Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information of Modeling of laser-pulse induced small water clusters-$(H_2O)_N$ ($_N$=1-10) decomposition on suitable metal cluster catalysts

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Laser Setting

People usually utilize intensity to describe the strength of laser field rather than the electric-field amplitude. The relationship between instantaneous electric field (*I(t)*) and amplitude(*E(t)*) in atomic units can be described as:

$$I(t) = \frac{c}{8\pi}E^2(t) \tag{1}$$

To describe the laser intensity in W/cm^2, a series of conversions should be performed. The dimensions of intensities are [W]/(L^{2}T), where [W] are the dimensions of energy. The relevant conversion factors are as follows:

$$\text{Hartree}/(a_0^2 \text{atomictime}) = 6.364086\times10^{15}\ \text{W/cm}^2 \tag{2}$$

$$\text{eV}/(\text{Å}^2(\hbar/eV)) = 2.4341348\times10^{12}\ \text{W/cm}^2 \tag{3}$$

$$I_0 = 3.51\times10^{16}\ \text{W/cm}^2(E_0^2)\quad \text{(a.u.)} \tag{4}$$

$$1E_0\text{(a.u.)}=1\ \text{Hartree/bohr/e} = 51.423\ \text{(V/Å)} \tag{5}$$

According to these equations, we can get the laser amplitudes and their intensities we used in this paper.

Table S1 Amplitude & intensity of the applied lasers

2.5	3.0	4.5	5	6	7	7.5	8	V/Å
0.83	1.19	2.69	3.32	4.78	6.50	7.47	8.49	$\times10^{14}$ W/cm^2

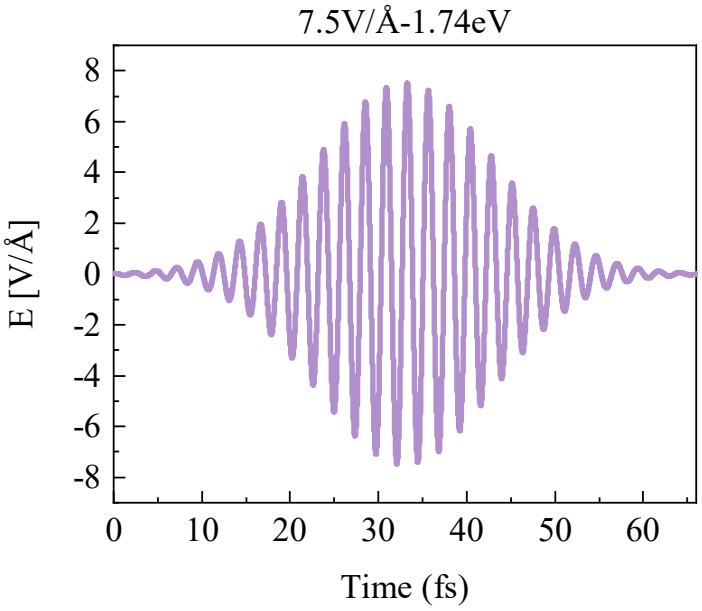


Figure S 1 Waveform of the incident laser pulse (7.5V/ Å-1.74eV-66fs).

The laser field reaches the maximum amplitude Emax = 7.5 V/Å at the time t0 = 33 fs, corresponding to a laser intensity of ~7.47 × 10^{14} W/cm^2.

Criteria for OH bond breakage

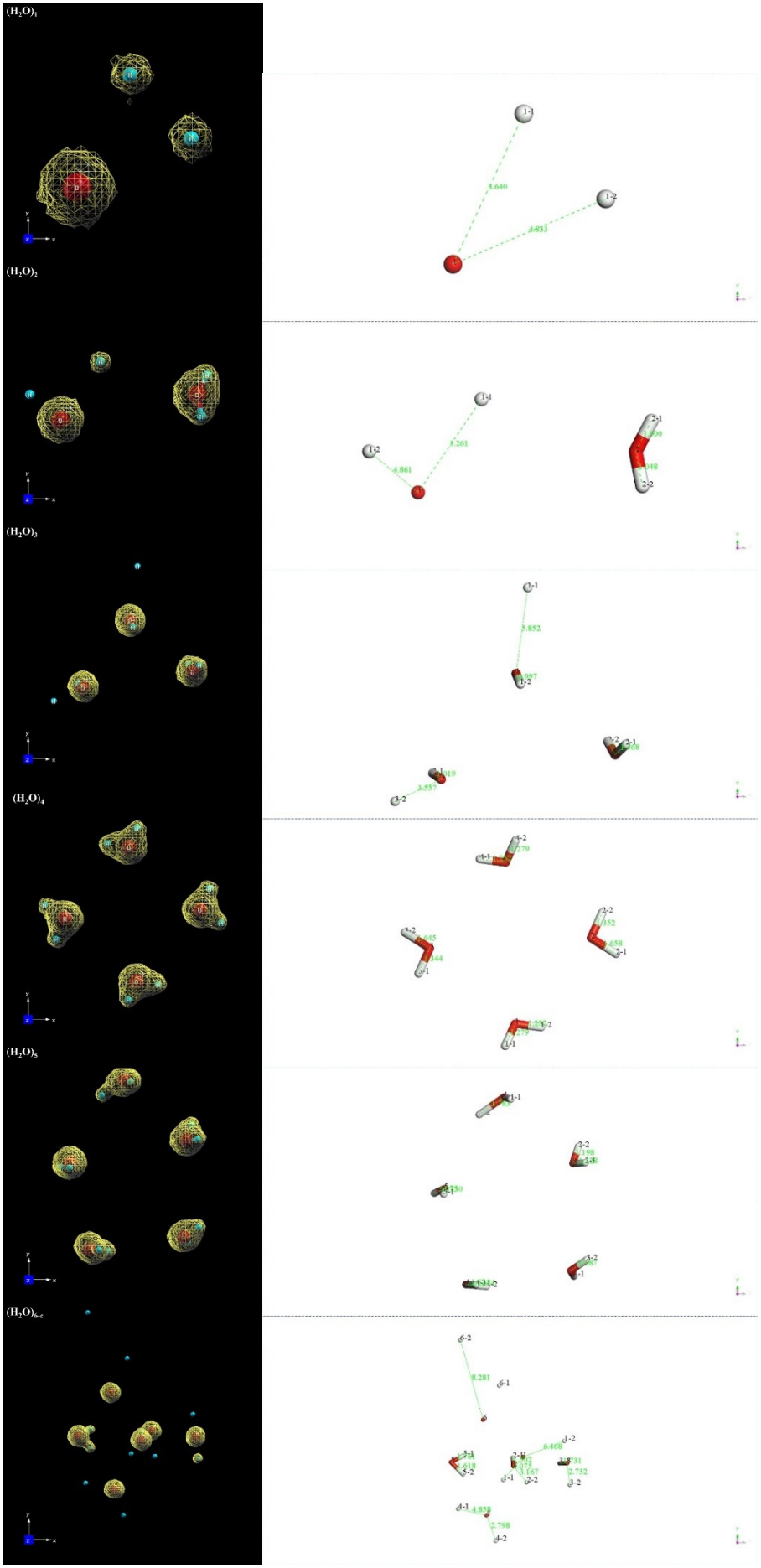
According to the report[1], the cleavage of an OH bond in a water molecule requires the adsorption of 100 kcal/mol of photon energy, which is about 4.86 eV. At present, the critical bond lengths for OH breakage in water molecules to determine the decomposition of water molecules are not uniform. For example, there are different published results as 2.00 Å[2], 2.84 Å[3], >3.00 Å[4, 5] and so on. In this paper, by calculating the photolysis of $(H_2O)_N$, ($_N$=1-10) water clusters under the condition of 7.5 V/Å-1.74 eV-66 fs pulsed laser, recording the final state ELF image of the water molecule dissociation and being marked with the structural images of the bond length shown in Figure S2, the maximum unbroken bond and the minimum broken bond of the OH bond length in each water cluster are summarized in the Table S1.

We regard the OH bonds that still have charge localization between OHs in the final ELF diagram as intact OH bonds, and the OH bonds that have no charge localization around the OH bonds as broken bonds. As can be seen from Figure S2, under the 7.5 V/Å-1.74 eV-66 fs laser, for single-molecule water $(H_2O)_1$, the two OH bonds are all broken; the water molecules are

completely decomposed; and the nearest distance between O and H atoms of original water molecule is 3.64 Å. For the dimer water cluster $(H_2O)_2$, only two OHs of one water molecule are broken; and the other water molecule remains intact, that is, 50% of the OH bonds are broken; Among them, the largest length of the unbroken OH bond could be 1.048 Å, and the nearest distance broken O and H atom of an original OH bond could be 3.261 Å. Similarly, for the maximum unbroken bond length, we can get 1.368 Å for the trimeric water cluster $(H_2O)_3$, 1.658 Å for the tetrameric water cluster $(H_2O)_4$, 1.783 Å for the pentameric water cluster $(H_2O)_5$, 1.761 Å for the caged hexameric water cluster $(H_2O)_{6\text{-}c}$, 1.752 Å for the prismatic hexameric water cluster $(H_2O)_{6\text{-}p}$, 1.761 Å for the heptameric water cluster ($H_2O)_7$, 1.62 Å for the octameric water cluster $(H_2O)_8$, 1.764 Å for the nonameric water cluster $(H_2O)_9$, and 1.453 Å for the decamer water cluster $(H_2O)_{10}$. For the broken bonds, the nearest distance between O and H atoms of original bond, we can get 3.640 Å, 3.261 Å, 3.557 Å, 3.261 Å, 1.847 Å, 1.819 Å, 1.834 Å, 1.929 Å and 1.906 Å as Minimum Broken Bond respectively. In short, among all the 11 water clusters, the minimum distance between the broken bonds is 1.819 Å, and the largest unbroken bond length is 1.783 Å. In conclusion, 1.8 Å could be set as the breaking critical bond length of the OH bond in the water molecule.

Table S 1 The length of the OH bond in the final state of the system when the water cluster $(H_2O)_N$, ($_N$=1-10) photolysis occurs

$(H_2O)_N$	Maximum Unbroken OH Bond	Minimum Broken **B**ond
$(H_2O)_1$	-	3.640 Å
$(H_2O)_2$	1.048 Å	3.261 Å
$(H_2O)_3$	1.368 Å	3.557 Å
$(H_2O)_4$	1.658 Å	-
$(H_2O)_5$	1.783 Å	-
$(H_2O)_{6\text{-}c}$	1.761 Å	3.261 Å
$(H_2O)_{6\text{-}p}$	1.752 Å	1.847 Å
$(H_2O)_7$	1.761 Å	1.819 Å
$(H_2O)_8$	1.620 Å	1.834 Å
$(H_2O)_9$	1.764 Å	1.929 Å
$(H_2O)_{10}$	1.453 Å	1.906 Å


(H2O)1
(H2O)2
(H2O)3
(H2O)4
(H2O)5
(H2O)6-c

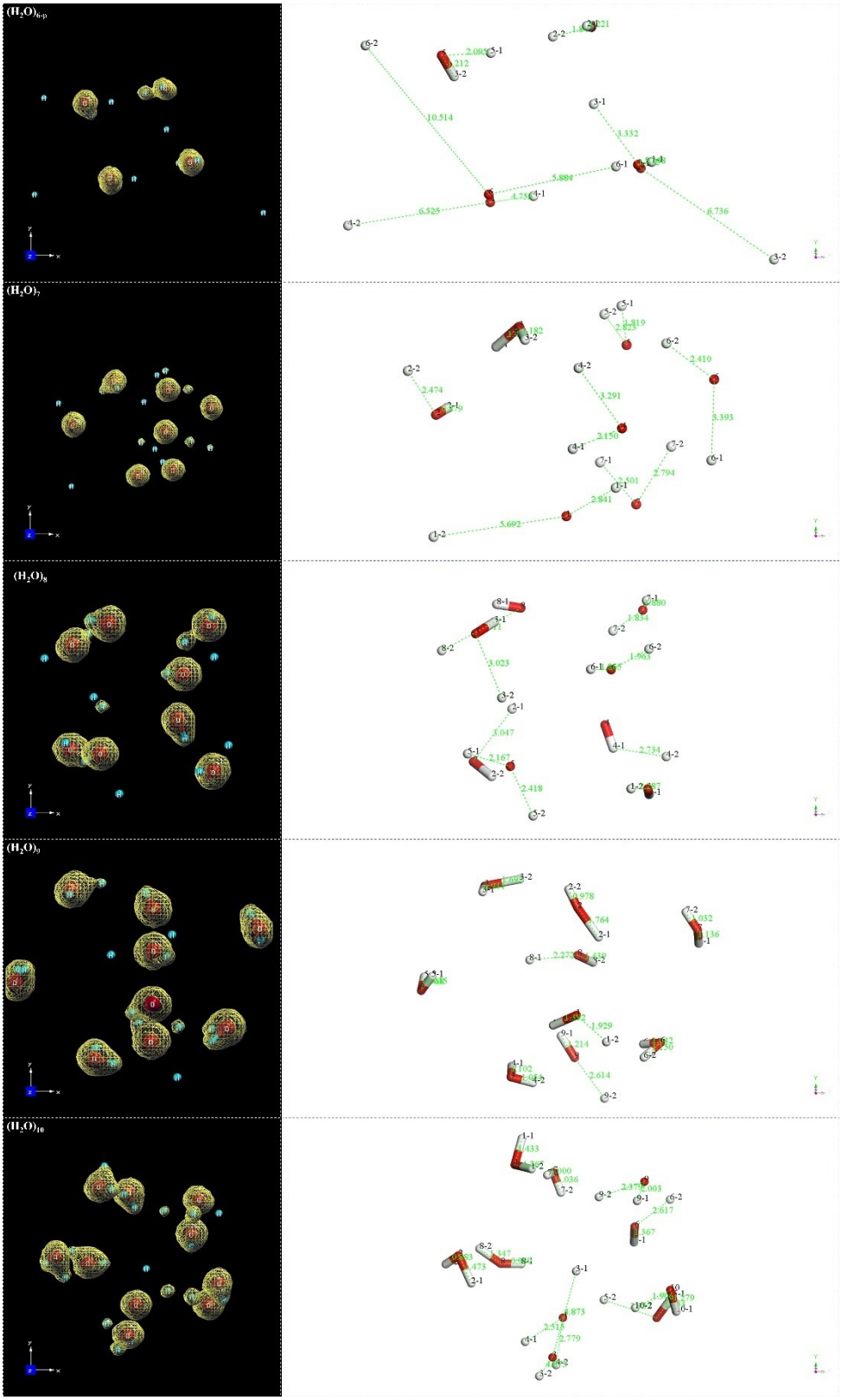
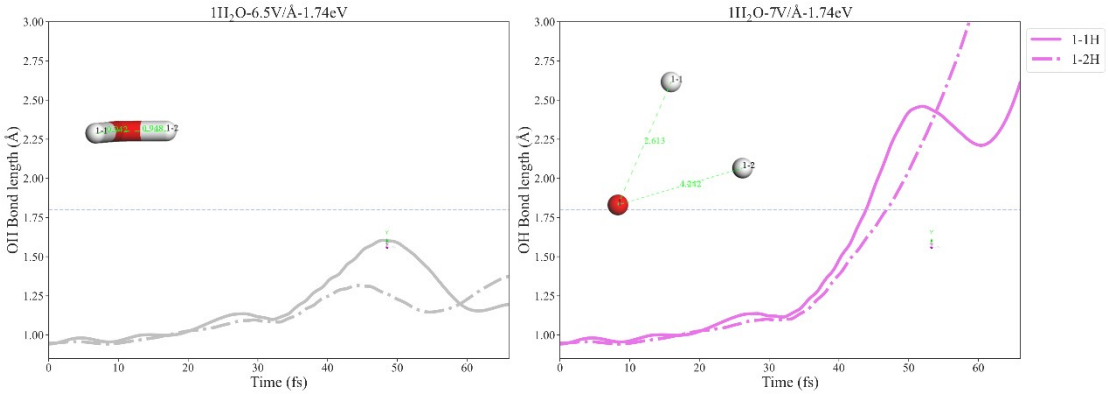


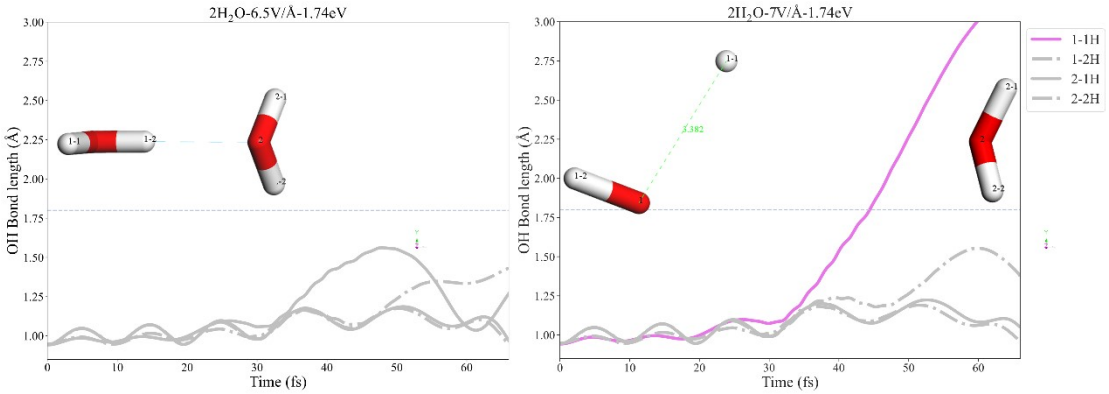
Figure S 2 Final ELF and structure diagram of Water cluster $(H_2O)_N$ ($_N$=1-10) under laser (laser: 7.5 V/Å-1.74 eV-66 fs)

Threshold identification

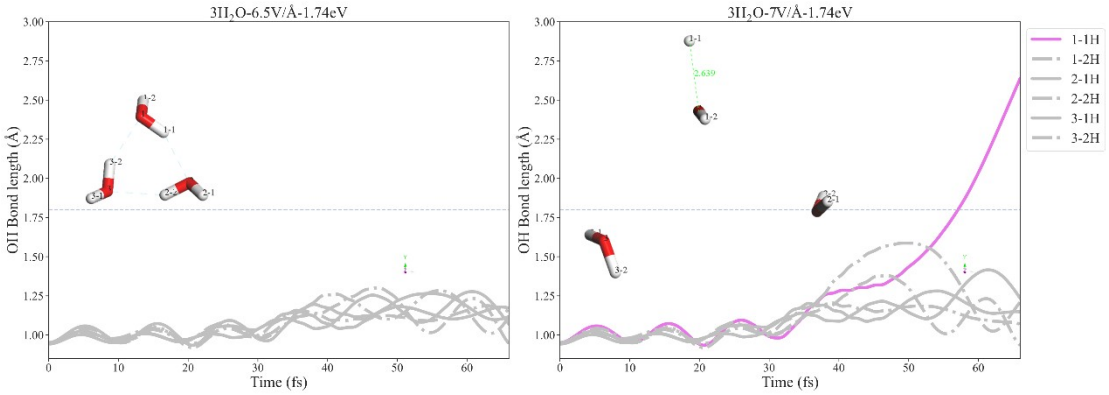
S3-1: $(H_2O)_1$-7V/Å -1.74 eV-66 fs



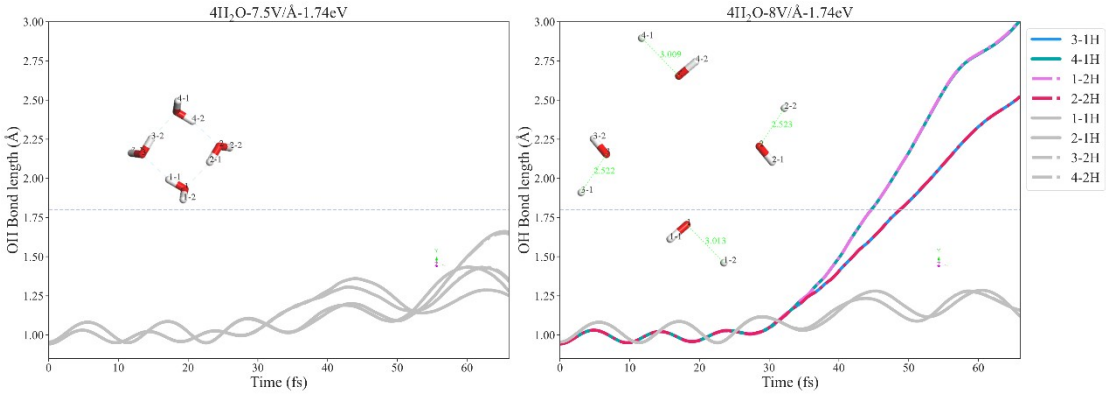
S3-2: $(H_2O)_2$-7 V/Å-1.74 eV



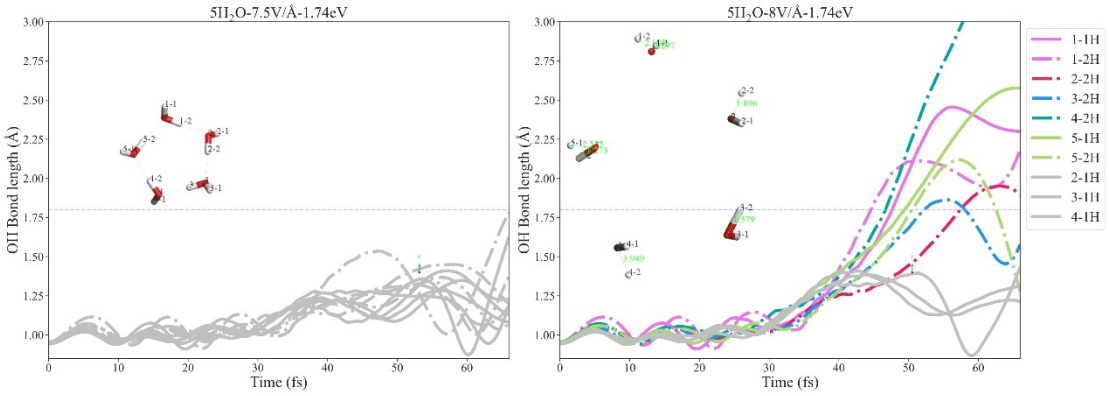
S3-3: $(H_2O)_3$-7 V/Å-1.74 eV



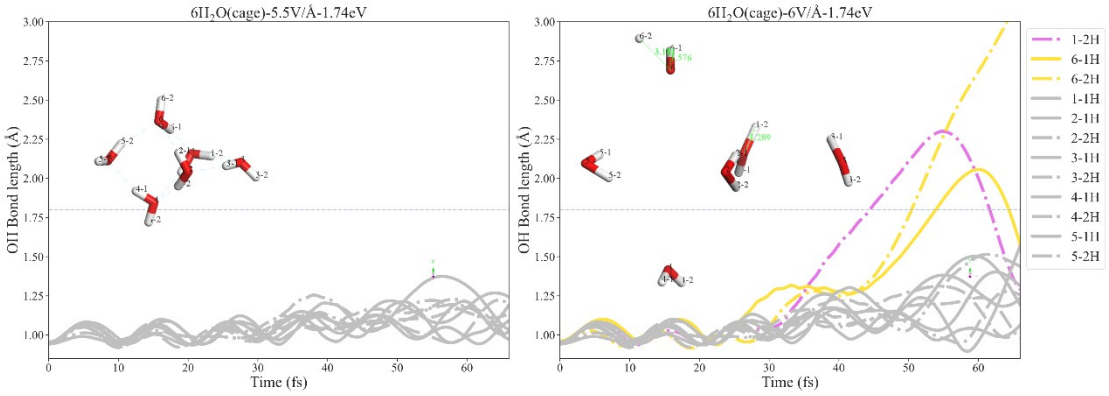
S3-4: $(H_2O)_4$-8 V/Å-1.74 eV



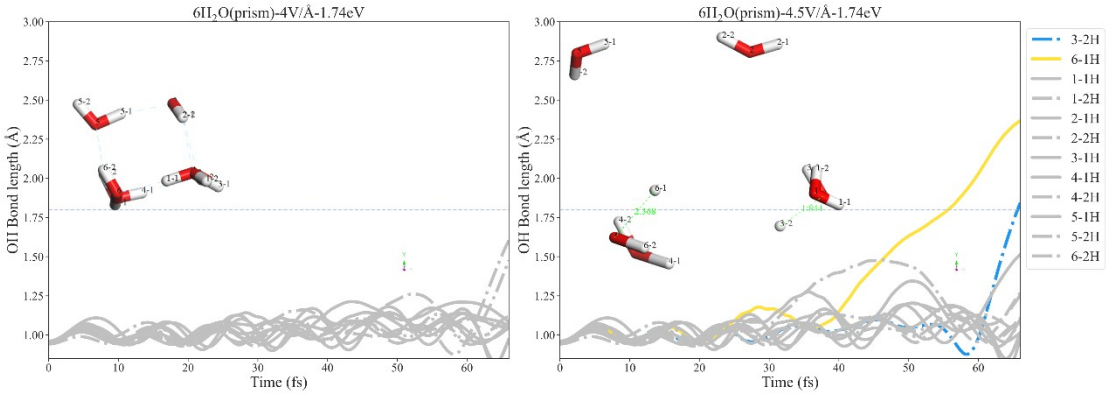
S3-5: $(H_2O)_5$-8 V/Å-1.74 eV



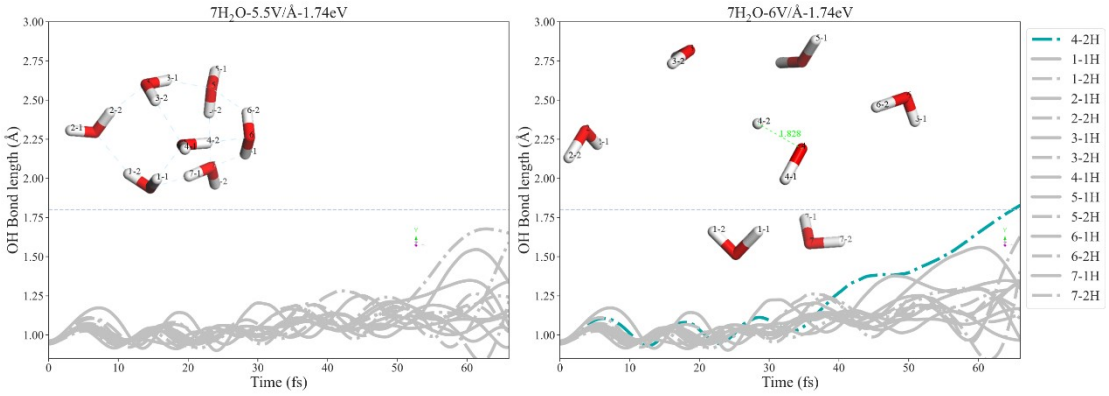
S3-6: $(H_2O)_{6\text{-}p}$-4.5 V/Å-1.74 eV



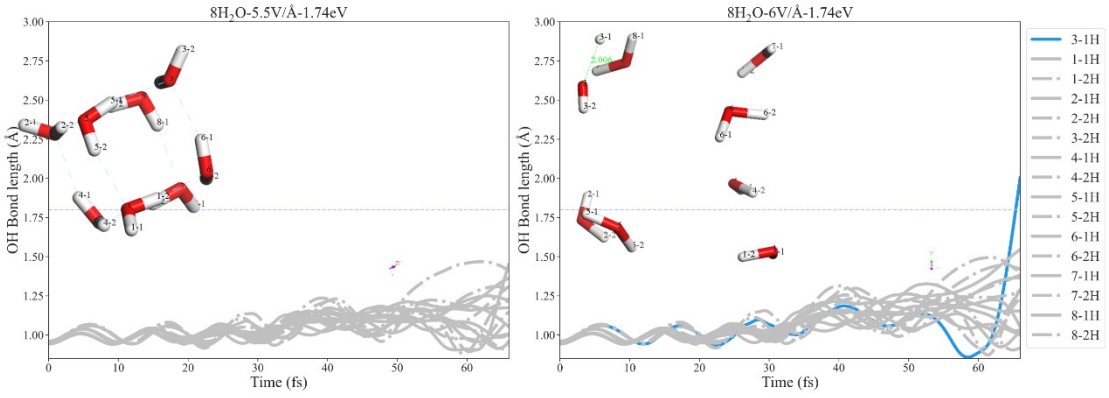
S3-7: $(H_2O)_{6\text{-}c}$-6 V/Å-1.74 eV



S3-8: $(H_2O)_7$-6 V/Å-1.74 eV



S3-9: $(H_2O)_8$-6 V/Å-1.74 eV



S3-10: $(H_2O)_1$-6.5V/Å -1.74 eV-200 f

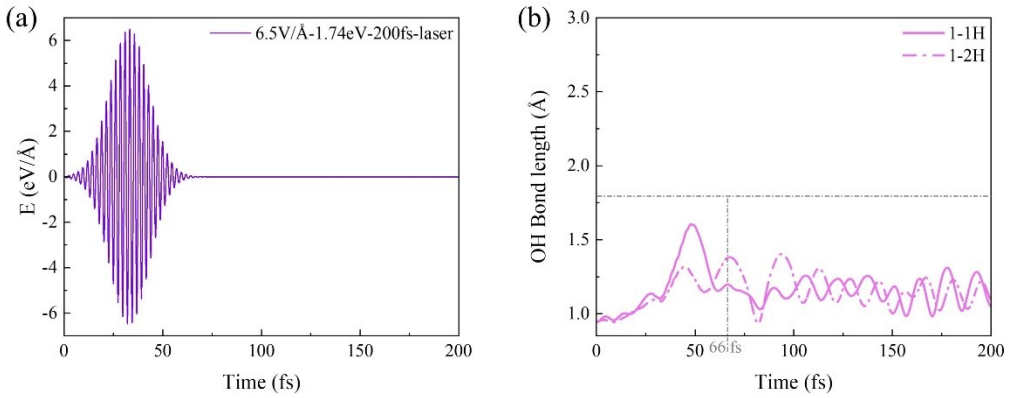


Figure S 3 Time evolution of the lengths of OH bonds of water clusters, (S2-1) H_2O (S2-2) $(H_2O)_2$ (S2-3) $(H_2O)_3$ (S2-4) $(H_2O)_4$ (S2-5) $(H_2O)_5$ (S2-6) $(H_2O)_{6\text{-}p}$ (S2-7) $(H_2O)_{6\text{-}c}$ (S2-8) $(H_2O)_7$ (S2-9) $(H_2O)_8$, in laser-induced photodissociation processes, where the intensities of 1.74 eV-66 fs-lasers are at their threshold (right) and 0.5 V/Å lower than their threshold; S2-10 Time evolution of the lengths of OH bonds of monomer water under the laser 6.5V/ Å -1.74 eV-66 fs propagating for 200 fs. The grey horizontal dotted line indicates the critical value. The insets are the initial snapshots (in the left panel) and final snapshots (in the right panel) of the dissociation process with atoms stamped.

Hydrogen Dissociation Dynamics from $(H_2O)_4$ Cluster

HOMO and LUMO orbitals of the $(H_2O)_4$ cluster before and after laser irradiation

Finally, to further examine the polarization and subsequent dissociation dynamics of the O–H bonds in the $(H_2O)_4$ cluster, the Kohn-Sham orbitals were computed as the wave function of time in Figure S4. We used the following visualization scheme with iso-value being 0.05 in Figure S4, and its color (red and green) represents its phase (positive and negative). At T = 0 fs, the highest occupied molecular orbital (HOMO) is occupied by a pair of lone pairs since the electron distribution is centered around the O atom but not on the O-H line indicating that the electrons of the HOMO orbital are not involved in the O-H bond formation. The Lowest Unoccupied Molecular Orbital (LUMO) locates the antibonding position of O-H, as the electron density is mainly concentrated in the connection of O and H atoms, but not between them. Over time, the

electrons distribution of HOMO and LUMO remains similar to the initial situation until the water molecule breaks. The distribution of positive charge in HOMO and LUMO is concentrated on the free H atoms.

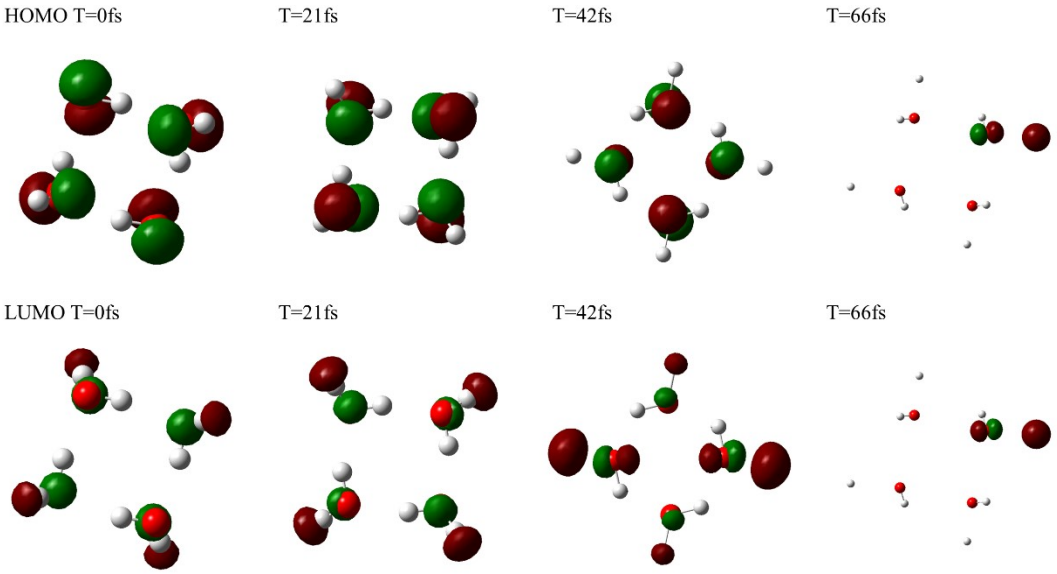


Figure S 4 Time evolution of charge distribution in HOMO (up) and LUMO (down) orbitals of $(H_2O)_4$ cluster in a laser-induced photodissociation process, where the intensities of 1.74 eV-66 fs-lasers are 8V/Å.

Compound structures with Ag_6 and $(H_2O)_4$

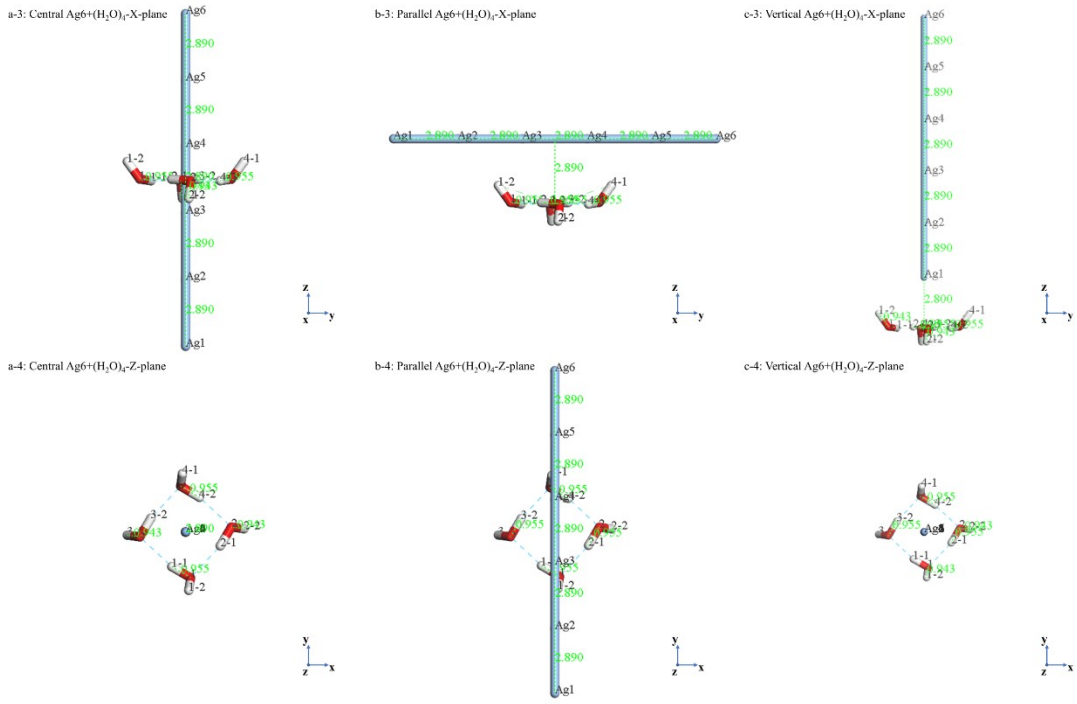


Figure S 5 The compound structures of (a) central (b)parallel and (vertical) Ag_6 chain and $(H_2O)_4$ cluster.

Adsorption Spectrum

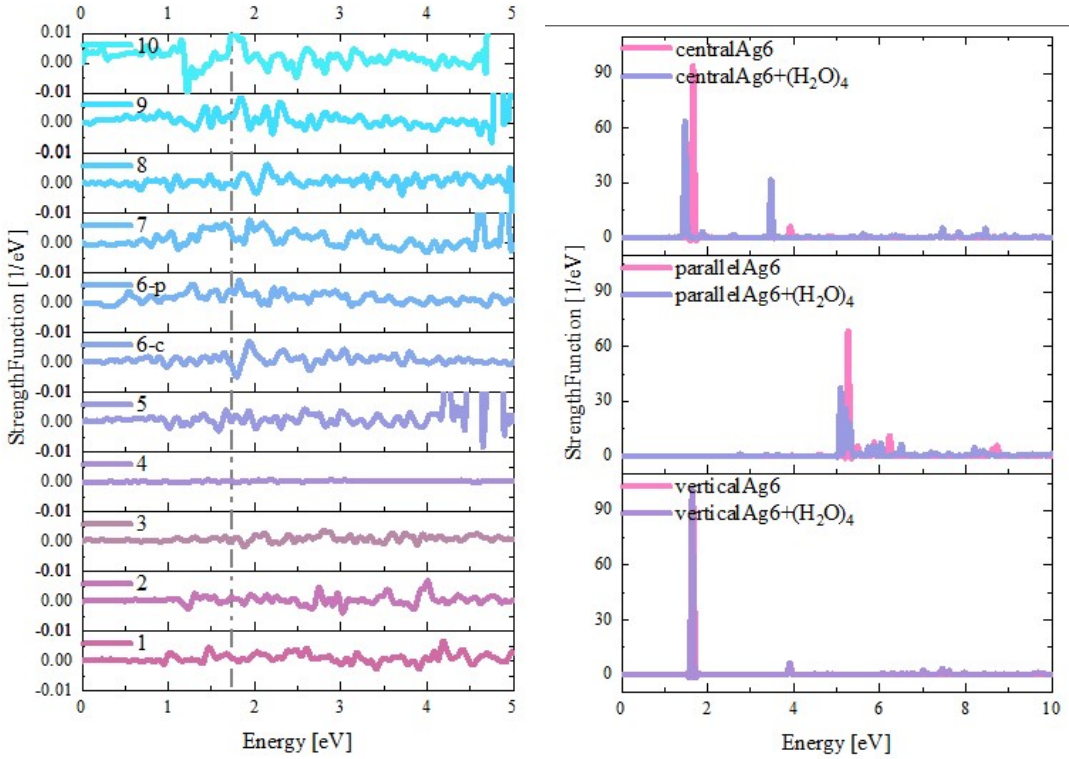


Figure S 6 Optical absorption spectrum of the pure water clusters (left) and compound structures of $(H_2O)_4$ cluster with Ag_6 chain rectangular monolayer phosphorene nanostructures to an impulse excitation polarized in theX-axis(a)andY-axis(b)directions.

[1] N.J. Turro, Modern Molecular Photochemistry, 1978).

[2] L. Yan, J. Xu, F. Wang, S. Meng, Plasmon-Induced Ultrafast Hydrogen Production in Liquid Water, Journal of Physical Chemistry Letters 9 (2018) 63-69.

[3] L. Yan, F. Wang, S. Meng, Quantum Mode Selectivity of Plasmon-Induced Water Splitting on Gold Nanoparticles, ACS Nano 10 (2016) 5452-5458.

[4] Y. Miyamoto, H. Zhang, X. Cheng, A. Rubio, Ab initio simulation of laser-induced water decomposition close to carbon nanotubes, Phys. Rev. B: Condens. Matter 99 (2019) 165424.

[5] Y. Miyamoto, H. Zhang, X. Cheng, A. Rubio, Modeling of laser-pulse induced water decomposition on two-dimensional materials by simulations based on time-dependent density functional theory, Physical Review B: Condensed Matter 96 (2017) 115451.