

VII-D Theory of Sum Frequency Generation Spectroscopy

Sum Frequency Generation (SFG) spectroscopy in combination of infrared and visible lights has a wide range of applications to study interfacial structure, including ambient and buried surfaces not accessible by most other techniques. In contrast to the recent experimental progress, however, theoretical study of SFG is still in a relatively primitive stage. We recently proposed two theories which allow us to calculate SFG spectra via *ab initio* molecular orbital theory and molecular dynamics simulation, and applied them to the experimental SFG spectrum of water surface with considerable success. This project aims at extending this theory in two ways: (1) development of fundamental SFG theory toward quantitative interpretation of the experiments, and (2) application to other interfacial structures of interest using large-scale computation.

VII-D-1 Toward Computation of Bulk Quadrupolar Signals in Vibrational Sum Frequency Generation Spectroscopy

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Although SFG is regarded as a surface-sensitive

spectroscopy, bulk contribution *via* quadrupole and other higher-order terms should not be negligible. Relative importance of surface and bulk signals has been a long standing issue, although quantitative discussion is rather scarce. This study provides theoretical expressions of the bulk signals, which are extension of our previous SFG theories and are readily implemented in molecular dynamics calculations.

VII-E Theory of Mass Transfer Kinetics at Liquid-Vapor Interfaces

Mass transfer kinetics at liquid-vapor interface is of fundamental importance in heterogeneous atmospheric chemistry, as it governs rates of heterogeneous reactions and nucleation. Observed uptake kinetics, however, is quite difficult to interpret in molecular level, since it is related to many kinetic factors including gas diffusion, liquid solubility and diffusion, interfacial mass accommodation, *etc.* We have demonstrated with the help of molecular dynamics and computational fluid dynamics calculations that those elemental kinetic resistances can be accurately decoupled in actual experimental conditions.

VII-E-1 Revised Kinetics in the Droplet Train Apparatus Due to a Wall Loss

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Heterogeneous uptake experiments become further complicated when a wall loss effect is involved in addition to the interfacial mass transfer. In most experimental analyses of the droplet train flow reactor, the wall loss rate is simply subtracted as a constant background, assuming that it is independent from the uptake rate constant into droplets. However, we showed that this usual assumption is flawed because of radial concentration gradient in the flow tube. Accurate treatment of the wall loss effect is demonstrated using computational fluid dynamics calculations.

VII-E-2 Uptake of the HO₂ Radical by Water: Molecular Dynamics Calculations and Their Implications to Atmospheric Modeling

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HO₂ plays many critical roles in radical-chain oxidation reactions in the troposphere. Although a substantial sink of HO₂ has been suggested to be the uptake into aerosols, its efficiency is largely uncertain. Therefore, we performed molecular dynamics calculations of HO₂ uptake into water surface, and found that the mass accommodation coefficient of HO₂ is close to unity. Implications of this result in the troposphere are examined by photochemical box model calculations for typical two cases of tropospheric boundary layers; remote marine air and polluted urban air. It is shown that HO₂ concentration is particularly sensitive to the heterogeneous uptake in the urban case.

VII-E-3 Mass Accommodation Coefficient of Water: Molecular Dynamics Simulation and Revised Analysis of Droplet Train/Flow Reactor Experiment

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Mass accommodation coefficient of water α has been studied for a century, in relation to the cloud formation kinetics and many other implications. Most recent experiment using droplet train flow reactor reported $\alpha = 0.23$ at room temperature, which appears inconsistent to molecular dynamics value, $\alpha \sim 1$. This study resolved this discrepancy by reanalyzing the gas diffusion and flow conditions in the experimental reactor. Accurate calculations of the gaseous diffusion resistance yielded a value of α close to unity, which is fully consistent to the molecular dynamics and some other experiments.