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Spectroscopic characterization of the conformational landscape of a tri-peptide, Z-Pro-Leu-Gly, in gas phase

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[Introduction] Precise information on conformational landscape of biological molecules is necessary to understand the relation between three dimensional structure and functions of these macro molecules. In general, structural information obtained from condensed phase investigation is the manifestation of complex nature of solvent interaction and contribution of all the conformers present in the medium. Alternatively, in bottom-up approach, one can start with isolated molecules devoid of any external perturbation and spectral congestion to understand the basic physics of intramolecular forces which govern their inherent structure. Precise understanding of the intrinsic hydrogen bonding (H-bond) network of bio-molecules is possible in the gas phase using molecular beam, mass-spectrometry, and laser spectroscopy. Herein, we report the IR spectroscopic and quantum chemical investigation of a tri-peptide Pro-Leu-Gly in gas phase. The N- terminal is protected by benzyloxycarbonyl (Z-) group which acts as a chromophore. Two different variant of the peptide (Z-PLG), either protected by $-NH_2$ group at C- terminal (Z-PLG- NH_2) or free (Z-PLG-OH), are being studied to understand the effect of terminal capping by $-NH_2$ group on the overall structure of the tri-peptide.

[Experiment and Theory] The mass selected resonance enhanced 2-photon ionization (R2PI) spectra of Z-PLG- NH_2 and Z-PLG-OH were recorded in a linear time-of flight mass spectrometer coupled to laser desorption source and supersonic jet expansion technique [1, 2]. The desorbed molecules were blown away with the supersonic expansion of Ar buffer gas and subsequently cooled down by collisions. UV-UV hole burning (HB) spectroscopy was employed to distinguish the electronic transitions of different conformers which are contributing simultaneously to the R2PI

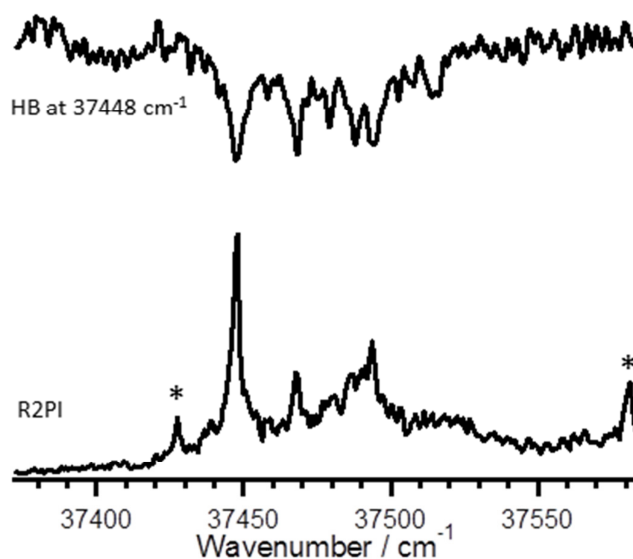


Figure 1 R2PI and UV-UV HB spectra of Z-PLG- NH_2

spectrum. Conformer selective IR spectra were recorded by IR-UV ion dip spectroscopy. Molecular dynamics simulation was carried out for the complete search of the local minima. Finally, energy

optimized structure and vibrational properties were calculated at the wB97XD/cc-pVDZ level to gain more insight into the experimental IR spectra and corresponding structure.

[Results and Discussion] The R2PI spectra of Z-PLG-NH₂ and Z-PLG-OH were recorded in the range of 37400 to 37600 cm⁻¹. A number of sharp electronic transitions are observed in the recorded spectral range for both species which indicates the formation of cold molecules under the jet-cooling effect.

Some of the possible conformers of the tri-peptide could be collapsed into different local minima structure due to jet-cooling effect and would simultaneously contribute to the recorded R2PI spectra. UV-UV HB spectra were recorded for each species to determine the number of different conformers coexist in the molecular beam and conformer specific assignment of electronic excitation spectrum. At least two conformers of Z-PLG-NH₂ (Figure 1)

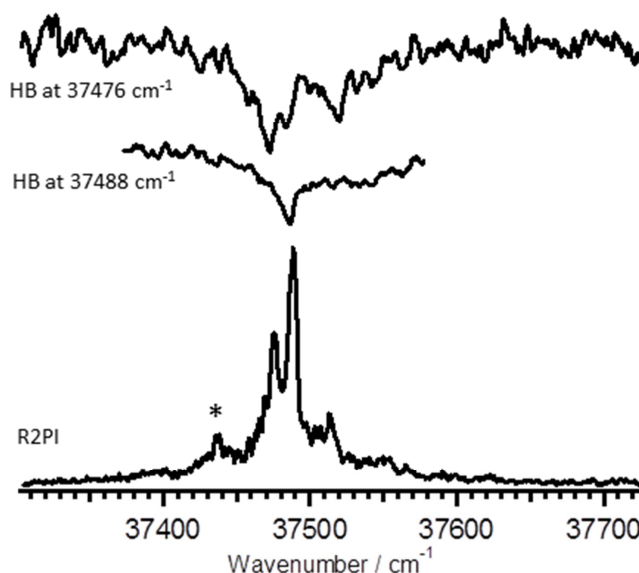


Figure 2 R2PI and UV-UV HB spectra of Z-PLG-OH

are being populated in the molecular jet under the experimental conditions. However, the signal intensity in R2PI spectrum is dominated by a single conformer which is further used to record the IR spectrum. Simultaneous population of at least three conformers of Z-PLG-OH was confirmed from the R2PI and HB spectra under the experimental conditions (Figure 2). The sensitive technique of IR-dip spectroscopy coupled with mass spectrometry was used here to derive the conformer specific IR spectra of Z-PLG-OH and Z-PLG-NH₂ in the N-H and O-H stretch range to identify the intramolecular H-bond network and the corresponding structure. The IR spectra were assigned considering the previous reports on N-H stretching frequencies of free amide group, O-H stretching frequency of free carboxylic group, H-bond induced shifts, and simulated IR spectra. Distinctly different H-bond network in Z-PLG-NH₂ and Z-PLG-OH is confirmed from the assignment of the observed IR spectra. Detail analysis of the IR spectra to assign the secondary structure of Z-PLG is in progress with molecular dynamics simulations and quantum chemical calculations, and would be discussed in the presentation.

[References]

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