INFRARED SPECTROSCOPY OF PHENOL-TRIETHYLSILANE DIHYDROGEN-BONDED CLUSTER

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Dihydrogen bond is a hydrogen bond between oppositely charged two hydrogen atoms, X-H$\cdots$H-Y, where X = O, N and Y = B, metal atoms, for example. In 2005, Ishikawa and coworkers reported the observation of the dihydrogen-bond system involving Si-H group as the proton acceptor[a]. They carried out infrared (IR) spectroscopy of phenol(PhOH)-Diethylmethylsilane(DEMS) clusters. All of the three isomers of PhOH-DEMS 1:1 clusters observed exhibit a small red-shift of $\tilde{\nu}_{\mathrm{OH}}$ of the PhOH moiety in the cluster compared with that of bare PhOH. The largest shift is -29 cm^{-1}. The small red-shift is considered to be the result of the competition between the O-H$\cdots$H-Si dihydrogen-bond and the dispersion interaction of alkyl group of DEMS with phenyl ring. It means that the strength of the O-H$\cdots$H-Si dihydrogen-bond is comparable to the dispersion force.

In the present study, we have performed fluorescence excitation (FE) and IR spectroscopies of phenol-triethylsilane(TES) to widen the knowledge of the dihydrogen bond. Similar to the case of PhOH-DEMS system, the electronic origin bands of three PhOH-TES isomers appear in the vicinity of that of PhOH monomer in the FE spectrum. In the present study, we have found an origin band of another PhOH-TES isomer showing a red-shift of -120 cm^{-1}. The shift of $\tilde{\nu}_{\mathrm{OH}}$ of this cluster is found to be -78 cm^{-1}. This value is much larger than those of the other PhOH-TES 1:1 clusters. It is expected that the spatial overlap of between the TES and the phenyl ring in this cluster is small so that the contribution of the O-H$\cdots$H-Si dihydrogen-bond becomes larger than the other isomers. We have performed density-functional-theory (DFT) calculation of the PhOH-TES clusters using M05-2X functional. The result of the DFT calculation supported the cluster structure and the large red-shift of $\tilde{\nu}_{\mathrm{OH}}$ of the newly found isomer of PhOH-TES.

[a] H. Ishikawa, A. Saito, M. Sugiyama, N. Mikami, *J. Chem. Phys.* **123**, 224309 (2005).