

FOURIER TRANSFORM MICROWAVE SPECTRA OF N₂-(CH₃)₂O

YOSHIYUKI KAWASHIMA, YOSHIO TATAMITANI, YASUMASA MORITA, *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*.

As an extension of the studies on the dynamical behavior of van der Waals complexes such as those on CO-DME, we have investigated nitrogen - dimethyl ether complex N₂-(CH₃)₂O, by using Fourier transform microwave spectroscopy. We have scanned the frequency region from 6 to 25 GHz and have found four sets of *a*-type rotational transitions ranging from $J = 2 \leftarrow 1$ up to $J = 6 \leftarrow 5$ for N₂-DME and ¹⁵N₂-DME and two sets for ¹⁵NN-DME. Two of the four sets (referred to as group I) of N₂-DME and ¹⁵N₂-DME have large centrifugal distortion constants. Each rotational transition of N₂-DME showed complicated splitting patterns due to the quadrupole coupling of the two nitrogen atoms and the number of hyperfine components was much smaller for group I than for the other (group II). This observation indicates that the group I complexes involve para-N₂ and the group II ortho-N₂. In the case of ¹⁵NN-DME only one type (corresponding to group II) of the complexes was detected because of the lack of symmetry. Some of the *a*-type transitions observed for ¹⁵N₂-DME consisted of closely spaced triplets; the splittings, which were nearly independent of the quantum numbers J , were ascribed to the internal rotation of the two methyl tops of DME. The observed transition frequencies of N₂-DME, ¹⁵N₂-DME, and ¹⁵NN-DME were analyzed for each set separately, by using an ordinary asymmetric-rotor Hamiltonian. The inertial defects $I_{cc} - I_{aa} - I_{bb}$ thus obtained for N₂-DME were -29.31 (10) and -30.97 (10) uÅ² for the two sets of group I and -9.98 (9) and -12.58 (11) uÅ² for group II. These results indicated that the heavy-atom skeleton of N₂-DME was not planar. The observed moments of inertia were analyzed to give the distance between the centers of gravity of the two component molecules, DME and N₂, to be approximately 3.45 Å. By assuming a Lennard-Jones-type potential the dissociation energy was estimated to be $E_B = 0.74 \sim 1.17$ kJ mol⁻¹, to be compared with the values 1.0 and 2.5 kJ mol⁻¹ for Ne-DME and Ar-DME, respectively. MP2/6-31++g(d, p) calculations suggest that N₂-DME is non-planar and is bound by a very flat potential energy surface, in qualitative agreement with our results.