

Supporting Information

-for-

Conformational structures of jet-cooled acetaminophen-water clusters: A gas phase spectroscopic and computational study

Ahreum Min,^{a,†} Ahreum Ahn,^{a,†} Cheol Joo Moon,^{a,†} Ji Hoon Lee,^a Yeon Guk Seong,^a Seong Keun Kim,^{b,*} Myong Yong Choi^{a,*}

^a Department of Chemistry (BK21+) and Research Institute of Natural Science, Gyeongsang National University, Jinju 52828, Republic of Korea.

^b Department of Chemistry, Seoul National University, Seoul 08826, Republic of Korea.

* To whom correspondence should be addressed: mychoi@gnu.ac.kr, Tel: +82-55-772-1492, Fax: +82-55-772-1489

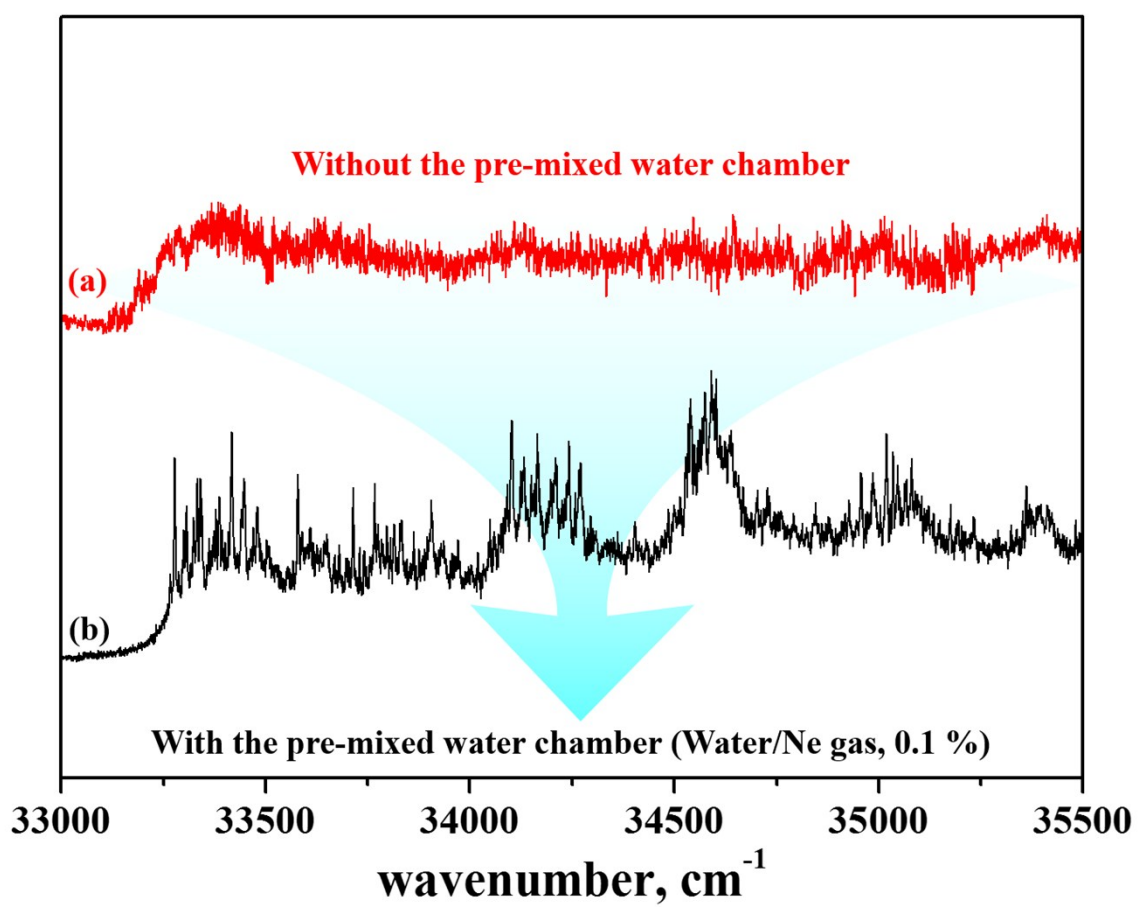


Figure S1. The R2PI spectra of $\text{AAP}-(\text{H}_2\text{O})_1$ without the pre-mixed water chamber (a) and with the pre-mixed water/Ne gas about 0.1 % (b) are compared.

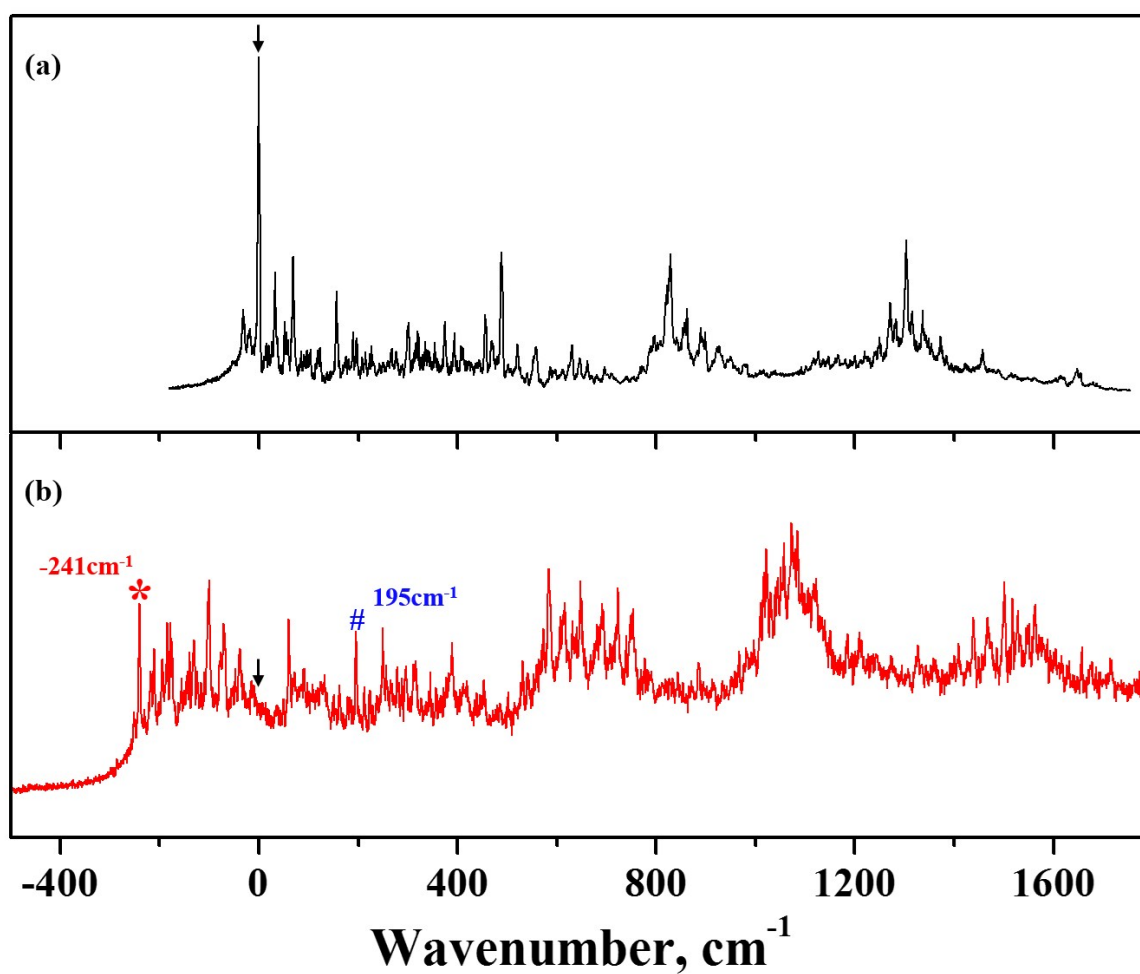


Figure S2. A comparison of the R2PI spectrum of (a) AAP and (b) $\text{AAP}-(\text{H}_2\text{O})_1$. The origin band of two conformer of $\text{AAP}-(\text{H}_2\text{O})_1$, “*” and “#” is shifted to red (-241 cm^{-1}) and blue (195 cm^{-1}), respectively, to those of the AAP marked by an down arrow.

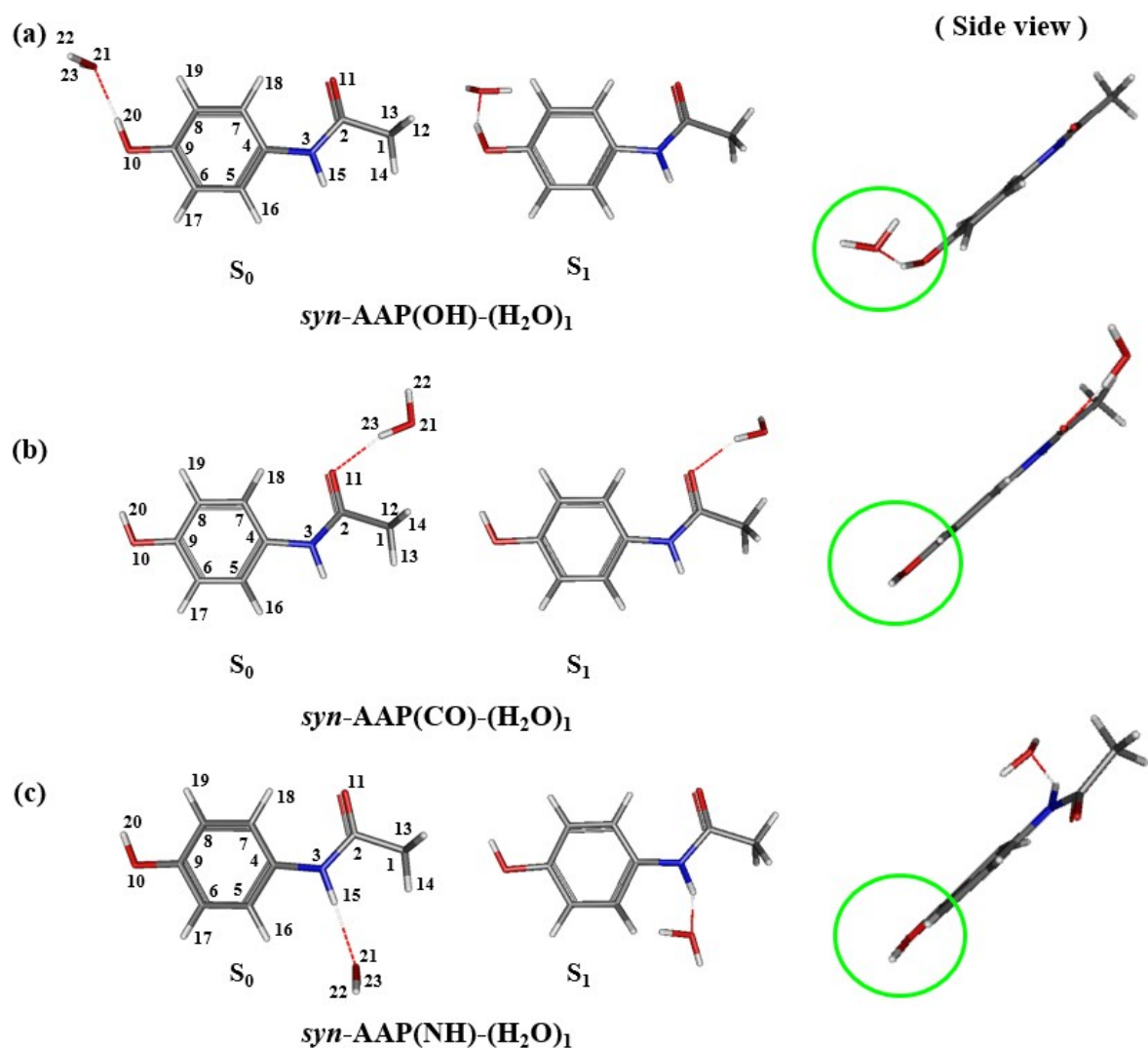


Figure S3. Fully optimized structures of 3 different *syn*-conformers of AAP-(H₂O)₁ in the ground (S_0) and excited (S_1) states, calculated at the wB97XD and TD-wB97XD level, respectively, with a 6-311++G(d,p) basis set. The side view shows the optimized structures of each *syn*-conformer in their S_1 state. The hydroxyl group (marked by an oval) of (a) AAP(OH)-(H₂O)₁ is significantly perturbed by the intermolecular hydrogen bond caused by the water molecule.

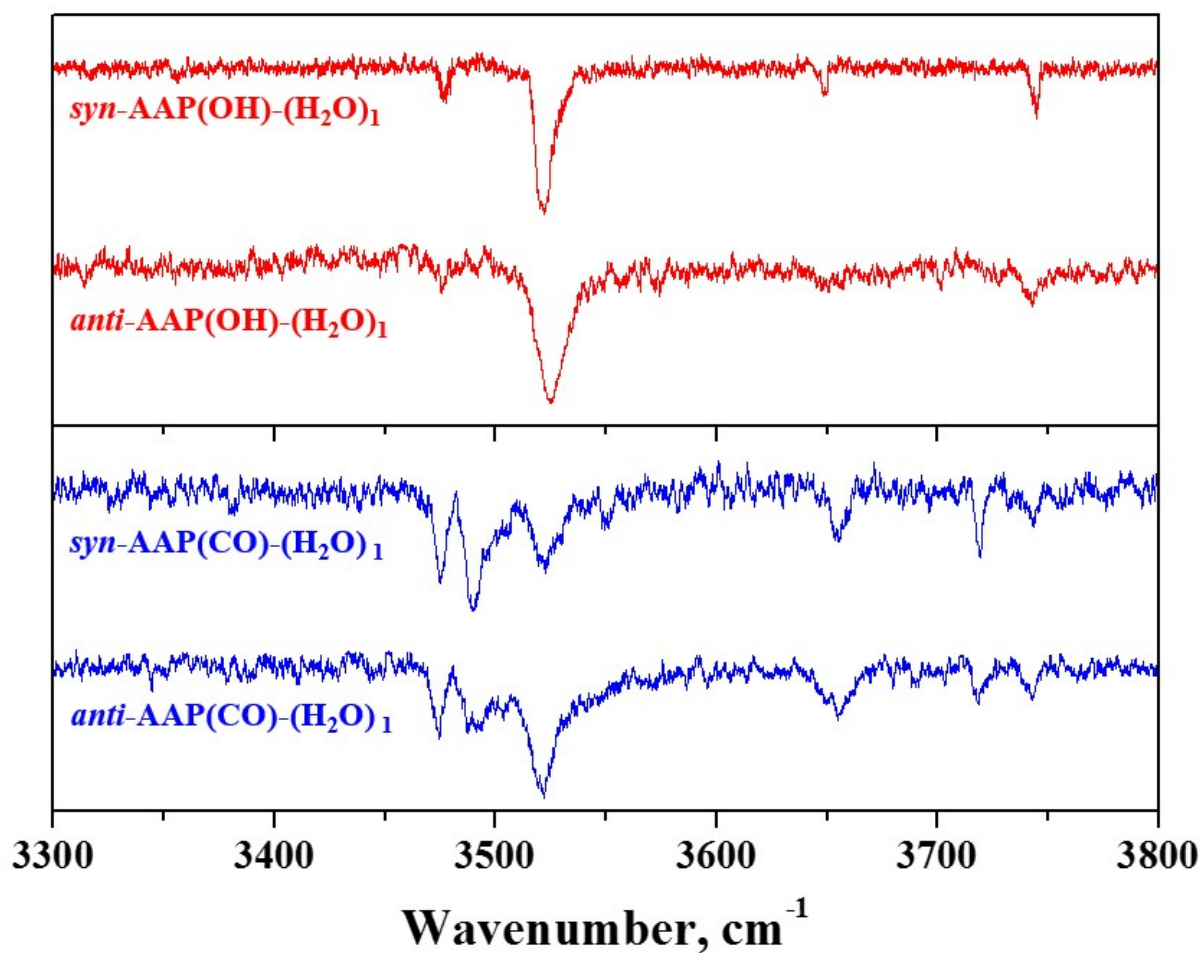


Figure S4. IR-dip spectra of the four conformers, *syn*- and *anti*- AAP(OH)-(H₂O)₁ and *syn*- and *anti*- AAP(CO)-(H₂O)₁.

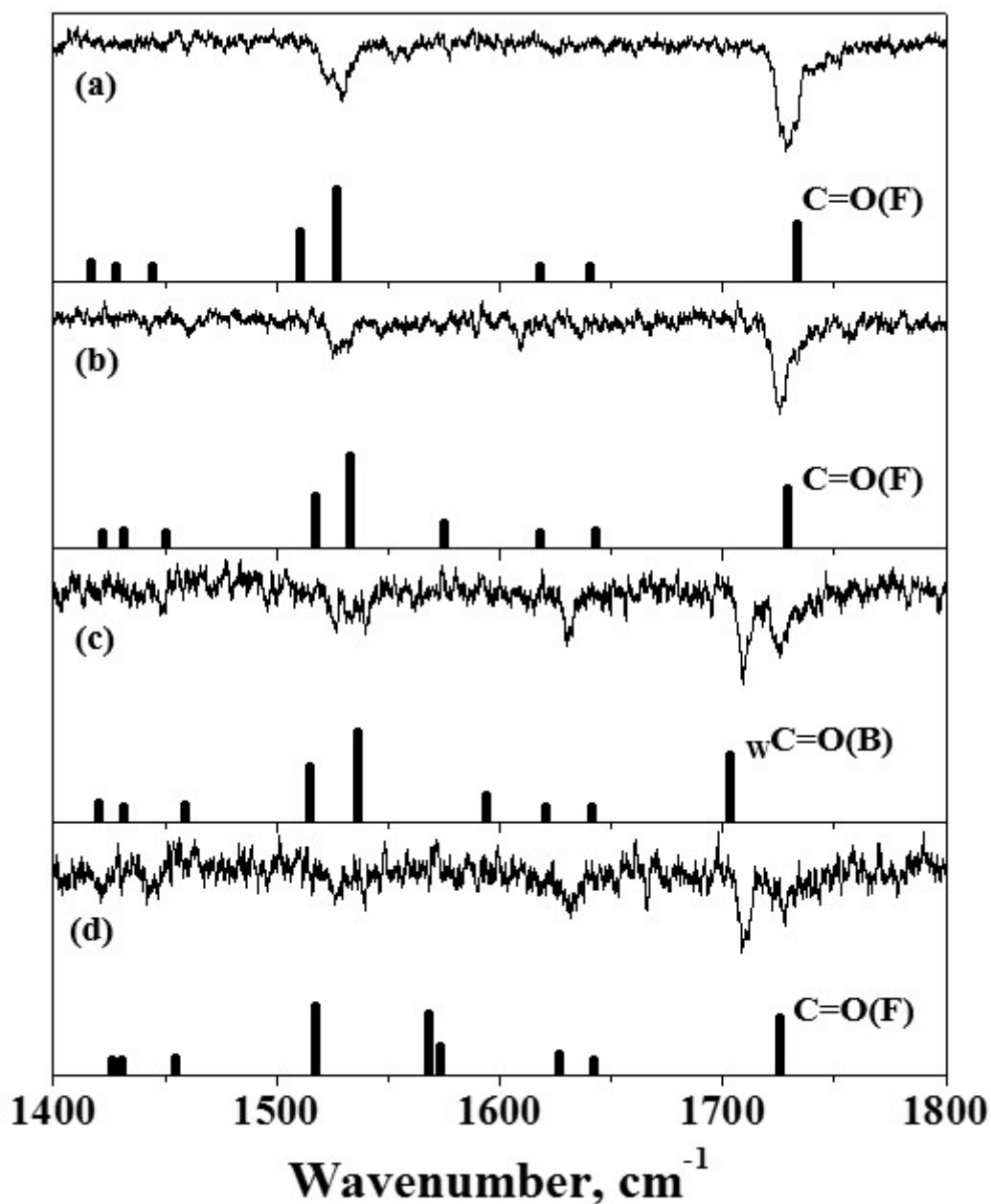


Figure S5. IR-dip spectra of (a) AAP, (b) AAP(OH)-(H₂O)₁, (c) AAP(CO)-(H₂O)₁, and (d) AAP(NH)-(H₂O)₁ in the region of 1400-1800 cm⁻¹. The calculated vibrational frequencies scaled by a factor 0.9659 are obtained with a wB97XD/6-311++G(d,p) level of theory.

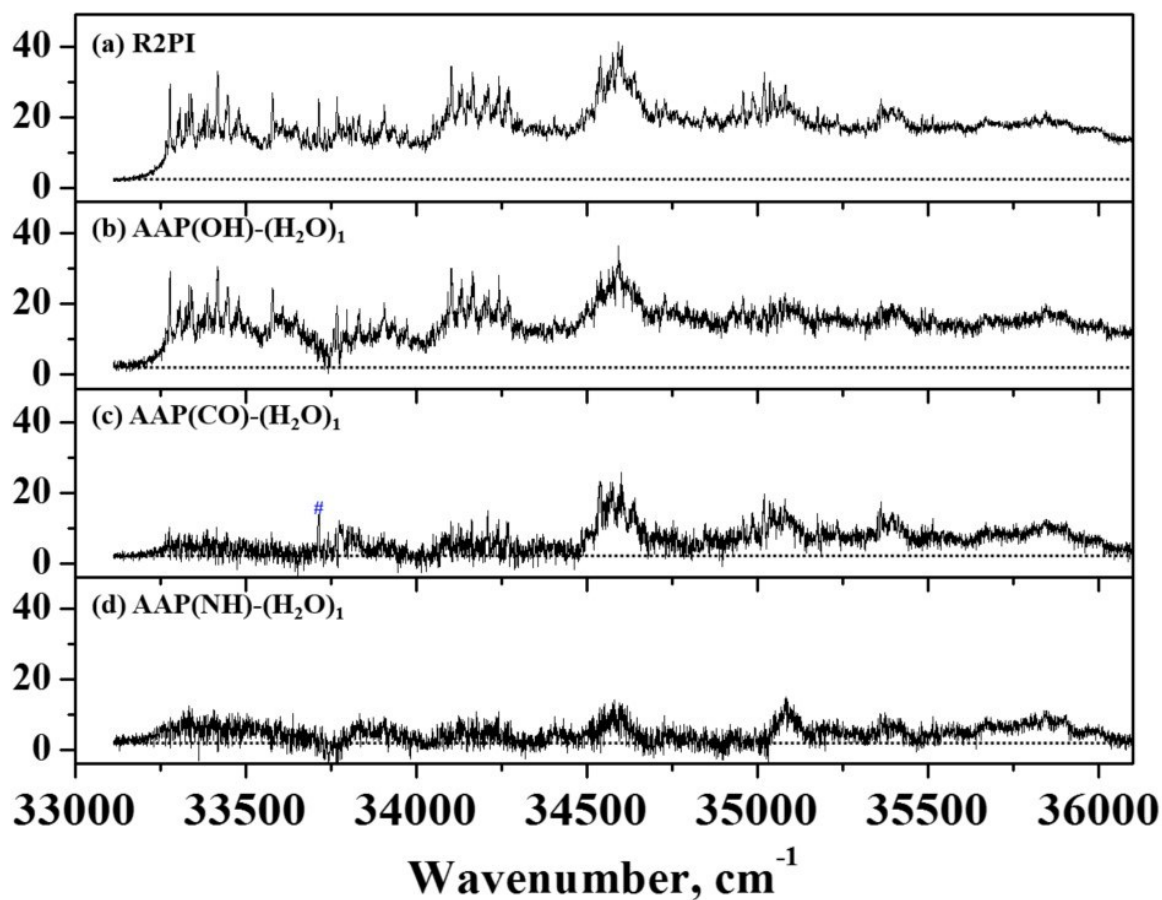


Figure S6. (a) R2PI and IR(on/off)-UV HB spectra of (b) AAP(OH)-(H₂O)₁, (c) AAP(CO)-(H₂O)₁, and (d) AAP(NH)-(H₂O)₁ in the region of 33000-36500 cm⁻¹. The IR(on/off)-UV HB spectra show the unique R2PI spectrum of each conformer since the specific IR band of specific conformer was pumped by the IR laser.

Figure S7. IR-dip spectra of AAP(OH)-(H₂O)₁ by fixing the UV laser on the (a) 0-0 band (33277 cm⁻¹) and (b) broad background (33283 cm⁻¹), respectively.

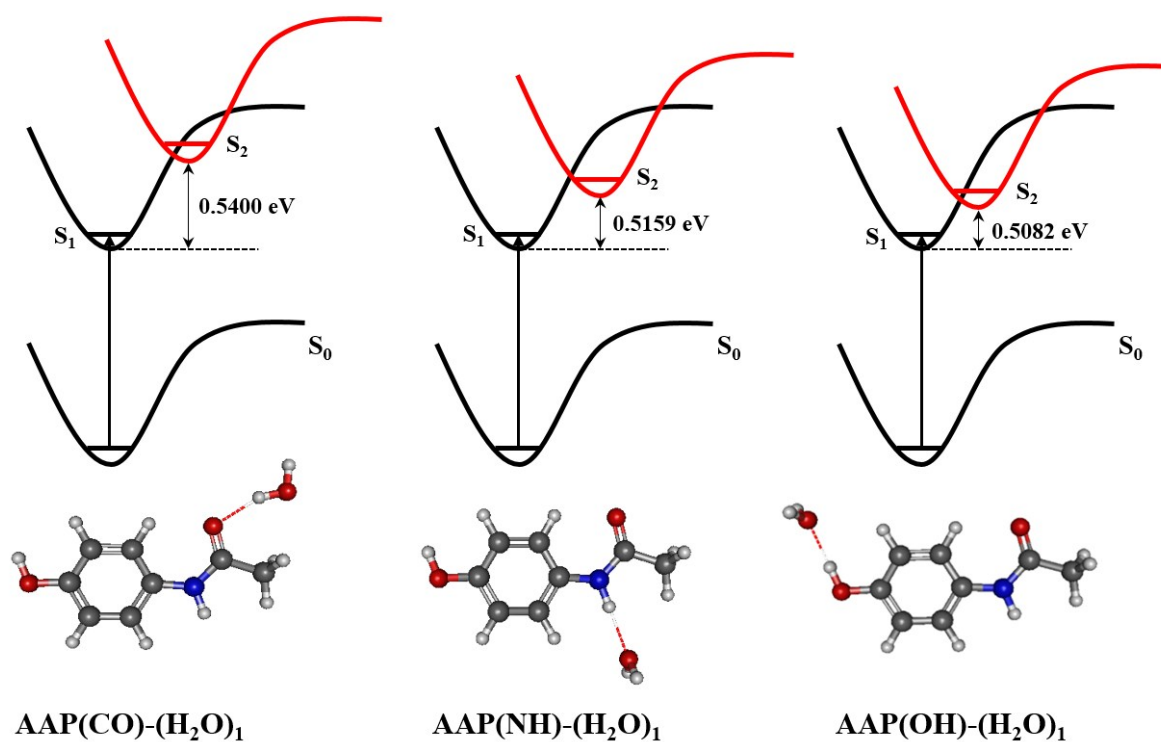


Figure S8. Schematic potential energy surfaces for the S₀ and two next-lying excited states of the AAP(CO, NH, OH)-(H₂O)₁ clusters at the wB97XD level of theory with a basis set of 6-311++G(d,p). The excitation energy gap of the AAP(CO, NH, OH)-(H₂O)₁ clusters in the lowest two excited states was calculated to be 0.5400, 0.5159, 0.5082 eV, respectively (see Table S1).

Table S1. The calculated excitation energy (eV) and energy gap (eV) between the next-lying excited states of the AAP(CO, NH, OH)-(H₂O)₁ clusters.

	AAP(CO)-(H ₂ O) ₁		AAP(NH)-(H ₂ O) ₁		AAP(OH)-(H ₂ O) ₁	
Excitation Energy (eV)^a						
S ₁ ← S ₀	π-π ₁ [*]	4.8554	π-π ₁ [*]	4.7887	π-π ₁ [*]	4.7827
S ₂ ← S ₀	π-π ₂ [*]	5.3954	π-σ [*]	5.3046	π-σ [*]	5.2909
S ₃ ← S ₀	π-σ [*]	5.6224	π-π ₃ [*]	5.3742	π-π ₃ [*]	5.3473
Difference Energy (eV)^b						
S ₂ - S ₁	ππ ₂ [*] - ππ ₁ [*]	0.5400	πσ [*] - ππ ₁ [*]	0.5159	πσ [*] - ππ ₁ [*]	0.5082
S ₃ - S ₁	πσ [*] - ππ ₁ [*]	0.7670	ππ ₃ [*] - ππ ₁ [*]	0.5855	ππ ₃ [*] - ππ ₁ [*]	0.5646

^a The excitation energy of the three lowest excited states are calculated at the wB97XD level of theory with a 6-311++G(d,p) basis set.

^b Energy gap between the two lowest excited states.