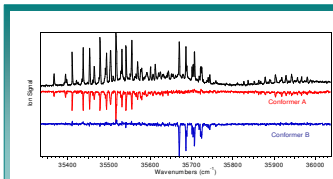


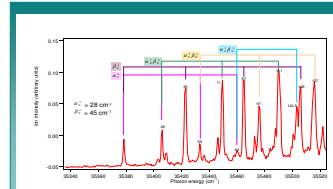
Conformational analysis of the flexible bichromophore: 3-(4-Hydroxyphenyl)-N-Benzyl-Propionamide

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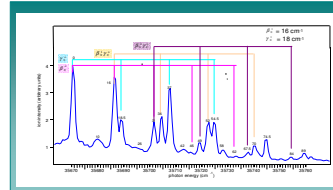
Experiment



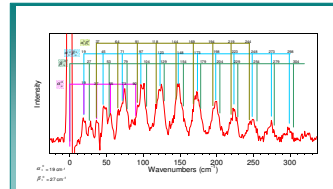
R2PI and HB spectra of Conformers A and B of HNBPA



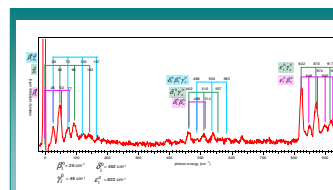
Excited state vibrational spectrum of Conformer A



Excited state vibrational spectrum of Conformer B



Dispersed Fluorescence of conformer A



Dispersed Fluorescence of conformer B

Bichromophoric systems are especially useful for examining the effects of electronic coupling. 3-(4-hydroxyphenyl)-N-benzyl-propionamide (HNBPA) is a biologically relevant bichromophore molecule that contains two spectroscopically distinguishable ultraviolet chromophores.

Professor Zwier's group¹ has studied HNBPA using one-color resonance two-photon ionization (R2PI)², UV-UV hole-burning(HB)³, and emission spectra by using a monochromator to disperse the fluorescence.

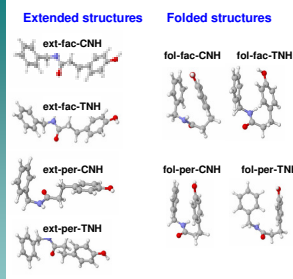
R2PI and UV-UV HB permit conformation-specific excitation and detection, taking advantage of the unique infrared and ultraviolet signatures of the individual conformations when cooled in a supersonic expansion. The dispersed fluorescence spectrum of conformer B does not show as many peaks as that of conformer A, leading us to conclude that the geometry distortion upon electronic excitation is much greater in A than B.

Theory

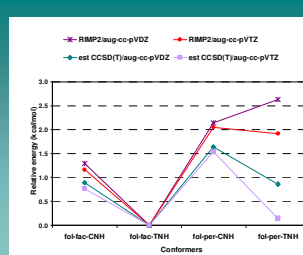
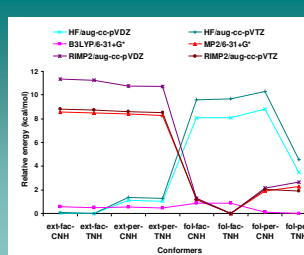
A major challenge in interpreting the spectra is the identification of the isomers responsible for the observed transitions. Here electronic structure calculations can be valuable.

I have optimized the geometries of eight conformers of HNBPA and have calculated the vibrational frequencies of these conformers using RIMP2/aug-cc-pVDZ³ method. Single-point energies were calculated using the RIMP2/aug-cc-pVTZ and CCSD(T) methods with RIMP2/aug-cc-pVDZ optimized geometries. Whereas the calculations with the HF method favor the extended structures, the opposite behaviors are found with the MP2 and CCSD(T) method.

Furthermore, in order to exploit the Frank-Condon progressions, I optimized the geometries of the excited states for the four folded structures of HNBPA.



Optimized 8 conformers of HNBPA using RIMP2/aug-cc-pVDZ method

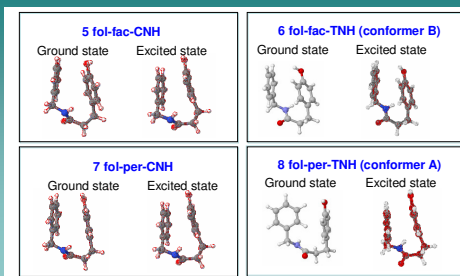


Relative energies of the 8 conformers of HNBPA using several electronic structure methods

S_0 (ground state)					S_1 (excited state)	
Exp.					Exp.	
Calc. (RIMP2/aug-cc-pVDZ)					Calc. (RIMP2/aug-cc-pVDZ)	
mode	Conformer A	Conformer B	fac-CNH	per-TNH	Conformer A	Conformer B
α	19	21	21	21	28	28
β	27	26	29	30	45	16
γ	48	37	44	51	18	18

The table summarizes the two lowest vibrational frequencies for each of the folded conformers as calculated at the RIMP2 level as well as the experimental frequencies for conformers A and B. Based on the comparison of the calculated and experimental results we assign A to the fol-per-TNH structure and B to the fol-fac-TNH conformer.

Excited state optimizations for the four folded structures with RICC2/aug-cc-pVDZ



[1] Perdue University
[2] Carney, J. R.; Zwier, T. S. J. Phys.Chem. A 2000, 104, 8677.
[3] Weigend, F.; H'aser, M. Theor. Chem. Acc. 1997, 97, 331.

