Supplementary material for:

Hydrogen Bonding in the Cyclic Complexes of Carboxylic Acid−Sulfuric Acid and Its Atmospheric Implications

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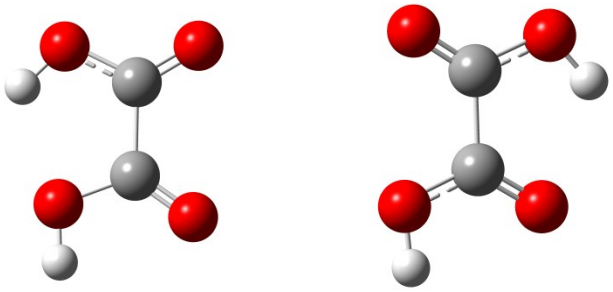
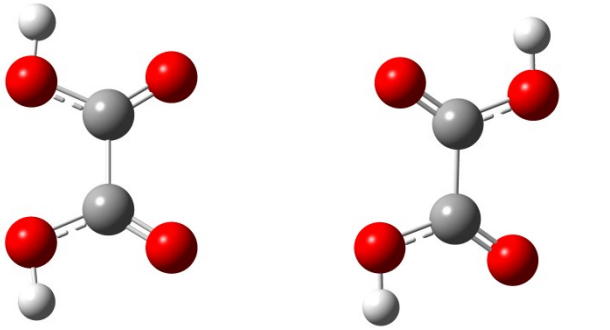
(a) 0.0 kJ mol^{-1} **(b) 5.3 kJ mol^{-1}**

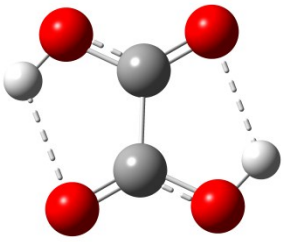
Fig. S1. Optimized two conformers of H_2SO_4 at the B3LYP-D3/aug-cc-pVTZ level (aug-cc-pV(T+d)Z basis set for sulfur). The relative energies of all the structures are calculated with respect to the most stable structure **a**.



(a) 25.2 kJ mol^{-1} **(b) 2.1 kJ mol^{-1}**

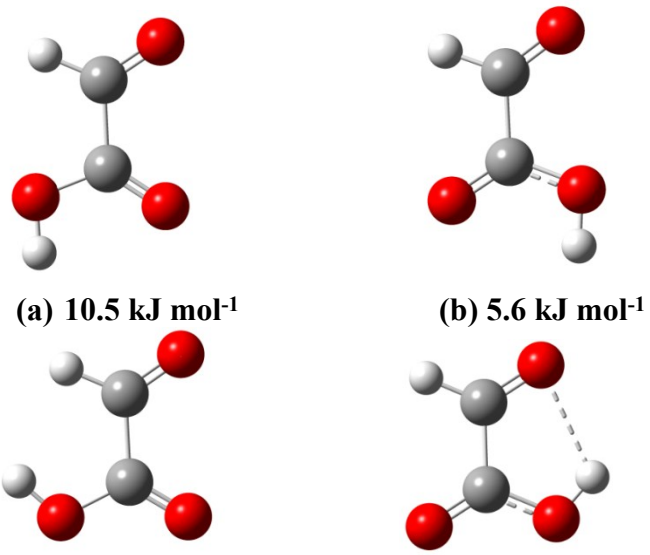


(c) 23.7 kJ mol^{-1} **(d) 18.3 kJ mol^{-1}**



(e) 0.0 kJ mol^{-1}

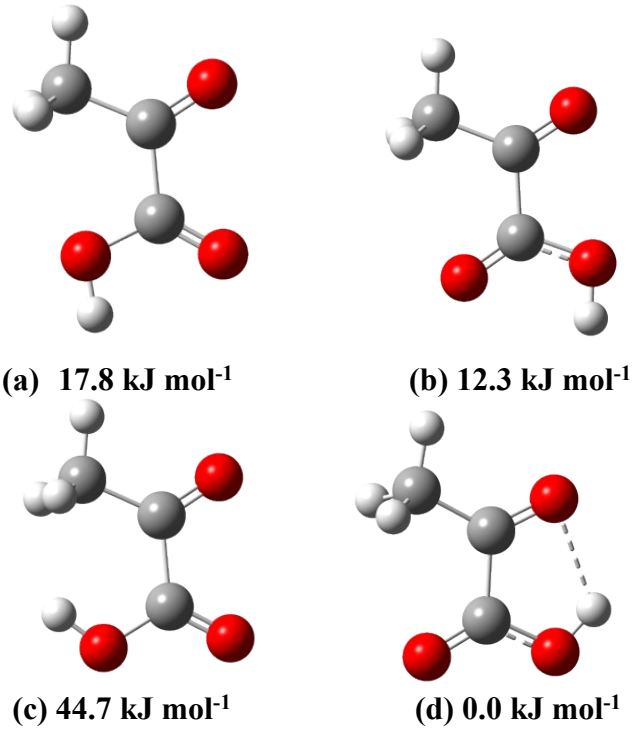
Fig. S2. Optimized five conformers of oxalic acid (OA) at the B3LYP-D3/aug-cc-pVTZ level. The relative energies of all the structures are calculated with respect to the most stable structure **e**.



(a) 10.5 kJ mol^{-1} **(b) 5.6 kJ mol^{-1}**

(c) 34.4 kJ mol^{-1} **(d) 0.0 kJ mol^{-1}**

Fig. S3. Optimized four conformers of glyoxylic acid (GA) at the B3LYP-D3/aug-cc-pVTZ level. The relative energies of all the structures are calculated with respect to the most stable structure **d**.



(a) 17.8 kJ mol^{-1} **(b) 12.3 kJ mol^{-1}**

(c) 44.7 kJ mol^{-1} **(d) 0.0 kJ mol^{-1}**

Fig. S4. Optimized four conformers of pyruvic acid (PA) at the B3LYP-D3/aug-cc-pVTZ level. The relative energies of all the structures are calculated with respect to the most stable structure **d**.

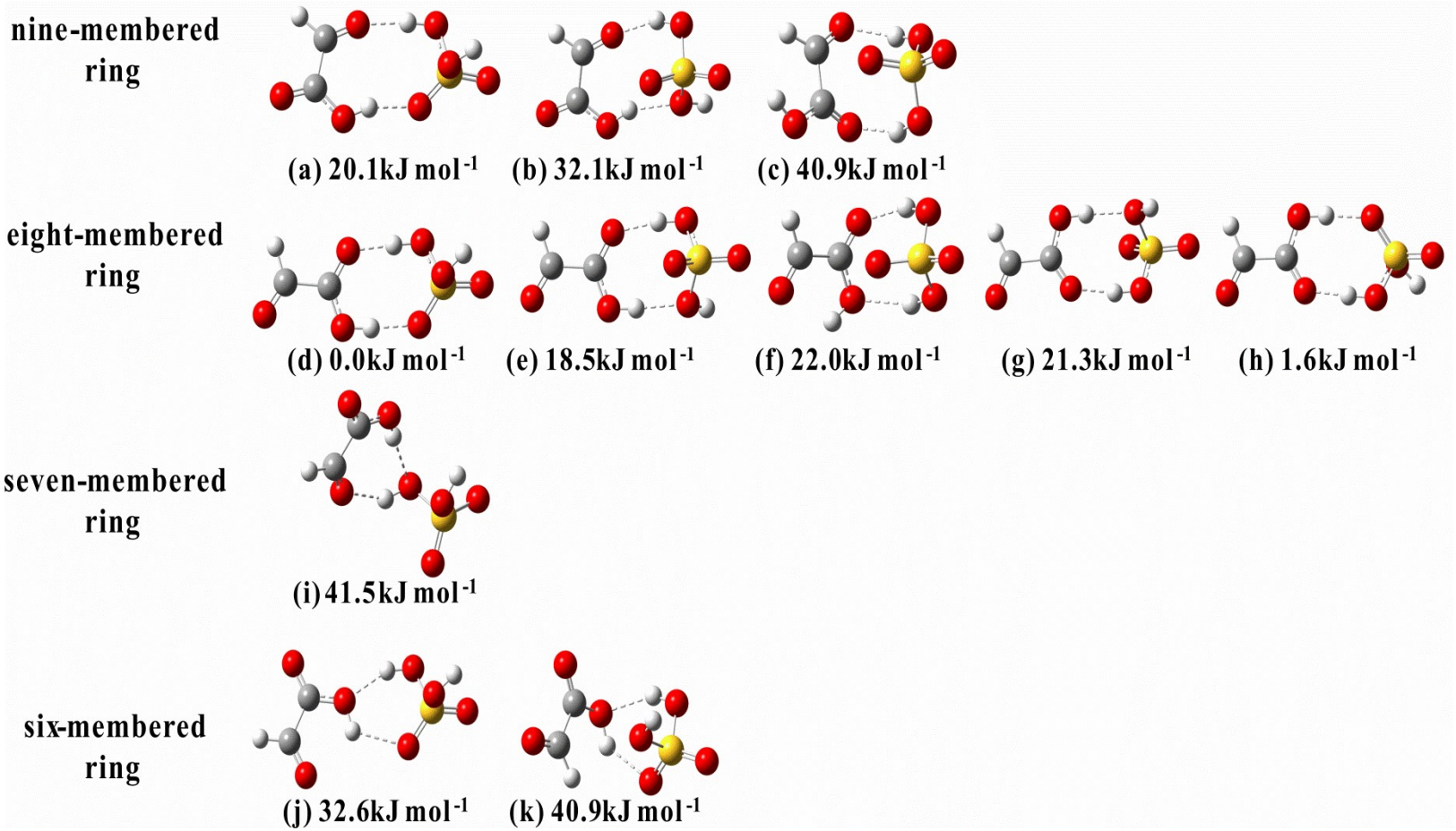


Fig. S5. Optimized structures of the glyoxylic acid (GA)−sulfuric acid complexes at the B3LYP-D3/aug-cc-pVTZ level (aug-cc-pV(T+d)Z basis set for sulfur). The relative energies of all the structures are calculated with respect to the most stable structure **d**.

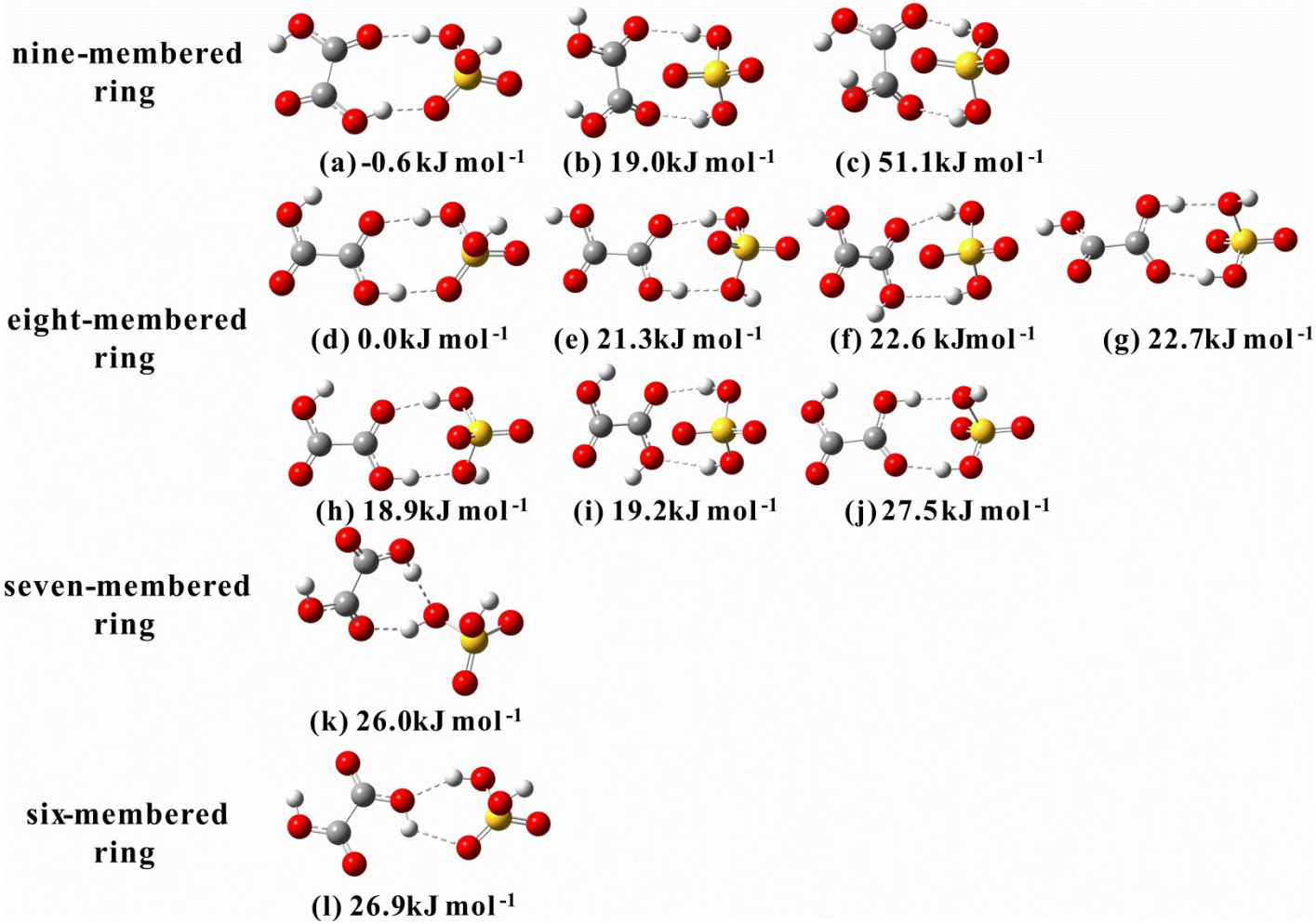


Fig. S6. Optimized structures of the oxalic acid (OA)−sulfuric acid complexes at the B3LYP-D3/aug-cc-pVTZ level (aug-cc-pV(T+d)Z basis set for sulfur). The relative energies of all the structures are calculated with respect to structure **d**.

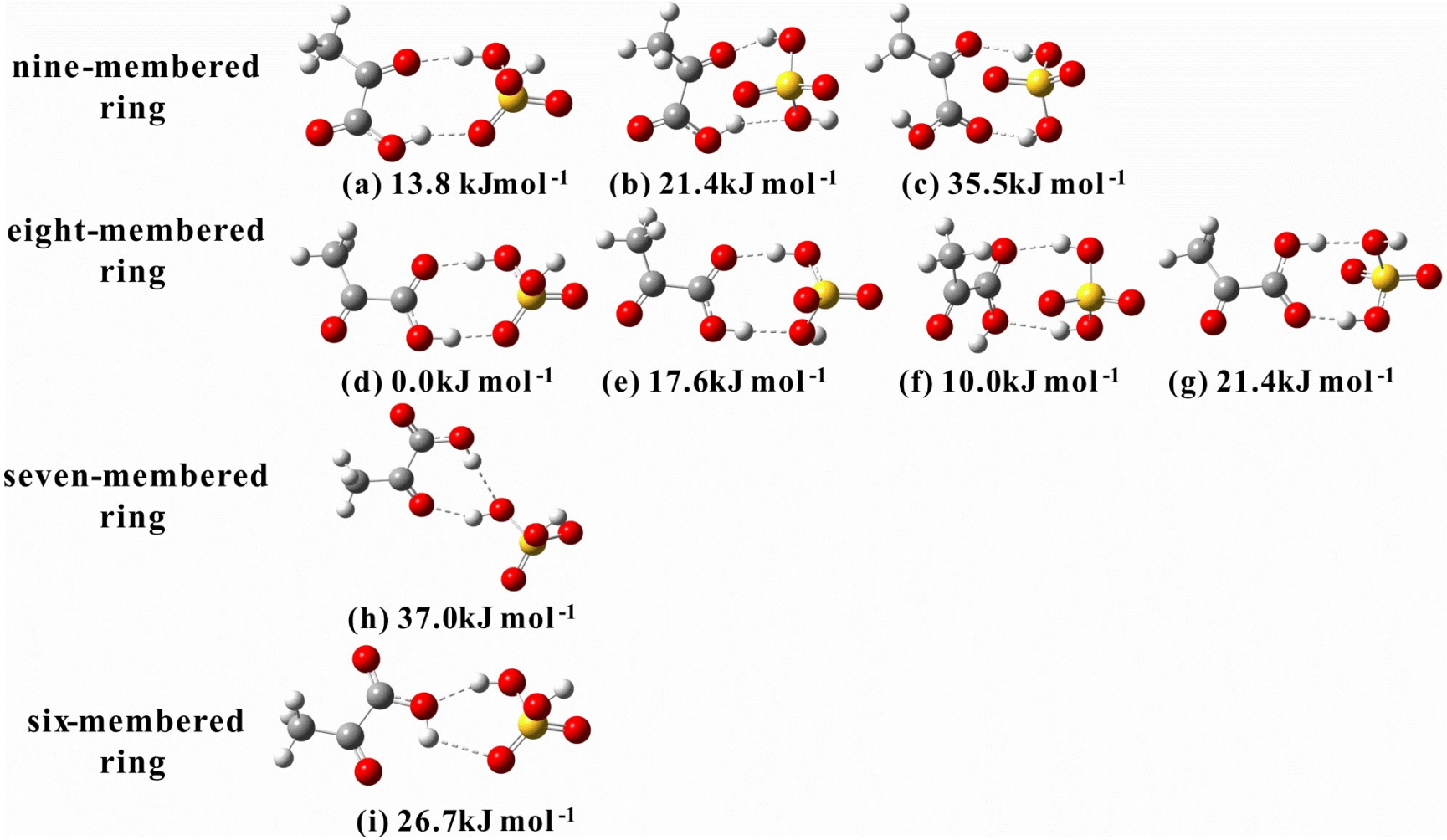


Fig. S7. Optimized structures of the pyruvic acid (PA)−sulfuric acid complexes at the B3LYP-D3/aug-cc-pVTZ level (aug-cc-pV(T+d)Z basis set for sulfur). The relative energies of all the structures are calculated with respect to the most stable structure **d**.

Table S1 Calculated binding energy (*BE*), enthalpy of formation (ΔH^{θ}_{298K}), Gibbs free energy of formation (ΔG^{θ}_{298K}) at the B3LYP/aug-cc-pVTZ level (aug-cc-pV(T+d)Z basis set for sulfur) [a]

Type	Conformer	*BE* [b]	*ZPVE*	ΔH^{θ}_{298K}	ΔG^{θ}_{298K}
Nine-membered ring	GA−H_2SO_4	-34.6	3.6	-33.1	6.9
	OA−H_2SO_4	-45.7	3.8	-44.7	-1.9
	PA−H_2SO_4	-35.2	3.3	-33.7	6.8
Eight-membered ring	GA−H_2SO_4	-54.3	3.9	-53.8	-9.7
	OA−H_2SO_4	-45.0	3.8	-44.5	0.2
	PA−H_2SO_4	-48.7	3.7	-48.1	-4.9
Seven-membered ring	GA−H_2SO_4	-14.2	2.7	-11.9	21.5
	OA−H_2SO_4	-22.1	3.6	-20.9	19.3
	PA−H_2SO_4	-15.7	2.4	-13.4	21.1
Six-membered ring	GA−H_2SO_4	-24.8	3.1	-22.8	14.3
	OA−H_2SO_4	-21.4	2.7	-19.2	17.8
	PA−H_2SO_4	-25.5	2.9	-23.3	13.2

[a] All energies are given in kJ mol^{-1}. [b] *BE* corrected with ZPVE.

Table S2 Calculated binding energy (*BE*), enthalpy of formation (ΔH^{θ}_{298K}), Gibbs free energy of formation (ΔG^{θ}_{298K}) at the M06-2X/aug-cc-pVTZ level (aug-cc-pV(T+d)Z basis set for sulfur) [a]

Type	Conformer	*BE* [b]	*ZPVE*	ΔH^{θ}_{298K}	ΔG^{θ}_{298K}
Nine-membered ring	GA−H_2SO_4	-51.6	3.5	-43.3	-3.6
	OA−H_2SO_4	-64.1	3.0	-56.2	-15.2
	PA−H_2SO_4	-53.6	3.3	-45.3	-5.7
Eight-membered ring	GA−H_2SO_4	-72.2	2.4	-64.8	-22.0
	OA−H_2SO_4	-62.5	1.9	-54.9	-12.5
	PA−H_2SO_4	-67.1	2.5	-59.8	-16.7
Seven-membered ring	GA−H_2SO_4	-30.5	3.4	-22.0	19.2
	OA−H_2SO_4	-38.8	2.7	-25.5	13.4
	PA−H_2SO_4 [c]	-27.7	1.9	-19.9	25.9
Six-membered ring	GA−H_2SO_4	-42.3	3.2	-33.8	4.0
	OA−H_2SO_4	-38.9	2.6	-30.2	7.4
	PA−H_2SO_4	-42.4	3.3	-33.9	4.5

[a] All energies are given in kJ mol^{-1}. [b] *BE* corrected with ZPVE. [c] Obtained from single-point M06-2X calculation at the B3LYP/aug-cc-pVTZ optimized structure.

Table S3 Calculated binding energy (*BE*), enthalpy of formation (ΔH^{θ}_{298K}), Gibbs free energy of formation (ΔG^{θ}_{298K}) at the ωB97X-D/aug-cc-pVTZ level (aug-cc-pV(T+d)Z basis set for sulfur) [a]

Type	Conformer	*BE* [b]	*ZPVE*	ΔH^{θ}_{298K}	ΔG^{θ}_{298K}
Nine-membered ring	GA−H_2SO_4	-42.2	3.3	-40.7	-0.9
	OA−H_2SO_4	-53.8	3.9	-52.9	-10.1
	PA−H_2SO_4	-42.8	3.6	-41.5	-0.6
Eight-membered ring	GA−H_2SO_4	-62.8	3.7	-62.2	-18.2
	OA−H_2SO_4	-52.8	3.8	-52.2	-7.8
	PA−H_2SO_4	-56.6	4.2	-56.2	-12.3
Seven-membered ring	GA−H_2SO_4	-20.7	3.1	-18.8	19.5
	OA−H_2SO_4	-26.9	3.7	-25.6	15.8
	PA−H_2SO_4 [c]	-19.5	2.3	-18.7	27.4
Six-membered ring	GA−H_2SO_4	-31.1	3.0	-29.1	7.8
	OA−H_2SO_4	-27.5	2.5	-25.4	11.3
	PA−H_2SO_4	-31.5	3.0	-29.5	7.0

[a] All energies are given in kJ mol^{-1}. [b] *BE* corrected with ZPVE. [c] Obtained from single-point ωB97X-D calculation at the B3LYP/aug-cc-pVTZ optimized structure.

Table S4 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of GA−H_2SO_4 nine-memebered ring system.

C	-2.80520400	-0.33235500	-0.00342100
O	-3.97944700	-0.54783100	0.14915100
O	-1.89488600	-1.27231400	-0.17276700
H	-0.97647700	-0.94694300	-0.29651100
C	-2.34823300	1.13356100	0.01691200
O	-1.20152500	1.50273300	-0.02496800
S	1.86905000	-0.14957100	-0.10254200
O	3.19914600	-0.30931700	-0.57363500
O	0.78397600	-0.93677100	-0.61104800
O	1.83129500	-0.39279100	1.47318200
H	2.67174400	-0.11068100	1.86368100
O	1.50859400	1.37127700	-0.23341600
H	0.53462000	1.48725300	-0.15409000
H	-3.19130000	1.83638000	0.09465900

Table S5 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of GA−H_2SO_4 eight-memebered ring system.

C	-2.00792200	0.18752400	-0.05906200
O	-1.27586700	1.16837800	-0.07333300
O	-1.64715500	-1.06006200	-0.15209300
H	-0.66004800	-1.14462600	-0.23367800
C	-3.52246400	0.41029700	0.08478800
O	-4.32194200	-0.47724800	0.12007500
S	1.95673200	-0.10727500	-0.08550200
O	3.26922800	-0.13190200	-0.62777900
O	1.02102400	-1.16773300	-0.35990400
O	2.04136200	-0.07767100	1.50796200
H	2.81690300	0.43534700	1.77925400
O	1.31155100	1.26084800	-0.43947500
H	0.31424700	1.24126700	-0.28783700
H	-3.78210900	1.48060600	0.15231800

Table S6 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of GA−H_2SO_4 seven-memebered ring system.

C	-2.58294000	-0.39283600	-0.00529500
O	-3.58282500	-0.87067900	0.45399400
O	-1.65039300	-1.10367500	-0.63670900
H	-0.89004400	-0.56440200	-0.92029400
C	-2.35863900	1.12238000	0.13642900
O	-1.37220400	1.70927600	-0.23104600
S	1.89513300	-0.04084200	0.05793100
O	2.72930000	-1.03586500	-0.52109600
O	0.95650900	-0.72366700	1.15849400
O	2.37646700	1.15569200	0.65221600
O	0.82900200	0.33944200	-1.07332500
H	0.29212800	1.11011300	-0.78697200
H	-3.20451100	1.62969000	0.62297300
H	0.84291900	-1.66340000	0.95036000

Table S7 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of GA−H_2SO_4 six-memebered ring system.

C	2.56624200	-0.60347400	0.00665200
O	3.07805300	-1.68209500	0.08435700
O	1.24482700	-0.41688100	-0.12551500
H	1.01061400	0.53201700	-0.16959100
C	3.38154500	0.69589700	0.05190800
O	2.85484600	1.77191300	-0.02388600
S	-2.00854200	0.12778400	-0.09494200
O	-3.29966200	0.16364800	-0.68898200
O	-1.38465400	-1.27647800	-0.45504200
O	-1.03124800	1.15025400	-0.30844700
O	-2.16672700	0.04270600	1.49134400
H	-2.97647900	-0.44325200	1.70634200
H	-0.41400400	-1.25355000	-0.31815400
H	4.46632400	0.54116800	0.15848600

Table S8 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of OA−H_2SO_4 nine-memebered ring system.

C	-2.44374500	-0.76308600	-0.01174200
O	-3.60406500	-1.07913500	0.10093100
O	-1.45382700	-1.60843800	-0.12184100
H	-0.55637900	-1.20699500	-0.21017200
C	-2.11043400	0.75672300	-0.02411800
O	-0.99859500	1.21441300	-0.12260200
S	2.15912300	-0.09512600	-0.08318700
O	3.49533000	-0.20784900	-0.55069000
O	1.16316800	-1.07455500	-0.41443400
O	2.15430700	-0.05810200	1.51155000
H	2.95041300	0.39565700	1.82573700
O	1.64310300	1.32705600	-0.47518900
H	0.66154400	1.36825800	-0.36398500
O	-3.19019500	1.50113000	0.08969400
H	-3.95027800	0.88712300	0.15522200

Table S9 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of OA−H_2SO_4 eight-memebered ring system.

C	-1.69324700	-0.10441300	-0.08308200
O	-1.04970800	0.93988600	-0.13175000
O	-1.22078100	-1.30918300	-0.12733800
H	-0.22784800	-1.30633700	-0.20338600
C	-3.23681300	-0.03797600	0.04748900
O	-3.93169000	-1.00412900	0.10922400
O	-3.68781500	1.21995400	0.08319600
H	-2.93264400	1.82724400	0.01748700
S	2.29050200	-0.05684900	-0.07807000
O	3.60406400	0.00148000	-0.61304600
O	1.43556300	-1.18920300	-0.32743800
O	2.35787300	0.02775300	1.51255800
H	3.10033200	0.59191100	1.77537300
O	1.54685000	1.25038200	-0.47890100
H	0.55762900	1.15558100	-0.33883700

Table S10 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of OA−H_2SO_4 seven-memebered ring system.

C	-2.27256000	-0.79201300	-0.06521900
O	-3.29784700	-1.28842700	0.32460600
O	-1.23237000	-1.48634000	-0.47876500
H	-0.46917900	-0.93440400	-0.74353900
C	-2.16650800	0.76275000	-0.09203600
O	-1.19405900	1.38048200	-0.45415300
S	2.21230200	0.07361300	0.05373700
O	3.19431500	-0.82233000	-0.45333900
O	1.46753300	-0.63076400	1.28501500
O	2.48861400	1.40306900	0.46874400
O	1.04540800	0.10971000	-1.03451000
H	0.39879500	0.83393800	-0.83725100
H	1.62048600	-1.58627900	1.24380200
O	-3.27263800	1.34108500	0.32508300
H	-3.90417900	0.63263800	0.55928100

Table S11 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of OA−H_2SO_4 six-memebered ring system.

C	-2.15879900	0.69504400	-0.02293900
O	-2.67184200	1.77697800	0.05553100
O	-0.84890200	0.49836100	-0.13534800
H	-0.62719300	-0.45516000	-0.18448900
C	-2.98489200	-0.61267900	-0.00003700
O	-2.46093000	-1.68808900	-0.07637800
S	2.39496700	-0.15051600	-0.08809500
O	3.68501800	-0.24128200	-0.67757300
O	1.84012100	1.28710400	-0.43924400
O	1.36963900	-1.12117200	-0.31605200
O	2.54861100	-0.08544100	1.49866400
H	3.38434300	0.35019000	1.72229600
H	0.87099500	1.31034900	-0.30717700
O	-4.29112900	-0.40689700	0.11071800
H	-4.45016700	0.55218400	0.15420300

Table S12 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of PA−H_2SO_4 nine-memebered ring system.

C	-2.45963800	-0.83540300	-0.00759000
O	-3.58963300	-1.22603000	0.12503000
O	-1.42080700	-1.64047300	-0.14029300
H	-0.55736400	-1.18784100	-0.24642400
C	-2.17536600	0.69183500	-0.01994900
O	-1.03710000	1.10723300	-0.08092400
S	2.20543600	-0.06155200	-0.09551200
O	3.53983200	-0.06325700	-0.58411200
O	1.24175800	-1.03536300	-0.51512700
O	2.22833100	-0.18350000	1.49604100
H	3.02578700	0.24626800	1.83863500
O	1.62710700	1.37658300	-0.32976400
H	0.64561500	1.35704200	-0.23815500
C	-3.37476800	1.57400800	0.05709800
H	-4.04476000	1.34796300	-0.77417200
H	-3.93870600	1.33983200	0.96133200
H	-3.07482100	2.61738500	0.04281100

Table S13 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of PA−H_2SO_4 eight-memebered ring system.

C	-1.67569000	-0.13826600	-0.08182600
O	-1.03210200	0.90338100	-0.12543900
O	-1.18688100	-1.34525300	-0.12923500
H	-0.19717900	-1.32917300	-0.19955500
C	-3.22383500	-0.09165100	0.04447500
O	-3.84847400	-1.11461000	0.12059700
S	2.31092900	-0.03489400	-0.07985800
O	3.61841900	0.06062100	-0.62781900
O	1.49291400	-1.19768900	-0.31009800
O	2.39800000	0.06140800	1.51172800
O	1.52296600	1.24242100	-0.47726200
H	0.52973400	1.11772100	-0.32960000
C	-3.81770100	1.28579400	0.06279900
H	-3.40176100	1.86025700	0.89193700
H	-3.54444400	1.82201600	-0.84744100
H	-4.89720200	1.21230100	0.15270200
H	3.12061000	0.65768600	1.75722200

Table S14 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of PA−H_2SO_4 seven-memebered ring system.

C	2.63134100	-0.84063100	-0.01604900
O	3.71601500	-1.28750700	0.23254400
O	1.56845800	-1.60566400	-0.26091700
H	0.77303500	-1.07863200	-0.44430600
C	2.39216100	0.69338900	-0.06456900
O	1.28045800	1.12945300	-0.28147300
S	-2.46373400	0.09749500	-0.02279600
O	-3.39553900	-0.73878900	-0.69920600
O	-2.17228700	-0.53292900	1.41671300
O	-2.66235100	1.48809900	0.19393500
O	-1.07072200	-0.11013300	-0.76195500
H	-0.43434700	0.60759500	-0.54942600
H	-2.39577500	-1.47505800	1.40073200
C	3.58826400	1.55058000	0.17123200
H	4.02268700	1.31277900	1.14368700
H	4.35918000	1.31402500	-0.56423100
H	3.31209800	2.59910400	0.11746900

Table S15 B3LYP-D3/aug-cc-pVTZ optimized cartesian coordinates (Å) of PA−H_2SO_4 six-memebered ring system.

C	-2.12690400	0.70746500	-0.03439300
O	-2.54846700	1.82423100	0.04804900
O	-0.82173300	0.42251000	-0.16424800
H	-0.68260800	-0.54496900	-0.21117800
C	-3.02079600	-0.55938200	-0.00258500
O	-2.48053300	-1.63619400	-0.09053300
S	2.43663100	-0.15659200	-0.08486500
O	3.74398400	-0.16500800	-0.64564900
O	1.80267900	1.24361500	-0.43895700
O	1.48041200	-1.18875900	-0.33565200
O	2.55755000	-0.09104000	1.50747400
H	3.35487700	0.40436800	1.74524800
C	-4.48863000	-0.32862600	0.13599800
H	-4.68582700	0.23471100	1.04976200
H	-4.83949700	0.29763500	-0.68617200
H	-5.01429000	-1.27852200	0.14793100
H	0.82808600	1.20067000	-0.32574600