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Bifunctional catalytic role of water clusters in the formation of acid rain

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Supporting information

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Methods

In this section, we briefly review the QCT methods used in this work, namely, the QTAIM and the IQA energy partition. The former method of wave function analysis leads to a division of the three-dimensional space into disjoint regions (Ω) identified with the atoms of chemistry. [1] These regions are proper subsystems, for which it is possible to compute the average values of quantum-mechanical observables, i.e., atomic properties, $\langle A \rangle_\Omega$ [2]. The addition of the quantities $\langle A \rangle_\Omega$ over all QTAIM atoms equals the expectation value of the corresponding operator for the whole electronic system. QTAIM provides a continuous link between the weak and strong regimes of interaction by means of a division of the Coulomb Hamiltonian into atomic components that can be assembled into functional groups or interacting monomers in crystals or molecular clusters. Another feature of QTAIM that we exploited in this investigation is the possibility to characterize different chemical bonds through the consideration of the integration of the Fermi and Coulomb holes in two different basins A and B, [3–5] leading to the delocalization indices

$$\delta(\mathrm{A},\mathrm{B}) = 2\left|\int_{\mathrm{A}}\int_{\mathrm{B}} \varrho(\mathbf{r}_1)\varrho(\mathbf{r}_2) f(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\right| \tag{S1}$$

in which $\varrho(\mathbf{r})$ is the charge distribution and $f(\mathbf{r}_1, \mathbf{r}_2)$ is the correlation factor [6]. The division of the real space established by QTAIM was used as a starting point to perform the Interacting Quantum Atoms (IQA) [7, 8] splitting of the Born-Oppenheimer electronic energy, E, as

$$E = \sum_{\mathrm{A}} E_{\mathrm{net}}^{\mathrm{A}} + \frac{1}{2}\sum_{\mathrm{A}}\sum_{\mathrm{B}\neq\mathrm{A}} E_{\mathrm{int}}^{\mathrm{AB}}, \tag{S2}$$

where $E_{\mathrm{net}}^{\mathrm{A}}$ is the net energy of basin A and $E_{\mathrm{int}}^{\mathrm{AB}}$ stands for the interaction energy between atoms A and B. Furthermore, $E_{\mathrm{int}}^{\mathrm{AB}}$, can be separated into classical ($V_{\mathrm{cl}}^{\mathrm{AB}}$) and exchange-correlation parts ($V_{\mathrm{xc}}^{\mathrm{AB}}$), so that,

$$E_{\mathrm{int}}^{\mathrm{AB}} = V_{\mathrm{cl}}^{\mathrm{AB}} + V_{\mathrm{xc}}^{\mathrm{AB}}, \tag{S3}$$

in which $V_{\mathrm{cl}}^{\mathrm{AB}}$ and $V_{\mathrm{xc}}^{\mathrm{AB}}$ are related to coulombic and covalent contributions to the interaction energy between atoms A and B respectively. The IQA partition energy also allows the grouping of QTAIM atoms to form superbasins $\mathscr{F}$, $\mathscr{G}$, $\mathscr{H}$... associated with molecules or functional groups whose self-energy can be written as

$$E_{\text{net}}^{\mathscr{G}} = \sum_{\text{A}\in\mathscr{G}} E_{\text{net}}^{\text{A}} + \frac{1}{2}\sum_{\text{A}\in\mathscr{G}}\sum_{\substack{\text{B}\in\mathscr{G}\\ \text{B}\neq\text{A}}} E_{\text{int}}^{\text{AB}}. \tag{S4}$$

This scale invariance enables the IQA approach to dissect the formation energy (ΔE) of molecular clusters or transition states $\mathscr{F}\cdots\mathscr{G}\cdots\mathscr{H}\cdots$

$$\mathscr{F} + \mathscr{G} + \mathscr{H} + \ldots \rightleftharpoons \mathscr{F}\cdots\mathscr{G}\cdots\mathscr{H}\cdots. \tag{S5}$$

As suggested in reference 9], we decomposed the energy associated with process (S5) in pairwise contributions

$$\begin{aligned}\Delta E &= \sum_{\mathscr{F}}\sum_{\mathscr{F}>\mathscr{G}} \left(E_{\text{int}}^{\mathscr{F}\mathscr{G}} + \left(\frac{E_{\text{int}}^{\mathscr{F}\mathscr{G}}}{\sum\limits_{\mathscr{H}\neq\mathscr{F}} E_{\text{int}}^{\mathscr{F}\mathscr{H}}} \right) E_{\text{def}}^{\mathscr{F}} + \left(\frac{E_{\text{int}}^{\mathscr{F}\mathscr{G}}}{\sum\limits_{\mathscr{H}\neq\mathscr{G}} E_{\text{int}}^{\mathscr{G}\mathscr{H}}} \right) E_{\text{def}}^{\mathscr{G}} \right) \\ &= \sum_{\mathscr{F}}\sum_{\mathscr{F}>\mathscr{G}} E_{\text{int}}^{\mathscr{F}\mathscr{G}\,\prime}.\end{aligned} \tag{S6}$$

wherein $E_{\text{def}}^{\mathscr{F}}$ is the deformation energy [7, 8] of moiety $\mathscr{F}$ in process (S5) and $E_{\text{int}}^{\mathscr{F}\mathscr{G}}$ is the IQA interaction energy of groups $\mathscr{F}$ and $\mathscr{G}$ within $\mathscr{F}\cdots\mathscr{G}\cdots\mathscr{H}\cdots$. Equation (S6) allows to interpret the IQA energy partition in a chemically appealing form, because the changes in the electronic energy associated to a given process can be conveniently analysed in terms of the strengthening or weakening of specific interactions among the monomers or functional groups comprising the system.

Computational details

All geometries and density functions of the studied systems were obtained using the MP2 [10]/aug-cc-pVTZ [11] approximation, as implemented in the Gaussian-09 program [12]. We used this method of electronic structure theory and basis set, because it describes properly hydrogen-bond cooperative effects [9, 13]. After the optimization of the geometry of every system of interest, we performed single point calculations at the same level of theory with the program Orca [14] to obtain the wave function files necessary to carry out the QTAIM and IQA wave function analyses of this study. We considered the Müller approximation [15] throughout the IQA energy partition. All the QCT calculations were done with the package Aimall [16].

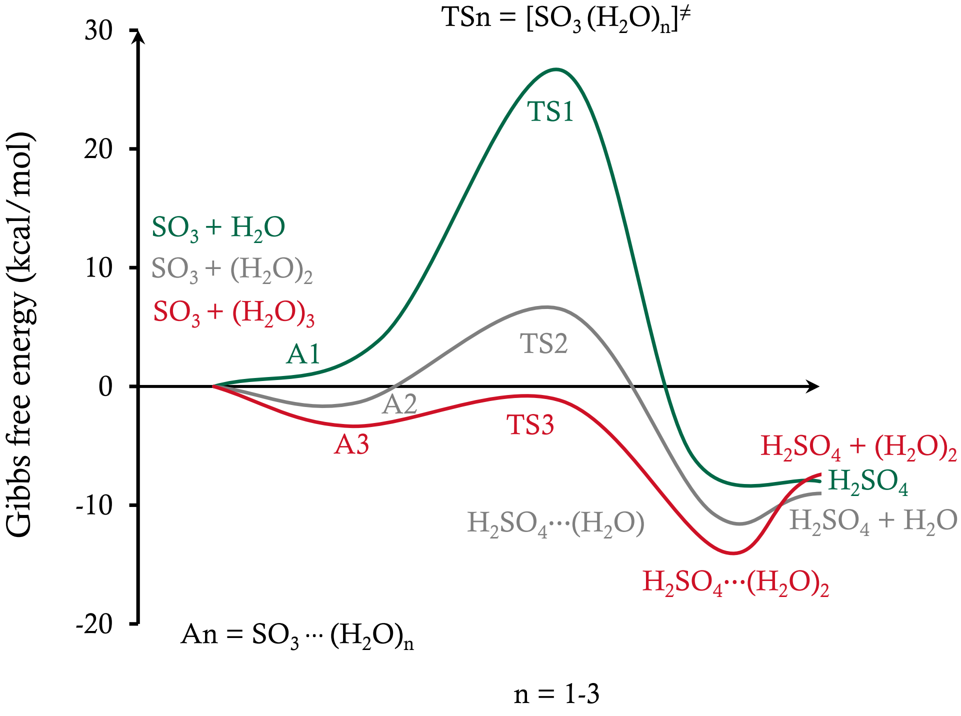

Figure S1: MP2/aug-cc-pVTZ Gibbs free energy profile for the reaction of SO_3 with $(H_2O)_n$ (n = 1–3) to form H_2SO_4. The free energy values are referred to the sum $G(SO_3) + G((H_2O)_n)$.

Thermodynamics and kinetics for the reactions $SO_3 + (H_2O)_n \rightarrow H_2SO_4 \cdots (H_2O)_{n-1}$ with n = 1 –3

The data in Table S1 show that the involvement of additional water molecules in equation (1) makes the formation of complexes An with $n = 1, 2, 3$ (Figures 1 and 2) more exothermic. In addition, the activation energies of the corresponding rate-limiting steps diminish with the number of H_2O molecules in the system. Similar trends are observed for the changes in the Gibbs free energies (Table S1 and Figure S1).

Concerning the process

$$SO_3 + H_2O \xrightarrow{(I)} SO_3 \cdots H_2O \xrightarrow{(II)} [SO_3 \cdots H_2O]^{\ddagger} \qquad (S7)$$

Figure 1 indicates that the activation energy required for the formation of the transition state $[SO_3 \cdots H_2O]^{\ddagger}$ exceeds largely that associated to the formation of the cluster $SO_3 \cdots H_2O$. Therefore, and as pointed out by Steudel [17], any activation of this molecular complex would lead

Table S1: Relative electronic energies, ΔE, enthalpies, ΔH, and Gibbs free energies, ΔG of species involved in equation (1) (in kcal mol^{-1}) with respect to the separated reactants (ΔH and ΔG values are given at 298.15 K). The activation energies for the rate-limiting steps can be obtained from the difference of the parameters corresponding to $[SO_3\cdots(H_2O)_n]^\ddagger$ and $SO_3\cdots(H_2O)_n$.

Water clusters	Species	ΔE	ΔH	ΔG	$-T\Delta S$
H_2O	$SO_3 + H_2O$	0.0	0.0	0.0	0.0
	$SO_3\cdots H_2O$	−7.4	−7.7	1.3	9.0
	$[SO_3\cdots H_2O]^\ddagger$	16.1	14.5	26.6	12.1
	H_2SO_4	−16.0	−17.4	−5.7	11.7
$(H_2O)_2$	$SO_3 + (H_2O)_2$	0.0	0.0	0.0	0.0
	$SO_3\cdots(H_2O)_2$	−13.4	−14.6	−1.3	13.3
	$[SO_3\cdots(H_2O)_2]^\ddagger$	−7.2	−9.7	6.5	16.2
	$H_2SO_4\cdots(H_2O)$	−23.6	−25.2	−10.7	14.5
	$H_2SO_4 + (H_2O)$	−12.9	−13.8	−9.0	4.8
$(H_2O)_3$	$SO_3 + (H_2O)_3$	0.0	0.0	0.0	0.0
	$SO_3\cdots(H_2O)_3$	−15.4	−16.2	−3.3	12.9
	$SO_3\cdots(H_2O)_3{}^\ddagger$	−14.9	−16.7	−1.2	15.5
	$H_2SO_4\cdots(H_2O)_2$	−26.1	−27.1	−14.0	13.1
	$H_2SO_4 + (H_2O)_2$	−8.2	−8.3	−7.4	0.9

to its dissociation rather than to the formation of the transition state $[SO_3\cdots H_2O]^\ddagger$, thereby precluding step (II) in reaction (S7). The addition of an extra H_2O molecule, i.e.,

$$SO_3 + (H_2O)_2 \xrightarrow{\text{(III)}} SO_3\cdots(H_2O)_2 \xrightarrow{\text{(IV)}} [SO_3\cdots(H_2O)_2]^\ddagger \tag{S8}$$

changes considerably the former scenario. In this case, the formation energy of the adduct $SO_3\cdots(H_2O)_2$ is large enough to enable the generation of $[SO_3\cdots(H_2O)_2]^\ddagger$ (grey curve in Figure 1) and hence the formation of H_2SO_4. The Gibbs free energy profiles in Figure (1) point nonetheless that

$$|\Delta G^\ddagger(\text{IV})| > |\Delta G(\text{III})| \tag{S9}$$

and that it is necessary an additional water molecule

$$SO_3 + (H_2O)_3 \xrightarrow{\text{(V)}} SO_3\cdots(H_2O)_3 \xrightarrow{\text{(VI)}} [SO_3\cdots(H_2O)_3]^{\ddagger} \tag{S10}$$

to invert the inequality (S9). The differences between Figures 1 and (S1) are of course due to the entropic component of ΔG. Table 1 indicates that $T\Delta S$ does not contribute to the spontaneity of processes (I)–(VI), and even makes the formation of the molecular cluster $SO_3\cdots H_2O$ endergonic. The negative sign of ΔS for the steps in equations (S7)–(S10) is consistent with the observation that the reaction rate of the reaction between SO_3 and H_2O increases as the temperature is decreased in the interval of -30 to $+60°$ C [18, 19]. In addition, when the temperature is lowered, the entropic component becomes less important and then it is expected that the inequality (S9) is inverted under these circumstances in agreement with the fact that the formation of H_2SO_4 is second order with respect to water. [18]

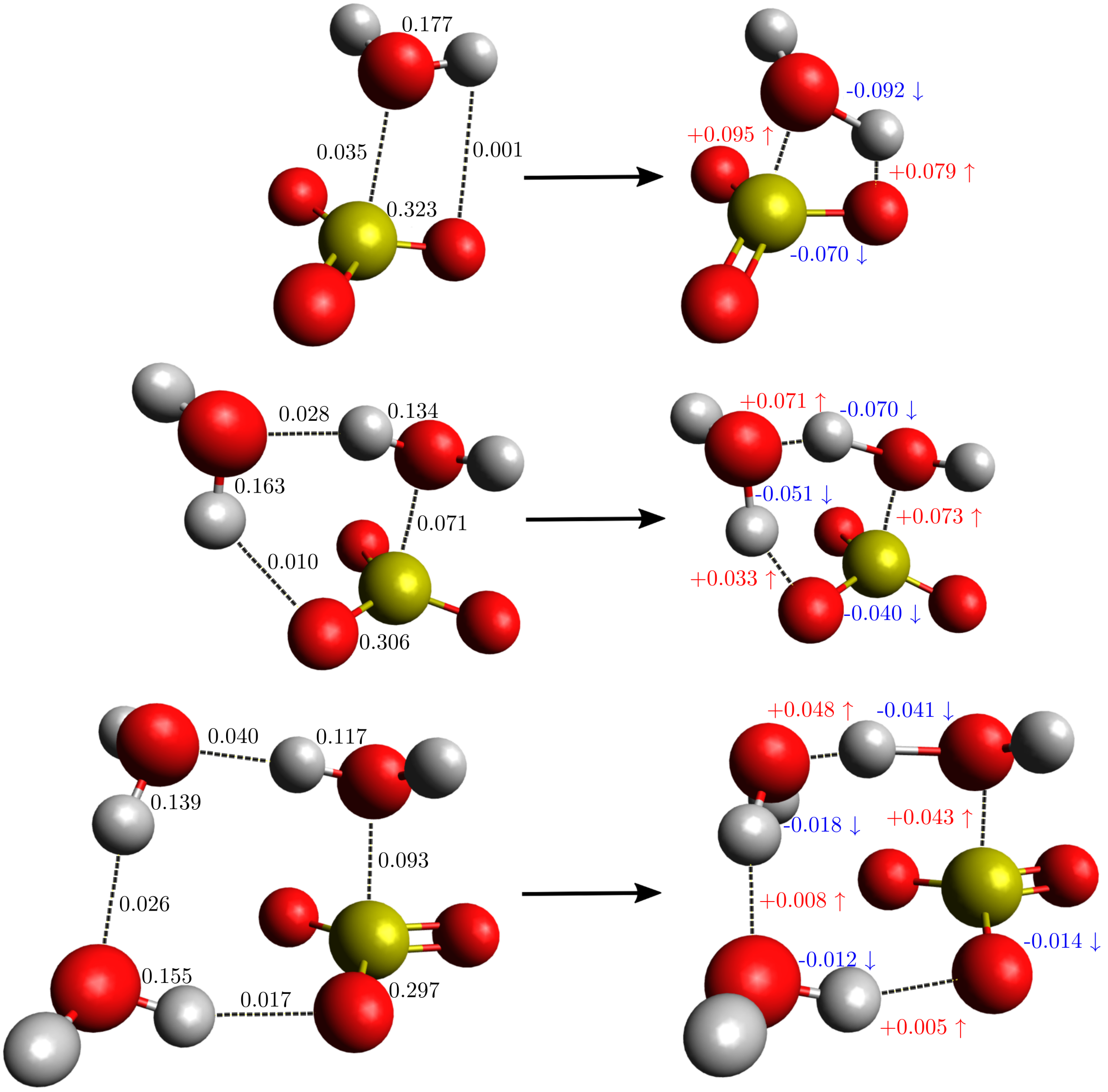

Figure S2: Left: Exchange-correlation component of the IQA interaction energy within the considered molecular clusters (Figure 2 (a)–(c) in the body of the paper) for the pairs of atoms entailed in the formation and breaking of chemical bonds in the considered rate-limiting steps of the formation of acid rain in equations (14)–(16). Right: Changes in $V_{\mathrm{xc}}^{\mathrm{AB}}$ after the formation of the corresponding transition states. Red/blue colour denote an increase/decrease in this quantity. The values are reported in atomic units.

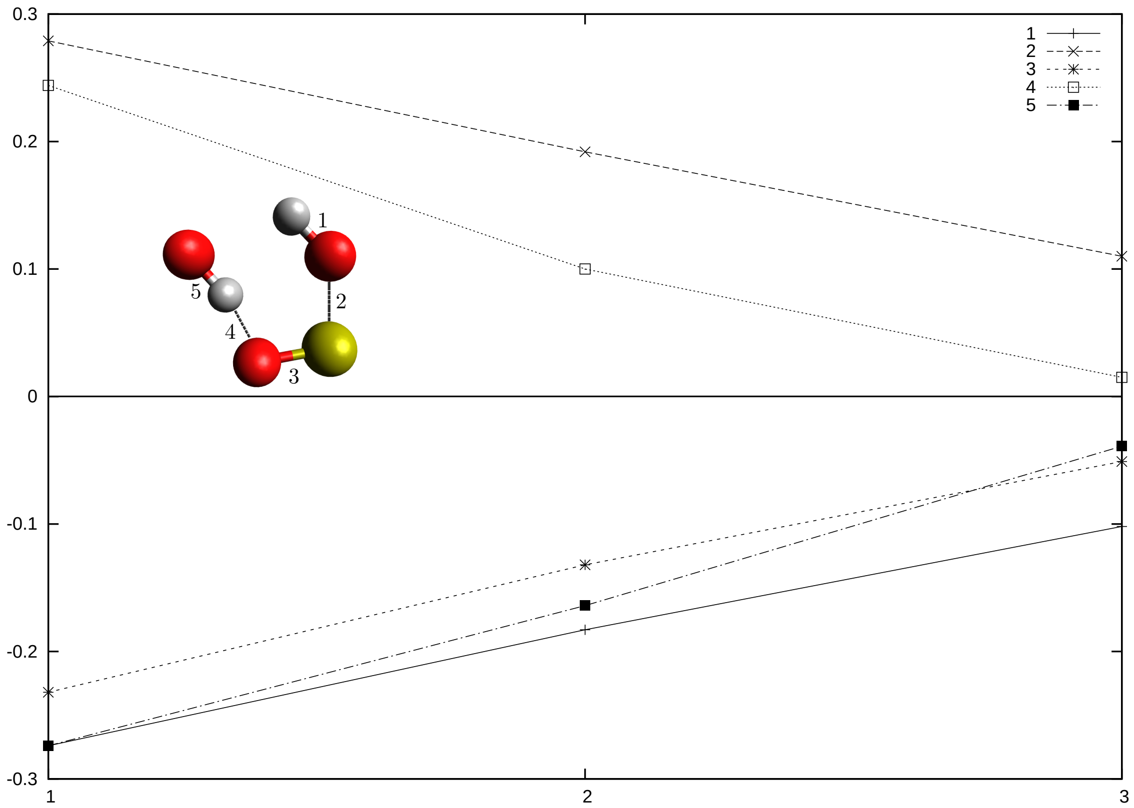

Figure S3: $\Delta\delta(A,B)$ for the broken (1 and 5) and formed (2 and 4) bonds in the formation of H_2SO_4 throughout the rate-limiting step as a function of the water molecules in the system. Bond 3 change its character from double to single in the process and bonds 1 and 5 are the same when n = 1. Atomic units are used throughout.

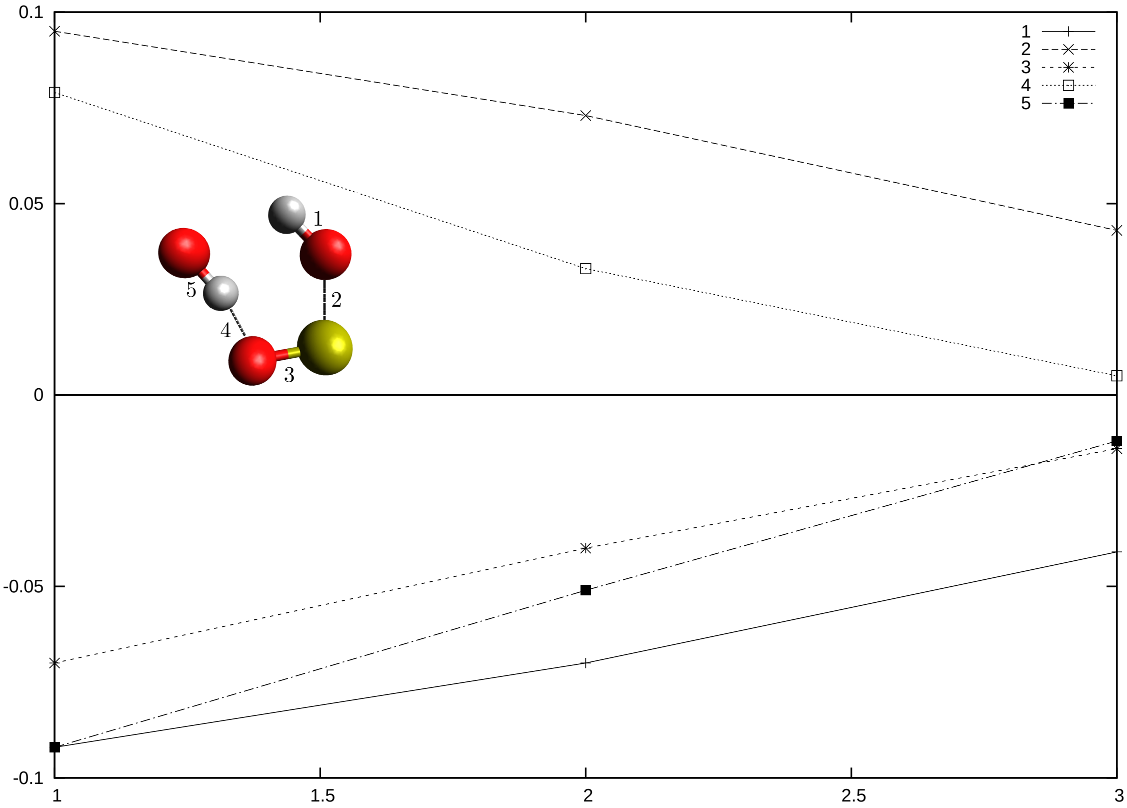

Figure S4: $\Delta V_{\mathrm{xc}}^{AB}$ for the broken (1 and 5) and formed (2 and 4) bonds in the formation of H_2SO_4 throughout the rate-limiting step as a function of the water molecules in the system. Bond 3 change its character from double to single in the process and bonds 1 and 5 are the same when n = 1. Atomic units are used throughout.

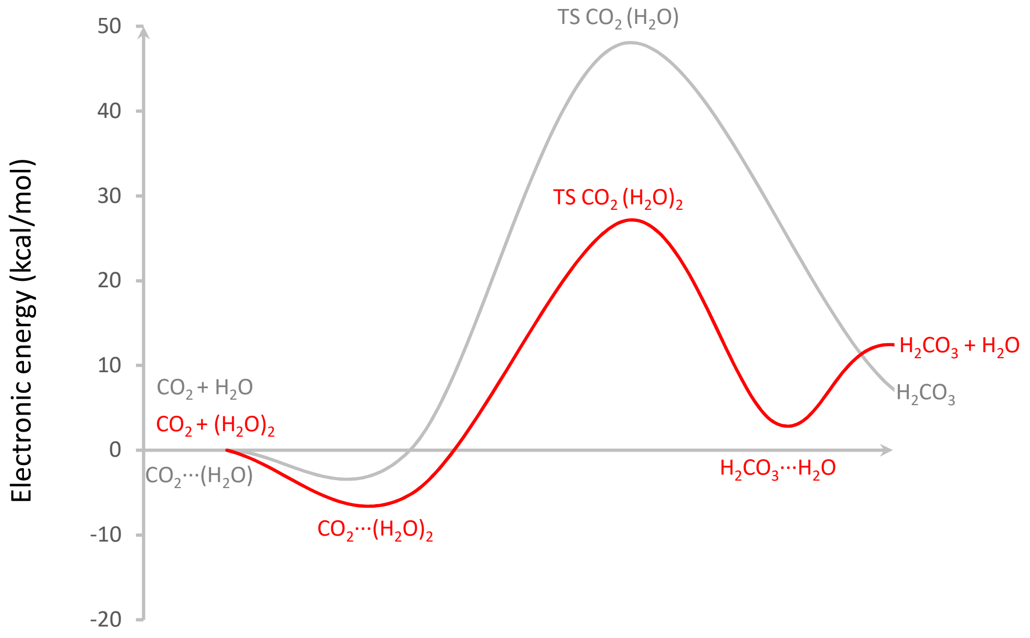

Figure S5: Potential energy curves for the formation of carbonic acid from the reaction of CO_2 with the water monomer and dimer. Every energy is referred to the corresponding value for the sum $E(SO_3) + E((H_2O)_n)$ with $n = 1, 2$.

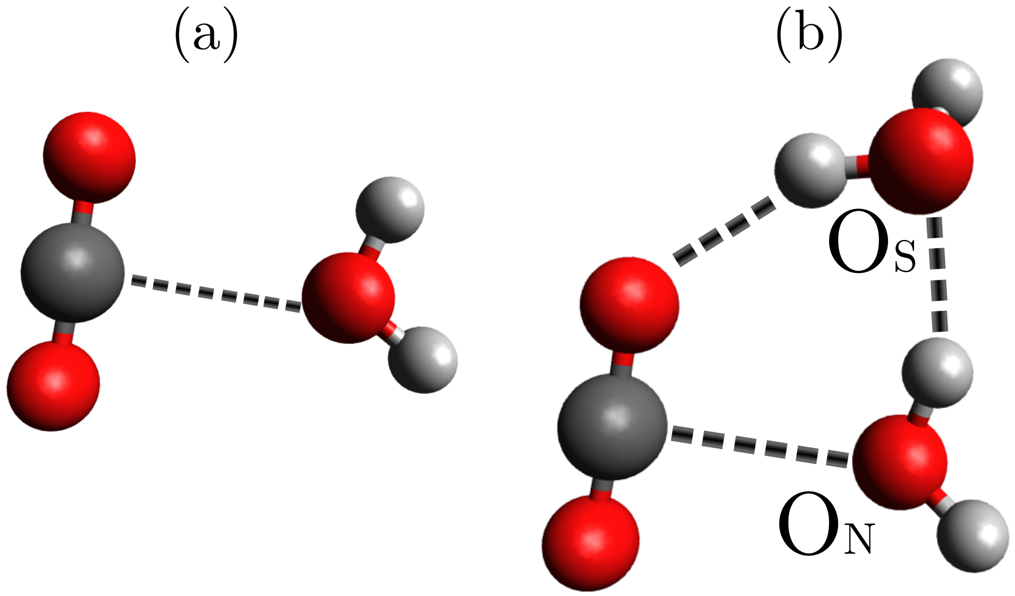

Figure S6: Molecular clusters of CO_2 with the water (a) monomer and (b) dimer.

Table S2: Pairwise IQA interaction energies $E_{\text{int}}^{\mathscr{F}\mathscr{G}\,\prime}$ (equation (8)) among the monomers in (a) the formation energy of the molecular complexes $H_2O\cdots CO_2$ and $(H_2O)_2\cdots CO_2$ along with (b) the rate-limiting steps in Figure S5. The first row and column of every chart indicate monomers $\mathscr{F}$ and $\mathscr{G}$ respectively. The labels, N, S, S1 and S2 are defined in Figure S6. The values are reported in kcal/mol.

(a) Molecular cluster

	$H_2O\cdots CO_2$	$(H_2O)_2\cdots CO_2$	
$\mathscr{G}\backslash\mathscr{F}$	H_2O(N)	H_2O(N)	H_2O(S)
SO_3	−2.57	−5.95	−4.89
H_2O(N)			5.84
Total	−2.57	−5.00	

(b) Transition state

	$[H_2O\cdots CO_2]^{\ddagger}$	$[(H_2O)_2\cdots CO_2]^{\ddagger}$	
$\mathscr{G}\backslash\mathscr{F}$	H_2O(N)	H_2O(N)	H_2O(S)
SO_3	38.82	6.31	−3.37
H_2O(N)			17.96
Total	38.82	20.90	

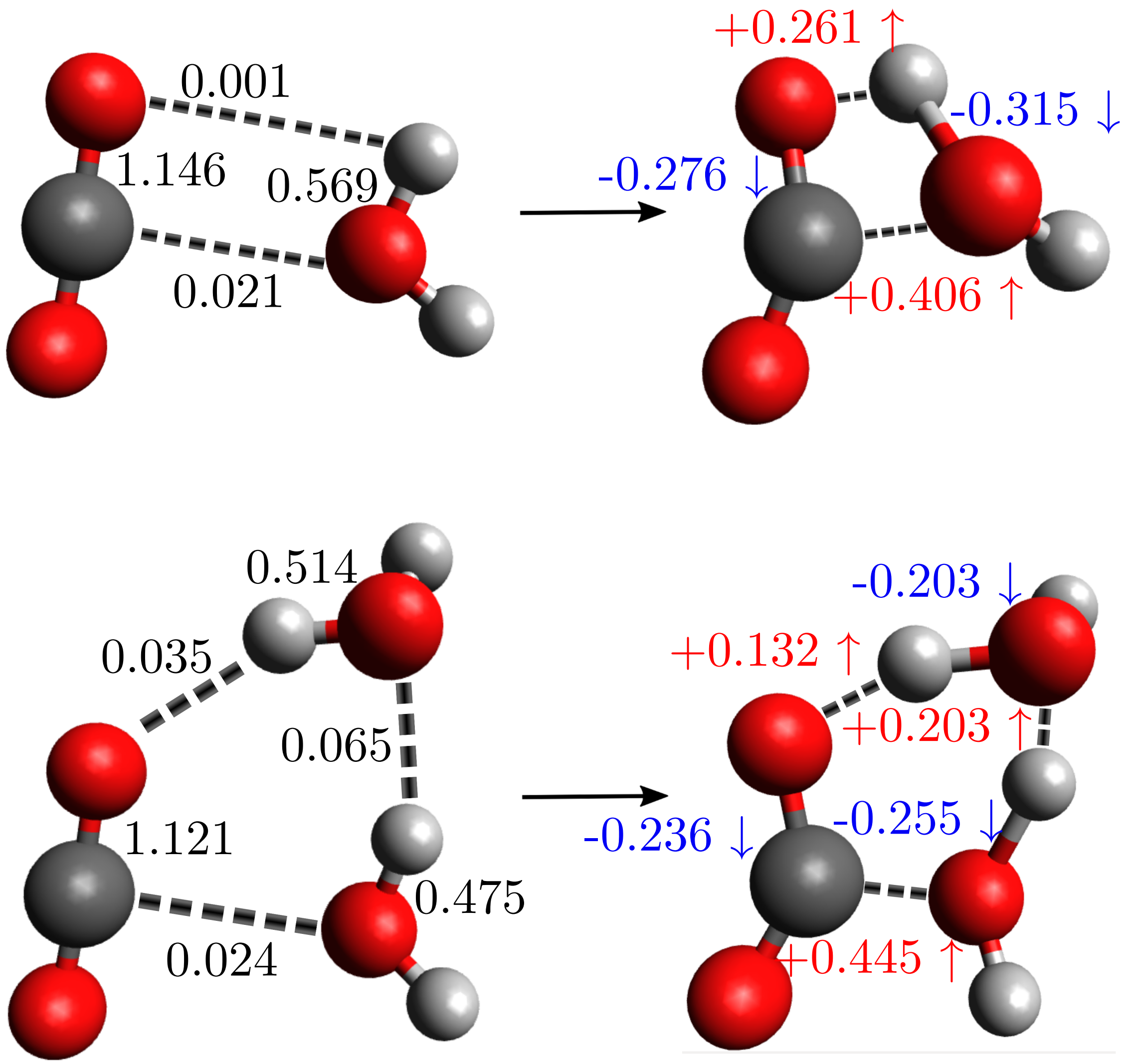

Figure S7: Left: Delocalization indices in the considered molecular clusters (Figure 6) for the pairs of atoms entailed in the formation and rupture of chemical bonds in the considered rate-limiting steps for the formation of carbonic acid Right: Changes in $\delta(A, B)$ indices after the formation of the corresponding transition states. The colour code is the same than in Figure 4 in the body of the manuscript.

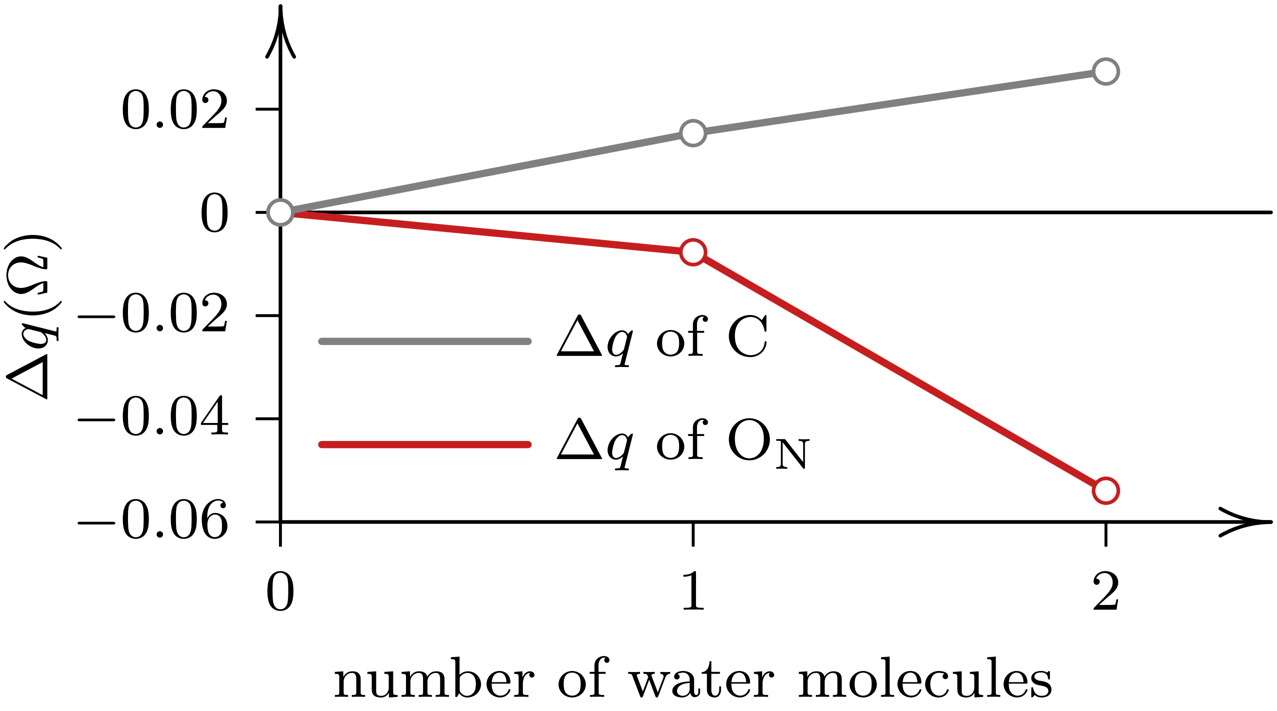

Figure S8: Changes in QTAIM charges of the carbon atom and the nucleophilic oxygen within the molecular clusters $(H_2O)_n \cdots CO_2$ n = 1, 2. Atomic units are used throughout.

Thermodynamic data and coordinates (ångströms) of all systems along with frequencies (cm^{-1}) of transtion states for the formation of H_2SO_4 and H_2CO_3

Formation of H_2SO_4

H_2O

```
E(MP2)= -76.3289923 Hartree
Zero-point correction=                           0.021409 (Hartree/Particle)
Thermal correction to Energy=                    0.024245
Thermal correction to Enthalpy=                  0.025189
Thermal correction to Gibbs Free Energy=         0.003111
Sum of electronic and zero-point Energies=            -76.307583
Sum of electronic and thermal Energies=               -76.304747
Sum of electronic and thermal Enthalpies=             -76.303803
Sum of electronic and thermal Free Energies=          -76.325882
Entropy=                                               46.468 Cal/Mol-Kelvin
```

XYZ coordinates

```
O                   0.00000000    0.11823600    0.00000000
H                   0.75813200   -0.47294400    0.00000000
H                  -0.75813200   -0.47294400    0.00000000
```

SO_3

```
E(MP2)= -623.0594395
Zero-point correction=                           0.012080 (Hartree/Particle)
Thermal correction to Energy=                    0.015641
Thermal correction to Enthalpy=                  0.016585
Thermal correction to Gibbs Free Energy=        -0.014358
Sum of electronic and zero-point Energies=           -623.047359
Sum of electronic and thermal Energies=              -623.043799
Sum of electronic and thermal Enthalpies=            -623.042855
Sum of electronic and thermal Free Energies=         -623.073797
Entropy=                                               65.125 Cal/Mol-Kelvin
```

XYZ coordinates

```
S                 0.00000200    0.00000000   -0.00000300
O                -0.72392400    1.25070100    0.00000200
O                -0.72118600   -1.25228200    0.00000200
O                 1.44510500    0.00158100    0.00000200
```

$(H_2O)_2$

```
E(MP2)= -152.6662408
Zero-point correction=                           0.046171 (Hartree/Particle)
Thermal correction to Energy=                    0.052056
Thermal correction to Enthalpy=                  0.053000
Thermal correction to Gibbs Free Energy=         0.019780
Sum of electronic and zero-point Energies=          -152.620070
Sum of electronic and thermal Energies=             -152.614185
Sum of electronic and thermal Enthalpies=           -152.613240
Sum of electronic and thermal Free Energies=        -152.646461
Entropy=                                              69.917 Cal/Mol-Kelvin
```

XYZ coordinates

```
O                -1.51284500   -0.00002500    0.12197600
H                -0.55937300    0.00000300   -0.04842600
H                -1.91287200    0.00016500   -0.75116100
O                 1.38503700    0.00002200   -0.11047100
H                 1.74734800   -0.76109400    0.35363000
H                 1.74736400    0.76095600    0.35391400
```

$(H_2O)_3$

```
E(MP2)= -229.0129338
Zero-point correction=                           0.072876 (Hartree/Particle)
Thermal correction to Energy=                    0.080431
Thermal correction to Enthalpy=                  0.081376
Thermal correction to Gibbs Free Energy=         0.043379
Sum of electronic and zero-point Energies=          -228.940058
Sum of electronic and thermal Energies=             -228.932502
Sum of electronic and thermal Enthalpies=           -228.931558
Sum of electronic and thermal Free Energies=        -228.969555
Entropy=                                              79.970 Cal/Mol-Kelvin
```

XYZ coordinates

O	-0.11465800	-1.60121300	0.10928600
H	0.66670600	-1.02107100	0.05722900
H	-0.00081800	-2.24308000	-0.59677600
O	-1.33359600	0.89935700	-0.09310900
H	-1.21730700	-0.06586600	-0.02247300
H	-2.00725400	1.12389900	0.55398500
O	1.44888800	0.69506600	-0.08237600
H	0.56622100	1.10329000	-0.02761000
H	1.98737600	1.15714800	0.56523500

H_2SO_4

```
E(MP2)= -699.4195426
Zero-point correction=                           0.039101 (Hartree/Particle)
Thermal correction to Energy=                    0.044262
Thermal correction to Enthalpy=                  0.045206
Thermal correction to Gibbs Free Energy=         0.010805
Sum of electronic and zero-point Energies=           -699.380442
Sum of electronic and thermal Energies=              -699.375280
Sum of electronic and thermal Enthalpies=            -699.374336
Sum of electronic and thermal Free Energies=         -699.408738
Entropy=                                               72.404 Cal/Mol-Kelvin
```

XYZ coordinates

S	-0.00000300	-0.00000900	-0.15929900
O	1.03486500	-0.68758000	0.84860900
O	-1.03482800	0.68764900	0.84858800
H	1.68383200	-0.01435200	1.10781300
H	-1.68381800	0.01447000	1.10786400
O	-0.65927600	-1.08398900	-0.82772400
O	0.65924300	1.08392300	-0.82783300

$SO_3 \cdots H_2O$

```
E(MP2)= -699.403375
Zero-point correction=                           0.036691 (Hartree/Particle)
Thermal correction to Energy=                    0.043430
```

```
Thermal correction to Enthalpy=                  0.044374
Thermal correction to Gibbs Free Energy=         0.005744
Sum of electronic and zero-point Energies=           -699.366684
Sum of electronic and thermal Energies=              -699.359945
Sum of electronic and thermal Enthalpies=            -699.359001
Sum of electronic and thermal Free Energies=         -699.397631
Entropy=                                               81.304 Cal/Mol-Kelvin
```

XYZ coordinates

S	0.45366800	-0.00000200	0.03199500
O	0.41115100	1.24776300	0.75821000
O	0.73375000	0.00006000	-1.38087200
O	0.41114500	-1.24783000	0.75810000
O	-1.90355400	0.00000800	-0.25560700
H	-2.23931700	0.76714500	0.22471000
H	-2.23931300	-0.76712000	0.22472700

$SO_3 \cdots (H_2O)_2$

```
E(MP2)= -775.7521759
Zero-point correction=                           0.063378 (Hartree/Particle)
Thermal correction to Energy=                    0.071853
Thermal correction to Enthalpy=                  0.072797
Thermal correction to Gibbs Free Energy=         0.029771
Sum of electronic and zero-point Energies=           -775.688798
Sum of electronic and thermal Energies=              -775.680323
Sum of electronic and thermal Enthalpies=            -775.679379
Sum of electronic and thermal Free Energies=         -775.722405
Entropy=                                               90.557 Cal/Mol-Kelvin
```

XYZ coordinates

S	-0.78182700	-0.22218600	-0.02108400
O	-1.77205400	0.56917400	-0.70832200
O	-0.93993300	-0.54100400	1.37391200
O	0.12506100	-1.03362700	-0.81535600
O	0.55544900	1.38045400	0.27557700
O	2.69113900	-0.12933400	-0.08097100
H	3.22176700	-0.48001800	0.64117400

H	2.11550800	-0.85720500	-0.36329700
H	0.43776700	1.96090900	-0.48976600
H	1.45687900	0.96599400	0.19051500

$SO_3\cdots(H_2O)_3$

```
E(MP2)= -852.1007116
Zero-point correction=                           0.088805 (Hartree/Particle)
Thermal correction to Energy=                    0.099521
Thermal correction to Enthalpy=                  0.100465
Thermal correction to Gibbs Free Energy=         0.052023
Sum of electronic and zero-point Energies=           -852.011907
Sum of electronic and thermal Energies=              -852.001191
Sum of electronic and thermal Enthalpies=            -852.000247
Sum of electronic and thermal Free Energies=         -852.048689
Entropy=                                              101.955 Cal/Mol-Kelvin
```

XYZ coordinates

O	2.14027000	1.37515100	0.06529000
H	2.40236200	0.42291200	0.05296300
H	2.25811300	1.66238100	0.97701800
O	-0.31528800	1.44914800	-0.59160100
H	0.68480200	1.45112500	-0.35432800
H	-0.39668600	1.42569600	-1.55645800
O	2.45884100	-1.27865300	-0.01433500
H	1.53009100	-1.48059500	-0.22772600
H	2.98763300	-1.79468800	-0.62918300
S	-1.06237800	-0.25540500	0.11957000
O	-0.25768900	-1.17761100	-0.67345300
O	-0.66068900	-0.02823100	1.48546000
O	-2.42398000	-0.03984700	-0.29328800

$[SO_3\cdots H_2O]^{\ddagger}$

```
E(MP2)= -699.3638423
Zero-point correction=                           0.034617 (Hartree/Particle)
Thermal correction to Energy=                    0.039313
Thermal correction to Enthalpy=                  0.040257
Thermal correction to Gibbs Free Energy=         0.006561
```

```
Sum of electronic and zero-point Energies=          -699.329225
Sum of electronic and thermal Energies=             -699.324529
Sum of electronic and thermal Enthalpies=           -699.323585
Sum of electronic and thermal Free Energies=        -699.357282
Entropy=                                              70.920 Cal/Mol-Kelvin
```

Frequencies

1578.3817i, 262.5096, 369.6208, 440.1638, 494.4950, 537.3829,
646.0225, 713.6963, 935.8817, 1022.5619, 1269.0623, 1297.2346,
1439.9231, 2031.5338, 3735.2216

XYZ coordinates

S	0.28007100	0.00135400	0.06214400
O	0.70164700	1.37708000	0.07814400
O	1.06585300	-1.01443400	-0.57301500
O	-0.56420000	-0.45005200	1.24162600
O	-1.37613900	0.00336600	-0.79763700
H	-1.60899100	0.92977300	-0.97989500
H	-1.48943400	-0.27912200	0.39264900

$[SO_3\cdots(H_2O)_2]^\ddagger$

```
E(MP2)= -775.7401914
Zero-point correction=                          0.061310 (Hartree/Particle)
Thermal correction to Energy=                   0.067643
Thermal correction to Enthalpy=                 0.068587
Thermal correction to Gibbs Free Energy=        0.030261
Sum of electronic and zero-point Energies=          -775.678881
Sum of electronic and thermal Energies=             -775.672549
Sum of electronic and thermal Enthalpies=           -775.671604
Sum of electronic and thermal Free Energies=        -775.709931
Entropy=                                              80.664 Cal/Mol-Kelvin
```

Frequencies

628.1436i, 36.0072, 316.0166, 330.4941, 415.7977, 442.8093, 496.3594,
514.4383, 532.7660, 594.6199, 599.8305, 667.6098, 747.7685, 1033.6417,
1041.9591, 1259.7697, 1333.0391, 1409.9013, 1568.6037, 1636.7155,
1817.5896, 2545.6501, 3758.6081, 3812.1007

XYZ coordinates

S	0.65020800	-0.14494400	0.01532100
O	1.75151700	0.53403500	0.65103900
O	0.80932200	-0.77330500	-1.27157000
O	-0.26136500	-0.86739100	0.94573700
O	-0.42532600	1.23101900	-0.42730900
O	-2.39810200	-0.02772400	0.09606600
H	-2.74770400	-0.49641600	-0.67440600
H	-1.65368600	-0.62464100	0.53332300
H	-0.18199800	1.95034800	0.17675100
H	-1.62830400	0.71674900	-0.23251200

$[SO_3\cdots(H_2O)_3]^\ddagger$

```
E(MP2)= -852.0980858
Zero-point correction=                          0.086977 (Hartree/Particle)
Thermal correction to Energy=                   0.096057
Thermal correction to Enthalpy=                 0.097001
Thermal correction to Gibbs Free Energy=        0.052764
Sum of electronic and zero-point Energies=          -852.011108
Sum of electronic and thermal Energies=             -852.002029
Sum of electronic and thermal Enthalpies=           -852.001085
Sum of electronic and thermal Free Energies=        -852.045322
Entropy=                                              93.104 Cal/Mol-Kelvin
```

Frequencies

389.5407i, 55.2342, 85.2337, 119.0799, 220.8217, 269.2085, 291.0123, 325.7169, 383.3699, 424.4931, 472.4496, 497.3682, 528.6456, 556.2404, 576.8422, 639.2642, 733.5166, 739.1792, 886.3369, 1024.7301, 1068.0045, 1162.7122, 1296.0566, 1387.2487, 1526.8181, 1647.5907, 1712.2269, 1767.6422, 2924.0126, 3455.4227, 3739.4336, 3771.5524, 3891.2441

XYZ coordinates

O	-1.84648900	-1.38139700	0.05300400
H	-2.22562000	-0.44055900	0.02160700
H	-1.53615800	-1.47930000	0.96938200
O	0.32614200	-1.12496600	-0.94760000

H	-0.82982000	-1.29354000	-0.52875900
H	0.39224600	-0.80891900	-1.86152000
O	-2.41747000	1.11267700	0.03300300
H	-1.49144900	1.41701300	-0.10177000
H	-2.96644000	1.61217400	-0.57796200
S	0.96960800	0.19000600	0.13549100
O	0.24319300	1.34703500	-0.40180300
O	0.45510800	-0.34725100	1.38353800
O	2.38245400	0.13803200	-0.13124700

$H_2SO_4 \cdots H_2O$

```
E(MP2)= -775.7692771
Zero-point correction=                           0.064204 (Hartree/Particle)
Thermal correction to Energy=                    0.072044
Thermal correction to Enthalpy=                  0.072988
Thermal correction to Gibbs Free Energy=         0.031899
Sum of electronic and zero-point Energies=           -775.705073
Sum of electronic and thermal Energies=              -775.697234
Sum of electronic and thermal Enthalpies=            -775.696289
Sum of electronic and thermal Free Energies=         -775.737378
Entropy=                                               86.478 Cal/Mol-Kelvin
```

XYZ coordinates

S	-0.58175100	-0.06608700	0.13209200
O	-1.78793100	-0.82705100	0.29211600
O	0.21876300	0.37109900	1.25141900
O	0.33145900	-0.84153600	-0.88551200
O	-0.93123200	1.28202200	-0.65954100
O	2.67306900	0.09287800	-0.12010700
H	3.40416200	-0.48066200	0.13018700
H	1.27768900	-0.55137500	-0.73077300
H	-1.67451300	1.08850700	-1.25197100
H	2.26765000	0.38161500	0.71208900

$H_2SO_4 \cdots (H_2O)_2$

```
E(MP2)= -852.1182656
Zero-point correction=                           0.089309 (Hartree/Particle)
```

```
Thermal correction to Energy=                    0.099702
Thermal correction to Enthalpy=                  0.100647
Thermal correction to Gibbs Free Energy=         0.052679
Sum of electronic and zero-point Energies=           -852.028957
Sum of electronic and thermal Energies=              -852.018563
Sum of electronic and thermal Enthalpies=            -852.017619
Sum of electronic and thermal Free Energies=         -852.065587
Entropy=                                              100.956 Cal/Mol-Kelvin
```

XYZ coordinates

```
O          2.76300       -1.11560        0.10530
H          2.46590        0.56900       -0.01360
H          3.25020       -1.60710       -0.56210
O         -1.13570        0.16290        1.47220
H          1.83640       -1.39710        0.01330
H         -1.96410        0.65270        1.59390
O          2.05010        1.46110       -0.07820
H          0.56650        1.28340       -0.40830
H          2.25280        1.90930        0.74850
S         -0.99720       -0.15530       -0.09750
O         -0.41530        1.16720       -0.67510
O         -0.00940       -1.20960       -0.14940
O         -2.30930       -0.33170       -0.65120
```

Formation of H_2CO_3

CO_2

```
E(MP2)= -188.3216406
Zero-point correction=                           0.009992 (Hartree/Particle)
Thermal correction to Energy=                    0.012965
Thermal correction to Enthalpy=                  0.013909
Thermal correction to Gibbs Free Energy=        -0.006146
Sum of electronic and zero-point Energies=           -188.311649
Sum of electronic and thermal Energies=              -188.308676
Sum of electronic and thermal Enthalpies=            -188.307731
```

```
Sum of electronic and thermal Free Energies=          -188.327787
Entropy=                                                 42.210 Cal/Mol-Kelvin
```

XYZ coordinates

```
C                  0.00000000    0.00016400   -0.00002000
O                  0.01482900   -0.05553200    1.16884200
O                 -0.01482900    0.05541000   -1.16882700
```

H_2CO_3

```
E(MP2)= -264.6390757
Zero-point correction=                          0.039408 (Hartree/Particle)
Thermal correction to Energy=                   0.043158
Thermal correction to Enthalpy=                 0.044103
Thermal correction to Gibbs Free Energy=        0.013491
Sum of electronic and zero-point Energies=            -264.599668
Sum of electronic and thermal Energies=               -264.595917
Sum of electronic and thermal Enthalpies=             -264.594973
Sum of electronic and thermal Free Energies=          -264.625584
Entropy=                                                 64.427 Cal/Mol-Kelvin
```

XYZ coordinates

```
C                 -0.06036800   -0.13353100    0.00004000
O                  1.27719900   -0.19166100   -0.00013500
O                 -0.77662900   -1.09541800    0.00004100
O                 -0.47763300    1.15773800   -0.00005900
H                  1.62295300    0.71054500    0.00092700
H                 -1.44424100    1.12536600    0.00005700
```

$CO_2 \cdots H_2O$

```
E(MP2)= -264.6551199
Zero-point correction=                          0.034144 (Hartree/Particle)
Thermal correction to Energy=                   0.040848
Thermal correction to Enthalpy=                 0.041792
Thermal correction to Gibbs Free Energy=        0.002664
Sum of electronic and zero-point Energies=            -264.620976
Sum of electronic and thermal Energies=               -264.614272
```

```
Sum of electronic and thermal Enthalpies=           -264.613328
Sum of electronic and thermal Free Energies=        -264.652456
Entropy=                                              82.351 Cal/Mol-Kelvin
```

XYZ coordinates

```
O                 -0.75374100    1.20335200   -0.00005500
O                  1.87828900   -0.12403300   -0.00035400
H                  2.63495500   -0.71718700    0.00059300
H                  2.26142800    0.75816100    0.00188400
O                 -1.06651000   -1.11520400    0.00009300
C                 -0.89344800    0.04101800    0.00000800
```

$CO_2 \cdot .. (H_2O)_2$

```
E(MP2)= -340.9962464
Zero-point correction=                          0.059536 (Hartree/Particle)
Thermal correction to Energy=                   0.068835
Thermal correction to Enthalpy=                 0.069779
Thermal correction to Gibbs Free Energy=        0.025053
Sum of electronic and zero-point Energies=          -340.936710
Sum of electronic and thermal Energies=             -340.927411
Sum of electronic and thermal Enthalpies=           -340.926467
Sum of electronic and thermal Free Energies=        -340.971194
Entropy=                                              94.135 Cal/Mol-Kelvin
```

XYZ coordinates

```
O                 -0.46168900   -1.22221000    0.09613400
O                  0.49518600    1.58041300    0.12204900
O                  2.42431600   -0.46996900   -0.15679300
H                  3.04638900   -0.76841200    0.51288500
H                  1.65052600   -1.03665200   -0.04628000
H                  0.63098900    2.44447100   -0.27461700
H                  1.33548300    1.10896400    0.00704100
O                 -2.27514000    0.24273700   -0.08900100
C                 -1.35413000   -0.46602400    0.00364400
```

$[CO_2 \cdots H_2O]^{\ddagger}$

```
E(MP2)= -264.5740618
Zero-point correction=                           0.033033 (Hartree/Particle)
Thermal correction to Energy=                    0.036803
Thermal correction to Enthalpy=                  0.037748
Thermal correction to Gibbs Free Energy=         0.006988
Sum of electronic and zero-point Energies=           -264.541029
Sum of electronic and thermal Energies=              -264.537258
Sum of electronic and thermal Enthalpies=            -264.536314
Sum of electronic and thermal Free Energies=         -264.567073
Entropy=                                               64.738 Cal/Mol-Kelvin
```

Frequencies

```
1684.9285i, 397.2061, 501.6286, 626.1690, 722.7938, 789.3887,
940.1567, 1264.6963, 1302.3902, 1984.8988, 2189.9317, 3780.6104
```

XYZ coordinates

```
C                 0.34864400    0.08459300   -0.00665700
O                -0.18156500    1.23401400    0.02344600
O                 1.36059700   -0.51507000   -0.00098500
O                -1.13158300   -0.69540800   -0.10723400
H                -1.19804700    0.53749500    0.03218000
H                -1.27340600   -1.23334100    0.68594800
```

$[\mathrm{CO_2}\cdots(\mathrm{H_2O})_2]^\ddagger$

```
E(MP2)= -340.9446818
Zero-point correction=                           0.058855 (Hartree/Particle)
Thermal correction to Energy=                    0.064083
Thermal correction to Enthalpy=                  0.065027
Thermal correction to Gibbs Free Energy=         0.030387
Sum of electronic and zero-point Energies=           -340.885827
Sum of electronic and thermal Energies=              -340.880598
Sum of electronic and thermal Enthalpies=            -340.879654
Sum of electronic and thermal Free Energies=         -340.914295
Entropy=                                               72.907 Cal/Mol-Kelvin
```

Frequencies

```
1092.4683i, 109.5954, 374.1202, 435.1393, 512.0622, 550.8642,
583.3398, 642.3378, 694.6013, 762.8424, 786.3042, 1044.0394,
1196.5627, 1336.8172, 1608.2170, 1738.4865, 2000.8529, 2289.1096,
3812.5949, 3839.3025
```

XYZ coordinates

O	-0.06087700	-1.18112700	0.11476800
O	0.04320300	1.11770300	0.18211700
O	2.04598400	-0.03608900	-0.20767700
H	2.63309100	-0.04452700	0.55806600
H	1.26237100	-0.75971500	-0.04452900
H	-0.43328600	1.82363200	-0.27360000
H	1.21552500	0.76663400	-0.06967400
O	-1.99203000	0.02748000	-0.13028000
C	-0.82799000	-0.20162800	0.02638500

$H_2CO_3\cdots H_2O$

```
E(MP2)= -340.9828527
Zero-point correction=                          0.064046 (Hartree/Particle)
Thermal correction to Energy=                   0.070926
Thermal correction to Enthalpy=                 0.071870
Thermal correction to Gibbs Free Energy=        0.033484
Sum of electronic and zero-point Energies=          -340.918807
Sum of electronic and thermal Energies=             -340.911927
Sum of electronic and thermal Enthalpies=           -340.910983
Sum of electronic and thermal Free Energies=        -340.949369
Entropy=                                              80.790 Cal/Mol-Kelvin
```

XYZ coordinates

O	-0.08183200	-1.11336600	-0.01147100
O	-0.19849200	1.10947200	-0.00714600
O	2.40984300	-0.02750300	-0.08121400
H	3.07684900	-0.15741900	0.59980700
H	0.85427100	-0.80956700	-0.03318700
H	-0.87775100	1.79811000	-0.00505600
H	2.07534000	0.86826000	0.04959700
O	-2.09786300	-0.12661600	0.02180800
C	-0.89699200	-0.07254600	0.00217200

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