Supplementary Information

Table 1 Parameters of the radial symmetry functions [1] of type G^2 describing the environment of the hydrogen and oxygen atoms, respectively, for each possible neighboring element. A radial shift $R_{\mathrm{shift}} = 0.0$ Bohr and a cutoff radius $R_{\mathrm{c}} = 19.0$ Bohr have been used for all symmetry functions.

central atom	neighbor	η [Bohr^{-2}]
H	H	0.200
		0.070
		0.030
		0.010
	O	0.200
		0.070
		0.030
		0.010
O	H	0.200
		0.070
		0.030
		0.010
	O	0.030
		0.010
		0.001

Table 2 Parameters of the angular symmetry functions [1] of type G^4 employed to describe the environment of each atom with respect to the elements of the neighboring atoms. A cutoff radius $R_c = 19.0$ Bohr has been used to define the atomic environments.

central atom	neighbors	η [Bohr^{-2}]	λ	ζ
H	HH	0.200	1.0	1.0
		0.070	-1.0	1.0
		0.010	1.0	4.0
		0.001	-1.0	4.0
	OH	0.200	1.0	1.0
		0.070	1.0	1.0
		0.030	1.0	1.0
		0.010	1.0	4.0
		0.070	-1.0	1.0
		0.030	-1.0	1.0
		0.010	-1.0	4.0
	OO	0.030	1.0	1.0
		0.030	-1.0	1.0
		0.001	1.0	4.0
		0.001	-1.0	4.0
O	HH	0.070	1.0	1.0
		0.030	1.0	1.0
		0.010	1.0	4.0
		0.070	-1.0	1.0
		0.030	-1.0	1.0
		0.010	-1.0	4.0
	OH	0.030	1.0	1.0
		0.030	-1.0	1.0
		0.001	1.0	4.0
		0.001	-1.0	4.0
	OO	0.030	1.0	1.0
		0.030	-1.0	1.0

Table 3 Theoretical vibrational frequencies of the neural network (NN) and DFT-optimized protonated water clusters along with the experimental values. No frequency scaling has been applied. For a visualization of the cluster geometries cf. Table 2 in main text. For comparison also the values of the neutral water monomer are given.

cluster	description	calculated [cm^{-1}]		experimental [cm^{-1}]		
		NN	DFT	Ref. [2]	Ref. [3]	Ref. [4]
H_2O	H_2O bend	1583	1590			1595
	H_2O symmetric	3706	3706			3652
	H_2O asymmetric	3809	3814			3756
H_3O^+	H_3O^+ bend	844	847			526
	H_3O^+ symmetric	3483	3478			3390
	H_3O^+ asymmetric	3565	3566			3519
$H_5O_2^+$	proton oscillation	1076	1111	1085	920	
	H_2O symmetric	3634	3637	3520	3609	
	H_2O asymmetric	3726	3722	3660	3684	
$H_7O_3^+$	H_3O^+ asymmetric	2139	2147	1880		
	H_3O^+ symmetric	2428	2373	2420		
	H_2O symmetric	3680	3681	3639	3637	
	H_3O^+ free OH	3723	3704	3580	3667	
	H_2O asymmetric	3768	3772	3742	3722	
$H_9O_4^+$	H_3O^+ asymmetric	2666	2638	2665		
	H_3O^+ symmetric	2851	2805			
	H_2O symmetric	3698	3690	3644	3645	
	H_2O asymmetric	3775	3781	3730	3730	
$H_{11}O_5^+$	H_3O^+ asymmetric	2515	2570	2860	2879	
	H_3O^+ symmetric	2852	2839		2967	
	H bond asymmetric	3480	3459	3195	3208	
	H bond symmetric	3525	3497			
	H_2O symmetric	3690	3684	3647	3647	
	OH asymmetric	3760	3754	3712	3736	
	OH symmetric	3764	3755			
	H_2O asymmetric	3761	3772	3740	3817	
$H_{13}O_6^+$	H_3O^+ asymmetric	2546	2575			
	H_3O^+ symmetric	2919	2886			
	H bond asymmetric	3298	3294			
	H bond symmetric	3379	3363			
	H_2O symmetric	3696	3700	3650	3651	
	H_2O asymmetric	3782	3796	3740	3741	
$H_{15}O_7^+$	H_3O^+ asymmetric	2505	2524			
	H_3O^+ symmetric	3738	2760			
	H bond stretch	3443	3431			
	OH stretch	3739	3749			
$H_{17}O_8^+$	H_3O^+ asymmetric	2505	2518			
	H_3O^+ symmetric	2767	2754			
	H bond stretch	3275	3300			
	OH stretch	3737	3753			

References

[1] J. Behler, *J. Chem. Phys.*, 2011, **134**, 074106.

[2] J. M. Headrick, E. G. Diken, R. S. Walters, N. I. Hammer, R. A. Christie, J. Cui, E. M. Myshakin, M. A. Duncan, M. A. Johnson and K. D. Jordan, *Science*, 2005, **308**, 1765.

[3] L. Yeh, M. Okumura, J. Myers, J. Price and Y. Lee, *J. Chem. Phys.*, 1989, **91**, 7319.

[4] G. M. Chaban, J. O. Jung and R. B. Gerber, *J. Phys. Chem. A*, 2000, **104**, 2772.