Time-resolved IR studies of a variety of IR probes for studying local electrostatics and solvent structures in myoglobin, reverse micelles, and peptides

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Over the years, ultrafast IR pump-probe and 2D-IR methods have been widely used to study ultrafast dynamics of biomolecules and their model systems. Although the technique itself has been found to be extremely powerful, a lot of potential applications of 2D-IR are yet to be discovered. Very often it is the case that the success of an experiment relies wholly upon the choice of a suitable IR probe that can specifically provide critical and site-specific information on local electrostatic environment and solvent (protein residue) structure. Although, many vibrational probes have been already studied, which include nitriles (CN), thio- (SCN) and selenocyanates (SeCN), or the very popular azides (N_3) [1], several new applications of those IR probes are presented and discussed here.

We introduce thio- and selenocyanate ions as the IR probes with very long vibrational lifetimes to study heme-bound high spin complexes of myoglobin and other hemoproteins.[2] We considered the azide stretch of hydrazoic acid to probe confinement effects on water structure and dynamics in reverse micelles.[3] More recently, we have put a lot of efforts in developing new IR probes based on isocyano(NC)-derivatized amino acids including β-isocyanoalanine and p-isocyanophenylalanine[4], which have been chosen as appropriate models for both aliphatic and aromatic amino acid residues in proteins. Considering their unique properties including large transition dipole, 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 proteins.

References

[1] H. Kim and M. Cho. " Infrared Probes for Studying the Structure and Dynamics of Biomolecules" Chem. Rev. , 113 (8), pp 5817–5847 (2013)

[2] M. Maj, Y. Oh, K. Park, J. Lee, K. Kwak and M. Cho „Vibrational dynamics of thiocyanate and selenocyanate bound to horse heart myoglobin" J. Chem. Phys. 140, 235104 (2014)

[3] J. Lee, M. Maj, K. Kwak and M. Cho „Infrared Pump-Probe Study of Nanoconfined Water Structure in Reverse Micelle" J. Phys. Chem. Lett., 5(19), 3404-3407 (2014)

[4] M. Maj, C. Ahn, D. Kossowska, K. Park, K. Kwak, H. Han and M. Cho „β-Isocyanoalanine as an IR Probe: Comparison of Vibrational Dynamics between Isonitrile and Nitrile-Derivatized IR Probes" (in press)