Manipulating Molecular Electronic Properties by Vibrational Excitations: Novel Spectroscopies and Microscopies

838. WE-Heraeus-Seminar

17 – 21 August 2025

at the Physikzentrum Bad Honnef, Germany

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HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 838. WE-Heraeus-Seminar:

Recent years have witnessed the development of novel powerful experimental techniques, that explore and exploit the coupling of vibrational and electronic degrees of freedom (vibronic couplings), using vibrational excitations to manipulate electronic properties of matter.

These developments originate from different scientific backgrounds with little overlap between the involved communities. On the technology side, these backgrounds comprise ultrafast laser spectroscopy, microscopy and photonics. On the application side, researchers target such different topics as cell biology, solid state physics, non-linear optics, chemical analytics, molecular physics, molecular biophysics or photochemistry.

The seminar aims at bringing together researchers and students from these different backgrounds who are united by the fact that they develop and apply techniques that exploit vibronic couplings, e.g. to access new observables and information in spectroscopy, to implement novel contrast mechanisms in microscopy, which are sensitive to molecular structure, to dramatically extend possibilities for multiplexing in microscopy and imaging, to overcome long standing barriers in selectivity and sensitivity of spectroscopies and microscopy and to develop new means of steering dynamics on the molecular level. At this seminar, we would like to explore the synergies and foster collaborations between these different areas of research.

Scientific Organizers:

Prof. Dr. Jens Bredenbeck	University of Frankfurt, Germany e-mail: bredenbeck@biophysik.uni-frankfurt.de
Prof. Dr. Wei Xiong	University of California, San Diego, USA e-mail: w2xiong@ucsd.edu

Introduction

Administrative Organization:

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Registration:

Mojca Peklaj (WE Heraeus Foundation)
at the Physikzentrum, Reception Office
Sunday (16:00 h - 21:00 h) and Monday morning

Program

Program

Sunday, 17 August 2025

16:00 – 21:00	Registration	
18:30	*BUFFET SUPPER and informal get together*	
20:30 – 20:45	Scientific Organizers	**Welcome and Introduction**

Session chairs: Jens Bredenbeck / Wei Xiong

20:45 – 21:30	Andrei Tokmakoff	**Enabling single molecule infrared spectroscopy through fluorescence detection**

Monday, 18 August 2025

08:00	*BREAKFAST*

Session chair: Wei Xiong

09:00 – 09:45	Jens Bredenbeck	**Subensemble selective dynamics through IR pre-excitation**
09:45 – 10:30	Julia Weinstein	**IR-control of photoinduced electron transfer in solution**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:45	Fabrizio Santoro	**Computing Vibronic Spectra after vibrational pre-excitation with FCclasses code**
11:45 – 12:30	Irene Burghardt	**Signatures of vibronic couplings in VIPER spectroscopy and VIPER mediated photocontrol**
12:30 – 12:40	**Conference Photo (in front of the main entrance)**	

Program

Monday, 18 August 2025

12:40 – 14:00 *LUNCH*

Session chair: Lu Wei

14:00 – 15:30 **Contributed Talks 1 - 3**

Hugo Levy Falk	**Hybrid Interfaces for Sensing and Control in Fluorescent Organic Molecules**
Beier Hu	**Unveiling the Impact of High-Frequency Vibrations on Electronic Properties in Soft Optoelectronic Materials**
Srijan Chatterjee (ONLINE)	**Mapping Vibronic Couplings in Mixed-Frequency Regimes Using Coherent Multidimensional Vibrational-Electronic Spectroscopy**

15:30 – 16:00 *COFFEE BREAK*

16:00 – 16:10 **Video WE Heraeus Foundation**

Session chair: Ricardo Fernández-Terán

16:10 – 18:10 **Hot Topic Talks**

Patrick Friebel	**THz vibrational dynamics of Liquid Crystals: from molecular origin to bulk response**
Timo Stern	**Simultaneous detection of FEIR and 2D-IR spectra and site-specific application to biomolecules**
Stefan Piontek	**Innovation in Ultrashort Broadband Mid-Infrared Pulses for Nonlinear Spectroscopy**
Luuk van Wilderen	**Vibronic couplings in a photoreceptor protein**

	Bin Yang	**Ultrafast Optical Gating of Single Photon Emission via Pump–Ionization–Probe Spectroscopy in CdSe/ZnS Quantum Dots**
	Ryan McDonnell	**Comparing one and two-photon transitions in vibronic coupling schemes**
	William Jeffries	**Decoding nanocrystal surface heterogeneity: insights from ligand vibrations and vibronic coherences**
19:00	*DINNER*	

Program

Tuesday, 19 August 2025

08:00	*BREAKFAST*	
Session chair: Jens Bredenbeck		
09:00 – 09:45	Jeremy Baumberg	**Exploiting Extreme Plasmonic Nanocavities to drive Collective Molecular Vibrations**
09:45 – 10:30	Christophe Galland	**Optical and electrical investigations of molecules in plasmonic nanojunctions**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 12:30	**Contributed Talks 4 - 6**	
	Carsten Fallnich	**A route to chip-based ultrafast light sources for coherent Raman imaging**
	Ricardo Fernández-Terán	**Towards Controlling Excited State Reactivity in Organic and Organometallic Systems: A Perspective Through Ultrafast Multidimensional Spectroscopies**
	Hanqing Xiong	**Recent progress in time-domain stimulated Raman excited fluorescence spectroscopy**
12:30 – 14:00	*LUNCH*	
Session chair: Christophe Galland		
14:00 – 14:45	Nicholas Chilton	**Vibronic coupling probed by single-crystal FIRMS**
14:45 – 15:30	**Poster Flash Talks**	
15:30 – 16:00	*COFFEE BREAK*	
16:00 – 18:00	**Poster Session**	
19:00	*DINNER*	

Program

Wednesday, 20 August 2025

08:00	*BREAKFAST*	
Session chair: Tim Zuehlsdorff		
09:00 – 09:45	Jiri Vanicek	**Vibrationally resolved electronic spectra from Hagedorn wavepacket dynamics**
09:45 – 10:30	Wei Xiong	**Nonlinear IR-visble interactions: From Multiplexing Imaging to Ultrafast Quantum Emitters**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:45	Lu Wei	**Functional bond-selective microscopy toward the single-molecule, super-resolution regime**
11:45 – 12:30	Renee Frontiera (ONLINE)	**Distinguishing spectator from driving vibrational modes in excited state photochemistry**
12:30 – 14:00	*LUNCH*	
14:00	**Excursion**	
19:00	*HERAEUS DINNER* *(social event with cold & warm buffet with complimentary drinks)*	

Program

Thursday, 21 August 2024

08:00	*BREAKFAST*	
Session chair: Hanqing Xiong		
09:00 – 09:45	Christopher Elles	**Manipulating reaction dynamics through vibronic coupling in higher-lying electronic states**
09:45 – 10:30	Tim Zuehlsdorff	**Modeling nonlinear optical spectroscopy signals in molecules beyond the Condon approximation**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:45	Junrong Zheng	**Mechanism of aggregation-induced emission and control of excited state dynamics**
11:45 – 12:30	**Discussion and Closing Remarks**	
12:30	*LUNCH*	

End of the seminar and departure

Posters

Poster Session, Tuesday, 19 August, 4 pm (CEST)

Dina Atwa Khalil	**Nonlinear Optical Properties of Hexagonal Boron Nitride Nanosheet Thin Films: A Femtosecond Z-scan Study**
Rahul Bhuyan	**The Role of the Dark States on Strong Exciton Photon Coupling Dynamics**
Malin Brütting	**Unveiling Myoglobin COnformations: 2DVE and VIPER spectroscopy**
Alyssa Cavazos	**Dynamical contributions to the vibrational absorption lineshape of an intramolecularly hydrogen bonded organic dye compound**
Viktoria Chatrchyan	**Quantum dynamical properties of Oligocene: from Spectroscopy to Machine Learning**
Avinash Chettri	**2D-IR spectroscopy reveals structural heterogeneity in GLFG-rich hydrogels as models for the nuclear pore complex**
Lara Denninger	**Same Same but Different: Vibronic Coupling to Selectively Target Subpopulations**
Ghada Elsayed	**Experimental exploration of third- order nonlinear properties of GQD prepared by pulsed laser ablation in liquid**
Alexander Fellows	**Azimuthal-Scanning and Phase-Resolved Vibrational Sum-Frequency Microscopy**
Patrick Friebel	**THz vibrational dynamics of Liquid Crystals: from molecular origin to bulk response**
Jin Guo	**Self-Calibrated Stimulated Raman Scattering Spectroscopy for Rapid Cholangiocarcinoma Diagnosis**

Poster Session, Tuesday, 19 August, 4 pm (CEST)

Nina Hagmeyer	Radiative and non-radiative decay in carbazole-substituted polychlorinated triphenyl methyl radicals
Markus Hinterthan	Probing Vibronic Dynamics in Rubrene Crystals via 2D-VE and VIPER Spectroscopy
Kuo Wei Huang	Structural analysis of transient reaction intermediate in formic acid dehydrogenation catalysis using two-dimensional IR spectroscopy
William Jeffries	Decoding nanocrystal surface heterogeneity: insights from ligand vibrations and vibronic coherences
Niklas Klosterhalfen	Nonradiative deactivation of photobasic Ru(II)- and Fe(II)-complexes
Joseph Kölbel	Illuminating Single- and Multi-Branched Donor–Acceptor Systems with Multidimensional Spectroscopies
Shilpa Kurupath Bhavadas	Mapping the vibration states in Retinal and Retinal Schiff Base by FSRS
Nick Sidney Lemberger	Special detector design for improved SRS imaging
Reece Marsden	Ab initio Magnetic Relaxation Prediction of Dysprosium Bis-Borolide Single-Molecule Magnets
Ryan McDonnell	Comparing one and two-photon transitions in vibronic coupling schemes
Ritesh Pant	Influence of Thermal Motion on Exciton Dynamics in Finite Molecular Chains

Poster Session, Tuesday, 19 August, 4 pm (CEST)

Helena Poulose	**Understanding Vibrational Strong Coupling through non-linear spectroscopy**
Debkumar Rana	**Interactions of Azide Anion with Imidazole in DMSO: Time-resolved IR Spectroscopy and Molecular Dynamics Simulation**
Till Stensitzki	**Exploring Uncharted Territory: 2D-IR spectroscopy in the 1100-1300 cm-1 region**
Timo Stern	**Simultaneous detection of FEIR and 2D-IR spectra and site-specific application to biomolecules**
Toby Thompson	**Electron and Nuclear Spin dynamics of Lanthanide Complexes in Solution**
Mathesh Vaithiyanathan	**In vivo 2D-IR Spectroscopy on Live Cells of E. coli Reveals a Remarkably Stable [FeFe] Hydrogenase Active Site**
Luuk Van Wilderen	**Vibronic couplings in a photoreceptor protein**
Kristin Wallmeier	**Epi-detected stimulated Raman photo-thermal microscopy**
Bin Yang	**Ultrafast Optical Gating of Single Photon Emission via Pump–Ionization–Probe Spectroscopy in CdSe/ZnS Quantum Dots**
Qirui Yu	**Mode-selective Fluorescence Modulation via Visible/IR Excitation and its Vibrational-electron Coupling Dynamics**

Abstracts of Lectures

(in alphabetical order)

Exploiting Extreme Plasmonic Nanocavities to drive Collective Molecular Vibrations

Jeremy J Baumberg

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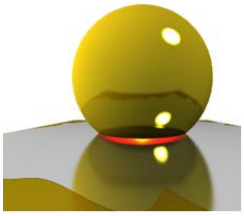
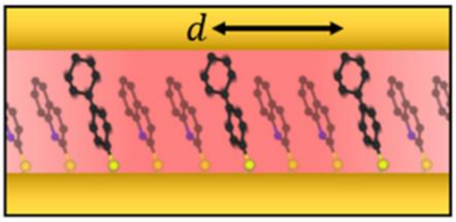
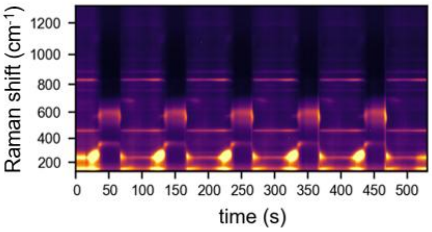
The ability to routinely confine light to nanoscale volumes around molecules using plasmonic nanocavities opens up a wide landscape to explore optomechanical coupling. In this talk I will explore the capabilities and vision.

We have exploited the nanoparticle-on-mirror configuration to create thousands of identical nanocavities.[1] Through this we are able to explore the coupling of vibrations through the plasmonic-enhanced dipolar interactions, which leads to vibrational energy shifts and retarded phase scattering.[2] We can also watch these vibrations in the situation of strong coupling into vibrational plasmon polaritons.[3] Exploring molecular vibrations at THz frequencies allows the collective motion of the entire molecular backbone to be probed, as well as the intermolecular interactions.[4] Using pulsed measurements we show how vibrational pumping depends on collective effects which scale with the number of identical molecules coupled together.[5,6] We also explore the vibrational coupling of molecules with radical electrons, to access a new generation of qubits which can operate at room temperature.[7]

We also show applications ranging from photocatalysis to sensing. These have been enabled by a new discovery that we can completely clean out and reinsert molecules in nanogaps repeatedly, producing ideal SERS substrates which can be operated in flow with electrochemical control.[8] Monolayers of water on the gold nanogap facets can be tracked, allowing their orientation and hydrogen-bonding to be studied in situ, and sensitising for ultralow gas/vapour detection.







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Subensemble selective dynamics through IR pre-excitation

Luuk J.G.W. van Wilderen, Lara Denninger, Hafiz M. A. Masood, Hendrik Brunst, and Jens Bredenbeck

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Manipulating UV/VIS spectra through vibrational pre-excitation is paving the way to novel spectroscopies and microscopies.[1-4] VIPER-2D-IR spectroscopy (Vibrationally Promoted Electronic Resonance) employs an initial IR excitation to change the electronic spectrum of the sample and shift it into resonance with a subsequent off-resonant UV/VIS pulse. The vibrationally pre-selected molecules are thus promoted to a higher electronic state.[1] As the IR spectrum is sensitive to even subtle structural differences, VIPER excitation allows to pick sub-ensembles such as conformers, isotopmomers or molecules in different hydrogen bonding environments to selectively study their photochemistry[5,6] or to obtain spectral diffusion[7] and chemical exchange[1] kinetics beyond the vibrational lifetime in a VIPER-2D-IR experiment.

While many experiments such as VIPER-2D-IR rely on IR-induced change of the UV/VIS spectrum, they do not measure this change explicitly. We use 2D vibrational-electronic (2D-VE) spectroscopy to explore the possibilities of manipulating electronic spectra by IR excitation in various systems, such as fluorophores, catalysts, photoswitches and photoreceptors. The mode dependence of the UV/VIS modulation and the role of vibrational dynamics such as intramolecular vibrational energy redistribution (IVR) and vibrational coherences are investigated, providing important insights for designing experiments based on IR-induced modulation of UV/VIS spectra.

References

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Signatures of vibronic couplings in VIPER spectroscopy and VIPER mediated photocontrol

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VIbrationally Promoted Electronic Resonance (VIPER) spectroscopy [1] exploits electronic-vibrational – i.e., vibronic – couplings and their impact on UV-Vis transitions, such that theoretical computation of these couplings provides the key to predicting the VIPER effect. Vibrational modes which are strongly coupled to an electronic transition give rise to significant spectral shifts, enabling off-resonant UV-Vis (1-photon) or near infrared (2-photon) excitation upon selective vibrational pre-excitation. Here, we describe the computation and analysis of vibrationally resolved 1-photon and 2-photon absorption spectra including IR pre-excitation, obtained for the full set of vibrational modes, i.e., tens to hundreds of modes for medium-sized chromophores [2,3]. The resulting theoretical VIPER spectra are in very good agreement with slices of 2D-Vibrational Electronic (2D-VE) spectra where VIPER excitation is followed by detection of the UV-Vis response. Furthermore, we describe the selection of sub-ensembles via VIPER, for example for chromophores in different hydrogen-bonded states, along with VIPER-induced selective photo-deprotection in a mixture of caged isotopologues, as demonstrated for the para-hydroxyphenacyl (pHP) photocage [4]. Finally, the interplay of the VIPER effect with intramolecular vibrational redistribution (IVR) and Fermi resonances is addressed.

References

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Mapping Vibronic Couplings in Mixed-Frequency Regimes Using Coherent Multidimensional Vibrational-Electronic Spectroscopy

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Understanding coupled nuclear and electronic motions is critical for controlling ultrafast processes in strongly coupled molecular and material systems. Two-dimensional vibrational pump, electronic probe (2DVE) spectroscopy offers a direct approach to study these processes by linking molecular vibrations (nuclear motion) with electronic transitions. This technique, initially demonstrated by Courtney et al., has proven instrumental in examining vibronic couplings in various molecular systems. [1-2]

In this study, we use femtosecond multidimensional 2D and 3D VE spectroscopy to understand the mechanism of vibronic coupling in 10-hydroxybenzo[h]quinoline (HBQ), a model system known for ultrafast proton transfer.[3] In HBQ, we observe strong coupling between the O-H stretching mode (vOH) and electronic excitations. Fourier analysis of our 1DVE data reveals coherent oscillations arising from low-frequency vibrational modes that modulate hydrogen bond distances, which in turn affect the detected electronic signal. Using 3DVE spectroscopy, we further map the couplings of the high frequency O-H stretch (w1), low-frequency skeletal modes (w2) and the electronic frequency (w3). Overall, our results represent a significant step in mixed-frequency methodology development and demonstrate the promise of harnessing coupled vibrations to alter electronic properties of molecules.

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Vibronic coupling probed by single-crystal FIRMS

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Vibronic coupling is a central component of energy transfer processes, and is a fundamental mechanism in dictating spin lifetimes in solid materials. Previously, we have used far infrared magnetospectroscopy (FIRMS) to probe vibronic coupling for a polycrystalline sample of the rare-earth molecular qubit [Yb(trensal)].[1] In that work we developed *ab initio* calculations of the FIRMS spectra to assign transitions, identifying an “envelope effect” that served to conceptually de-couple the FIRMS intensity from the underlying vibronic coupling strength. All features that we discussed were assigned to an intra-Kramers doublet origin, whereby the vibronic transition involves a low-energy EPR-like transition within the ground Kramers doublet and simultaneous excitation of a high-energy optical phonon mode. However, that assignment was quite difficult as it was on the basis of what “looked best”. In this work we have now performed single crystal FIRMS measurements on the same molecular material, which allows us to directly prove from the experiments that our previous assignments of all intra-Kramers vibronic transitions were correct, and furthermore directly shows very weak coupling between vibrational modes: i.e., the usual assumptions of uncoupled harmonic oscillators appears to be well justified by our experimental data. Improved ab initio simulation of FIRMS maps are demonstrated on the basis of embedded periodic calculations of the vibronic coupling for the molecular crystal.[2]

References

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Manipulating reaction dynamics through vibronic coupling in higher-lying electronic states

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The coupling between vibrational and electronic degrees of freedom in a molecule provides an opportunity to selectively control chemical reactions by enhancing or suppressing specific nuclear motions upon optical excitation. In general, optical excitation promotes a molecule to an electronically excited state, where the ensuing dynamics depend on the details of the adiabatic potential energy surface that dictates the motions of the nuclei. Accessing higher-lying electronic states raises the possibility of new reaction channels, but is often limited by rapid internal conversion to the lowest excited state, a manifestation of Kasha's rule. We have shown that sequential excitation with two photons can overcome this limitation by accessing higher-lying electronic states from non-equilibrium geometries in order to sample new regions of the excited-state potential energy surfaces.[1] In short, this approach takes advantage of time-evolving Franck-Condon factors to control the outcome of a reaction by selectively altering the vibronic coupling that is responsible for the dynamics in the upper state. Understanding the dynamics in these higher-lying states presents many challenges, both experimental and theoretical, due to the large density of states above S_1, strong non-adiabatic coupling among these states, and fleeting lifetimes. Therefore, in order to probe the vibronic interactions that are responsible for launching new reaction channels, we use time-resolved resonance Raman scattering (i.e., FSRS) to directly probe the motions of the wave packet following sequential excitation to the higher-lying states.[2,3,4] Analogous to ground-state resonance Raman spectroscopy, the resonance condition in the FSRS measurement probes the topology of the upper-state potential energy surface, and therefore provides an insightful window on the dynamics in the higher-lying state and the ability to selectively control reactions based on vibronic coupling interactions.

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A route to chip-based ultrafast light sources for coherent Raman imaging

C. Fallnich[1,2], **K. Wallmeier**[1], **M. Gao**[1], **N.S. Lemberger**[1],
M. Timmerkamp[1], **N.M. Lüpken**[1]

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Shoebox-sized all-fiber light sources based on dispersively matched mode-locked lasers pumping an optical parametric oscillator (OPO) do become prominent driving sources for coherent Raman scattering (CRS) [1], as fast tuning to different vibrational resonances in less than about 5 ms across a tuning range of 2700 cm^{-1} enables a wide field of applications. The next innovation for an even broader use of CRS, e.g. in chemical research, biology, medicine, and forensics, will come with down-scaling system dimensions of ultrafast dual-wavelength light sources by transitioning from fiber- to chip-based approaches. With a 20 mm long silicon nitride (SiN) waveguide and a narrowband pump laser, idler pulses with an energy of up to 210 pJ and a spectral bandwidth down to 11.2 cm^{-1} were obtained for CRS spectroscopy and microscopy with a signal-to-noise ratio of up to 13.4 [2]. Even a two-wavelength pair SiN-OPO has been realized by exploiting both fundamental transverse modes of a single SiN waveguide within a single cavity including a tunable birefringence to generate two independently tunable idler pulses with arbitrary frequency spacing between zero and 65 THz in the wavelength region from 1.11 to 1.46 μm [3]. All above so-called hybrid fiber-waveguide OPOs show a route to fully chip-based ultrafast light sources for CRS, because increasing their oscillation threshold via reduced efficiency of the feedback loop revealed the feasibility of OPO integration on a single chip for pulse repetition rates around 100 MHz [4]. Together with current improvements towards chip-based mode-locked light sources [5,6], compact matchbox-sized light sources seem to become realistic, paving the way towards robust and low-price lab-on-a-chip CRS applications.

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Towards Controlling Excited State Reactivity in Organic and Organometallic Systems: A Perspective Through Ultrafast Multidimensional Spectroscopies

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Controlling excited-state reactivity through bond-specific IR excitation is a fundamental research focus.[1] Our work explores excited-state dynamics in organic and organometallic chromophores, including electron/charge transfer, excited-state symmetry breaking (ES-SB), and proton transfer. We studied donor–acceptor–donor (D–A–D) chromophores exhibiting ES-SB,[2,3] and donor–acceptor (D–A) chromophores with electron or charge transfer. We aim to probe in these molecules how selective IR excitation of C≡C stretches influences their excited-state behaviorm with the aim of influencing their photodynamics. Modifications introducing rotational asymmetry revealed intriguing differences, and further investigations examined the role of redox states in ES-SB dynamics.

Parallel studies on symmetric Pt(II) bis-acetylide complexes assessed how ligand arrangement (*cis* vs *trans* geometry), conjugation length, and substituents affect the observed photodynamics and potential for ES-SB.[4] Another system involved proton transfer (PT) in a symmetric molecule with two PT sites, where ultrafast single-sided PT and isomerisation occur. Multipulse experiments tracked ground-state back-PT and explored triggering a second PT.

Using time-resolved spectroscopy (including tr2DIR, 2D-VE), we analyzed relaxation dynamics, vibronic couplings, and solvation effects, focusing on C≡C stretches (1950–2250 cm^{-1}) involved in charge transfer. Combined with calculations and spectroelectrochemistry, these methods provide unique insights not available otherwise.

ES-SB dynamics in D–A–D systems showed strong solvent dependence, but permanent control over photoexcitation outcomes remains elusive. Ongoing studies on other systems aim to generalize this approach and further guide molecular design.

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Distinguishing spectator from driving vibrational modes in excited state photochemistry

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Our depiction of chemical reactions typically involves plotting a potential energy surface against some reaction coordinate. This convenient representation is essential for accurate determination of reaction rates; however, it generally lacks specificity on the nature of the multiple nuclear coordinates involved in the reaction mechanism. Quantitative measurements of the multidimensional character of potential energy surfaces can provide fundamental understanding into reaction mechanisms, and suggest future directions for reaction design and control. Here, we use femtosecond stimulated Raman spectroscopy with mode-selective amplification in order to directly quantify the contribution of specific nuclear coordinates to a chemical reaction. We either amplify or suppress a single vibrational mode through impulsive Raman excitation, and use femtosecond Raman probes to monitor the impacts on a photoinduced chemical reaction. In this way we can distinguish driving modes, which are those that are crucial for reaction progress, from spectator modes, which are those that are merely along for the ride. We demonstrate this approach on several chemical processes, including photoinduced spin transformations, exciton transport, and photoinduced charge transfer. Overall our work shows the utility of vibrational spectroscopy and structural analysis in determining reaction mechanisms, and shows how spectroscopic-based insights can be used for rational molecular design.

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Optical and electrical investigations of molecules in plasmonic nanojunctions

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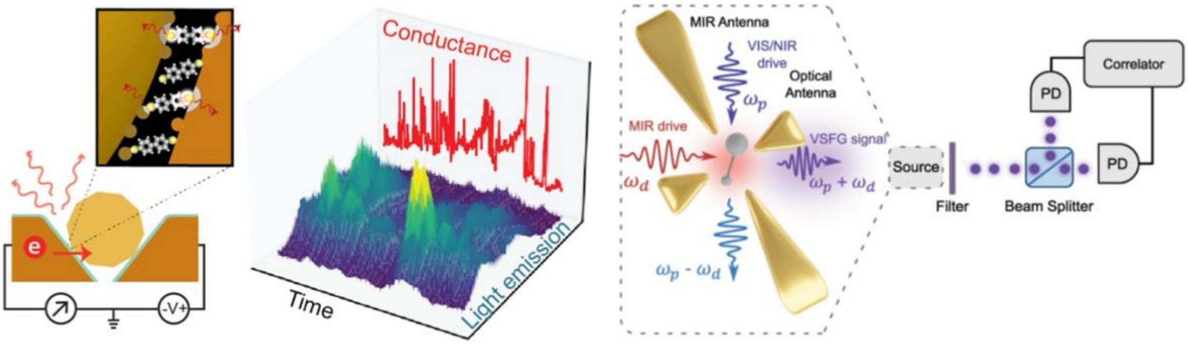
Plasmonic nanojunctions are formed by nanoscale gaps between metallic nanostructures. They boost light-matter interaction by orders of magnitude, offering unrivaled performance when it comes to amplifying incoming and outgoing optical signals from individual molecules. Moreover, they can be electrically connected to simultaneously probe electron transport through the guest molecules. In this talk, I will summarize our recent experiments aimed at probing the vibrational, optical, and electrical response of a small number of molecules trapped in a plasmonic nanojunction [1]. I will focus on the use of dual-resonant plasmonic antennas that enable resonant mid-infrared excitation of vibrational modes simultaneously with surface-enhanced Raman scattering or fluorescence measurements [2], with the prospect of adding electrical gates. The platform is a powerful testbed for molecular and nano-science, and the strong anharmonicity of molecular vibration is seen as a resource for applications in molecular quantum optics and molecular optomechanics [3].



Left: The dynamics of single molecule-gold contacts is imprinted on the conductance and electro-luminescence of the nanojunction [1]. Right: Proposal for anharmonic vibrational photon blockade in single-molecule mid-infrared upconversion [3]

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Unveiling the Impact of High-Frequency Vibrations on Electronic Properties in Soft Optoelectronic Materials

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Selective excitation of vibrational states in soft photovoltaic materials has emerged as a powerful tool for modulating key electronic properties, including charge transfer, carrier mobility, and recombination dynamics. To address this, we conduct vibrationally promoted electronic resonance spectroscopy (VIPER) with action detection to directly capture the transient dynamics of vibrational–electronic coupling, particularly, under operando conditions of functional materials/devices.

We first resolve time-dependent vibronic coupling lasting for 300 fs in perovskite nanocrystals ($FAPbBr_3$). Through temperature-dependent VIPER dynamics and anisotropy analysis via traditional two-dimensional infrared vibrational spectroscopy (2DIR), we conclude that fast vibronic coupling arises from the break of hydrogen bond (N–H•••X) triggered by the reorientation of the FA cation, which in turn results in electronic bandgap fluctuations.

Building on this foundation, we extend this novel vibrational spectroscopy to non-fullerene organic systems, which inherently possess richer vibrational structures and stronger electron–phonon coupling due to their diverse bonding configurations and conformational flexibility. We experimentally confirm the electronic transition pathway could be modulated by specific high-frequency mode within the fingerprint region in organic donor-acceptor bulk heterojunction. The observed mode-selectivity highlights the significance of vibration control in soft materials, offering valuable insights for material design and device performance optimisation.

Hybrid Interfaces for Sensing and Control in Fluorescent Organic Molecules

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The physics of single molecules involves complex interactions between electronic and vibrational modes. In particular, at liquid-helium temperatures, polycyclic aromatic hydrocarbons present a lifetime-limited optical transition, making them a platform of choice for the generation of undistinguishable photons and for quantum sensing [1, 2]. Our recent theoretical work on a framework for a vibronic model of molecules [3] highlights the possibility of inducing a coherent interaction using laser excitation. We particularly highlight the similarity between this system and a cavity QED system, where the electronic two-level transition plays the role of the two-level atom, and the vibrational mode corresponds to the cavity bosonic mode. The coherent population of the vibrational mode alters the fluorescence of the molecule and thus provides indirect evidence that the system enters this regime.

I will present our latest experimental results on the characterization and manipulation of vibronic coupling on a single molecule of dibenzoterrylene embedded in an anthracene nanocrystal. In particular, I will discuss the use of continuous-wave and pulsed excitation schemes in the high-saturation regime, providing insights on the cooperativity of the system and our work toward coherent excitation of vibrational modes. Additionally, I will present our efforts towards porting these techniques to engineered long-lived vibrational states, as was previously proposed in other theoretical works [4]. Finally, I will discuss the potential of this system for leveraging the vibrational modes of the molecule in order to realize THz to optical transducers.

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Computing Vibronic Spectra after vibrational pre-excitation with FCclasses code

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Vibrational pre-excitation can modulate the shape and intensity of electronic spectra. We have recently released a new version of our code Fcclasses 3.0 [1] which implements time-independent (TI) and time-dependent (TD) approaches for the computation of vibronic spectra. The code assumes harmonic approximation for the potential energy surfaces of both the initial and final states of the transition, but it allows the possibility that normal modes and frequencies of the two staes are different. FCclasses 3.0 can simulate a number of spectroscopies, and namely one-photon absorption (OPA), emission, electronic circular dichroism (ECD), circularly polarized luminescence (CPL), two-photon absorption (TPA), two-photon circular dichroism (TPCD), magnetic circular dichroism (MCD) and Resonance Raman, both at 0 Kelvin and considering an initially thermally equilibrated distribution.

In order to aid the interpretation of VIPER spectroscopies the code implements also the possibility to compute spectra at 0K from initial states vibrationally excited along a single mode or pair of modes, both in Franck-Condon (FC) and in Herzberg-Teller (HT) approximation. This implementation has been used in combination with OPA [2] and TPA [3], but it is ready to be used with any of the spectroscopies known to FCclasses. In the same way the code can also compute non-radiative decay rates from vibrationally excited states.

In this contribution we will illustrate the capabilities of FCclasses for computing vibrationally pre-excited electronic spectra and we also discuss some a priori criteria to predict the possible impact of the pre-excitation of different vibrations [2-3].

Finally, we will also show recently proposed mixed quantum-classical strategies to perform these computations for flexible molecules, characterized by soft anharmonic modes and also in explicit homogeneous and heterogeneous environments [4].

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Enabling single molecule infrared spectroscopy through fluorescence detection

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Fluorescence-encoded infrared spectroscopy (FEIR) is a new nonlinear vibrational technique that can be used for single-molecule spectroscopy of solution-phase chemical dynamics. By upconverting an IR vibrational excitation to an electronic excited state, fluorescence emission can be used as a high sensitivity readout of vibrational spectra. Using single-molecule fluorescence detection and confocal microscopy, FEIR brings the sensitivity of vibrational spectroscopy to a nanomolar concentration where a single fluorophore exists in the probe volume. This opens the possibility of investigating chemical dynamics on the angstrom length scale where vibrational spectroscopy is sensitive.

This presentation will review the experimental and theoretical principles of FEIR as applicable to the design of single molecule experiments and describe experiments to study diffusion-controlled bimolecular reactions in solution. Analogous to fluorescence correlation spectroscopy (FCS), our FEIR correlation spectroscopy experiments use FEIR photon emission trajectories from state-specific vibrational probes to track changes during a reaction and through the equilibrium fluctuations of FEIR intensity.

Vibrationally resolved electronic spectra from Hagedorn wavepacket dynamics

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Hagedorn functions are carefully constructed generalizations of Hermite functions to the setting of many-dimensional squeezed and coupled harmonic systems [1]. I will describe recent developments that allowed application of Hagedorn wavepackets to vibronic spectroscopy of even anharmonic systems. To evaluate time correlation functions needed for computing spectra, we first derived efficient recursive expressions for the overlaps between Hagedorn bases associated with different Gaussians [2]. To succinctly highlight advantages of Hagedorn wavepackets, I will focus on applications to single vibronic level (SVL) fluorescence experiments, in which the electronically excited initial state is also excited in one or several vibrational modes. In displaced, squeezed, and Duschinsky-rotated globally harmonic systems, Hagedorn functions are exact solutions to the time-dependent Schrödinger equation and can be propagated with the same equations of motion as a simple Gaussian wavepacket; emission spectra from arbitrary vibronic levels can be evaluated using a single trajectory. After validating the method by comparing it with exact quantum calculations [3], we applied it to compute SVL spectra of anthracene by performing wavepacket dynamics on a 66-dimensional harmonic potential energy surface constructed from density functional theory calculations [4]. However, real molecules have anharmonic surfaces. To partially describe effects of anharmonicity on spectra, we combined the Hagedorn approach with local harmonic approximation of the potential [5] and with on-the-fly ab initio dynamics, which allowed us to compute SVL fluorescence spectra of difluorocarbene, a floppy molecule with a very anharmonic potential energy surface [6]. Time permitting, I will also briefly mention other improvements and applications to other spectroscopies, such as evaluating Herzberg-Teller and resonance Raman spectra.

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Functional bond-selective microscopy toward the single-molecule, super-resolution regime

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Advances in optical spectroscopy and microscopy have revolutionized our understanding of biological functions at the sub-cellular levels. In this talk, I will present BonFIRE - a Bond-selective Fluorescence-detected InfraRed-Excited imaging technique that integrates mid-infrared and near-infrared double-resonance excitation to achieve single-molecule sensitivity across a broad range of vibrational modes. This microscopy platform unlocks a suite of capabilities, including single-molecule infrared spectral profiling, wide-field super-multiplex imaging, vibrational lifetime imaging, and two-dimensional vibronic fluorescence mapping. These features collectively should enable unprecedented insights into heterogeneous cellular interactions and microenvironments.

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IR-control of photoinduced electron transfer in solution

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A. Auty,[1] G.Wu,[1] J. Shipp,[1] C. Royle,[1] R. Fernandez-Teran,[1] T. Cheng[1]
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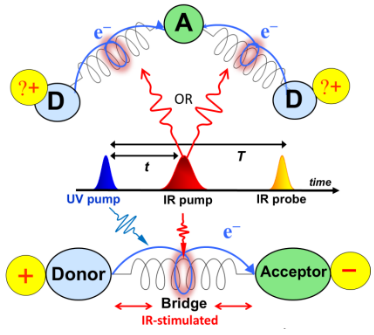
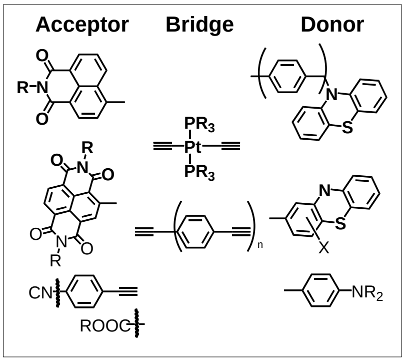
The ability to direct the outcome of photochemical reactions has long been considered one of the “Holy Grails” of photochemistry. Ultrafast photoinduced electron transfer in Donor-Bridge-Acceptor systems, operating in non-BO regime, offers an exciting opportunity for such a control.[1-4] In DBAs, an electronic excitation populates a charge-transfer excited state. This state branches into several singlet and/or triplet states, including a full charge-separated state, D^+BA^-. The IR-excitation of bridge vibrations during branching can potentially alter the rates of charge transfer[4] or the yield of the product states.[1-3] To realise this idea, a pulse sequence **{fs UV/Vis$_{pump}$}–{narrow-band IR$_{pump}$} – {broadband IR$_{probe}$}**.



We observed a drastic decrease (up to 100%) of the population of the charge-separated state in the systems with a Pt(II) trans-acetylide bridge, B = **C≡C-Pt-C≡C,** when the bridge vibrations (~2000 cm^{-1}) are pumped as the excited state landscape evolves. We developed a large library of such **D-B-A** systems, in which IR-perturbation changes the product state population, yet so far we only observe a *decrease* in the population of the charge-separated state.



In the related “fork” systems with two pathways, and two **D**-moieties (Fig 1, top) where the two acetylide bridges differ by ^{13}C-substitution, transient IR-perturbation of one of the bridges also causes a *decrease* in the population of the relevant D^+BA^- state. The D-B-As where B = $(\text{-C≡C-Ph})_n$ (including TICT systems, e.g. Me_2N-Ph-C≡C-Ph-CN), also show susceptibility to IR-perturbation.

The range of open questions include: the role of *vibronic coupling*; the importance of *strong coupling* between D-B and B-A; and the role of low-frequency modes in the effects observed. The experimental and DFT data indicate that the mechanism of IR-control depends on the system, and we hope to discuss this at the meeting.

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Recent progress in time-domain stimulated Raman excited fluorescence spectroscopy

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The pursuit of better sensitivity has always been one of the central themes in Raman spectroscopy. Recently, all-far-field single-molecule Raman spectroscopy has been demonstrated by a novel hybrid spectroscopy that couples Raman scattering with fluorescence emission. However, such frequency-domain spectroscopy lacks efficient hyperspectral excitation methods and encounters intrinsic strong fluorescence backgrounds from electronic transitions, hindering its applications in advanced Raman spectroscopy and microscopy. In this talk, we will present the ultrafast time-domain spectroscopy counterpart named transient stimulated Raman excited fluorescence (T-SREF): excited by two successive broadband femtosecond pulse pairs (i.e., the pump and Stokes pulses) with time-delay scanning, we successfully encoded Raman free-induction decays into fluorescence emissions of fluorophores through vibrational wave packet interference, resulting in background-free spectra of the corresponding Raman modes after the Fourier transform. T-SREF achieves background-free Raman spectra of electronic-coupled vibrational modes with sensitivity up to the level of a few molecules, imaging applications in molecular dynamics sensing will be discussed.

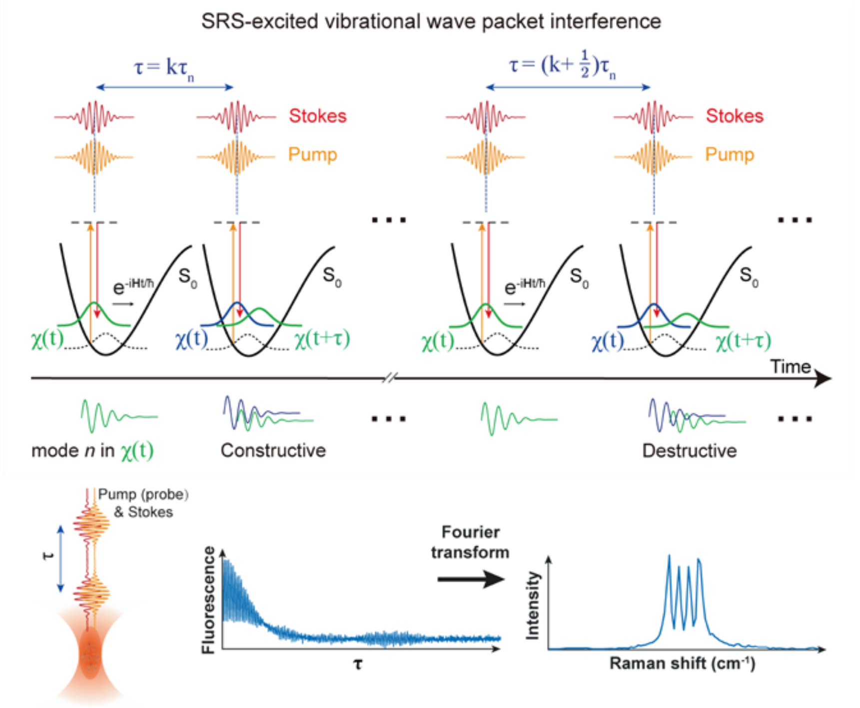

Figure 1: Principle of transient stimulated Raman excited fluorescence spectroscopy.

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Nonlinear IR-visble interactions: From Multiplexing Imaging to Ultrafast Quantum Emitters

Bin Yang[1], Chenglai Wang[1], Chang Yan[1] and Wei Xiong[1]

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Nonlinear interactions between infrared and visible light with matter can manipulate both electronic and vibrational properties, opening new avenues for analytical differentiation and active photonic control. In this talk, I will highlight two examples:1. Multiplexed Detection via Vibronic Coupling and Strong-Field Ionization: By exploiting vibronic coupling and strong-field ionization, we developed a fluorescence imaging strategy—MD-WISE—that enables multiplexing across visible, infrared, and temporal domains.[1] 2. Ultrafast Single-Photon Emitters: We demonstrate the generation of ultrafast single-photon emitters through strong-field IR–visible interactions on nanoparticles, offering a new platform for nonlinear quantum photonics.[2]

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Mechanism of aggregation-induced emission and control of excited state dynamics

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Abstract: The aggregation of molecules into nanostructures often results in fluorescence quenching, whereas a small group of exceptions do the opposite. Using ultrafast uv-vis and infrared multi-pulse mixing sequences and non-linear spectroscopic techniques, we carried out a detailed study of the evolution dynamics of molecular electronic excited states, revealing the mechanism of aggregation-induced emission of TPE molecules, and discovering that the fluorescence of the AIE molecules are of anti-Vavilov's rule. Based on the mechanism, we are able to tune photochemical reactions by mode-selective vibrational excitations.

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Modeling nonlinear optical spectroscopy signals in molecules beyond the Condon approximation

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Theoretical spectroscopy plays a crucial role in understanding light-driven properties of materials and molecules. Truly predictive modeling of optical properties of systems in the condensed phase, such as solvated molecules, is however highly challenging, as direct couplings of the electronic states to the complex environment must be accounted for. Additionally, non-Condon effects due to vibrationally induced symmetry breaking[1], or nonadiabatic effects due to multiple explicitly coupled electronic excited states[2,3] influence light-induced energy relaxation dynamics in a wide range of molecular systems and are notoriously difficult to model. In this talk, I will showcase several approaches recently developed by us to address this challenge. These can be grouped into *static methods*[4] based on parameterizing harmonic model Hamiltonians from vibrational normal mode calculations, or *dynamic methods*[2,3] based on sampling fluctuations of the excitation energies and transition dipole moments of molecules in the condensed phase along ground state molecular dynamics trajectories. Spectra are then computed either in the adiabatic picture, where non-Condon effects are accounted for through Herzberg-Teller type couplings, or in the diabatic picture, where the exact quantum dynamics of the system is solved using powerful tensor-network approaches. All developed approaches are implemented on graphics processing units (GPUs), enabling the rapid computation of linear and nonlinear optical spectra in a wide range of complex systems. We demonstrate the strengths of the developed approaches on several model systems, including modeling the finite temperature 2D electronic spectrum (2DES) for the Q_x band of porphyrin, or the solvent-driven quenching of dual fluorescence in the proflavine molecule[5].

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Abstracts of Posters

(in alphabetical order)

"Nonlinear Optical Properties of Hexagonal Boron Nitride Nanosheet Thin Films: A Femtosecond Z-scan Study"

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Hexagonal boron nitride nanosheets (h-BNNs) have emerged as promising two-dimensional materials with exceptional optical properties, yet their nonlinear optical (NLO) characteristics remain largely unexplored. This study presents the first comprehensive investigation of the NLO properties of h-BNN thin films using the Z-scan technique with femtosecond laser excitation. h-BNN thin films were fabricated via mechanical exfoliation and characterized using UV-visible spectroscopy, transmission electron microscopy, and Raman spectroscopy to confirm their morphology and crystal structure. The nonlinear optical response was systematically evaluated using 100 fs laser pulses across excitation wavelengths ranging from 740 to 820 nm at a fixed average power of 1 W. The results demonstrate a linear decrease in the nonlinear absorption coefficient with increasing excitation wavelength. The h-BNN thin films exhibited remarkable optical limiting behavior characterized by reverse saturable absorption, indicating strong potential for laser protection applications. These findings establish h-BNNs as viable candidates for next-generation optical limiting devices and highlight their promise as sensitive optical components in photonic applications. The wavelength-dependent nonlinear response observed in h-BNN thin films provides valuable insights into their optical properties and opens new avenues for their implementation in advanced optical systems requiring precise power regulation and laser safety protocols.

The Role of the Dark States on Strong Exciton Photon Coupling Dynamics

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Strong exciton-photon coupling occurs when molecular transition dipole moment and electromagnetic field interaction energy exceeds energy dissipation in an optical cavity, spectroscopically observed as excited-state splitting into polaritons. For N molecules strongly coupled to a cavity mode, this creates N+1 hybrid states: two polaritons (upper and lower) acquire all oscillator strength, while the remaining N-1 states form an optically inactive "exciton reservoir" at the molecular energy level, critical for relaxation dynamics.[1] The relaxation from the exciton reservoir to the lower polariton is slow, making the dynamics of polaritonic relaxation primarily dependent on this relaxation rate. The rate of relaxation from the exciton reservoir to the lower polariton is mainly influenced by the size of the exciton reservoir. Therefore, understanding the effect of the size of the exciton reservoir on polaritonic photophysics is crucial.

In my presentation, I will demonstrate that polaritonic emission is inversely proportional to the size of the exciton reservoir.[2] Furthermore, I will present a kinetic model I developed to analyze angle-dependent lower polariton emission quantum yields. This model allows me to measure the relative size of the exciton reservoir and the lower polaritonic state with cavity detuning.[3] My research reveals that the size of the exciton reservoir decreases as the overlap between the absorption of the molecular transition and the lower polariton increases. Conversely, the size of the lower polariton increases with this overlap. Additionally, I will demonstrate how to use the source term method to quantitatively model the lower polariton emission in both transverse electric and transverse magnetic polarizations.[4]

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Unveiling Myoglobin COnformations: 2DVE and VIPER spectroscopy

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Structure determines function. This is of central importance to proteins, as for instance mutations or misfolded proteins can lead to disfunctional proteins. Many proteins such as Myoglobin (Mb) are known to exist in different conformations, which are in fast equilibrium. If these conformations are near the heme and associated ligand, each may exhibit a different vibronic coupling. With Two-Dimensional Vibrational Electronic (2DVE) spectroscopy, these different ligand-binding substates can be investigated and even studied selectively through VIbrationally Promoted Electronic Resonance (VIPER) spectroscopy.

2DVE spectroscopy probes the interaction between vibrational modes and the electronic absorption spectrum.[1] VIPER spectroscopy combines a resonant IR with an off-resonant Vis pump pulse. The IR excitation induces a redshift in the visible absorption spectrum through vibronic coupling, bringing the initially off-resonant Vis pulse into resonance, allowing for electronic transition. Tuning the IR pump enables selective excitation of compounds that share similar visible spectra but differ in the infrared.[2] However, this approach has only been successfully applied to small molecules so far. The goal of this work is to test it on a small protein (MbCO) for the first time, paving the way for future applications on other proteins.

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Dynamical contributions to the vibrational absorption lineshape of an intramolecularly hydrogen bonded organic dye compound

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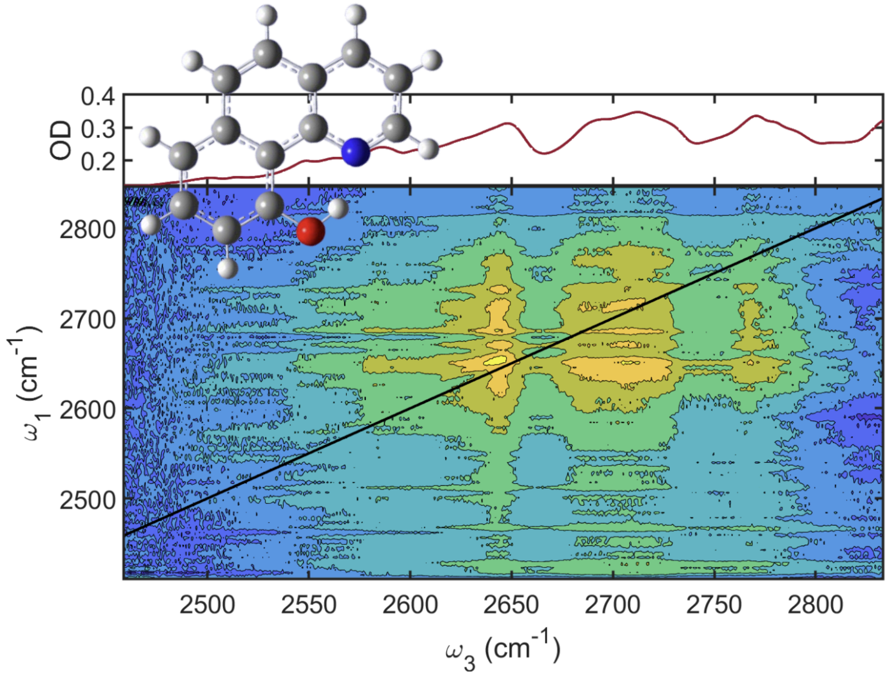
Understanding how dynamical processes in chemical systems are captured by linear spectra is a fundamental underpinning of molecular spectroscopy. Here, we investigate what dynamics contribute to the unique absorption lineshape in the OH stretch region of an intramolecularly hydrogen bonded compound, 10-hydroxybenzo[h]quinoline (HBQ). Broadband IR pump-probe and 2DIR spectroscopic measurements confirm an OH stretch lifetime of ~1.5 ps. Oscillations in the pump-probe and 2DIR signals over t_2 correspond to a low-frequency skeletal mode at 250 cm^{-1} which modulates the hydrogen bond distance. This structural modulation broadens the range of frequencies sampled by OH stretch. Spectroscopic experiments are supplemented by ab initio molecular dynamics (AIMD) simulations to further explain the extremely broad feature and substructure "finger" motif present in the linear spectra. Calculations and experimental measurements confirm that the frequency of the OH stretch is dependent on the hydrogen bond distance.



Quantum dynamical properties of Oligocene: from Spectroscopy to Machine Learning

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Femtosecond transient absorption spectroscopy is a powerful technique for probing ultrafast molecular dynamics. However, interpreting the resulting data typically demands extensive human expertise, comprehensive literature analysis, and substantial computational effort to support theoretical models. To address this challenge, we developed a deep neural network capable of real-time analysis of experimental data, enhanced by quantum-mechanical descriptors, to predict the relaxation kinetics of organic chromophores with over 80% accuracy. The evaluation of the neural network on simulated data confirmed the significant improvement of the prediction (6-8%), underscoring the value of hybrid data integration. This model was applied to transient absorption of a group of recently developed oligocenes due to their intriguing photodimerization properties. The results showed a non-trivial dependence of the multi-step photodimerization efficiency on the number of aromatic rings in linear oligocenes. The analysis suggests a complicated relation between formation yield and the stability of the side products for different molecule size. This property leads to similarly efficient dimerization in molecules with five and nine aromatic rings and almost completely prevents the dimerization of the seven-ring molecule.

2D-IR Spectroscopy reveals structural heterogeneity in GLFG-rich hydrogels as models for the nuclear pore complex

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The nuclear pore complex (NCP) allows regulated exchange of material from the nucleus to the cytoplasm and vice versa thereby playing a key role in maintaining cellular metabolism. This complex molecular machinery allows unregulated entry of materials with sizes < 5 nm simultaneously serves as a macromolecular sieve for cargos whose sizes exceeds the desired limit [1,2].

The properties of this molecular sieve are determined primarily by intrinsically disordered proteins (IDPs, specifically nucleoporins) with the characteristic repeat sequence GLFG/ FG / GxFG. Upon a hydrophobic collapse these IDPs form a mesh-like network permitting the cargo-regulating functionality of the NPC.

Purified nucleoporins as well as peptides with repeats of the sequence motif FG or GLFG form hydrogels in vitro and hence can also be interesting as biomimetic materials[3]. The investigation of secondary structure elements or mesoscale structures, like fibrils, and related structural dynamics is difficult to access by typical structure-sensitive methods. To unravel the dominant secondary structures in GLFG-based gels (as models for the sieve in the NPC) we have studied single GLFG repeats with differing N- and C-Terminal residues by FTIR spectroscopy and 2D-IR spectroscopy.

The 2D-IR spectra reveal the formation of fiber containing β-sheets in one of the GLFG sequence whereas non-fibrous β-sheets primarily constitute the other two sequences with unstructured regions composed of random coils and turns sharing commonality in all three sequences. The gel-like structures undergo a reversible phase-transition upon temperature change which can be followed in detail by the 2D-IR data.[4] Our findings show that amino-acid sequences which are not integral to the GLFG sequence may also play a vital role in determining the overall macrostructure of the NPC.

Overall, the results demonstrate how 2D-IR can reveal predominant intrinsic structures in systems which appear heterogenous on larger lengths scales and serve as an example for studying phase transformations in biology.

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Same Same but Different: Vibronic Coupling to Selectively Target Subpopulations

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Achieving selective electronic excitation of specific molecules or subpopulations within a mixture is particularly challenging when their UV/VIS spectra are nearly identical. **VI**brationally **P**romoted **E**lectronic **R**esonance (VIPER) excitation exploits the fact that a vibrational excitation by IR light can modulate the UV/VIS spectrum via vibronic couplings.[1-3] A selective vibrational excitation can therefore control which molecules or subpopulations undergo electronic excitation.

2D Vibrational-Electronic (2D-VE) spectroscopy provides direct insight into IR-induced UV/VIS modulations (which we termed the VIPER effect), which are fundamental for the success of selective VIPER excitation. Applying this to a hydrogen-bonded complex between the Schreiner thiourea catalyst[4] and a coumarin dye in dynamic equilibrium, we observe distinct spectral shifts linked to IR selection of free versus H-bonded populations. Notably, a 2D-VE band, absent in FTIR spectra, suggests Fermi resonance involving a weakly IR-active mode strongly coupled to the electronic transition. Our results also demonstrate direct coupling of a vibrational mode to an electronic transition is not essential for subpopulation selection. We found vibrational energy transfer (VET) from the catalyst to the substrates through hydrogen bonds also to manipulate the UV/VIS spectrum.

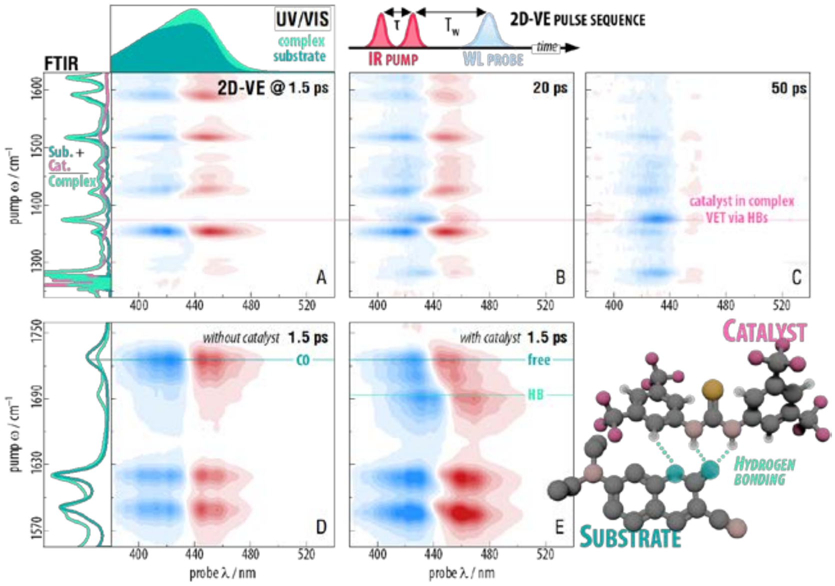

Figure 1 *Hydrogen bonding between a coumarin substrate and a Schreiner catalyst investigated with 2D-VE spectroscopy. (A-C) 2D-VE spectra in presence of the catalyst, VET from the substrate to the catalyst allow us to use vibrations for selection which are not directly coupled to the electronic transition.(D-E) 2D-VE spectra without and with catalyst in the C=O stretching region, (E) shows the coexistence of a free and H-bonded C=O band, an additional 2D-VE band appears from a Fermi resonance coupled to an electronic transition appears.*

In summary, our study shows how 2D-VE spectroscopy can be used to identify vibrations suitable for selectively exciting subpopulations in VIPER 2D-IR experiments, as demonstrated for the catalyst-bound or free subpopulation of substrate molecules. Selection can be based on direct vibronic couplings or VET. These findings open the door to exploring the role of structural heterogeneity of substrate-catalyst complexes in photocatalysis.

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Experimental exploration of third- order nonlinear properties of GQD prepared by pulsed laser ablation in liquid

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Graphene quantum dots (GQDs) have recently significant attentions because of their unique optical properties, particularly their strong nonlinear optical (NLO) properties. In this study we explore the optical properties of GQDs synthesized via pulsed laser ablation in liquid, straight forward and eco friendly technique that allows production of highly pure GQDS nanoparticles without any reagent or caping agent. UV- visible absorption spectroscopy, transmission electron microscopy (TEM), Raman spectroscopy, confirming their edge state dominant structure. Nonlinear optical properties were measured using Z-Scan technique with nanosecond laser at wavelength 1064 nm (pulse duration of 10 ns). GQDS exhibited strong reversable saturable absorption, and large nonlinear third- order susceptibility $\chi^{(3)}$. This study highlights the promising GQDs in optical limiting, ultrafast photonics, and laser protection application.

Azimuthal-Scanning and Phase-Resolved Vibrational Sum-Frequency Microscopy

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Structural heterogeneity is an abundant feature in a wide range of materials and interfaces, manifesting as variations in density, composition, and crystalline packing. These variations are prevalent in both molecular systems such as self-assembled mono/bilayers, and atomic structures such as 2D materials. The heterogeneity in these systems can have a profound impact on their macroscopic properties but characterising it can be a formidable challenge. For example, they can be extremely difficult to image with conventional optical or scanning probe microscopies, and their spectroscopic signals (e.g. Raman or second-harmonic generation) are often feeble.

Here, we introduce phase-resolved and azimuthal-scanning sum-frequency (SFG) microscopy as a technique to characterise the structure of these systems. By combining a resonant IR excitation of the molecular vibrations or lattice phonons that substantially enhances the second-order signals, with an off-resonant visible upconversion, we image the resulting SFG signals in a wide-field optical microscope. By further heterodyning the signals, we also obtain phase resolution that enables the characterisation of absolute orientations. Finally, through azimuthal-scanning, whereby the SFG images are recorded as a function of sample rotation, the SFG signals can be separated into their components from the different crystalline packing symmetries.

This technique is demonstrated on both a phase-separated chiral lipid monolayer and CVD-grown monolayer flakes of hexagonal Boron Nitride (hBN). For the lipid sample, we fully characterise the heterogeneity in density, composition, and 3D packing structure, showing domains with substantial compositional enrichment and mesoscopic chiral crystalline packing. For the hBN, we isolate and fully determine the crystallographic axes of its 3-fold D_{3h} symmetry, showing the dominance of 'zig-zag' terminated crystal edges with N termination. By further coupling this technique with electronic excitation using a tuneable visible source, such a 'doubly-resonant' SFG approach has significant potential to expand this structural characterisation to also include the manipulation and characterisation of electronic properties.

THz vibrational dynamics of Liquid Crystals: from molecular origin to bulk response

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The Liquid Crystal (LC) phase is characterized by a hybrid of properties commonly attributed to solids and liquids. In these phases of matter, anisotropic molecules retain their ability to flow, but show a combination of macroscopic positional and orientational order. This ability to tune the collective degree of order by tuning the LC phase for a given molecular species provides a unique platform to investigate the interplay between vibrational dynamics on a molecular level and the collective macroscopic properties. The vibrational dynamics of complex molecules is known to be strongly delocalized over intra- and intermolecular modes in the low THz regime, hence THz spectroscopic methods are the ideal tool to probe for these dynamics. Table top THz emitters and detectors have reached a level of maturity that allows for a broad range of investigations.

Here, we present investigations into linear and nonlinear spectroscopic responses of benchmark thermotropic LC systems. In particular, we studied 8CB (4 -Octyl-4-biphenylcarbonitrile) consisting of an alkyl chain, a bi-phenyl group, and a cyano group, 8OCB (4′-octyloxy-4-cyanobiphenyl) presenting one additional oxygen, and PCH5 (4-(trans-4-Pentylcyclohexyl) benzonitrile) with one phenyl group exchanged for a cyclo-hexane group. These molecules have been chosen thanks to their structural similarities in order to disentangle the influence of the molecular composition on the intermolecular response. We probe these systems from two points of view. Firstly, we look at the linear absorption in a broadband (1-7.5THz) Time Domain Spectroscopy (TDS) setup, which spans both intra- and intermolecular vibrations. Secondly, we use the same setup to drive these modes coherently with strong THz pulses of up to 2 MV/cm in the interaction region, in order to induce a nonlinear response and to follow the relaxation of the bulk in a time resolved manner by looking at the transiently induced birefringence in a Kerr-type geometry.

Self-Calibrated Stimulated Raman Scattering Spectroscopy for Rapid Cholangiocarcinoma Diagnosis

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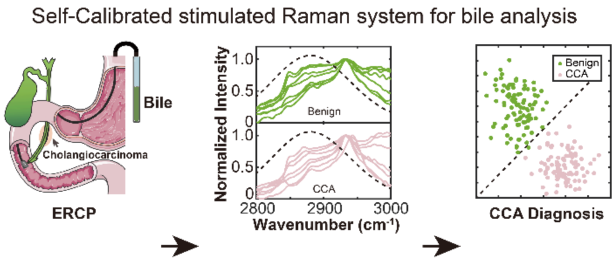
Abstract: Cholangiocarcinoma (CCA) is an aggressive malignancy with poor clinical outcomes. The current "gold standard" diagnostic approach, endoscopic retrograde cholangiopancreatography (ERCP)-obtained biopsy, has a relatively low sensitivity (i.e., ~ 50%). Here, we developed a bile-based diagnostic system using transient stimulated Raman scattering (T-SRS). Except for the tolerance to autofluorescence inheriting from traditional SRS spectroscopy, T-SRS features quantum-limit spectral line shapes, and is further improved with self-calibration ability in this research. These advantages make the acquired Raman spectra insensitive to the drifting of excitation parameters, facilitating long-term reliability. Based on the T-SRS spectra in the C-H stretching region from 76 bile samples accumulated over more than one year, we demonstrated high accuracy (i.e., 85% ± 3%) and sensitivity (i.e., 87% ± 9%) for classification between CCA and benign diseases. The T-SRS acquisition only requires ~9-μL bile samples and features drastically improved time cost. This study suggests the self-calibrated T-SRS analysis of the bile sample offers a promising approach for rapid CCA diagnosis.


Self-Calibrated stimulated Raman system for bile analysis

Radiative and non-radiative decay in carbazole-substituted polychlorinated triphenyl methyl radicals

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Vibronic coupling is ubiquitous in the context of electronic spectroscopy. It is one of the main interactions determining the shape of absorption spectra but also non-radiative decay and, hence, excited-state dynamics. Based on that, the field of optical spectroscopy constantly deals with vibronic coupling and especially its consequences for the photophysics of molecules.

In the field of light-emitting devices (LEDs), these photophysics play a key role in the selection of suitable materials. Due to their favorable emission properties, polychlorinated triphenylmethyl radicals have become a promising class of compounds in this context. Among them, donor-acceptor motifs showing high emission quantum yields and enhanced stability have been developed. Following this approach, we examined the photophysical properties of three donor-acceptor structures: the literature-reported carbazole-substituted tris(2,4,6-trichlorophenyl)methyl radical (TTM-Cz)[1] and two derivatives where one TTM unit has been replaced by either a pyridine (PyBTM-Cz) or by a pyrimidine (PymBTM-Cz) unit.

We found that the emission quantum yields differ significantly across the radical series with TTM-Cz exhibiting the highest emission quantum yield and PymBTM-Cz the lowest emission quantum yield. Femtosecond transient absorption spectroscopy in toluene and dichloromethane was performed to get a deeper insight into the excited-state dynamics of the radicals and to explain their different emission behavior. We found a strong correlation of the emission quantum yields and the excited-state lifetimes of the compounds indicating that additional non-radiative decay pathways are present in PyBTM-Cz and PymBTM-Cz and are responsible for their faster relaxation. The TA data suggest that the observations are related to different excited-state geometries, namely a change in the dihedral angle between the carbazole and the triarylmethyl moieties for TTM-Cz which is not observed for PymBTM-Cz.

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Probing Vibronic Dynamics in Rubrene Crystals via 2D-VE and VIPER Spectroscopy

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In polyacene crystals like rubrene one high energy excited state can be split into two triplet excited states [1] in a process called singlet fission (SF). This could potentially improve e.g. solar cell efficiency by generating multiple excited states from one single photon absorption. A recent paper by Maslennikov et al. [2] found that the branching between different singlet fission pathways in rubrene can be controlled by the excitation photon energy.

2D vibrational-electronic (2D-VE) spectroscopy [3] visualizes the modulation of the electronic state by vibrational excitation. Here we propose the mapping of the ground state vibrational modes in rubrene coupling to electronic excited states to explore its SF pathways. In a follow-up vibrationally promoted electronic resonance (VIPER) [4] experiment an IR and a UV/VIS photon (vibronically coupled) are combined to reach the electronically excited state, which is then probed in the IR, tracking the dynamics of the selected SF pathway.

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Structural analysis of transient reaction intermediate in formic acid dehydrogenation catalysis using two-dimensional IR spectroscopy

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To reduce the environmental footprint of modern societies and address the limitations of fossil resources, the projected increase in global energy demand must go along with implementing low-carbon energy production and carrier systems. Formic acid has great potential for use as a low-carbon hydrogen and energy carrier, as well as an e-fuel. We have developed a new class of phosphorus–nitrogen PN^3P-Ru complexes, which efficiently catalyze the formic acid dehydrogenation reaction with turnover numbers (TONs) exceeding 30 million. The molecular structure of a catalytically active key intermediate was determined in solution using 2D IR spectroscopy, which measures vibrational cross-angles. The spectroscopic studies show that the complex features a formate ion directly attached to the Ru center as a ligand, and a proton added to the imine arm of the (pseudo)dearomatized PN^3P^* ligand. During the catalytic process, the imine arm is reversibly protonated and deprotonated; furthermore, it also interacts with the protic substrate molecules (H_2O or HCOOH), effectively serving as a local proton buffer to offer remarkable stability.

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Decoding nanocrystal surface heterogeneity: insights from ligand vibrations and vibronic coherences

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Experimental evidence is presented for ligand-exciton vibronic coupling governing ultrafast charge localization in oleate-capped cadmium sulfide (CdS) nanocrystals (NCs) under varied charged surface environments. Using two-dimensional electronic-vibrational (2D EV) spectroscopy, we directly resolve correlations between electronic and vibrational degrees of freedom and map carboxylate vibrational modes to excitonic states. Resonant excitation of the 1S exciton manifold induces extinction changes in carboxylate modes associated with both asymmetric and symmetric stretching vibrations. Notably, the symmetric vibrations are preferentially anharmonically coupled to high-frequency CH stretches extended from the NC surface and overlapping the 1Pe–1Se intraband transition, thereby serving as a unique excitonic reporter of picosecond biexciton recombination via Auger processes. These results demonstrate that specific ligand populations—and the symmetry of surface-bound transition dipoles—play a critical role in directing ligand-exciton vibronic couplings and nonradiative relaxation channels in photoexcited NCs. Moreover, our findings reveal that these couplings are sensitive to different surface charging environments, highlighting their utility in characterizing NC surface heterogeneity and charge trapping. Finally, we introduce our early developments in mixed-frequency vibrational-electronic microscopy for probing excitation energy transport in semiconductor solids. Collectively, these insights—uniquely resolved by coherent multidimensional vibronic spectroscopies—advance our understanding of complex ligand–nanocrystal interactions and are integral to the design of next-generation nanocrystal photocatalysts and photovoltaic materials.

Nonradiative deactivation of photobasic Ru(II)- and Fe(II)-complexes

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Acid-base reactions are at the heart of many chemical and biological processes. The ability to spatially and temporally control them by the use of photoacids or photobases, meaning molecules which have a decreased or increased pK_a in the excited state, opens up a variety of possibilities in polymer sciences, electrochemistry or photolithography. While organic photobases are extensively studied, their metal-coupled counterparts are still not well understood and only a few reports exist.[1]

In this contribution we study novel Ru(II)- and Fe(II)-complexes, which, due to the inclusion of pyrazine moieties in their ligand design, can act as photobases. Within the group of complexes that we studied, the subsequent excited-state proton transfer (ESPT) reaction is particularly evident for $[Ru(dqpyz)_2]^{2+}$ (dqpyz=2,6-di(quinolin-8-yl)pyrazine), since this complex becomes non-emissive upon protonation. This particular property allowed us to determine its pK_a* value of 8.6 by pH-titration. We were further able to determine the time constant of the ESPT reaction via transient absorption (TA) spectroscopy, which yielded a value of 246 ps in acidic aqueous media.[2]

Further, we present ideas and design principles on how to transfer this concept to earth-abundant Fe(II) complexes on the example of the structurally analogous $[Fe(dqpyz)_2]^{2+}$. Here we also observed a nonradiative decay. However, the reason for this is entirely different, since this complex does not undergo ESPT, but instead relaxes back to the ground state via a competing deactivation channel.

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Illuminating Single- and Multi-Branched Donor–Acceptor Systems with Multidimensional Spectroscopies

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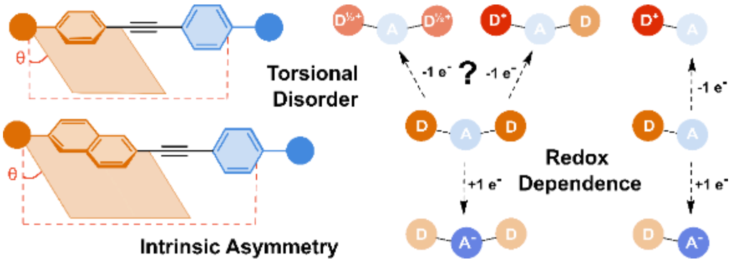
We are investigating Donor–Acceptor (D–A) and Donor–Acceptor–Donor (D–A–D) systems linked via acetylene bridges. Starting from fluorenone acceptor-based D–A–D systems,[1] we focus on the corresponding single-branched D–A counterparts with 4-NR_2-phenyl donor units, studying the influence of the alkyl chain length on the excited-state dynamics and spectral properties. In a second step, we expand the scope of D–A molecules by introducing different donor chromophores with intrinsic asymmetry, whilst completing the survey by varying the acceptor core. Using time-resolved infrared spectroscopy (TRIR) as well as transient electronic absorption spectroscopy (TA), we explore the surprisingly complex behaviour of single-branched D–A systems in the excited state, as a function of both solvent polarity and the identities of donor and acceptor.

The presence of the acetylene bridges leads to a wide distribution of dihedral angles between the donor and acceptor planes in the ground state. In the excited state, however, the rotational barrier is significantly increased.[2] In the phenyl-substituted molecules, rotation around the C-C bond produces a symmetric modulation of the conjugation of the system, whilst in the novel naphthyl-substituted molecules this modulation is asymmetric. This in turn gives rise to increased differences in both the electronic absorption spectra and the observed dynamics as a function of the D–A torsion angle (θ). Transient two-dimensional infrared (t2DIR) spectroscopy is uniquely suited to study this phenomenon, in combination with excitation wavelength dependence studies. Furthermore, we explore the effects of electrochemically reducing or oxidizing suitable D–A and D–A–D molecules. These spectroelectrochemical (SEC) investigations allow us to determine the influence of single-electron transfer upon the excited state behaviour, as well as its potential to induce or inhibit symmetry breaking in both ground and excited states in case of the D–A–D systems—akin to inorganic mixed-valence complexes.



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Mapping the Vibrational States in Retinal and Retinal Schiff Base by FSRS

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Retinal, polyene aldehyde chromophore of visual rhodopsins, undergoes ultrafast isomerization via its π→π* manifold and subsequent ground-state recovery through the $1Ag^-$ potential. Protonation of the C15 imine to form the retinal Schiff base (RSB) red-shifts absorption into the visible and introduces a localized n→π* excited state on the imine nitrogen. Here, we combine Femtosecond Stimulated Raman Spectroscopy (FSRS) and broadband transient absorption (TA) to directly map the energy ordering, structural evolution, and lifetimes of the key electronic states and track the ground state $^1Ag^-$ recovery in free retinal versus RSB. Through FSRS, we resolve mode-specific dynamics of the C=C and C=N stretches, revealing that RSB's imine stretch emerges within 400 fs, which is not visible in free retinal. TA spectra show a single broad excited-state absorption at ~480 nm for retinal, while RSB exhibits a characteristic doublet at ~480/520 nm tied to n→π* mixing. We propose a scheme depicting the energy ordering of the vibrational states in Retinal and RSB based on the evidence from FSRS and TA measurements. These complementary vibrational and electronic fingerprints elucidate how protonation modulates photochemical pathways.

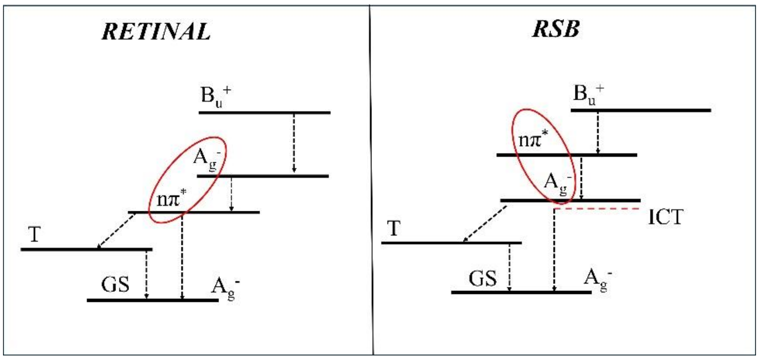

Fig1. The proposed scheme

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Special detector design for improved SRS imaging

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Stimulated Raman scattering (SRS) microscopy offers label-free and chemically selective imaging but its low scattering cross-section, laser and detector noise, and spatially variable transmission losses from tissue scattering and absorption collectively limit SNR, imaging speed, and quantitative comparability. In order to overcome these issues, we implemented and demonstrated an autobalanced detector that is able to cancel the laser excess noise allowing for shot noise limited SRS detection (Fig. 1a) with noisy light sources such as fiber- or chip-based lasers [1,2]. An autobalanced detector works by monitoring the Stokes transmission to automatically correct for losses with a PID loop and variable electronic gain in order to keep proper balancing while scanning heterogeneous samples. By cascading an autobalanced detector with a second modified autobalancer module that additionally measures and corrects for losses on the pump beam, full suppression of artifacts caused by spatially varying transmission losses in the microscope and sample is possible. Using our modified autobalanced detector, we not only demonstrated shot noise limited detection, but were also able to remove chemically unspecific shadows and image gradients from a chicken tissue sample (Fig. 1b), resulting in significant improvement of the detection of lipids across the field of view matching the expectation of a homogeneous distribution across the cells.

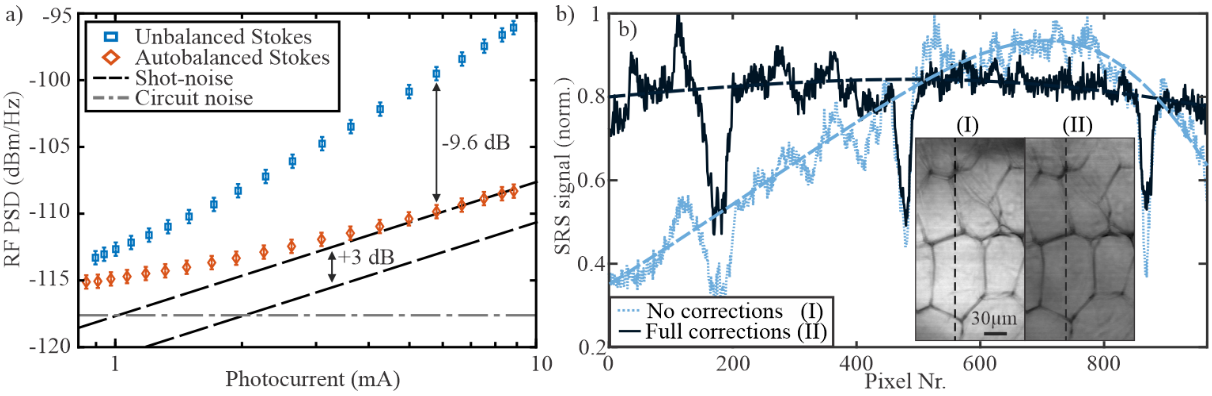

Fig. 1: a) Measured noise on the Stokes beam with (orange diamonds) and without (blue squares) autobalanced operation. b) SRS image of sliced chicken tissue at 2850 cm^{-1} (see insert) and corresponding profile view with pump and Stokes transmission correction disabled (light blue dotted line) and enabled (black solid line).

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Ab initio Magnetic Relaxation Prediction of Dysprosium Bis-Borolide Single-Molecule Magnets

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At the macroscopic scale magnetism arises from the cooperative interaction of many magnetic centres. In contrast the magnetic properties of paramagnetic metal ion complexes originate at the molecular level in species known as single molecule magnets (SMMs).[1] Among the plethora of SMM complexes, Dy(III) cyclopentadienyl $(CpR_5)^-$ sandwich compounds have been at the forefront in terms of performance in which a strong axial ligand-field is enforced by the ligand resulting in a large magnetic anisotropy barrier.[2,3] As such, one aspect of design strategy of dysprosium SMMs involves increasing the axial ligand-field to maximise this barrier. The magnetic relaxation mechanism in SMMs is driven by different temperature-dependent mechanisms based on spin-phonon interactions. Thus, to calculate magnetic relaxation rates we need an accurate description of the spin-phonon coupling.

This work aims to computationally investigate a series of borolide Cp ligands with different substituents and predict their effects on the magnetic relaxation. A previous study on the $[K(18\text{-crown-6})][Dy(BC_4Ph_5)_2]$ complex substituted a carbon in the Cp ring for a boron resulting in a higher charge dianionic pentaphenylborolide $(BC_4Ph_5)^{2-}$ ligand.[4] However the electron withdrawing phenyl groups pulls electron density from the ring centres hindering strength of the imposed ligand field and did not increase the magnetic relaxation barrier. Our study has determined which substitution patterns on borolide Cp ligands maximises the charge density on ring centres and should increase the barrier for relaxation. In order to calculate relaxation rates, we described both the electronic structure and the spin-phonon coupling of our target systems. We did this by creating a frozen solution system using a quantum mechanics (QM)/ molecular mechanics (MM) methodology,[5] calculate the electronic structure at the CASSCF-SO level and evaluate the spin-phonon coupling *via* the linear vibronic coupling (LVC) method using analytical crystal field parameter derivatives.[6]

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Comparing one and two-photon transitions in vibronic coupling schemes

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Vibronic coupling mechanisms are hypothesized to regulate chemical reactivity and relaxation mechanisms in molecular and materials systems. Multicolor, coherent Raman methods were developed long ago to resolve vibronic coupling mechanisms in prototypical organic systems (e.g., pentacene, azulene) by one-photon transitions. [1] More recently, coherent hyper-Raman spectroscopies have been proposed as a method to resolve vibronic coupling in molecular and materials systems by one- and two-photon transitions. [2] Here, we will apply multicolor, mixed time-frequency domain coherent anti-Stokes and Stokes Raman spectroscopy (CARS, CSRS) [1], hyper difference frequency generation (HDFG) spectroscopy [2], and triple sum frequency generation (TSF) spectroscopy [3,4] to resolve vibronic coupling in biologically relevant molecules (cyanocobalamin) and heterometallic systems (diruthenium tetra diphenylformamidate azide, $Ru_2(dpf)_4N_3$). Additionally, we will demonstrate the feasibility of HDFG as a probe of one- and two-photon transitions, non-Condon effects, and their impact on resolving vibronic coupling mechanisms in molecular systems. [2]

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Influence of Thermal Motion on Exciton Dynamics in Finite Molecular Chains

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In molecular aggregates, electronic excitation energy is transferred through transition dipole–dipole interactions [1]. The strength of these interactions depends on both the intermolecular separations and relative orientations of transition dipoles. At finite temperatures, these quantities fluctuate due to motion of molecules, rendering the coupling time-dependent [2, 3]. We investigate how such thermal vibrations, treated classically, influence the transport of an exciton in a one-dimensional chain of molecules. For this we consider two simple models of molecular motion: (i) longitudinal vibrations along the aggregation direction (ii) torsional motion of planer monomers in a plane orthogonal to the aggregation direction.

We find that in the absence of intramolecular vibrations, and when the molecular motion is slow enough to be considered adiabatic with respect to the exciton dynamics, site populations exhibit beatings that are more prominent at the boundries. The amplitude of these beatings depends on factors such as temperature, on-site disorder strength, and the length of the chain. As the molecular motion becomes fast compared to exciton timescale, the dynamics gradually become diffusive due to dephasing induced by rapid flucutations in molecular positions.

In the present work, we have ignored the effect of intramolecular vibrations on exciton dynamics, although these are known to play a crucial role in transport [4]. In the next step to this exploration, we will thus extend the quantum dynamics calculations for excitation transport to an open quantum system technique, such as non-Markovian quantum state diffusion [5], combined with classical molecular dynamics for the centre-of-mass motion of molecules.

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Innovation in Ultrashort Broadband Mid-Infrared Pulses for Nonlinear Spectroscopy

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While femtosecond pulses in the mid-infrared (mid-IR) have been available for non-linear spectroscopists performing vSFG and 2DIR measurements in the past, low signal levels and complex experimental setups can limit the rate at which researchers can collect data.

We present a new platform for generating tunable 2.5 – 15 µm mid-IR pulses using Yb-doped femtosecond lasers as the pump source.[1] By mixing the output of a short (~40 fs) pulse fixed at 2 µm pump with a tunable seed of longer duration (~200 fs), we can generate sub 100 fs tunable mid-IR pulses with a significant bandwidth (~200-300 cm^{-1} FWHM). The generation of such broadband pulses removes the need to stitch multiple IR probe pulses from various selected OPA central wavelengths together. Despite the lack of efficient compression techniques available in the mid-IR, our design produces sub-100 fs pulses. This facilitates high temporal resolution time-resolved vibrational spectroscopies, where vibrational lifetimes can be on the order of ~100 fs for highly coupled systems.[2, 3]

Multi-uJ level femtosecond mid-IR pulses, ideal for pump and probing in the vibrational region are generated at repetition rates up to 400 kHz.[4] The generation of such pulses at hundreds of kHz drastically reduces acquisition times compared to previous work carried out at 1 kHz. Providing a platform which ensures mechanical stability, regulated component and housing temperature, and beam tracking for pump beam insertion ensures ease of operation. The system has undergone rigorous testing to combine high performance with high reliability. We hope it will empower spectroscopists in various fields to reduce experimental acquisition times by orders of magnitude.

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Understanding Vibrational Strong Coupling through non-linear IR spectroscopy

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The emerging field of polariton chemistry opens up a way to tune molecular properties and steer chemical reactions by manipulating quantum light-matter interactions[1], i.e. vibropolaritons formed under vibrational strong coupling (VSC). The confined electromagnetic field in Fabry-Perot cavities can strongly couple with vibrational transitions of molecules, generating these quasi light-matter states, characterised by vacuum rabi splitting into lower and upper polarition states that exhibit molecular and photonic character simultanously. However, the underlying mechanism behind how the formation of vibropolaritons effects the reaction dynamics of molecules remains to be understood. Applying ultrafast nonlinear IR spectroscopy, in particular 2D-IR, to study molecular reactivity under strong coupling conditions could provide mechanistic insight to how the energy distribution is modulated when these delocalized hybrid states are formed and might reveal the fundamental mechanisms of how they modulate chemical reactions[2] . Here, we aim to study a self condensation reaction of an organic molecule under VSC by steady-state IR supported by theoretical modelling, nonlinear IR pump-probe and two-dimensional infrared spectroscopy, and with the long-term aim to understand how cavity properties modulate the reaction dynamics.

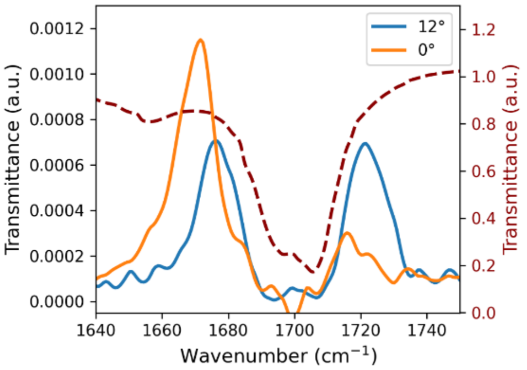

Figure: Steady state IR spectrum for strongly coupled Benzaldehyde at 12 degree angle of incidence

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Interactions of Azide Anion with Imidazole in DMSO: Time-resolved IR Spectroscopy and Molecular Dynamics Simulation

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Azide anion (N_3^-) is an excellent vibrational probe for the investigation of ion-pairs interaction in solution [1]. In DMSO, azide ion forms contact ion pairs with positive counter ions as evidenced by two different well-separated features in the FT-IR spectra. In our study, we have used the asymmetric stretching mode of the N_3^- to explore the interaction of N_3^- with Imidazole (HIm). HIm contains a five membered heterocyclic ring with two N-atoms at the 1- and 3- positions which participate in hydrogen bonding interaction. In our study, we show that HIm interacts both with solvent-separated and contact ion-pair N_3^-. which is supported by the molecular dynamics simulation. From the time-resolved IR spectra, it is clear that the vibrational population relaxation times of solvent-separated and contact ion-pair azide are getting faster in presence of HIm. To clarify the role of counter ions, we have selected different counter ions (Na^+, Li^+, Mg^{2+}, Ca^{2+}) based on their different sizes and charges. The vibrational lifetime of the contact ion-pair N_3^- is relatively longer compare to solvent separated ion pair as the vibrational energy dissipation of the azide mode to the neighbouring solvent bath modes is restricted by the metal counter ions. By adding HIm, we see HIm helps azide anion modes to dissipate the energy faster. We will further explore the impact of solvent fluctuations and spectral diffusion using 2D IR spectroscopy.

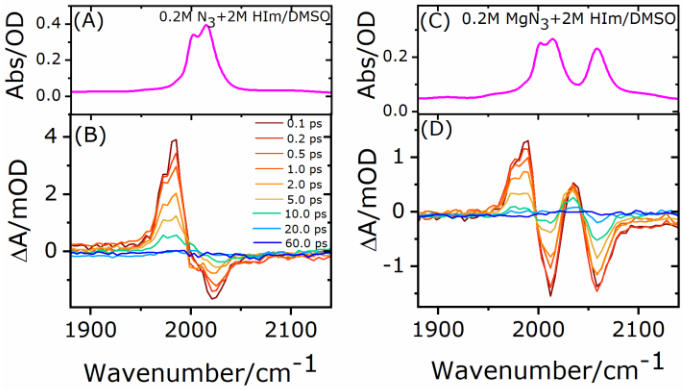

Fig. 1 (A) and (C) The magenta solid line shows the spectral range of the linear absorption of the azide asymmetric stretching mode when HIm is added with N_3 and Mg-N_3. Transient IR pump-probe spectra of (B) 0.2M N_3 with 2M HIm (D) 0.2M Mg-N_3 with 2M HIm in DMSO after excitation at 2000 cm^{-1}. The change of absorbance is plotted against a probe frequency for the pulse delay times given in the inset of the panel.

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Exploring Uncharted Territory: 2D-IR Spectroscopy in the 1000 cm^{-1} - 1300 cm^{-1} Region

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The spectral region between 1000 cm^{-1} - 1300 cm^{-1} contains vibrational frequencies of many important groups like the stretching mode of phosphate groups or sulfonates. However, due to significant experimental difficulties, only two groups successfully conducted 2D-IR experiments in this region. The group of Elsaesser, who studied phosphates with 2D-IR [1-4] and the group of Baiz, who measured DMSO [5]. As a result of the experimental challenges, all these studies are limited to one or two waiting times.

By using an optimized setup, we were able to record 2D-IR spectra in this region with higher SNR in shorter time. We use the setup to track ATP to ADP conversion [6] of hexokinase and to look and the effect of ions on the sulfonate vibration by measuring polarization resolved 2D-IR spectra spanning multiple waiting times, providing novel insights into molecular dynamics in this previously inaccessible spectral region.

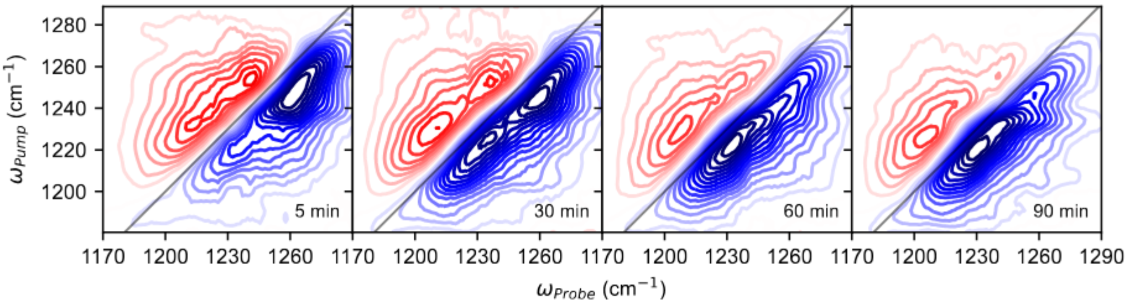

Figure 1: The conversion of ATP to ADP by the enzyme Hexokinase tracked by 2D-IR spectroscopy over 90 min.

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Simultaneous detection of FEIR and 2D-IR spectra and site-specific application to biomolecules

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Fluorescence-encoded infrared (FEIR) spectroscopy is a technique that uses the sensitivity of fluorescence to investigate vibrational dynamics in solution.[1–3] Here, we present the development of a versatile experimental setup capable of simultaneously measuring FEIR and 2D infrared (2D-IR) spectra. The setup is designed to operate with sample concentrations below 20 µM. The combination of a non-collinear optical parametric amplifier (NOPA) in the visible, as well as a OPA in the infrared, enables the measurement of a wide range of different molecular systems. The simultaneous detection capability allows us to compare FEIR and 2D-IR measurements under identical experimental conditions. By resolving the vibrations and couplings of the chromophore within a protein LOV domain, we demonstrate the potential of FEIR to isolate local vibrational features in complex biological systems.

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Electron and nuclear spin dynamics of lanthanide complexes in solution

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Nuclear spin relaxation in paramagnetic metal complexes is driven by their electron spin dynamics, making these dynamics key to their use as MRI contrast agents. The lanthanide-based PARASHIFT agents, capable of giving simultaneous information on pH, temperature and agent location, rely on the longitudinal component of this paramagnetic relaxation enhancement to boost signal strength.[1] Their electron spin dynamics are driven by nuclear motion via the ligand field interaction, but describing this vibronic coupling is far more challenging than in the well-understood solid-state case. The nuclei cannot be treated harmonically and the standard assumptions used to formulate the electron spin dynamics, namely the high-field and Redfield limits, do not apply.[2] Prior attempts at approaching this problem have been limited by the use of simple, fitted models of the varying ligand field,[3] or by available computational resources.[4] Our approach begins with ab initio MD, utilizing periodic DFT, to obtain a classical description of the vibrational degrees of freedom, including explicit solvent interactions. Electronic structure is then evaluated at the CASSCF-SO level of theory, allowing the projection of spin Hamiltonian parameters describing the varying ligand field. The resulting simulations offer unprecedented insight into the behaviour of near-equilibrium electron spin dynamics in these systems, including significant deviation from monoexponential character. They can also be used to predict nuclear relaxation rates beyond the classic Solomon-Bloembergen-Morgan theory. These rates demonstrate excellent agreement with experiment including their dependence on magnetic field strength. The simulations therefore allow us to elucidate the behaviour and relative importance of the mechanisms contributing to the paramagnetic relaxation enhancement, including the short-term dynamics of the electron spin (the dipolar mechanism) and the rotational modulation of the chemical shielding anisotropy due to its long-term average (the Curie mechanism).

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In vivo 2D-IR Spectroscopy on Live Cells of *E. coli* Reveals a Remarkably Stable [FeFe] Hydrogenase Active Site

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While *in vitro* studies have extensively characterized [FeFe] hydrogenases[1], structural, dynamical, and functional properties of its active site *in vivo* remain unexplored. We apply *in vivo* 2D-IR spectroscopy to track CO/CN vibrations (1800–2100 cm^{-1}) of the active site, exploiting a spectral window free from cellular absorption. By comparing the inhibited H_{ox}-CO state of the isolated enzyme with the enzyme in live *E. coli* cells, we aimed to uncover cytoplasm-induced shifts in CO/CN frequencies, suggesting environmental tuning of the H-cluster. Likewise, the excited-state absorptions could reveal altered anharmonic coupling of ligands, and enhanced spectral broadening could reflect dynamic protein-solvent interactions.

Surprisingly, spectroscopic properties in vitro and in vivo turned out to be very similar. The results challenge assumptions about cellular perturbations of metalloenzyme structure and dynamics and suggest that the [FeFe] hydrogenase active site is remarkably unaffected by cytoplasmic factors. In a wider sense, our work establishes *in vivo* 2D-IR spectroscopy as a powerful tool to validate *in vitro* models under physiological conditions [2].

Keywords: *FeFe-hydrogenase, 2D-IR, H_{ox}-CO, in vivo spectroscopy.*

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Vibronic couplings in a photoreceptor protein

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The local embedding of a chromophore in a protein matrix can significantly influence the optical properties of the chromophore. Structural changes in the local environment would therefore lead to different vibronic couplings. In the case of a protein such as the AsLOV domain, different protein-chromophore conformations exist in the electronic ground state [1]. In our study, the vibronic couplings of the electronic ground state as well as the signaling state of the protein are investigated for the first time by 2D-VE (vibrational pump-electronic probe) spectroscopy. The data show that the couplings are significantly different in each photocycle state. Although they also show that the vibronic couplings of two known ground-state chromophore conformers are relatively similar, they demonstrate that each conformation is spectrally resolved and therefore independently accessible by VIPER excitation (i.e. in an IR pump - VIS pump - IR probe experiment). The latter approach would enable conformer-selective excitation, so that the photocycle of each conformation can be resolved independently. This is an advantage over conventional resonant electronic excitation with VIS pump - IR probe spectroscopy, where all conformations evolve simultaneously. VIPER can then help to assign vibrational modes that are essential for selective VIPER excitation to study the photocycle of different conformers. Zooming into the functional role of protein heterogeneity in this fashion paves the way for protein engineering studies in general, aiming for example to increase product yield in enzymes.

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Epi-detected stimulated Raman photothermal microscopy

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Stimulated Raman photothermal (SRP) microscopy [1] enables increased sensitivity compared to stimulated Raman scattering (SRS) by probing the heat accumulation within the sample during the SRS process. We further developed the technique of SRP microscopy by implementing an SRP setup in epi-direction, allowing for the chemically-selective investigation also of non-transmissive samples without the need for an additional aperture as used in forward-detected SRP microscopy. For the epi-SRP setup, a laser diode at 976 nm wavelength was added as a continuous-wave probe beam to an SRS setup. The pump beam was amplitude-modulated with a mechanical chopper and a laser-scanning microscope was used for sample investigation. By using a quarter-wave plate in combination with a polarizing beam splitter in the probe light path, the back-reflected probe light was extracted for detection with a home-built photodetector and the generated signal was processed with a lock-in amplifier.

Epi-SRP spectroscopy was performed with a sample of pure dDMSO in order to verify the chemically-selective signal. The acquired spectrum (Fig. 1a) showed the two expected and distinct Raman peaks at 2130 cm^{-1} and 2250 cm^{-1} with line widths of 12.3 cm^{-1} and 32.1 cm^{-1}, respectively. Additionally, an epi-SRP microscopy image (Fig. 1b) was acquired at 2125 cm^{-1}, showing a PMMA bead embedded in dDMSO. The resulting image contrast of roughly 9 was increased compared to a corresponding epi-SRS image (Fig. 1c) with a contrast of only 4 [2]. Additionally, for a pure oil sample a signal-to-noise ratio of an epi-SRP signal of roughly 33 dB could be achieved. Therefore, the presented epi-SRP scheme demonstrated a high performance with real-time signal detection for a broad range of applications.

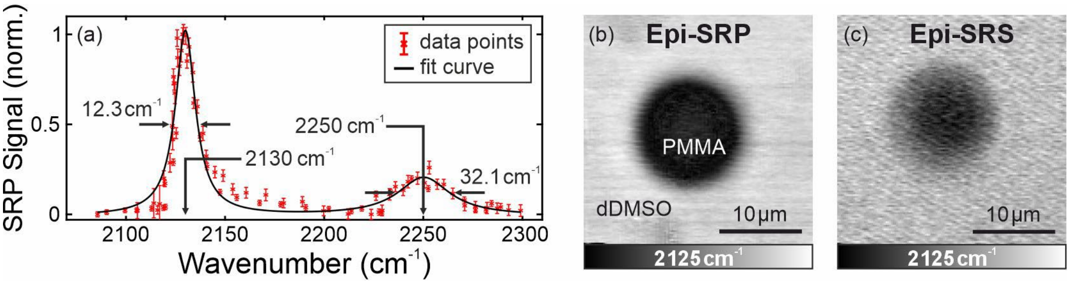

Fig. 1: (a) Epi-SRP spectrum of dDMSO. (b) Epi-SRP and (c) epi-SRS image of a PMMA bead in dDMSO at 2125 cm^{-1} with increased contrast for the epi-SRP image.

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Ultrafast Optical Gating of Single Photon Emission via Pump–Ionization–Probe Spectroscopy in CdSe/ZnS Quantum Dots

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We present a novel single-molecule pump–ionization–probe (SM-PIP) technique that enables direct investigation of and manipulate the ultrafast excited exciton dynamics in individual CdSe/ZnS core–shell quantum dots (QDs). Our approach employs non-resonant, strong-field mid-infrared pulses to ionize or dissociate excited excitons, thereby circumventing the limitations imposed by energy level matching and optical selection rules in conventional resonance-based methods. This allows access to non-radiative states, delocalized carriers, and field-induced escape channels that are typically hidden from standard ultrafast spectroscopy. Beyond tracking exciton dynamics and carrier trapping processes, SM-PIP enables quantitative evaluation of exciton dissociation and charge injection in core–shell quantum dot systems, and importantly, facilitates ultrafast optical gating of single-photon emission on the femtosecond timescale. This technique thus provides a powerful and sensitive approach to reveal previously inaccessible photophysical parameters at the single-particle level.

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Mode-selective Fluorescence Modulation via Visible/IR Excitation and its Vibrational-electron Coupling Dynamics

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It is an efficient way to achieve vibrational-electron coupling by synchronizing femtosecond visible pulse and high-power tunable narrow-band picosecond mid-IR pulse to selectively excite specific vibrational modes. With this double excitation method, we successfully observed the simultaneous fluorescence enhancement, blueshift and linewidth broadening in fluorescein dianion solution. Through scanning IR frequencies, tuning the time delay between two pulses and other ultrafast spectroscopies, the findings indicate that the fluorescence enhancement is caused by an increase in the Franck-Condon factor due to vibrational excitation of the electronic ground state. Various effects, including modulation peak shifts and delayed maximum, are also observed as the vibrations couple with each other and relax to lower frequency intermediate states. The fluorescence blueshift and broadening are due to the selective IR excitation of different aggregates.

Using another common dye, Coumarin 6, combing IR pump/visible-IR probe spectroscopy, the influence to electron response by vibrational pre-excitation is investigated. The results show that the significant red-edge absorption increase originate from two distinct mechanisms. The multi-photon absorption, which occurs only when visible and IR pulse temporally overlaps, predominates when the visible photon energy is relatively low. While vibrational relaxation, through internal energy redistribution and solvent dissipation, generates different vibrational intermediate states within hundreds of femtoseconds to tens of picoseconds, and deeply affect the electron transition process. It shows that the dynamics of fluorescence enhancement closely correlated with the absorbance changes, suggesting that the absorbance increase induced by IR pre-excitation play a decisive role in fluorescence modulation.

This work demonstrates that the fluorescence enhancement induced by visible/IR double excitation is not a simple sum-frequency effect. The vibrational relaxation will lead to profound influence on electron states and further luminescence. These contribute to a deeper understanding to the dynamics of vibrational-electron coupling, and provide new opportunities for applications in molecular sensing and bond-selective imaging.

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