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Solvent and Peptide Conformational Fluctuations Revealed with Two-Dimensional Infrared Spectroscopy ZIAD GANIM, ANDREI TOKMAKOFF, Department of Chemistry, Massachusetts Institute of Technology — Two-dimensional nonlinear infrared spectroscopy (2D-IR) is emerging as a new biophysical tool that offers the sensitivity to protein secondary structure and fast time resolution of linear Fourier transform infrared spectroscopy (FT-IR), but with the added ability to separate overlapping contributions and reveal vibrational couplings. Amide I nonlinear spectroscopy has been used to probe the thermal stability of proteins and peptides and reveal a detailed picture of how the beta-sheet of ubiquitin unfolds from nanoseconds to milliseconds. We show that the standard techniques that are sufficient in calculating FT-IR spectra from a static structure fail to reproduce observed 2D-IR lineshapes. By combining DFT parameterized semi-empirical models and structure trajectories from molecular dynamics simulations, we obtain good agreement with experimental FT-IR and 2D-IR spectra of trpzip2, a model beta-hairpin. We then demonstrate how hydrogen bonding, conformational variation, and their fluctuations are each manifested in 2D-IR spectra. This methodology provides a means of calculating FT-IR and 2D-IR spectra directly from any atomistic molecular dynamics simulation - allowing richer data analysis and a means of validating mechanistic predictions from simulations.

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