INTERMOLECULAR INTERACTION BETWEEN CO OR CO_2 AND ETHER OR THIOETHER OR PROPYLENE OXIDE IN A COMPLEX, INVESTIGATED BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND $ABINITIO$ CALCULATIONS

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In sharp contrast with the hydrogen bond, which has been well established to be one of the strongest interactions between two atomic and/or molecular species, weak interactions between two closed-shell molecules have not been understood in detail. We have thus carried out a systematic study on complexes shown in the title; examples include the CO-ethylene oxide (EO), CO-ethylene sulfide (ES), CO-dimethyl ether (DME), CO-dimehtyl sulfide (DMS), CO_2-EO, CO_2-ES, CO_2-DME, and CO_2-propylene oxide (PO) complexes. From their Fourier transform microwave spectra, we determined the r_s structure, the force constant of the van der Waals stretching mode, and the dissociation energy by analyzing the observed rotational and centrifugal distortion constants. We have also carried out ab initio molecular orbital calculations at the level of MP2 with basis sets 6-311++G(d, p) and aug-cc-pVDZ using the Gaussian 09 package. In most cases, the MP2/6-311++G(d, p) calculations yield rotational constants in better agreement with the experimental values, than the other basis set, in other word, the molecular structures calculated using this basis set are close to those experimentally found for the ground state. The estimated bond dissociation energies including the zero-point vibrational energy corrections ΔZPV and the basis set superposition errors (BSSE) calculated with the counterpoise correction (CP) are in good agreement with the observed binding energies E_B. We have applied an NBO analysis to the complexes to calculate the stabilization energy CT (= $\Delta E_{\sigma\sigma*}$), which we found are closely correlated with the binding energies E_B. We have thus achieved a consistent overview on the intermolecular interaction in the complexes under consideration.