

Electronic Supplementary Information of

Influence of the microsolvation on hemibonded and protonated hydrogen sulfide:

**Infrared spectroscopy of $[(\text{H}_2\text{S})_n(\text{X})_1]^+$ and $\text{H}^+(\text{H}_2\text{S})_n(\text{X})_1$ ($n = 1$ and 2 , $\text{X}=\text{water}$,
methanol, and ethanol).**

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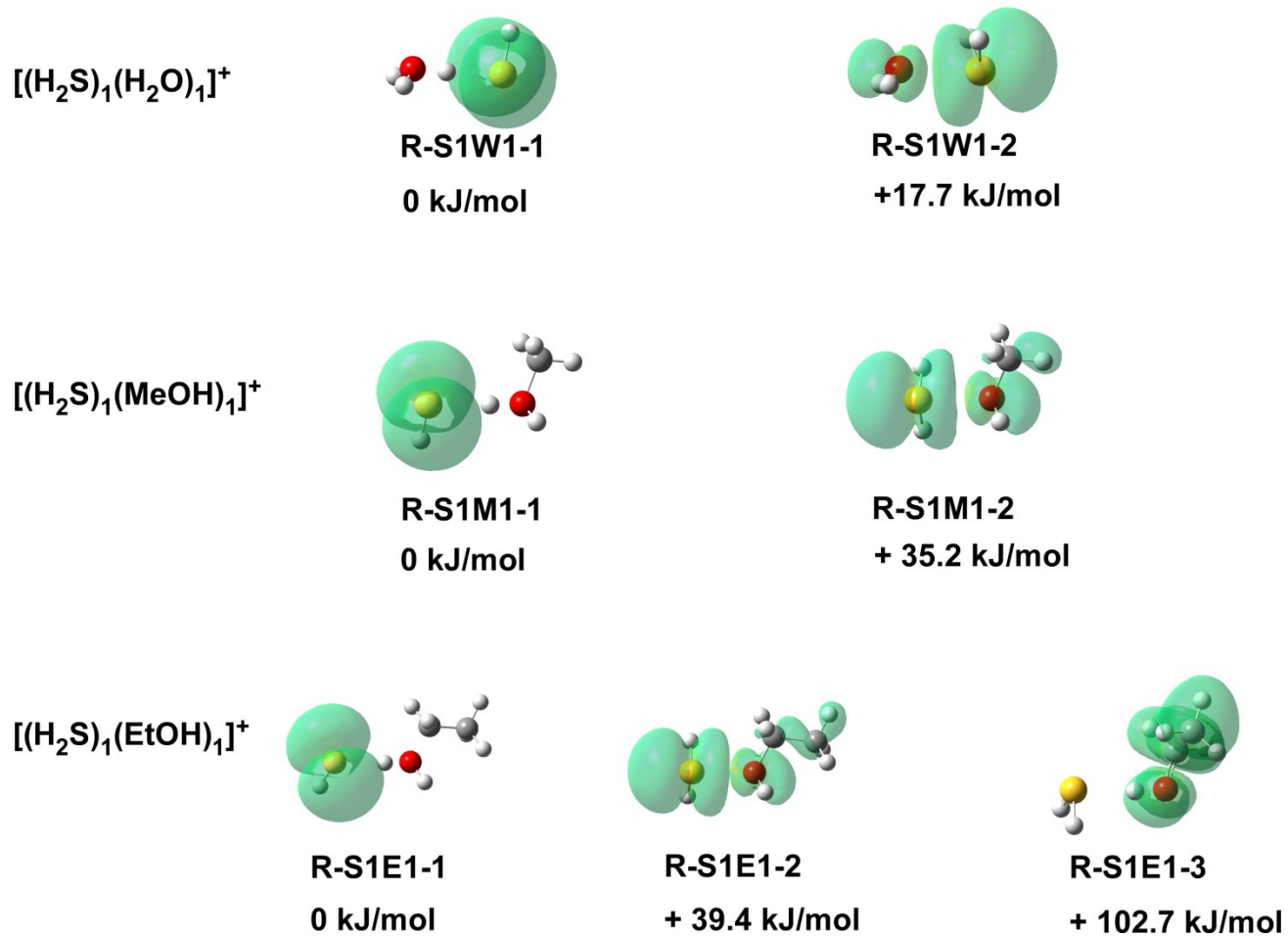


Figure S1. Spin density (isovalue = 0.0004) of stable structures of $[(\text{H}_2\text{S})_1(\text{X})_1]^+$ (X = water, methanol, and ethanol). The calculations were performed at MP2/aug-cc-pVDZ.

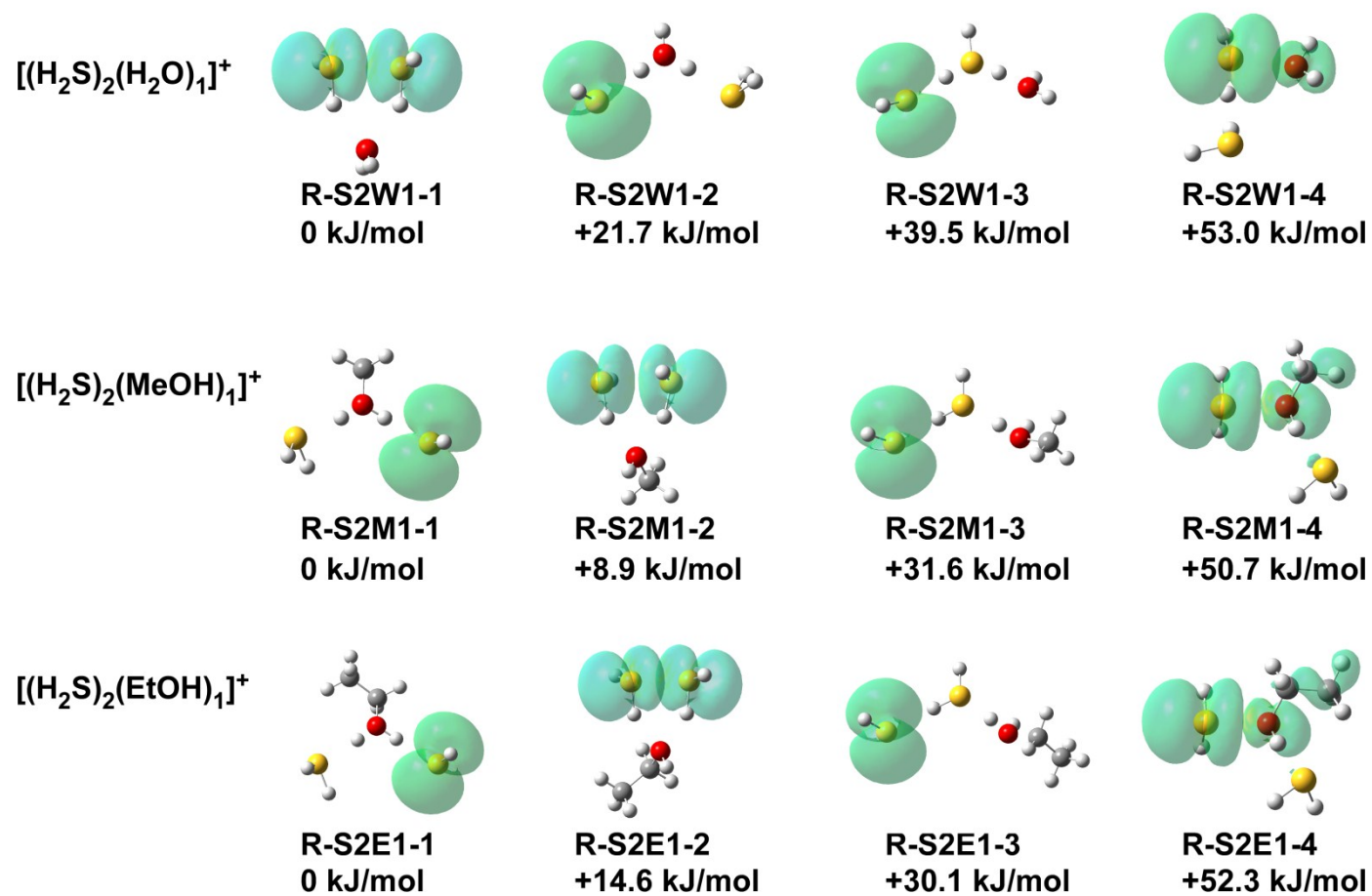


Figure S2. Spin density (isovalue = 0.0004) of stable structures of $[(\text{H}_2\text{S})_2(\text{X})_1]^+$ (X = water, methanol, and ethanol). The calculations were performed at MP2/aug-cc-pVDZ.

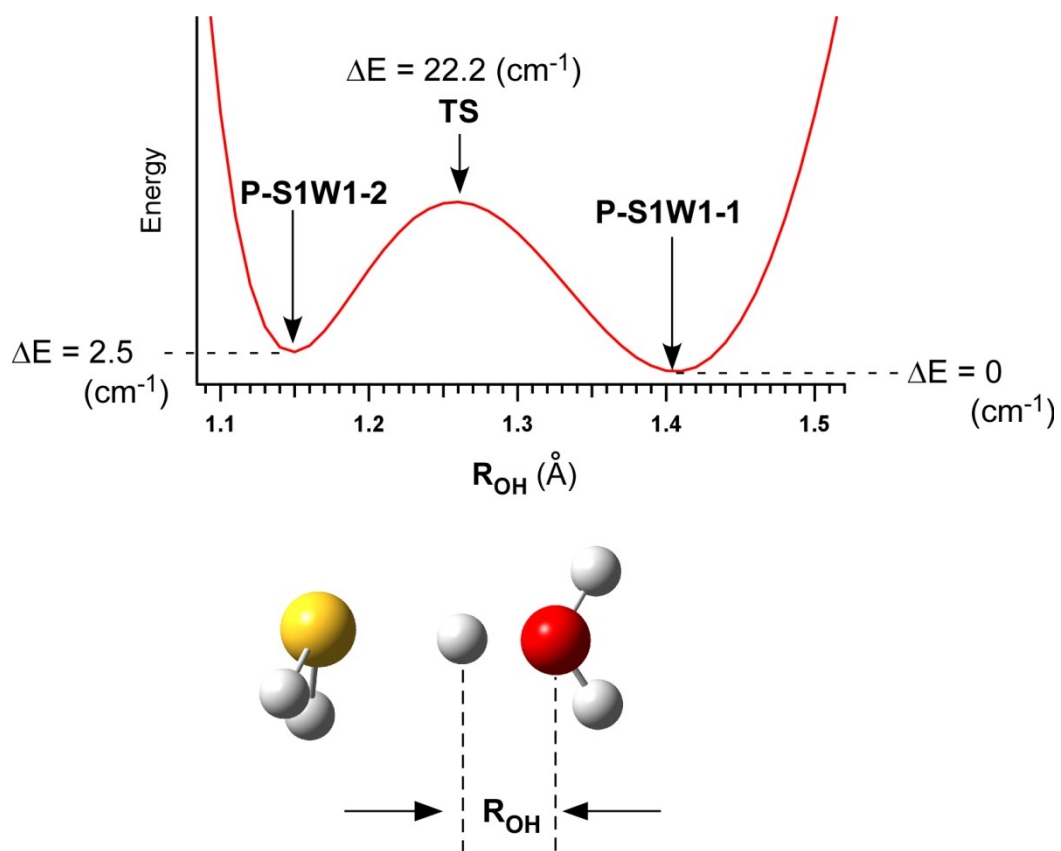


Figure S3. One dimensional potential of $\text{H}^+[(\text{H}_2\text{S})_1(\text{H}_2\text{O})_1]$. While R_{OH} is scanned, all other structural parameters are optimized. Two minima in the potential correspond to **P-S1W1-1** and **PS1W1-2** in Fig. 9 of the main text.

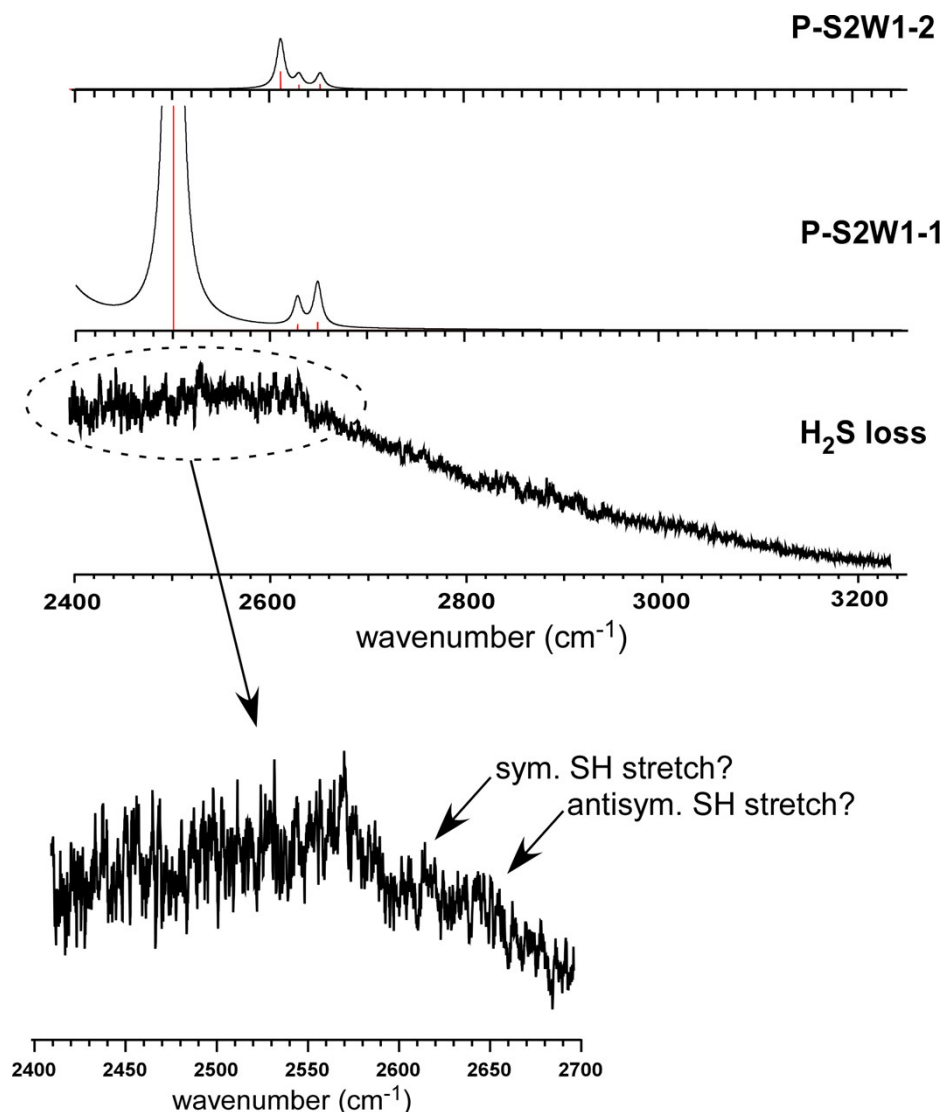


Figure S4. Observed and simulated IR spectra of $\text{H}^+[(\text{H}_2\text{S})_2(\text{H}_2\text{O})_1]$ in the SH stretch region. The observed spectra were measured by monitoring the H_2S loss channel. The simulated spectra are based on the stable structures shown in Fig. 13 in the main text. All the calculations were performed at the MP2/aug-cc-pVDZ level. The calculated harmonic frequencies were scaled by the factor of 0.954. The lowest column is the expanded observed spectrum in the free SH region. The small shoulders at around 2600-2650 cm^{-1} indicated by the arrows might be assigned to the symmetric and antisymmetric SH stretch bands of neutral H_2S moiety. However, clear assignments of the SH stretches are difficult because of the overlap with the strong absorption of hydrogen-bonded OH stretch band.