TWO-DIMENSIONAL INFRARED SPECTROSCOPY OF TYROSINE-CONTAINING PEPTIDES

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The aromatic side chains of amino acids such as Phe, Trp and Tyr are of importance to molecular recognition, folding and stabilization of peptides and proteins. Study of ultrafast dynamics and interactions of the aromatic side chains will contribute to fundamental understanding of these biophysical and chemical processes. To this end, we applied two-dimensional infrared (2D-IR) spectroscopy to probe vibrational dynamics of the amide-I and tyrosine ring modes in Ac-Tyr-NHMe and Tyr-Ala. The population relaxation times of these modes exhibit solvent dependence, suggesting the presence of different relaxation pathways in D_2O and DMSO-d_6. Intramolecular vibrational energy transfer between the amide-I and tyrosine ring mode was observed in 2D-IR spectra taken at different waiting times. Spectral diffusion of the tyrosine ring mode in solvents and membrane mimetics reveals the influence of local environments on conformational fluctuations of the aromatic side chains.