FOURIER TRANSFORM MICROWAVE SPECTRUM OF $CO_2$ -$(CH_3)_2$ S

YOSHIYUKI KAWASHIMA and TAKAYUKI MORITANI, *Department of Applied Chemistry, Faculty of Engineering, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-0292, JAPAN*; EIZI HIROTA, *The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, JAPAN.*

In spite of the fact that the oxygen and sulfur atoms belong to the same group in the periodic table, oxygen-containing molecules and their corresponding sulfur analogues often exhibit characteristic differences in their chemical and physical properties. We have been interested in these differences and have investigated, in a systematic way using Fourier transform microwave (FTMW) spectroscopy combined with ab initio molecular orbital calculations, complexes consisting of dimethyl ether (DME)/dimethyl sulfide (DMS) and ethylene oxide (EO)/ ethylene sulfide (ES), each being attached to either one of rare gas atoms (Rg), CO, $N_2$, or $CO_2$[a]. Among others the $CO_2$-DMS complex should be mentioned, which, in sharp contrast with its counterpart: $CO_2$-DME [b]. behaves anomalously, presumably because of low-frequency internal motions, and we have decided to explore it in detail by a FTMW spectrometer. We have generated the $CO_2$-DMS complex by supersonic expansion of a $CO_2$ and DMS mixture diluted with Ar, and have scanned the frequency region from 5 to 24 GHz to record the rotational spectra of the complex. We have found it difficult to fit the observed transition frequencies to the ordinary rotational Hamiltonian, but have succeeded to assign 75 transitions by sum rules among the observed transition frequencies. We are suspecting the anomalous behavior of the complex to be caused by a low-frequency torsion of the moieties. In the case of the $CO_2$-DME, the internal rotations of the two methyl groups of the DME were shown to be locked to the $CO_2$ by hydrogen bonding, whereas, for the $CO_2$-DMS, we have observed internal-rotation splittings of the two methyl groups of the DMS, indicating the structure of the $CO_2$-DMS complex being considerably different from that of the $CO_2$-DME. We will report the structure at the potential minima and the internal motion of the $CO_2$-DMS, in comparison with the results predicted by quantum chemical calculations.

[a] Y. Kawashima, A. Sato, Y. Orita, and E. Hirota *J. Phys. Chem. A* **116**, 1224 2012.
[b] J. J. Newby, R. A. Peebles, and S. A. Peebles *J. Phys. Chem. A* **108**, 11234 2004.