COMPARISON OF SPECTROSCOPIC AND AB INITIO STRUCTURES FOR THE HYDROGEN-BONDED COMPLEX TRIMETHYLAMINE-HYDROGEN SULFIDE

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Rotational spectra have been recorded for six isotopomers of the trimethylamine-hydrogen sulfide complex using a Fourier-transform microwave spectrometer. The spectra were found to be characteristic of a symmetric top, (B + C)/2 = 1395.463 (1) MHz, and are indicative of free internal rotation of trimethylamine within the complex. A structure with a single, linear hydrogen bond (R_{N-S} = 3.36 (5) Åbest reproduces the moments of inertia of the six isotopic species, including three distinct deuterated complexes. The experimental structure is compared to the ab initio structure optimized at the MP2/6-31G(d,p) level, which predicts R_{N-S} = 3.328 Å. MP2/aug′-cc-pVTZ calculations were used to determine the binding energy of the complex and the barrier to an internal tunneling motion which exchanges the two H_2S hydrogens.