

## FLUORESCENCE DIP INFRARED SPECTROSCOPY OF THE $S_1$ STATES OF INDOLE AND ITS DERIVATIVES

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Fluorescence dip infrared spectroscopy (FDIRS) has been used as the primary technique in supersonic expansions to determine the ground state conformations of indole, 3-methylindole, tryptamine, n-acetyltryptophan amide (NATA) and n-acetyltryptophan methylamide (NATMA). In each of these molecules two close-lying excited states,  $^1L_a$  and  $^1L_b$ , are present, and play an important role in the spectroscopy and photophysics of the molecules. The relative separation of the  $^1L_a$  and  $^1L_b$  states is highly sensitive to the type of side chain attached to the C3 position of indole. Recently, a third excited state ( $\pi\sigma^*$  transition localized in the NH bond) that is dissociative along the NH-stretching mode of the indole ring has been predicted to exist in this energy region<sup>a</sup>. We have applied the FDIR technique to the  $S_1$  state of the above molecules to study this process. The excited state spectra are marked by the absence of the indole-NH stretching mode, suggesting dissociation along this coordinate. The strength of coupling to the dissociative state varies significantly depending on the type of side chain attached to the indole ring. The excited state spectra range from a sharp band in indole, to a broad unresolved continuum in which all of the NH stretches are washed out in NATA and NATMA.

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<sup>a</sup>A.L. Sobolewski, W. Domcke, Chem. Phys. Lett. 315 (1999) 293.