

## THE MYSTERIOUS CASE OF THE MISSING NH STRETCH TRANSITION

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The ground and excited state IR vibronic spectra of jet-cooled methyl anthranilate (MA) in the hydride stretch ( $2400\text{--}3800\text{ cm}^{-1}$ ) and mid-IR ( $1400\text{--}1800\text{ cm}^{-1}$ ) regions have been recorded and many of the peaks have been assigned. The key exception, and the subject of this talk, is the H-bonded NH stretch on the  $S_1$  excited surface. In contrast to the  $S_0$  surface, where the NH stretches of  $\text{-NH}_2$  can be modeled assuming symmetric and asymmetric stretch vibrations, on the  $S_1$  surface only the free NH stretch is observed. Time-dependent density functional electronic structure calculations combined with both normal mode and VPT2 results predict an extremely bright transition between  $2900\text{ cm}^{-1}$  and  $3100\text{ cm}^{-1}$  depending on the level of theory for the hydrogen bonded NH stretch. No corresponding transition is observed experimentally. To explain the discrepancy between the experimental and calculated intensities of the dislocated NH stretch transition in the  $S_1$  excited state a model is proposed based on the adiabatic separation of the NH stretch and other internal coordinates. In this model, the excitation of the NH stretch leads to dramatic structural reorganization, this leading to many Franck-Condon factors that, in turn, lead to substantial shared intensity of the initial bright state over hundreds of wavenumbers, thereby diluting the band sufficiently that it is no longer apparent in the spectra.