Computational vibrational spectroscopy for various IR probes

Jun-Ho Choi[1,2] and Minhaeng Cho[1,2]

[1]Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science, Seoul 136-713, Republic of Korea
[2]Department of Chemistry, Korea University, 136-713, Seoul, Republic of Korea

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Various IR probes such as -CN, -SCN, $-N_3$ compounds, amide I in peptide and CO in MbCO were widely used to obtain information on protein structure and dynamics from their vibrational spectrum. The band shape and peak position are found to be sensitive to the local electrostatic environment around a given IR probe. The 2D IR spectroscopic measurement can be used in probing protein conformational change in time and protein unfolding pathway by employing femtosecond laser pulses. But, it is not straightforward to extract directly useful information on peptide structure and dynamics from experimental results obtained by vibrational spectroscopic measurements mainly due to congestion of vibrational bands. Therefore, the theoretical approach based upon the vibrational analysis is needed. There are a variety of complicated issues to be resolved in describing numerically vibrational spectrum, that is, the solvatochromic frequency shift due to interaction between peptide and water, motional narrowing, intermolecular vibrational coupling between neighboring peptides.[1]

To tackle these issues, QM mechanical calculation has successfully used for a given molecular system. For the proteins under solution, the structure is constantly changed making hydrogen bonding interaction with water molecules and interaction between neighboring peptides. This solvent or peptide induced interactions cause the frequency shift and change of band shape in the vibrational spectrum. But it is not practical to carry out QM calculation considering explicitly solvent molecules for protein-solvent system because of computational cost due to its large molecular size and varying configurations under solution.

Recently, we have developed a systematic way to numerically simulate linear and nonlinear vibrational spectrum considering fully solvent effects and peptide-peptide interaction by the hybrid method combining electronic structure calculation, molecular dynamics (MD) simulation, and theoretical models for vibrational solvatochromism.[1] This theoretical approach has been widely applied to simulate linear and nonlinear vibrational spectra of amide I vibrational modes of proteins,[1] various IR probes containing -CN, -SCN, $-N_3$ groups[2,3], and CO stretch mode in MbCO protein[4]. It was shown that the distributed interaction site model developed by us work properly in describing solvent induced frequency shift as well as calculating fluctuation amplitude of a variety of IR probe frequencies in liquid water. For MbCO protein system, the vibrational substates associated with differnent conformations of CO bound Myoglobin were investigated performing MD simulation studies for the wild-type and the double mutant. The numerically

simulated IR and 2D IR spectra for MbCO mutant are plotted in figure 1. Comparing to experimentally measured IR and 2D IR spectra for various IR probes, it is shown that this theoretical method can be successfuly used in reproducing the protein vibrational spectra and extracting critical information on protein structure and dynamics with the vibrational analysis.

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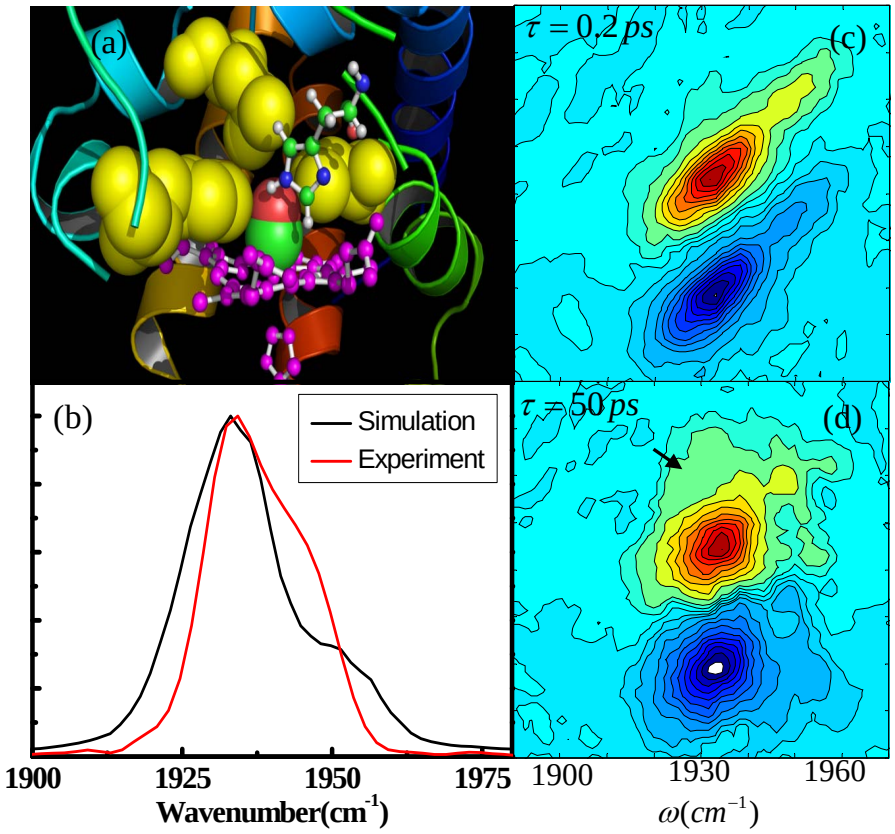

Figure 1. Snap shot structure of active site (a), simulated IR spectrum in (b), and 2D IR spectrum in (c) and (d) of the double mutant MbCO. The arrow represents growth of cross peak in the 2D IR spectrum.

References

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