Advances in Applied Nonlinear Spectroscopy:
07:00pm - 09:00pm USA / Canada - Pacific - August 13, 2023 | Location: Hall F, South Bldg. (Moscone Center)
Steve Baldelli, Organizer; Dr. Wei Zhao, Organizer
Division: [ANYL] Division of Analytical Chemistry
Session Type: Poster - In-person
Division/Committee: [ANYL] Division of Analytical Chemistry

The symposium will cover a broad range of topics in applied nonlinear spectroscopy, including but not limiting to coherent multidimensional spectroscopy (CMDS), sum frequency generation (SFG), femtosecond stimulated Raman spectroscopy (FSRS), and coherent nonlinear optical imaging.

Sunday
3924108 - Real and imaginary spectra of thin films via nonlinear, interferometric SFG | Poster Board #3714
07:00pm - 09:00pm USA / Canada - Pacific - August 13, 2023 | Location: Hall F, South Bldg. (Moscone Center)
Rebecca Davies, Presenter; Joam Marmolejos; Emma Gubbins; Mary Shultz
Division: [ANYL] Division of Analytical Chemistry
Session Type: Poster - In-person
Vibrational sum frequency generation (SFG) is a proven, powerful technique for semiquantitative, surface-sensitive detection of molecular species. Complex SFG
has recently been utilized for more quantitative measurements with the goal of
deconvoluting spectral resonances, measuring vibrational mode lifetime, and
collecting orientation information for surface moieties. Many complex SFG
methods suffer from significant phase error in determination of surface
molecules’ orientation and have trouble distinguishing overlapping signals. The
SBW-M Interferometer has been designed and implemented for direct
measurement of real and imaginary SFG spectra and nano-scale phase
accuracy. The interferometer has been utilized in measurements of
octadecyltrichlorosilane (OTS) thin films and is useful for backside-attack of buried
catalytic film interfaces for water purification and energy applications.

Sunday 3924250 - Difference phase interference mode into ultrafast SFG spectroscopy
system to study molecular dynamics of CO2 conversion | Poster Board #3716
07:00pm - 09:00pm USA / Canada - Pacific - August 13, 2023 | Location: Hall F,
South Bldg. (Moscone Center)
Sahar Shata, Presenter; Mary Shultz
Division: [ANYL] Division of Analytical Chemistry
Session Type: Poster - In-person
Phase-sensitive sum-frequency generation spectroscopy is a unique tool to
interrogate the vibrational structure of surface interfaces. A precise
understanding of the interfacial structure often relies on accurately determining
the phase of the non-linear susceptibility χ(2), which has recently been
demonstrated using a nonlinear interferometer in conjunction with a frequency-
scanning picosecond laser system. At the current work, the non-linear
interferometer is combined with ultrafast, broadband, sum-frequency generation
spectroscopy system (up to 11000 nm). The time and phase-resolved spectra of
the vibrational response from CO2 reduction reacting molecules are investigated
and the results will be compared to those obtained using other reported
traditional phase-sensitive measurements. Our overarching goal is to optimize
the CO2 conversion, reduction, reaction into value-added products using an eco-
friendly combination of sunlight as the source of energy and ultra-nano, single-
atom, TiO2 photocatalyst as the reaction promoter. Results investigate and
discuss the origin of the phase uncertainties for CO2 reduction reaction into CO
and provide guidelines for further practical experimental and technical
improvements.

Sunday 3924599 - Withdrawn
07:00pm - 09:00pm USA / Canada - Pacific - August 13, 2023 | Location: Hall F,
South Bldg. (Moscone Center)
Division: [ANYL] Division of Analytical Chemistry
Session Type: Poster - In-person
The symposium will cover a broad range of topics in applied nonlinear spectroscopy, including but not limiting to coherent multidimensional spectroscopy (CMDS), sum frequency generation (SFG), femtosecond stimulated Raman spectroscopy (FSRS), and coherent nonlinear optical imaging.

Tuesday

3918112 - X-ray/XUV floquet state multidimensional spectroscopy, an analogue of MQC NMR

John Wright, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

There is great interest in developing fully coherent multidimensional X-ray/XUV spectroscopic techniques because of their capability for achieving atomic spectral resolution. Current proposals rest on using sequentially and coherently driven core excitations with multiple X-ray/XUV excitation pulses and measuring the output using time domain Fourier transform methods. In this paper, we propose an alternative method that creates an entanglement of core and optical transitions to form a Floquet state that creates directional and coherent output beams. Multidimensional spectra are obtained by measuring the output beams’ intensity while tuning the optical frequencies across resonances. This approach expands on previous optical pump-XUV probe spectroscopy of MoTe₂ by theoretically demonstrating its multidimensional capabilities. Both parametric and non-parametric pathways are proposed in order to optimize the resolution of inhomogeneous broadening and k-selective features.

Tuesday

3921141 - Nonlinear interferometer for complex spectral measurement: a sensitive probe of complex interfaces

Mary Shultz, Presenter; Patrick Bisson; Joam Marmolejos; Rebecca Davies; Emma Gubbins; Ziqing Xiong; Sahar Shata
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

Soft interfaces with multiple species are common in biology, the environment, and technological applications. Probing interfaces, particularly when buried
between two condensed phases presents many challenges. The only current method available for probing such interfaces with molecular specificity is the vibrational spectroscopy, sum frequency generation (SFG). SFG attains surface sensitivity due to its nonlinear nature. Unfortunately, due to nonlinearity, separating overlapping resonances is difficult, usually leading to nonunique separation. This problem has long been recognized by SFG practitioners and several methods for determining the complex components of the signal have been devised. None produce an accurate, absolute measurement of the complex signal. This contribution reports a nonlinear interferometer, that not only addresses this complex measurement issue, but due to exquisite phase accuracy, also detects low concentration interfacial species plus interactions via frequency shifts and lifetime broadening. The nonlinear interferometer has been demonstrated in both scanning and broadband SFG systems. This contribution reports on results from thin films and other interfaces including buried interfaces that significantly challenge current spectral interference techniques.

Tuesday 3920417 - Time-resolved nonlinear spectroscopy of excess electrons in aliphatic ionic liquids
09:00am - 09:30am USA / Canada - Pacific - August 15, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Andrew Healy; Katie Huber; David Blank, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
Applications of ionic liquids have become common in radiolytic environments such as solar cells and nuclear reactors. The photodetachment of an electron from an ion in the liquid creates an initially delocalized and highly reactive species that subsequently localizes to a cavity in less than a picosecond. This is followed by relaxation and cooling that spans decades in time. We apply pump-probe spectroscopy to quantify the reactivity and localization time scales. In order to gain more detailed insight into the structure of the excess electron we apply resonance-enhanced femtosecond stimulated Raman spectroscopy (FSRS) to probe the structure and dynamics following photodetachment in aliphatic ionic liquids. The results will be discussed in the context of the molecular structure of these liquids, and how this structure evolves during the course of electron localization and solvation.

An example of time-resolved resonance Raman spectroscopy of the electrons following photodetachment at 266 nm from a pyrrolidinium dicyanamide ionic liquid (molecular structure shown at the right).

Tuesday 3918651 - High resolution two dimensional infrared spectroscopy for exploring rovibrational coupling
Peter Chen, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

HR-2DIR spectroscopy is a new nonlinear spectroscopic technique that can be used to study the relationship between peaks in different parts of the infrared spectrum. For example, it can be used to determine which peaks in the mid infrared region are related to which peaks in the near infrared. This talk will discuss the use of HR-2DIR for exploring the coupling between rovibrational peaks in the gas phase molecules. The shapes of the resulting 2D rovibrational patterns help show which peaks belong together and provide information on the rovibrational motions that create them.

Tuesday

Intermission
10:00am - 10:10am USA / Canada - Pacific - August 15, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

Tuesday

3925722 - Spatiotemporal probes of electronic and thermal energy transduction and transport
10:10am - 10:40am USA / Canada - Pacific - August 15, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Stephanie Hart; Hannah Weaver; Leo Hamerlynck; Erin Moloney; Rongfeng Yuan; Elena Vasquez; Naomi Ginsberg, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

Very few materials are able to absorb visible light without dissipating some of the resulting energy into phonon modes, and these excited modes have the capability to act back on the electronic excitation that is generated. By the same token, very few probes of photophysical processes in materials are able to directly probe the coexistence of both electronic and thermal departures from equilibrium or directly visualize the impact of the spatiotemporal interaction of electronic and thermal excitations. Through a range of examples, I will nevertheless describe such a capability that leverages not only the ~ps time resolution associated with electronic to thermal energy transduction but that also provides direct spatial maps of localized photoinduced electronic and temperature profiles and their coupled evolution.
3922325 - Stimulated Raman excited fluorescence: Combining the best of two worlds
10:40am - 11:10am USA / Canada - Pacific - August 15, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Dr. Wei Min, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
The pursuit of a hybrid spectroscopy that combines the superb sensitivity of fluorescence and the high chemical specificity of Raman scattering has lasted for more than 40 years. It was only recently that the stimulated Raman excited fluorescence (SREF) process was successfully observed in a broad range of fluorophores (Nature Photonics, 2019). SREF allows single-molecule vibrational spectroscopy and imaging in the optical far field without relying on plasmonic enhancement. In this talk, we will present the core technology of SREF, and then discuss its exciting applications including single-molecule spectroscopy, super-resolution microscopy, super-multiplexed imaging and functional sensing.

Tuesday
3919310 - Surface enhanced coherent Raman scattering: Blessing or curse?
11:10am - 11:40am USA / Canada - Pacific - August 15, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Eric Potma, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
Coherent Raman scattering (CRS) techniques are recognized for their ability to induce and detect vibrational coherences in molecular samples. The generation of coherent light fields in CRS produces much stronger signals than what is common in incoherent Raman spectroscopy, while also enabling direct views of evolving molecular vibrations. Despite the attractive attributes of CRS spectroscopy, the technique’s sensitivity is insufficient for performing measurements on single molecules, thus precluding the ability to coherently drive, manipulate and observe individual vibrational quantum oscillators with light. The single-molecule sensitivity that has been achieved in surface-enhanced Raman scattering (SERS) with the aid of plasmonic antennas suggests that a similar approach may be used to push CRS techniques to the single-molecule detection limit. Compared with SERS, however, experimental successes in surface-enhanced coherent Raman scattering (SE-CRS) are few, and a theoretical understanding of surface-enhancement in CRS is still incomplete. In this presentation, we discuss some of the principles and challenges in SE-CRS and summarize the latest advances in the quest of performing routine CRS experiments on single molecules.

Tuesday
3903821 - Nonlinear optical turn-on probes for membrane lipids imaging in live cells
Imaging biological tissues at the microscopic scale is a major need in biomedical and clinical applications. Fluorescence microscopy has been widely used, but traditional fluorophores are often constrained by problems such as photobleaching, phototoxicity, and excitation saturation. Besides, nonlinear optical bioimaging techniques have been developed to improve the resolution and penetration depth. It is highly desirable to develop nonlinear optical probes for their widespread applications.

This study describes organic nanocrystals as turn-on probes excited by two-photon for membrane imaging in live cells. We developed two types of organic nanocrystals as second harmonic generation (SHG) probes for the imaging of live cells. The organic nanocrystals consist of (N-(4-sulfobutyl)-4-(6-(4-(dibutylamino)phenyl)hexatrienyl)pyridinium (RH237) and 4-Dimethylamino-4′-nitrostilbene (DANS) molecules, respectively. The structure of nanocrystals increases the orderly arrangement of organic molecules and improves the polarization rate of nanomaterials, thus effectively increasing the SHG signal. These probes are applied to the nonlinear optical imaging of live tumor cells. The DANS nanocrystals, as lipid layer turn-on probes, show great SHG signals on the cell membrane and two-photon excited fluorescence (TPEF) signals inside the cell. The emitted signals of SHG and TPEF can be received and recognized simultaneously under femtosecond laser scanning with the wavelength of 960 nm. Compared with inorganic probes, organic probes have a better potential for biological application considering biocompatibility, targeting marker capability and metabolic properties. The organic probes in this work exhibit turn-on optical signals when interacting with cell membranes, making these nonlinear probes attractive for bioimaging.
Understanding highly concentrated water-in-salt and acid solutions using ultrafast optical heterodyne detected optical Kerr experiments

02:00pm - 02:30pm USA / Canada - Pacific - August 15, 2023 | Location: Room 2005, West Bldg. (Moscone Center)

Michael D Fayer, Presenter; Sebastian Fica Contrares; Aaron Charnay; Junkun Pan
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

The role of ions in aqueous systems is important in chemistry, biology, and geology and is the subject of a vast amount of research. Recently, highly concentrated “water-in-salt” electrolytes have been of interest, which can make water-in-salt electrolytes attractive for applications, e.g., safer and more environmentally friendly battery technology. However, there remains a substantial deficit in our understanding of these systems. We report the dynamics of concentrated lithium chloride and lithium bromide aqueous solutions over a range of moderate to high concentrations, e.g., 1-29 to 1-3.3 LiCl-water. At the highest concentrations, there are far too few water molecules to solvate the ions. The experiments employed optically heterodyne-detected optical Kerr effect (OHD-OKE) experiments, a non-resonant technique able to observe dynamics over a wide range of time scales and signal amplitudes. While the pure water decay is a biexponential, the LiCl-water and Li-Br decays are tetra-exponentials. The faster two decays arise from water dynamics, while the slower two decays reflect the dynamics of the ion-water network. The slower dynamics, which do not have counterparts in pure water, arise from ion-water complexes and at the highest concentrations, an extended ion-water network. Comparisons are made between the concentration dependence of the observed dynamics and simulations, which enable the assignment of dynamics to contact ion pairs and large ion-water clusters. The concentration dependences of the correlation time of the slowest two processes is directly correlated with the bulk viscosity, providing an atomistic level understanding of the viscosity. Experiments are also present for highly concentrated HCl solutions. The results are compared to 2D IR measurements and ab initio MD simulations of proton hopping. These results show that the same structural dynamics of the hydronium-water-chloride network drive proton hopping and are responsible for the bulk viscosity.
labeled with visible cyanine fluorescent dyes. Such studies can provide important information about the distributions of local DNA backbone conformations at specific positions relative to single-stranded (ss) – double-stranded (ds) DNA junctions, which are relevant to protein-DNA assembly and function. Obtaining complementary information about the local conformations of DNA bases is more challenging because of experimental difficulties associated with performing ultrafast measurements in the ultraviolet (uv) regime. Here we report a two-photon excitation (2PE) approach to 2DFS, which avoids many of the obstacles associated with ultrafast measurements on uv-absorbing chromophores. 2PE-2DFS uses a train of four laser pulses (with center wavelength ~680 nm, and relative phases swept at radio frequencies) to excite two-photon absorbing optical transitions in the fluorescent guanine analogue 6-methyl isoxanthopterin (6-MI, with peak absorbance ~340 nm). We detect via fluorescence the rephasing (RP), non-rephasing (NRP) and double-quantum coherence (DQC) signal pathways as a function of the inter-pulse delays. Our results indicate that 2PE-2DFS spectra contain information about the electronic structure of the 6-MI chromophore and its interactions with the local environment. Such 2PE-2DFS experiments can provide new information about the local conformations of base stacking interactions within 6-MI dimer-substituted DNA constructs, which will complement previous studies of the local conformations of cyanine-labeled DNA sugar-phosphate backbones.

Tuesday
3922494 - Probing peptide-membrane interactions and molecular conformations by two-dimensional infrared spectroscopy
03:00pm - 03:30pm USA / Canada - Pacific - August 15, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Dr. Nien-Hui Ge, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
Two-dimensional infrared (2D IR) spectroscopy is a powerful technique for studying ultrafast vibrational dynamics and molecular structure. The frequency-frequency correlation function determined from waiting time dependence 2D spectra provides insight into local environment fluctuation. The diagonal and cross peaks in 2D spectra reveal rich information about conformational distribution and molecular interactions. This talk will report two recent applications: i) insertion of a peptide tyrosine sidechain into phospholipid bilayers with different charged headgroups and ii) conformations of a structure unit with unique thermal contracting properties. Experimental results are compared with computational results from quantum chemical calculations and spectral simulation.

Tuesday
3926447 - Extended lifetime 2D IR spectroscopic probe of protein dynamics
Application of infrared spectroscopy to study proteins is challenged by the complexity from spectral congestion. Vibrational probe groups that absorb in a transparent window of protein spectra provide a route to site-selective analysis of single locations. While many such probes have been developed, the duration over which they may be used to measure equilibrium dynamics is limited by the typically short vibrational lifetimes. We report synthesis and characterization of the seleno analog of the popular vibrational probe cyanocysteine. Due to well-known heavy atom decoupling, the cyano vibration of cyanoselenocysteine is anticipated to increase the vibrational lifetime by an order of magnitude, with potential to extend study of equilibrium protein dynamics to the nanosecond timescale.

Room temperature ionic liquids (RTILs) have had much attention paid to them due to the ease of which they can be tuned to perform in many different applications ranging from using them as a green solvent system to the use of RTILs as electrolytes in electrochemical devices. In practice RTILs are hygroscopic and as such, the influence of water in RTILs must be understood. In this talk, I will discuss the effects of limited amounts (under 21.6% \( \chi_{\text{water}} \)) of water on 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF\(_4\)) and 1-butyl-3-methylimidazolium dicyanamide (BmimDCA) room-temperature ionic liquid (RTIL) mixtures. The RTILs were characterized by tracking changes in the vibrational features observed in the linear infrared (IR) and two-dimensional infrared (2D IR) spectra of the dicyanamide anion (DCA). Peak shifts with increasing water suggest the formation of water associated and “dry” DCA populations. Further results showed clear differences in the dynamic behavior of
these different populations of DCA at low (defined here as below 2.5% $\chi_{\text{Water}}$), mid (defined here as between 2.5% $\chi_{\text{Water}}$ and 9.6% $\chi_{\text{Water}}$), and high (defined here as between 11.6% $\chi_{\text{Water}}$ and 21.6% $\chi_{\text{Water}}$) range water concentrations. Vibrational relaxation is accelerated with increasing water content for water-associated populations of DCA, indicating water facilitates population relaxation, possibly through the provision of additional bath modes. Conversely, spectral diffusion of water-associated populations slowed dramatically with increasing water, suggesting water drives the formation of distinct and non- or very slowly interchangeable local solvent environments.

**Tuesday**

3921945 - Functional stimulated Raman imaging for subcellular bioanalysis  
04:40pm - 05:10pm USA / Canada - Pacific - August 15, 2023 | Location: Room 2005, West Bldg. (Moscone Center)  
Dr. Lu Wei, Presenter  
Division: [ANYL] Division of Analytical Chemistry  
Session Type: Oral - In-person  
In this talk, we will discuss our recent efforts toward functional SRS imaging and sensing empowered by integrating new spectroscopy, chemistry, and chemical probes. We will present our results for Raman-guided intracellular metabolic mapping; quantitative subcellular analysis of cytoplasmic aggregates; photo-activatable and photo-switchable SRS spectral-imaging; intracellular sensing through alkyne-HDX; and toward super-resolution chemical imaging.

**Tuesday**

3914626 - Analyzing structural heterogeneity in nucleic acids using ultrafast fluorescence upconversion spectroscopy  
05:10pm - 05:40pm USA / Canada - Pacific - August 15, 2023 | Location: Room 2005, West Bldg. (Moscone Center)  
Julia Widom, Presenter  
Division: [ANYL] Division of Analytical Chemistry  
Session Type: Oral - In-person  
The biological macromolecules DNA and RNA play critical roles in cellular function, and often adopt specific structures in order to do so. Many of the methods that have been developed to probe nucleic acid structure and dynamics are based on fluorescence detection. Standard fluorescence spectroscopy is subject to both ensemble and time averaging, with neither static nor dynamic heterogeneity being resolvable. Single-molecule fluorescence measurements overcome the problem of ensemble averaging, but typically can not resolve dynamics that are faster than the microsecond-to-millisecond time-scale. Ultrafast fluorescence spectroscopy can access sub-picosecond time-scales and can dissect structural heterogeneity by resolving the distinct excited state lifetimes and relaxation pathways exhibited by fluorescent probes in different structural contexts. Specifically, fluorescence upconversion spectroscopy measures the spectrum of fluorescence emitted at different times after excitation.
by mixing the emitted fluorescence with a delayed “gate” pulse. I will present work in which we utilized fluorescence upconversion spectroscopy to probe DNA and RNA labeled with cyanine dyes in different structural contexts. Cy3 was investigated in single- and double-stranded DNA and in an RNA-DNA hybrid, with and without a second Cy3 in close proximity. In addition to yielding excited state lifetimes, these measurements resolve the Stokes shift of Cy3 on the ~10 ps time-scale. This approach will be generalized to interrogate unknown nucleic acid structures, and will be coupled with Förster resonance energy transfer to reveal correlations between the local environment of the probe and the global structure of the nucleic acid.

Tuesday
3918334 - Determining the impact of gold nanoparticles on amylin aggregation via 2D IR spectroscopy
05:40pm - 06:00pm USA / Canada - Pacific - August 15, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Kayla Hess, Presenter; Lauren Buchanan
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
The uses of nanoparticles (NPs) have increased in a variety of industries, making it necessary to understand the health and safety risks they can pose. That includes investigating the interactions of NPs with biological media, as NPs are known to induce protein structural changes after adsorbing proteins onto their surfaces. These changes can alter native protein function or modulate the aggregation of proteins; thus, the interactions of aggregation-prone amyloidogenic proteins are of particular concern. Amyloidogenic proteins are associated with diseases such as Alzheimer’s and type II diabetes and are characterized by their formation of extended β-sheet structures known as fibrils. During amyloid aggregation, cytotoxic intermediates known as soluble oligomers form; NPs can interact with these species, possibly changing the lifetime or cytotoxic potential of the intermediates. This work focuses on characterizing how gold NPs alter the aggregation mechanism and polymorph formation of human islet amyloid polypeptide (hIAPP) using two-dimensional infrared spectroscopy and isotope labeling. The incorporation of $^{13}$C$^{18}$O isotope labels allows for residue specific kinetic and structural information to be obtained, including the identification of oligomeric species. Our initial results show that gold NPs inhibit the aggregation of hIAPP and alter the transition dipole strength of the aggregated fibrils, suggesting the formation of a more ordered system. A separate isotope-labeled hIAPP species has shown that gold NPs prolong the presence of a β-sheet intermediate. Additional kinetics studies are underway to fully understand how gold NPs modulate the aggregation mechanism and influence the final fibril structure of hIAPP.

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**Wednesday**

**3925269 - Ultrafast spectroscopy of molecules with quantum light and optical cavities**

08:00am - 08:30am USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)

Shaul Mukamel, Presenter; Bing Gu; Yonghao Gu; shichao sun; Feng Chen; Haiwang Yong; Vladimir Chernyak

Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

Nonlinear spectroscopy has been instrumental for probing dynamical processes in a wide variety of material systems ranging from atoms, molecules to biological complexes. These techniques mostly rely on coherent laser pulses with well-defined electric field and phase. Employing quantum light in nonlinear molecular spectroscopy has brought many novel opportunities to enhance the signal-to-noise ratio, the resolution, and the selectivity of transition pathways. In this talk, we will show how photoelectron signals generated by time-energy entangled photon pairs can monitor ultrafast excited state dynamics of molecules with high joint spectral and temporal resolutions, not limited by the Fourier uncertainty of classical light. This technique scales linearly with the pump intensity, allowing the study of fragile biological samples with low photon fluxes. Optical cavities provide another means for controlling the photochemistry and photophysics of molecules by making use of strong light–matter coupling without chemical modifications or strong external laser pulses. Here, we present a quantum dynamical study on the charge migration in molecules by coupling to an optical cavity, which can activate and enhance the targeted charge migration modes that are originally inactivated or suppressed.

**Wednesday**

**3918265 - Coherent effects in sum frequency generation microscopy of surfaces**

08:30am - 09:00am USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)

Steve Baldelli, Presenter

Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
Second-order nonlinear optics has become a valuable method to investigate surfaces and interfaces. The characterization of the heterogeneity on these systems is important to provide the correct interpretation of the spectroscopic signals and therefore the surface chemistry. Thus surface-sensitive nonlinear optical microscopy has been developed. In second-order nonlinear optical microscopy, the direct conversion of $\chi^{(2)}_{\text{eff}}$ into chemically relevant information is challenging and a major contributor is the coherent nature of the nonlinear signal. The coherence properties affect the spatial, spectral, and resolution interpretation of the images. The effects of coherence in several microscopy techniques are discussed with most considerations on imaging microscopy. This paper describes and discusses several key influences of coherence in sum frequency generation spectroscopy (SFG) used for surface microscopy. Coherent illumination of the sample with spatially structured or smooth beams results in potential edge diffraction effects and spatial coherence across the field of view. Also discussed are spectral coherence effects that occur in nonlinear spectroscopy and the resulting influence on the image. Knowledge of these coherence effects leads to a more accurate interpretation of the SFG image.

**Wednesday**

**3918261 - Multi-dimensional Widefield infrared-encoded spontaneous emission microscopy**

09:00am - 09:30am USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)

Chang Yan; Wei Xiong, Presenter

Division: [ANYL] Division of Analytical Chemistry

Session Type: Oral - In-person

Photoluminescence (PL) imaging is a powerful technique with broad applications in visualizing biological activities, detecting chemical species, and characterizing materials. However, traditional PL imaging is often limited by the number of independently resolvable chromophores within the detection spectral windows, which can constrain the information that can be encoded in an image. To address this limitation, we have developed a novel PL microscopy technique called Multi-Dimensional Widefield Infrared-encoded Spontaneous Emission (MD-WISE) microscopy, which is based on the nonlinear interactions between mid-infrared and visible excitations on matters. Unlike traditional PL imaging techniques that rely on a single variable to distinguish chromophores, MD-WISE microscopy employs three independent variables: the temporal delay between the infrared and the visible pulses, and the optical frequencies of the two pulses. This method enables the discrimination of chromophores with nearly identical emission spectra, and it operates under widefield imaging conditions, allowing for high-speed multiplexing. MD-WISE microscopy relies on two mechanisms: modulating the optical absorption cross sections of molecular dyes by exciting specific vibrational functional groups, and reducing the PL quantum yield of semiconductor nanocrystals through strong field ionization of excitons. The potential applications of MD-WISE microscopy are significant. By demonstrating the capacity to register multi-dimensional information into PL
images, it has the potential to expand the number of species and processes that can be simultaneously tracked in high-speed widefield imaging applications. Overall, MD-WISE microscopy represents a significant advancement in the field of PL imaging and has the potential to impact a wide range of scientific disciplines.

Wednesday

3921123 - Designing plasmonic photocatalysts with ultrafast SERS
09:30am - 10:00am USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Renee Frontiera, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
This talk will focus on our development and application of ultrafast surface-enhanced Raman spectroscopy (SERS) as a probe of plasmon-molecule dynamics. Plasmonic nanomaterials are extremely promising for solar energy conversion applications, due to their massive optical cross sections, generation of highly non-equilibrium nanoscale environments, and facile tunability across the solar spectrum. However, guiding principles on how to best design a plasmonic photocatalyst for a specific chemical reaction are lacking, in part due to a lack of quantitative metrics as to how these reactions proceed. Ultrafast SERS is ideally suited to provide these insights as it is capable of tracking molecular dynamics in plasmonic hot spots. We have used this technique to quantify photoreduction potentials and to develop new methods to control plasmon-to-molecule energy flow. Overall, this technique provides a unique window into the rapidly evolving and highly coupled plasmonic molecular system.

Wednesday

Intermission
10:00am - 10:10am USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

Wednesday

3922509 - Probing hydration structures of biomolecules at interfaces
10:10am - 10:40am USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Elsa Yan, Presenter; Ethan Perets; Daniel Konstantinovsky; Sharon Hammes-Schiffer
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
The challenge of comprehending the role of water in biological processes still stands as a challenge in the life sciences. The study of water structures in
hydration shells of biomolecules in their natural environments remains difficult due to the excessive background noise from aqueous surroundings. Furthermore, when biological molecules exist at interfaces, the hydrogen bonding network of water is abruptly terminated, creating additional complexity, resulting in biomolecular hydration that varies at interfaces when compared to bulk solutions. Here, we apply a combination of experimental and computational techniques using chiral vibrational sum frequency generation (chiral SFG) spectroscopy to analyze the hydration structures of proteins and DNAs at aqueous interfaces. Our findings indicate that the chiral SFG signals of water O-H stretches emanate from the first hydration shells of these biomolecules, and that these molecules transfer their chirality to the surrounding water solvent. This transfer of chirality is significant because it implies that a comprehensive description of biomacromolecule chirality should include their hydration. Our work introduces opportunities for utilizing chiral SFG to tackle research challenges in biology, such as folding of biomolecules at aqueous interfaces and the molecular origins of homochirality in life.

Wednesday
3918297 - Coherent phonon spectroscopy of single colloidal quantum dots
10:40am - 11:10am USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Elad Harel, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
The electronic states of semiconductor quantum dots are coupled to phonons, which are quantized vibrations of the host lattice. Phonons generate sidebands in the photo-emission spectrum whose states can exchange energy with the quantized electronic states. Further, they lead to dephasing of the QD exciton through carrier-phonon scattering. While the importance of phonons has been well-known, single quantum dot experiments have thus far relied on low-temperature photoluminescence where phonon sidebands may be observed in some instances. Here, we demonstrate that phonons in the ultralow frequency region may be measured directly on a single colloidal quantum dot, CdSe/ZnS, with a diameter of 5-7 nm at room temperature. The phonon spectrum is measured by examining the scattering of a probe pulse induced by a time-delayed pump pulse at the single quantum dot level, which is then subsequently measured by correlated high-resolution transmission electron microscopy (TEM). Correlating the phonon spectrum with TEM reveals significant inhomogeneity in the phonon modes due to variance in size, shape, etc. of the core-shell QD. The ability to correlate the phonons to the atomic structure of the QD is an important step in understand and controlling the role of phonons in their optical properties.

Wednesday
3926657 - Photonic electrochemistry
Voltage ranks among the most foundational properties in science and engineering. Without voltage, biological cells are dead, batteries don't work, and the lights are out. Today's voltage measurements are either invasive (requiring electrical leads stuck into the sample) or time-limited (requiring slow electrokinetic or scanning methods, or dyes that quickly bleach). What is needed is a quantitative, non-invasive, label-free, and direct measurement of absolute voltage. Our proof-of-concept pilot using nJ laser pulses in a non-imaging geometry shows measurements of a sample's nonlinear optical amplitude and phase directly yield the total potential of an oxide:water interface in just a few seconds (JACS, 144, 16338, ’22; JPCL, 12, 5649, ‘21; JPCL, 10, 2328, '19; Nat. Comm. 8, 1032, '17). The method fully recapitulates X-ray and electrical impedance measurements, which are much slower. New developments aimed at elucidating the molecular origin of the electrochemical overpotential that hampers progress in the areas of electrolyzers (nickel) and solar photoanodes (iron oxides) are discussed.

Wednesday

3917362 - Investigation of tetracycline's impact on the bacterial membrane with second harmonic scattering
11:40am - 12:00pm USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
**Eleanor Page, Presenter; Tessa Calhoun**
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
The growing threat of antibiotic resistance continues to drive drug development research. To develop more successful antibiotics, the interactions between these small molecules and bacterial membranes need to be uncovered. We monitor the effect of tetracycline (Tc), a broad-spectrum antibiotic, on the membrane of live *S. aureus* cells using second harmonic scattering (SHS), which is especially sensitive to changes in the cell interface environment due to its symmetry dependence. While a previous study proposed that Tc resides within the hydrophobic portion of the membrane, causing overall distortion, our SHS results have shown that there is a more complex interaction occurring.

**Advances in Applied Nonlinear Spectroscopy:**
02:00pm - 06:00pm USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Steve Baldelli, Organizer; Dr. Wei Zhao, Organizer; Carlos Baiz, Presider; Robert Felsted, Presider
Division: [ANYL] Division of Analytical Chemistry
The symposium will cover a broad range of topics in applied nonlinear spectroscopy, including but not limiting to coherent multidimensional spectroscopy (CMDS), sum frequency generation (SFG), femtosecond stimulated Raman spectroscopy (FSRS), and coherent nonlinear optical imaging.

**Wednesday**

**3914604 - Two-dimensional electronic-vibrational spectroscopy: A method to study the dynamics of complex systems**

02:00pm - 02:30pm USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)

Dr. Graham R. Fleming, Presenter; Cristina Leonardo; Shiun-Jr Yang

Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

Two dimensional electronic vibrational (2DEV) spectroscopy involves electronic excitations and infrared detection to produce 2D maps of excitation frequencies vs. detection (IR) frequencies. Because the factors that shift electronic absorption frequencies are often uncorrelated with the environmental influences on vibrational frequencies, the resolution of 2EDV spectra is far superior to degenerate four-wave mixing methods such as 2D electronic spectroscopy for congested spectra of molecular complexes, for example. In addition, 2DEV spectra record cross correlations rather than autocorrelations via the lineshape. I will illustrate the power of 2DEV spectroscopy via an analysis of the Photosystem II supercomplex which contains over 200 chlorophyll molecules.

**Wednesday**

**3907328 - Femtosecond stimulated Raman spectroscopy (FSRS)**

02:30pm - 03:00pm USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)

Richard Mathies, Presenter

Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

For chemists interested particularly in following reaction dynamics with time resolved structural techniques, femtosecond stimulated Raman spectroscopy or FSRS is particularly useful. By employing a broad-band fs stimulated Raman probe pulse followed by dispersion and spectral detection of the probe, high time precision transient vibrational (aka structural) information is obtained (see figure). This talk will review how FSRS, inspired by early fs dynamic absorption spectroscopy experiments, was first performed in the early 2000’s (1,2). These works demonstrated the successful development of apparatus that obtained high time-resolution vibrational spectra of polyene systems beyond the traditional uncertainty principle limits of ps vibrational spectroscopy. The early technologies and theoretical descriptions will be found in refs. 3-4. Applications to chemical isomerization reactions and to biochemical isomerizations in bacteriorhodopsin,
rhodopsin and GFP followed. For references on this early work see reviews 5-7. For more recent reviews on the application of FSRS to a variety of solution and solid-state materials see refs 8-9.

Wednesday

3929164 - 2D spectroscopy, a quantitative theory of luminescence, and ultrafast thermodynamics
03:00pm - 03:30pm USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Sarang Yeola; Callum Douglass; Aman Agrawal; David M Jonas, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

Chemists have generally treated absorption and luminescence as practically independent even though we have quantum pictures of absorption and emission between a pair of electronic states. The practical independence arises for a variety of reasons: many molecules exist in multiple forms that do not equilibrate on the luminescence timescale; others luminesce after a photochemical reaction, so that the emitting molecule is not the same as the absorbing molecule; sometimes molecular environments are heterogeneous. Remarkably, by spreading heterogeneity out in a second dimension, 2D spectroscopy has revealed a model-free single-molecule relationship between molecular absorption and emission that requires only weak excitation, thermalized spectra, and retention of molecular identity between absorption and emission. This no-adjustable-parameters theory of luminescence provides an opportunity to build on state-of-the-art calibration procedures for fluorescence spectrometers that were developed about a decade ago through efforts led by NIST (USA) and BAM (Germany). These have enabled new thermodynamic insights into molecular systems on the luminescence timescale.

Wednesday

3917270 - Enhancing signal-to-noise ratios in third-order nonlinear spectroscopy: new optical implementations and machine learning
03:30pm - 04:00pm USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Carlos Baiz, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

Ultrafast spectroscopy often requires measuring weak nonlinear optical signals, which are typically about three orders of magnitude lower in amplitude compared to the incoming pulses. Measuring such nonlinear signals often require very stable laser setups as well as long data acquisition times. Laser intensity fluctuations, thermal fluctuations, and optical drift are typical challenges. In this talk, I will present a new implementation of two-dimensional infrared spectroscopy (2D IR) in which we apply rapid-scanning techniques using a pulse
shaper to reduce noise in spectra and suppress scatter and combine this with a background-free detection that enables control of the local-oscillator intensity independent from the signal. In addition, I will describe new machine-learning approaches to improve signals by capturing spatial and temporal correlations in the fluctuations of the laser pulses, as well as adversarial neural network techniques to reconstruct 2D IR spectra. The machine learning methods are general and can be applied to many nonlinear techniques and a range of different optical setups.

Wednesday
Intermission
04:00pm - 04:10pm USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person

Wednesday
3925401 - Resolution of parallel relaxation pathways in transition metal complexes with 2D electronic spectroscopy
04:10pm - 04:40pm USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Gabriela Schlau-Cohen, Presenter
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
Transition metal-based charge-transfer complexes represent a broad class of inorganic compounds with multiple photochemical applications. Ruthenium- and iridium-based polypyridyl complexes have favorable photophysical properties but are limited by low natural abundance. Analogous compounds based on earth-abundant elements, such as the canonical [Fe(bpy)₃]²⁺, are of increasing interest, but optimizing their photophysical properties requires baseline knowledge of their behavior. The dynamics of [Fe(bpy)₃]²⁺ within the ligand-field manifold are well studied, but the dynamics within the metal-to-ligand charge-transfer (MLCT) states have remained elusive due to the sub-100 fs lifetime of these states. Here, we monitor the dynamics of the MLCT states of [Fe(bpy)₃]²⁺ using 2D electronic spectroscopy (2DES). First, we resolved a peak consistent with a ¹MLCT→³MLCT transition, indicating that intersystem crossing takes place within the charge-transfer manifold. Second, we showed that the stabilization of the radical anion correlated with the inertial response time of the solvent, suggesting it plays a mechanistic role. Resolution of these dynamics highlights the ability of 2DES to deconvolve the excited-state dynamics of charge-transfer complexes that are otherwise difficult to observe.

Wednesday
3926840 - Extracting energy from singlet fission materials
Singlet exciton fission (SF) is a unique energy conversion process that generates a pair of spin-triplet excitons from a single spin-singlet exciton. SF can potentially be harnessed to produce high-efficiency photovoltaic devices and new materials for quantum computing and sensing applications, but an improved understanding of how excitons move in SF materials and how these materials can be interfaced with modern electronics is needed. In this presentation, I will highlight methods employed by my group to track both exciton transport within SF materials and energy transfer from SF materials to silicon, the workhorse component of modern electronics. Using transient absorption microscopy, we have quantified rates of exciton diffusion within single perylenediimide crystals that undergo SF. We find that equilibration between SF and its inverse process, triplet fusion, plays a critical role in driving triplet exciton transport as it allows triplets to effectively diffuse by converting into singlet excitons that can more rapidly diffuse. Such singlet-mediated triplet diffusion has previously been observed in acene single crystals, but our work highlights that this mechanism is likely generalizable to a wider variety of SF materials. I will also describe transient reflectivity measurements performed on perylenediimide thin films deposited on silicon(111) substrates. We find that photoexcitation of perylenediimide thin films leads to an enhancement of charge carrier generation in silicon, suggesting excitons produced in the perylenediimide layer can photosensitize charge carrier production in silicon. Prospects for enhancing carrier generation by chemically functionalizing silicon with molecules that can enhance electronic coupling between silicon and a perylenediimide overlayer will be discussed. Our work highlights that by making careful design choices, the prospects for incorporating SF materials into modern electronics are indeed bright.
given a sequence. Errors in thermodynamic predictions can lead to miscalculations of important energetic parameters that impact applications, including the duplex melting temperature. Many are due to a lack of measurements that can monitor DNA melting temperatures at the level of a single base pair. Here, we show how the C2=O stretching vibration of the thymine base may serve as a molecular thermometer to provide a direct measurement of local base pair rupture using nucleobase isotope editing and variable temperature ATR FTIR spectroscopy.

Wednesday
3929235 - Can 2DFT spectroscopy detect vibronic coherence in photosynthetic complexes under physiological conditions?
05:40pm - 06:00pm USA / Canada - Pacific - August 16, 2023 | Location: Room 2005, West Bldg. (Moscone Center)
Aman Agrawal, Presenter; Prof. Vivek Tiwari; David M Jonas
Division: [ANYL] Division of Analytical Chemistry
Session Type: Oral - In-person
A few groups have reported quantum beat oscillations with picosecond decay times in femtosecond 2D spectra of the FMO complex from green sulfur bacteria at 77K. The strongest oscillations are attributed to coherence arising from anti-correlated vibrations on the ground electronic state. Recently, Miller and coworkers recorded 2D spectra of FMO complex at physiological temperature and reported that any anti-correlated vibrational oscillations, if present, must be below the level 5% in their 2D spectra. These results motivated simulation and comparison of 2D spectra at 80K and 300K for a dimer model that is loosely based on FMO. The model parameters are based on one pair of excitons in the FMO complex from green sulfur bacteria and were previously used to show that the 2D quantum beat oscillations in low temperature 2D spectra arise from the stimulated Raman excitation of anti-correlated vibrational wavepackets on the ground electronic state of the dimer, in which neither pigment is excited. The 2D spectra at 300K are broadened and show oscillations in the 2D amplitude that are smaller than at 80K and below the noise floor of the recent 2D experiment at physiological conditions. The anti-correlated vibrational enhancement of the strongest oscillations on the Stokes' cross-peak disappears and the phase of the oscillations changes. From an analysis of the Feynman diagrams, this is attributed to the out-of-phase cancellation of anti-correlated oscillations for overlapping 2D peakshapes. These results show that vibronic decoherence of anti-correlated vibration is not needed to explain the experimental 2D spectra, so that the role of anti-correlated vibration in energy transfer at physiological conditions remains an open question.