Abstract Submitted
for the TSS08 Meeting of
The American Physical Society

Ultraviolet, Infrared, and Raman Spectra of Pyridine and Its Fluoro Derivatives JAAN LAANE, PRAVEEN BOOPALACHANDRAN, KATHLEEN MCCANN, Texas A&M University — The vapour-phase infrared and ultraviolet absorption spectra of pyridine, pyridine-d_5, 2-fluoropyridine, and 3-fluoropyridine have been recorded. The high-temperature Raman spectra of these vapour phase samples have also been collected. DFT and ab initio calculations for each molecule were carried out for both the ground and $S_1(n,\pi^*)$ electronic excited states in order to calculate the molecular structures and vibrational frequencies, and this facilitated the assignment of the vibrational data. Comparison of the assignments for the $S_1(n,\pi^*)$ states with the electronic ground state provided an understanding of how the bonding of the molecules changes in the electronic excited states, where the molecules become much less rigid and floppy. Investigation of the ν_{18} out-of-plane ring-bending mode for pyridine-d_0 and $-d_5$ allowed their potential energy function to be determined, and this demonstrated that pyridine is quasi-planar with a barrier to planarity of 3 cm^{-1} in the $S_1(n,\pi^*)$ state. The decrease from 403 cm^{-1} (S_0) to 59.5 cm^{-1} (S_1) for the ν_{18} vibration of pyridine reflects the decreased rigidity in the excited state.

Jaan Laane
Texas A&M University

Date submitted: 11 Feb 2008 Electronic form version 1.4