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

Electronic Supplementary Information (ESI)

Structures and energetics of hydrated deprotonated *cis*-pinonic acid anion clusters and their atmospheric relevance

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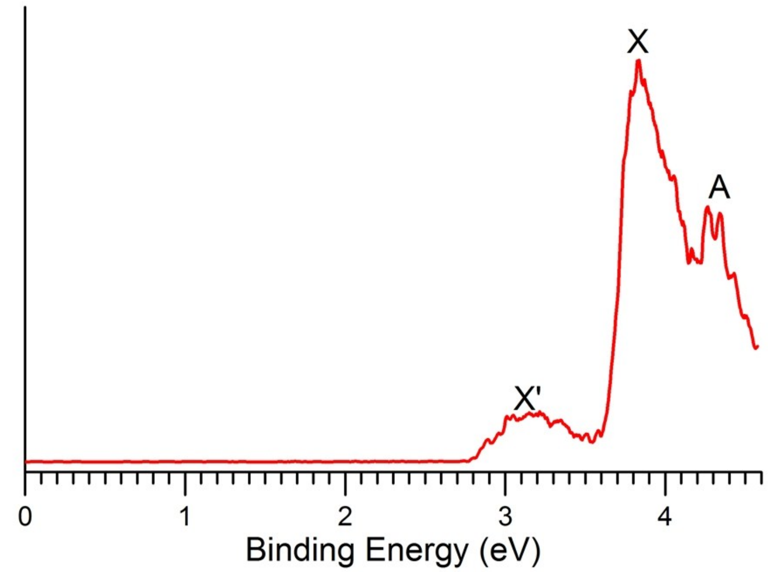
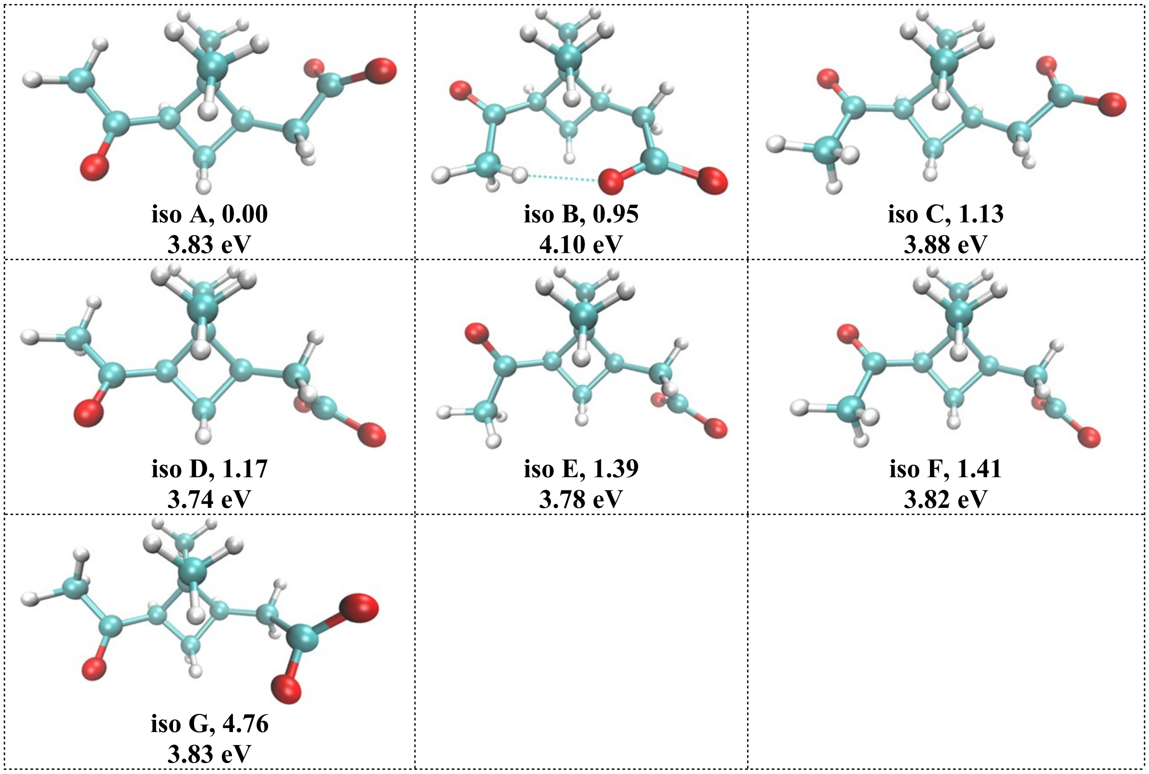


Figure S1. The 20 K NIPE spectrum of bare *cis*-pinonate at 266 nm.



iso A, 0.00
3.83 eV

iso B, 0.95
4.10 eV

iso C, 1.13
3.88 eV

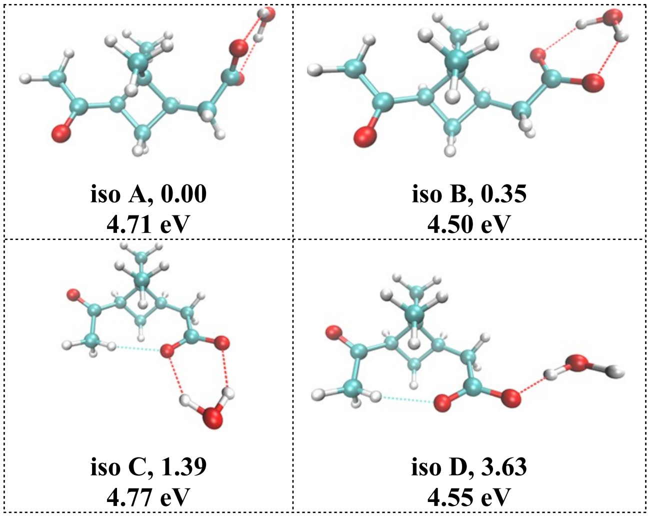
iso D, 1.17
3.74 eV

iso E, 1.39
3.78 eV

iso F, 1.41
3.82 eV

iso G, 4.76
3.83 eV

Figure S2. Seven low-lying conformers of bare *cis*-pinonate optimized at B3LYP/6-31++G(d,p) level of theory. Relative energies are obtained at the same level and are in kcal/mol.



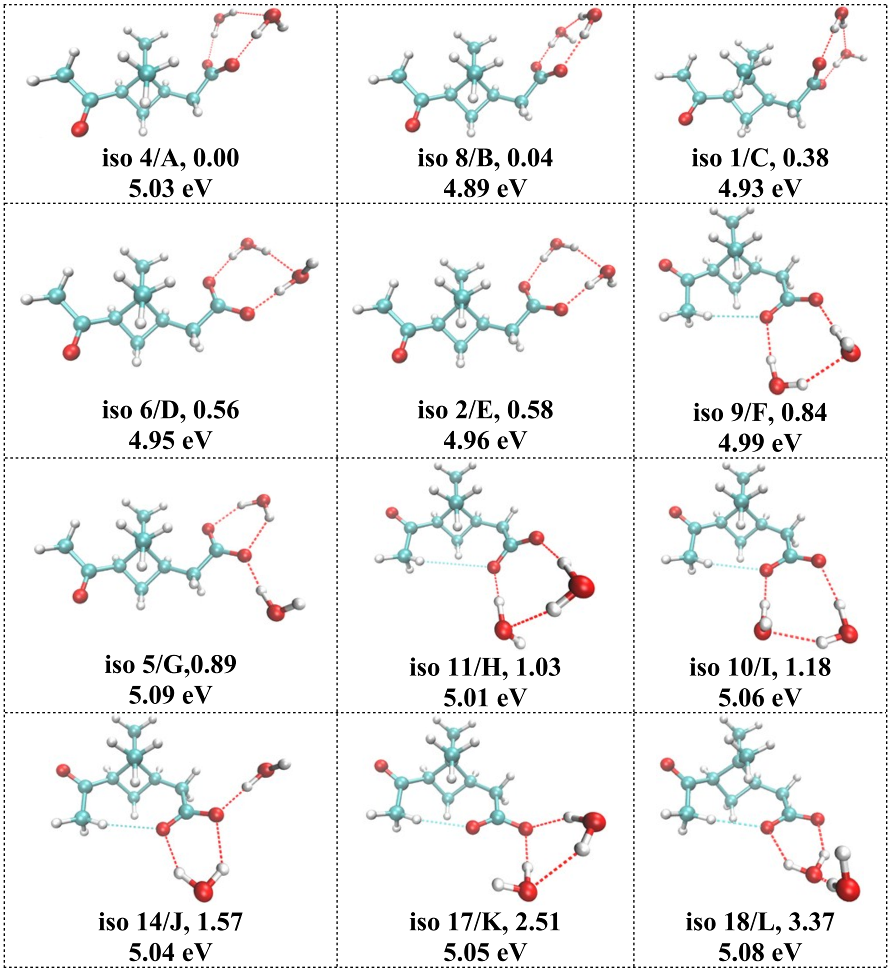
iso A, 0.00
4.71 eV

iso B, 0.35
4.50 eV

iso C, 1.39
4.77 eV

iso D, 3.63
4.55 eV

Figure S3. Complete list of the isomers of *c*PA^{-}(H$_2$O)$_1$ optimized at B3LYP/6-31++G(d,p) level of theory. Relative energies are obtained at the same level and are in kcal/mol.



iso 4/A, 0.00
5.03 eV

iso 8/B, 0.04
4.89 eV

iso 1/C, 0.38
4.93 eV

iso 6/D, 0.56
4.95 eV

iso 2/E, 0.58
4.96 eV

iso 9/F, 0.84
4.99 eV

iso 5/G,0.89
5.09 eV

iso 11/H, 1.03
5.01 eV

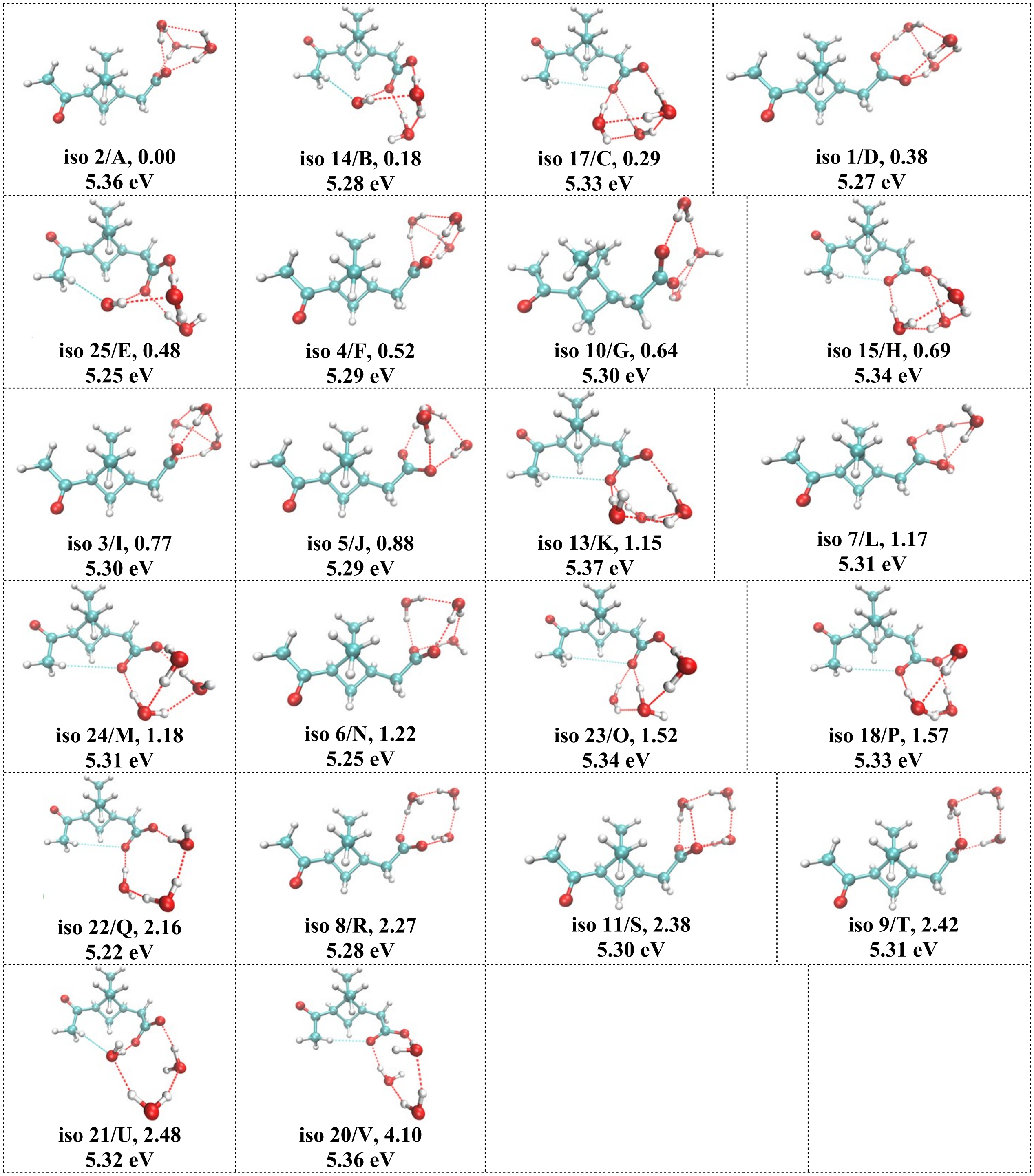
iso 10/I, 1.18
5.06 eV

iso 14/J, 1.57
5.04 eV

iso 17/K, 2.51
5.05 eV

iso 18/L, 3.37
5.08 eV

Figure S4. Complete list of the isomers of *c*PA^{-}(H$_2$O)$_2$ optimized at B3LYP/6-31++G(d,p) level of theory. Relative energies are obtained at the same level and are in kcal/mol.



iso 2/A, 0.00
5.36 eV

iso 14/B, 0.18
5.28 eV

iso 17/C, 0.29
5.33 eV

iso 1/D, 0.38
5.27 eV

iso 25/E, 0.48
5.25 eV

iso 4/F, 0.52
5.29 eV

iso 10/G, 0.64
5.30 eV

iso 15/H, 0.69
5.34 eV

iso 3/I, 0.77
5.30 eV

iso 5/J, 0.88
5.29 eV

iso 13/K, 1.15
5.37 eV

iso 7/L, 1.17
5.31 eV

iso 24/M, 1.18
5.31 eV

iso 6/N, 1.22
5.25 eV

iso 23/O, 1.52
5.34 eV

iso 18/P, 1.57
5.33 eV

iso 22/Q, 2.16
5.22 eV

iso 8/R, 2.27
5.28 eV

iso 11/S, 2.38
5.30 eV

iso 9/T, 2.42
5.31 eV

iso 21/U, 2.48
5.32 eV

iso 20/V, 4.10
5.36 eV

Figure S5. Complete list of the low-lying isomers of *c*PA^{-}(H_2O)$_3$ optimized at B3LYP/6-31++G(d,p) level of theory. Relative energies are obtained at the same level and are in kcal/mol.

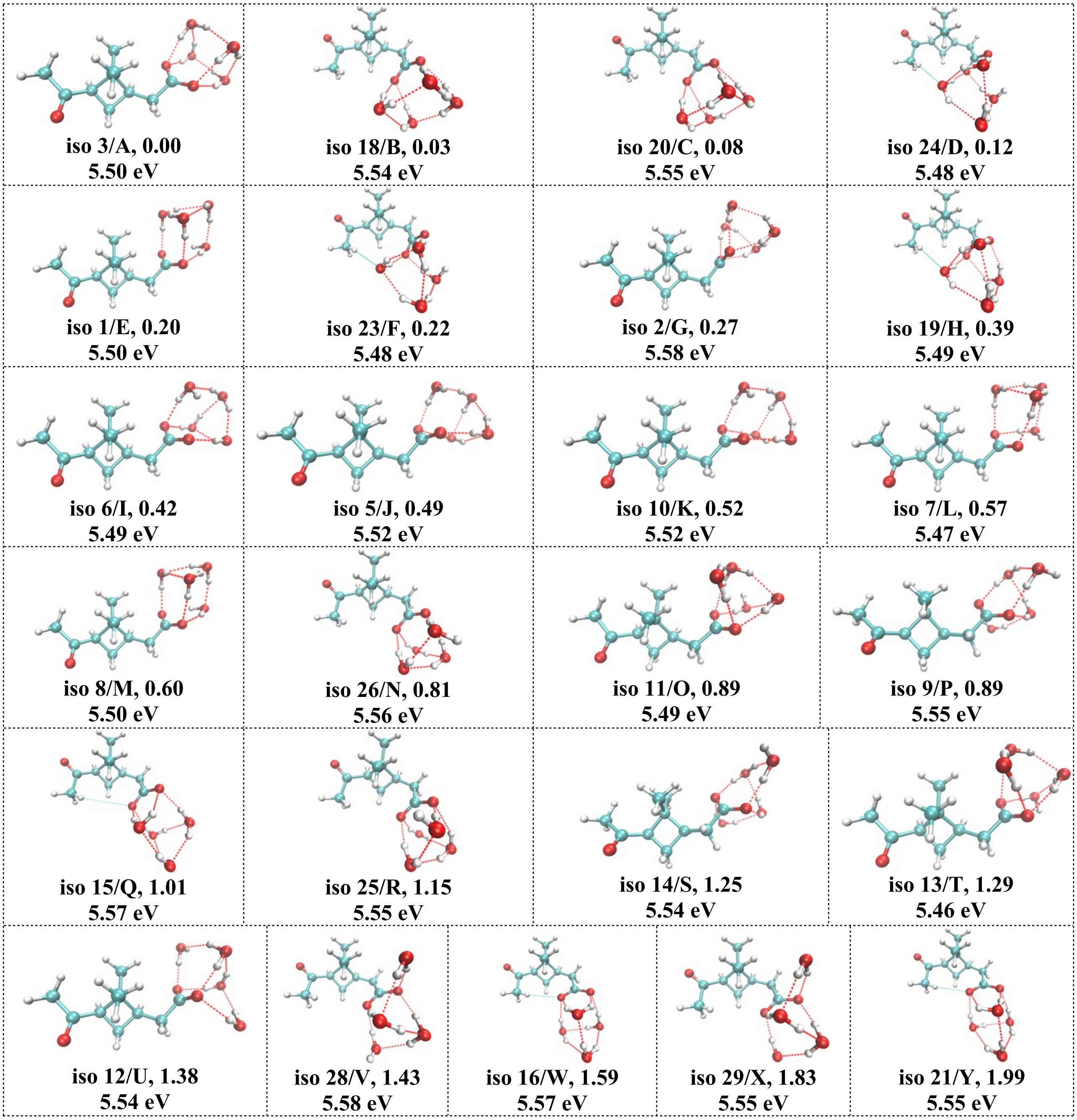
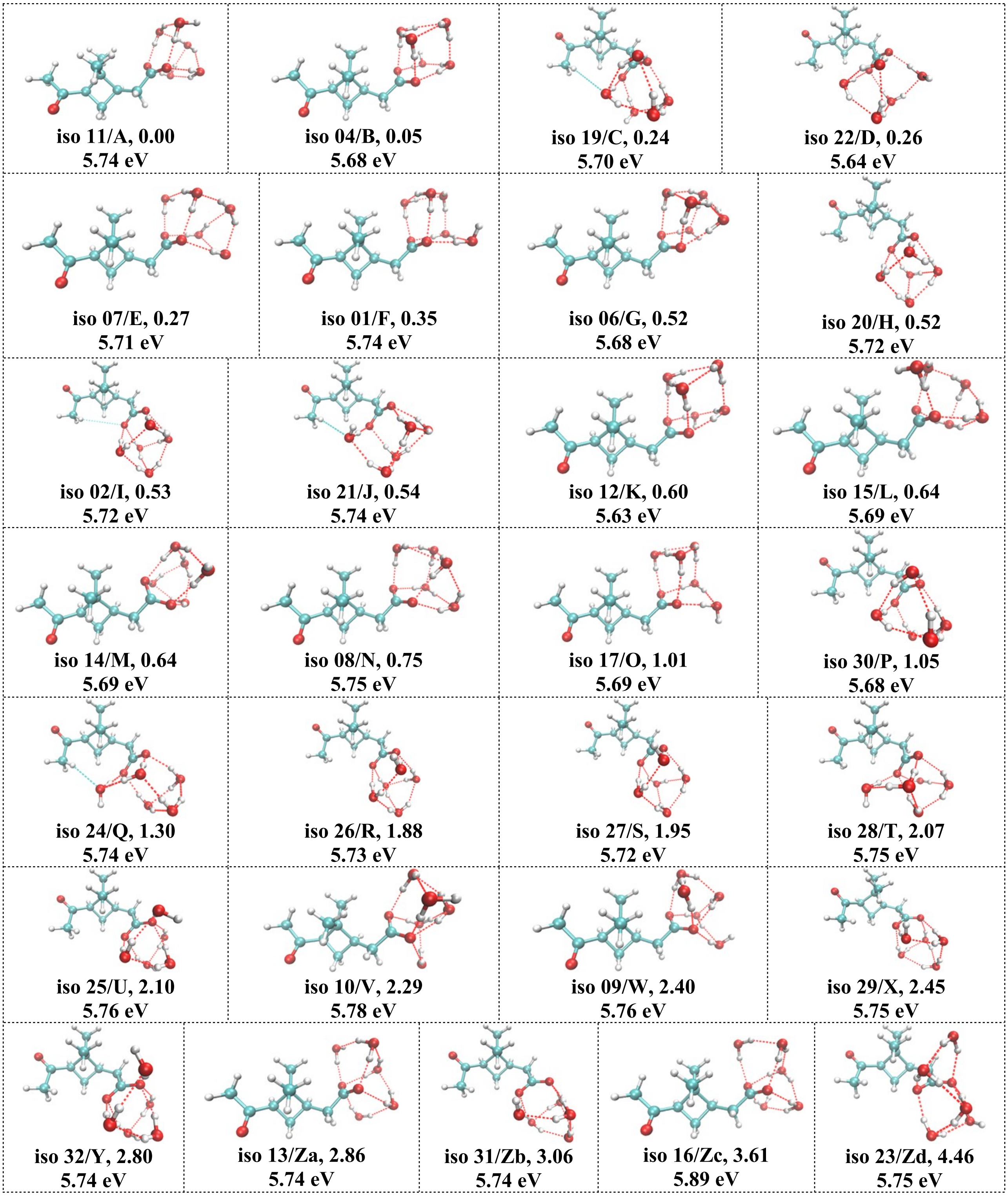

iso 3/A, 0.00
5.50 eV
iso 18/B, 0.03
5.54 eV
iso 20/C, 0.08
5.55 eV
iso 24/D, 0.12
5.48 eV
iso 1/E, 0.20
5.50 eV
iso 23/F, 0.22
5.48 eV
iso 2/G, 0.27
5.58 eV
iso 19/H, 0.39
5.49 eV
iso 6/I, 0.42
5.49 eV
iso 5/J, 0.49
5.52 eV
iso 10/K, 0.52
5.52 eV
iso 7/L, 0.57
5.47 eV
iso 8/M, 0.60
5.50 eV
iso 26/N, 0.81
5.56 eV
iso 11/O, 0.89
5.49 eV
iso 9/P, 0.89
5.55 eV
iso 15/Q, 1.01
5.57 eV
iso 25/R, 1.15
5.55 eV
iso 14/S, 1.25
5.54 eV
iso 13/T, 1.29
5.46 eV
iso 12/U, 1.38
5.54 eV
iso 28/V, 1.43
5.58 eV
iso 16/W, 1.59
5.57 eV
iso 29/X, 1.83
5.55 eV
iso 21/Y, 1.99
5.55 eV

Figure S6. Complete list of the low-lying isomers of *c*PA^{-}(H_2O)$_4$ optimized at B3LYP/6-31++G(d,p) level of theory. Relative energies are obtained at the same level and are in kcal/mol.



iso 11/A, 0.00
5.74 eV

iso 04/B, 0.05
5.68 eV

iso 19/C, 0.24
5.70 eV

iso 22/D, 0.26
5.64 eV

iso 07/E, 0.27
5.71 eV

iso 01/F, 0.35
5.74 eV

iso 06/G, 0.52
5.68 eV

iso 20/H, 0.52
5.72 eV

iso 02/I, 0.53
5.72 eV

iso 21/J, 0.54
5.74 eV

iso 12/K, 0.60
5.63 eV

iso 15/L, 0.64
5.69 eV

iso 14/M, 0.64
5.69 eV

iso 08/N, 0.75
5.75 eV

iso 17/O, 1.01
5.69 eV

iso 30/P, 1.05
5.68 eV

iso 24/Q, 1.30
5.74 eV

iso 26/R, 1.88
5.73 eV

iso 27/S, 1.95
5.72 eV

iso 28/T, 2.07
5.75 eV

iso 25/U, 2.10
5.76 eV

iso 10/V, 2.29
5.78 eV

iso 09/W, 2.40
5.76 eV

iso 29/X, 2.45
5.75 eV

iso 32/Y, 2.80
5.74 eV

iso 13/Za, 2.86
5.74 eV

iso 31/Zb, 3.06
5.74 eV

iso 16/Zc, 3.61
5.89 eV

iso 23/Zd, 4.46
5.75 eV

Figure S7. Complete list of the low-lying isomers of $c\text{PA}^{-}(\text{H}_2\text{O})_5$ optimized at B3LYP/6-31++G(d,p) level of theory. Relative energies are obtained at the same level and are in kcal/mol.

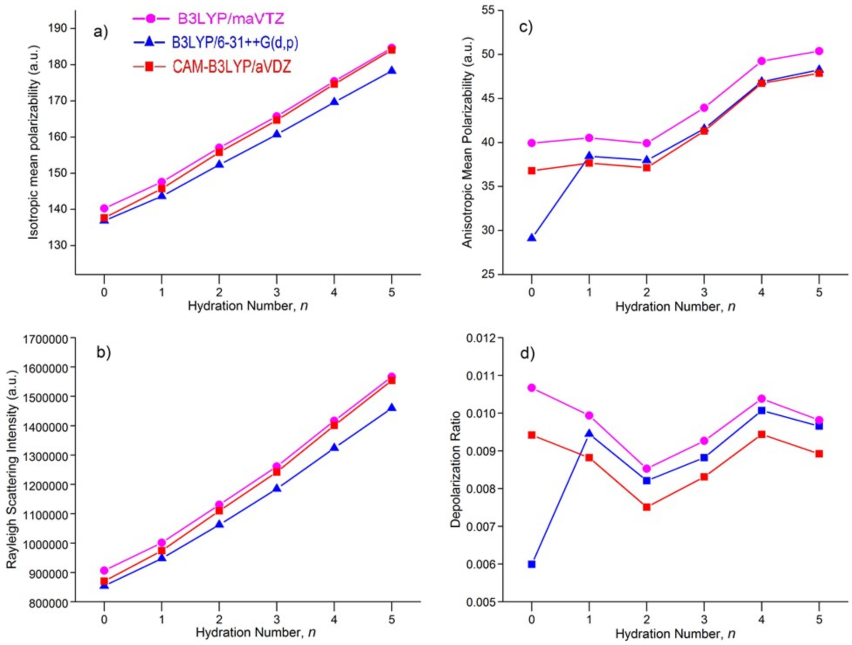


Figure S8. The Rayleigh light scattering properties of the *cis*-pinonate hydrates at three different theoretical levels: the isotropic mean ($\bar{\alpha}$) (a), and anisotropic ($\Delta\alpha$) polarizabilities (b); as well as the Rayleigh light scattering intensities of natural light (R_n) (c) and depolarization ratios (ρ_n).

Table S1. Comparison of experimental VDE to calculated ones for the bare *c*PA⁻ at different theoretical levels. The structure is optimized with B3LYP/6-31++G(d,p) method. The highlighted entry shows the theoretical method and calculated values using this method that agree best with the experiments.

Methods	VDE (eV)	
Experiment	3.82 ± 0.05	
	iso1	**iso2**
B3LYP/6-31++G(d,p)	3.83	4.10
B3LYP/6-311++G(d,p)	3.86	4.13
B3LYP/maug-cc-pVTZ	3.83	4.11
M06-2X/6-311++G(d,p)	4.02	4.30
M06-2X/maug-cc-pVTZ	4.05	4.53
PW91/6-311++G(d,p)	3.56	3.67
PW91/maug-cc-pVTZ	3.54	3.64

Table S2. Comparison of experimental TDE and VDE to calculated ones for $CH_3CO_2^-(H_2O)_1$ at various theoretical levels. The highlighted entry shows the theoretical method and calculated values using this method that agree best with the experiments.

Methods	TDE (eV)	VDE (eV)
Experiment[a]	4.08 ± 0.05	4.3 ± 0.1
B3LYP/6-31++G(d,p) // B3LYP/6-31++G(d,p)	4.15	4.41
B3LYP/6-311++G(d,p) // B3LYP/6-31++G(d,p)	4.15	4.43
B3LYP/aug-cc-pVTZ // B3LYP/6-31++G(d,p)	4.07	4.36
B3LYP/maug-cc-pVTZ // B3LYP/6-31++G(d,p)	4.08	4.37
M06-2X/6-311++G(d,p) // B3LYP/6-31++G(d,p)	4.30	4.79
M06-2X/aug-cc-pVTZ // B3LYP/6-31++G(d,p)	4.28	4.76
M06-2X/maug-cc-pVTZ // B3LYP/6-31++G(d,p)	4.29	4.77
PW91/6-311++G(d,p) // B3LYP/6-31++g(d,p)	3.97	4.12
PW91/aug-cc-pVTZ // B3LYP/6-31++G(d,p)	3.89	4.06
PW91/maug-cc-pVTZ // B3LYP/6-31++G(d,p)	3.90	4.07
CCSD(T)/6-311++G(d,p) // B3LYP/6-31++G(d,p)	3.96	4.22
CCSD(T)/aug-cc-pVTZ // B3LYP/6-31++G(d,p)	4.19	4.45
CCSD(T)/ maug-cc-pVTZ // B3LYP/6-31++G(d,p)	4.11	4.37
PW91/6-311++G(d,p) // PW91/6-311++G(d,p)	3.76	4.11

[a] The experimental values are taken from Chem. Phys. Lett. 477, 41 (2009).

Table S3. Thermochemical parameters for the sequential hydration of *cis*-pinonate and evaporation rates of the water molecule from the *cis*-pinonate hydrates calculated at ambient conditions (298.15 K and 1 atm).

n	BE[a] (kcal/mol)		ΔH[a] (kcal/mol)		ΔG[a] (kcal/mol)		ΔS[a] (cal/mol/K)		γ (s^{-1})[b]	
	$c\mathrm{PA}^{-}(\mathrm{H_2O})_{n-1} + \mathrm{H_2O} \rightarrow c\mathrm{PA}^{-}(\mathrm{H_2O})_n$									
	Calc.[c]	Calc.[d]	Calc.[c]	Calc.[d]	Calc.[c]	Calc.[d]	Calc.[c]	Calc.[d]	Calc.[c]	Calc.[d]
1	15.94	14.26	-16.58	-14.90	-7.49	-5.81	-30.48	-30.48	1.67×10^{5}	3.06×10^{6}
2	12.89	11.82	-13.52	-12.56	-4.84	-3.79	-29.09	-29.09	1.45×10^{7}	9.30×10^{7}
3	11.27	9.58	-12.24	-10.54	-1.36	0.34	-36.50	-36.50	5.22×10^{9}	9.86×10^{10}
4	11.20	9.52	-12.00	-10.32	-2.30	-0.62	-32.53	-32.53	1.06×10^{9}	1.93×10^{10}
5	10.47	9.22	-11.21	-9.97	-2.65	-1.42	-28.69	-28.69	5.80×10^{8}	5.80×10^{8}

[a] Binding energy, Enthalpy, Gibbs free energy, and Entropy changes are obtained by using the following equation:

$\mathrm{BE}[c\mathrm{PA}^{-}(\mathrm{H_2O})_n] = \mathrm{E}[c\mathrm{PA}^{-}(\mathrm{H_2O})_{n-1}] + \mathrm{E}(\mathrm{H_2O}) - \mathrm{E}[c\mathrm{PA}^{-}(\mathrm{H_2O})_n]$ (with ZPE correction)

$\Delta\mathrm{H}[c\mathrm{PA}^{-}(\mathrm{H_2O})_n] = \mathrm{H}[c\mathrm{PA}^{-}(\mathrm{H_2O})_n] - \mathrm{H}[c\mathrm{PA}^{-}(\mathrm{H_2O})_{n-1}] - \mathrm{H}(\mathrm{H_2O})$ (with ZP Enthalpy correction)

$\Delta\mathrm{S}[c\mathrm{PA}^{-}(\mathrm{H_2O})_n] = \mathrm{S}[c\mathrm{PA}^{-}(\mathrm{H_2O})_n] - \mathrm{S}[c\mathrm{PA}^{-}(\mathrm{H_2O})_{n-1}] - \mathrm{S}(\mathrm{H_2O})$

$\Delta\mathrm{G} = \Delta\mathrm{H} - \mathrm{T}\Delta\mathrm{S}$, T = 298.15 K

[b] The evaporation rates are estimated using previously described approach. Ref. *Atmos. Chem. Phys.* **2012**, *12*, 225-235.

[c] B3LYP/6-31++G(d,p) level of theory.

[d] B3LYP/maug-cc-pVTZ//6-31++G(d,p) level of theory.