Electronic Supplementary Information:

# Theoretical calculation of the vibrational state dependent photodetachment spectra of X<sup>-</sup>H<sub>2</sub>O, X=F, Cl, Br

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Comparison of the 4 dimensional vibrational calculation using B3LYP and MP2, comparison of the vibrational state dependent photodetachment spectra with DVR grid, the binding energies, figure of the vibrational state dependent photodetachment spectra for low frequencies, one dimensional cut of the potential energy curve, molecular orbitals of X<sup>-</sup>H<sub>2</sub>O, XYZ geometries of the calculated structures are provided.

## **Comparison of the vibrational calculations**

For the calculation of the vibrational state dependent photodetachment spectra, we need to obtain accurate vibrational wavefunctions. For X<sup>-</sup>H<sub>2</sub>O system, Ar-tagging experimental spectra have been performed by Horvath et al.<sup>1,2</sup> for high frequency vibrations. Therefore, we first tested the calculated peak positions for 4 selected vibrations calculated by B3LYP/6-31+G(d,p) and MP2/6-311++G(3df,3pd). Considering their importance, we selected, the H<sub>2</sub>O in plane wagging, H<sub>2</sub>O out of plane wag, H<sub>2</sub>O bending, and IHB OH stretching modes. For Cl<sup>-</sup>H<sub>2</sub>O and Br<sup>-</sup>H<sub>2</sub>O, as given in Table S1 and S2, the peak positions calculated by B3LYP and MP2 are within  $\sim 30 \text{ cm}^{-1}$  of each other, thus considering the computational efficiency we use the B3LYP method for the 6-dimentional calculation. On the other hand, for F<sup>-</sup>H<sub>2</sub>O, given in Table S3, the MP2 and B3LYP values show much larger variations, and we decided to use MP2 for the 6-dimentional vibrational calculation. Another important observation, is that the fundamental H<sub>2</sub>O in plane wagging peak positions vary greatly compared to the 6-dimensional results in Table 1 of the main text. This signifies the huge coupling between the H<sub>2</sub>O in plane wagging and the X<sup>-</sup>...H<sub>2</sub>O van der Waals stretching mode.

Table S1: The calculated 4-dimension vibrational peak position in cm<sup>-1</sup> and absorption intensity in km mol<sup>-1</sup> for Cl<sup>-</sup>H<sub>2</sub>O at B3LYP/6-31+G(d,p) and MP2/6-311++G(3df,3pd) level of theory.

Assignment	B3LYP/6-31+G(d,p)		MP2/6-311++G(3df,3pd)		Experimental
	Peak	Intensity	Peak	Intensity	peak position
	position		position		
(0,1,0,0,0,0)	542	62	571	52	
(0,0,1,0,0,0)	715	128	739	88	738
(0,0,2,0,0,0)	1392	68	1435	72	1404
(0,0,0,1,0,0)	1647	97	1661	94	1653
(0,0,0,2,0,0)	3286	27	3310	17	3289
(0,0,0,0,1,0)	3125	1012	3127	1052	3146

Table S2: The calculated 4-dimension vibrational peak position in cm<sup>-1</sup> and absorption intensity in km mol<sup>-1</sup> for Br<sup>-</sup>H<sub>2</sub>O at B3LYP/6-31+G(d,p) and MP2/6-311++G(3df,3pd) level of theory.

Assignment	B3LYP/6-31+G(d,p)		MP2/6-311++G(3df,3pd)		Experimental
	Peak	Intensity	Peak	Intensity	peak position
	position		position		
(0,1,0,0,0,0)	531	55	524	50	
(0,0,1,0,0,0)	673	106	652	87	664
(0,0,2,0,0,0)	1308	57	1275	50	1262
(0,0,0,1,0,0)	1634	92	1647	101	1647
(0,0,0,2,0,0)	3279	139	3311	360	3238
(0,0,0,0,1,0)	3203	794	3261	492	3296

Table S3: The calculated 4-dimension vibrational peak position in cm<sup>-1</sup> and absorption intensity in km mol<sup>-1</sup> for F<sup>-</sup>H<sub>2</sub>O at B3LYP/6-31+G(d,p) and MP2/6-311++G(3df,3pd) level of theory.

Assignment	B3LYP/6-31+G(d,p)		MP2/6-311++G(3df,3pd)		Experimental
	Peak	Intensity	Peak	Intensity	peak position
	position		position		
(0,1,0,0,0,0)	742	29.5	774	19	
(0,0,1,0,0,0)	1173	109	1232	109	1250
(0,0,0,1,0,0)	1668	226	1671	38	1650
(0,0,0,2,0,0)	3311	8	3320	2	
(0,0,0,0,1,0)	1505	1664	1360	2875	1523
(0,0,0,0,2,0)	3013	50	2857	132	2815-2930

### **Binding Energies**

In the table below, we list the zero-point corrected binding energies for the X<sup>-</sup>H<sub>2</sub>O cluster calculated using B3LYP and MP2 methods.

Table S4: The zero-point corrected binding energies, in kcal mol<sup>-1</sup>, for X<sup>-</sup>H<sub>2</sub>O calculated using B3LYP/6-31+G(d,p) and MP2/6-311++G(3df,3pd) level of theory. The single point basis set super position counter poise correction energies, in kcal mol<sup>-1</sup>, are given in parenthesis.

	B3LYP	MP2
F <sup>-</sup> H <sub>2</sub> O	28.20 (0.75)	28.47 (2.72)

Cl <sup>-</sup> H <sub>2</sub> O	13.62 (0.16)	14.20 (1.30)
Br <sup>-</sup> H <sub>2</sub> O	12.77 (1.25)	12.03 (0.89)

#### **Convergence of the photodetachment spectra**

For the calculation of the vibrational state dependent photodetachment spectra, we must check the convergence of the discrete variable representation (DVR) grid points. In the main text we report results obtained from 9 grid points per each degree of freedom. In Figure S1 we compare the F<sup>-</sup>H<sub>2</sub>O results obtained using 11 grid points for the three lowest vibrational modes and 15 grid points for the three high frequency vibrational modes. Here we used the MP2/6-311++G(3dp,3pd) to calculate the required potential energy surface for the anion ground electronic state, while B3LYP/6-31+G(d,p) were used for the vertical detachment energies. It can be observed that the bigger grid will give more smooth curves, but the difference in the two spectra V's small enough that the general trend can be obtained from the 9 grid point results.



Figure S1: Calculated vibrational state dependent photodetachment spectra of  $F^-H_2O$ . The quantum numbers for the vibrational state are given on the left. The solid line results are for the 9 grid point results while the dotted line results are for the bigger grid.

In Figure S2 we present the difference photodetachment spectr b to clarify the variations from the results of the zero-point vibration. In Figure S3 and S4 the results for the excitation of the low frequency modes, as well as their difference spectra are presented. One can notice that other than the out of plane wagging which breaks the ionic hydrogen bonding (IHB) in X<sup>-</sup>H<sub>2</sub>O, the variation from the zero-point vibration is small.



Figure S2 Difference between the photodetachment spectra obtained for the vibrational excited state and the vibrational ground state for the H<sub>2</sub>O bending (dark blue), IHB OH stretching (red), H<sub>2</sub>O bending overtone (light blue) and the free OH stretching (brown) for (a)  $F^-H_2O$ , (b) Cl<sup>-</sup>H<sub>2</sub>O, and (c) Br<sup>-</sup>H<sub>2</sub>O. When calculating the difference spectra we did not correct for the energy shift due to the vibrational excitation.



Figure S3 Calculated vibrational state dependent photodetachment spectra of (a)  $F^{-}H_2O$ , (b)Cl<sup>-</sup>H\_2O, and (c) Br<sup>-</sup>H\_2O. The quantum numbers for the vibrational state are given on the left and the gray spectra at the bottom is the calculated spectra for the respective halogen anion. The black dashed spectra is the experimental results of Yang et al.<sup>3</sup> for F<sup>-</sup>H\_2O, and Cl<sup>-</sup>H\_2O. The black dotted spectra is the experimental results of Markovich et al.<sup>4</sup> for Cl<sup>-</sup>H\_2O and Br<sup>-</sup>H\_2O. The color coding of the vibrational state matches those given in Figure 1 of the main text.



Figure S4 Difference between the photodetachment spectra obtained for the vibrational excited state and the vibrational ground state for the X<sup>-</sup>...H<sub>2</sub>O van der Waals stretching (light green), H<sub>2</sub>O in plane wag (yellow), H<sub>2</sub>O out of plane wag (dark green) and H<sub>2</sub>O out of plane wag overtone (black) for (a) F<sup>-</sup>H<sub>2</sub>O, (b) Cl<sup>-</sup>H<sub>2</sub>O, and (c) Br<sup>-</sup>H<sub>2</sub>O. When calculating the difference spectra we did not correct for the energy shift due to the vibrational excitation.

In Figure S5 we plot the potential energy curve along the IHB OH stretching and  $H_2O$  bending normal mode for X<sup>-</sup>H<sub>2</sub>O and XH<sub>2</sub>O while keeping all other degrees of freedom in their equilibrium values. One can clearly notice that in the case of F<sup>-</sup>H<sub>2</sub>O, the elongation of the IHB OH results in a large decrease in the neutral potential energy curve which is due to the fact that formation of FH...OH is exothermic compared to F...H<sub>2</sub>O. For ClH<sub>2</sub>O and BrH<sub>2</sub>O, the IHB OH curve has a more sharp increase compared to their anion counterpart. On the other hand, for the bending modes in Cl<sup>-</sup>H<sub>2</sub>O and Br<sup>-</sup>H<sub>2</sub>O, the anion state has a tighter feature compared to the neutral state.



Figure S5 One dimensional potential energy cut along the IHB OH stretching and  $H_2O$  bending normal mode. The solid line is for the anion (left axis) and the dotted line (right axis) is for the neutral.

## Details on the excited electronic states of XH<sub>2</sub>O

In Figure S6, we present the highest occupied molecular orbital (HOMO) and the 3 orbitals below that for X<sup>-</sup>H<sub>2</sub>O (X=F, Cl, and Br) calculated using Hartree Fock (HF) with the 6-311++G(3df,3pd) basis set. The ground electronic state, first, second, and third excited states of the neutral XH<sub>2</sub>O calculated using the EOM-CCSD mainly corresponds to the ionization from HOMO, HOMO-1,HOMO-2, and HOMO-3. Other than the case for F<sup>-</sup>H<sub>2</sub>O, which shows large charge transfer with the water molecule, HOMO, HOMO-1, and HOMO-2 correspond to the valance p-orbitals of the halogen atom, while HOMO-3 is the out of plane 2p-orbital of the oxygen atom of H<sub>2</sub>O.



Figure S6 The highest occupied molecular orbital (HOMO) and MOs below the HOMO calculated by HF/6-311++G(3df,3pd) for (a)-(d)  $F^-H_2O$ , (e)-(h)  $Cl^-H_2O$ , and (i)-(l)  $Br^-H_2O$ .

# **XYZ** geometries

The XYZ geometries of X<sup>-</sup>H<sub>2</sub>O are given in Å for F<sup>-</sup>H<sub>2</sub>O, Cl<sup>-</sup>H<sub>2</sub>O, and Br<sup>-</sup>H<sub>2</sub>O at B3LYP/6-31+G(d,p) and MP2/6-311++G(3df,3pd) level of theory.

F-(H <sub>2</sub> O) B3LY	(P/6-31+G(d,p))		
F	0.047385	1.242434	0.000000
0	0.047385	-1.207506	0.000000
Н	0.095724	-0.143291	0.000000
Н	-0.901260	-1.378574	0.000000
F <sup>-</sup> H <sub>2</sub> O MP2/6	-311++G(3df,3p	od)	
F	0.048232	1.226272	0.000000
0	0.048232	-1.192962	0.000000
Н	0.073042	-0.125515	0.000000
Н	-0.892983	-1.367235	0.000000
Cl <sup>-</sup> H <sub>2</sub> O B3LY	P/6-31+G(d,p)		
Ο	0.028811	2.020869	0.000000
Н	0.215440	1.046495	0.000000

Н	-0.935726	2.032434	0.000000	
Cl	0.028811	-1.132110	0.000000	
Cl <sup>-</sup> H <sub>2</sub> O MP2/6	5-311++G(3df,3p	d)		
Ο	0.030556	1.980687	0.000000	
Н	0.162438	1.002537	0.000000	
Н	-0.926347	2.028277	0.000000	
Cl	0.030556	-1.110371	0.000000	
Br <sup>-</sup> H <sub>2</sub> O B3LYP/6-31+G(d,p)				

	-		
0	0.017373	2.622607	0.000000
Н	0.200148	1.651816	0.000000
Н	-0.947185	2.643835	0.000000
Br	0.017373	-0.722186	0.000000

#### Br<sup>-</sup>H<sub>2</sub>O MP2/6-311++G(3df,3pd)

0	0.017399	2.587157	0.000000
Н	0.192910	1.622453	0.000000
Η	-0.941070	2.589364	0.000000
Br	0.017399	-0.711688	0.000000

# References

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