

Femtosecond time-resolved spectroscopy of various IR probes for studying structure and dynamics of myoglobin, reverse micelles and peptides.

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Femtosecond infra-red spectroscopy, due to its inherent sub-picosecond resolution, has been extensively applied to studying ultrafast conformational changes and solvation phenomena in various molecular systems. To provide site-specific information on local electrostatic environment and solvation structure, small IR probes that act as antennae, sensing local electric field and hydrogen-bonding interactions, have been introduced into a variety of molecules, comprising the structure of peptides, proteins and nucleotides. [1]

Many vibrational probes have been studied so far, which include nitriles (CN), thio- (SCN) and selenocyanates (SeCN), or the very popular azides (N₃). Although the vibrational properties of the above mentioned probes have been well-characterized, many potential applications have emerged over the years, and many are still yet to be found.

In the present study, we apply thiocyanate and selenocyanate ions as long-living vibrational probes to study dynamics of high-spin complexes of myoglobin protein with 2D-IR spectroscopy.[2,3] We also consider the azide stretch of hydrazoic acid (HN₃) as a highly sensitive probe to study water dynamics in confined environments of reverse micelles. [4]

Recently, we have developed new IR probes based on terminally-blocked isocyano(NC)-derivatized amino acids, i.e. β-isocyanoalanine and p-isocyanophenylalanine[5], which can be site-specifically introduced into both aliphatic and aromatic residues in proteins. Considering their unique properties including large intensity, exceptionally high sensitivity to hydrogen-bonding environment, and relatively long vibrational lifetime, we believe that such isonitrile non-natural amino acids will become very popular IR probes for studying ultrafast dynamics of biomolecules.

References

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