LASER SPECTROSCOPY OF A DOUBLY-SUBSTITUTED AROMATIC WITH TWO FLEXIBLE SIDE CHAINS: INTRACHAIN AND INTERCHAIN CONFORMATIONAL PREFERENCES

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Building on previous studies of the spectroscopy and isomerization dynamics of small biologically relevant molecules, we have been motivated to study molecules designed to be prototypical of different types of potential energy landscapes. In that spirit, O-acetamidoethyl-N-acetyltyramine (OANAT) possesses two flexible side chains of similar size, substituted at opposite ends of a phenyl ring, which intuitively should have two largely decoupled regions of the potential energy surface involving coordinates localized on one or the other side chain. In addition, the chains have sufficient length and H-bonding capacity to fold back over the phenyl ring, forming interchain hydrogen bonds. Resonant two-photon ionization and UV-UV holeburning spectroscopy identifies six conformational isomers of OANAT. Resonant ion-dip infrared spectroscopy identified three of these six as independent chain conformers, and three as possessing interchain H-bonds. To better understand the independent chain class, single chain molecules containing one or the other peptide mimetic side chains of OANAT were also studied. These molecules include the alkyl chain species N-phenethyl-acetamide (NPEA, 1 conformer) and N-(p-methoxyphenethyl-acetamide) (NMPEA, 3 conformers), and the alkoxy chain species N-(2-phenoxyethyl)-acetamide (NPOEA, 4 conformers). The electronic and infrared spectra for these molecules are presented along with DFT, TDDFT, MP2, RIMP2, and RICC2 calculations. The S_0-S_1 conformer origins of OANAT and NPOEA were spread over 1000 and 750 cm^{-1}, respectively, encouraging use of relative origin position as a diagnostic for conformational assignment. Based on the full body of spectroscopic evidence, structural assignments for these molecules are made and will be discussed.