OBSERVATION OF SINGLE AND DOUBLE IONIC H-BONDS IN PROTONATED DIPEPTIDE IONS USING IR-IR DOUBLE RESONANCE SPECTROSCOPY

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Isomer-specific vibrational predissociation spectra are reported for the gas-phase GlySarH$^+$ and SarSarH$^+$ [gly=glycine; sar=sarcosine] ions prepared by electrospray ionization and tagged with weakly bound D_2 adducts using a cryogenic ion trap. The contributions of individual isomers to the overlapping vibrational band patterns are isolated using a pump-probe photochemical hole-burning scheme involving two tunable infrared lasers. These patterns are then assigned by comparison with harmonic (MP2/6-311+G(d,p)) spectra for various possible conformers. In the case of GlySarH$^+$, a 9 cm^{-1} splitting of the OH stretches associated with the C-terminal acid group is traced to cis- and trans-isomers with respect to rotation about the amide bond. The SarSarH$^+$ ion displayed three distinct band patterns, two of which are assigned to variations of the analogous cis-conformer while the third arises from a trans-configuration. Two distinct types of hydrogen bonding are observed: one involving the usual single intramolecular hydrogen bond (IHB) between the protonated amine and the nearby amide oxygen and another, only displayed in the cis-configuration, which features two amino NHs acting as IHB donors. The latter results in formation of 5- and 8-membered intramolecular cycles, tethered by H-bonds to the amide oxygen and to the acid carbonyl, respectively. When the N-H bonds to the acid group, red-shifts are clearly recovered for both the H-bond donor (NH) and acceptor (C=O) groups involved in the linkage.