Division of Environmental Chemistry
– Solution and Interface Chemistry –

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Scope of Research

　　We investigate chemical phenomena in condensed phases. (1) To understand the chemical structure, property and reactions in a two-dimensional molecular aggregate, the keywords of molecular interactions and orientation are focused on, and the fluctuated molecular aggregates are investigated by using originally developed spectroscopic and theoretical techniques. (2) The structure, dynamics, and reaction of solutions with nano-scale inhomogeneity and/or with fine tunability are investigated by computer simulation, and statistical-mechanical theory of solutions, and NMR spectroscopy.

KEYWORDS

Infrared and Raman Spectroscopy	Free Energy
Surface and Interface Chemistry	Solvation
Nano Particle and Fibril Analysis	Solution Theory

Selected Publications

Shimoaka, T.; Itoh, Y.; Hasegawa, T., Dynamic Rearrangement of Stearic Acid Molecules Adsorbed on a Gold Surface Induced by Ambient Water Molecules Studied by Infrared Spectroscopy, *J. Phys. Chem. C*, **116,** 17142-17148 (2012).

Itoh, Y.; Hasegawa, T., Polarization Dependence of Raman Scattering from a Thin Film Involving Optical Anisotropy Theorized for Molecular Orientation Analysis, *J. Phys. Chem. A*, **116,** 5560-5570 (2012).

Muro, M.; Harada, M.; Okada, T.; Hasegawa, T., Molecular Rearrangement in a Zinc Stearate Langmuir Film Dependent on a Film Preparation Method Studied Using Polarization-Modulation Infrared Reflection Absorption Spectroscopy and X-ray Absorption Fine Structure, *J. Phys. Chem. B*, **116,** 3148-3154 (2012).

Matubayasi, N.; Takahashi, H., Free-energy Analysis of the Electron-density Fluctuation in the Quantum-mechanical/Molecular-mechanical Simulation Combined with the Theory of Energy Rrepresentation, *J. Chem. Phys.*, **136,** [044505-1]-[044505-10] (2012).

Shintani, M.; Matsuo, Y.; Sakuraba, S.; Matubayasi, N., Interaction of Naphthalene Derivatives with Lipid in Membrane Studied by [1]H-Nuclear Overhauser Effect and Molecular Dynamics Simulation, *Phys. Chem. Chem. Phys.*, **114,** 14049-14060 (2012).

Kimura, H.; Yasaka, Y.; Nakahara, M.; Matubayasi, N., Nuclear Magnetic Resonance Study on Rotational Dynamics of Water and Benzene in a Series of IonicLliquids: Anion and Cation Effects, *J. Chem. Phys.*, **137,** [194503-1]-[194503-10] (2012).

Spectroscopic Observation of Dynamic Rearrangement of Adsorbed Molecules on Imperfectly Hydrophilic Gold Surface

Molecular adsorbates of stearic acid on a imperfectly hydrophilic gold surface prepared as an imperfect Langmuir-Blodgett (LB) film is found to exhibit dynamic molecular rearrangement when the humid atmosphere about the sample is changed. The gold surface was prepared by solvent cleaning in a sonication bath. The molecular adsorbates stored in a thoroughly dried sample room of FT-IR is found to have a unique adsorption structure; the hydrocarbon chains have a nearly parallel orientation to the substrate surface while the molecules are highly packed to have the orthorhombic subcell packing, which is confirmed by infrared reflection-absorption (RA) spectrometry. When the sample is pulled into an ambient air, the adsorption structure exhibits a drastic change in about only fifteen minutes, which is pursued by polarization-modulation infrared reflection-absorption spectrometry (PM-IRRAS). The spectra clearly indicate that the molecular stance has largely been changed to have a standing-up orientation, whereas the molecular conformation is largely degraded. When the sample is got back to the dried sample room, the molecular conformation largely improves while the standing orientation is kept. These irreversible changes are induced by ambient water molecules adsorbed on the lying stearic acid molecules, which was monitored by analyzing absorption bands of the hydronium ion.
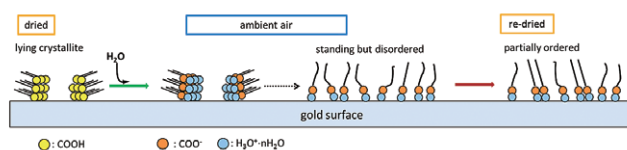

Figure 1. Schematic illustrations of the adsorbed stearic acid molecules on gold as a function of the environmental condition.

Interaction of Small Molecule with Lipid Membrane through Combined [1]H-Nuclear Overhauser Effect Measurement and Molecular Dynamics Simulation

The location, orientation, and dynamics of hydrophobic small molecule in lipid membrane are studied through combined use of the solution-state ^{1}H-NMR and MD simulation. 1-Naphthol and 1-methylnaphthalene were adopted as the small molecule with or without hydrophilic group. The nuclear Overhauser effect (NOE) measurement was performed for large unilamellar vesicle (100 nm in diameter) composed of dimyristoylphosphatidylcholine (DMPC) and the naphthalene derivative. The transient NOE-SE (spin echo) scheme was employed to quantitatively determine the NOE cross relaxation rate constant between DMPC and the naphthalene derivative. The observed NOE shows that both the naphthalene derivatives distribute over wide domain across the normal of the essentially planar membrane ranging from the hydrophobic core to the hydrophilic headgroup. The experimental NOE information was further refined in combination with the analysis of time correlation functions in MD simulation. It was found that 1-naphthol exhibits slight preference of its OH group pointing toward the hydrophilic domain of membrane and that no definite preference can be concluded for the orientation of 1-methylnaphthalene. When 1-naphthol and 1-methylnaphthalene are compared, the NOE is the stronger for 1-naphthol due to the restricted motion by the OH group. The slowdown of the 1-naphthol motion is also evidenced by the ^{1}H spectral line width.
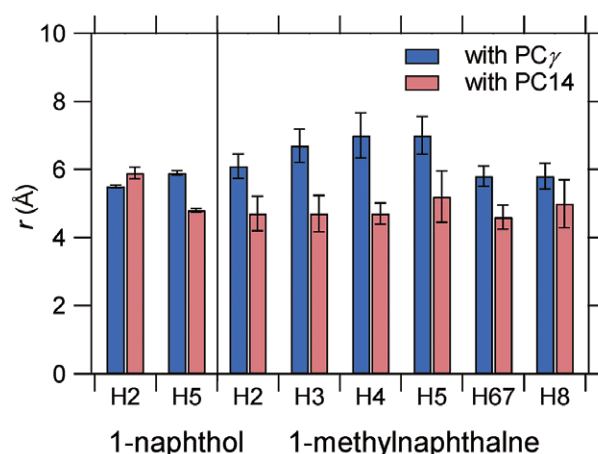

Figure 2. The distances r from DMPC terminal positions (PCγ and PC14) estimated by combining the experimental NOE cross relaxation rate constant and the simulated correlation time.