.14	3.96	1.58	0.96		
H (9)	3.35	3.11	3.33	3.86	2.6	1.76	1.19	1.77	
Cl (10)	4.22	3.36	2.98	3.42	2	3.15	2.77	3.23	1.57

Distance Matrix (Å) of the $[(Cl^{-})(H_{3}O^{+})]_{2} \rightarrow (symmetric)[(HCl)(H_{2}O)]_{2}$

Transition State (B3LYP-D3, 6-311G**)

Table S2. The distances (in Ångstroms) between the atoms in the computed transition state (B3LYP-D3, 6-311G**). Marked in color:distances between each of the two transferred protons (H(2) and H(9)) and the other atoms in the system. Marked in the same color: distances that are equal due to the symmetry of the cluster with regard to the protons being transferred.

2. Transition state of the reaction $[(F)(H_3O^+)]_4 \rightarrow (symmetric)[(HF)(H_2O)]_4$

The geometry of the computed transition state (BLYP-D3, 6-311G**) of this reaction is presented in Figure S3. It has an imaginary frequency of -244.21 cm⁻¹. It is higher in energy by 0.08 eV than the ionic isomer, and is 0.1 eV higher in energy than the corresponding H-bonded isomer (isomer (e)). It is highly symmetrical, as the partial-charges on each of the four oxygen atoms are equal, as well as the partial-charges on each of the four oxygen atoms are equal, as well as the partial-charges on each of the four oxygen atoms are equal, as well as the partial-charges on each of the four fluorine atoms.

NBO analysis³ shows that this structure is closer to the ionic isomer than to the H-bonded isomers: besides a slight rise in the absolute value of partial charges on the oxygen atoms, and a slight reduction in the absolute value of partial- charges on the chlorine atoms, the charge partition is the same as in the ionic isomer.

The distances between the atoms are presented in Table S4. It can be seen that atoms that are symmetric with regard to the four protons being transferred share a very similar distance from the protons (marked in the same color).



Figure S3. The geometry of the computed transition state of the reaction $[(F^{-})(H_3O^{+})]_4 \rightarrow (symmetric)[(HF)(H_2O)]_4$, including partial-charges on the flourine and oxygen atoms.

Distance Matrix (Å) of the $[(F^{-})(H_3O^{+})]_4 \rightarrow (symmetric)[(HF)(H_2O)]_4$

	F(1)	H(2)	O(3)	H(4)	H(5)	F(6)	H(7)	O(8)	H(9)	H(10)
H(2)	1.27									
O(3)	2.39	1.12								
H(4)	2.76	1.68	1							
H(5)	2.74	1.68	1.02	1.59						
F(6)	3.48	2.86	2.55	2.88	1.58					
H(7)	2.88	2.76	2.97	3.36	2.22	1.29				
O(8)	2.58	2.96	3.53	3.91	3.03	2.39	1.11			
H(9)	1.61	2.23	3.04	3.49	2.82	2.74	1.67	1.01		
H(10)	2.87	3.33	3.88	4.01	3.45	2.77	1.68	1.01	1.59	
F(11)	3.53	3.92	4.36	4.11	4.08	3.56	2.9	2.56	2.85	1.58
H(12)	2.91	3.37	3.93	3.57	3.95	3.93	3.35	2.99	2.84	2.22
O(13)	2.57	3.02	3.63	3.2	3.95	4.37	3.91	3.6	3.14	3.06
H(14)	2.87	2.88	3.2	2.54	3.57	4.14	3.99	3.96	3.55	3.49
H(15)	1.6	2.26	3.09	2.92	3.49	4.06	3.51	3.14	2.46	2.87
H(16)	4.09	3.53	3.17	2.93	2.46	1.63	2.29	3.11	3.51	2.91
O(17)	4.34	3.89	3.59	3.09	3.11	2.58	3.03	3.62	3.95	3.16
H(18)	4.13	3.98	3.96	3.54	3.52	2.88	2.88	3.18	3.58	2.5
H(19)	3.79	3.23	2.9	2.17	2.75	2.87	3.31	3.83	3.86	3.45
F(20)	3.56	2.93	2.6	1.65	2.88	3.57	3.96	4.38	4.12	4.08

Transition State (BLYP-D3, 6-311G**)

	F(11)	H(12)	O(13)	H(14)	H(15)	H(16)	O(17)	H(18)	H(19)
H(12)	1.24								
O(13)	2.38	1.14							
H(14)	2.75	1.7	1						
H(15)	2.75	1.7	1.01	1.59					
H(16)	2.91	3.36	3.92	3.53	4.02				
O(17)	2.62	2.98	3.55	3.07	3.89	1.01			
H(18)	1.68	2.28	3.1	2.89	3.52	1.58	1		
H(19)	2.87	2.71	2.89	2.18	3.22	1.72	1.17	1.71	
F(20)	3.52	2.92	2.62	1.67	2.9	2.79	2.37	2.77	1.19

Table S4. The distances (in Ångstroms) between the atoms in the computed transition state (BLYP-D3,
 6-311G**). Marked in the same color: distances that are very similar due to the symmetry of the cluster with regard to the protons being transferred.

3. Equilibrium structures of asymmetric [(HCl)(H₂O)]₂ clusters

There are two known asymmetric isomers of $[(HCl)(H_2O)]_2$. These isomers were identified experimentally.^{1,2} However, only one of these structures is a minimum structure in the B3LYP-D3 potential (6-311G** basis set), and is presented in Figure S5. This isomer is higher in energy than the symmetric H-bonded structure by 0.017 eV, and lower in energy than the ionic structure by 0.035 eV. None of the forty trajectories initiating with the ionic isomer (twenty at 200K and twenty more at 300K) resulted in a transition into this asymmetric configuration. Moreover, none of the forty trajectories that were initiated with this isomer resulted in proton transfers.



Figure S5. One of the two asymmetric isomers of the H-bonded [(HCl)(H₂O)]₂, calculated using the B3LYP-D3 potential, and the 6-311G** basis set.

4. Number of transitions during the one picosecond trajectory of the reaction $[(F^{-})(H_3O^{+})]_4 \rightarrow (symmetric)[(HF)(H_2O)]_4$

The number of transitions observed during each trajectory of the reaction $[(F^{-})(H_3O^{+})]_4 \rightarrow (symmetric)[(HF)(H_2O)]_4$ at 200K and at 300K is presented in Figure S6. We differentiated here between transition into conformer (d) and transitions into conformer (e).



Figure S6. The number of transitions observed in each trajectory of the reaction $[(F^{-})(H_3O^{+})]_4 \rightarrow (symmetric)[(HF)(H_2O)]_4$ at 200K and at 300K. Pie charts show the percentage of concerted transitions (brown), partially concerted transitions (purple), and non-concerted transitions (pink).

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