

Spectroscopic Studies of the Electronic Excited States of Pyridine-d₀ and -d₅, 2-Fluoro- and 3-Fluoropyridine, and 1,3-Benzodioxan

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The infrared and ultraviolet absorption spectra and the Raman spectra of vapor-phase pyridine, pyridine-d₅, 2-fluoropyridine, and 3-fluoropyridine have been recorded and analyzed. The UV spectrum of pyridine is shown below. DFT calculations for each molecule have also been carried out for both the ground and S₁(n,π*) electronic excited states. Vibrational assignments for the S₁(n,π*) states have been made and compared to the ground state. In the electronic excited state the molecules become much less rigid and floppy. Investigation of the ν₁₈ out-of-plane ring-bending mode for pyridine-d₀ and -d₅ 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 S₁(n,π*) state. The decrease from 403 cm⁻¹ (S₀) to 59.5 cm⁻¹ (S₁) for the ν₁₈ vibration of pyridine reflects the decreased rigidity in the excited state.

The jet-cooled laser induced fluorescence and UV absorption spectra of 1,3-benzodioxan have also been analyzed. Many of the vibronic levels in the S₁(π,π*) state were assigned for the three low-frequency out-of-plane ring motions, and these were used to better understand the structure in the electronic excited state. Theoretical calculations predict barriers to planarity of 9.3 kcal/mole and 8.0 kcal/mole for the S₀ and S₁(π,π*) states, respectively, and the experimental data are consistent with these values.

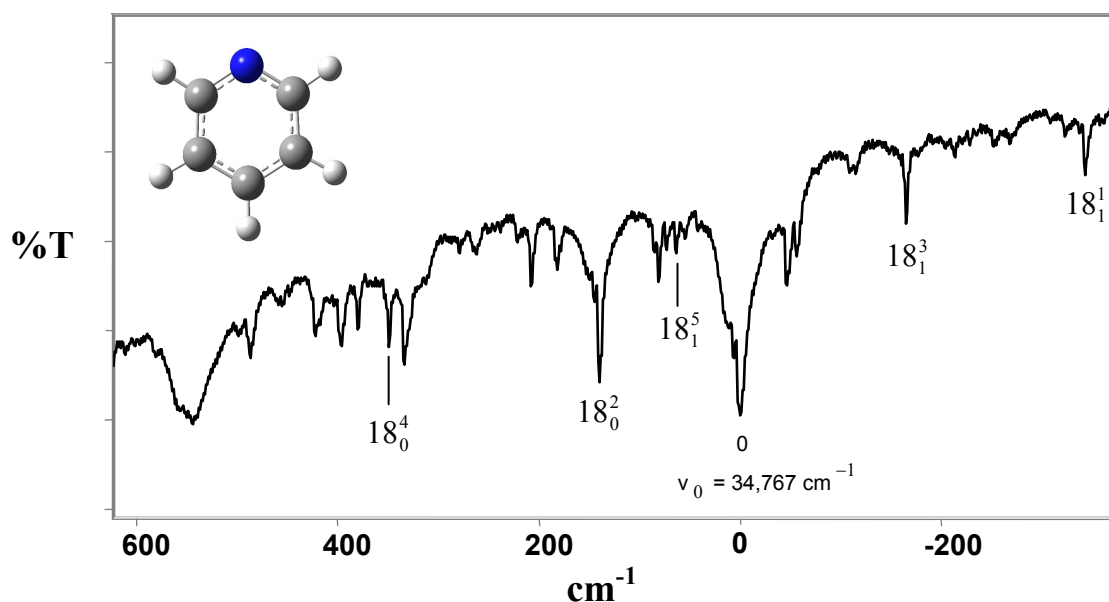


Fig. 1: The UV spectrum of pyridine.