1P005

Infrared spectroscopy of protonated and ionic hydrogen sulfide clusters H$^+$(H$_2$S)$_n$ and (H$_2$S)$_n$ ($n{\leq}6$)

(Tohoku Univ.) Dandan Wang, Asuka Fujii

Sulfur centered hydrogen bond (SCHB) has recently attracted much interest since SCHB is ubiquitous and significant in biological systems. Sulfur plays a crucial role in protein folding process and serves as an active bonding site of protein[1]. While sulfur belongs to the same group as oxygen, its heavier atomic weight suggests that dispersion should be more important in SCHB than in typical hydrogen bonds[2]. Therefore, exploration of the particularity and generality of SCHB in comparison with conventional hydrogen bond is of great interest. Several spectroscopic studies on SCHB model clusters have recently been reported[2,3]. However, the property of SCHB, especially its preferred network structures and influence of the excess charge (proton), is still elusive. In the present study, as benchmark systems for networks formed by SCHB, we study structures of protonated and ionic hydrogen sulfide clusters, H$^+$(H$_2$S)$_n$ and (H$_2$S)$_n$$^+$, by infrared (IR) spectroscopy combined with ab initio calculations.

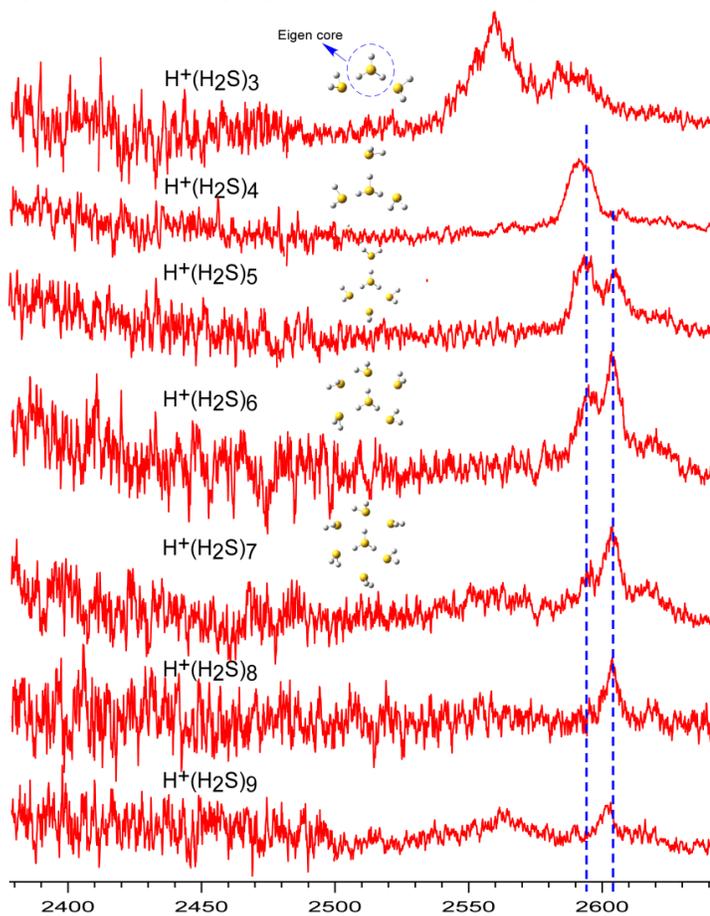

Figure 1. Overview of the vibrational predissociation spectra of H$^+$(H$_2$S)$_n$(n=3 to 9) in SH stretching region of neutral H$_2$S and the calculated lowest-energy structures from size 3 to 7.

Figure 1 shows the observed IR spectra of size-selected H$^+$(H$_2$S)$_n$ (n=3-9) in the SH stretch region. The spectra were measured by IR dissociation spectroscopy, and the H$_2$S loss channel was monitored. All the bands higher than 2580 cm^{-1} are assigned to free SH stretches of neutral H$_2$S moieties in the clusters[3]. The strong band at 2560 cm^{-1} in the spectrum of n=3 disappears in the larger sizes. Therefore, this band is attributed to the free SH stretch of the Eigen type ion core (H$_3$S$^+$). This also indicates that the first H-bond solvation shell of the ion core is completed

in $H^+(H_2S)_4$, as shown in Figure 1 (H-bonded SH bands of the ion core are expected below 2000 cm^{-1}). The free SH band at 2594 cm^{-1} is then attributed to those of the first H-bond shell (ν_1, sym. stretch).

In n=5, a new free SH band strongly appears at 2604 cm^{-1}, but H-bonded SH bands, which are expected at around 2550 cm^{-1} or lower for 2-coordinated H_2S site, are absent. This means the second H-bond solvation shell of the ion core is not formed in n=5. Optimized structure search at the MP2/aug-cc-pVDZ level suggests that in n>4, further H_2S prefers to directly solvate the ion-core by the charge-dipole interaction rather than the second H-bond solvation shell formation. This calculation result explains well the observed spectra, and the band at 2605 cm^{-1} is attributed to the ν_1 sym. stretch of H_2S in the "charge-dipole shell". Both in the H-bond and charge-dipole shells, only the ν_1 band strongly appears and the ν_3 band is much weaker or almost disappears. The same trend has been observed for H_2O directly solvating a protonated or positively charged site.

In the size range of n=5-8, the basic spectral motifs are kept, but a remarkable intensity ratio change happens between the two free SH bands with increase of the size. The intensity of the band at 2594 cm^{-1} is gradually overtaken by the band at 2604 cm^{-1}. This spectral change shows the filling process of the charge-dipole shell. At n=9, a somewhat broadened band appears at 2564 cm^{-1}, and this band is assigned to an H-bonded SH band. This is the beginning of the second H-bond shell formation. Therefore, there would be 4 sites for the charge-dipole solvation of the ion core (3 are in the plane of the first H-bond shell, and 1 is under the umbrella of the ion core), and totally 7 H_2S molecules directly solvate the Eigen type ion core. To form such a dense solvation structure around the ion core, not only the charge dipole interaction but also dispersion should play an important role. This is proved by the fact that the B3LYP calculation, which is known to lack the contribution of dispersion, largely underestimates the stability of the charge-dipole solvation structures. In the previous theoretical study of $H^+(H_2S)_n$ at the HF level[4], which has been the unique study on the structures of $H^+(H_2S)_n$ so far, also could not find this type of solvation structures.

We also note that no evidence for the Zundel type ion core (H_2S-H^+-H_2S) formation is obtained in the observed size range (n=3-9), though the Zundel ion core is most stable in $H^+(H_2O)_6$[5]. Moreover, the observed network structures of $H^+(H_2S)_n$ is totally different from those of $H^+(H_2O)_n$ in n>4.

Spectra and structures of $(H_2S)_n^+$ radical cluster ions will also be discussed in the presentation.

References:

[1] S. Ghosh, S. Bhattacharyya, S. Wategaonkar. J. Phys. A 2015, 119, 10863-10870.
[2] H. S. Biswal, S. Bhattacharyya, A. Bhattacherjee, S. Wategaonkar. Int. Rev. Phys. Chem. 2015, 34, 99-160.
[3] A. Bhattacherjee, Y. Matsuda, A. Fujii, S. Wategaonkar. J. Phys. Chem. A 2015, 119, 1117-1126.
[4] S. Yamabe, T. Minato, M. Sakamoto, K. Hirao. Can. J. Chem. 1985, 2571-2574.
[5] J. M. Headrick, E. G. Diken, R. S. Walters, N. I. Hammer, R. A. Christie, J. Cui, E. M. Myshakin, M. A. Duncan, M. A. Johnson, K. D. Jordan. Science 2005, 308, 1765-1769.