INTERNAL AND EXTERNAL PERTURBATIONS IN ELECTRONIC SPECTROSCOPY. THE STARK SPECTRUM OF INDOLE-NH_3.[a]

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Hydrogen bond pairs involving the chromophore indole have been extensively studied in the gas phase. Here, we report new rotationally resolved data on the indole-NH_3 hydrogen bond pair in the absence and presence of an electric field. The electronic origin of this complex recorded at high resolution reveals two overlapping spectra, a consequence of NH_3 internal rotation. The barrier to internal rotation is predicted by theory to be below 20 cm^{-1}in the ground state, therefore requiring a revision of the standard rigid rotor Hamiltonian. Conducting the expeirment in the presence of an applied electric field further perturbs the already congested spectrum, but allows for the permanent dipole moments of the complex to be measured. Efforts to understand the unique perturbations that arise from both internal (molecular frame) and external (laboratory frame) sources will be discussed.

[a]Work supported by NSF (CHE-0911117).