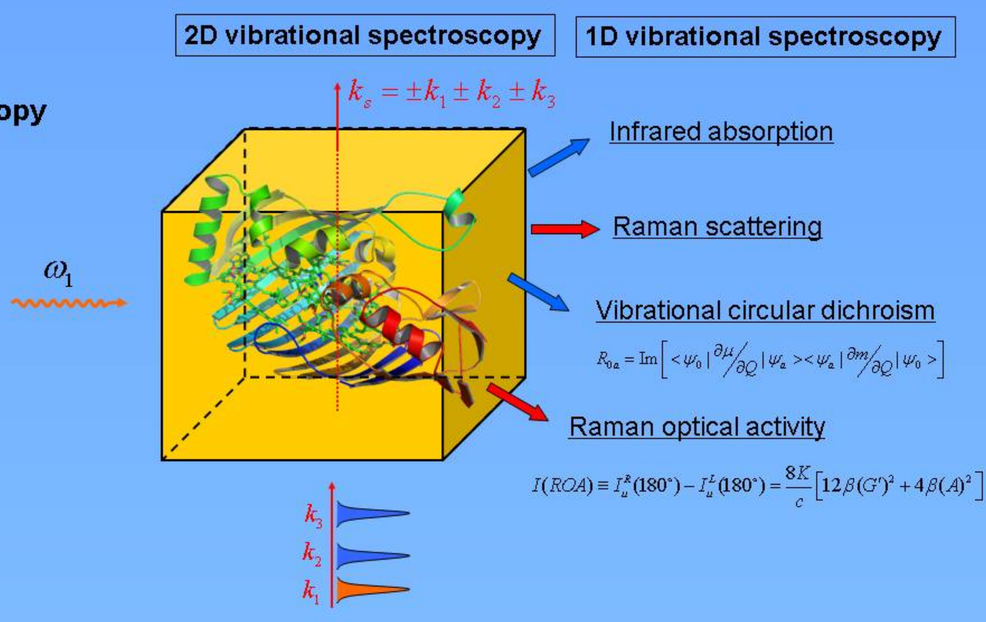
# Computational Spectroscopy

## I. Introduction

**Development of computational algorithm for simulating linear and nonlinear spectroscopy**

| Previous work | Our work |
|---|---|
| Limitation of QM calculation due to large size of a polypeptide | Numerical simulation for a protein: Hessian matrix reconstruction |
| Corruption of TDC approximation | Use of coupling constant map obtained from ab-initio calculation |
| Assumption of peak shape: Gaussian and Lorentzian function | Correlation function formalism: Molecular dynamic simulation |




## II. Computational Methods

**Algorithm for numerically simulating vibrational spectra**

Hessian matrix reconstruction: QM calculation

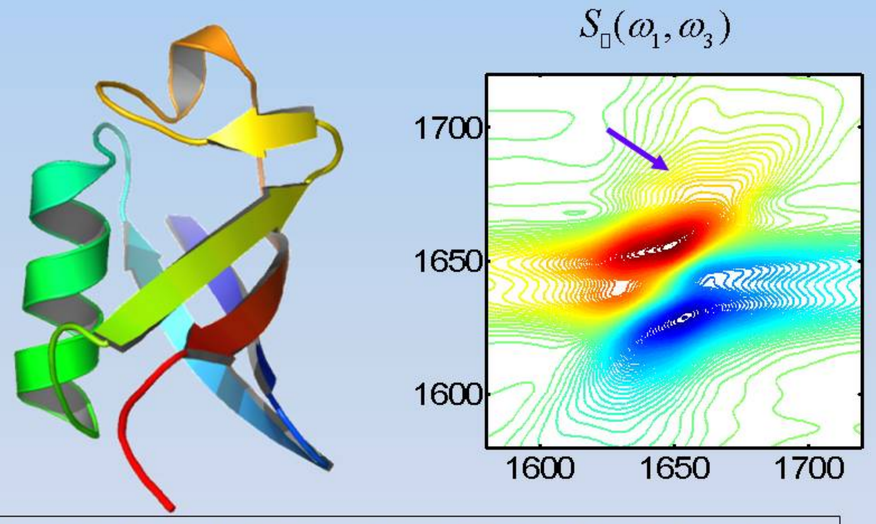
Theoretical approximation: Electrostatic model, TDC

Solute-solvent interaction: MD calculation, Electrostatic model

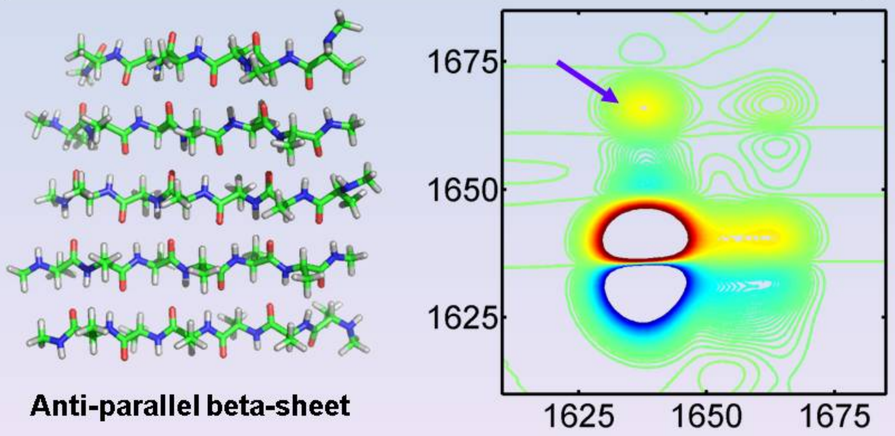
Evaluation of transition dipole, magnetic dipole, tensors: Fragment analysis, QM calculation

Simulation of linear vibrational spectroscopy:
IR, VCD, Raman, ROA, CP-IR-Vis-SFG
Simulation of nonlinear vibrational spectroscopy:
2D IR, 2D CP-PE, 2D SFG

**Simulated 2D IR photon echo spectra of a protein ubiquitin**




Cross peak indicated by arrow reveals the existence of beta-sheet

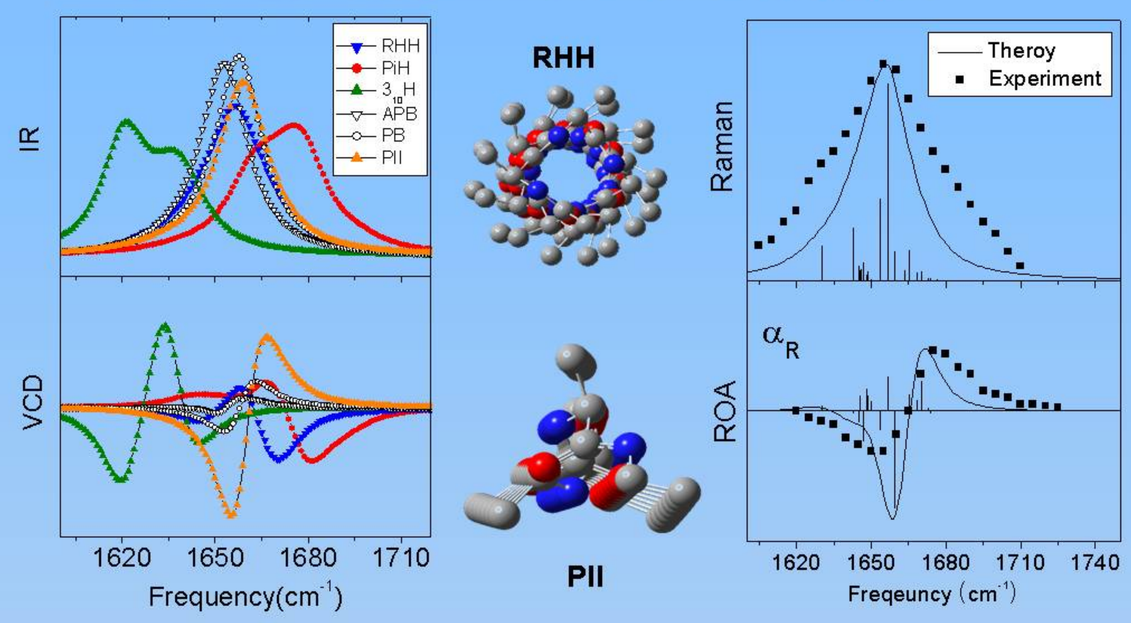



Anti-parallel beta-sheet

J.Chem.Phys. (2007)

## III. Application to Biomolecule

**Simulated IR, VCD, Raman, ROA spectra of polypeptide**

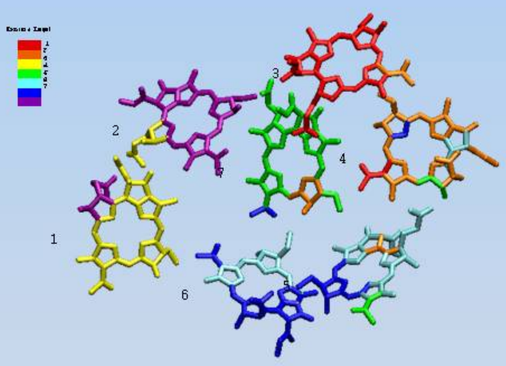



*Biopolymer (2006)*

*J.Chem.Phys. (2009)*

Simulated linear vibrational spectra show good agreement with the experiment

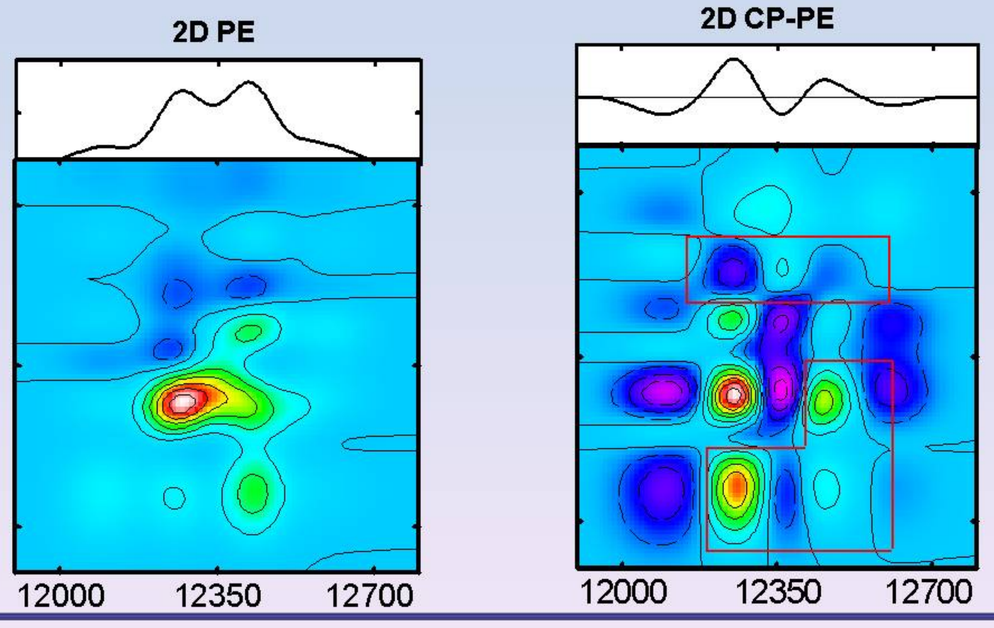
**Simulated 2D CP-PE spectra for FMO protein: Novel spectroscopy**




| Linear polarized beam | Circularly polarized beam |
|---|---|
| 1D IR, UV spectroscopy | Circular dichroism |
| 2D PE spectroscopy | 2D CP-PE spectroscopy |

Novel 2D CP-PE spectroscopy provide more crucial information on structure and dynamics of biomolecule than conventional 2D PE.

*Chem.Phys. (2008), Acc.Chem.Res. (2009)*

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