ROTATIONAL SPECTRA OF CH_3CCH-NH_3, NCCCH-NH_3, AND NCCCH-OH_2

A.R. Hight Walker, R. Omron, G.T. Fraser, R.D. Suenram, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; G. Hilpert, *Institut für Angewandte Physik, Universität Bonn, Wegelerstraße 8, D-53115 Bonn, Germany.*

Microwave spectra of NCCCH-NH_3, CH_3CCH-NH_3, and NCCCH-OH_2 have been recorded using a pulsed-nozzle Fourier-transform microwave spectrometer. The complexes, NCCCH-NH_3 and CH_3CCH-NH_3, are found to have symmetric-top structures with the acetylenic proton hydrogen-bonded to the nitrogen of the NH_3. The data for CH_3CCH-NH_3 are further consistent with free or nearly free internal rotation of the methyl top against the ammonia top. For NCCCH-OH_2, the acetylenic proton is hydrogen-bonded to the oxygen of the water. The water complex has a dynamical C_{2v} structure, as evidenced by the presence of two nuclear-spin modifications of the complex. The hydrogen-bond lengths and hydrogen-bond stretching force constants are 2.212 Å and 10.8 N/m, 2.322 Å and 6.0 N/m, and 2.125 Å and 9.6 N/m, for NCCCH-NH_3, CH_3CCH-NH_3, and NCCCH-OH_2, respectively. For the cyanoacetylene complexes, these bond lengths and force constants lie between the values for the related hydrogen cyanide and acetylene complexes of NH_3 and H_2O. The NH_3 bending and weak-bond stretching force constants for CH_3CCH-NH_3 are less than those found in NCCCH-NH_3, NCH-NH_3, and HCCH-NH_3, suggesting that the hydrogen bonding interaction is particularly weak in CH_3CCH-NH_3. The weakness of the bond is partially a consequence of the orientation of the monomer electric dipole moments in the complex. In CH_3CCH-NH_3 the antialigned monomer dipole moments leads to a repulsive dipole-dipole interaction energy, while in NCH-NH_3 and NCCCH-NH_3 the aligned dipoles give an attractive interaction.