GSS Summer School Advanced Module:

"Single-conformation spectroscopy of biomolecular building blocks"

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The aim of our Advanced Module lab course is to familiarize the participating students with the laser spectroscopic double-resonance techniques that are used in our group to obtain conformer-specific UV and IR spectra of biomolecular building blocks in molecular beams.

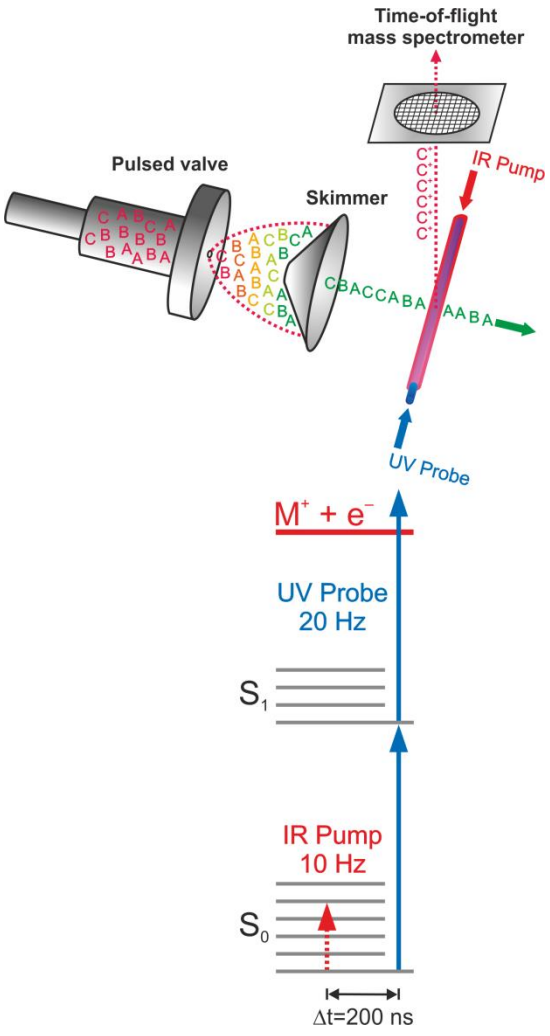

Figure 1: Experimental setup and Jablonski diagram for IR-UV double-resonance spectroscopy

Molecular beam single-conformation spectroscopy[1–3] provides the unique opportunity to single out the UV, IR, and Raman spectra of each individual conformer present in a mixture of conformers. Experimentally, single-conformation spectroscopy consists of a series of single- and double-resonance laser spectroscopic experiments that have to be carried out in a prescribed succession to obtain state-selective, mass-resolved, and conformer-specific UV, IR, and Raman spectra of cold, isolated molecules and microsolvated clusters in molecular beams. First in the succession of experiments, the mass-selected UV spectrum is recorded via resonantly enhanced two-photon ionization (R2PI). In a second step, the UV spectrum is dissected into its constituent single-conformation UV spectra via a UV-UV double-resonance technique termed UV-UV hole-burning spectroscopy. These single-conformation UV spectra provide conformation-specific electronic/vibronic transitions that serve as "monitor" transitions in the subsequent IR-UV and Raman-UV double-resonance experiments (Figure 1). The assignment of these single-conformation IR and Raman spectra through quantum chemical *ab initio* and density functional theory (DFT) calculations allows us to determine the conformational preferences of isolated flexible molecules and the isomeric structures of their microsolvated complexes.

Single-conformation spectroscopy combines laser spectroscopic double-resonance techniques with mass spectrometric ion detection in a time-of-flight mass spectrometer to record conformation-specific UV, IR, and Raman spectra (Figure 2).

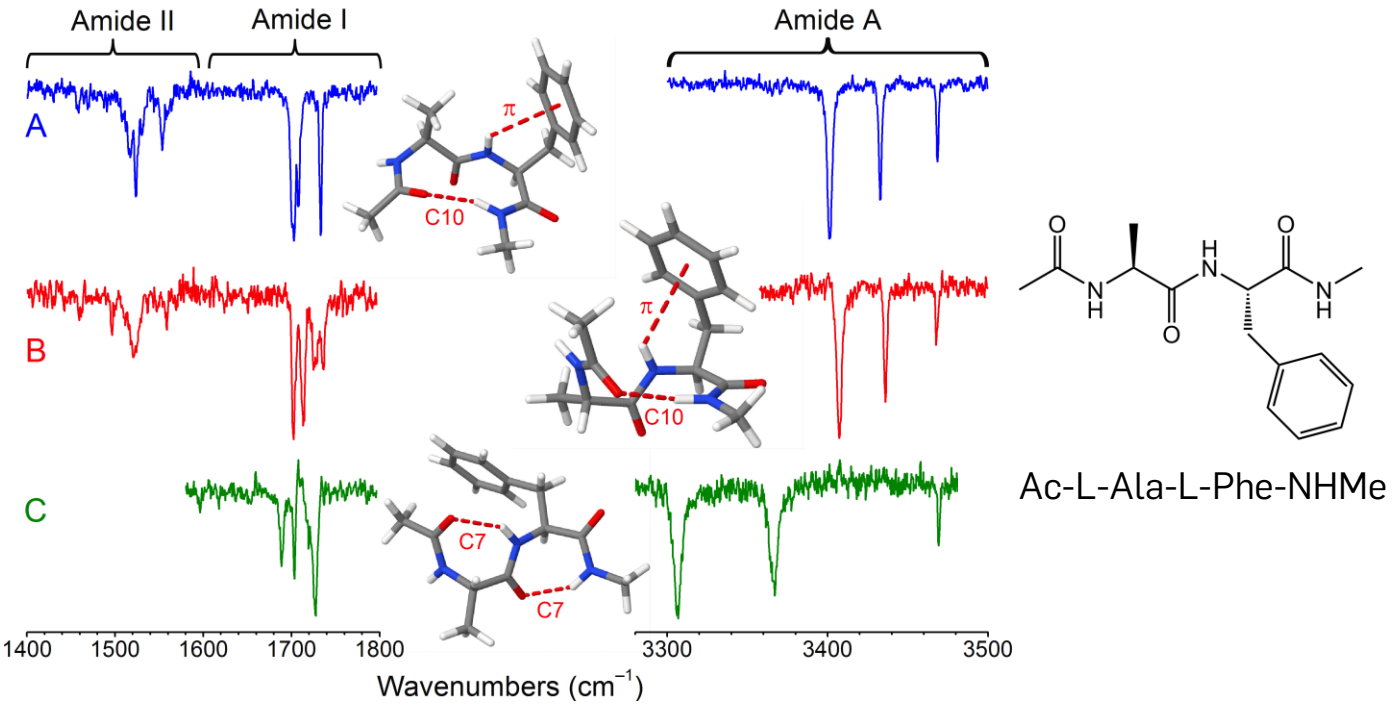

Figure 2: Single-conformation IR spectra of the three conformers of the dipeptide Ac-L-Ala-L-Phe-NHMe in the N–H stretch (amide A), C=O stretch (amide I), and N–H bend (amide II) regions.

Our Advanced Module lab course, therefore, aims as well at introducing the participating students into high-vacuum molecular beam methods and mass spectrometric ion detection techniques.

References

(1) T.S. Zwier, *J. Phys. Chem. A*, **2006**, *110*, 4133.

(2) M.S. de Vries, P. Hobza, *Annu. Rev. Phys. Chem.*, **2007**, *58*, 585.

(3) J.P. Simons, *Mol. Phys.*, **2009**, *107*, 2435.