

One Day Meeting on Spectroscopy, Photonics and Dynamics (SPD-2020)

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Abstracts

IL-1

What new we learn from extended dynamic Stokes shift measurements and large-scale atomistic simulation in DNA?

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Water around biomolecules is special both in terms of its structure and dynamics. The questions that how water and ions around these biomolecules behave in terms of their structure and dynamics, and how they affect the biomolecular functions have triggered tremendous research activities worldwide. Such activities not only unfolded important static and dynamic properties of water and ions around these biomolecules, but also provoked heated debate regarding their explanation and role in biological functions. DNA being negatively charged interacts strongly with surrounding dipolar water and positively charged counterions, leading to complex electrostatic coupling of water and ions with the DNA. In this talk I will show that several previous studies on dynamic Stokes shifts in DNA provided incomplete picture of DNA solvation, which triggered debated views in literature. It will be shown that by performing dynamic Stokes shifts over extended time-range from ~100 fs to 10 ns, together with large-scale atomistic simulation, one can obtain a complete understanding of the DNA solvation. It will be shown how DNA sequence and backbone fluctuations can induce local solvation dynamics near minor groove. Remarkably however, we see that the nature of slow solvation dynamics in DNA minor groove is universal as measured in minor groove created by small oligonucleotide or by nucleosomal DNA.

IL-2

Probing the origin of self trapped excitons in 1d hybrid lead halide perovskites

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Lead halide perovskites have emerged as an interesting class of materials because of their photo-physical properties like high PL quantum yield, narrow emission bandwidth, low threshold lasing, high PCE, etc. These properties are due to their intrinsic defect tolerant band structure as compared to conventional semiconductors. Lead halide perovskites crystallize in a variety of structures ranging from 3D to 0D. Lower dimensional lead halide perovskites (2D, 1D, 0D) show some interesting optoelectronic properties. The optical properties in lower-dimensional lead halide perovskites strongly depend upon A-site cation, which is not the case in 3D analogs. In addition to quantum confinement, the lower dimensional perovskites also show dielectric confinement.

We synthesized strongly confined one dimensional (1D) Pyridinium lead bromide (PyPbBr₃) perovskite single crystals. Due to strong confinement in two dimensions and the presence of an aromatic cation, these perovskite crystals show interesting optical properties. A strong and highly Stokes shifted PL emission is observed, at room temperature. The origin of this emission is attributed to exciton self-trapping. We used Optically Heterodyned-Optical Kerr Effect Spectroscopy (OH-OKE) to understand the mechanistic origin of this self-trapped excitonic emission and the role of aromatic π -electron cloud in exciton self-trapping.

IL-3

Tryptophan Radical Cation Mediates Charge Transfer Chemistry at the Cu-active site in Azurin

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Azurin is a blue copper protein having cysteine as one of the active site ligand which generates S-to-Cu²⁺ ligand-to-metal (LMCT) band at 628 nm leading to its blue color.¹ It has been hypothesized that the Cu²⁺ active site electronically couples to the protein scaffold with a spatial lengthscale of >10 Å.² However little is known about the exact electronic nature of the coupling, and the ensuing photo-excited charge transfer dynamics leading to protein-centered charge intermediates. Here using femtosecond broadband transient absorption spectroscopy we observe evidence for rapid relaxation between two distinct CT states in the LMCT manifold with a 300-fs time constant followed by recombination of charges in sub-picosecond timescales. Remarkably, we see the presence of a Tryptophan cation radical

signature which forms within 100 femtoseconds substantiating the presence of long-range ($>10 \text{ \AA}$) electronic coupling for the first time between the copper active site and Trp48 residue. The Fourier transform Raman spectra obtained from impulsively excited LMCT state unequivocally shows the presence of Raman frequencies corresponding to Trp cation radical along with vibrational modes assigned to the Cu-active site.³ Our results indicate the surprising delocalization length scale of the initially populated CT state, and thereby highlighting the possibilities of using Azurin photochemistry for energy conversion technologies.

References

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IL-4

Optical studies of I-III-VI₂ Nanocrystals

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I-III-VI₂ semiconductor quantum dots offer significant advantages over more conventional II-VI QDs, however their physical properties remain poorly understood. I will discuss recent progress made towards understanding the physical properties of I-III-VI₂ semiconductor nanocrystals. The presentation will try to provide a picture of the electronic structure and photophysics of I-III-VI₂ QDs as inferred from spectroscopic studies. The implications of these properties for devices will be discussed.

IL-5

Probing isotope-specific heavy and semi-heavy water by cavity ring-down spectroscopy

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Cavity ring-down spectroscopy (CRDS), an optical cavity-enhanced absorption spectroscopy technique, directly measures the rate of absorption of light rather than the magnitude of absorption when the light is circulating in a high-finesse optical cavity. Because of its unique approaches, this technique readily offers 10 to 100 million times better detection sensitivity when it is compared with the traditional absorption spectroscopy techniques. In this talk, I will discuss the underlying mechanisms of the triple-oxygen (¹⁶O, ¹⁷O and ¹⁸O) isotopic content of deuterated (D) isotopologues of water in H-D exchange reactions in the gas-phase.

We have demonstrated the high-resolution gas-phase spectral analysis of doubly (D_2O) and singly (HDO) deuterated isotopologues of water in the region around 7.8 μm using quantum cascade laser (QCL)-based CRDS technique. The isotopic fractionations among doubly and singly deuterated species of water, $D_2^{16}O$, $HD^{16}O$, $HD^{17}O$, and $HD^{18}O$ in the gas-phase were carried out by probing the fundamental and hot band transitions in the ν_2 (bending) mode of D_2O and the fundamental ν_2 transitions for the other water isotopes. We subsequently investigated the fractionations of different D-enriched water isotopologues for the H-D exchange reaction using various mixtures of D_2O in H_2O . We explored the potential role of triple-oxygen isotopic contents through enrichments and depletions of $HD^{16}O$, $HD^{17}O$ and $HD^{18}O$, involved in the H-D reaction. Our direct and quantitative experimental evidences reveal a new picture of gas-phase isotopic fractionation chemistry in a mixture of light and heavy water (H_2O - D_2O). I will also talk about the isotope-specific water metabolism linking biological and physiological processes in human body. Finally, I will briefly talk about separation of D_2O into its Ortho and Para isomers.

References

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IL-6

Dynamical exchange of protein corona improves cell internalization

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It is practically impossible to avoid the formation of protein corona surrounding nanoparticle when it enters into the biological fluid. Several approaches in recent past, including the pre-coating by antibody, PEG or proteins helped in reducing such corona formation and thus improving the cell internalization and targeting ability, however, nanoparticle based chemotherapy still remain a great challenge for clinical trials. Here, instead of avoiding corona formation, we rather show that the dynamical exchange of the loosely adsorbed proteins onto the glutathione-folic acid functionalized nanocarrier (NC) helped in increasing the cell internalization dramatically. Using fluorescence lifetime imaging microscopy (FLIM) and super resolution radial fluctuation (SRRF), we show, how the cell internalization improves the efficacy of drug delivery into the cancer cell.

IL-7

Plasmon-exciton coupling in dispersionless plasmonic structures

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Surface plasmon polaritons (SPPs) are charge density waves localized at a metal-dielectric interface. Geometry defined dispersion in patterned surfaces (plasmonic crystals) were used in physics, chemistry, biology and engineering studies. After briefly introducing the broadband, dispersionless plasmonic structure, in this talk I will present some intriguing results related to beam shifts and charge transport in PIQC - organic semiconductor complexes. These studies address the question, “is there strong coupling between the vacuum states of plasmons and the excitons in organic semiconductors that modulates the conductivity?”

IL-8

Non-linearity and temperature dependence of light shifts in magnetic resonance and optical spectroscopy

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We theoretically investigated the non-linearity of drive influenced shifts in a fluctuation regulated environment and study the temperature dependence of the shifts using a recently proposed fluctuation regulated quantum master equation (frQME). Our result agrees with the known form of the shifts in the low temperature regime. However, in the high temperature regime we find the shifts decay following a power-law ($1/T^2$) behavior. The shifts are obtained in a closed generic form over the entire detuning range of the drive. It turns out that at very high detuning being the environmental correlation time scale) our result produces the known form of the shifts whereas on the other regime i.e. near resonance condition a non-linear dependence of the shifts is found on the inverse detuning frequency which explains the departure from the known linear form of the shifts.

IL-9

Emerging Two-Dimensional Lateral Heterostructures

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Atomically thin two-dimensional (2D) transition metal dichalcogenides (TMD) heterostructures have made tremendous research interest for fascinating physical properties and emerging applications in ultra-smart and flexible optoelectronic devices, including

transistors, diodes, memory devices, LEDs, solar cells, photodetectors, quantum emitters and sensors. 2D lateral and vertical heterostructures can offer exciting opportunities to manipulate the formation, confinement and transport of electrons, holes, excitons and polaritons at the ultimate thickness limits. Unlike vertical heterostructures, lateral heterostructures with atomically sharp interface can be fabricated only via direct growth. To dates, several proof-of-concept 2D devices rely mostly on mechanical exfoliation of different van der Waals materials. This approach can result in interfacial contamination during the transfer process, and lacks scalability. In addition, the cumulative properties of these heterostructures are dominated by the precise positioning of individual atomic layers and their coupling strength. Furthermore, the optoelectronic performance of most 2D heterostructure based devices falls far below the theoretical predicted values owing to several intrinsic and extrinsic factors. These major issues will be discussed.

Recently, we demonstrated a novel, simple and scalable protocol for the direct fabrication of wide range of high-quality lateral TMDs heterostructures in the form of $\text{MoX}_2\text{-WX}_2$ (where X= Se or S), only changing the reactive gas environment in the presence of water vapor.^{1,2} These TMD heterostructures are extensively characterized through Raman and Photoluminescence spectroscopy and correlated with the electrical and structural characteristics. The extent of the spatial modulation of individual TMD domains as well as their optical and electronic transition characteristics across the heterojunctions are studied in detail.^{1,2} Tip-enhanced photoluminescence (TEPL) imaging, with sub-wavelength spatial resolution,^{3,4} has been used to correlate the nanoscale optical properties with that of structural characteristics of the $\text{MoX}_2\leftrightarrow\text{WX}_2$ transition, in the 2D plane.⁴ Electrical transport measurements revealed diode-like responses across the 2D lateral junctions. We found that bilayer heterostructures are as robust as monolayer, in terms of optoelectronic characteristics such as observation of room temperature electroluminescence.² This study will further supplement the quantitative evaluation of optical properties of various 2D heterostructures for the development of more complex and atomically thin in-plane superlattices and optoelectronic devices.

References

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IL-10

Omnidirectional transport and navigation of Janus particles through a nematic liquid crystal film

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I will present some recent results on the electric field driven transport properties of Janus particles. In a striking departure from conventional electrophoresis, we show that metal-dielectric Janus particles can be piloted at will through a nematic liquid crystal film, in the plane perpendicular to an imposed AC electric field. We achieve complete command over particle trajectories by varying field amplitude and frequency, exploiting the sensitivity of electro-osmotic flow to the asymmetries of particle and defect structure. We propose a new method for measuring the induced electrostatic dipole moment of the Janus particles, through competition between elastic and electrostatic interactions. These findings open unexplored directions for the use of colloids and liquid crystals in controlled transport and assembly.

IL-11

Targeting the pathogenic fibrillation of α -synuclein using non-toxic and ultra-small luminescent gold nanoclusters

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Misfolding and aggregation of the neuronal protein α -Synuclein (A-Syn) has been directly linked to the pathogenesis of Parkinson's disease (PD)-the second most common neurodegenerative disorder. So that identifying (or synthesizing) molecules to modulate the pathogenic aggregation of A-Syn has been extensively investigated as a means to tackle PD pathogenesis, leading to reports on various kinds of anti-aggregation agents. However, none so far have made it to becoming an actual disease-modifying drug for PD; one major reason being the difficulty in transporting most therapeutics across the blood-brain barrier (BBB). In this context, nanomaterials, particularly the *non-toxic and ultra-small BBB-permeable* gold nanoclusters, are promising candidates to be used against the pathogenic aggregation of A-Syn. In the present work, we show for the first time, how two easily synthesizable, biocompatible and ultra-small gold nanoclusters effectively modulate the fibrillation of A-Syn *in vitro* producing less toxic aggregates. They also alleviate cytotoxicity caused by pre-fibrillar and fibrillar aggregates of A-Syn to cultured human neuronal cells. In addition, we utilize the inherent strong luminescence of one of the AuNCs to detect its BBB permeability (in mice) by simple fluorescence measurement. Thus, our findings point towards the prospective use of non-toxic ultra-small gold nanoclusters as potential drugs against PD and other Synucleinopathies; while also exploring a new scope of their application.

IL-12

Inhibition of the host inflammatory response by bacterial deamidases

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The deamidase OspI from enteric bacteria *Shigella flexneri* deamidates a glutamine residue in the host ubiquitin-conjugating enzyme UBC13 and converts it to glutamate (Q100E). Consequently, its polyubiquitination activity in complex with the RING-finger ubiquitin ligase TRAF6 and the downstream NF- κ B inflammatory response is inactivated. The precise role of deamidation in inactivating the UBC13/TRAF6 complex is unknown. We report that deamidation inhibits the interaction between UBC13 and TRAF6 RING-domain (TRAF6^{RING}) by perturbing both the native and transient interactions. Deamidation creates a new intramolecular salt-bridge in UBC13 that competes with a critical intermolecular salt-bridge at the native UBC13/TRAF6^{RING} interface. Moreover, the salt-bridge competition prevents transient interactions necessary to form a typical UBC13/RING complex. Repulsion between E100 and the negatively charged surface of RING also prevents transient interactions in the UBC13/RING complex. Our findings highlight a mechanism where a post-translational modification perturbs the conformation and stability of transient complexes to inhibit protein-protein association.

Reference

Mohanty P, Rashmi A, Habibullah BI, Geetha Surendran A, Das R, (2019), "Deamidation disrupts native and transient contacts to weaken the interaction between UBC13 and RING-finger E3 ligases," *eLife* 8: e49223.