FOURIER TRANSFORM MICROWAVE SPECTRA OF CO-DIMETHYL SULFIDE AND CO-ETHYLENE SULFIDE

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In order to understand the dynamical behavior of van der Waals complexes and to obtain information on the potential function for internal motions in complexes, we have previously investigated the tunneling-rotational spectra of CO-dimethyl ether (DME) observed by FTMW spectroscopy and have confirmed the heavy-atom skeleton of the complex to be essentially planar at the equilibrium.[a] In the present study we extended the investigation to carbon monoxide-dimethyl sulfide (DMS): CO-$(CH_3)_2S$ and carbon monoxide-ethylene sulfide (ES,thiirane): CO-$(CH_2)_2S$ complexes. We observed strong $c$-type and weak $a$-type transitions of CO-DMS and its isotopic species containing naturally abundant $^{34}S$ and $^{13}CH_3$ and concentrated $^{13}CO$ and $C^{18}O$, by a FTMW spectrometer in the frequency region from 7 to 25 GHz. In sharp contrast with CO-DME, we found the CO moiety in CO-DMS located in a plane perpendicular to the C-S-C plane and bisecting the CSC angle of DMS. For the CO-ES complex, we scanned the frequency region from 5 to 30 GHz by using a sample containing ES and CO diluted with Ar. We first identified the $b$-type $Q$-branch transitions around 30 GHz and then extended the observation to strong $b$-type and less intense $a$-type transitions, however, $c$-type transitions were not observed at all. We also observed $b$-type transitions of the $^{34}S$ species in natural abundance. By analyzing the observed spectra we concluded the CO moiety of CO-ES located in a plane perpendicular to the C-S-C plane of ES, as in the case of CO-DMS. An $ab\ initio$ MO calculation at the level of MP2/6-311G($d$, $p$) yielded a structure which, when optimized, was in good agreement with the experimental result. From the observed spectroscopic parameters, we have calculated the distance, the stretching force constant, and the binding energy of the bond between the constituents of the CO-DMS and CO-ES complexes and have found that the distances of the two complexes were almost equal, but the bonding was stronger in CO-ES than in CO-DMS.

[a] Y. Kawashima, Y. Morita, Y. Tatamitani, N. Ohashi, and E. Hirota, *J. Chem. Phys.* 127, 194302 (2007).