Spectroscopic Observation of Two-Center Three-Electron Bonded (Hemibonded) Structures of the $(H_2S)_n^+$ Clusters in the Gas Phase

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[Abstract] The stable hemibonded core $(H_2S \therefore SH_2)^+$ formation in $(H_2S)_n^+$ (n = 3− 6) is demonstrated in the gas phase. The spectral feature of the free SH stretches of the clusters shows that the hemibond motif of the ion core is held up to the completion of the first H-bonded solvation shell. All the observed spectra are well reproduced by the minimum energy hemi-bonded structures, and no sign of the proton-transferred type ion core H_3S^+-SH are found. The hemibond character of the ion core is also supported by the spin density calculations.

[Introduction] When lone pair orbitals of a neutral molecule and its radical cation are overlapped and molecular orbitals are formed, the bonding σ orbital is doubly occupied while the antibonding σ* orbital is singly occupied. The formal bond order of this interaction is ½, indicating the formation of a stable bond between the two molecules.[1-3] Such a bond is called two-center three electron (2c-3e) bond or hemibond. Since the first characterization of the hemibond by Linus Pauling in the early 1930s,[4] the hemibond of radical cations has attracted strong interest in biological, atmospheric, and radiation chemistry due to its role in the reactivity of the radical cation.[5,6] However, spectroscopic observations of hemibonded structures have been very scarce. In the present study, we apply infrared predissociation spectroscopy combined with quantum chemical calculations to $(H_2S)_n^+$ (n = 3 - 6) radical ion clusters, and prove their hemibond ion core.[7]

[Results and Discussion] To verify which type of ion core, as shown in Figure 1, is favoured in $(H_2S)_n^+$ (n = 3 − 6) in the gas phase is the most critical part in this study. Figure 2 shows the observed IR spectra of $(H_2S)_n^+$ in the SH stretch region. The broad absorption below 2500 cm^{-1} is attributed to hydrogen-bonded SH stretches of the

hemibonded type   proton-transferred type

Fig. 1. Two possible structural motifs of $(H_2S)_2^+$

ion core. The free SH stretch bands appear above 2500 cm^{-1}. Among the free SH bands, the lowest frequency band at around 2560 cm^{-1} in each size (the band in the red dotted block) is assigned to free SH stretches of the ion core. The two relatively higher frequency bands at around 2595 and 2610 cm^{-1} (the bands in the blue and green dotted blocks) are assigned to the symmetric
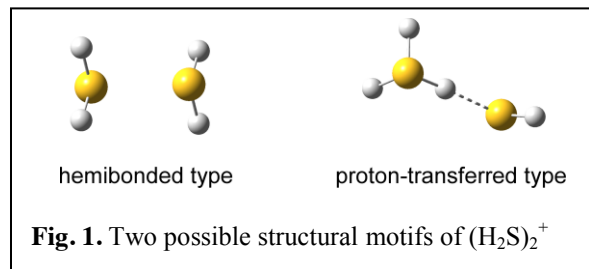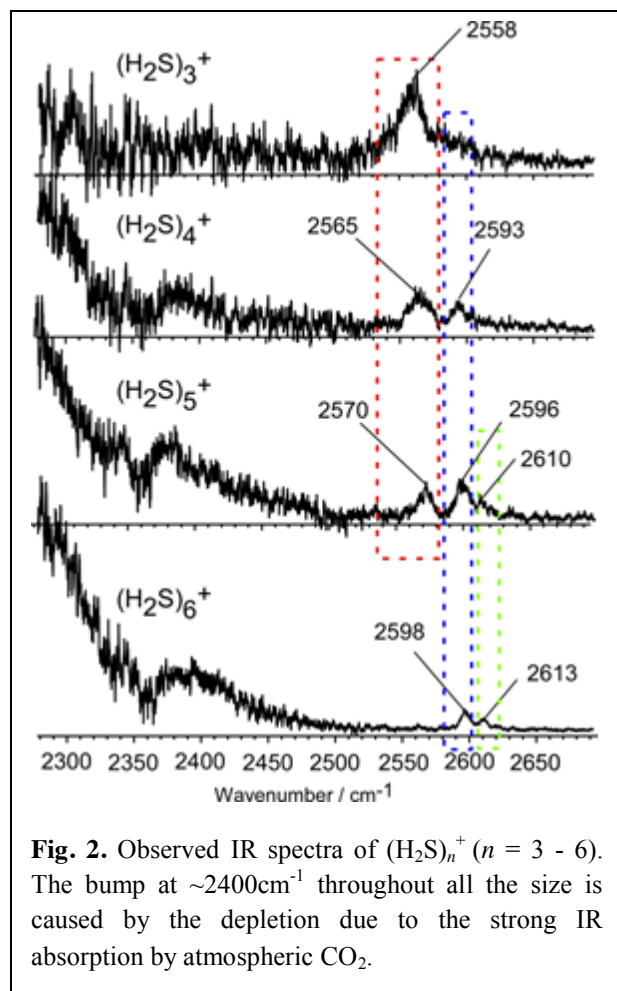
Fig. 2. Observed IR spectra of $(H_2S)_n^+$ ($n = 3 - 6$). The bump at $\sim 2400 cm^{-1}$ throughout all the size is caused by the depletion due to the strong IR absorption by atmospheric CO_2.
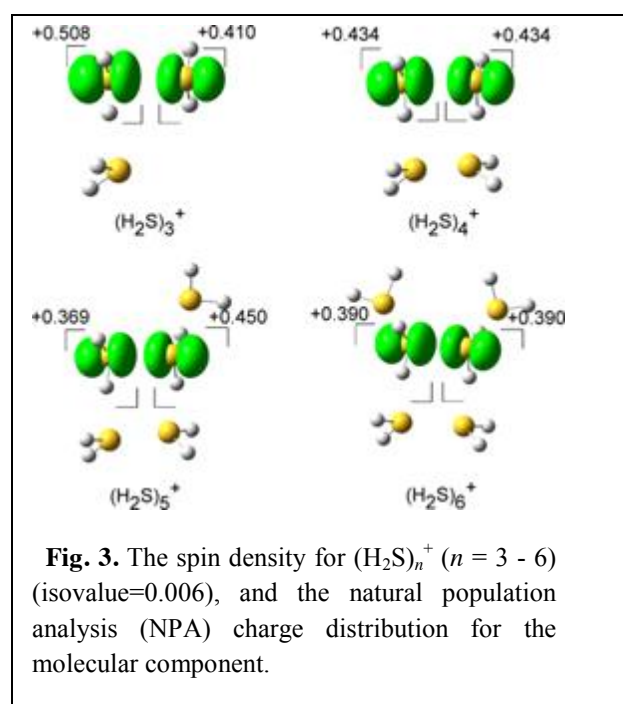

Fig. 3. The spin density for $(H_2S)_n^+$ ($n = 3 - 6$) (isovalue=0.006), and the natural population analysis (NPA) charge distribution for the molecular component.

(ν_1) and asymmetric (ν_3) SH stretch bands of the neutral H_2S moiety, respectively, which is solvating the ion core as an acceptor of an H-bond. Herein, the most striking feature in the spectra is the free SH stretch band of the ion core. This band should disappear when the number of neutral H_2S molecules in the cluster is enough to solvate all the SH bonds of the ion core. Whatever the ion core is the hemibonded or proton-transferred type, the free SH of the ion core should exist in $(H_2S)_3^+$. Assuming the ion core is the proton-transferred type, the free SH stretch in the core is expected to disappear at $n = 4$. In the observed spectra, however, the free SH band actually disappears at $n = 6$. This clearly demonstrates that the ion core of the clusters is the hemibonded type $(H_2S \therefore SH_2)^+$ which has four SH bonds.

This conclusion is further confirmed by the harmonic simulated spectra of the most stable hemibonded structures. In addition, as seen in Figure 3, the calculated spin density is almost equally delocalized on the two H_2S molecules. This is another reinforced evidence of the hemibonded structure.

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