Spectral Signatures of 3\textsubscript{10}- and $\alpha$-Helices Revealed by Two-Dimensional Infrared Spectroscopy\textsuperscript{1} NIEN-HUI GE, HIROAKI MAEKAWA, Department of Chemistry, University of California at Irvine, CLAUDIO TONIOLO, Department of Chemistry, University of Padova, Italy, QUIRINUS BROXTER-MAN, DSM Research, Life Sciences, Advanced Synthesis and Catalysis, The Netherlands — Femtosecond two-dimensional infrared (2D IR) spectroscopy is applied to the amide I modes of the homo-octapeptide Z-[L-(\text{Me})Val\textsubscript{8}-OtBu in CDCl\textsubscript{3}, TFE and HFIP solutions to acquire 2D spectral signatures that distinguish between 3\textsubscript{10}- and $\alpha$-helix structures. Suppression of diagonal peaks by controlling polarizations of IR pulses clearly reveals cross-peak patterns that are crucial for structural determination. A doublet feature is observed when the peptide forms a 3\textsubscript{10}-helix in CDCl\textsubscript{3} and TFE, and when it is at the initial stage of $3\textsubscript{10}$- to $\alpha$-helix transition in HFIP. In contrast, the 2D IR spectrum shows a multiple peak pattern after the peptide has become an $\alpha$-helix in HFIP. This is the first report on the experimental 2D IR signature of a 3\textsubscript{10}-helical peptide. These results for a model octapeptide demonstrate the powerful capability of 2D IR spectroscopy to discriminate between different helical structures.

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