

UC San Diego –National Sun Yat-sen University

2019 Bilateral Research Symposium

Atmospheric Science Breakout Session II

SATURDAY MORNING, MARCH 9, 2019

CAICE, CONFERENCE ROOM

UREY HALL ANNEX 3060

9:30 - 12:30 Atmospheric Science II (co-Chairs: Kim Prather, Chia-Chen Wang)

- Vicki Grassian, Professor, Department of Chemistry and Biochemistry, UC San Diego
“Aerosol Chemistry and Impacts”
- Chia C. Wang, Professor, Department of Chemistry, NSYSU
“Probing the Interfacial Solvation Properties and Surface pH of Solute-containing Aqueous Nanoaerosols”
- Robert Continetti, Professor, Department of Chemistry and Biochemistry, UC San Diego
“Aerosol Spectroscopy and the Dynamics of Nanoparticle Collisions”
- Chao-Yu Chung, Professor, Department of Chemistry, NSYSU
“Probing the Reactive Radicals with Infrared Off-axis Cavity Output Spectroscopy (OA-ICOS)”
- Ming-Jung Wu, Professor and Dean, College of Science, NSYSU
“Transition Metal-Catalyzed Cyclization of Ene-dienes to Benzopyranones, Carbazoles, Benzothiophenes and Indeno[1,2-c]chromenes”
- Wei Xiong, Professor, Department of Chemistry and Biochemistry, UC San Diego
“Salting Up of Proteins at the Air/Water Interface”
- Dr. Arnab Bagchi, Department of Chemistry, NSYSU
“Ozonolysis of Terpenes and Formation of Aerosols studied via Time-resolved Fourier Transform Infrared Spectroscopy”

ABSTRACTS

Aerosol Chemistry and Impacts

Vicki Grassian

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This talk will discuss some recent laboratory studies on the chemistry and global impacts of several important classes of atmospheric aerosols, namely mineral dust, sea spray and aqueous aerosols. In particular, new studies of mineral dust aerosol sulfur oxidation chemistry including the formation of organosulfur compounds, ice nucleation of mineral dust and sea spray aerosol, and pH effects in aqueous aerosols will be highlighted in this talk.

Probing the Interfacial Solvation Properties and Surface pH of Solute-containing Aqueous Nanoaerosols

Chia C. Wang

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An in-depth understanding of the fundamental energetic and structural properties at or near the interface of nanoscaled aqueous aerosols is of fundamental and crucial importance in understanding the impacts of organic species, either of biogenic or anthropogenic origins in intervening the cloud formation microphysics and the intrinsic nature of clouds. To address these issues, we applied aerosol VUV photoelectron spectroscopy to investigate the valence electronic structures and interfacial characteristics of pure and several organic-containing aqueous nanoaerosols that are of atmospheric significance. To assess the intrinsic structural and energetic properties of pure water droplets in the nanoscaled size regime and how they may be modified due to the presence of solutes, we studied the VUV photoelectron spectrum of pure H₂O and D₂O nanoaerosols. Both the fully vibrationally-resolved fine structures of gaseous water features and the partially vibrationally-resolved condensed water features were obtained. The partially vibrational resolved photoelectron spectral features of water nanodroplets imply that the condensed water in the form of nanoscaled water droplets may not be entirely disordered. The possible origins for the observed isotopic effect, as well as the micro-hydration structure and nature of water nanodroplets will be discussed. Considering that many organic species emitted from anthropogenic activities may encounter fine water nanodroplets and form aqueous aerosols in the atmosphere, we studied the valence photoelectron spectroscopy of phenol and three dihydroxybenzene isomers including catechol, resorcinol, and hydroquinone aqueous nanoaerosols at varying pH conditions. It reveals that the hydration extents, pH values, deprotonation status, and numbers/relative arrangements of -OH groups are crucial factors affecting the ionization energies of phenolic aqueous nanoaerosols and thus their redox-based activities. The multi-faceted implications of the present study in the aerosol science, atmospheric/marine chemistry, and biological science will be addressed.

Keywords: Aerosols; Aerosol VUV photoelectron spectroscopy; Aqueous Aerosols; Valence electronic structures; Surface pH; Interfacial solvation structures

Aerosol Spectroscopy and the Dynamics of Nanoparticle Collisions

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Two new directions for the characterization of aerosol chemistry and dynamics will be reviewed in this presentation. In the first instance, a new electrodynamic balance apparatus optimized for the study of the spectroscopy and phase-change dynamics of aqueous particles relevant to sea-spray aerosol will be discussed. Droplets of model compounds in the 50 micron size range with control of the relative humidity, gas composition and temperature can be achieved with this device. The initial measurements examining the translational diffusion of D₂O through H₂O in sucrose, citric acid and ternary sucrose-salt solutions will be presented.

In the second instance, a new single-particle dust accelerator/decelerator will be discussed. This apparatus allows the examination of the impact dynamics of micron and sub-micron-sized nanoparticles. The mass and charge of single nanoparticles can be measured using charge detection mass spectrometry and the particle then accelerated or decelerated to the desired final velocity for studies of particle impact with surfaces. Applications to measurements of the coefficient of restitution for polystyrene latex spheres, tin nanoparticles, and ice particles will be presented.

Probing the Reactive Radicals with Infrared Off-axis Cavity Output Spectroscopy (OA-ICOS)

Shei-Saint Chen, Wei-ling Tseng, Chi-Pang Huang, and Chao-Yu Chung

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The reactive intermediates in the gaseous phase usually are difficult to be detected, so that a sensitive spectroscopic tool is needed to tackle this issue. We are planning to establish an infrared off-axis cavity output (OA-ICOS) spectrometer to capture the reactive intermediates, such as simplest Criegee intermediate, CH_2OO , from the photolysis of a mixture of CH_2I_2 and O_2 .

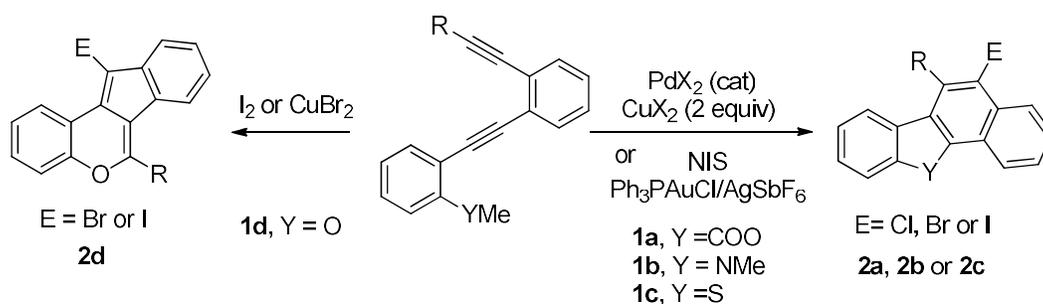
Keywords: Criegee; CH_2OO ; OA-ICOS

Transition Metal-Catalyzed Cyclization of Ene-diynes to Benzopyranones, Carbazoles, Benzothiophenes and Indeno[1,2-c]chromenes

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Recently, we found that treatment of methyl 2-[(2-(2-alkynylphenyl)ethynyl)benzoates 1a, N,N-dimethyl 2-[(2-(2-alkynylphenyl)ethynyl)anilines 1b with ten mol% of PdX₂ (X = Cl or Br) and two equivalents of CuX₂ (X = Cl or Br) at refluxing CH₃CN or THF for one hour gave the halogenated dibenzo[b,d]pyran-6-ones 2a and benzo[a]carbazoles 2b in good chemical yields, respectively. On the other hand, Treatment of 2-(2-(2-(2-substituted ethynyl)phenyl)ethynyl)thioanisoles 1c with NIS using Ph₃PAuCl/AgSbF₆ as the catalyst gave benzo[b]naphtho[2,1-d]thiophenes 2c in good yields. Interestingly, the reaction of (2-(2-(2-substituted ethynyl)phenyl)ethynyl)anisoles 1d with I₂ or CuBr₂ gave halogenated indeno[1,2-c]chromene derivatives 2d, respectively. The reaction mechanism and the electronic effects on the cyclization modes will also be discussed.



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Salting Up of Proteins at the Air/Water Interface

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Vibrational sum frequency generation (VSFG) spectroscopy and surface pressure measurements are used to investigate the adsorption of a globular protein, bovine serum albumin (BSA), at the air/water interface with and without the presence of salts. We find at low (2-5 ppm) protein concentrations, which is relevant to environmental conditions, both VSFG and surface pressure measurements of BSA behave drastically different than at higher concentrations. Instead of emerging to the surface immediately, as observed at 1000 ppm, the adsorption kinetics is on the order of tens of minutes at these lower concentrations. Most importantly, salts strongly enhance the presence of BSA at the interface. This “salting up” effect differs from the well-known “salting out” effect as it occurs at protein concentrations well-below where “salting out” occurs. “Salting up” is a new type of salt-driven interfacial phenomenon and can potentially explain surface enrichment of proteins in aqueous systems.

Ozonolysis of Terpenes and Formation of Aerosols studied via Time-resolved Fourier Transform Infrared Spectroscopy

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Biogenic alkenes, which are among the most abundant volatile organic compounds, are readily oxidized by ozone to generate secondary organic aerosols in the atmosphere. We have investigated the ozonolysis of α -pinene in the aerosol phase at temperatures ranging from 298 K to 200 K using a combined rapid scan Fourier transformed infrared (FTIR) spectroscopy and theoretical calculations. By means of time resolved spectroscopic analysis, larger secondary organic aerosols (SOA) were found to evolve with the progress of reaction; whereas several intermediate peaks were witnessed during the early stage of reaction when carried out at lower temperatures. The transient signals have been assigned to the key reaction intermediates, such as the primary ozonides (POZ), Criegee Intermediates (CI), secondary ozonides (SOZ) and hydroperoxides (HP) on the basis of good agreement between experimental and DFT calculated results. A detailed calculation at the M062X/-31+G(d,p) level of theory reveals that HP and SOZ intermediate formation pathways are competitive and energetically favorable during the course of α -pineneozonolysis reaction. However at lower temperatures multiphase chemistry play vital role in controlling the chemical reactions and kinetics of the processes thereby accounting for the longer lifetimes of the intermediates observed at lower temperatures. Our study showed prompt unimolecular decay of CI forming hydroperoxides through 1,4-hydrogen shift where the role played by the quantum mechanical tunneling has been investigated. We have also found water as an efficient catalyst for the unimolecular decay of CI. We provide new insights into the reaction mechanism for α -pineneozonolysis at the molecular level, which sheds new light on the effects of SOA formation caused by the ozonolysis of VOCs.

Keywords: *α -pineneozonolysis; Secondary organic aerosols (SOA); Criegee Intermediates (CI); Secondary ozonides (SOZ) and hydroperoxides (HP); Rapid-scan Fourier Transform Infrared Spectroscopy; DFT calculations*