

# EAWCD 2024

## The 24th East Asia Workshop on Chemical Dynamics

 March 18 ~ 20

# ABSTRACT BOOK



中央研究院  
ACADEMIA SINICA



中央研究院 原子與分子科學研究所  
Institute of Atomic and Molecular Sciences  
Academia Sinica

# EAWCD 2024 Program

## March 18 (Monday)

08:30 ~ 09:00	Registration
09:00 ~ 09:10	Welcome opening speeches
	Chair: Takuya Horio (Kyushu University)
09:10 ~ 09:50	<b>Thomas Schultz (Ulsan National Institute of Science and Technology)</b> <i>Correlating Parent-Fragment Relationships in Molecular Cluster Photoionization</i>
09:50 ~ 10:30	<b>Pei-Ling Luo (Academia Sinica)</b> <i>A new approach to kinetic studies of radical-radical reactions using time-resolved dual-comb spectroscopy</i>
10:30 ~ 10:50	Coffee break
	Chair: Gabriel da Silva (The University of Melbourne)
10:50 ~ 11:30	<b>Christopher S. Hansen (University of New South Wales)</b> <i>Fluoroform (CHF<sub>3</sub>) production from CF<sub>3</sub>CHO photolysis and implications for the decomposition of hydrofluoroolefins in the atmosphere</i>
11:30 ~ 12:10	<b>Jae Woo Park (Chungbuk National University)</b> <i>Multireference Quantum Chemistry for Exploring Potential Energy Surfaces (II) Large Active Spaces</i>
12:10 ~ 13:30	Lunch and Group photo
	Chair: Chia C. Wang (National Sun Yat-sen University)
13:30 ~ 14:10	<b>Toshiki Sugimoto (Institute for Molecular Science)</b> <i>Sum-frequency generation vibrational spectroscopy for pioneering many-body physico-chemical properties of interfacial molecular systems: Advancement from far-field to near-field scheme</i>
14:10 ~ 14:50	<b>Yu-Chieh Wen (Academia Sinica)</b> <i>Momentum-dependent nonlinear optics of electrical double layer</i>
14:50 ~ 15:30	<b>Jongcheol Seo (Pohang University of Science and Technology)</b> <i>Ion behavior in the Evaporating Charged Droplets Generated by Electrospray Ionization</i>
15:30 ~ 15:50	Coffee break
	Chair: Taiha Joo (Pohang University of Science and Technology)
15:50 ~ 16:30	<b>Chun-Fu Chang (National Yang Ming Chiao Tung University)</b> <i>Effects of the Intermolecular Interactions on the Ultrafast Photoreaction Dynamics of Schizorhodopsin</i>
16:30 ~ 17:10	<b>Korenobu Matsuzaki (RIKEN)</b> <i>Inhomogeneity of hydrated electrons revealed by transient two-dimensional electronic spectroscopy</i>
17:10 ~ 17:50	<b>JunWoo Kim (Chungbuk National University)</b> <i>Coherent vibrational spectroscopy for exploring chemical reactivity</i>
18:30	Dinner ( By invitation only )

# EAWCD 2024 Program

## March 19 (Tuesday)

Chair: Kaito Takahashi (Academia Sinica)

**09:00 ~ 09:40** **Yuan-Pin Chang (National Sun Yat-sen University)**  
*Studying Heterogeneous Reactions in microdroplets via Aerosol Optical Tweezers (and the lessons I've learned)*

**09:40 ~ 10:20** **Martina Lessio (University of New South Wales)**  
*Computational insights into the catalytic hydrogenolysis of plastic waste using ruthenium nanoparticles*

**10:20 ~ 10:50** **Coffee break**

Chair: Yuan-Chung Cheng (National Taiwan University)

**10:50 ~ 11:30** **Kiyoshi Miyata (Kyushu University)**  
*Elucidation and Control of Microscopic Mechanisms in Molecular Photofunctional Materials*

**11:30 ~ 12:10** **Daeheum Cho (Kyungpook National University)**  
*Time-resolved Spectroscopic Measurement and Optical Cavity Manipulation of Ultrafast Phenomena*

**12:10 ~ 13:30** **Lunch**

Chair: Li-Kang Chu (National Tsing Hua University)

**13:30 ~ 14:10** **Tak W. Kee (University of Adelaide)**  
*Evolving Hydrogen Gas Using Triplet Excitons of an Organic Photocatalyst*

**14:10 ~ 14:50** **Woojae Kim (Yonsei University)**  
*Peculiar Photophysics of 2,2'-Bianthracene: Symmetry-Breaking Charge Transfer, Triplet Formation Dynamics, and Their Connection to Conformational Diversity*

**14:50 ~ 15:30** **Masahiro Shibuta (Osaka Metropolitan University)**  
*Ultrafast photoexcited state dynamics at organic molecular films studied by time-resolved photoelectron spectroscopy and microscopy*

**15:30 ~ 15:50** **Coffee break**

Chair: Oh-Hoon Kwon (Ulsan National Institute of Science and Technology)

**15:50 ~ 16:30** **Charlotte Petersen (The University of Melbourne)**  
*Measuring amorphous structure: How thermal vibrations reveal structural change*

**16:30 ~ 17:10** **Tzu-Hsiung Yang (National Tsing Hua University)**  
*What Can Generative Models Do for Quantum Information Processing? A Study Case on the Design of Molecular Qubits with Long Coherence Time*

**17:10 ~ 17:50** **I-Chung Lu (National Chung Hsing University)**  
*Unveiling the Mysteries of Matrix-Assisted Ionization in Mass Spectrometry for Enhanced Efficiency and Fundamental Insights*

**18:30** **Dinner ( By invitation only )**

# EAWCD 2024 Program

## March 20 (Wednesday)

Chair: Manho Lim (Pusan National University)

**09:00 ~ 09:40** **Felix J. Rizzuto (University of New South Wales)**  
*Photo-control of DNA assemblies through time and space*

**09:40 ~ 10:20** **Tomotsumi Fujisawa (Saga University)**  
*Raman optical activity spectroscopy of biological photoreceptors*

**10:20 ~ 10:50** **Coffee break**

Chair: Chung-Hsin Yang (National Sun Yat-sen University)

**10:50 ~ 11:30** **Junming Ho (University of New South Wales)**  
*Self-consistent fragment charges – A simple strategy to accelerate quantum chemistry calculations*

**11:30 ~ 12:10** **Takeshi Iwasa (Hokkaido University)**  
*Light-matter interaction with near-field: dynamics and spectroscopy*

**12:10 ~ 12:20** Closing

**12:20 ~ 13:00** **Lunch**

**13:40 ~ 16:30** Cultural Activity

**17:30** Dinner ( By invitation only )

# Correlating Parent-Fragment Relationships in Molecular Cluster Photoionization

J.C. Lee<sup>#</sup>, B.R. Özer, I. Heo, and T. Schultz

Ulsan National Institute of Science and Technology (UNIST), Korea

<sup>#</sup> Now at: Dept. of Chem. and Biosciences, ETH Zürich, Switzerland

e-mail: schultzt@gmail.com



Traditional spectroscopic methods are ill-suited for the investigation of heterogeneous samples. Spectroscopic signals carry no label to identify the signal origin and guesswork is required to assign an observed spectroscopic signal to a specific sample component. This is a big problem for molecular cluster spectroscopy: cluster sources emit a heterogeneous range of cluster structures and sizes. By correlating mass signals with rotational Raman spectra, we label each ion signal with the spectroscopic fingerprint of its neutral parent molecule. This creates a new capability to track fragmentation reactions for many species in a complex sample. A measurement for carbon disulfide clusters (see Figure) resolved 28 distinct ionization and fragmentation channels [1].

Rotational Raman spectra were measured with an infinite interferometer, reaching sub-kHz resolution over a 500 GHz spectral range [2]. This is 2 orders-of-magnitude better than the best FTIR data. The measurement principle and some further applications will be outlined.

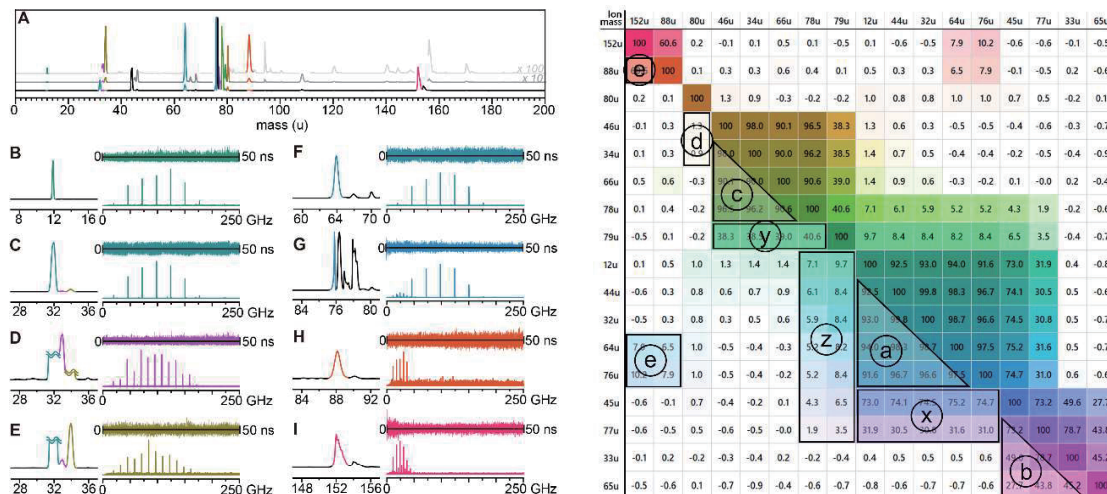


Fig. 1: (Left, A) Mass spectrum. (B-I) delay-dependent ion signal modulation and rotational Raman spectra for highlighted ions. (Right) Correlation map for selected ions reveals fragmentation channels, e.g., for the  $^{12}\text{C}^{32}\text{S}_2$  isotopologue (a), the  $^{12}\text{C}^{32}\text{S}_2$  isotopologue (b), and the  $\text{CS}_2$  dimer (e).

## References

[1] J.C. Lee, B.R. Özer, I. Heo, T. Schultz, arXiv:2402.08398. URL:

<https://doi.org/10.48550/arXiv.2402.08398>

[2] T. Schultz, I. Heo, J.C. Lee, B.R. Özer. *J. Korean Phys. Soc.* **82**, 919–927 (2023).

# A new approach to kinetic studies of radical-radical reactions using time-resolved dual-comb spectroscopy

**Pei-Ling Luo**

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei,  
Taiwan

e-mail: [plluo@gate.sinica.edu.tw](mailto:plluo@gate.sinica.edu.tw)



Radical-radical reactions play the important roles in many chemical reaction systems, but the kinetic studies of radical-radical reactions are typically challenging due to the difficulty of simultaneous determination of multiple unstable radicals. Herein, we propose a new approach to kinetic studies of radical-radical reactions by means of synchronized two-color time-resolved dual-comb spectroscopy (TR-DCS).<sup>1,2</sup> With this new approach, we currently have achieved the kinetic studies of the radical-radical reaction between OH and HO<sub>2</sub> via direct concentration measurements of OH and HO<sub>2</sub> radicals generated in the reaction system of the 248-nm photolysis of H<sub>2</sub>O<sub>2</sub>. Both OH and HO<sub>2</sub> can be quantified using the measured time-resolved dual-comb spectra and the line strengths of their fundamental transitions. In addition to introducing the capability of the novel spectroscopic technique with TR-DCS, detailed kinetic analysis on the reaction OH + HO<sub>2</sub> will also be presented.

## References

1. P.-L. Luo and I.-Y. Chen, *Anal. Chem.* **94**, 5752 (2022).
2. C.-W. Chang, I.-Y. Chen, C. Fittschen, and P.-L. Luo, *J. Chem. Phys.*, **159**, 184203 (2023).

# Fluoroform ( $\text{CHF}_3$ ) production from $\text{CF}_3\text{CHO}$ photolysis and implications for the decomposition of hydrofluoroolefins in the atmosphere

**Christopher S. Hansen**

UNSW Sydney

e-mail: [christopher.hansen@unsw.edu.au](mailto:christopher.hansen@unsw.edu.au)

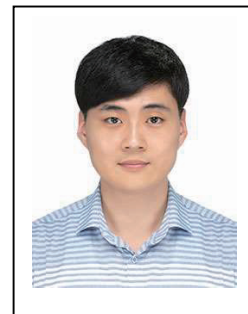


Hydrofluoroolefins (HFOs) are the leading synthetic replacements for compounds successively banned by the Montreal Protocol and amendments. HFOs readily decompose in the atmosphere to form fluorinated carbonyls, including  $\text{CF}_3\text{CHO}$  in yields up to 100%, which is then photolysed. A longstanding issue, critical for the transition to safe industrial gases, is whether atmospheric decomposition of  $\text{CF}_3\text{CHO}$  yields any quantity of  $\text{CHF}_3$  (HFC-23), which is one of the most environmentally hazardous greenhouse gases. This talk will describe the outcomes of a comprehensive, and largely unpublished, experimental investigation that combined velocity-mapped ion imaging (VMI), a new technique (purpose built) for determining relative photolysis quantum yields in a molecular beam, synchrotron multiplexed photoionisation mass spectrometry, Fourier-transform Infrared (FTIR) spectroscopy with *in situ* photolysis, chirped-pulse Fourier-transform microwave spectroscopy, and sophisticated atmospheric modelling to confirm that this reaction occurs under atmospheric conditions and provide pressure-dependent quantum and molar yields.

# Multireference Quantum Chemistry for Exploring Potential Energy Surfaces (II) Large Active Spaces

## Jae Woo Park

Department of Chemistry, Chungbuk National University (CBNU),  
Cheongju 28644, Korea  
e-mail: jaewoopark@cbnu.ac.kr



Limitations in the active space size are one of the significant difficulties in employing multireference quantum chemistry methods for studying chemical dynamics. Many approximate configuration interaction (CI) methods, such as density-matrix renormalization group (DMRG) or selected CI (SCI) theories, have been recently developed to overcome such difficulty. In this talk, I will present the recent progress in our group in developing and improving the adaptive sampling configuration interaction (ASCI) method [1–2] for obtaining the CASSCF-level results,[3–4] chemically accurate results with dynamical correlations,[5] and excited state potential energy surfaces.[6] I will also discuss the future research directions for studying chemical dynamics with the developed methods.

## References

1. Tubman, N. M.; Lee, J.; Takeshita, T. Y.; Head-Gordon, M.; Whaley, K. B. **J. Chem. Phys.** 145, 044112 (2016).
2. Levine, D. S.; Hait, D.; Tubman, N. M.; Lehtola, S.; Whaley, K. B.; Head-Gordon, M. **J. Chem. Theory Comput.** 16, 2340 (2020).
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4. Park, J. W. **J. Chem. Theory Comput.** 17, 4092 (2021).
5. Park, J. W. **J. Chem. Theory Comput.** 19, 6263 (2023).
6. Kim, S. Y.; Park, J. W. **J. Chem. Theory Comput.** 19, 7260 (2023).



# Sum-frequency generation vibrational spectroscopy for pioneering many-body physico-chemical properties of interfacial molecular systems: Advancement from far-field to near-field scheme

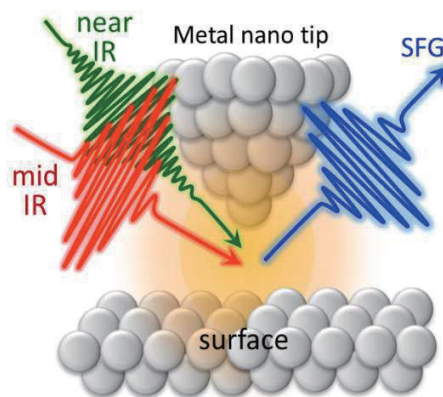
**Toshiki Sugimoto**

Institute for Molecular Science, [toshiki-sugimoto@ims.ac.jp](mailto:toshiki-sugimoto@ims.ac.jp)



Interfacial molecules are ubiquitous in nature and play crucial roles in various fields such as physics, chemistry, and biology. The widespread impacts of interfacial molecules on many phenomena have motivated intensive experimental efforts to elucidate microscopic origins of their unique properties. So far, we have conducted sum-frequency generation (SFG) vibrational spectroscopy of water molecules on model metal surfaces (Pt(111) & Rh(111)) as benchmark systems of interfacial water [1,2] to investigate how unique hydrogen-bond network with preferential proton order is formed in response to interaction with material surfaces. However, SFG molecular spectroscopy has been mostly limited to the observation of ensemble-averaged structures and properties due to the inherent limitation derived from the low spatial resolution under the diffraction limit of light.

Plasmons optically excited at the nanogap between metallic nanoprobe tip and surface induce localization of electric field of incident light and significantly enhance spectroscopic signals from the nanogap, enabling nanoscale mapping of various spectral signals in combination with a scanning probe microscope. Recently, we found that plasmonic tip enhancement of the second-order nonlinear optical signal occurs not only in the visible region but also in the near- and mid-infrared region; such broadband nonlinear optical property is directly affected not only by the nanometer-scale sharpness of tip apices but also by the micrometer-scale surface geometry of tip shafts [3]. Then, by irradiating mid- and near-infrared femtosecond pulses on gold tips for scanning tunneling microscope (STM), we have obtained vibrational SFG nanoscopic signals (Fig. 1) for several representative molecules adsorbed on plasmonic Au surfaces and non-plasmonic Pt surfaces.



**Fig. 1** Tip-enhanced SFG

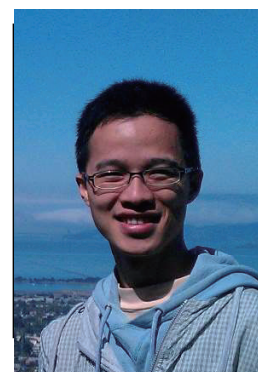
## References

- [1] T. Sugimoto et al., *Nature Phys.* **12**, 1063 (2016).
- [2] T. Sugimoto et al., *Phys. Chem. Chem. Phys.* **22**, 16453 (2020).
- [3] S. Takahashi et al., *J. Phys. Chem. Lett.* **14**, 6919–6926 (2023).

# Momentum-dependent nonlinear optics of electrical double layer

**Y.-C. Wen**

Institute of Physics, Academia Sinica, Taiwan  
e-mail: ycwen@phys.sinica.edu.tw



Electrical double layer (EDL) controls the energy transfer and chemical reaction pathway at many aqueous interfaces, yet to characterize the interface-specific hydrogen-(H-)bonding network and ionic structure therein remains a challenge. Nonlinear optics is known as a perceptive probe to the interfacial properties, whereas the structural identification of an EDL is difficult owing to interference of various nonlinear optical responses. In this talk, I shall report our recent development of a sum-frequency (SF) spectroscopic scheme with varying photon momenta as an all-optic solution for retrieving the vibrational spectra of the bonded water layer and the ion diffuse layer, and hence microscopic structural and charging information about an interface. Application of the method to a model surfactant–water interface reveals a hidden weakly-donor-H-bonded water species, suggesting an asymmetric hydration-shell structure of fully solvated surfactant headgroups. In another application to a zwitterionic phosphatidylcholine lipid monolayer–water interface, we find a highly polarized bonded water layer structure associating to the phosphatidylcholine headgroup, while the diffuse layer contribution is experimentally proven to be negligible. Our all-optic method offers an in situ microscopic probe of electrochemical and biological interfaces and the route toward future imaging and ultrafast dynamics studies.

## References

1. Y. Hsiao, T.-H. Chou, A. Patra, and Y.-C. Wen\*, “Momentum-Dependent Sum-Frequency Vibrational Spectroscopy of Bonded Interface Layer at Charged Water Interfaces”, *Sci. Adv.*, 9, eadg2823 (2023).

# Ion behavior in the Evaporating Charged Droplets Generated by Electrospray Ionization

**Seongjae Jang and Jongcheol Seo\***

Department of Chemistry, POSTECH, Republic of Korea

e-mail: [jongcheol.seo@postech.ac.kr](mailto:jongcheol.seo@postech.ac.kr)



Charged droplets generated during electrospray ionization (ESI) represent one of the most intriguing yet challenging chemical/physical environments, providing unique confinement for molecules within a container characterized by a highly dynamic air-liquid interface. Notably, the rapid and continuous evaporation of interfacial solvents accelerates non-equilibrium behaviors of molecules and/or ions, differing significantly from those in bulk solutions. This results in substantial impacts on the solute-liquid interface within the droplets. Thus, investigating the behaviors of molecules and ions in charged micro-/nanodroplets during the electrospray ionization process can offer new insights into the chemical dynamics of various molecules and ions within these highly fluctuating airborne droplets.

Recently, our group has observed specific behaviors of iodide ( $I^-$ ) ions at (i) the air-liquid interface, and (ii) the solute-liquid interface in evaporating charged micro-/nanodroplets using ion mobility spectrometry-mass spectrometry (IMS-MS). Initially, we investigated the cluster ion formation of alkali halide salts,  $(MX)_nM^+$  or  $(MX)_nX^-$  (where  $M = Na, K, \text{ or } Cs$ ;  $X = Cl \text{ or } I$ ), during the electrospray ionization process. In this study, we confirmed that ion emissions at the interface (ion emission mechanism, IEM) of charged droplets predominantly yield small cluster ions ( $n < 3$ ) with a distinct preference for iodides over other halides. This preference dramatically decreases for larger cluster ions ( $n > 4$ ), which are presumed to be residual ions following complete solvent evaporation (charged residue mechanism, CRM). Additionally, we observed a significantly enhanced affinity of iodides for compact native protein ions in charged droplets. Iodides, known as representative chaotropic ions, are typically associated with protein denaturation. However, our findings indicate that compact and native protein ions in IMS-MS analyses bind numerous iodides, unlike denatured, chain-like protein ions, which do not bind iodide at all. This selective binding is not observed with other halides.

The detailed ion behavior and dynamics inferred from our experimental observations have been further corroborated by molecular dynamics simulations, confirming the ions' affinity towards interfaces as the primary cause of the specific behavior of iodides at the air-liquid and liquid-solute interfaces. These observations of ion behaviors at the interface of charged droplets could be pivotal for examining ions' surface propensity, modeling ion transport across interfaces, and investigating the detailed folding structures of biomolecular ions in droplets.

# Effects of the Intermolecular Interactions on the Ultrafast Photoreaction Dynamics of Schizorhodopsin

**Chun-Fu Chang<sup>1</sup>, Masae Konno<sup>2,3</sup>, Keiichi Inoue<sup>2</sup>, Tahei Tahara<sup>4,5</sup>**

<sup>1</sup> Department of Applied Chemistry, National Yang Ming Chiao Tung University

<sup>2</sup> The Institute for Solid State Physics, The University of Tokyo

<sup>3</sup> PRESTO, Japan Science and Technology Agency

<sup>4</sup> Molecular Spectroscopy Laboratory, RIKEN

<sup>5</sup> Ultrafast Spectroscopy Research Team, RAP, RIKEN  
e-mail: chunfuc@nycu.edu.tw



Intermolecular interactions play important roles in determining the properties of biological systems, such as protein structures and enzyme activities. Here, we study the effects of the intermolecular interactions on the ultrafast dynamics of schizorhodopsin (SzR). SzR is a recently discovered microbial rhodopsin subfamily.<sup>1</sup> While most of the microbial rhodopsins function as light-driven outward proton ( $H^+$ ) pumps for synthesizing ATP, SzR acts as a light-driven inward  $H^+$  pump. An x-ray crystallography study revealed the protein structure around the retinal chromophore of SzR is different from bacteriorhodopsin (BR) (Fig. 1),<sup>2</sup> resulting in unique chromophore–protein interactions that may be responsible for the unusual  $H^+$ -pumping direction. We study the primary photoreaction dynamics of SzR and its C75S mutant by femtosecond time-resolved absorption (TA) spectroscopy.<sup>3</sup> The obtained TA data revealed that SzR exhibits much slower and less efficient photoisomerization than typical outward  $H^+$ -pumping rhodopsins,<sup>4</sup> which further slows down in the C75S mutant. We also performed impulsive stimulated Raman measurements to clarify the effect of the cysteine residue on the retinal chromophore and found the interaction with Cys75 flattens the retinal chromophore of SzR.<sup>3</sup>

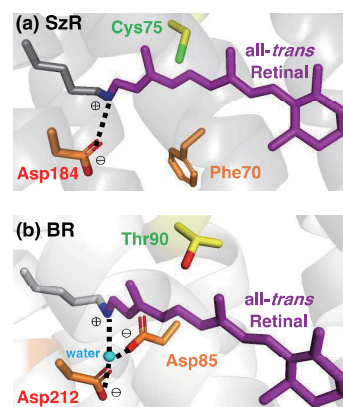


Fig. 1. Comparison of the protein structure around the retinal chromophore. (a) SzR (PDB ID: 7E4G) and (b) BR (PDB ID: 1C3W). The residues at the homologous positions are labeled with the same color. The dashed lines represent the hydrogen bonds.<sup>3</sup>

## References

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2. A. Higuchi *et al. Proc. Natl. Acad. Sci. U.S.A.* **118** (14), e2016328118 (2021).
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4. C.-F. Chang *et al. Angew. Chem. Int. Ed.* **61** (2), e202111930 (2022).

# Inhomogeneity of hydrated electrons revealed by transient two-dimensional electronic spectroscopy

**Korenobu Matsuzaki**,<sup>1,2</sup> **Hikaru Kuramochi**,<sup>3,4</sup> and **Tahei Tahara**<sup>1,2</sup>

<sup>1</sup>Molecular Spectroscopy Laboratory, RIKEN, Japan

<sup>2</sup>RIKEN Center for Advanced Photonics, RIKEN, Japan

<sup>3</sup>Institute for Molecular Science, Japan

<sup>4</sup>The Graduate University for Advanced Studies, Japan

e-mail: kmatsuzaki@riken.jp



When an electron is released into liquid water, it gets swiftly solvated in a cage made of approximately four water molecules. This simple anionic species is called a hydrated electron, and it is an intriguing system as a real-world realization of a particle in a spherical box. One of the peculiar properties of hydrated electrons is that their absorption spectrum has a very broad bandwidth. Such a broad bandwidth is due to either homogeneous or inhomogeneous broadening mechanisms, i.e., the absorption spectrum consists of either a single spectral component or multiple spectral components. In spite of the apparent simplicity of the system and even after decades of experimental as well as theoretical investigations, the origin of the broad absorption bandwidth has not been clearly understood yet.

Recently, we developed transient two-dimensional electronic spectroscopy (tr-2DES), which enables us to obtain 2DES spectra of short-lived transient species. We utilized this novel experimental method to examine the longstanding problem concerning the absorption spectrum of hydrated electrons. The obtained tr-2DES spectra of hydrated electrons enabled us to conclude without any ambiguity that the broad absorption bandwidth of hydrated electrons is due to the inhomogeneous broadening mechanism [1].

## References

1. K. Matsuzaki, H. Kuramochi, and T. Tahara, *in preparation*.

# Coherent vibrational spectroscopy for exploring chemical reactivity

**Jun Woo Kim**

Department of Chemistry, Chungbuk National University, South Korea  
e-mail: jwkim0@cbnu.ac.kr



Time-resolved multidimensional spectroscopy is a powerful tool for investigating the photoinitiated chemical dynamics of molecular ensembles. Typically, the recorded multidimensional spectrum reflects the molecular properties at transient equilibria due to the distinct properties of each individual molecule in the ensemble. However, when the molecular system interacts with an ultrashort optical pulse, it becomes possible to observe coherent electronic or vibrational features within the relevant coherence time.

Despite the dominance of system-bath interaction in breaking down the coherence of photoexcited molecules, chemical reactions often serve as dephasing sources. Clarifying the correlation between dephasing and a chemical reaction enables the deduction of the reaction mechanism. We focus on studying ultrafast photophysics using coherent vibrational spectroscopy to identify nuclear motions strongly correlated with the photophysics by analyzing the vibrational coherence of photoexcited molecular systems. In this presentation, we will introduce studies on the photoinitiated libration of transition dipole moment [1] and ultrafast internal conversion (unpublished). Finally, we will briefly introduce practical single-photon femtosecond time-resolved spectroscopy, a novel approach suggested here for the first time.

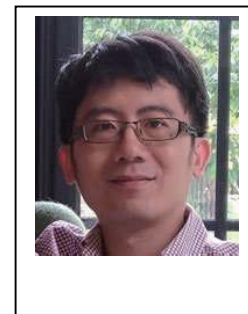
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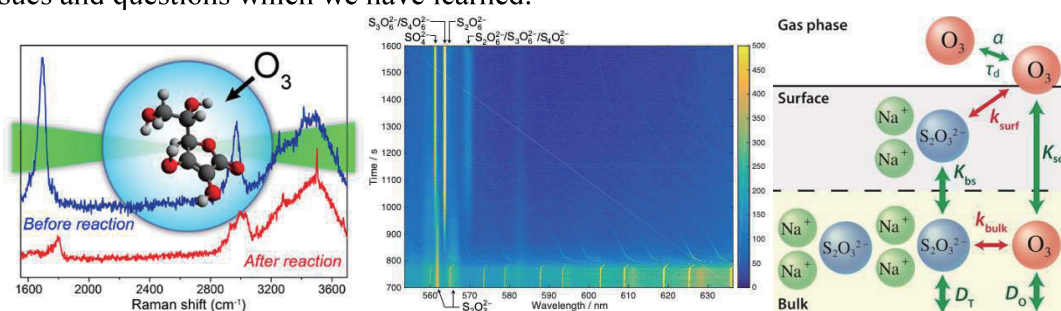
# Studying Heterogeneous Reactions in microdroplets via Aerosol Optical Tweezers (and the lessons I've learned)

**Yuan-Pin Chang**

Department of Chemistry, National Sun Yat-sen University, Kaohsiung, Taiwan  
ypchang@mail.nsysu.edu.tw



This study used aerosol optical tweezers coupled with Raman spectroscopy to study heterogeneous oxidation reactions in optically trapped single microdroplets, such as the oxidation reactions of ascorbic acid, cysteine, thiosulfate, nitrite and sulfite with ozone, as well as the uptakes of VOCs. The aim is to elucidate the role of interface and bulk reactions in aerosol chemistry and the complicate interplays between physicochemical properties and chemistry of aerosol. The Raman spectra of optically trapped single microdroplets allows for retrieving various physicochemical properties of individual single microdroplets, such as droplet radius, refractive index, solute concentrations, pH, ionic strength, diffusivity ... etc. Furthermore, a multi-layer kinetic model for aerosol chemistry is used to simulate the reactions of ozone on the aerosol surface and in the bulk phase under different conditions, allowing for clarifying the roles of surface and bulk reactions. These results demonstrate that the application of aerosol optical tweezers coupled with Raman spectroscopy can be a versatile tool to elucidate the aerosol reaction kinetics. Finally, this presentation will share not only our experiences of experiments and kinetic simulations, and also the remaining issues and questions which we have learned.



**Figure 1** (Left) Raman spectra of single optically trapped ascorbic acid microdroplet before and after ozonolysis. (Middle) Raman spectra time series of a single  $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$  droplet exposed to  $\text{O}_3$  after  $\sim 800$  s. (Right) Schematics of multiphase kinetics model utilized to retrieve the interface kinetics.

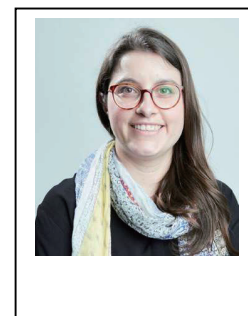
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3. Y.-P. Chang, S.-J. Wu, M.-S. Lin, C.-Y. Chiang, and G. G. Huang, **Phys. Chem. Chem. Phys.**, *23*, 10108 (2021).

# Computational insights into the catalytic hydrogenolysis of plastic waste using ruthenium nanoparticles

Fabio Colasuonno, Sohaib Umer, Martina Lessio

School of Chemistry, UNSW Sydney, Kensington, NSW, Australia  
e-mail: [martina.lessio@unsw.edu.au](mailto:martina.lessio@unsw.edu.au)



Catalytic hydrogenolysis on supported metal nanoparticles has recently emerged as a promising technique for the conversion of polyolefin-based plastic waste into useful products under moderate conditions.<sup>1,2</sup> However, more control over the product distribution is needed in order for this process to be employable at the industrial scale. Fundamental mechanistic insights are critical to achieve such control, with computational methods being the ideal tool to gain these insights. In this contribution, I will present our recent work on ruthenium-catalysed hydrogenolysis of polyolefin-based plastic waste. Here, we first use periodic density functional theory (DFT) to accurately assess the activity of different Ru facets towards H<sub>2</sub> splitting and determine the resulting surface coverage of atomic hydrogen under operating conditions according to a recent protocol developed in our group.<sup>3</sup> The atomic hydrogen surface coverage is known to significantly influence reaction outcomes and selectivity and is thus a critical parameter for predicting and understanding the catalytic performance of different facets and designing the best possible catalysts. Another critical aspect investigated in this study is the plastic polymer cleavage mechanism as this can shed light on the selectivity of the hydrogenolysis process towards high-value products. Here, we present preliminary DFT results on the full reaction pathway for butane (as a proxy of polyethylene) cleavage on the most stable Ru facet.

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# Elucidation and Control of Microscopic Mechanisms in Molecular Photofunctional Materials

**Kiyoshi Miyata**

Affiliation (times new roman 12pt)  
e-mail: kmiyata@chem.kyushu-univ.jp



Microscopic understanding of exciton physics in molecular materials for optoelectronics is a great challenge because of their complexity resulting from strong electron-phonon coupling and perhaps interaction to spin degree of

freedom, electron spin-flip of intersystem crossing in molecular optoelectronic materials are strongly connected to molecular geometries in the excited states and vibronic coupling, and singlet fission, ultrafast generation of a correlated triplet pair state from a singlet excited state, is viewed as an extreme example of a concerted process of electron-phonon-spin degrees of freedom. Here, I would like to discuss a few topics mainly focusing on triplet excited state based photofunctions (Figure 1), Reverse intersystem crossing (RISC), room temperature phosphorescence (RTP), triplet-triplet energy transfer (TTET), and singlet fission (SF), investigated by ultrafast spectroscopy.

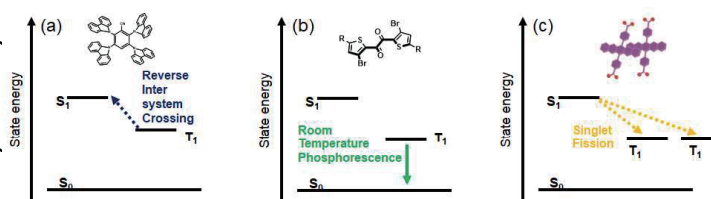
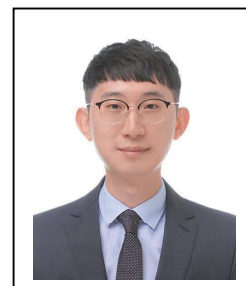


Figure 1. Extended Jablonski diagram and related functions. (a) Thermally activated delayed fluorescence, (b) Room temperature phosphorescence, and (c) Singlet fission.

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# Time-resolved Spectroscopic Measurement and Optical Cavity Manipulation of Ultrafast Phenomena



**Daeheum Cho**

Department of Chemistry, Kyungpook National University, Republic of Korea

e-mail: daeheumc@knu.ac.kr

Conical intersection dynamics are of central interest for understanding the function and the relaxation mechanisms of photoexcited molecules in virtually all photochemical processes. Direct real-time measurement and characterization are essential to monitor conical intersections and their paths. In this talk, various time-resolved X-ray spectroscopic techniques, such as X-ray absorption, X-ray Raman, and X-ray circular dichroism, and X-ray diffraction technique will be discussed. The techniques employ hard X-ray narrowband/broadband probe fields to probe electronic coherences at the level crossing region via X-ray chromophore. The signal carries phase information of the valence-to-core electronic coupling in the vicinity of conical intersections.

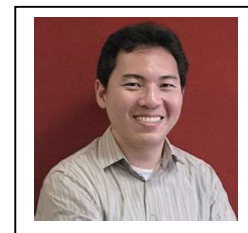
Optical cavity manipulation of conical intersections will be discussed as a platform for manipulating the excited-state dynamics of molecules via strong light–matter coupling. We employ optical absorption and two-multiphoton electronic spectroscopy simulations to investigate the effect of optical cavity coupling in the nonadiabatic dynamics of photoexcited pyrazine. We observe the emergence of a novel polaritonic conical intersection between the electronic dark state and photonic surfaces as the cavity frequency is tuned. Moreover, the absorption spectrum and excited-state dynamics could be systematically manipulated by tuning the strong light–matter interaction.

# Evolving Hydrogen Gas Using Triplet Excitons of an Organic Photocatalyst

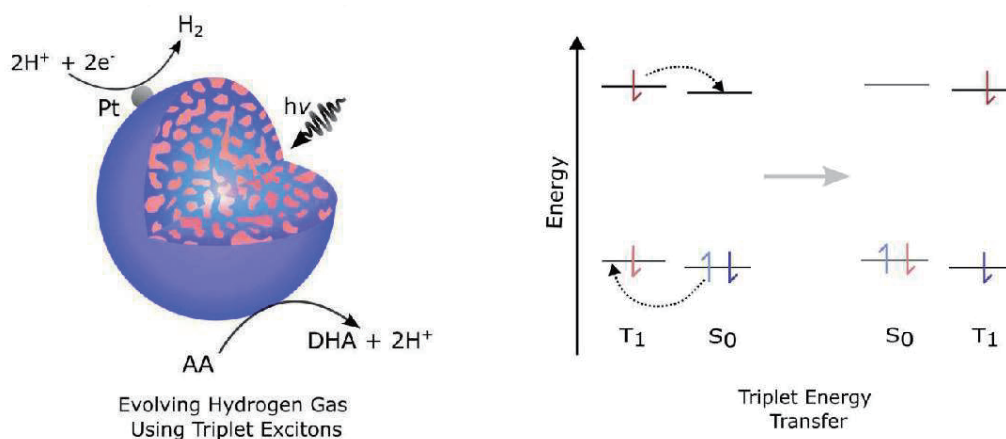
**Harrison J. McAfee, David M. Huang, Tak W. Kee**

*Department of Chemistry, The University of Adelaide, South Australia, Australia.*

e-mail: tak.kee@adelaide.edu.au



Hydrogen gas ( $H_2$ ) is an important energy source that is attracting significant attention because it is a carbon-free fuel. However, the current methods of producing  $H_2$ , which are powered by fossil fuels, release a high level of carbon dioxide. A cost-effective and green alternative to current methods is photocatalytic  $H_2$  evolution using nanoparticles of organic semiconductors. Typically, this process uses light to generate singlet excitons, which then undergo charge separation at interfaces between electron donor and acceptor materials. The generated charges can migrate to the photocatalyst's surface to facilitate redox reactions (left figure). For example, the generated electron can migrate to the surface bound platinum co-catalyst to reduce protons to form  $H_2$ . In this presentation, however, we discuss a novel approach of using triplet energy transfer (right diagram) to generate triplet excitons of an organic semiconductor to increase the efficiency of  $H_2$  evolution. Triplet excitons are longer-lived species than singlet excitons due to their spin-forbidden relaxation to the ground state. As a result, the longer triplet exciton lifetime may allow a higher probability for charge separation than that using singlet excitons. The use of triplets could pave the way for singlet fission, a process that converts a singlet into two triplets, to be explored for maximising the efficiency of  $H_2$  evolution in organic semiconductors.



# Peculiar Photophysics of 2,2'-Bianthracene: Symmetry-Breaking Charge Transfer, Triplet Formation Dynamics, and Their Connection to Conformational Diversity

**Byongjoo Kang, Woojae Kim**

Department of Chemistry, Yonsei University, Korea  
e-mail: woojae@yonsei.ac.kr



Here, we delve into symmetry-breaking charge transfer (SB-CT) and triplet formation dynamics, particularly their interplay with conformational diversity in 9,9',10,10'-tetraphenyl-2,2'-bianthracene (TPBA). TPBA distinguishes itself from the traditional 9,9'-bianthracene through its notably planar structure, attributed to the diminished steric hindrance between its anthracene chromophores.<sup>1,2</sup> This structural attribute engenders pronounced short-range CT coupling, underpinned by significant overlap integrals of electron and hole, in stark contrast to the 9,9'-bianthracene, which is characterized by dominant long-range Coulombic coupling. As a result, TPBA shows an adiabatic mixture of locally-excited and CT diabats, with the degree of their contribution being influenced by the dielectric properties of the surrounding medium. Our research further uncovers that the SB-CT reaction in TPBA is mainly affected by solvation dynamics. Remarkably, we observe that triplet formation in TPBA follows an unprecedented multiexponential behavior, and its efficiency significantly varies with solvent polarity. This can be rationalized by considering the multiple conformers and their energetic landscapes.

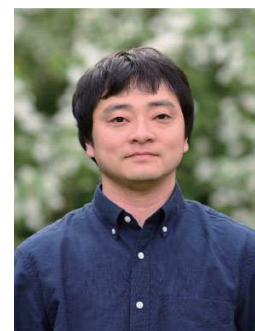
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# Ultrafast photoexcited state dynamics at organic molecular films studied by time-resolved photoelectron spectroscopy and microscopy

**Masahiro Shibuta**

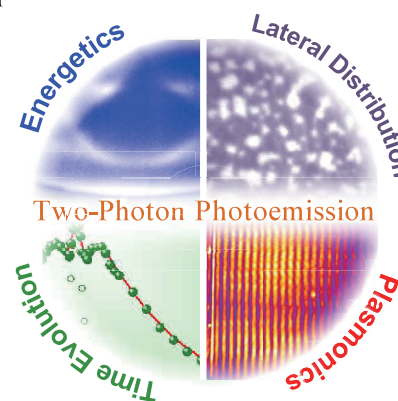
Department of Engineering, Osaka Metropolitan University, Japan  
e-mail: shibuta@omu.ac.jp



Studying of the ultrafast electron dynamics at organic surfaces and interfaces is of high importance because it governs the functionalities of photoconversion devices. Since the growth of the organic layer exhibits inhomogeneity, time-resolved spectroscopy should be combined with microscopic way to observe the local phenomena. Two-photon photoemission spectroscopy (2P-PES) is a powerful method for studying the ultrafast electron dynamics, in which a first photon excites an electron in a targeted system and the excited electron is extracted by the aftercoming second photon. Using the optics for photoelectron emission microscopy as 2P-PEEM, the local excited-state dynamics can also be resolved with  $\sim 100$  nm resolution [1].

On the fullerene  $C_{60}$  layer, our 2P-PES and 2P-PEEM characterized the photocarrier generation in the  $C_{60}$  layers with high energy, spatial, and temporal resolutions [1,2]. In addition, momentum-resolved 2P-PES showed a variety of highly-dispersive conduction bands in a well-assembled  $C_{60}$  film; the nearly free-electron-like character originates from the diffuse superatomic molecular orbitals of  $C_{60}$  [3]. In case of the pentacene, 2P-PEEM reflects the lateral distribution of excitons in the nanocrystal grown on a substrate. Importantly, time-resolved 2P-PEEM captured the evolution of hot electrons expanding into the substrate in 1 ps or sub  $\mu\text{m}$  ranges [4].

We have also demonstrated that 2P-PES and 2P-PEEM are valuable to observe plasmonic phenomena, which enhance the functionalities of organic system [5,6]. These methodologies probing 2P-photoemission have high potential to reveal the optical and plasmonic properties of various functional nanoscale systems.



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# Measuring amorphous structure: How thermal vibrations reveal structural change

**Charlotte Petersen,<sup>a</sup> Peter Harrowell<sup>b</sup>**

<sup>a</sup> School of Chemistry, University of Melbourne, Melbourne, Victoria 3010 Australia; <sup>b</sup> School of Chemistry, University of Sydney, Sydney, New South Wales 2006 Australia.  
e-mail: charlotte.petersen@unimelb.edu.au



Predicting the rigid behaviour of glass from its disordered, amorphous atomic structure remains a significant challenge in materials science. In the absence of periodic order, defining, let alone measuring, structure in glass materials presents the first stumbling block. Scattering experiments that measure the static structure factor are the standard structural determination tool for crystalline materials. However, their utility is limited for amorphous materials, where the lack of periodic order means structural signatures become washed out.

Recent progress has connected the presence of localised soft normal modes to the dynamics of glass.<sup>1</sup> Building on this success, the capacity of a configuration to restrain particle motion has been formalised as a structural order parameter that characterises the solidification of a liquid into an amorphous solid on cooling.<sup>2</sup> We have recently demonstrated computationally that the Debye-Waller factor, which quantifies particle vibrations from the static structure factor, is a suitable experimentally accessible structural order parameter to characterise solidification.<sup>3</sup> The Debye-Waller factor can be extracted from static measurements if the scattering at individual wavevectors is considered.

In this talk, I will discuss our ongoing work to connect this new measure of structure to behavior. In particular, can the Debye-Waller factor be used to predict rigidity? By varying the constraints in our system, we can quantify the effect on both structure and properties.

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# What Can Generative Models Do for Quantum Information Processing? A Study Case on the Design of Molecular Qubits with Long Coherence Time

**Tzuhsiung Yang**

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan  
e-mail: [tyang@mx.nthu.edu.tw](mailto:tyang@mx.nthu.edu.tw)



There is a growing interest in quantum information processing (QIP). Numerous advantages have been demonstrated such as single molecule nuclear resonance of protein, quantum entanglements of qubits, and the detection of single neuron action potential. It has been shown that transition metal (TM) complexes with more than one unpaired electron are potential quantum information carriers for their scalability, solubility, and tunable coherence time, which is achieved through modulating their axial (D) and rhombic (E) zero-field splitting (ZFS) parameters *via* adjusting their first coordination sphere.[1]

In this talk, I will present out recent work on the computational screening and generative model enabled design of TM complex based molecular qubits. We first collected 139 of non-hydrogen-containing ligands from experimentally synthesized TM complexes. We then built 556 TM complexes using these ligands along with  $Ti^{2+}$ ,  $V^{3+}$ ,  $Cr^{4+}$ , and  $Mn^{5+}$  ( $d^2$  ions). D and E ZFS parameters were then calculated using spin-orbit coupling (SOC) Hamiltonian with quasi-degenerate perturbation theory (QDPT) treatment on N-electron valence second order perturbation (NEVPT2) corrected energies of the complete active space self-consistent field (CASSCF) wavefunctions on top of density functional theory (DFT) optimized geometries. Inverse correlation between the calculated absolute D values and the first vertical excitation gaps ( $E_g$ ) was observed, except at large  $E_g$ . Large E values are achievable at low absolute D values, which drastically decay as the absolute values of D increases. Variational Autoencoder (VAE) models were then applied to generate novel TM complexes with optimized D values and maximized E values.

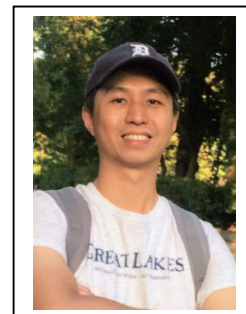
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# Unveiling the Mysteries of Matrix-Assisted Ionization in Mass Spectrometry for Enhanced Efficiency and Fundamental Insights

**I-Chung Lu**

Department of Chemistry, National Chung Hsing University  
e-mail: iclu@nchu.edu.tw



Mass spectrometry (MS) offers universal detection by measuring the mass-to-charge ratio of matter, identifying chemical compositions with high sensitivity and an extensive dynamic range. Depending on the chemical characters and approach, various strategies are employed to ionize analytes for mass analysis. In some ionization techniques, matrix molecules facilitate the transfer of protons or alkali ions to the analyte during the ionization process. At EAWCD 2019, we introduced matrix-assisted ionization (MAI), utilizing a home-built charge detector to observe charge transfer during the sublimation of a volatile matrix in a vacuum. This sublimation-induced ionization allowed proton transfer without additional electric field or thermal energy for subsequent mass analysis. The driving force behind this ionization remained unclear, and existing studies were insufficient. We recently identified potential proton sources for protonated analyte ions in the MAI process by isotope labeling experiments. This breakthrough provides an understanding of optimization to increase signal intensity tenfold in MAI-MS and illuminates the relationship between tunneling effects and ionization. In this presentation, we aim to revisit questions posed four years ago. The sublimation leading to charged substances may be a frequent but underexplored natural phenomenon, holding research value in both application and fundamental studies.

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# Photo-control of DNA assemblies through time and space

Willi Ragnar Berg, Laura Wimberger, Jonathon Beves, Felix J. Rizzuto



<sup>1</sup>School of Chemistry, University of New South Wales, Sydney, Australia, 2052

e-mail: *Contact emails:* [f.rizzuto@unsw.edu.au](mailto:f.rizzuto@unsw.edu.au)

The programmability of DNA and its compatibility with oscillatory biological systems makes it an ideal material for generating out-of-equilibrium systems. However, the interactions and functionality of DNA are limited to the binary recognition of four nucleic acids. Expanding upon this DNA alphabet (to include metal ions, small molecules, and artificial nucleobases) diversifies the types of chemistries that can be performed with DNA, and its ability to form new structural motifs for programmable nanotechnology applications.

In this talk, I'll discuss how visible light, small molecules, and protons can be used synergically as stimuli to create out-of-equilibrium DNA architectures.<sup>1-3</sup> By programming these nanomaterials in both time and space, these single-stranded and DNA origami systems are capable of life-like properties – they can grow, 'evolve' and repair themselves by accessing unique assembly pathways under kinetic control. This new method of annealing nanomaterials has recently led to the development of more sophisticated out-of-equilibrium systems, including new modes of organizing DNA origami units into hierarchical structures under spatiotemporal control. We can now form polymers and matrices of DNA origami away from equilibrium, enabling new possibilities in tissue scaffolding and catalysis.

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# Raman optical activity spectroscopy of biological photoreceptors

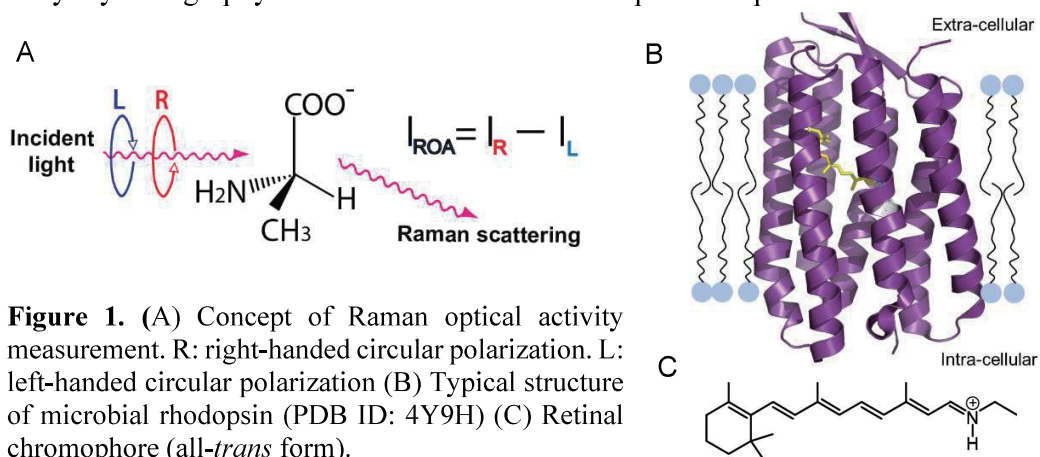
**Tomotsumi Fujisawa**

Department of Chemistry and Applied Chemistry, Faculty of  
Science and Engineering, Saga University  
e-mail: tfuji@cc.saga-u.ac.jp



Photoreceptor proteins bind light-absorbing chromophores as the cofactors to utilize photon energy for their biological functions. A protein environment generally causes a structural deformation of the chromophore and this structural change is considered to be important to play their physiological roles. The conformation of chromophore in the protein is closely related to which color of light the chromophore is sensitive to as well as how the chromophore reacts. In order to capture this conformation of photoreceptors, Raman optical activity (ROA) spectroscopy can be powerful,<sup>1-3</sup> due to its capability of reporting the three-dimensional molecular structures most sensitively.

ROA spectroscopy detects the small difference of Raman intensities obtained with right- and left-circularly polarized incident lights (Figure 1A). In this study, we applied ROA spectroscopy to microbial rhodopsins, a seven-transmembrane photoreceptor family that binds retinal chromophore (Figure 1B and 1C). We show that the ROA spectra provide the three-dimensional structural information of the retinal chromophore, which is not obtained by X-ray crystallography or conventional vibrational spectroscopies.



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# Self-consistent fragment charges – A simple strategy to accelerate quantum chemistry calculations

**Junming Ho**

School of Chemistry, University of New South Wales,  
Kensington NSW 2052, Australia.  
e-mail: [junming.ho@unsw.edu.au](mailto:junming.ho@unsw.edu.au)



One of the Holy Grails in computational chemistry is to be able to make highly accurate prediction of molecular properties and reaction outcomes. Whilst quantum chemical methods are in principle very accurate, they have very high computational cost that prohibits their application to realistic systems such as solution-phase and enzymatic reactions.

Over the last few decades, approximate approaches such as hybrid quantum mechanics/molecular mechanics (QM/MM; Nobel Prize 2013) and fragmentation methods have been introduced to overcome the steep scaling cost of quantum chemical methods. However, these methods usually suffer from slow convergence which makes their performance less predictable.

In this talk, I will introduce a simple approach for improving the description of electrostatic interactions that accounts for mutual polarisation effects. I will demonstrate how the approach can be used to accelerate the QM region size convergence of QM/MM models of solution-phase reactions<sup>1</sup> and many-body expansion calculation of the energies of water clusters. The cost of this self-consistent fragment charge approach scales linearly with the size of the system and can be applied to both covalent and non-covalent systems.

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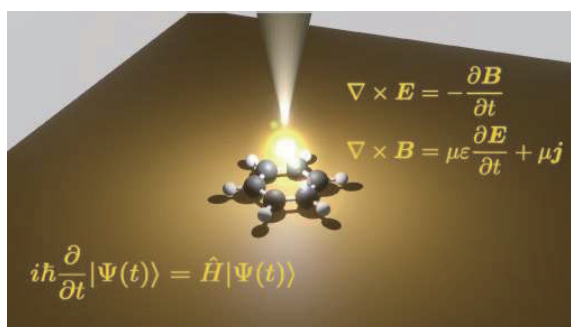
# Light-matter interaction with near-field: dynamics and spectroscopy

**Takeshi Iwasa**

Department of Chemistry, Faculty of Science, Hokkaido University  
e-mail: tiwasa@sci.hokudai.ac.jp



Near field, a localized non-propagating light field allows us to study molecules below the diffraction limit. Recent experiments utilizing scanning tunneling microscopy offer a unique platform for nanoscale spectroscopy and microscopy [1-2], as well as photochemistry [3-4] down to single molecule even with sub-molecular resolutions. From the theoretical perspective, near-field requires us to reformulate the light-matter interaction beyond the dipole approximation. In this paper, first principles studies based on the multipolar Hamiltonian for electronic and vibrational excitations and their applications to near-field IR and Raman spectroscopies will be shown [5-8]. In addition, some of our recent theoretical efforts on energy migration at atomistic scale, optical forces for molecular manipulations [9], as well as for optimal control with near-field toward photochemical applications will be shown.



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