Conformational dynamics of thiopeptides: From transient absorption to transient 2D-IR spectroscopy

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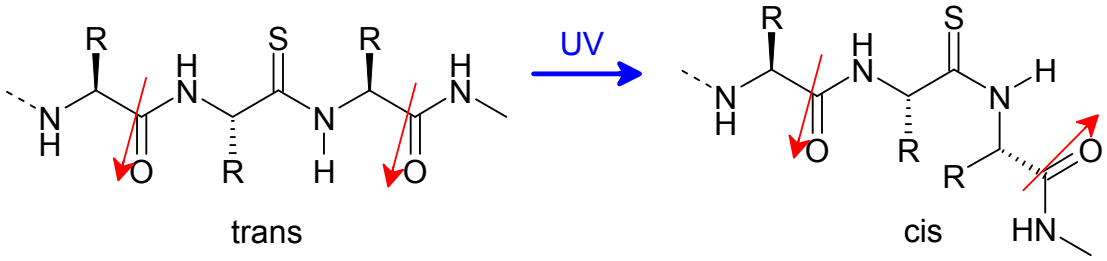
Two dimensional infrared spectroscopy allows us to measure the coupling and relative orientation of vibrational transition dipole moments on ultrafast timescales. This is particularly useful for obtaining structural information on small peptides, where the dihedral angles of the peptide bond are directly linked to the coupling between the amide I vibrations of neighbouring units[1]. We have recently demonstrated that 2D-IR spectra may also be recorded for transient species[2,3], which opens up a new way for following ultrafast structural changes in the course of a photoreaction.

Molecular photoswitches provide an efficient tool for inducing conformational change in polypeptides on a fast timescale[2,4]. Typical azobenzene-based photoswitches are, however, rather bulky and their incorporation may strongly perturb the native structure of the molecule under investigation. As an alternative, we here use the trans-cis isomerization of a thio substituted peptide unit as the least invasive phototrigger possible[5,6]. The amide I vibrators are spaced by only one thiopeptide unit and change their relative orientation and coupling upon its photoisomerization (see figure). Conformational changes may thus be followed in an essentially native peptide. Independent of isomerization, the additional uv-transition dipole moment also provides valuable information for the determination of the ground state conformation of the molecule in transient 2D-IR spectroscopy.



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