

NITROGEN MOLECULE-DIMETHYL SULFIDE COMPLEX INVESTIGATED BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND AB INITIO CALCULATION

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This paper presents an extension of the preceding talk on the FTMW spectroscopy of N₂-ES (ethylene sulfide), namely the results on N₂-DMS (dimethyl sulfide). We have previously investigated two N₂ complexes: N₂-DME (dimethyl ether), for which we reported a preliminary result,^a and N₂-EO (ethylene oxide).^b We have observed the ground-state rotational spectrum of the N₂-DMS complex, i.e. *c*-type transitions in the frequency region from 5 to 24 GHz, which we assigned to the normal, ¹⁵N₂-DMS, and ¹⁵NN-DMS species of the N₂-DMS. We have found both the ortho and para states for the ¹⁴N₂-DMS and ¹⁵N₂-DMS species. In the case of the ¹⁵N₂-DMS, some transitions with $K_a = 2$ and 3 were observed slightly split by the internal rotation of the two methyl tops of the DMS. The observed spectra of the ¹⁵N₂-DMS were analyzed by using the XIAM program. In the case of the para state of the ¹⁵N₂-DMS, three rotational and five centrifugal distortion constants with the V_3 barrier to the methyl group internal rotation, whereas, in the case of the ortho state of the ¹⁵N₂-DMS, two more centrifugal distortion constants, Φ_{JK} and Φ_{KJ} , were needed to reproduce the observed spectra. For the N₂-DMS complex, we concluded that the N₂ moiety was located in a plane perpendicular to the C-S-C plane and bisecting the CSC angle of the DMS.

We have carried out ab initio molecular orbital calculations at the level of MP2 with basis sets 6-311++G(d, p), aug-cc-pVDZ, and aug-cc-pVTZ, to complement the information on the intracomplex motions obtained from the observed rotational spectra. We have applied a natural bond orbital (NBO) analysis to the N₂-DMS and N₂-ES to calculate the stabilization energy CT ($=\Delta E_{\sigma\sigma^*}$), which was closely correlated with the binding energy E_B , as found for other related complexes.

^aY. Kawashima, Y. Tatamitani, Y. Morita, and E. Hirota, *61st International Symposium on Molecular Spectroscopy*, TE10 (2006)

^bY. Kawashima and E. Hirota, *J. Phys. Chem. A* **2013** 117 13855