



Physical Chemistry Graduate Student Awards Seminar

KV Reddy Award Presentations

Hanming Yang - Cavagnero Group

“Enhanced Nuclear-Spin Hyperpolarization of Amino Acids and Proteins via Reductive Radical Quenchers”

Low-concentration photochemically induced dynamic nuclear polarization (LC-photo-CIDNP) has recently emerged as an effective tool for the hyperpolarization of aromatic amino acids in solution, either in isolation or within proteins. One factor limiting the maximum achievable signal-to-noise ratio in LC-photo-CIDNP is the progressive degradation of the target molecule and photosensitizer upon long-term optical irradiation. Fortunately, this effect does not cause spectral distortions but leads to a progressively smaller signal buildup upon long-term data-collection (e.g., 500 nM tryptophan on a 600 MHz spectrometer after ca. 200 scans). Given that it is still generally desirable to minimize the extent of photodamage, we report that low- μM amounts of the reductive radical quenchers vitamin C (VC, i.e., ascorbic acid) or 2-mercaptoethylamine (MEA) enable LC-photo-CIDNP data to be acquired for significantly longer time than ever possible before. This approach increases the sensitivity of LC-photo-CIDNP by more than 100%, with larger enhancement factors achieved in experiments involving more transients. Our results are consistent with VC and MEA acting primarily by reducing transient free radicals of the NMR molecule of interest, thus attenuating the extent of photodamage. The benefits of this reductive radical-quencher approach are highlighted by the ability to collect long-term high-resolution 2D ^1H - ^{13}C LC-photo-CIDNP data on a dilute sample of the drkN SH3 protein (5 μM).

Feng Pan - Goldsmith Group

“Exploring plasmonic-photonic interaction using single-particle microresonator spectroscopy”

Plasmonic-photonic coupled systems are versatile platforms for the study and control of nanoscale light-matter interactions because of small mode volume or high-quality factor in their respective component cavities. Among these systems a coupled plasmonic-photonic cavity combining ultrahigh quality whispering-gallery mode and ultrasmall plasmonic mode is attractive to achieve optimal photonic performance. Constructing such an optimal system requires rigorous understanding of critical system parameters in the coupled cavity, such as dissipation rates and couplings, etc. However, the inability to easily measure and tune these parameters renders this task challenging. Here, we present a method to simultaneously measure absorption and two-sided optical transmission in a coupled plasmonic-photonic resonator consisting of plasmonic gold nanorods deposited on a toroidal whispering-gallery-mode optical microresonator. Our analytical model predicts and explains distinct line shapes observed and quantifies the contribution of each system parameter. This combined approach enables us to determine all system parameters with a dynamic range spanning 9 orders of magnitude. A full description of plasmonic-photonic energy dynamics in this weakly coupled optical system is a necessary step for future applications that rely on tunability of dissipation and coupling. In this talk I will also briefly show our efforts to tune the coupling in this plasmonic-photonic system.

Hartl Award Presentation

Xianyuan Zhao - Nathanson Group

Competition between Br⁻ and Cl⁻ as Counterions to a Cationic Surfactant

We use neutral impact ion scattering spectroscopy (NICISS) to measure the elemental depth profiles of a cationic surfactant, tetrahexylammonium bromide (THABr), dissolved together with NaCl/NaBr salt mixture in liquid glycerol. By analyzing the energy loss of helium atoms backscattered from the surface of solution, the depth profiles of oxygen, carbon, chloride, and bromide are mapped at the Angstrom scale. These profiles are then used to analyze how solvent, surfactant, and counterions populate the surface region. The experiments cover a series of solutions with a fixed surfactant concentration (0.01 M THABr) and fixed salt mixture total concentration (0.30 M NaCl + NaBr), while gradually changing the NaCl:NaBr ratio from all NaBr to nearly all NaCl. Br⁻ is found to be more attracted to THA⁺ than is Cl⁻ by a factor of 2 to 3, indicating that Br⁻ outcompetes Cl⁻ as a counterion for THA⁺. The total adsorption of THA⁺ is also enhanced when the salt mixture contains more Br⁻. Glycerol solvent molecules are concomitantly repelled from the surface as THA⁺ replaces glycerol at larger Br⁻ bulk concentrations. As partial proof of the validity of the NICISS study, the adsorption of THA⁺ and the depletion of glycerol are consistent in terms of a volume trade-off. These structural analyses are in accord with previous reactivity studies of gaseous Cl₂ and N₂O₅ at THA⁺-coated glycerol containing differing fractions of Cl⁻ and Br⁻ ions.