

Supporting information for

SO₂ capture by ionic liquid and spectroscopic speciation of sulfur (IV) therein

Yoshiro Yasaka,* Koki Watanabe, and Yoshifumi Kimura*

*Department of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, Doshisha University,
Kyotanabe, Kyoto 610-0321, Japan*

Corresponding Authors

Yoshifumi Kimura and Yoshiro Yasaka

Department of Molecular Chemistry and Biochemistry

Faculty of Science and Engineering

Doshisha University

Kyoto 610-0321, Japan

Table S1. Thermal energies for the optimized structures of monomers and clusters using aug-cc-pVTZ basis set and B3PW91 functional

	E in vapor (hartree)	E in SCRF water (hartree)
SO ₂	-548.587924	-548.593472
CO ₂	-188.570869	-188.573349
H ₂ O	-76.411785	-76.418394
HCO ₃ ⁻	-264.434037	-264.536980
HSO ₃ ⁻	-624.472227	-624.568445
HOSO ₂ ⁻	-624.476141	-624.572371
S ₂ O ₅ ²⁻	-1172.417332	-
(HOSO ₂) ₂ ²⁻ symmetric	-	-1249.154095
(HOSO ₂) ₂ ²⁻ asymmetric	-	-1249.154649
(HOSO ₂ ⁻)SO ₂	-1173.089803	-1173.171224
(HSO ₃ ⁻)SO ₂	-1173.083120	-1173.165021

Table S2. Thermal energies for the optimized structures of monomers and clusters using 6-311G+(d,p) basis set and B3PW91 functional. (T) and (G) mean the all trans and all gauche conformations of alkyl-chains of the phosphonium cation.

	E (hartree)
SO ₂	-548.540968
CO ₂	-188.554120
H ₂ O	-76.403810
HCO ₃ ⁻	-264.411579
HSO ₃ ⁻	-624.407775
HOSO ₂ ⁻	-624.419833
[P ₄₄₄₈] ⁺ (T)	-1129.100874
[P ₄₄₄₈]HCO ₃ (T)	-1393.647760
[P ₄₄₄₈]HSO ₃ (T)	-1753.636099
[P ₄₄₄₈]HOSO ₂ (T)	-1753.651688
[P ₄₄₄₈] ⁺ (G)	-1129.091735
[P ₄₄₄₈]HCO ₃ (G)	-1393.636698
[P ₄₄₄₈]HSO ₃ (G)	-1753.623588
[P ₄₄₄₈]HOSO ₂ (G)	-1753.641198

Table S3. Calculated geometries of (a) HCO_3^- , (b) HSO_3^- , and (c) HOSO_2^- by DFT calculations using B3PW91 functional. Figures S1 and S2 show the geometrical parameter definitions. Distances in angstroms with a two atom sequence denoting a bond. Angles in degrees with a three atom sequence denoting a bond angle and a four-atom sequence denoting a dihedral angle. In cases of cluster with a cation, the distance to the phosphonium atom is also denoted.

(a) HCO_3^-

	aug-cc-pVTZ		6-311G+(d,p)		
	in vacuum	in SCRF water	in vacuum	with $[\text{P}_{4448}]^+$ (T)	with $[\text{P}_{4448}]^+$ (G)
HO_1	0.9621	0.9635	0.9623	0.9634	0.9634
CO_1	1.4389	1.4035	1.4434	1.3841	1.3846
CO_2	1.2488	1.2485	1.2492	1.2534	1.2524
CO_3	1.2329	1.2420	1.2324	1.2479	1.2484
HO_1C	101.82	105.47	102.09	104.60	104.62
O_1CO_2	113.51	115.62	113.33	116.36	116.43
O_1CO_3	114.19	114.29	114.08	115.22	115.12
O_2CO_3	132.31	130.09	132.59	128.42	128.45
HO_1CO_2	-0.01	-0.02	0.00	-0.27	-0.29
HO_1CO_3	180.00	179.99	180.00	179.8	179.61
CP				3.8785	3.8767

(b) HSO_3^-

	aug-cc-pVTZ		6-311G+(d,p)		
	in vacuum	in SCRF water	in vacuum	with $[\text{P}_{4448}]^+$ (T)	with $[\text{P}_{4448}]^+$ (G)
HS	1.3747	1.3625	1.3815	1.3680	1.3682
SO_1	1.4722	1.4738	1.4794	1.4845	1.4794
SO_2				1.4830	1.4925
SO_3				1.4783	1.4738
HSO_1	103.81	104.78	103.76	105.21	105.28
HSO_2				105.04	104.43
HSO_3				105.51	105.66
O_1SO_2	114.49	113.73	114.53	112.79	112.31
O_1SO_3				113.56	114.74
O_2SO_3				113.67	113.26
SP				4.0129	4.1527

(c)HOSO₂⁻

	aug-cc-pVTZ		6-311G+(d,p)		
	in vacuum	in SCRF water	in vacuum	with [P ₄₄₄₈] ⁺ (T)	with [P ₄₄₄₈] ⁺ (G)
HO ₁	0.9662	0.9679	0.9672	0.9648	0.9647
SO ₁	1.7597	1.7249	1.7920	1.7935	1.7938
SO ₂	1.5020	1.5028	1.5069	1.5068	1.5060
SO ₃	1.4888	1.4962	1.4969	1.4988	1.4994
HO ₁ S	100.44	104.48	101.78	106.56	106.44
O ₁ SO ₂	99.11	100.48	99.72	101.13	101.15
O ₁ SO ₃	103.15	102.79	103.52	97.28	97.26
O ₂ SO ₃	112.12	110.77	112.14	111.26	111.26
HO ₁ SO ₂	12.88	15.14	29.05	63.46	62.61
HO ₁ SO ₃	-102.53	-99.18	-86.7	176.89	176.05
SP				4.1544	4.1587

Table S4. Raman bands observed experimentally. Only the bands assigned to anionic species are listed for those of $[P_{4448}]HCO_3$ and $[P_{4448}]HSO_3$. The Raman shifts of $[P_{4448}]Br$ are the apparent peak positions, and those of $[P_{4448}]HCO_3$ and $[P_{4448}]HSO_3$ are those obtained by multi-peak fittings after the subtraction of cation bands. The region of CH stretching vibrations is omitted.

$[P_{4448}]Br$	$[P_{4448}]HCO_3$	$[P_{4448}]HSO_3$ $q_{SO_2} = 0.98$	$[P_{4448}]HSO_3$ $q_{SO_2} = 1.57$
249 s		315 s	314 s
			430~470 s
		505 s	503 s
	621 m		635 m
642 shoulder			
694 shoulder			
716 vw			
		725 m	723 m
752 w			
810 vw			
844 vw			
870 s			
893 s			
970 w			
	996 s		
1012 w			
1033 w			
		1029 w	1029 w
		1048 s	1046 s
1053 s			
		1079 m	1078 s
1087 shoulder			
1101 s			
1116 shoulder			
		1120 m	1119 m
			1144 s
1170 w			
1201 w			
1236 w			
	1262 s		
1278 s			
1304 s			
1311 s			
1348 w			
1411 w			
1449 s			
	1655 m		
	1672 m		
		2444 m	2447 m

Table S5. Vibrational frequencies for HCO_3^- , HSO_3^- , and HOSO_2^- for the optimized structure by the DFT calculations using B3PW91 functional with different basis-sets and solvent model.

HCO_3^-

Assgnt ^a	aug-cc-pVTZ in vacuum	aug-cc-pVTZ in SCRF water	6-311G+(d,p) in vacuum
$\delta\text{OC(OH)}$	548	563	551
ρOH	551	526	527
$\nu\text{CO} + \delta\text{CO}_2$	630	654	630
$\delta_s \text{CO}_3$ (umbrella)	827	826	823
$\nu\text{CO} + \delta\text{CO}_2$	863	914	861
δCOH	1194	1197	1197
$\nu_s\text{CO}_2$	1309	1316	1312
$\nu_{\text{as}}\text{CO}_2$	1773	1692	1791
νOH	3822	3811	3842

HSO_3^-

Assgnt ^a	aug-cc-pVTZ in vacuum	aug-cc-pVTZ in SCRF water	6-311G+(d,p) in vacuum
δSO_2 E	484	481	478
$\delta_s\text{SO}_3$ A ₁	614	600	609
$\nu_s\text{SO}_3$ A ₁	1031	1029	1011
δOSH E	1099	1105	1096
$\nu_a\text{SO}_3$ E	1225	1189	1205
νSH A ₁	2389	2501	2377

HOSO_2^-

Assgnt ^a	aug-cc-pVTZ in vacuum	aug-cc-pVTZ in SCRF water	6-311G+(d,p) in vacuum
ρOH	215	122	149
$\delta\text{OS(OH)}$	356	362	361
$\omega\text{SO}_2 + \nu\text{S(OH)}$	393	413	376
$\delta\text{SO}_2 + \nu\text{S(OH)}$	525	528	505
$\delta_s\text{SO}_2(\text{OH})$	591	591	558
$\delta\text{SOH} + \nu\text{SO}$	1005	1000	986
$\delta\text{SOH} + \nu_s\text{SO}_2$	1096	1070	1076
$\delta\text{SOH} + \nu_{\text{as}}\text{SO}_2$	1155	1106	1125
νOH	3769	3752	3779

^a Notation of vibrational modes : ν , stretching; δ , bending; τ , twisting; ω , wagging; ρ , rocking; s, symmetric; a, asymmetric.

Table S6. Calculated geometries of HOSO₂⁻ dimer (symmetric and asymmetric) by DFT calculations using B3PW91 functional and aug-cc-pVTZ in SCRF model water. Figures S6(a) and(b) show the geometrical parameter definitions. Distances in angstroms with a two atom sequence denoting a bond. Angles in degrees with a three atom sequence denoting a bond angle and a four-atom sequence denoting a dihedral angle.

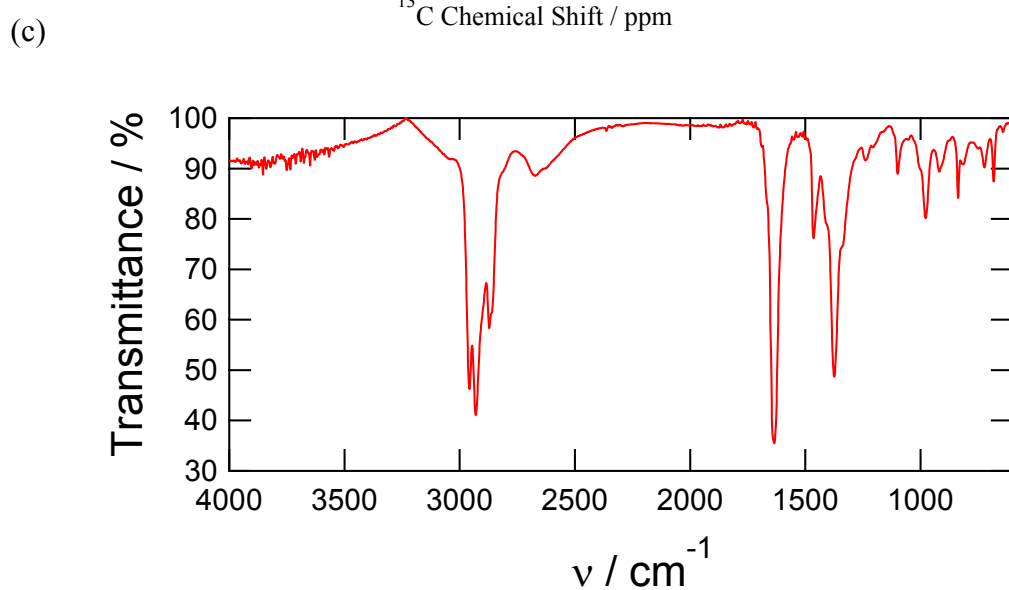
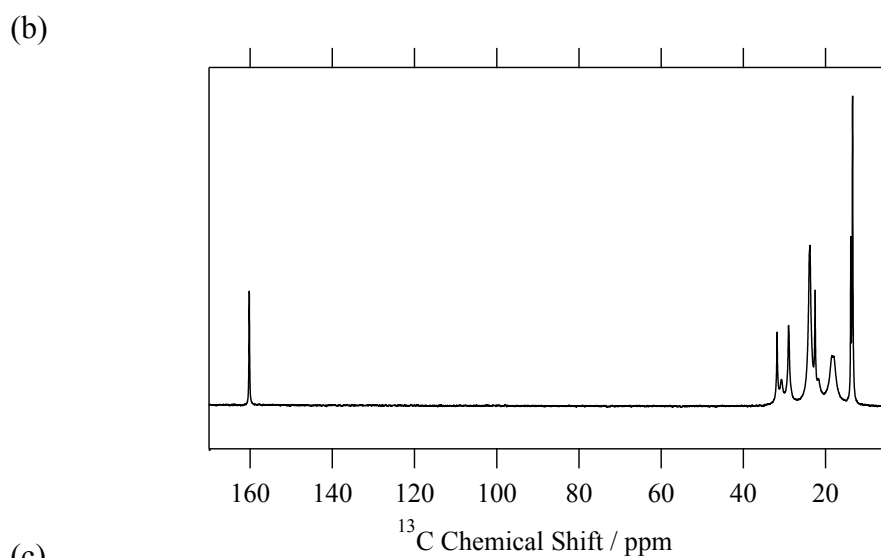
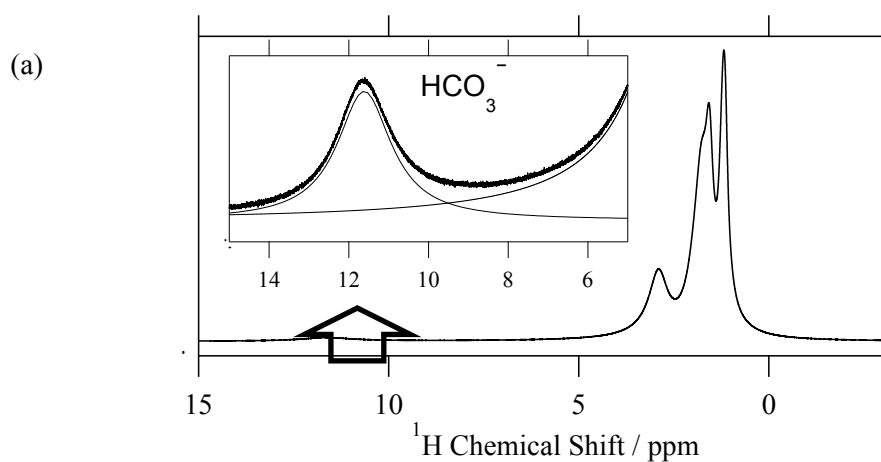
	Symmetric dimer	Asymmetric dimer
H ₁ O ₁	1.0026	0.9986
H ₂ O ₅	1.0026	0.9984
O ₂ H ₂	1.6781	1.6760
O ₅ H ₁	1.6783	1.7017
S ₁ O ₁	1.6649	1.6663
S ₁ O ₂	1.5224	1.5217
S ₁ O ₃	1.5023	1.5015
S ₂ O ₄	1.6649	1.6773
S ₂ O ₅	1.5224	1.5194
S ₂ O ₆	1.5023	1.4960
H ₁ O ₁ S ₁	109.49	109.95
H ₂ O ₄ S ₂	109.49	107.48
O ₁ S ₁ O ₂	102.67	102.86
O ₁ S ₁ O ₃	104.46	104.37
O ₂ S ₁ O ₃	109.07	109.05
O ₄ S ₂ O ₅	102.67	102.25
O ₄ S ₂ O ₆	104.46	100.31
O ₅ S ₂ O ₆	109.07	109.83
O ₂ H ₂ O ₄	176.07	176.59
O ₅ H ₁ O ₁	176.13	173.06
S ₁ O ₂ H ₂	121.53	126.14
S ₂ O ₅ H ₁	121.57	120.49
H ₁ O ₁ S ₁ O ₂	-45.55	-46.94
H ₁ O ₁ S ₁ O ₃	68.26	66.89
H ₂ O ₄ S ₂ O ₅	45.47	-57.71
H ₂ O ₄ S ₂ O ₆	-68.35	-170.81
O ₁ S ₁ O ₂ H ₂	52.57	29.75
O ₃ S ₁ O ₂ H ₂	-57.83	-80.62
O ₄ S ₂ O ₅ H ₁	-52.53	43.09
O ₆ S ₂ O ₅ H ₁	57.87	148.94
S ₂ O ₅ O ₁ S ₁	57.52	19.05
S ₂ O ₄ O ₂ S ₁	-57.51	31.68

Table S7. Calculated geometries of complex of HOSO_2^- and SO_2 , $\text{S}_2\text{O}_5^{2-}$, and SO_2 by DFT calculations using B3PW91 functional and aug-cc-pVTZ. Figures S7(a-d) show the geometrical parameter definitions. Distances in angstroms with a two atom sequence denoting a bond. Angles in degrees with a three atom sequence denoting a bond angle and a four-atom sequence denoting a dihedral angle.

	HS_2O_5^-		$\text{S}_2\text{O}_5^{2-}$	SO_2
	$\text{HOSO}_2^- + \text{SO}_2$	$\text{HOSO}_2^- + \text{SO}_2$		
HO_1	0.9826			
HS_1		1.3641		
O_5H	1.8560	3.0727		
S_1S_2	2.5220	3.2522	2.4050	
S_1O_1	1.6535	1.4607	1.4929	
S_1O_2	1.4712	1.4603	1.4964	
S_1O_3	1.4677	1.5074	1.4964	
S_2O_4	1.4735	1.4604	1.5070	1.4474
S_2O_5	1.4948	1.4635	1.5069	1.4474
HO_1S_1	103.31			
HS_1O_1	26.96	105.35		
HS_1O_2		105.78		
HS_1O_3		102.69		
$\text{O}_1\text{S}_1\text{O}_2$	106.99	116.83	112.42	
$\text{O}_1\text{S}_1\text{O}_3$	105.03	113.12	112.42	
$\text{O}_2\text{S}_1\text{O}_3$	115.98	111.54	111.63	
$\text{O}_4\text{S}_2\text{O}_5$	113.78	114.73	111.58	118.22
O_1HO_5	146.22			
HS_1S_2		84.45		
$\text{O}_1\text{S}_1\text{S}_2$	94.17	87.44	111.58	
$\text{O}_2\text{S}_1\text{S}_2$	109.45	148.72	104.08	
$\text{O}_3\text{S}_1\text{S}_2$	121.68	37.37	104.08	
$\text{S}_1\text{S}_2\text{O}_4$	105.80	120.99	104.52	
$\text{S}_1\text{S}_2\text{O}_5$	91.97	88.06	104.51	
$\text{HO}_1\text{S}_1\text{O}_2$	-99.02			
$\text{HO}_1\text{S}_1\text{O}_3$	137.17			
$\text{HO}_1\text{S}_1\text{S}_2$	12.78			
$\text{O}_1\text{S}_1\text{S}_2\text{O}_4$	100.66	-137.42	58.68	
$\text{O}_2\text{S}_1\text{S}_2\text{O}_4$	-149.68	5.39		
$\text{O}_3\text{S}_1\text{S}_2\text{O}_4$	-9.87	-2.52		
$\text{O}_1\text{S}_1\text{S}_2\text{O}_5$	-14.75	104.67	-58.68	

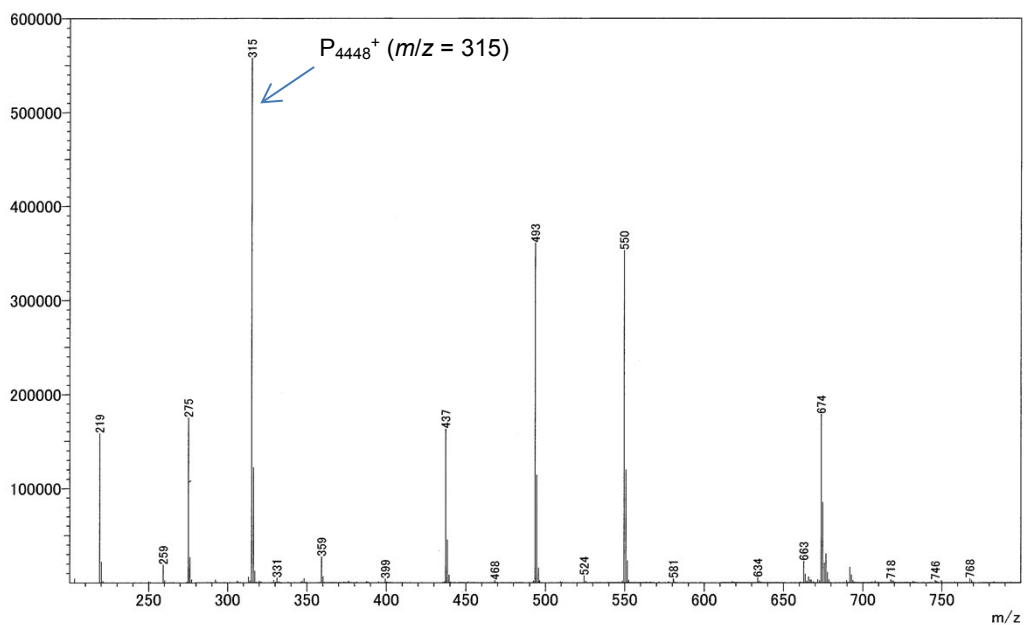
$O_2S_1S_2O_5$	-125.27	-112.51
$O_3S_1S_2O_5$	94.91	-120.42
$HS_1S_2O_4$		116.88
$HS_1S_2O_5$		-1.03

Figure S1. Characterization of $[P_{4448}][HCO_3^-]$. (a) 1H NMR spectrum at 25 °C (no solvent), (b) ^{13}C NMR spectrum at 23 °C (no solvent), (c) ATR-IR spectra (measured by JASCO FT/IR-4200) at 23 °C (no solvent) and mass spectrum measured by SHIMADZU LCMS-2020 on (d) positive and (e) negative mode.



Peak (cm^{-1}); 640(vw), 683(w), 721(w), 753(vw), 814(w), 837(m), 920(w), 976(m), 1006(shoulder), 1097(w), 1236(vw), 1333(shoulder), 1374(s), 1413(shoulder), 1465(m), 1635(vs), 2678(broad), 2857(shoulder), 2871(s), 2930(s), 2957(s)

(d)



(e)

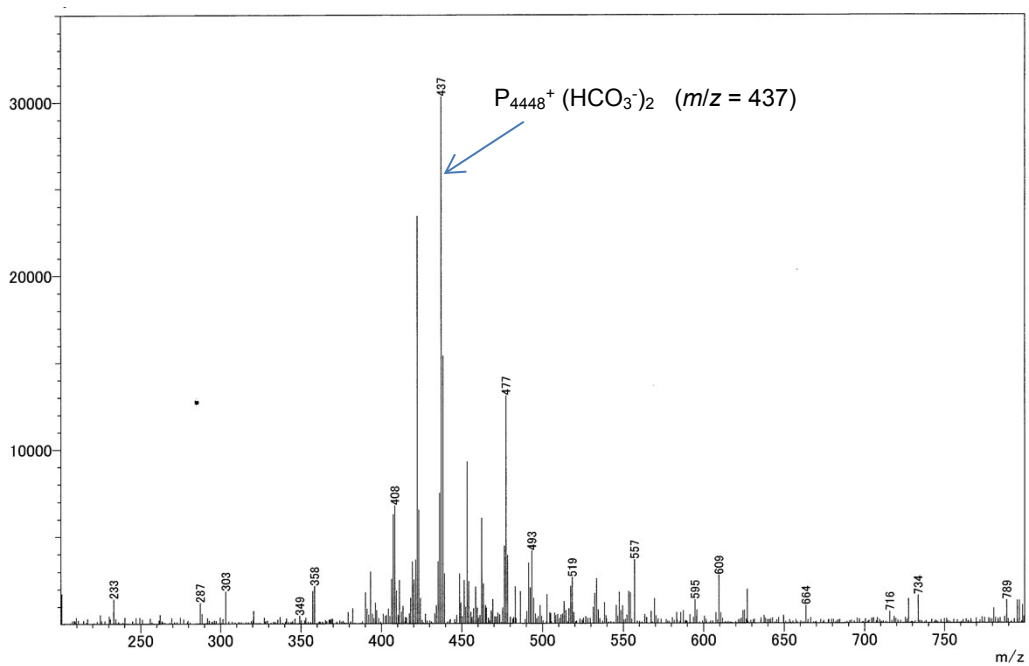


Figure S2 ^{13}C NMR spectra of SO_2 -loaded ionic liquid (left: bicarbonate, right: P_{4448} cation). The spectra were collected at 25 °C except for $q_{\text{SO}_2} = 0$ (23 °C). The cation peaks sharpen at increased SO_2 loadings because of the decrease in viscosity. The chemical shift reference was taken by the terminal methyl carbons of the P_{4448} cation.

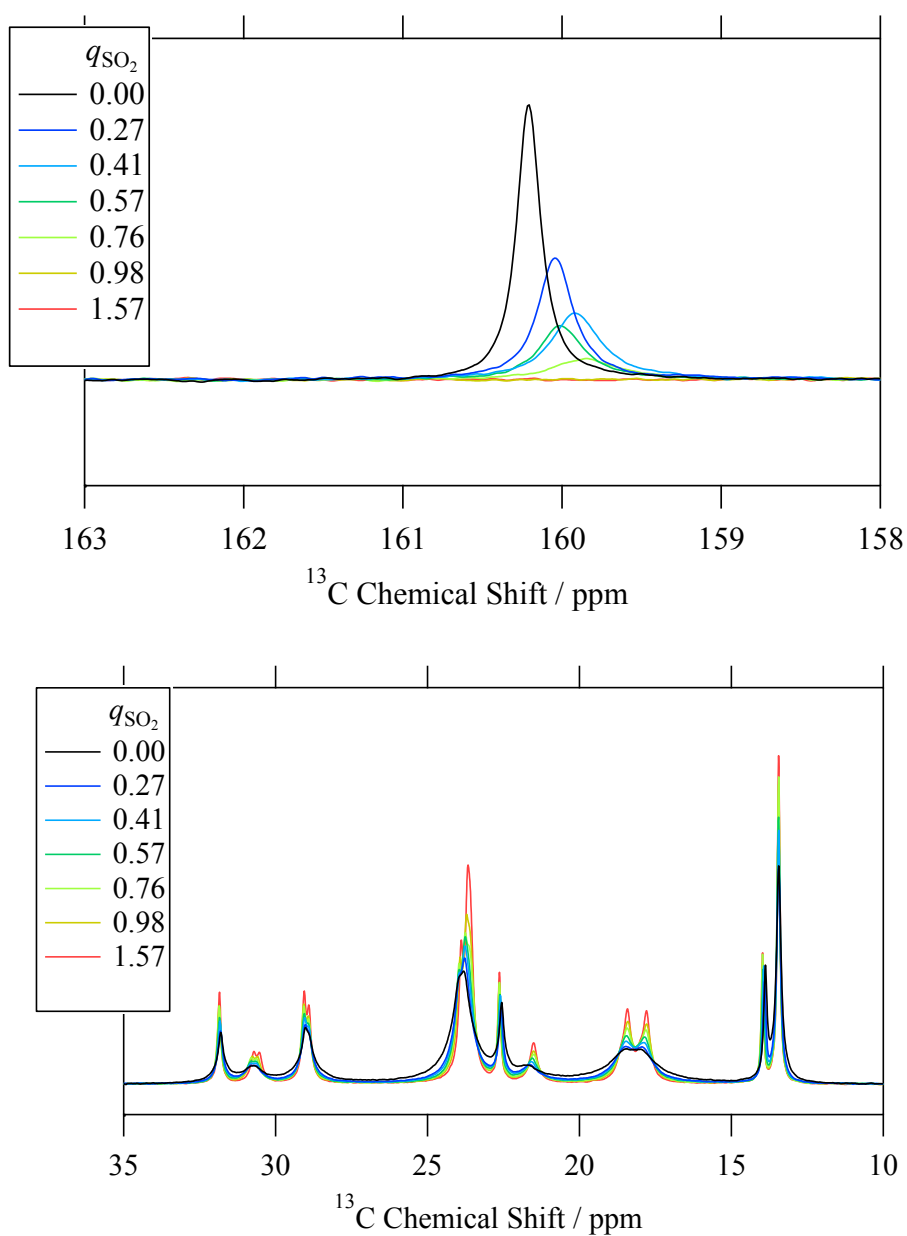


Figure S3. ^1H NMR spectra at 298-338 K. The peak at 10 ppm assigned to the HSO_3^- isomer broadens at higher temperature due to the increase in the isomer exchange rate. The peak assigned to the hydroxyl protons (HOSO_2^- , HCO_3^-) shifts from 7.7 to 6.6 ppm as the temperature is raised

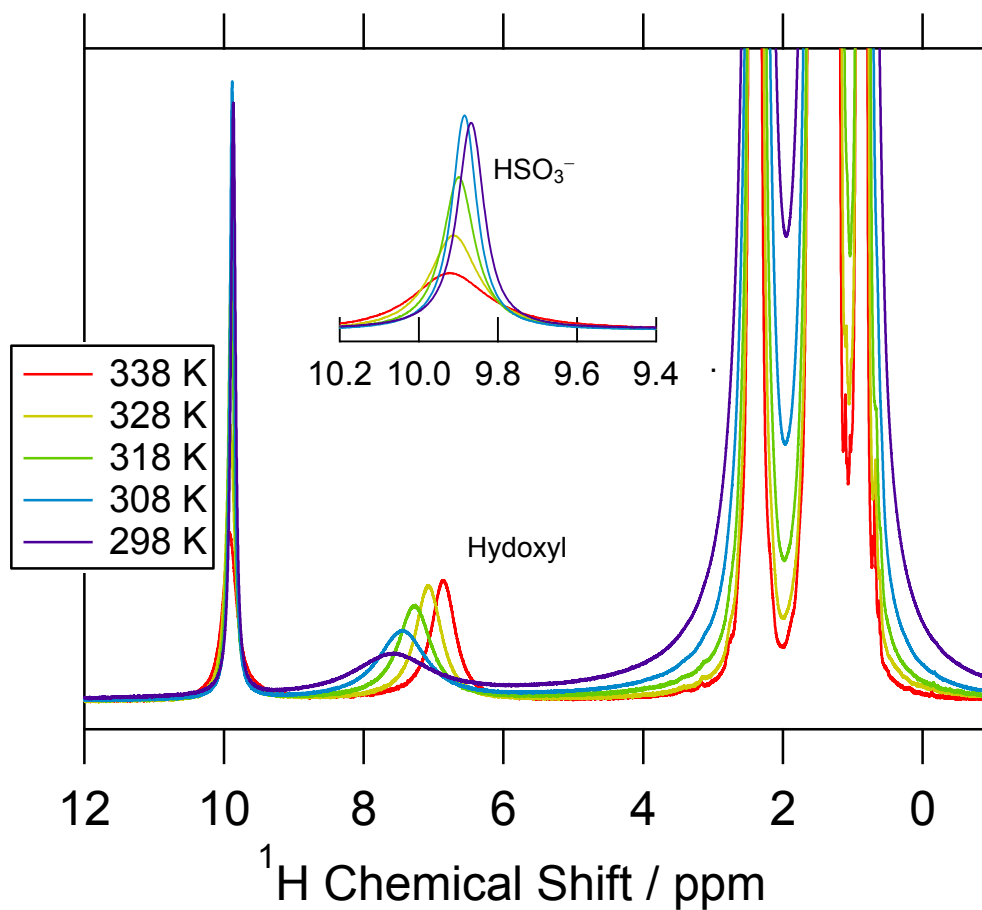
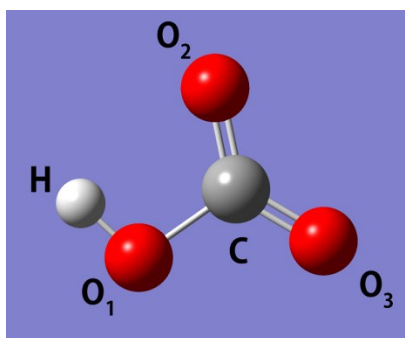
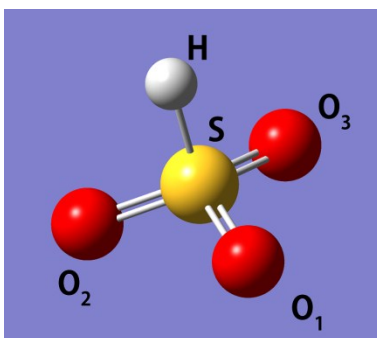


Figure S4. Images of the optimized structure of (a) HCO_3^- , (b) HSO_3^- , and (c) HOSO_2^- by the DFT calculations using B3PW91 functional and aug-cc-pVTZ basis set.

(a)



(b)



(c)

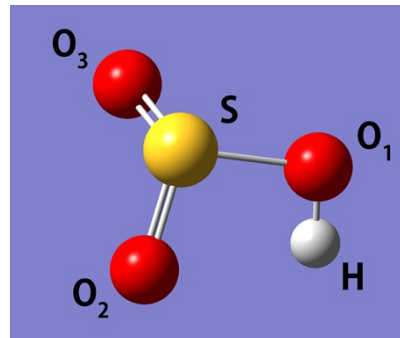
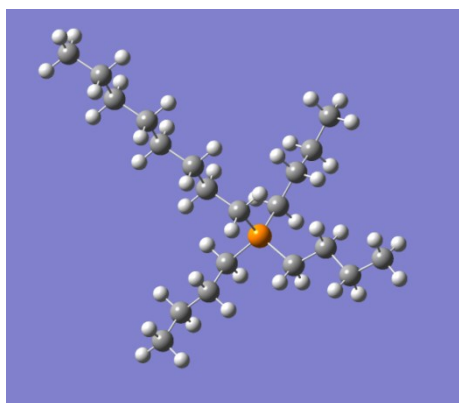
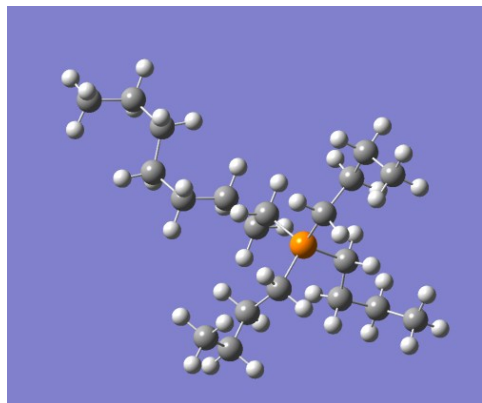


Figure S5. Images of the optimized structures of (a) all trans conformations and (b) all gauche conformations of alkyl-chains of cation ($[P_{4448}]^+$), together with the clusters of all trans $[P_{4448}]^+$ with (c) HCO_3^- , (d) HSO_3^- , and (e) $HOSO_2^-$, by the DFT calculations using B3PW91 functional and 6-311G+(d,p) basis set.

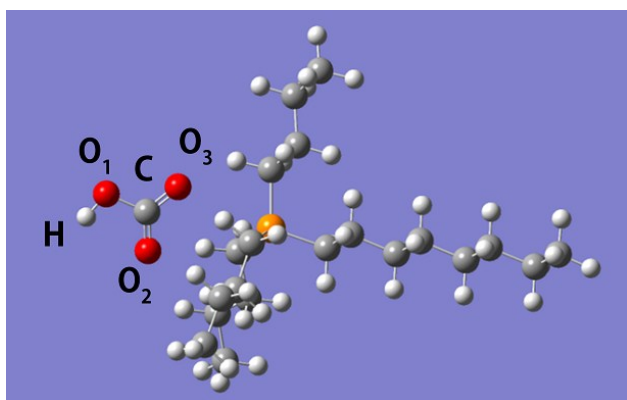
(a)



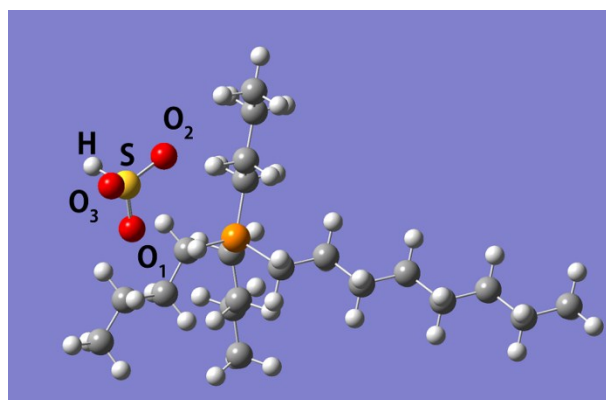
(b)



(c)



(d)



(e)

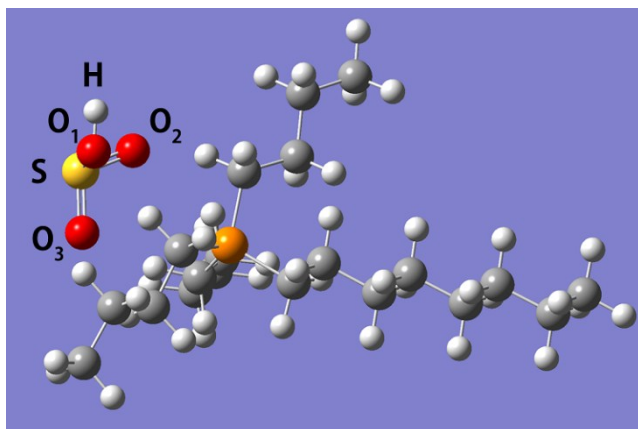


Figure S6. Comparison between the theoretical and experimental Raman spectra of $[P_{4448}]^+$.

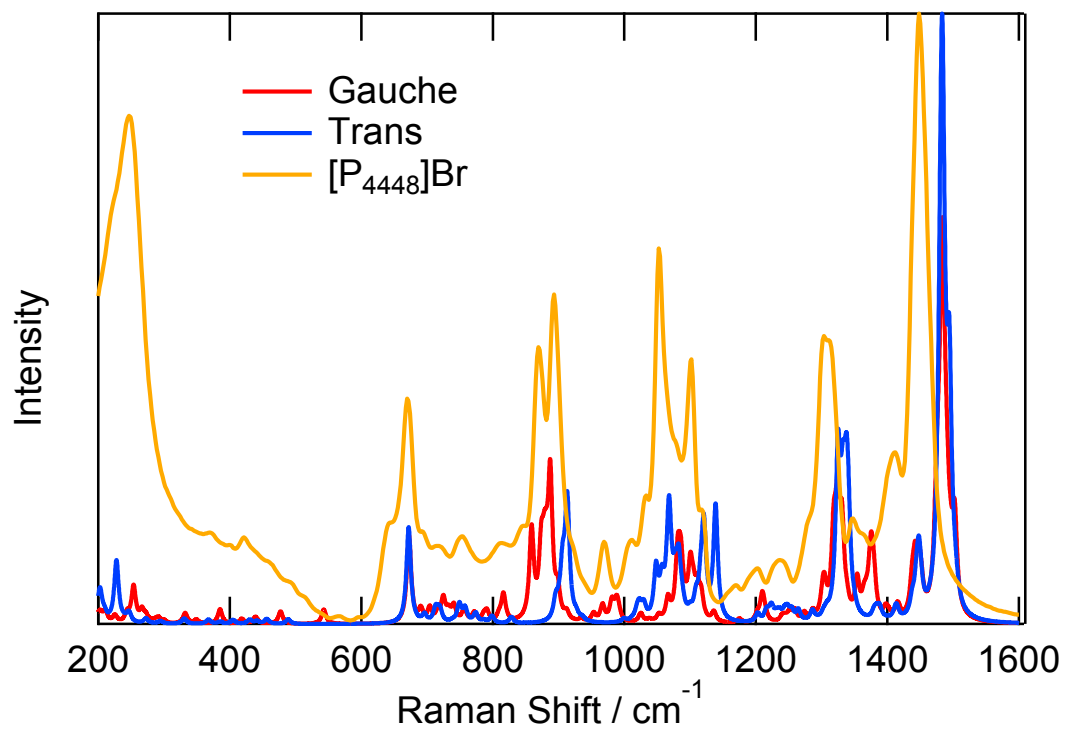


Figure S7. (a) Typical example of the multi-peak fitting in the finger-print region. (b) Vibrational frequencies of the SH stretching with different q_{SO_2} . In doing the multi-peak fit of the spectrum, we have used the macro function incorporated into the Igor 6.22 A (Wavemetric). The difference spectra of the finger-print region were further divided into several regions in order to making the multi-peak fit without using any complex baseline function. Most complex part was the region from 1020 cm^{-1} to 1180 cm^{-1} where several bands overlaps. We have assumed that five different bands with different shapes contribute the spectrum for the spectra with $q_{SO_2} \leq 1$. The band shape functions were chosen to fit the spectrum (Gaussian (band I, 1029 cm^{-1}), exponentially modified Gaussian (ExpModGauss) (band II, 1048 cm^{-1}), Voigt (band III, 1079 cm^{-1}), Gaussian (band IV, 1099 cm^{-1}), and Voigt (band V, 1119 cm^{-1}). The band IV at 1099 cm^{-1} is very weak and made minor contribution to the total spectrum, but it was necessary to fit the whole spectrum reasonably. Since the band shape at 1048 cm^{-1} is asymmetric, the ExpModGauss function was employed to fit the band. The Gaussian width parameters for band I and band IV, the Gaussian width and the exponential component of a ExpModGauss function for band II, and the width and shape (mixing ratio of Gaussian and Lorentzian) parameters of a Voigt function (band III and V) were fixed to optimized values for each band through the fitting all spectra with different values of q_{SO_2} . In the fitting of the SH stretching mode, an ExpModGauss function was employed to represent the asymmetric nature of the band.

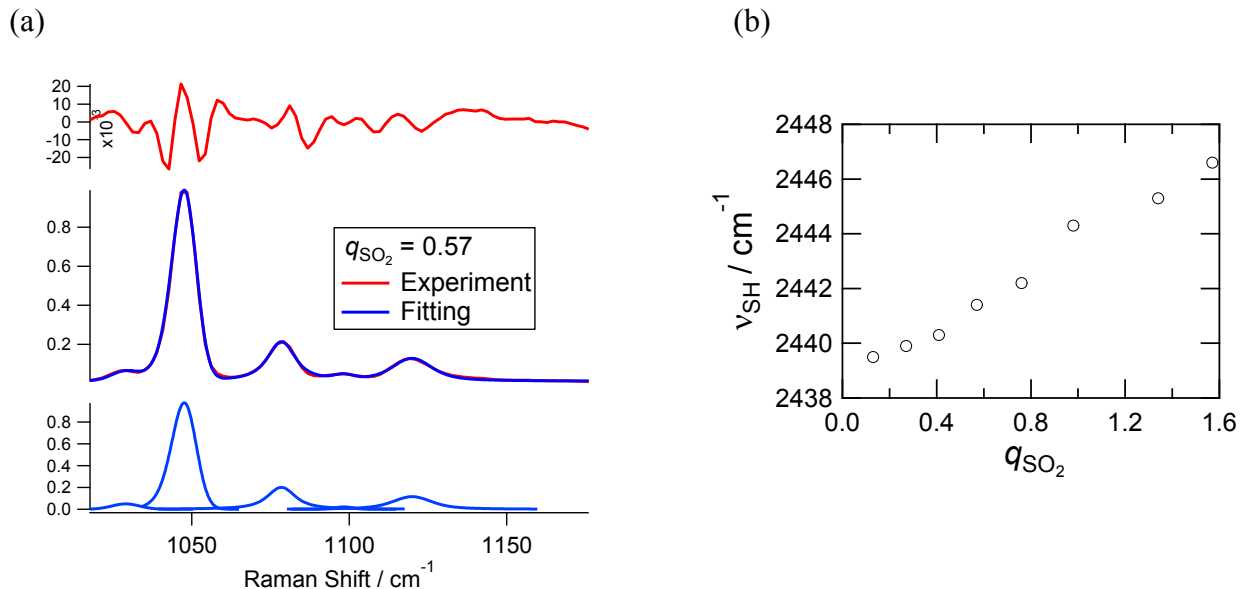


Figure S8. Vibrational spectra (Raman activities) of different anions with $[P_{4448}]^+$ and without $[P_{4448}]^+$. The vibrational modes that mainly derive from the anion species are selected and depicted. The upper panel shows the difference of the normalized Raman spectra of $[P_{4448}]\text{HCO}_3$ with different q_{SO_2} from that of neat $[P_{4448}]\text{HCO}_3$.

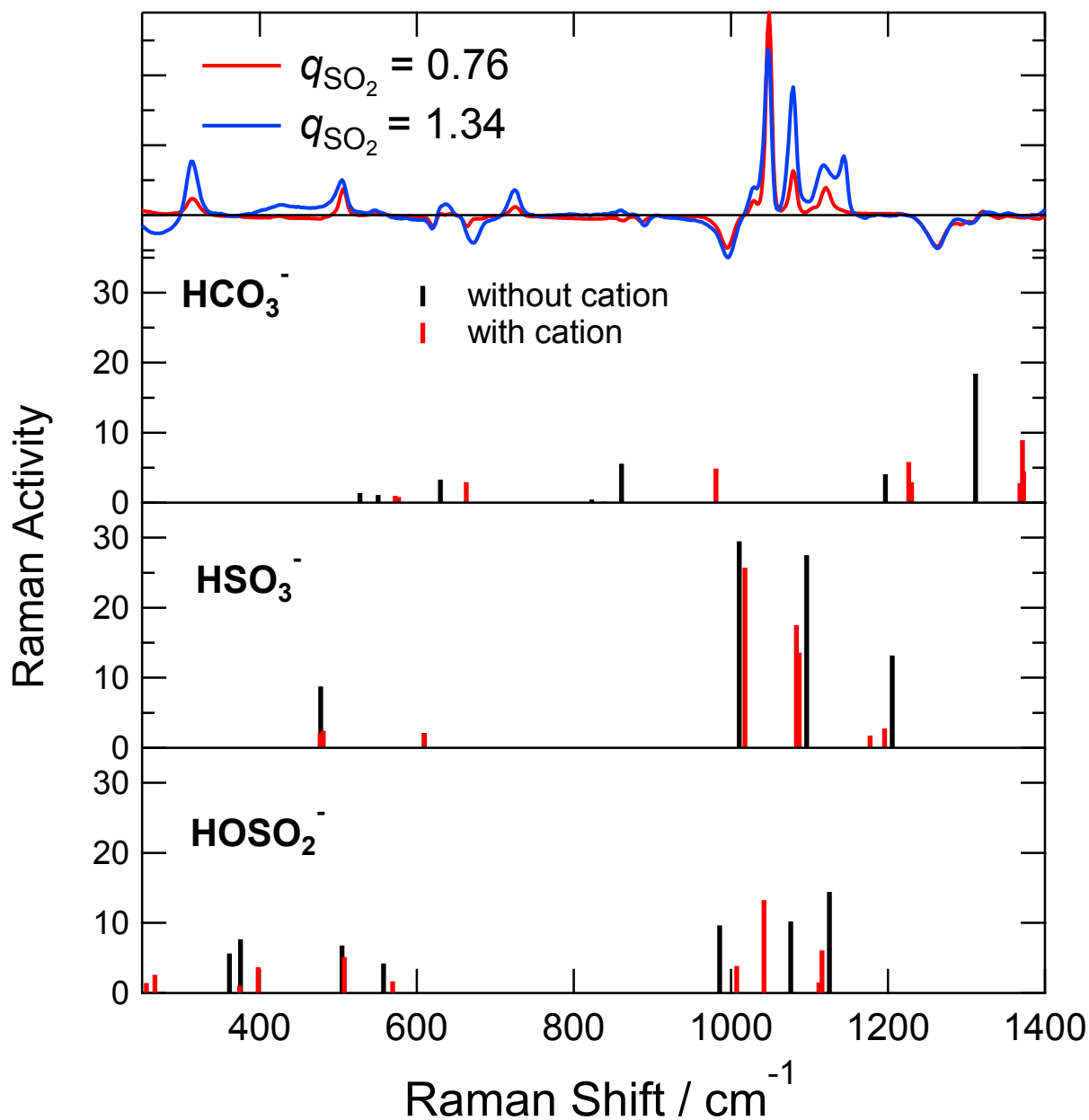
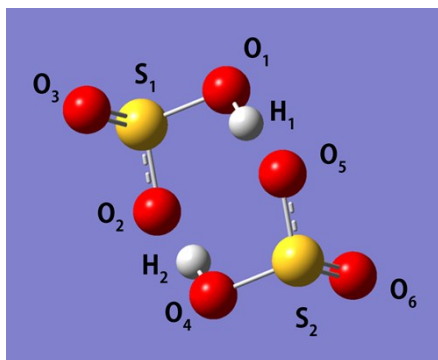


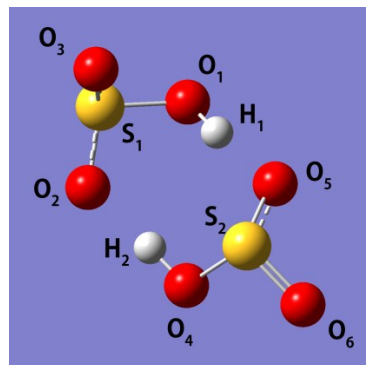
Figure S9. Optimized structures of the dimers of HOSO_2^- (symmetric (a) and asymmetric (b))and (c) vibrational spectra (Raman activities) of different anions calculated by DFT with B3PW91 functional and aug-cc-pVTZ basis set in SCRF water. The upper panel shows the difference of the normalized

Raman spectra of $[\text{P}_{4448}]\text{HCO}_3$ with different q_{SO_2} from that of neat $[\text{P}_{4448}]\text{HCO}_3$.

(a)



(b)



(c).

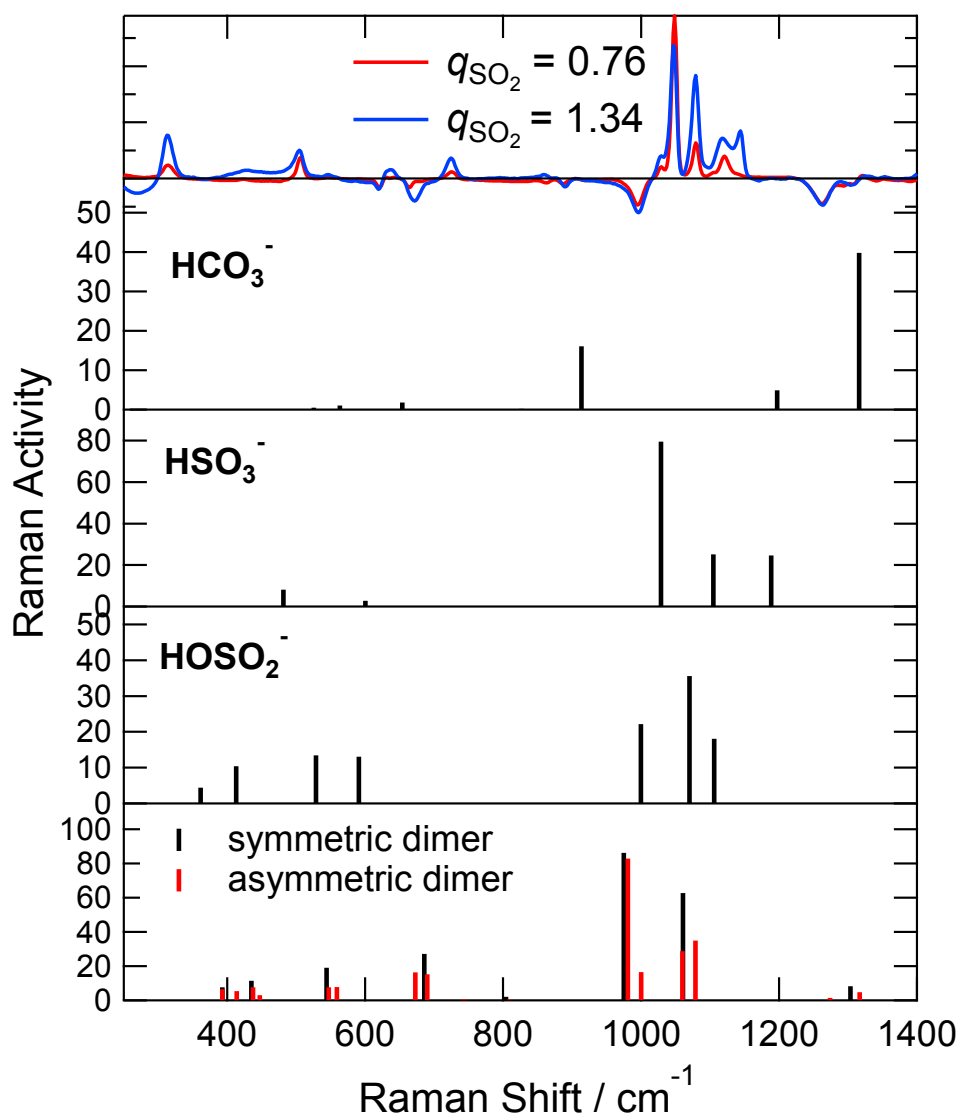


Figure S10. Optimized structures of (a) the complex of HOSO_2^- and SO_2 , (b) the complex of HSO_3^- and SO_2 , (c) $\text{S}_2\text{O}_5^{2-}$ and (d) SO_2 , and (e) vibrational spectra (Raman activities) of HSO_3^- , HOSO_2^- , the complex of HOSO_2^- and SO_2 , the complex of HSO_3^- and SO_2 , $\text{S}_2\text{O}_5^{2-}$, and SO_2 by DFT with B3PW91 functional and aug-cc-pVTZ basis set.

