

FOURIER TRANSFORM MICROWAVE SPECTRA OF CO₂-ETHYLENE SULFIDE, CO₂-ETHYLENE OXIDE AND CO₂-PROPYLENE OXIDE COMPLEXES

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

We have previously examined the difference in roles of O and S in structure and dynamics of the CO-ethylene oxide (EO) and CO-ethylene sulfide (ES) complexes^a. We have extended the investigation to CO₂-EO and CO₂-ES for comparison. We have also observed the CO₂-propylene oxide (PO) complex, which is an important intermediate in the reaction of PO with CO₂ leading to polycarbonate. Both *a*-type and *b*-type transitions were observed for the CO₂-EO and CO₂-ES, but no *c*-type transitions were observed at all. We also detected the ³⁴S and ¹³C isotopic species in natural abundance and the species containing ¹⁸OCO and C¹⁸O₂, which were synthesized by burning paper in an ¹⁸O₂ and ¹⁶O₂ mixture. By analyzing the observed spectra we concluded the CO₂ moiety of CO₂-EO and CO₂-ES located in a plane *perpendicular* to the three-membered ring and bisecting the COC or CSC angle of EO or ES, respectively, as in the case of CO-EO and CO-ES complexes. An *ab initio* MO calculation at the level of MP2/6-311G(*d*, *p*) yielded an optimized structure in good agreement with the experimental result. We have derived from the observed spectra the distance, the stretching force constant, and the binding energy of the bonds between the constituents of the CO₂-EO and CO₂-ES complexes and have found that the distances of the two complexes were shorter by 0.2 Å than those in CO-EO and CO-ES, respectively, and that the intermolecular bonds were two times stronger in the CO₂ complexes than in the corresponding CO complexes. We have concluded from the observed spectra that the CO₂ moiety in CO₂-PO is located on the PO three-membered ring plane opposite to the methyl group. The constituents in CO₂-PO were more weakly bound than those in CO₂-EO and CO₂-ES.

^aS. Sato, Y. Kawashima, Y. Tatamitani, and E. Hirota, *63rd International Symposium on Molecular Spectroscopy*, WF05 (2008).