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

Electronic Supplementary Information for

Structures of Protonated Hydrogen Sulfide Clusters, $H^+(H_2S)_n$, Highlighting the Nature of Sulfur-Centered Intermolecular Interactions

Dandan Wang and Asuka Fujii*

Department of Chemistry, Graduate School of Science, Tohoku University

Sendai 980-8578, Japan

*Author to whom correspondence should be addressed. Email: asukafujii@m.tohoku.ac.jp

Contents

Figure SI-2 Comparison between the experimental and simulated spectra of $H^+(H_2S)_6$ in the full SH stretch region.

Figure SI-3 Comparison between the experimental and simulated spectra of $H^+(H_2S)_7$ in the full SH stretch region.

Determination of the reasonable level of theory in the present study

21 calculation levels were adopted to energy-optimize the structure of $H^+(H_2S)_3$ with the Eigen type ion-core for evaluation of the calculation method on the present system. Results are summarized in Table SI-1. First, the scaling factor for each calculation level was determined by the sym. stretch band (ν_1) of free SH in H-bonded H_2S; we fitted the average of the calculated frequencies of the two H-bonded H_2S molecules in $H^+(H_2S)_3$ to the experimental value (2585 cm^{-1}). Then, the calculated frequency of free SH in H_3S^+ was scaled by this factor, and the resultant frequency was compared with the experimental value (2558 cm^{-1}). The deviation of the calculated value from the experimental one, Δ_{E-C}, is listed in Table SI-1. It is seen that the MP2 method shows the good agreement irrespective of the basis sets. Thus, MP2/aug-cc-pVDZ, which has been frequently employed for analyses of neutral SCHB systems,[1] was selected for the level of theory in the following analyses.

Reference

1. H. S. Biswal, S. Bhattacharyya, A. Bhattacherjee and S. Wategaonkar, *Int. Rev. Phys. Chem.* 2015, **34**, 99-160.

Table SI-1 Calculated free SH stretch frequencies of $H^+(H_2S)_3$ at different calculation levels. All units are in cm^{-1}.

Calculation level	Stretch of free SH in H_3S^+ [a]	ν_1 in H-bonded H_2S [a],[b]	Scaling factor [c]	Δ_{E-C} [d]
B3LYP/6-311++G(3df,2p)	2659	2674	0.9667	-12
B3LYP/6-311++G(d,p)	2650	2664	0.9703	-13
B3LYP/aug-cc-pVDZ	2675	2696	0.9588	-7
CAM- B3LYP /6-311++G(3df,2p)	2694	2718	0.9511	-4
CAM - B3LYP /6-311++G(d,p)	2689	2714	0.9525	-3
CAM - B3LYP /aug-cc-pVDZ	2675	2697	0.9585	-6
M06-2X/6-311++G(3df,2p)	2700	2745	0.9417	15
M06-2X/6-311++G(d,p)	2688	2740	0.9434	22
M06-2X/aug-cc-pVDZ	2666	2706	0.9553	11
MP2/6-311++G(3df,2p)	2727	2752	0.9393	-3
MP2/6-311++G(d,p)	2773	2806	0.9212	4
MP2/aug-cc-pVDZ	2711	2736	0.9448	-3
MPW1PW91/6-311++G(3df,2p)	N/A	N/A	N/A	N/A
MPW1PW91/6-311++G(d,p)	2694	2707	0.9549	-15
MPW1PW91/aug-cc-pVDZ	2681	2690	0.961	-18
LC-ωPBE/6-311++G(3df,2p)	2755	2781	0.9295	-3
LC-ωPBE /6-311++G(d,p)				
LC-ωPBE /aug-cc-pVDZ	2843	2766	0.9346	-99
ωB97XD/6-311++G(3df,2p)	2734	2754	0.9386	-8
ωB97XD/6-311++G(d,p)	2730	2768	0.9339	8
ωB97XD/aug-cc-pVDZ	2721	2746	0.9414	-4

[a] Values without scaling.

[b] Averaged values between two frequencies of the two acceptor H_2S molecules.

[c] Scaling factors are determined by fitting the observed sym. stretch frequency of free SH in H-bonded H_2S (2585 cm^{-1}) by the corresponding calculated frequency.

[d] Δ_{E-C} is difference between the observed free SH frequency in H_3S^+ (2558 cm^{-1}) and calculated one scaled by the factor determined for the free SH band of the H-bonded H_2S.

Table S1-2 Calculated SH stretch harmonic vibrational frequencies (in cm^{-1}) of $H^+(H_2S)_n$ (n = 3 – 8) at the MP2/aug-cc-pVDZ level with the scaling factor 0.945. Corresponding optimized structures are shown in Figure 2 in the main text. Frequencies of the observed bands are also shown in parentheses.

	3	**4**	**5-1**	**5-2**	**6**	**7**	**8**	**9**
Stretch of H-bonded SH in H_3S^+	1702 1849	1985[a] 1985[a] 2094	1883 2043 2131	1935 2009 2142	1897 2014 2185	2047 2119 2224	2088 2148 2260	
Stretch of H-bonded SH in neural H_2S								(2564)
Stretch of free SH in H_3S^+	2563 (2558)							
Sym. stretch of free SH in H-bonded H_2S	2585 2586 (2590)	2591[a] 2591[a] 2591[a] (2592)	2589 2593 2594	2591[a] 2591[a] 2593	2590 2593 2595	2590 2591[a] 2591[a]	2590 2591 2593	
			(2593)		(2594)	(2594)		
Sym. stretch of free SH in charge-dipole bound H_2S			2600	2605	2601 2605	2599 2603[a] 2603[a]	2596 2600 2603[a] 2603[a] (2603)	(2603)
			(2605)		(2603)	(2603)		
Asym. stretch of free SH in H-bonded H_2S	2609 2610	2614[a] 2614[a] 2614[a]	2618 2619 2621	2616 2618 2619	2619[a] 2619[a] 2620	2616 2618 2619	2620 2621 2623	
Asym. stretch of free SH in charge-dipole bound H_2S			2627	2631	2627 2630	2625 2627 2629	2622 2625 2629 2631	

[a] Degenerated frequencies .

Table SI-3 Calculated SH stretch harmonic vibrational frequencies (in cm^{-1}) and their assignments of all the isomers of $H^+(H_2S)_5$ shown in Figure 3 in the main text (and in Figure SI-1). The calculation level is MP2/aug-cc-pVDZ and the scaling factor of 0.945 is applied.

	5-1	**5-2**	**5-3**	**5-4**	**5-5**	**5-6**	**5-7**
Stretch of H-bonded SH in H_3S^+	1883 2043 2131	1935 2009 2142	1886 2026 2121	1900 1977 2106	1727 2070 2135	1525 2013	1323 2130
Stretch of H-bonded SH in neutral H_2S			2565	2539 2546	2433	2463	2440
Stretch of free SH in H_3S^+						2556	2581
Sym. stretch of free SH in H-bonded H_2S	2589(1st shell)[a] 2593(1st shell) 2594(1st shell	2591(1^{st} shell) 2591(1^{st} shell) 2593(1^{st} shell)	2592(1^{st} shell) 2593(1^{st} shell) 2603(2^{nd} shell)[b] 2605(2^{nd} shell)[b]	2592(1^{st} shell) 2603(2^{nd} shell)[b] 2604(2^{nd} shell)[b] 2605(2^{nd} shell)[b]	2592(1^{st} shell) 2593(1^{st} shell) 2602(2^{nd} shell)	2591(1^{st} shell) 2603(2^{nd} shell)	2594(1^{st} shell) 2603(2^{nd} shell)
Stretch of free SH in the 1^{st} shell H-bonded H_2S			2603[b] 2605[b]	2603[b] 2604[b] 2605[b]	2599	2593	2588
Sym. stretch of free SH in charge-dipole bound H_2S	2600	2605				2597	2599
Asym. stretch of free SH in H-bonded H_2S	2618(1^{st} shell) 2619(1^{st} shell) 2621(1^{st} shell)	2616(1^{st} shell) 2618(1^{st} shell) 2619(1^{st} shell)	2617(1^{st} shell) 2630(2^{nd} shell)	2616(1^{st} shell) 2630(2^{nd} shell)	2616(1^{st} shell) 2616(1^{st} shell) 2626(2^{nd} shell)	2615(1^{st} shell) 2628(2^{nd} shell)	2617(1^{st} shell) 2628(2^{nd} shell)
Asym. stretch of free SH in charge-dipole bound H_2S	2627	2631				2622	2625

[a] The H_2S molecules in the "1^{st} shell" are highlighted by the dotted red circle in Figure 3 in the main text (and in Figure SI-1), while the molecules outside the circle belong to the "2^{nd} shell".

[b] The stretch frequency of free SH in the 1^{st} shell H-bonded H_2S is mixed with the sym. stretch of free SH in 2^{nd} shell H-bonded H_2S for isomer **5-3**. Therefore, for these two types of stretch, only single band exists for each. This case is the same for structure **5-4**.

Table SI-4 Calculated SH stretch harmonic vibrational frequencies (in cm^{-1}) and their assignments of all the isomers of $H^+(H_2S)_6$ shown in Figure 5 in the main text (and in Figure SI-2). The calculation level is MP2/aug-cc-pVDZ and the scaling factor of 0.945 is applied.

	6-1	**6-2**	**6-3**	**6-4**	**6-5**	**6-6**	**6-7**
Stretch of H-bonded SH in H_3S^+	1897 2014 2185	2022 2129 2198	1890 2050 2123	1873 1965 2066	1785 2121 2207	1806 1949 2124	1655 1818
Stretch of H-bonded SH in neutral H_2S			2544 2549	2544 2551	2491	2482 2496	2494 2507
Stretch of free SH in H_3S^+							2556
Sym. stretch of free SH in H-bonded H_2S	2590(1^{st} shell) 2593(1^{st} shell) 2595(1^{st} shell)	2589(1^{st} shell) 2594(1^{st} shell) 2595(1^{st} shell)	2592(1^{st} shell) 2604(2^{nd} shell)	2603(2^{nd} shell) 2604(2^{nd} shell)	2594(1^{st} shell) 2595(1^{st} shell) 2604(2^{nd} shell)	2593(1^{st} shell) 2598(2^{nd} shell)[a] 2599(2^{nd} shell)[a] 2604(2^{nd} shell)	2604(2^{nd} shell) 2605(2^{nd} shell)
Stretch of free SH in the 1^{st} shell H-bonded H_2S			2607 2612	2605 2606	2597	2598[a] 2599[a] 2603	2597 2599
Sym. stretch of free SH in charge-dipole bound H_2S	2601 2605	2604 2605	2604		2599		2592
Asym. stretch of free SH in H-bonded H_2S	2619(1^{st} shell) 2619(1^{st} shell) 2620(1^{st} shell)	2618(1^{st} shell) 2619(1^{st} shell) 2622(1^{st} shell)	2617(1^{st} shell) 2630(2^{nd} shell)	2630(2^{nd} shell)	2618(1^{st} shell) 2619(1^{st} shell) 2629(2^{nd} shell)	2617(1^{st} shell) 2625(2^{nd} shell) 2628(2^{nd} shell)	2629(2^{nd} shell) 2630(2^{nd} shell)
Asym. stretch of free SH in charge-dipole bound H_2S	2627 2630	2630 2631	2630		2624		2619

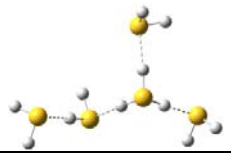
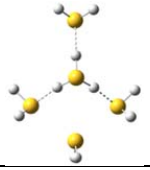
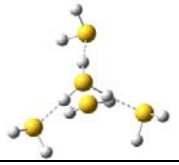
[a] The stretch frequency of free SH in the 1^{st} shell H-bonded H_2S is mixed with the sym. stretch of free SH in 2^{nd} shell H-bonded H_2S for isomer **6-6**. Therefore, for these two types of stretch, only single band exists for each.

Table SI-5 Calculated SH stretch harmonic vibrational frequencies (in cm^{-1}) and their assignments of all the isomers of $H^+(H_2S)_7$ shown in Figure 6 in the main text (and in Figure SI-3). The calculation level is MP2/aug-cc-pVDZ and the scaling factor of 0.945 is applied.

	7-1	**7-2**	**7-3**	**7-4**	**7-5**	**7-6**	**7-7**	**7-8**
Stretch of H-bonded SH in H_3S^+	2047 2119 2224	1946 1973 2082	2041 2072 2151	2014 2117 2189	1607 2186 2236	2069 2177 2223	1996 2085 2213	1897 1973 2088
Stretch of H-bonded SH in neutral H_2S		2539 2556 2560 2563	2539 2563	2568	2487		2511	2493 2501 2600
Sym. stretch of free SH in H-bonded H_2S	2590(1^{st} shell) 2591(1^{st} shell) 2591(1^{st} shell)	2588(1^{st} shell) 2603(2^{nd} shell)	2603(2^{nd} shell) 2604(2^{nd} shell)	2593(1^{st} shell) 2595(1^{st} shell) 2602(2^{nd} shell)[a] 2604(2^{nd} shell)[a]	2595(1^{st} shell) 2596(1^{st} shell) 2603(2^{nd} shell)	2591(1^{st} shell) 2592(1^{st} shell) 2593(1^{st} shell)	2590(1^{st} shell) 2594(1^{st} shell) 2604(2^{nd} shell)	2591(1^{st} shell) 2598(2^{nd} shell) 2603(2^{nd} shell)
Stretch of free SH in the 1^{st} shell H-bonded H_2S		2609 2611	2606 2611	2602[a] 2604[a]	2573		2602	2606
Sym. stretch of free SH in charge-dipole bound H_2S	2599 2603 2603	2604	2603 2604	2600 2605	2598 2603	2602 2605 2605	2596 2601	2604
Asym. stretch of free SH in H-bonded H_2S	2616(1^{st} shell) 2618(1^{st} shell) 2619(1^{st} shell)	2629(2^{nd} shell) 2630(2^{nd} shell)	2620(1^{st} shell) 2629(2^{nd} shell)	2617(1^{st} shell) 2620(1^{st} shell) 2630(2^{nd} shell)	2619(1^{st} shell) 2621(1^{st} shell) 2628(2^{nd} shell)	2618 2619 2620	2613(1^{st} shell) 2621(1^{st} shell) 2630(2^{nd} shell)	2620(1^{st} shell) 2624(2^{nd} shell) 2628(2^{nd} shell)
Asym. stretch of free SH in charge-dipole bound H_2S	2625 2627 2629	2630	2629 2630	2626 2630	2625 2629	2627 2628 2630	2622 2627	2630

[a] The stretch frequency of free SH in the 1^{st} shell H-bonded H_2S is mixed with the sym. stretch of free SH in 2^{nd} shell H-bonded H_2S for isomer **7-4**. Therefore, for these two types of stretch, only single band exists for each.

Table SI-6 Relative energies among the optimized structures of $H^+(H_2S)_5$ by various calculation methods. All units are in kJ/mol.

	5-5 	**5-2** 	**5-1** 
with dispersion correction			
MP2/aug-cc-pVDZ	9.56	1.48	0
M062x/aug-cc-pVDZ	20.5	8.72	0
M062X/6-311++G(3df,2p)	12.3	0.436	0
M062x/6-311++g(d,p)	17.5	8.39	0
ωB97xD/aug-cc-pVDZ	3.85	0.971	0
ωB97XD/6-311++G(3df,2p)	2.81	0	1.26
ωB97XD/6-311++g(d,p)	5.47	0	0.683
without dispersion correction			
B3LYP/aug-cc-pVDZ	0	3.58	N/A
B3LYP/6-311++G(3df,2p)	2.66	0	N/A
B3LYP/6-311++G(d,p)	0	N/A	N/A

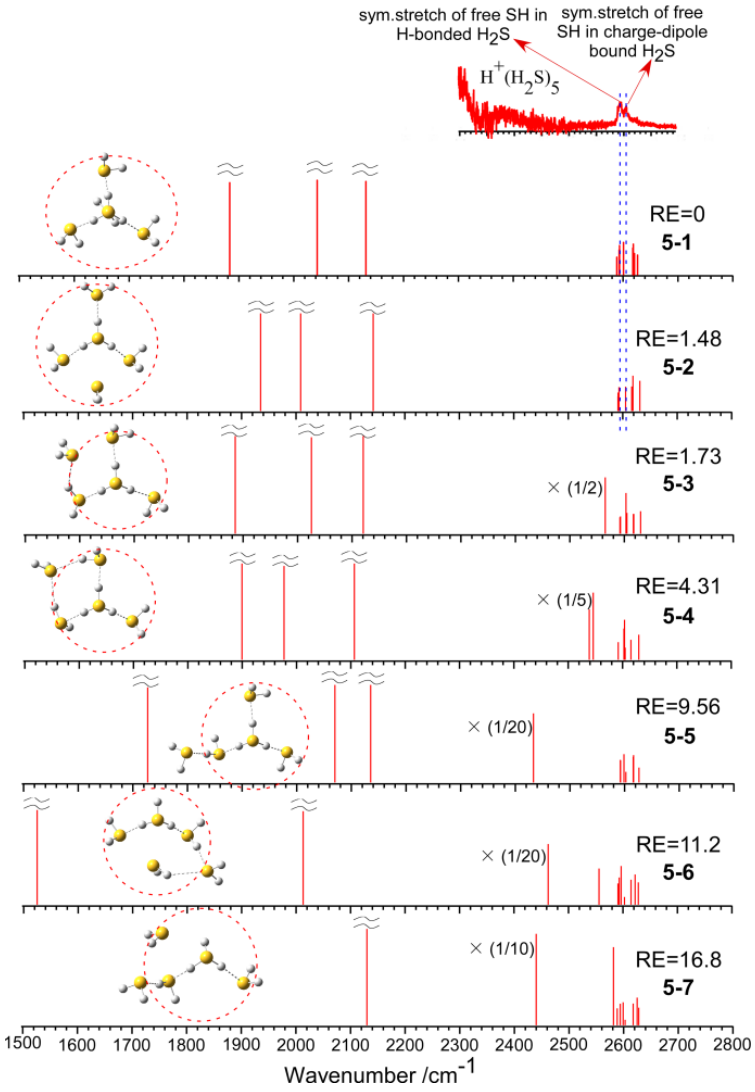


Figure SI-1 Comparison between the experimental and simulated IR spectra of $H^+(H_2S)_5$ in the full SH stretch region. The simulation was performed at the MP2/aug-cc-pVDZ level with the scaling factor 0.945. Relative energies (RE) are in kJ/mol. For the stretches of H-bonded SH in the ion core, H_3S^+, their intensities are about 100~400 times greater than that of the free SH stretches in the neutral H_2S moiety, so these sticks are simply cut off for a clear presentation. Another H-bonded SH stretch in the ion core for **5-7** is located at 1323 cm^{-1}. Note that the structures with the second H-bonded shell formation (**5-3** to **5-7**) show H-bonded SH stretch bands of the neutral H_2S moiety (their intensities are scaled in the simulated spectra). Red dotted circles indicate the first solvation shell.

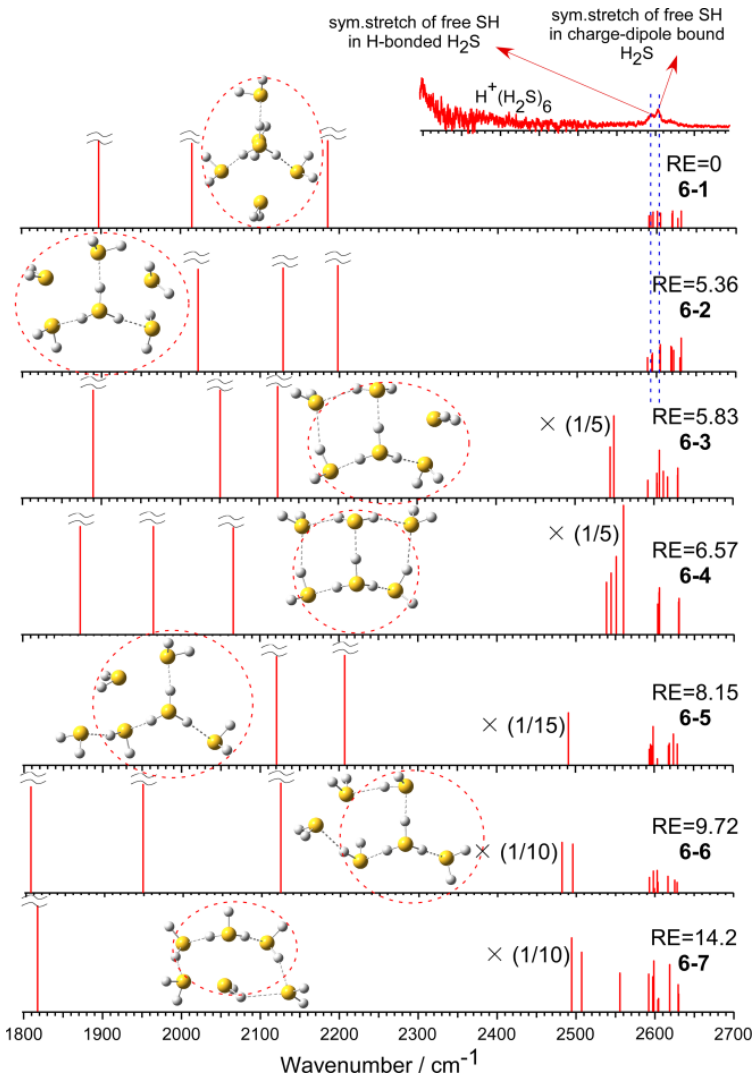


Figure SI-2 Comparison between the experimental and simulated IR spectra of $H^+(H_2S)_6$ in the full SH stretch region. The simulation was performed at the MP2/aug-cc-pVDZ level with the scaling factor 0.945. Relative energies (RE) are in kJ/mol. Another H-bonded SH stretch in the ion core for **6-5** is located at 1785 cm^{-1}, and that for isomer **6-7** is at 1655 cm^{-1}. Note that the structures with the second H-bonded shell formation (**6-3** to **6-7**) show H-bonded SH stretch bands of the neutral H_2S moiety (their intensities are scaled in the simulated spectra). Red dotted circles indicate the first solvation shell.

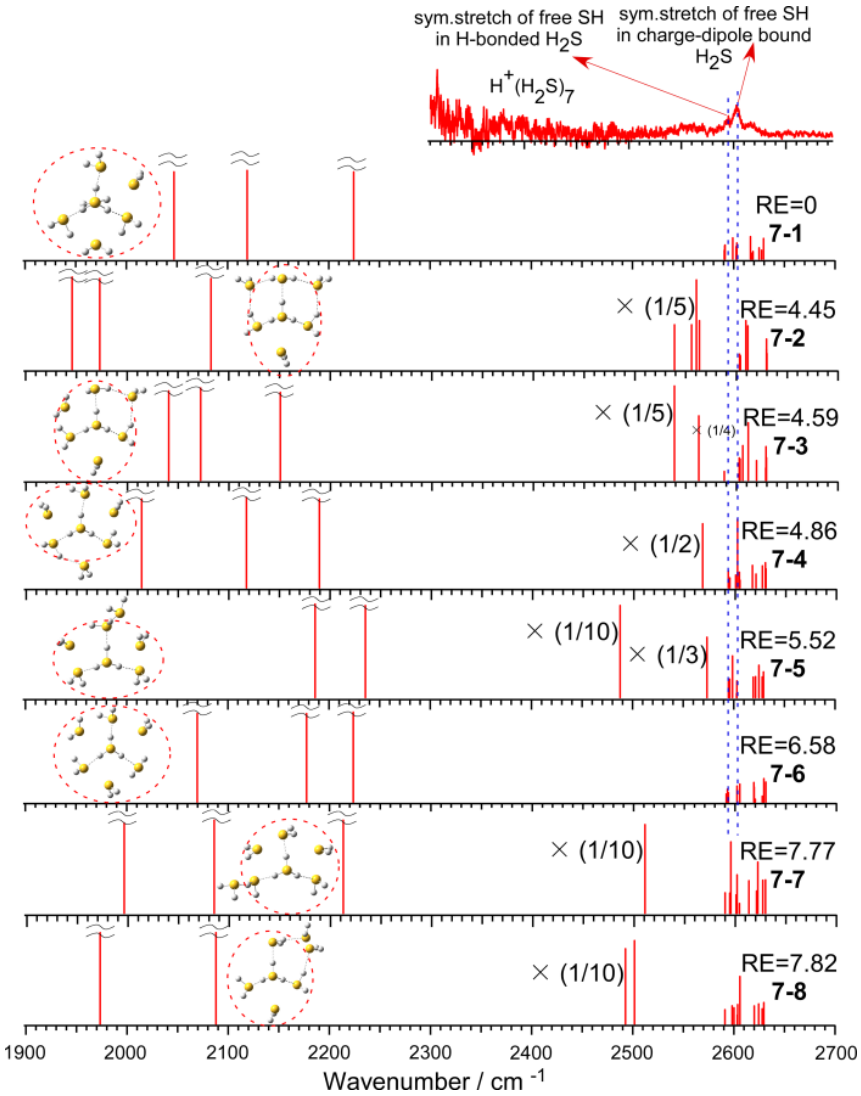


Figure SI-3 Comparison between the experimental and simulated IR spectra of $H^+(H_2S)_7$ in the full SH stretch region. The simulation was performed at the MP2/aug-cc-pVDZ level with the scaling factor 0.945. Relative energies (RE) are in kJ/mol. Another H-bonded SH stretch in the ion core for **7-5** is located at 1607 cm^{-1}, and that for isomer **7-8** is at 1897 cm^{-1}. Note that the structures with the second H-bonded shell formation (**7-2** to **7-5**, **7-7** and **7-8**) show H-bonded SH stretch bands of the neutral H_2S moiety (their intensities are scaled in the simulated spectra). Red dotted circles indicate the first solvation shell.