Laser spectroscopic investigation of sulfur-centered intermolecular interactions in the gas phase

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論 文 内 容 要 旨

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学位論文の 題　　　目	**Laser spectroscopic investigation of sulfur-centered intermolecular interactions in the gas phase** （硫黄を含む分子間相互作用の気相レーザー分光研究）		

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1. Introduction

Sulfur is a biologically abundant element, which are involved in amino acids, disulfide bridges, etc. Sulfur-centered hydrogen bonds（SCHBs）have first been well established by crystallography of proteins and organic molecules. SCHBs play profound roles in stabilization of protein structures and selective binding of ligands at the active site of proteins. SCHBs are

known to be unconventional hydrogen bonds (HBs) due to the small electronegativity of sulfur. However, understanding of such particular and weak interactions has been still limited, especially from the aspect of molecular level in the gas phase. Some unexpected properties of SCHBs have been known.[1] For example, it has been reported that the strengths of the S···H−O and O···H−O HBs in DMS-HNO$_3$ and DME-HNO$_3$, respectively, are very close to each other. The magnitude of the S−H···π interaction is the largest one among the X−H···π (X = C, N, O, and S) type interactions. In addition, sulfur is frequently concerned with a hemibond (two-center three-electron, 2c-3e, bond) in radical (cation) systems, which has been suggested in various areas such as free-radical chemistry, biochemistry, organic reactions, radiation chemistry, and so on. [2,3] For instance, it has been supposed that the temporary formation of hemibonds, such as S∴π, O∴S, can serve as relay stations in the long-range electron (hole) transport in protein. However, so far, its nature has been hardly elucidated by experimental observations since only broadened electronic transitions have been a unique spectral signature of hemibonds. Therefore, in the present work, we planned a systematic study on SCHBs and sulfur-sulfur hemibonds in the gas phase. Protonated and radical cation clusters of hydrogen sulfide, $H^+(H_2S)_n$ and $(H_2S)_n^+$, were chosen as the simplest model systems, and their intermolecular structures were studied by infrared (IR) spectroscopy and quantum chemical calculations.

2. Experimental and theoretical methods

IR spectra of size-selected $H^+(H_2S)_n$ and $(H_2S)_n^+$ clusters were measured in the SH stretch region by infrared (IR) photodissociation spectroscopy combined with tandem mass spectrometry. The charged clusters were generated by pulsed discharge to a supersonic jet expansion of a H$_2$S/Ar gaseous mixture, and the cluster size selection was performed by a tandem type quadrupole mass spectrometer. The mass resolution of the mass spectrometer was set to high enough to separate $H^+(H_2S)_n$ and $(H_2S)_n^+$. In theoretical computations, possible stable isomers were extensively searched at the MP2/aug-cc-pVDZ level, which has the excellent balance of accuracy and time-consuming. Harmonic vibrational simulations of the stable isomers were also performed. The dissociation energies of the clusters were also evaluated with the zero point energy and basis set superposition error corrections. In addition, the natural band orbital (NBO) and spin density analysis were taken to get a more insight into the intermolecular interactions. With regard to the radical cation system, $(H_2S)_n^+$, since the unrestricted wave functions in MP2 tend to be contaminated by states of higher spin multiplicity, a computational cost-effective double hybrid DFT functional, UB2PLYPD, which

has demonstrated to treat the spin contamination well, was also employed to guarantee the validity of the results. The observed spectra consist fairly well with the theoretical results.

3. Results and discussions

A. Structures of $H^+(H_2S)_n$

Sulfur belongs to the same group as oxygen, and the H-bond coordination property of H_2S is expected to be same as that of H_2O. Thus, the well-studied protonated clusters $H^+(H_2O)_n$ can be a reference to consider structures of $H^+(H_2S)_n$. Comparison between $H^+(H_2O)_n$ and $H^+(H_2S)_n$ will be highly helpful to illustrate the unique properties of intermolecular structures constructed by SCHBs.

In the observed spectrum of $n = 3$, as shown in Fig.1, three features are seen; intense and broadened absorption below ca. 2400 cm^{-1} and two relatively sharp bands at 2558 and 2585 cm^{-1}. The broadened absorption is obviously attributed to the tail of strong H-bonded SH stretch bands of the protonated ion core. Its peak is expected to be lower than 2300 cm^{-1}, which is the low frequency limit of the reliable measurement by the present experiment system.

Fig. 1 Vibrational predissociation spectra of size-selected $H^+(H_2S)_n$ ($n = 3 - 9$) with their simulated stick spectra based on the most stable energy-optimized structures. The optimized structures for the simulations are shown in Fig. 2. The harmonic vibration modes are calculated at the MP2/aug-cc-pVDZ level (scaled by 0.945) and are presented as colored sticks. Orange stick: free SH stretch of the Eigen type ion core H_3S^+; Blue sticks: sym. stretch (v_1) of free SH in H-bonded H_2S; Red sticks: sym. stretch (v_1) of free SH in charge-dipole bound H_2S; Green sticks: asym. stretch (v_3) of free SH in both H-bonded and charge-dipole bound H_2S molecules.

of the reliable measurement by the present experiment system. Extremely broadened absorption of such an ion core vibration has also been reported for $H^+(H_2O)_3$. The sharp band at 2558 cm^{-1} in the spectrum of $n = 3$ suddenly disappears in $n \geq 4$. The absence of the band for $n \geq 4$ gives unambiguous implication that this band is attributed to the free SH stretch of the
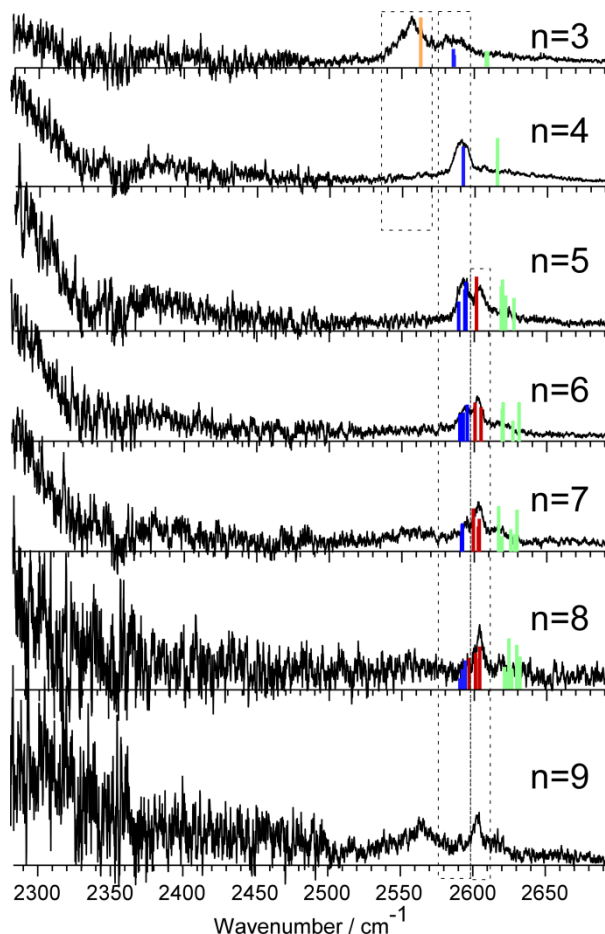
ion core, and the ion core is the Eigen type, H_3S^+. This is because the first H-bonded solvation shell of the Eigen type ion core should be completed at $n = 4$. This spectral assignment is also supported by the good agreement with the simulated spectra based on the minimum energy structures. Therefore, the development of the proton solvation structure in $H^+(H_2S)_n$ is parallel to that in $H^+(H_2O)_n$ at $n = 3$ and 4. In the structures of $n = 3$ and 4, free SH should exist in the neutral moiety (H-bonded shell) and the observed bands at 2585 and 2590 cm^{-1}, respectively, are uniquely assigned to their stretch vibration (symmetric stretch, v_1). Free SH stretch bands of neutral H_2S monomer (v_1 and asym. stretc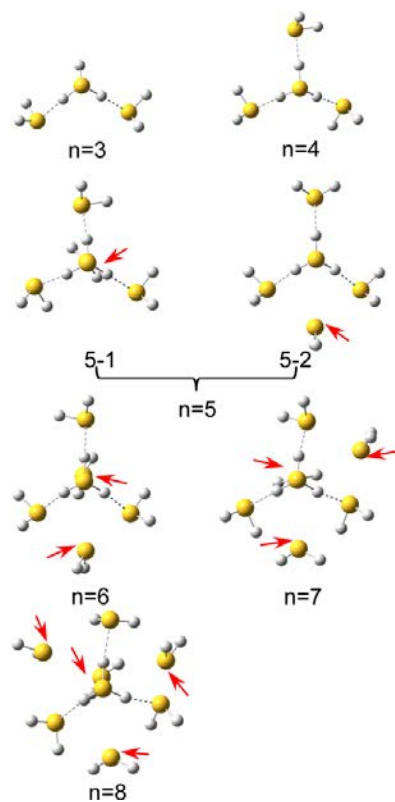h v_3) have been reported at 2614 and 2628 cm^{-1}, respectively, and the small low-frequency shifts are attributed to the influence of the excess charge in the ion core.

As seen in the spectrum of $n = 5$ in Fig. 1, a new free SH band strongly appears at 2605 cm^{-1}. If the second H-bonded shell begins to form following the completion of the first shell at $n = 4$, an H-bonded SH band of the neutral moiety (H-bonded SH of the first shell molecule) is expected in the frequency region lower than the free SH band (< 2585 cm^{-1}). However, such a band is totally absent. This suggests that the second H-bonded shell is not formed in $n = 5$ and the solvation structure is quite different from that of $H^+(H_2O)_5$, in which the fifth H_2O interacts only with the first solvation shell by an H-bond. To uncover the structure of $H^+(H_2S)_5$, we turn to quantum chemical calculations at the MP2/aug-cc-pVDZ level. We find that a charge-dipole shell is energetically preferred over the 2nd HB solvation shell, and in the charge-dipole shell of $H^+(H_2S)_5$, the fifth H_2S can locate either under

Fig. 2 Energy-optimized structures (MP2/aug-cc-pVDZ) of $H^+(H_2S)_n$ ($n = 3 − 8$) identified by the observed IR spectra. H_2S molecules bound by the charge-dipole interactions are denoted by red arrows.

the umbrella of the H_3S^+ moiety (5-1) or in the same plane as the H-bonded shell molecules (5-2). The charge-dipole shell formation following the first H-bonded shell completion is demonstrated for the first time in the present work.

In the size range of $n = 6 − 8$, the basic spectral motifs are kept, as shown in Fig. 1, but a remarkable intensity ratio change happens between the two free SH bands of neutral H_2S with increasing of the cluster size. The intensity of the H-bonded shell band is gradually overtaken by the charge-dipole shell band. This spectral change clearly exhibits the filling process of the charge-dipole shell. By calculation, we searched the structures of $n = 6− 8$, and the most stable one in each size shows the development of the charge dipole shell. At $n = 9$, a new band appears at around 2570 cm^{-1}. This band is assigned to an SH stretch H-bonded to a neutral H_2S moiety, and demonstrates the beginning of the 2nd H-bond shell formation.

The overview of the solvation structure evolution of $H^+(H_2S)_n$ till the first solvation shell completion is illustrated in Fig.2. We find some quite unique properties of $H^+(H_2S)_n$. From the aspect of configuration, only the Eigen type ion core is observed for $H^+(H_2S)_n$ ($n = 3$ - 8). The charge-dipole shell is preferred rather than the 2nd HB solvation shell after the 1st HB solvation shell. As a result, in comparison with $H^+(H_2O)_n$, a more closely solvated structure is finally formed in $H^+(H_2S)_8$, in which 7 molecules directly interact with the Eigen type ion core. We ascribe this characteristic of the structures of $H^+(H_2S)_n$ mainly to the large polarizability of sulfur. The magnitude of the H-bonds between the ion core and the 1st shell is largely enhanced by the excess charge of the core, relative to the H-bonds between the 1st and 2nd H-bonded shells which are those between essentially neutral molecules. Meanwhile, the magnitude of H-bonds between neutral H_2S molecules is much smaller than those of H_2O molecules. Thus, the charge-dipole interaction

Fig. 3 Observed IR spectra of $(H_2S)_n^+$ (n=3-6) and the corresponding structures as well as the harmonic simulations at MP2/aug-cc-pVDZ. The green block of the observed spectra is assigned to free SH stretch of the ion core. The red block is the sym. stretch of free SH of H-bonded neutral H_2S. The blue block is the asym. stretch of free SH of H-bonded neutral H_2S.

with the ion core, or rather charge induced dipole interaction can be superior to the H-bond between the first and second shells. The charge dipole shell should be also reinforced by dispersion with neighboring sulfur atoms.
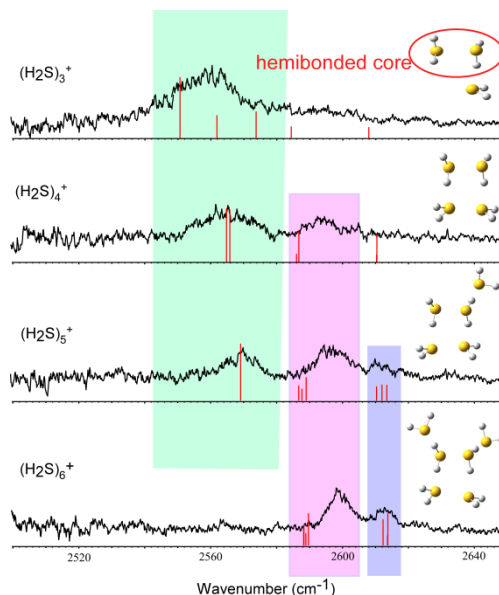
B. Hemibond formation in H$^+$(H$_2$S)$_n$

To investigate the sulfur-involved hemibond, we take (H$_2$S∴SH$_2$)$^+$ as the simplest model. The observed IR spectra of (H$_2$S)$_n^+$ (n = 3-6) are shown in Fig.3. The bands higher than 2550 cm^{-1} are attributed to free SH stretches, and they are categorized into three different types of vibrations. The most striking feature in the spectra is in the free SH stretch band of the ion core highlighted by the green block. The disappearance of the free SH band of the ion core at n = 6 demonstrates that the ion core of the clusters has the hemibond motif (H$_2$S∴SH$_2$)$^+$.

Theoretical calculations also supported that the hemiboned type motif is favored over the proton-transferred type (H$_3$S$^+$-SH). In addition, the spin (unpaired electron) density is almost equally delocalized over the two H$_2$S molecules, as seen in Fig.4. Upon the solvation of the ion core, the positive charge is dominantly localized on the ion core. Therefore, it is concluded that the hemibond motif of the ion core can be held at least up to the completion of the 1st H-bonded solvation shell. This result consists with the previous observation of the electronic transition attributed to hemibonded H$_2$S radical cations in solution. [2]
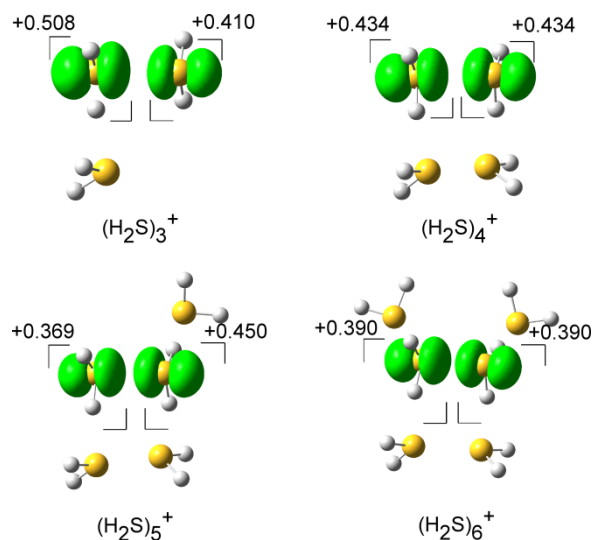

+0.508   +0.410   +0.434   +0.434

(H$_2$S)$_3^+$ (H$_2$S)$_4^+$

+0.369   +0.450   +0.390   +0.390

(H$_2$S)$_5^+$ (H$_2$S)$_6^+$

Fig. 4 The spin density for (H$_2$S)$_n^+$ (n = 3 - 6) (isovalue = 0.006), and the natural population analysis (NPA) charge distribution for the molecular component.

Reference

[1] H. S. Biswal, *et al.*, *Int. Rev. Phys. Chem.* 2015, **34**, 99-160.
[2] (a) S. A. Chaudhri, *et al.*, *J. Am. Chem. Soc.* 1984, **106**, 5988-5992. (b) M. Bonifacic, *et al.*, *J. Phys. Chem.* 1985, **89**, 3910-3914.
[3] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, 1960.

論文審査の結果の要旨

　硫黄は酸素と同族であるが、電気陰性度や分極率に大きな違いがある。そのため、酸素原子を硫黄原子に置換した化合物はこの置換により様々な化学的性質を変化させるが、近年、硫黄を含む系における、特異な分子間相互作用に注目が集まっている。特に硫黄を含む水素結合は、sulfur-centered hydrogen bonds（SCHBs）と呼ばれ、酸素を含む系における典型的な水素結合との性質の相違に大きな興味がもたれ、生体関連分子には硫黄原子を含むものが多くあることから、その生命現象における役割も注目されている。また、ラジカル（カチオンで）に対して想定される半結合（あるいは2中心3電子結合）と呼ばれる非古典的共有結合は、酸素原子間では実際の形成が難しいが、硫黄原子間でははるかに安定に存在できることが指摘されている。しかしこれらの研究の多くは凝集相における観測や理論計算に基づくものが多く、他の競合因子の存在や計算精度の信頼性等の点で、様々に議論の余地を残している。

　本研究は、気相のクラスターを利用して硫黄を含む系における特異な分子間相互作用の解明を企図したものである。もっとも単純な代表として硫化水素に着目し、特に余剰電荷を含む場合に焦点を絞り、硫化水素のプロトン付加およびラジカルカチオンクラスター（$H^+(H_2S)_n$ および $(H_2S)_n^+$）の分子間構造を赤外分光法と量子化学計算との組み合わせにより探った。

　プロトン付加クラスターでは、$H^+(H_2S)_n$ の構造は対応する水のプロトン付加クラスター $H^+(H_2S)_n$ とは大きく異なることが分かった。いくつかのサイズの水クラスターで現れる Zundel 型のイオンコア $(H_2O-H^+-OH_2)$ は $H^+(H_2S)_n$ では観測されず、また水素結合による第1溶媒和殻の完成後、次の水素結合溶媒和殻の生成に先立ち、電荷―（誘起）双極子と分散力に起因する特異な第2溶媒和殻が生成することが分かった。これは水素結合とファンデルワールス力が直接競合する、硫黄原子を含む系の特異な性質を示すものとして非常に興味深い。

　またラジカルカチオンクラスターにおいては、2分子による半結合イオンコア $(H_2S\therefore SH_2)^+$ の生成を SH 伸縮振動の特徴から実験的に立証し、プロトン移動が競合できる系における半結合形成の直接的証拠をはじめて得ることに成功した。加えて、この半結合が第一溶媒和殻の完成にいたるまで安定であることも示した。

　これらの結果は余剰電荷を含む系における硫黄原子の関わる分子間相互作用の性質を厳密な議論を可能とする気相で初めて検証したものであり、多くの全く新たな知見を含むその意義は大きい。本論文は王丹丹氏が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって，王丹丹氏提出の博士論文は，博士（理学）の学位論文として合格と認める。