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Benzene-(H₂S)_n クラスターのレーザー分光研究

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Laser Spectroscopic Investigation of Benzene-(H₂S)_n Clusters

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【Abstract】 Electronic and infrared spectroscopy of benzene-(H₂S)_n in the gas phase was performed. Tentative assignments of the electronic spectra were obtained by the combination of infrared-ultraviolet double resonance spectroscopy and MP2/6-311++G(d,p) level calculations. We found that the 6^1_0 band of the S₁-S₀ electronic transition of benzene-(H₂S)₁ shows a blue-shift relative to that of the benzene monomer. This suggests that the electrostatic term is dominant for benzene-(H₂S)₁. On the other hand, the band of benzene-(H₂S)₂ is red-shifted, suggesting increase of contribution of dispersion to the intermolecular interaction.

【Introduction】

Noncovalent interactions involving aromatic side chains of amino acids are one of the most significant decisive factors in the dynamics of protein folding. One of such interactions is the SH···π interaction. It has been confirmed by the database searches (Brookhaven Protein Data^[1] and Cambridge Crystallographic Database^[2]) that the SH···π contact exists more frequently than expected from the random association of amino acids. However, understanding of the property of the SH···π interaction has been still limited because of the shortage of experimental characterization and difficulty in theoretical computations. Thus, in this study, we focus on benzene-(H₂S)_n clusters in the gas phase as the simplest prototype of the SH···π interaction. We perform electronic and infrared (IR) spectroscopy of benzene-(H₂S)_n and discuss stable structures of the cluster and the property of the interaction between benzene and H₂S.

【Methods】

Benzene-(H₂S)_n clusters were produced by a supersonic jet expansion. Mass-selected multiphoton ionization spectra of the S₁-S₀ transition and infrared-ultraviolet double resonance (IR-UV) spectra of the clusters were measured. Stable cluster structures were searched at the MP2/6-311++G(d,p) level of theory, and their IR spectra were calculated under the harmonic approximation.

【Discussion】

Fig.1 shows the electronic spectra of benzene-(H₂S)_n around the S₁-S₀ 6¹₀ band measured by monitoring (upper) benzene⁺ and (lower) [benzene-(H₂S)₁]⁺ channels. In the spectrum by monitoring [benzene-(H₂S)₁]⁺, the 6¹₀ band of the benzene monomer is seen because of the collision after ionization of benzene. Around the monomer band, six dominant bands due to clusters are seen at +61, +32, +11 cm⁻¹ in the blue side and -14, -74, -97 cm⁻¹ in the red side. The electronic spectrum by monitoring [benzene-(H₂S)₂]⁺ channel is totally broadened but its absorption is mainly weighted in the red side of the monomer band.

To figure out the assignments of the electronic spectra, we employed IR-UV spectroscopy in the SH stretch region. The IR-UV spectra in the SH stretch region are shown in **Fig.2**. There are three major features marked by blue lines in the spectra. The bands around 2603 and 2630 cm⁻¹ are assigned to the sym. stretch (or SH•••π bonded SH) and asym. stretch of H₂S, respectively. That around 2587 cm⁻¹ is the stretch of H-bonded SH in benzene-(H₂S)₂. These assignments are verified by the theoretical calculations at the MP2/6-311++G(d,p) level. We tentatively assign the +32 cm⁻¹ band to the 6¹₀ band of benzene-(H₂S)₁, and -74 cm⁻¹ to benzene-(H₂S)₂ (the -97 cm⁻¹ band would be due to a higher cluster). It is very interesting that the band shift direction changes with the cluster size. A similar blue shift is seen in benzene-(H₂O)₁, and a red-shift occurs in benzene-Ar. While the electrostatic interaction plays an important role in the former case, dispersion is dominant in the latter. The observed shift behavior suggests that the electrostatic term is dominant for benzene-(H₂S)₁ while the contribution of dispersion is largely enhanced in benzene-(H₂S)₂.

【References】

- [1] Bernstein, F. C. et al. *J. Mol. Biol.* **112**, 535(1977).
 [2] Allen, F. H. *Acta Crystallogr. B* **58**, 380(2002).

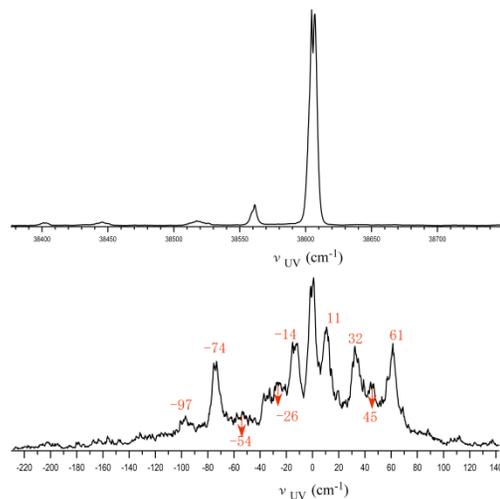


Fig. 1 S₁-S₀ electronic spectra of benzene-(H₂S)_n measured by monitoring the benzene⁺ channel (upper) and [benzene-(H₂S)₁]⁺ channel (lower). The abscissa in the lower panel is the relative frequency to the monomer band.

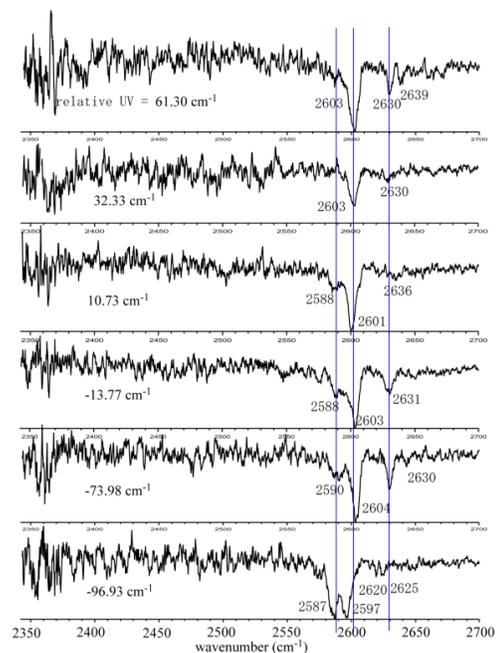


Fig. 2 IR-UV spectra of benzene-(H₂S)_n in the SH stretch region.