Probing Binding-Site Preferences in Propiolic Acid Complex with Water at 0.4 K

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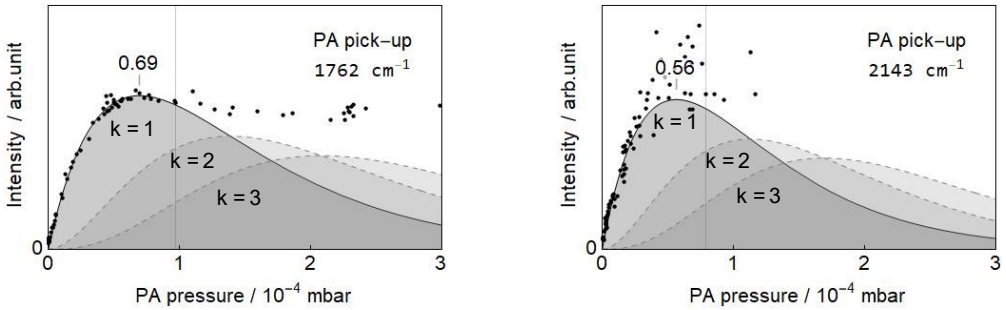

Figure S1. Pickup curves measured for the IR bands of PA monomer due to C=O and C≡C stretching modes. Laser was fixed at a particular resonant frequency: A_1 (1762 cm^{-1}, left) and A_3 (2143 cm^{-1}, right). Measurements were performed at *m/z* = 53. Cluster size is denoted by *k*.

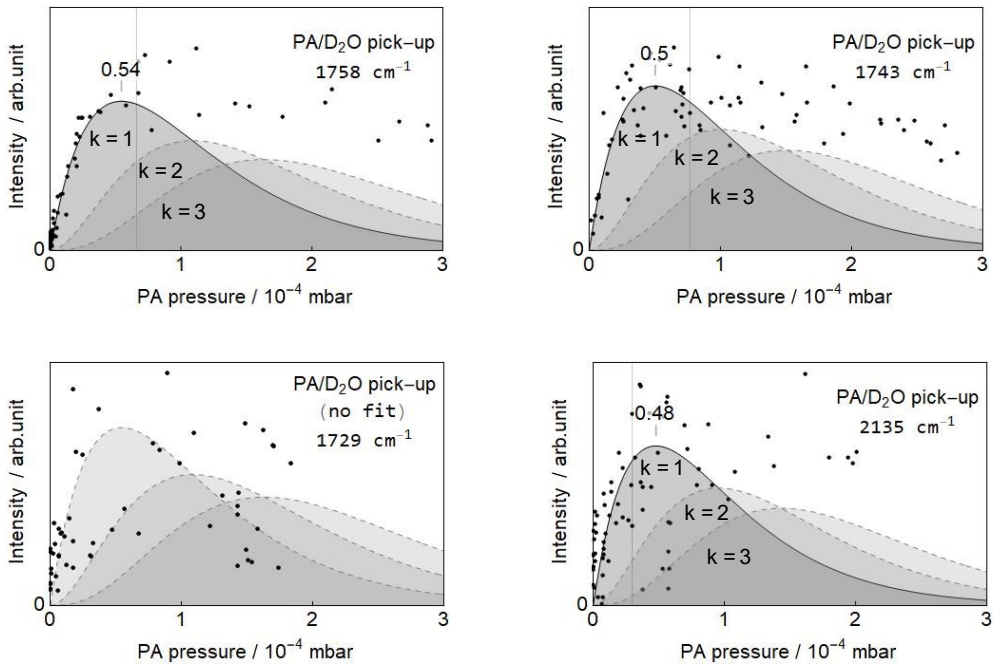

Figure S2. Pickup curves for the IR features, a_1 (1758 cm^{-1}, top left), a_2 (1743 cm^{-1}, top right), a_3 (1729 cm^{-1}, bottom left), a_4 (2135 cm^{-1}, bottom right), originating from the PA···D_2O complex are measured varying the PA partial pressures where the D_2O partial pressure was maintained constant at 3.0 $\times 10^{-5}$ mbar. Measurements were performed at *m/z* = 53. Number of PA molecule in the cluster is denoted by *k*.

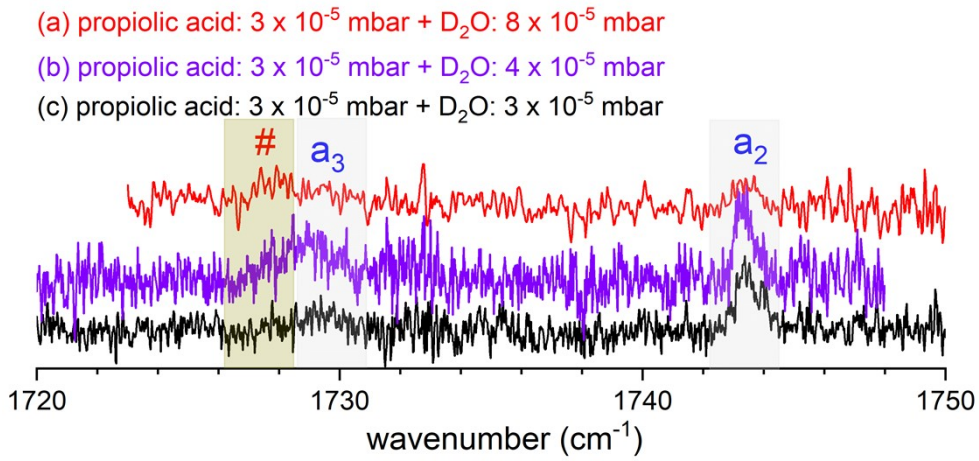

Figure S3a. Mass-selective (*m/z* = 53) infrared spectra of the PA···D_2O complex recorded in the 1720–1750 cm^{-1} region at a constant pickup pressure of PA (3×10^{-5} mbar), while varying the D_2O pickup pressure: (a) 3×10^{-5} mbar (black), (b) 4×10^{-5} mbar (violet), and (c) 8×10^{-5} mbar (red). The shaded grey regions correspond to peaks a_2 and a_3, whose intensity variation with increasing D_2O pressure indicates their assignment to the 1:1 PA···D_2O complex. The PA pressure maintained at 3×10^{-5} mbar ensures single-molecule doping, as demonstrated in Figure S2. The feature marked with # (follow light green shaded area) arises likely from larger PA···$(D_2O)_n$ clusters ($n \geq 2$).

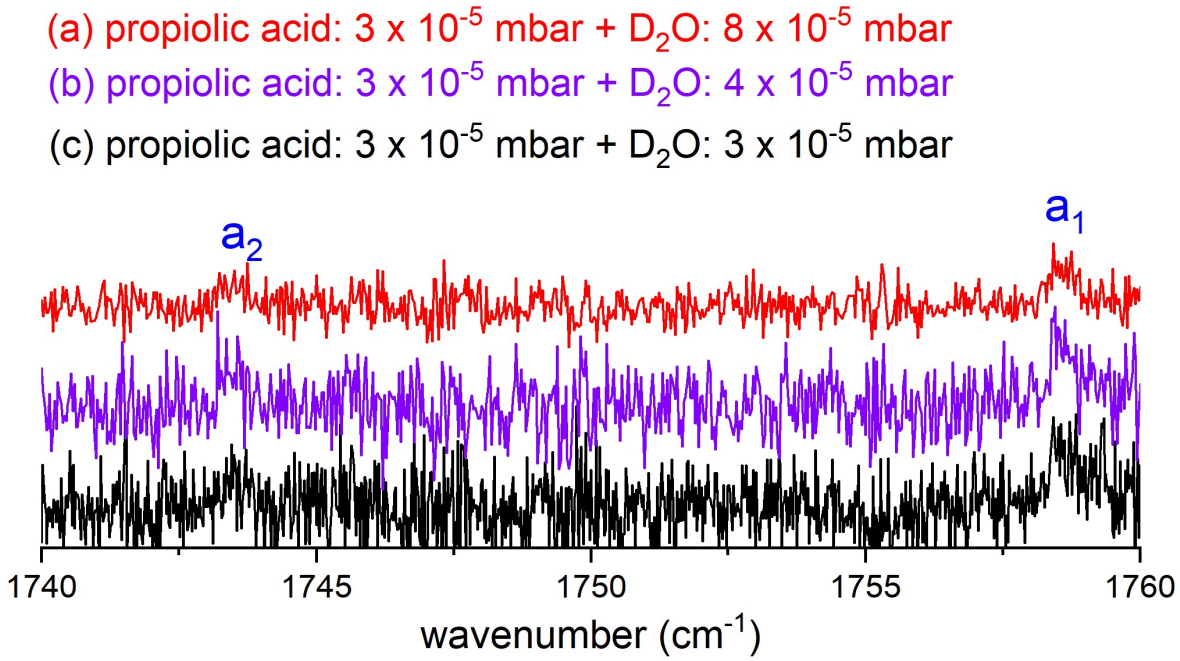

Figure S3b. Mass-selective (*m/z* = 53) infrared spectra of the PA···D_2O complex recorded in the 1740–1760 cm^{-1} region at a constant pickup pressure of PA (3 × 10^{-5} mbar), while varying the D_2O pickup pressure: (a) 3 × 10^{-5} mbar (black), (b) 4 × 10^{-5} mbar (violet), and (c) 8 × 10^{-5} mbar (red). The PA pressure maintained at 3 x 10^{-5} mbar ensures single-molecule doping, as demonstrated in Figure S2.

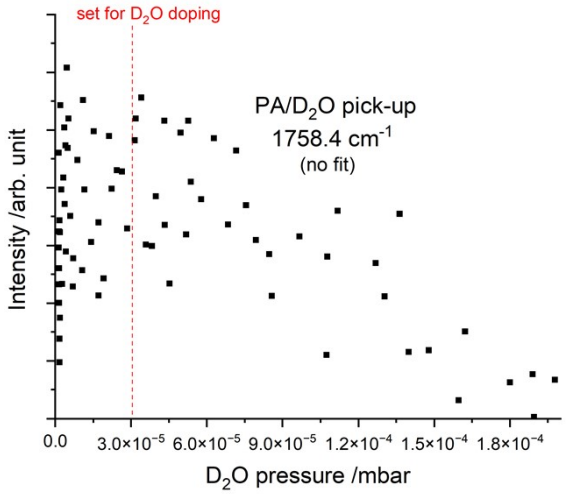

Figure S3c: Pickup curve for the strongest IR features a_1 (1758 cm^{-1}) originating from the PA···D_2O complex is measured varying the D_2O partial pressures: Here, the PA partial pressure was maintained constant at 3.0 ×10^{-5} mbar. Measurements were performed at *m/z* = 53. This pick-up curve has not been fit due to marginal signal to noise ratio. The D_2O pressure maintained for the single doping of D_2O molecule is denoted by dotted line.

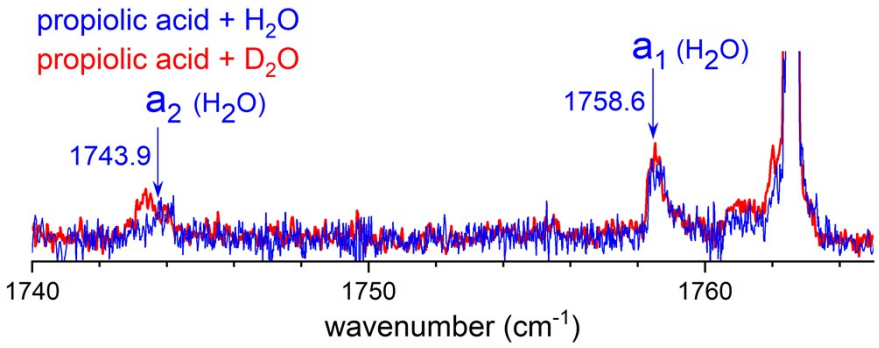

Figure S4. Mass-selective (*m/z* = 53) IR spectra of the PA···H_2O complex (blue trace) in the C=O stretching region, recorded following sequential pickup of PA (partial pressure: 3×10^{-5} mbar) and H_2O (partial pressure: 3×10^{-5} mbar) in helium nanodroplets. For comparison, the spectrum of the PA···D_2O complex is shown in red maintaining the same pick up pressures. A slight isotopic shift (~ 0.6 cm^{-1}) for the band a_2 is observed between the PA···H_2O and PA···D_2O complexes, whereas no significant shift is evident for band a_1.

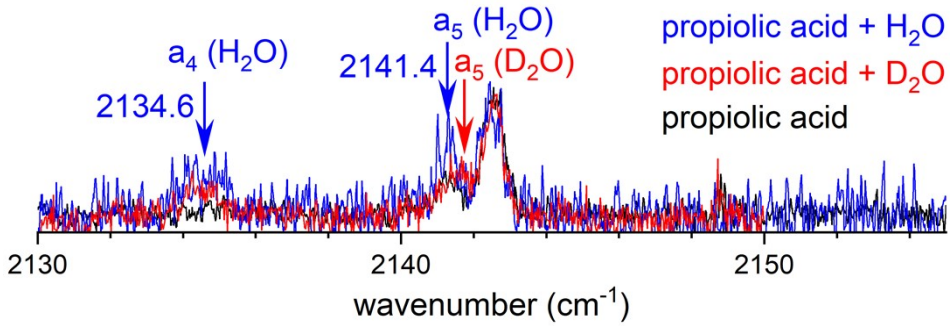

Figure S5. Mass-selective (*m/z* = 53) IR spectra of the PA···H_2O complex (blue trace) in the C≡C stretching region, recorded following sequential pickup of PA (partial pressure: 3×10^{-5} mbar) and H_2O (partial pressure: 3×10^{-5} mbar) in helium nanodroplets. For comparison, the spectra of the PA···D_2O complex and the PA monomer are shown in red and black, respectively. A slight isotopic shift (~ 0.3 cm^{-1}) for the band a_5 is observed between the PA···H_2O and PA···D_2O complexes, whereas no such shift is evident for band a_4.

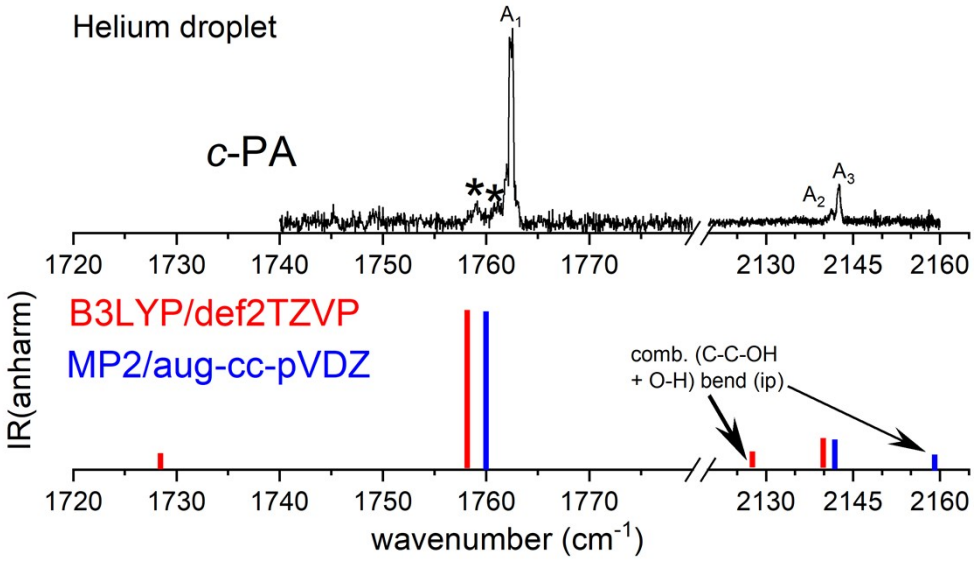

Figure S6. IR spectrum of the PA monomer recorded inside helium droplets (top panel) compared to MP2 (blue) and DFT (red) computed anharmonic IR spectra (bottom trace) of the *cis*-PA conformer.

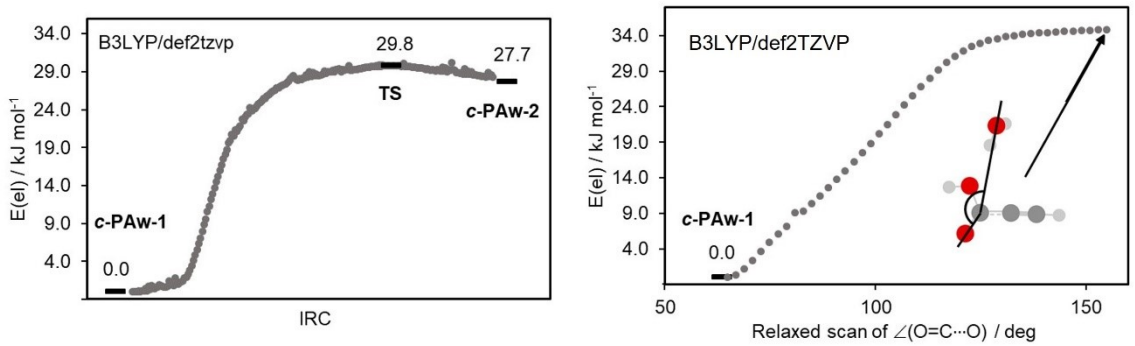

Figure S7. Energy diagrams displaying the IRC of ***c*-PAw-2 → *c*-PAw-1** (left panel) and relaxed scan of increasing the C=O···O angle of ***c*-PAw-1** (right panel). The level of theory used is B3LYP/def2TZVP.

Table S1a. Plausible structures of PA···D_2O complexes considering both, the cis- and trans-conformations of of PA. The ZPE-corrected relative energies (ΔE_0, kJ/mol) obtained with D3-B3LYP/cc-pVTZ and *MP2/aug-cc-pVDZ* are in parentheses.

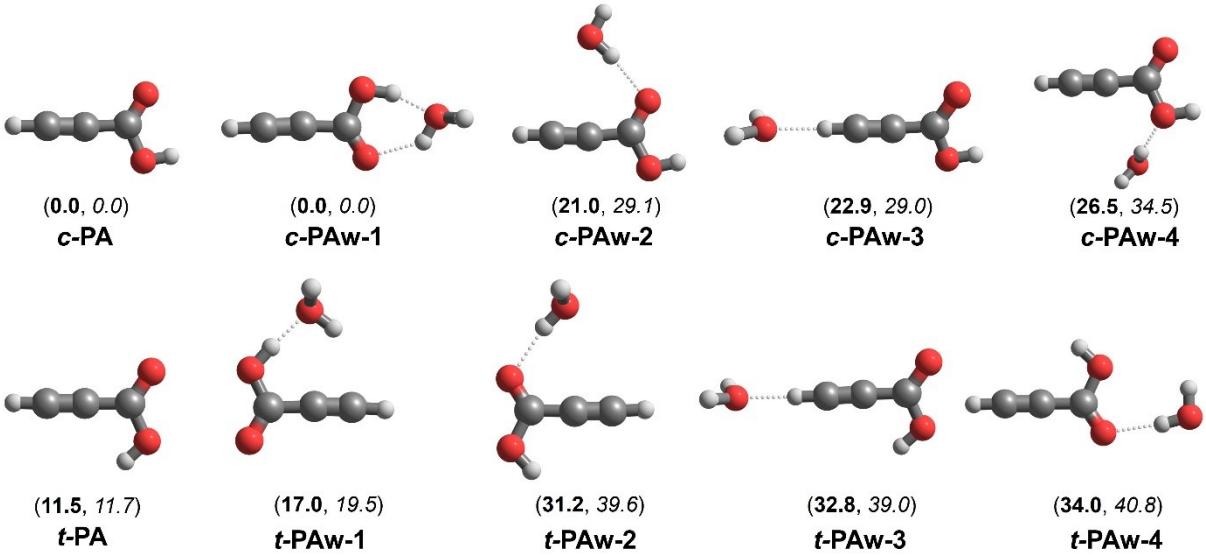

Table S1b. The optimized (in MP2/aug-cc-pVDZ level) XYZ coordinates for the lowest energy structures of PA monomers and 1:1 PA···D_2O complexes.

PA

	X	**Y**	**Z**
***c*-PA**			
C	2.201651000	-0.042263000	-0.000002000
H	3.275630000	-0.083838000	0.000002000
C	0.968864000	-0.016978000	0.000002000
C	-0.482341000	0.117484000	0.000001000
O	-1.079329000	1.181442000	-0.000001000
O	-1.090261000	-1.099953000	0.000000000
H	-2.047956000	-0.917523000	-0.000003000
***t*-PA**			
C	-2.176091000	-0.008385000	0.000106000
H	-3.250935000	0.017973000	0.000140000
C	-0.942863000	-0.062843000	0.000066000
C	0.520370000	-0.129196000	-0.000024000
O	1.140770000	1.087849000	-0.000057000
H	0.463917000	1.784373000	-0.000011000
O	1.156546000	-1.162825000	-0.000070000

1:1 PA···D_2O

	X	Y	Z
***c*-PAw-1**			
C	2.983443000	-0.037710000	0.005753000
H	4.057438000	-0.071966000	0.006527000
C	1.750556000	-0.019268000	0.003419000
C	0.296391000	0.093852000	0.001562000
O	-0.287396000	1.177535000	0.000169000
O	-0.304843000	-1.105760000	0.001910000
H	-1.284278000	-0.937928000	0.003147000
H	-2.286185000	0.755909000	-0.014344000
H	-3.456427000	-0.024153000	0.628066000
O	-2.809371000	-0.064663000	-0.088054000
***c*-PAw-2**			
C	-0.192621000	2.147060000	0.000005000
H	-0.662187000	3.113993000	0.000003000
C	0.368031000	1.049010000	0.000002000
C	0.860472000	-0.316848000	0.000003000
O	0.138022000	-1.306919000	0.000018000
O	2.213208000	-0.375243000	-0.000014000
H	2.443029000	-1.322905000	-0.000012000
H	-3.289149000	-1.219866000	-0.000013000
H	-1.816455000	-0.822027000	0.000005000
O	-2.712547000	-0.445904000	-0.000009000
***c*-PAw-3**			
C	-0.211864000	0.038598000	0.010146000
C	1.022029000	0.061119000	0.006687000
H	2.102972000	0.066217000	0.002780000
C	-1.664610000	0.112566000	0.019460000
O	-2.311345000	1.146502000	0.079521000
O	-2.225917000	-1.127775000	-0.047838000
H	-3.189227000	-0.979630000	-0.036099000
O	4.217025000	0.093773000	-0.000720000
H	4.790050000	0.324341000	0.742119000
H	4.795481000	0.142194000	-0.772920000
***c*-PAw-4**			
C	0.932741000	2.173424000	0.058434000
H	0.972461000	3.247678000	0.060962000
C	0.871538000	0.941892000	0.061725000
C	0.880398000	-0.512676000	0.015264000
O	1.780997000	-1.196270000	-0.435826000
O	-0.268163000	-1.026123000	0.553660000
H	-0.197758000	-1.995417000	0.470813000
H	-2.088244000	-0.153083000	0.078295000
H	-3.337463000	0.703960000	0.258171000
O	-2.944966000	0.045020000	-0.327930000

	X	Y	Z

***t*-PAw-1**

C	0.281866000	0.998847000	-0.003013000
C	-0.241341000	2.118546000	-0.010039000
H	-0.674777000	3.102553000	-0.021713000
C	1.004315000	-0.286425000	0.001752000
O	2.220756000	-0.337559000	0.040313000
O	0.229872000	-1.387542000	-0.040294000
H	-0.724285000	-1.134085000	-0.059345000
O	-2.395828000	-0.578737000	-0.069753000
H	-3.004003000	-0.895316000	0.611918000
H	-2.304374000	0.371735000	0.094802000

***t*-PAw-2**

C	0.379981000	0.991910000	-0.000005000
C	-0.055781000	2.146317000	-0.000003000
H	-0.448127000	3.147430000	-0.000001000
C	0.821270000	-0.398626000	-0.000009000
O	0.061227000	-1.352077000	-0.000052000
O	2.167888000	-0.583453000	0.000039000
H	2.602616000	0.285455000	0.000068000
O	-2.705668000	-0.320951000	0.000018000
H	-1.853673000	-0.789448000	-0.000017000
H	-3.361211000	-1.029204000	0.000005000

***t*-PAw-3**

C	-0.189224000	0.093773000	0.007377000
C	1.045816000	0.059946000	-0.000556000
H	2.127626000	0.053917000	-0.006013000
C	-1.651076000	0.116818000	0.015966000
O	-2.325564000	1.125754000	0.063601000
O	-2.233797000	-1.120385000	-0.035136000
H	-1.531140000	-1.790124000	-0.067663000
O	4.230987000	0.041147000	-0.000233000
H	4.772248000	0.324168000	0.748171000
H	4.790142000	0.201070000	-0.771619000

***t*-PAw-4**

C	-1.819615000	-0.140193000	0.000055000
C	-3.049851000	-0.235402000	0.000216000
H	-4.120187000	-0.338636000	0.000354000
C	-0.364358000	-0.024341000	-0.000129000
O	0.396027000	-0.974408000	-0.000275000
O	0.110909000	1.253197000	-0.000130000
H	-0.638714000	1.871166000	0.000009000
O	3.312573000	-0.200093000	0.000255000
H	2.396830000	-0.522144000	-0.000012000
H	3.208946000	0.759666000	0.000000000

Table S2. ZPE-corrected relative energies (ΔE_0) for the lowest energy isomers of propiolic acid (PA) monomer, and PA···D_2O dimers calculated at MP2 levels. The hydrogen bond (r_{HB}), the C=O ($\boldsymbol{r_{C=O}}$) and acidic O-H ($\boldsymbol{r_{O-H}}$) bond distances are in picometer (pm). The interaction energies (D) at MP2 level are provided in kJ/mol.

Species	***Isomers***	**MP2/aug-cc-pVDZ**					
		ΔE_0 (kJ/mol)	**r_{HB} (pm)**	**D^a (kJ/mol)**	**D^b (kJ/mol)**	**r_{O-H} (pm)**	**$r_{C=O}$ (pm)**
PA	*c*-PA	0.0	-	-	-	-	-
	t-PA	11.7	-	-	-	-	-
PA···D_2O	*c*-PAw-1	0.0	176 & 204	37.3	32.6	99	123
	c-PAw-2	21.0	201	16.3	12.4	98	123
	c-PAw-3	22.9	211	14.6	11.3	97	122
	c-PAw-4	26.5	207	10.8	6.0	98	122

[a] ZPE corrected
[b] ZPE-BSSE corrected