FOURIER TRANSFORM MICROWAVE SPECTRA OF CO-$(CH_3)_2O$

YOSHIYUKI KAWASHIMA, YASUMASA MORITA, YOSHIO TATAMITANI, *Department of Applied Chemistry, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-0292, JAPAN*; and EIZI HIROTA, *The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, JAPAN*.

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 chosen carbon monoxide - dimethyl ether complex CO-$(CH_3)_2O$ as examples of the complexes consisting of a diatomic and a C_{2v} molecule and have investigated them by Fourier transform microwave spectroscopy. We have observed two sets of 30 a-type transitions, not only for the normal species, but also for the ^{13}CO and C^{18}O species, in the frequency region from 3.8 to 25 GHz, ranging from $J = 1 \leftarrow 0$ up to $J = 7 \leftarrow 6$. The splittings between the two sets of the same rotational transitions varied from 5 to 20 MHz and the two components were assigned to the symmetric and antisymmetric states of a double-minimum internal motion. The observed transition frequencies were analyzed for each set separately, by using an ordinary asymmetric-rotor Hamiltonian. The inertial defects $I_{cc} - I_{aa} - I_{bb}$ thus obtained were -5.763 (16) and -5.764 (23) uÅ^2 for the two states, which indicated that the heavy-atom skeleton of CO-DME was essentially planar. The observed moments of inertia were analyzed to give the distance between the centers of gravity of the two component molecules, DME and CO, to be 3.68 Åand the angle between CO and a-axis to be 75°, C of CO being closer to DME. Most a-type transitions were observed as closely spaced triplets; the splittings were ascribed to the internal rotation of the two methyl tops of DME, but were nearly independent of the quantum numbers J and K. By assuming a Lennard-Jones-type potential the dissociation energy has been estimated to be E_B = 1.6 kJ mol^{-1} (1.0 and 2.5 kJ mol^{-1} for Ne-DME and Ar-DME, respectively). MP2/6-31++g(d,p) calculations suggest that CO-DME is a planar complex, in agreement with our results.