ABSTRACTS

2nd Workshop on Molecular Quantum Technology #MQT2022

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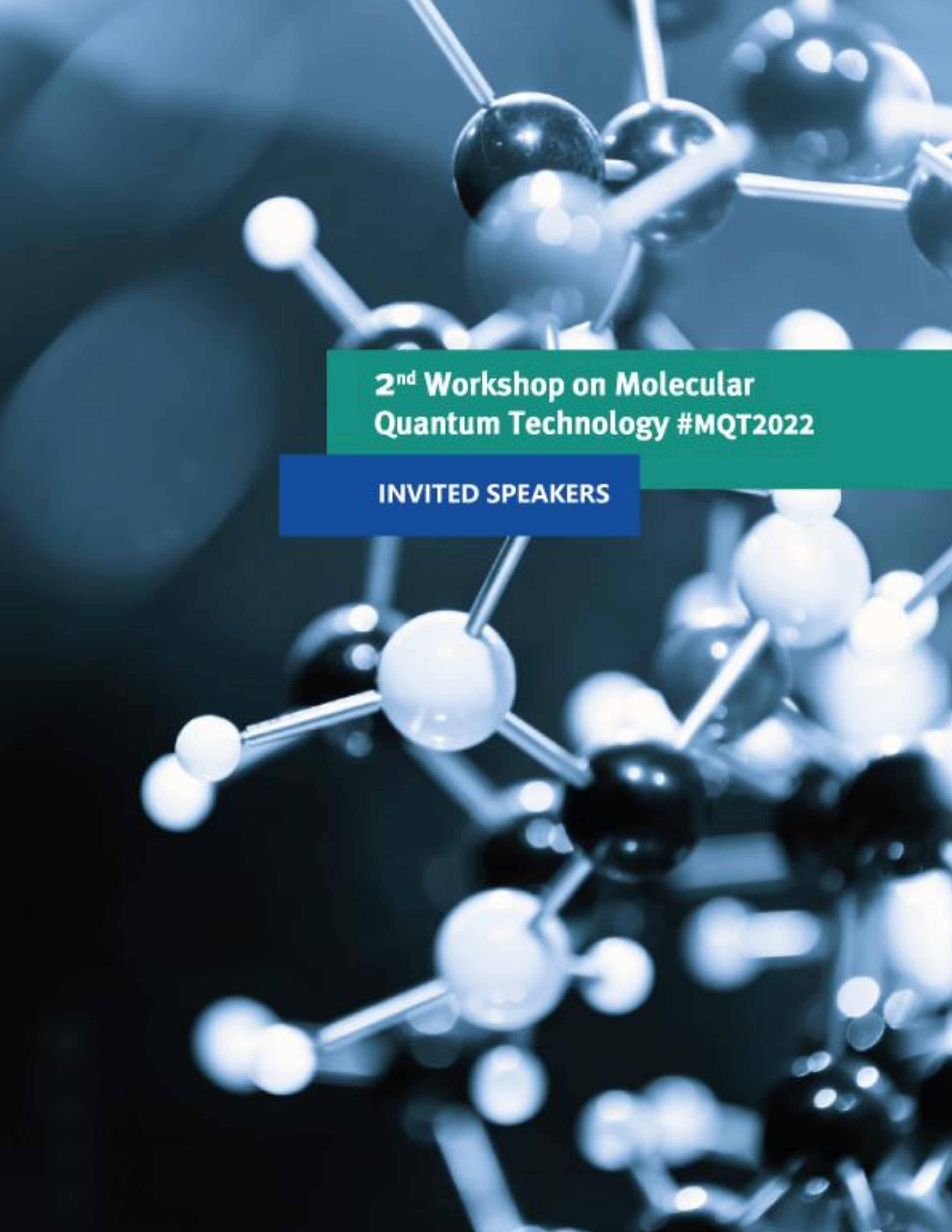
INDEX

INVITED SPEAKERS 6



2nd Workshop on Molecular Quantum Technology #MQT2022

INVITED SPEAKERS

1) Daniel Aravena, Universidad de Santiago de Chile

Spin Transport and Magnetoresistance in Inorganic Complexes

Daniel Aravena,[a] Albert C. Aragonès,[b] Eliseo Ruiz,[c] Ismael Diéz-Pérez[d]

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A series of combined experimental and theoretical studies about spin transport though first row transition metal complexes are presented. The first article focuses on the spin dependent transport in a spin-crossover Fe^{II} complex.[1] Experiment and theory agree on a higher conductance for the high spin state, which current is strongly spin polarized. Following studies explore the effect of different transition metals in both conductance and spin filtering and different conductance pathways related with metals and ligands. [2-4] Non-equilibrium Green Functions combined with Density Functional Theory (NEGF+DFT) results point to different contact positions and changes in coordination number as key aspects controlling electron transport. These conditions affect the frontier orbital alignment with respect to the Fermi level of the electrodes and modify the relevant transmission channels of the molecule.

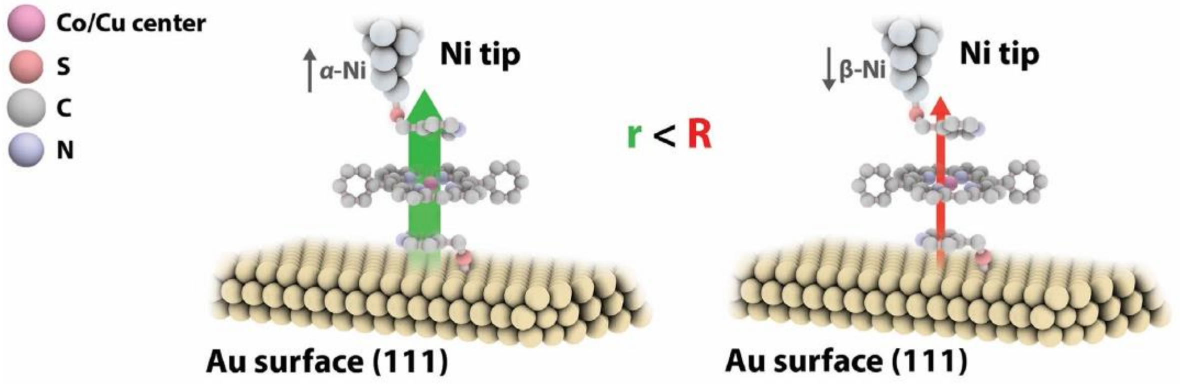

Figure 1. Representation of the magnetoresistance effect in [Cu/Co(DPP)] systems.[4]

[1] Aragones A, Aravena D, Cerda J, Acis-Castillo Z, Li H, Real JA, Sanz F, Hihath J, Ruiz E, Díez-Pérez I; *Nano Lett.* 16, 218–226 (2016).
[2] Aragones AC, Aravena D, Valverde-Muñoz FJ, Real JA, Sanz F, Díez-Pérez I, Ruiz E; *J. Am. Chem. Soc.*, 139, 5768–5778 (2017).
[3] Aragonès AC, Martín-Rodríguez A, Gonzalez-Campos A, Aravena D, Aliaga-Alcalde N, Ruiz E, Díez-Pérez I, *Angew. Chem. Int. Ed.*, 59, 19193-19201 (2020).
[4] Aragonès AC, Martín-Rodríguez A, Aravena D, di Palma G, Qian W, Puigmartí-Luis J, Aliaga-Alcalde N, González-Campo A, Díez-Pérez I, Ruiz E, *Angew. Chem. Int. Ed.*, 60, 25958-25965 (2021).

2) Alexey Belyanin, Texas A&M University

Quantum dynamics of molecules and quantum dots in dissipative nanocavities

M. Tokman, A. Behne, M. Erukhimova, Q. Chen, Y. Wang, A. Belyanin

Department of Physics & Astronomy, Texas A&M University, College Station, TX, USA

Strong coupling between quantum emitters such as molecules or quantum dots and a quantized electromagnetic field in a nanocavity drastically modifies both intramolecular electron-vibrational coupling and collective many-emitter dynamics. While the treatment of open quantum systems with many degrees of freedom is usually heavily numerical, here we develop a version of the stochastic Schroedinger-Langevin formalism which allows one to find semi-analytic solutions for nonperturbative nonlinear dynamics. We illustrate it with two examples. In the first example, the strong coupling regime is realized at the nonlinear resonance between electron, photon, and vibrational degrees of freedom. When the strength of such a parametric three-wave interaction is higher than the dissipation rates, entangled electron-photon-phonon states of GHZ type are formed and the emission spectra acquire a multi-peak structure. In the second example, we study quantum dynamics of many emitters strongly coupled to a spatially nonuniform field of a plasmonic nanocavity and taking into account the spread of their transition frequencies, dissipation, and decoherence for all degrees of freedom. We show how dissipation drives the system into robust many-emitter dark states that are decoupled from the cavity field. The ability to generate and control such states is an important problem for plasmonic nanocavities where the dissipation of a cavity mode is much faster than the relaxation in quantum emitters.

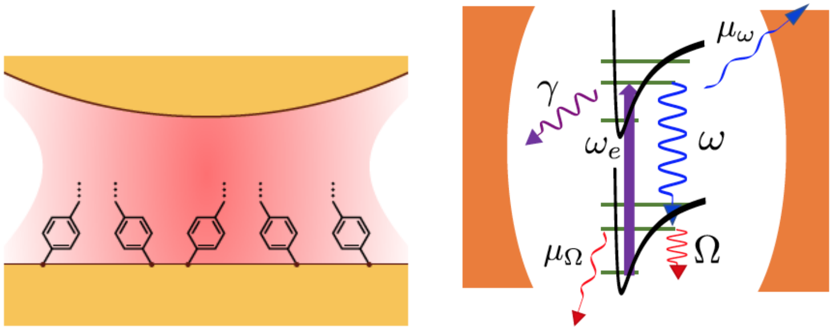

Figure 1. A sketch of an ensemble of molecules in a nonuniform field of a plasmonic nanocavity (left) and nonlinear resonance for a molecule in a cavity (right) showing the decay of the electron excitation at frequency ω_e into a cavity mode photon at frequency ω and a phonon of a given vibrational mode at frequency Ω.

[1] M. Tokman, A. Behne, B. Torres, M. Erukhimova, Y. Wang, and A. Belyanin, Dissipation-driven formation of entangled dark states in strongly-coupled inhomogeneous many-qubit systems in solid-state nanocavities, Phys. Rev. A submitted; https://arxiv.org/abs/2207.09523
[2] M. Tokman et al., The universal model of strong coupling at the nonlinear parametric resonance in open cavity-QED systems, Phys. Rev. A 105, 053707 (2022).
[3] M. Tokman et al., Generation and dynamics of entangled fermion-photon-phonon states in nanocavities, Nanophotonics 10, 491 (2021).

3) Joshua Caldwell, Vanderbilt University

Strong Coupling and Extreme Anisotropy in Infrared Nanophotonics

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The field of nanophotonics is based on the ability to confine light to sub-diffractional dimensions. In the infrared this requires the compression of the wavelength to length scales well below that of the free-space values. Two predominant forms of polaritons, the plasmon and phonon polariton, which are derived from light coupled with free carriers or polar optic phonons, respectively, are broadly applied in the mid- to long-wave infrared. However, the short scattering lifetimes of free-carriers results in high losses and broad linewidths for the former, while the fast dispersion and narrow band of operation for the latter result in significant limitations for both forms. We will discuss the opportunity to implement polaritonic strong coupling between different media in an effort to dictate the polaritonic dispersion relation, and thus, the propagation and resonant properties of these materials. The talk highlights the role of strong coupling between both plasmon and phonon polaritons in the context of infrared emitters in the form of localized phonon polariton nanostructures[1] and Tamm phonon polaritons.[2] Further, by employing the extreme anisotropy of low-symmetry monoclinic to triclinic crystals, novel optical phenomena such as hyperbolicity and shear polaritons.[3] These hyperbolic shear polaritons result in a frequency-dependent shear force resulting in a rotation of the optical axis and thus, the polariton propagation direction and wavelength (Fig. 1). Implementation of strong coupling between free carrier plasmas and hyperbolic shear polaritons promise dynamic control of the polariton propagation.

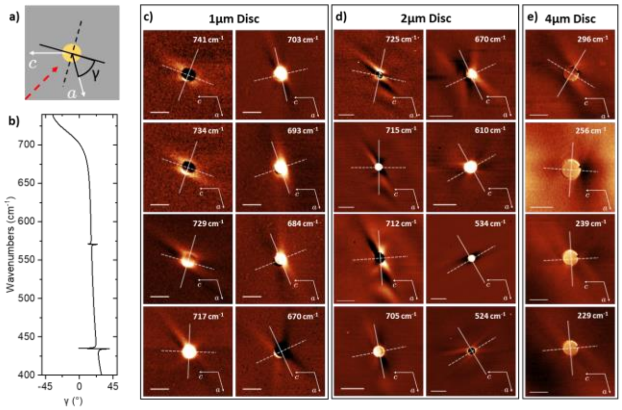

Figure 1: Frequency-dependent rotation of HShP propagation. *a) Schematic of the frequency-dependent rotation of the polariton propagation axis. b) Plot of the permittivity rotation angle γ of the polariton at $k/k_0 = 20$, marking the opening angle of the hyperbolic dispersion across the HShP range. c-e) Rotated polariton axis plotted, as in (a)*

1. Lu, G. *et al.* Engineering the Spectral and Spatial Dispersion of Thermal Emission via Polariton–Phonon Strong Coupling. *Nano Lett.* **21**, 1831–1838 (2021).
2. He, M. *et al.* Deterministic Inverse Design of Tamm Plasmon Thermal Emitters with Multi-Resonant Control. *Nat. Mater.* **20**, 1663–1669 (2021).
3. Passler, N. C. *et al.* Hyperbolic Shear Polaritons in Low-Symmetry Crystals. *Nature* **602**, 595–600 (2022).

4) Jianshu Cao, Massachusetts Institute of Technology

Quantum coherence in vibrational polaritons: reactivity, cooperativity, and molecular coupling

Jianshu Cao[a]

[a] Department of Chemistry, MIT

The strong light-matter interaction opens new possibilities of quantum control, but also presents new challenges. Inspired by recent experiments and numerical simulations, we are working on four theory projects: (1) Floquet theory, (2) photon counting statistics, (3) disordered polaritons, and (4) vibrational polariton chemistry. In this talk, I will first summarize the four projects and then focus on our recent efforts to understand coherent vibrational polariton dynamics in the vibrational strong coupling (VSC) regime.

Our quantum transition state theory (TST) calculation [1] attributes the VSC modification of reaction rates to vibrational frequency shifts in the reactive well and reactive barriers. The vibrational perturbation analysis predicts the dependences of reactivities on temperature, cavity frequency, and light-matter coupling strength. In comparison, application of the generalized resonance energy transfer (gRET) theory [2] explains the resonant and cooperative effects in vibrational energy relaxation in cavities, as shown in recent simulations. Though the two papers reveal complimentary perspectives of VSC polariton dynamics, new mechanisms [3] are needed to explore the broad range of intriguing phenomena reported in the VSC regime.

(1) Yang and Cao, JPC Lett 11, 7204 (2021) Quantum Effects in Chemical Reactions under Polaritonic Vibrational Strong Coupling.
(2) Cao, JPC Lett 13, 10963 (2022) Generalized Resonance Energy Transfer Theory: Applications to Vibrational Energy Flow in Optical Cavities.
(3) Cao and Pollak (in preparation).

5) Simon Cornish, Durham University

Controlling ultracold RbCs molecules for applications in quantum technology

Simon L. Cornish[a]

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Ultracold polar molecules are an exciting new platform for quantum technologies. The combination of rich internal structure of vibration and rotation, controllable long-range dipole-dipole interactions and strong coupling to applied electric and microwave fields has inspired many applications. These include sensitive imaging of electromagnetic fields, quantum simulation of strongly interacting many-body systems, the study of quantum magnetism, quantum metrology and molecular clocks and quantum computation.

In Durham, we study ultracold ground-state RbCs molecules formed by associating Rb and Cs atoms using a combination of magnetoassociation and STIRAP [1]. This talk will report our progress on controlling the molecules for applications in quantum technology. Specifically, we will discuss how we have mastered the ac Stark shift due to the trapping light [2] to demonstrate robust storage qubits in the molecule [3] and will describe the development of magic traps that support long rotational coherences [4]. Finally, we will describe new experiments that produce single molecules in optical tweezers starting from a single Rb and a single Cs atom [5]. Together these results demonstrate the key elements of a quantum processor based upon ultracold RbCs molecules.

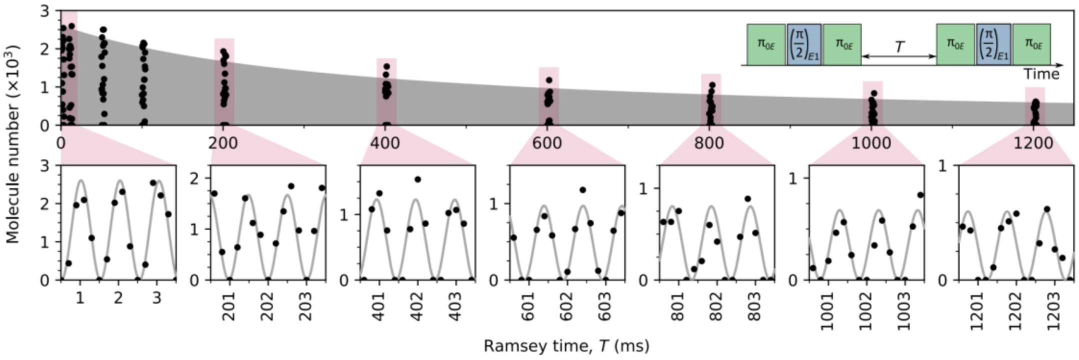

Figure 1. Robust storage qubit in ultracold RbCs molecules showing long-lived coherence.

[1] P.K.Molony *et al*., “Creation of Ultracold RbCs Molecules in the Rovibrational Ground State”, Phys. Rev. Lett. 113, 255301 (2014).

[2] P.D.Gregory *et al*., “ac Stark effect in ultracold polar RbCs molecules”, Phys. Rev. A 96, 021402(R) (2017).

[3] P.D.Gregory *et al*., “Robust storage qubits in ultracold polar molecules”, Nature Physics 17, 1149-1153 (2021).

[4] Q.Guan *et al*., “Magic conditions for multiple rotational states of bialkali molecules in optical lattices”, Phys. Rev. A 103, 043311 (2021).

[5] R.V.Brooks *et al*., “Preparation of one Rb and one Cs atom in a single optical tweezer”, New J. Physics 23, 065002 (2021).

6) Eugenio Coronado, Universitat de Valencia

Molecular Spins for Quantum Technologies

Eugenio Coronado[a]

[a] Instituto Ciencia Molecular (ICMol). Universidad de Valencia

Spins provide one of the simplest platforms to encode a quantum bit (qubit), the elementary unit of future quantum computers. A challenge in this topic is to control the quantum decoherence in these spin qubits by minimizing the sources of decoherence (dipolar spin-spin interactions, hyperfine interactions and spin-phonon interactions). This loss of quantum information by interaction with the environment can be quantified by the phase memory time T_2. Here, I will show how a molecular approach can be exploited to design robust molecular quantum spin systems [1] showing enhanced decoherence, allowing to control the spin state through an external electric field [2], or hosting more than one spin qubit in order to implement quantum logic gates [3].

[1] E. Coronado, *Nat. Rev. Mater.* 5, 87-104 (2020)
[2] J. Liu *et al. Nat. Phys.* 17: 1205-1209 (2021)
[3] A. Gaita-Ariño *et al. Nat. Chem.* 11, 301-309 (2019)

7) Gilad Haran, Weizmann Institute of Science

Plasmonic Cavities: Strong Coupling and Beyond

Gilad Haran[a]

[a] Department of Chemical and Biological Physics, Weizmann Institute of Science

Plasmonic structures concentrate electromagnetic fields to deep sub-diffraction volumes. We will first discuss how this nanofocusing can strongly couple plasmonic cavities and individual quantum emitters. In particular, we present our studies of colloidal quantum dots within silver bowtie structures. Light scattering spectra of individual devices clearly showed a dip indicative of vacuum Rabi splitting even in the presence of a single quantum dot (1). We further found that electron energy-loss spectroscopy (EELS) within the electron microscope can probe this coupling with a nanometric spatial resolution (2). This allowed us to demonstrate Rabi splitting of dark modes that do not couple radiatively to the far field. Photoluminescence measurements revealed the non-classical nature of emission from coupled quantum dots, and demonstrated how the interaction of emitters with the cavity alters pathways of excited-state relaxation quite dramatically (3). Finally, unpublished studies (4) on giant electrochemical tuning of the resonances of plasmonic cavities will be presented- we hypothesize that differential charging is responsible for these surprising results.

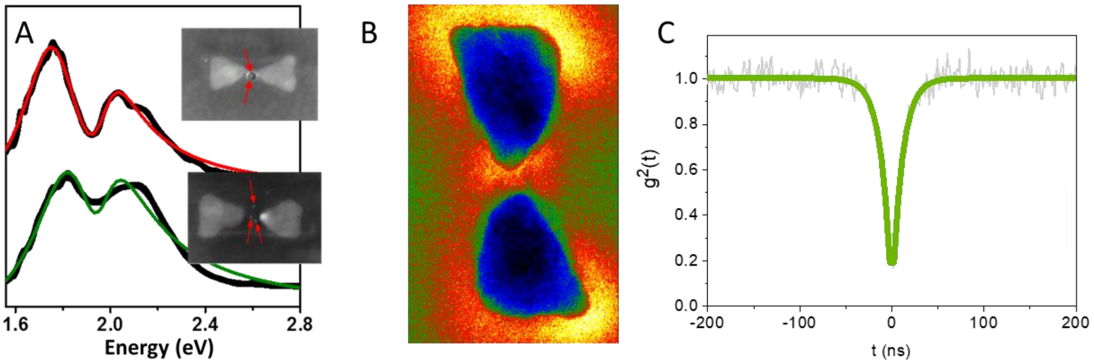

Figure: Probing strong coupling in plasmonic cavities. (A) Scattering spectra of plasmonic bowties with QDs inserted in their gaps. Top- two QDs. Bottom- three QDs. The spectra show Rabi splitting. (B) EELS map of the electric field around a bowtie at 1.55 eV. (C) Second-order correlation function of a single QD within a bowtie, demonstrating antibunching at t=0.

(1) K. Santhosh, O. Bitton, L. Chuntonov, G. Haran, Vacuum Rabi splitting in a plasmonic cavity at the single quantum emitter limit. *Nature communications* **7**, ncomms11823 (2016).

(2) O. Bitton, S. N. Gupta, L. Houben, M. Kvapil, V. Krapek, T. Sikola, Vacuum Rabi splitting of a dark plasmonic cavity mode revealed by fast electrons. *ArXiv* **1907.10299** (2019).

(3) S. N. Gupta, O. Bitton, T. Neuman, R. Esteban, L. Chuntonov, J. Aizpurua, G. Haran, Complex plasmon-exciton dynamics revealed through quantum dot light emission in a nanocavity. *Nature communications* **12** (2021).

(4) A. Vaskevich, A. Basu, L. Chuntonov, I. Ashiri-Kaplan, G. Haran, Unpublished (2022).

8) Stephen Hill, Florida State University

Molecular Spin Clock Transitions

Stephen Hill

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shill@magnet.fsu.edu

This talk will focus on recent efforts aimed at protecting molecular spin qubits from decoherence caused by surrounding electron and nuclear spins (the spin bath), with emphasis on so-called clock transitions – avoided level crossings associated with the Zeeman splitting of spin states [1]. Spin clock transitions provide an optimal operating point at which the transition frequency, f, becomes insensitive to the local magnetic field, B_0. In this way, a clock qubit is immune to magnetic noise [2]. There are several strategies for generating spin clock transitions. All that is needed is an interaction term in the spin Hamiltonian that does not commute with the Zeeman interaction. For molecules with integer spin states, zero-field splitting interactions do the job. Alternatively, clock transitions may be generated in molecules possessing half-integer spin states via the on-site hyperfine interaction, a strategy that is employed widely in trapped-ion quantum devices. Crucially, in the molecular case, the hyperfine interaction can be synthetically controlled to maximize unpaired electron spin density at the relevant nucleus. A recent example involving a $\mathrm{Lu^{II}}$ ($[\mathrm{Xe}]4f^{14}5d^{1}$) organometallic compound has demonstrated that this is possible by varying the degree of *s*-orbital mixing into the formal spin-bearing *d*-orbital [3]. This approach has the added advantage of increasing the *s*-orbital character, thus reducing spin-orbit coupling that, in turn, suppresses spin-lattice relaxation. The talk will provide an overview of various synthetic strategies that have been employed for developing molecular clock qubits, together with the spectroscopic studies that demonstrate their enhanced coherence. The findings are supported by exact quantum dynamics simulations that demonstrate decoupling of a spin qubit from the nuclear bath at a clock transition [4].

In collaboration with: Bill Evans, Filipp Furche, Lauren Sanchez, Jason Yu, Jessica White (UC Irvine, USA); Jeff Long, Danh Ngo (UC Berkeley, USA); Eugenio Coronado, Alex Gaita-Ariño, Yan Duan (University of Valencia, Spain); Hai-Ping Cheng, Silas Hoffman, Xiaoguang Zhang, Jia Chen (University of Florida, USA); Krishnendu Kundu, Jakub Hrubý, Jonathan Marbey, Dorsa Komijani, Muhandis Shiddiq (Florida State University, USA).

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[1] Gaita-Ariño et al., Nat. Chem. **11**, (2019); https://doi.org/10.1038/s41557-019-0232-y
[2] Shiddiq et al., Nature **531**, 348 (2016); https://doi.org/10.1038/nature16984
[3] Kundu et al., Nat. Chem. **14**, 392 (2022); https://doi.org/10.1038/s41557-022-00894-4
[4] Kundu et al., arXiv:2106.05185 [quant-ph]; https://arxiv.org/abs/2106.05185

9) Tijs Karman, Radboud University

Microwave shielding of ultracold molecules

Tijs Karman

RU Nijmegen, the Netherlands.

Ultracold polar molecules are a promising platform for applications such as precision measurement, quantum computing, and quantum simulation. In typical experiments, the molecules' lifetime is limited by loss due to molecule-molecule collisions. These losses prevent evaporative cooling of molecules and spoil resonances that could otherwise be used to tune interactions.

In this talk I will discuss "microwave shielding", a scheme for inducing repulsive interactions between molecules that protect them from collisional loss [1]. Microwave shielding has recently been realized experimentally [2]. Shielding not only suppresses collisional loss, but also boosts elastic collisions. This enables evaporative cooling of fermionic NaK molecules to quantum degeneracy [3]. I will also discuss recent results on controlling interactions between microwave-shielded molecules [4].

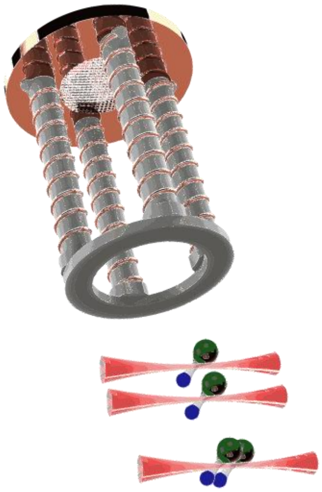

Figure 1. Microwave shielded CaF molecules in optical tweezers

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[2] Anderegg *et al.* Science **373**, 779 (2021)
[3] Schindewolf *et al.* Nature **607**, 677 (2022)
[4] Chen *et al.* arXiv:2210.13324

10) Stéphane Kená-Cohen, Polytechnique Montreal Technological University

Quantifying scattering rates in the electronic strong light-matter coupling regime

Stéphane Kéna-Cohen

[a] Polytechnique Montréal, Department of Engineering Physics, Montréal, QC CANADA

One of the most interesting features of exciton-polaritons is their ability to condense into a single macroscopic quantum state: a so-called polariton Bose-Einstein condensate. Under non-equilibrium conditions, the density at which condensation occurs is intrinsically linked to the ratio between the scattering rate from localized “dark” molecular excitations to the polariton lifetime. While a variety of theoretical approaches have been introduced to describe the former, there has yet to be a quantitative comparison of such rates with experiment. We will describe 3 different approaches that allow for direct measurements of these scattering rates. We will show that these rates are generally slow and radiative in nature. This inefficacy is, to some extent, linked to the large N problem, and this intrinsically limits the impact that polaritons have on the kinetics of electronically excited molecule. We will discuss the consequences that this has had on previous attempts to modify photophysical processes using strong light-matter coupling and possible solutions.

11) Kevin Kubarych, University of Michigan

Vibrational Polariton Dynamics Probed with 2D-IR Spectroscopy

Rong Duana, Joseph N. Mastrona,b, Yin Songb, Kevin J. Kubarych

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b Department of Physics, University of Michigan, Ann Arbor, MI

We will present our efforts to understand vibrational strong coupling and the resulting ultrafast dynamics in both single and dual-mode scenarios. We have found subtle issues in the role of weakly coupled molecules in producing nonlinear spectral contributions that can mask the interesting polartion and dark state signal. We have attempted to resolve the question of the importance of so-called "Rabi contraction" by implementing a double-quantum coherence sequence that accesses vibrational polaritonic states without producing excited state populations. Last, we present "dual-mode" polartions (Fig. 1) where we couple distinct vibrational states to different optical cavity modes, and use 2D-IR to track the coupling of these two polaritonic subsystems. The dual-mode polaritons have distinct dark state reservoirs which are themselves coupled (anharmonically though the bare molecules), providing an interesting new dimensión of polariton dynamics.

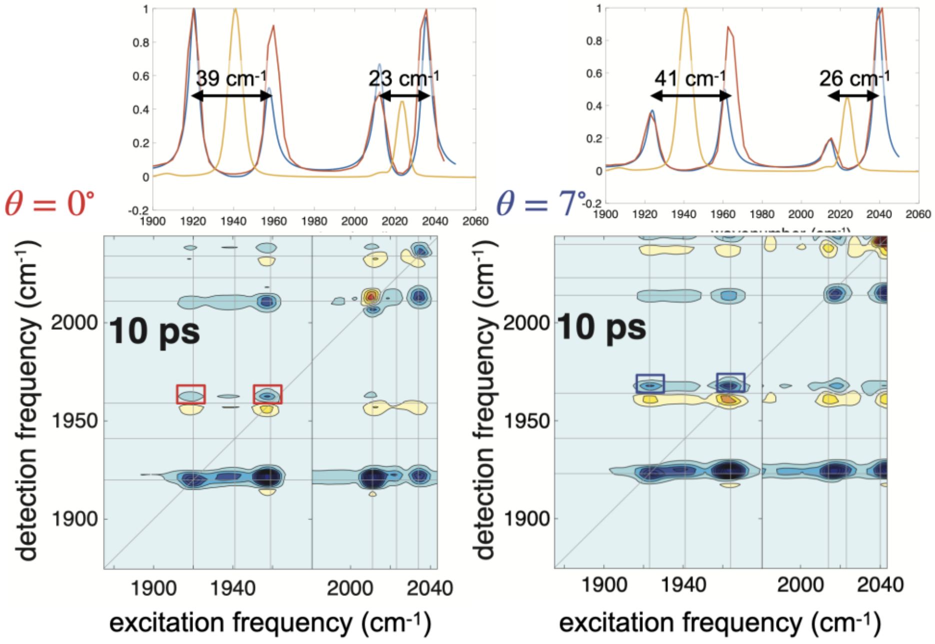

Figure 1: FT-IR and fully collinear 2D-IR spectra of dual mode polaritons formed by coupling two different molecular transitions to two adjacent cavity modes. Angle dependent hybridization leads to change in the spectra and the dynamics. Cross peaks between the two polariton branches indicate coupling through the shared common ground state.

12) Shaul Mukamel, University of California Irvine

Monitoring Coherences in Elementary Molecular Events by Ultrafast Nonlinear X-ray Spectroscopy

Daniel Keefer, Haiwang Yong, Shichao Sun, Stefano Cavaletto, Jeremy R. Rouxel,
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Novel X-ray pulse sources, specifically from free-electron lasers (FELs) and high-harmonic generation (HHG) setups make it possible to monitor molecular events on unprecedented temporal, spatial and energetic scales. In this talk, we survey recent theoretical developments that design, simulate and predict spectroscopic signals that reveal detailed information about different aspects of ultrafast molecular transformations. The first is TRUECARS and based on an X-ray stimulated Raman process between electronic states to probe their coherences in a background-free measurement.[1] A hybrid broadband/narrowband X-ray probe field provides the necessary joint temporal and spectral resolutions.[2] The measurement can be performed in different modes, either with two phase-controlled coherent X-ray pulses,[1,2] or with stochastic, SASE-generated X-ray fields in a covariance-based setup.[3] Next, different implementations of ultrafast homodyne- and heterodyne-detected X-ray (XRD) and electron diffraction (UED) are discussed. Besides following photochemical reactions in real-time via a series of femtosecond-resolved diffraction patterns,[4-6] a combination of UED and XRD is demonstrated to be sensitive *only* and directly to nuclear wavepackets.[7] Both for TRUECARS and for XRD, quantum optimal control is presented as a potent tool to selectively amplify and isolate desired contributions, such as the intrinsically weak coherences that may be buried beneath a stronger, less interesting population background.[8,9] For all techniques, the signal formalism and simulation procedure are discussed, as well as pulse requirements for experimental realization, followed by examples on ultrafast molecular processes such as uracil photorelaxation, azobenzene photoisomerization, thiophenol S-H bond cleavage, electronic coherences in dimers and dendrimers, and Mg-phthalocyanine ring current migration. The novel X-ray techniques discussed here contain direct signatures of conical intersections and other elementary molecular phenomena which so far remained elusive, corroborating the unique capabilities and groundbreaking potential of ultrafast X-ray probes.

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[3] S. M. Cavaletto, D. Keefer, S. Mukamel, *Phys. Rev. X.* **11**, 011029 (2021)
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[6] J. R. Rouxel, D. Keefer, S. Mukamel, *Struct. Dyn.* **8**, 014101 (2021).
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[11] S. Sun, H. Yong, F. Chen, S. Mukamel, *Chem. Sci.*, 2022 DOI: 10.1039/d2sc02768b

13) Prineha Narang, Harvard University

Ab initio approaches to molecular quantum matter and quantum information science

Prineha Narang, UCLA

In this talk, I will present theoretical and computational approaches to describe excited-states in quantum matter, and predicting emergent states created by external drives. Understanding the role of such light-matter interactions in the regime of correlated electronic systems is of paramount importance to fields of study across condensed matter physics, quantum optics, and ultrafast dynamics[1]. I will discuss our work at the intersection of *ab initio* cavity quantum-electrodynamics and electronic structure methods to treat electrons, photons and phonons on the same quantized footing, accessing new observables in strong light-matter coupling. Current approximations in the field almost exclusively focus on electronic excitations, neglecting electron-photon effects, for example, thereby limiting the applicability of conventional methods in the study of polaritonic systems, which requires understanding the coupled dynamics of electronic spins, nuclei, phonons and photons. With our approach we can access correlated electron-photon and photon-phonon dynamics[2–4], essential to our latest work on driving quantum materials far out-of-equilibrium to control the coupled electronic and vibrational degrees-of-freedom [5–7]. In the second part of my talk, I will demonstrate how the same approach can be generalized in the context of control of molecular quantum matter and molecular quantum transduction. As a first example, I will discuss a cavity-mediated approach to break the inversion symmetry allowing for highly tunable even-order harmonic generation (e.g. second- and fourth-harmonic generation) naturally forbidden in such systems. This relies on a quantized treatment of the coupled light-matter system, similar to the driven case, where the molecular matter is confined within an electromagnetic environment and the incident (pump) field is treated as a quantized field in a coherent state (with just a few photons). When the light-molecule system is strongly coupled, it leads to two important features: (i) a controllable strong-coupling-induced symmetry breaking, and (ii) a tunable and highly efficient nonlinear conversion efficiency of the harmonic generation processes[8]. Both have implications for molecular quantum architectures. Being able to control molecules at a quantum level gives us access to degrees of freedom such as the vibrational or rotational degrees to the internal state structure. Finally, I will give an outlook on connecting ideas in cavity control of molecules with quantum information science.

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14) Abraham Nitzan, University of Pennsylvania

Collective response in light-matter interaction: The interplay between strong coupling, local dynamics and disorder

Abraham Nitzan
University of Pennsylvania and Tel Aviv University

Because molecular size is much smaller than optical wavelength molecules can interact with light collectively. Actual manifestations of such collective response depend on other factors such as dephasing and disorder. Under strong (molecules-light) coupling conditions such collective response can be more pronounced because collective mode are energy-shifted from the spectrum of individual emitters and appear as polaritonic spectral features in linear and non-linear optical signals. In this talk I will describe our recent studies of several phenomena that reflect this interplay between collective response, local dynamics and (static and dynamic) disorder.

15) Hossein Sadeghpour, Institute for Theoretical Atomic Molecular & Optical Physics

Few-body and many-body games in a quantum gas with Rydberg impurities

H. R. Sadeghpour*

ITAMP - Harvard University

Cold Rydberg atoms are the Swiss-army knife for engineering precise quantum interactions in atomic and molecular systems. I will describe how elementary Rydberg interactions in the quantum limit can lead to the emergence of few-body and the many-body collective phenomena in ultracold degenerate gases and how they may be exploited to simulate indirect quantum magnetization, such as chiral interaction, with Rydberg atoms as delocalized impurities.

* I was not the only dude who made the above possible; the significant figures are: Richard Schmidt (T), Seth Ritthenhouse (T), Rosario Gonzalez (T), Eugene Demler (T), Peter Schmelcher (T), Jim Shaffer (E), Tom Killian (E)…

16) Johannes Schachenmayer, University of Strasbourg

Exploring the role of entanglement in disordered polaritonic chemistry

J. Schachenmayer

CNRS, CESQ/ISIS, Université de Strasbourg

To gain insight on fundamental physical processes in polaritonic chemistry, we study a bottom-up approach with minimal quantum many-body models that include electronic, photonic and vibrational degrees of freedom in their simplest form. In this talk, for such models, I discuss the fundamental modifications of localization properties in disordered setups due to the presence of a cavity-coupling. As a new feature, I show how dark eigenstates acquire an unexpected "semi-localized" behavior with unusual properties in terms of level statistics and other localization quantifiers [1]. I then discuss how such states may play a crucial role for cavity-modified vibrational dynamics and lead e.g. to a breakdown of Born-Oppenheimer type approaches due to disorder-enhanced entanglement between electro-photonic and vibrational degrees of freedom [2].

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17) Blake Simpkins, U.S. Naval Research Laboratory

Suppressed reactivity via cavity-induced selective vibrational cooling

B. S. Simpkins,[1] W. Ahn,[2] J. F. Triana,[3] F. Recabal,[3] A. D. Dunkelberger,[1] J. C. Owrutsky,[1] F. Herrera[3,4]

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Molecular vibrations can couple to optical cavities to create new hybrid states called polaritons. The magnitude of this coupling, measured as the vacuum Rabi splitting (Ω), correlates with modified materials processes such as photon emission, molecular energy transfer, and chemical reaction rates. In this talk, I will first discuss modeling and active control of cavity coupling to molecular vibrations. Next, I will discuss results indicating modified chemical reaction rates for an alcoholysis addition reaction forming urethane monomers. Cavity tuning was used to selectively couple to reactant, solvent, and product vibrational modes resulting in a chemical response that is cavity tuning dependent. An open quantum system model attempting to rationalize such reaction suppression is presented which identifies bond-selective cooling via cavity-induced stationary population redistribution as the culprit.

18) Michal Tomza, University of Warsaw

Quantum-chemical calculations for ultracold molecular physics experiments

Michał Tomza[a]

[a] Faculty of Physics, University of Warsaw, Poland

I will present how molecular electronic structure and quantum scattering calculations can support and explain ultracold quantum physics experiments. Quantum-chemical calculations of potential energy curves [1], permanent and transition electric dipole moments [2], fine and hyperfine coupling constants [3] provide parameters for effective Hamiltonians describing nuclear dynamics. Multichannel quantum scattering calculations give scattering lengths, elastic, inelastic, and reactive rate constants [4,5,6]. I will discuss the capabilities and limits of state-of-the-art methods applied to neutral and ionic systems based on alkali-metal and alkaline-earth-metal atoms, and present our recent results for ongoing experimental effors.

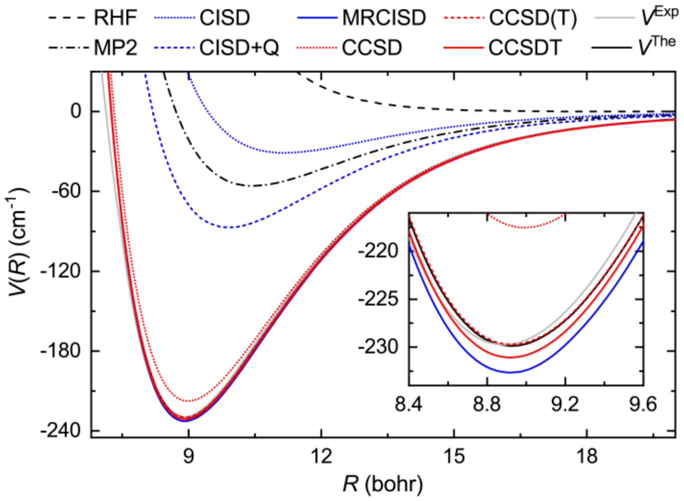

Figure 1. Interaction energy as a function of the internuclear distance for the a$^3\Sigma^+$ electronic state of the NaLi molecule from calculations at different levels of theory.

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19) Marissa Weichman, Princeton University

New Platforms for Polariton Reaction Dynamics

Marissa L. Weichman[a]

[a] Princeton University, Department of Chemistry

Polaritons are hybrid light-matter states with unusual properties that arise from strong interactions between a molecular ensemble and the confined electromagnetic field of an optical cavity. Cavity-coupled molecules appear to demonstrate energetics, reactivity, and photochemistry dramatically distinct from their free-space counterparts, but the mechanisms and scope of these phenomena remain open questions. Validating proposed mechanisms for cavity chemistry will require a new body of experimental work directly surveying strongly-coupled reaction trajectories on clean, easily-modeled reactive potentials, working in close partnership with theory. Here, we discuss two new platforms to investigate condensed-phase and gas-phase molecular reaction dynamics under vibrational strong coupling.

In the condensed phase, we have set out to survey cavity-altered reactivity in radical hydrogen-abstraction processes. These reactions have well-characterized potential energy surfaces; they can be initiated with photolysis and tracked directly on ultrafast timescales; they are exothermic and proceed rapidly so dynamical signatures are not washed out; and they are accessible to theory, enabling detailed interpretation of reaction pathways. We run our reactions in dichroic microcavities that permit vibrational strong coupling in the infrared in combination with broadband optical access in the visible and ultraviolet. We are using ultrafast transient absorption measurements to examine intracavity reaction rates with the goal of pinpointing precisely how these trajectories may be influenced by strong light-matter interactions.

We will also discuss our recent demonstration of gas-phase molecular polaritons. While polaritons are now well-established in solution-phase and solid-state samples, they have not yet been reported in isolated gas-phase molecules, where attaining sufficiently strong light-matter interactions is a challenge. We show that the strong-coupling regime can be accessed in the gas phase at low temperatures where molecules are found in only a few lowest-energy quantum states and their absorption linewidths are narrow. We have built an apparatus that combines a cryogenic buffer gas cell with a feedback-stabilized optical cavity to reach this regime. This new infrastructure allows us to cavity-couple individual rotational-vibrational states, access a range of coupling strengths and detunings from resonance, and tune both molecular and cavity linewidths. We expect that this platform will enable surveys of cavity-altered molecular reactivity, dynamics, and photophysics with quantum-state-specificity and without the complications of solution-phase environment.

20) Hannah Williams, Durham University

Laser Cooling Molecules

Hannah J. Williams [a]

[a] Durham University, UK

Ultracold molecules offer an exciting prospect for the future of Quantum Science and Technology. In this talk I will focus on laser cooling of molecules, which twenty years ago was considered an impossibility. To build an experimental platform capable of applied quantum science we need to fulfil various criteria, notably, cold, trapped molecules in programable internal states, with strong controllable interactions. I will share the progress that we, as a community, have made and the vision for the future.

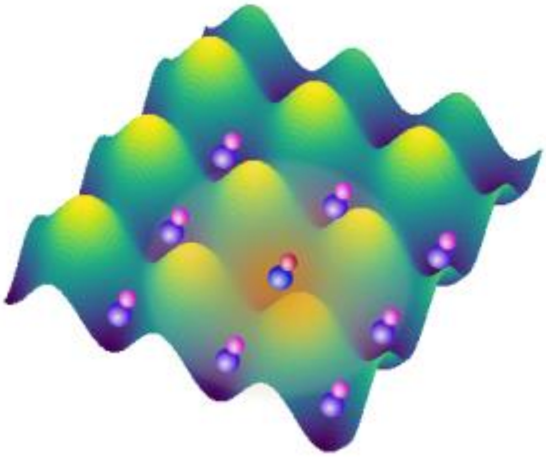

Figure 1. Dipolar molecules interacting in an array

21) Joel Yuen-Zhou, University of California San Diego

Collective dynamics Using Truncated Equations (CUT-E): simulating the collective strong coupling regime with few-molecule models

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The study of molecular polaritons beyond simple quantum emitter ensemble models (e.g., Tavis Cummings) is challenging due to the large dimensionality of these systems (the number of molecular emitters per cavity mode is $N \approx 10^6 - 10^{10}$), as well as the complex interplay of molecular electronic and nuclear degrees of freedom, which is absent or much reduced in atomic and solid-state polariton systems, respectively. A very important question is the extent to which single-molecule models can be used for interpretation or prediction of molecular polaritonic phenomena. In this talk, I will describe how to exploit permutational symmetries to drastically reduce the computational cost of *ab-initio* quantum dynamics simulations for large N [1]. In particular, we find that using an effective single molecule to calculate the dynamics in the collective regime is formally justified when $N \to \infty$. Based on this result, which we call Collective dynamics Using Truncated Equations (CUT-E), I discuss how to seamlessly modify existing single-molecule strong coupling calculations to generate the corresponding effective models as well as the crucial differences in phenomena predicted by each type of calculation. I will also explain how to systematically derive finite N corrections to the dynamics, and show that addition of an extra surrogate molecule is enough to account for couplings that scale as $O\left(\frac{1}{\sqrt{N}}\right)$. As interesting applications of this formalism, I will describe how to use it to develop much needed intuition to generate robust strategies for polariton chemistry, and to apply it to describe a cavity-assisted energy funneling mechanism between different molecular species.

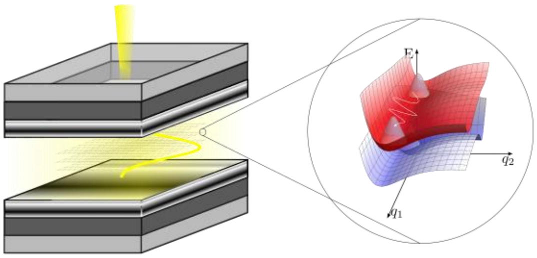

Figure 1. N molecules with complex potential energy surfaces in a cavity. The dynamics of this system can be efficiently simulated by exploiting permutational symmetries.

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2nd Workshop on Molecular Quantum Technology #MQT2022

CONTRIBUTED SPEAKERS

1) Katy Aruachan, Universidad de Santiago de Chile

Semi-empirical spin-lattice relaxation models for molecular spin qubits in metal-organic frameworks

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[4] Millennium Institute for Research in Optics (MIRO), Chile.

Understanding the mechanisms that determine spin-lattice T_1 relaxation times for molecular spin qubits in metal-organic framework (MOF) crystals is critical for near-term applications in precision measurements and quantum information processing [1]. Recent spin-echo experiments on the spin relaxation of vanadyl-based qubits as a function of magnetic field and temperature has stimulated the development of phenomenological and ab-initio quantum mechanical modeling techniques [1-3]. We propose a semi-empirical approach for building Redfield quantum master equations based on a stochastic fluctuation model for the molecular gyromagnetic tensor due to the interaction of molecular spin impurities with crystal lattice vibrations. The spin relaxation rates are obtained from a semi-empirical bath autocorrelation function that captures the experimental temperature dependence through a fitting procedure. These model spectral densities are used for computing the spin population and decoherence dynamics of vanadyl-based spin qubits beyond cryogenic temperatures (>50 K) and high magnetic fields, where vibrational Raman fluctuations and the Zeeman effect dominate the relaxation dynamics. Our results quantitatively agree with experiments [3] and represent a solid foundation for the theoretical characterization of other spin qubits in MOFs, for the rational design of novel quantum magnetometers based on this material class.

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2) Anael Ben-Asher, Universidad Autónoma de Madrid

Single-Photon Emission due to non-Hermitian Anharmonicity

Anael Ben-Asher[a], Antonio I. Fernández-Domínguez[a], Johannes Feist[a]

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Single-photon sources play a vital role in light-based quantum-information systems [1]. One well-known design for such sources is a coupled emitter-cavity system in the strong-coupling regime. Single-photon emission is then achieved through the photon blockade phenomenon, where the absorption of one photon induces large enough energy shifts in the system to prevent the absorption of subsequent photons [2,3]. We here propose a novel non-Hermitian photon blockade mechanism that works in the weak-coupling regime and does not require strong coupling. This mechanism does not rely on changes in the absorption energy, but on changes of the absorption bandwidth of the states and can be understood as the detuning of the effective state energies in the complex plane. We demonstrate an implementation of this idea using hybrid metallodielectric cavities that incorporate photon modes with different loss rates and show that high-purity single-photon emission at high repetition rates could be achievable in such systems.

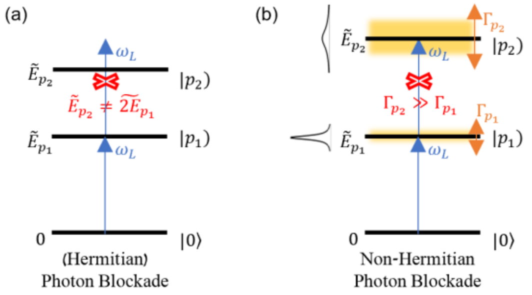

Figure 1. The two mechanisms for photon blockade: (a) the well-known (Hermitian) mechanism and (b) the novel non-Hermitian mechanism.

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3) Burak Gürlek, Max Planck Institute for the Science of Light

Engineering Organic Molecules with Long-Lived Quantum Coherence

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Single organic molecules in the solid-state are one of the promising optical platforms for realizing quantum networks owing to their remarkable coherent properties and flexibility in their chemical synthesis [1]. However, the molecular excited states associated with the strong Fourier-limited zero-phonon lines of these systems decay within nanoseconds, posing a challenge for practical applications in quantum technologies.

In this theoretical work, we propose a new molecular system with quantum coherences up to millisecond time scales. Here, we exploit the inherent optomechanical character of organic molecules in a solid organic crystal [2]. The proposed scheme consists of a single organic molecule in a host matrix with a structured phononic environment. By suppressing phononic decay channels, we realize and exploit long optomechanical coherence times up to milliseconds for storing and retrieving information. We show that the resulting long-lived vibrational states facilitate reaching the strong optomechanical regime at the single photon level. The proposed system shows the promise of organic molecules for achieving unexplored optomechanical phenomena and long-lived quantum memories.

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4) Shubham Jain, University of Maryland

Noise in quantum rigid rotors

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Molecular rotational state spaces, modeled by infinite dimensional Hilbert spaces of quantum rigid rotors, present new grounds for robust quantum information processing. They are, however, prone to noise induced by the environment that surrounds them. As a step towards making qubits realizable through these rotor space configurations, we study and contrast the nature of two different types of noise that molecules would be prone to. The first is a generalization of the brownian center of mass motion for quantum rigid bodies in a thermal environment[1]. This kind of noise is found to be local in the angular position and angular momentum phase space of the rotor and hence, compatible with already existing molecular codes[2]. The second noise models blackbody radiation affecting the molecules[3],[4]. We show that this kind of noise can be highly non-local in the molecule's phase space and characterize instances where conventional (i.e., exact) error-correction can fail. We comment on the different strategies that can circumvent this no-go result.

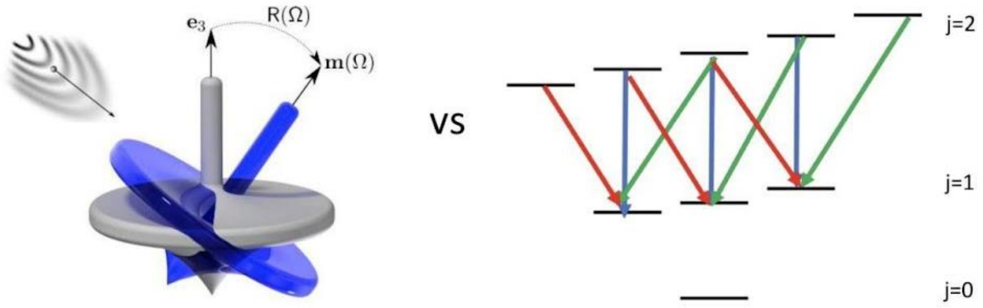

Figure 1. Visualization of the two types of noise - Quantum brownian motion[1] and Black body radiation in the presence of an environment

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5) Markus Raschke, University of Colorado, Boulder

Quantum vibrational microscopy and sensing

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The quest from low-loss quantum materials to efficient heat transport, high conductivity transistors, and chemical reactions all rely on understanding and engineering the *local density of vibrational modes*. In this talk, I will discuss the use of molecular vibrations and IR resonant nano-wire coupled molecular interactions as *sensors* and *local probes* for inter- to intra-molecular coupling, thermalization, and dissipation. This includes the development of new nano-imaging techniques that provide a qualitatively new window into the spatial, temporal, and low energy spectral vibrational landscape of molecular and other quantum materials. These new *vibrational quantum scopes* harness ideas developed in the context of *quantum optomechanical control of motion* to image the elementary processes of vibrational and polaron dynamics in ultrafast vibrational nano-movies with nanometer and femtosecond spatio-temporal resolution.

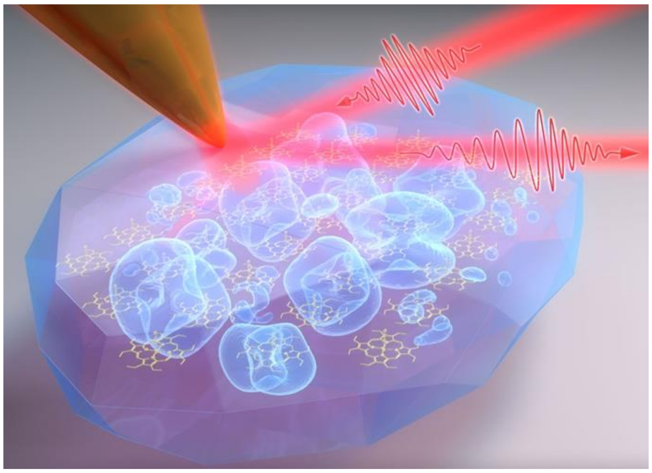

Figure 1. Infrared nano-imaging of spatial delocalization of the vibrational wavefunction, serving as quantum sensor and molecular ruler of molecular disorder, crystallinity, and intermolecular coupling that control the properties of functional molecular materials at their elementary level.

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6) Kai Schwennicke, University of California San Diego

Enantioselective Topological Frequency Conversion

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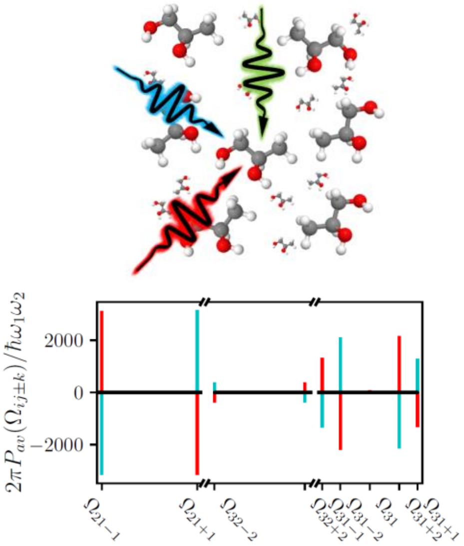

spectrum for *R*- (red) and *S*- (Cyan) 1,2-propaindiol. The spectrum differs in sign for the two enantiomers.

Two molecules are enantiomers if they are nonsuperimposable mirror images of each other. These chiral molecules possess “handedness”, interacting differently with left- and right-handed circularly polarized light. This optical activity can be used to discriminate between enantiomers; however, traditional linear techniques depend on the weak interaction between molecules and the magnetic component of the electromagnetic field. Because of this, other techniques that rely solely on electric dipole interactions have been recently advocated. For example, microwave three-wave mixing (MTWM) has been shown to be a promising enantioselective nonlinear technique [1].

In our work we present a new method that is reminiscent to MTWM, where we couple the rotational energy levels of the enantiomers to three linearly polarized fields whose field amplitudes are slowly modulated [2]. In the limit that the modulation fields can be treated adiabatically and are incommensurate (their ratio is irrational), we find that the power exchanged between driving fields is proportional to a Chern number. This is reminiscent of the phenomenon called Topological Frequency Conversion [3]. Interestingly, we can analytically show that the Chern number has the same symmetry as other nonlinear chiral optical techniques, in that it is proportional to sign of the three light matter coupling. As a result, the Chern number differs in sign for the two enantiomers, and the power exchanged between driving fields is in opposite directions for the two molecules (see Fig. 1).

Due to the topological nature of this phenomenon, this symmetry persists in the presence of slight changes to the optical set up. Thus, we propose utilizing this method for a sensitive measurement of enantiomeric excess. More importantly, this work highlights the underexplored connection between topological physics and molecular chirality.

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7) Karolina Slowik, Nicolaus Copernicus University

Low-dimensional material structures with adatoms: how electron tunnelling influences optical properties

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Depending on their chemical compounds and geometry, low-dimensional material structures such as 1D atomic chains or 2D nanoflakes offer a variety of electronic, optical and material properties. They can be used as elementary metal/semiconductor/insulator building blocks in heterostructures realizing nanoscaled optoelectronics. They may support topological properties or plasmonic optical response. The latter can be tuned by electronic or optical means or in presence of atomic defects (adatoms) [1]. In reverse, a flake or chain can be exploited to modulate the dynamics of adatoms positioned in its vicinity [2].

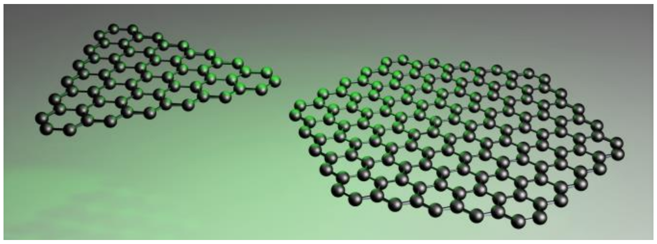

Figure 1. Visualizations of triangular and hexagonal graphene flakes.

Here, we investigate how coupling selected flakes and neighbouring adatoms modulates their plasmonic response and emission properties The key element we take into account is the electron tunnelling, or hopping, between the flake and the adatom, investigated within the tight-binding-based formalism [2]. We characterize the absorption spectra in presence of adatoms and the spontaneous emission properties of hybrid adatom+nanoflake structures.

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8) Ruth Tichauer, Universidad Autónoma de Madrid

Enhanced Exciton Transport under Strong Light-Matter Coupling: Insights from Multi-Scale MD Simulations

Ruth H. Tichauer[a,b], Ilia Sokolovskii[b], Johannes Feist[a], Gerrit Groenhof[b]
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While inherent disorder in organic materials limits the propagation length of energy carriers, coupling photoactive molecules to nanophotonic structures in the strong light-matter coupling regime has the potential to open a new era in energy harvesting [1] and transport [2,3] as the new hybrid light-matter states that form, polaritons, possess a low effective mass and high group velocities. What is more, the large binding energy of Frenkel excitons makes organic materials promising candidates for future applications as polariton formation takes place at ambient conditions. While ballistic transport was observed for inorganic quantum wells strongly coupled to an optical Fabry-Pérot cavity [4], measurements performed with organic materials [2] report diffusive motion that allows the excitation to reach much shorter distances than foreseen from the group velocity of polaritons and at time scales that surpass the intrinsic polariton lifetime.

Here, we resolved these controversies by means of atomistic multi-scale molecular dynamics simulations [5,6,7] of ensembles of Rhodamine molecules strongly coupled to the confined light modes of a Fabry-Pérot cavity. Our results [8] suggest that while *bright* polaritons propagate at their respective group velocities, population transfers between these states and the overwhelming majority of stationary *dark* states leads to the diffusive rather than ballistic propagation of excitations in the strong coupling regime. Additionally, the finite lifetime of the cavity photon sets an upper limit to the distance that can be reached. Nevertheless, while dark states limit polariton propagation they protect the excitation from decaying through the imperfect mirrors in low-Q cavities which is at the origin of the apparent *long lifetime* of the lower polariton branch.

The atomistic insights from our simulations not only help to better understand and interpret experimental observations, but also pave the way towards rational design of molecule-cavity systems for achieving coherent long-range energy transport.

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9) Johan Triana, Universidad de Santiago de Chile

Controlling the infrared vacuum field via molecular polaritons in the strong coupling regime

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The generation of non-classical light and optical phase control are two areas of intense research in quantum optics and nanophotonics. Although efforts have primarily focused on the optical regime, novel nanoscale devices offer new possibilities for studying quantum optical effects in the mid-infrared region. We propose novel schemes for modifying the photon statistics of an electromagnetic field of an infrared Fabry-Pérot cavity by driving one cavity mirrors with ultrafast UV pulses that adiabatically modulate the cavity resonance frequency. Under strong coupling of the mid-infrared vacuum with molecular vibrations, we demonstrate that large modifications of the Mandel factor and squeezing parameter are possible by initializing the system in the ground and first excited polariton eigenstates [1]. For open cavities architectures such as nanoantennas with tip nanoprobes, we show that a new type of infrared blockade effect can be exploited to generate nonlinear coherent phase shift of the infrared near field, with the shift depending on the power of an ultrafast infrared driving pulse [2]. Our work opens new routes for designing infrared quantum devices with possible applications in quantum metrology, quantum information processing and quantum state preparation.

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10) Giacomo Valtolina, Fritz-Haber-Institut der Max-Planck-Gesellschaft

Towards cavity-controlled ultracold chemistry

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Ultracold molecules hold great potential for future quantum technologies but chemical reactions have so far hampered their applications[1]. Recently, the development of several shielding methods has enabled the stabilization of molecular quantum gases against chemical reactions[2,3,4]. This approach allowed the attainment of quantum degeneracy in quantum gas of fermionic molecules by evaporative cooling[2]. Leveraging on these results, we are building a new experimental apparatus with ultracold bosonic molecules strongly coupled to an optical cavity. Cavity-control of ultracold reactions offers new opportunities for the creation of a stable, strongly dipolar gas of bosonic molecules at high density.

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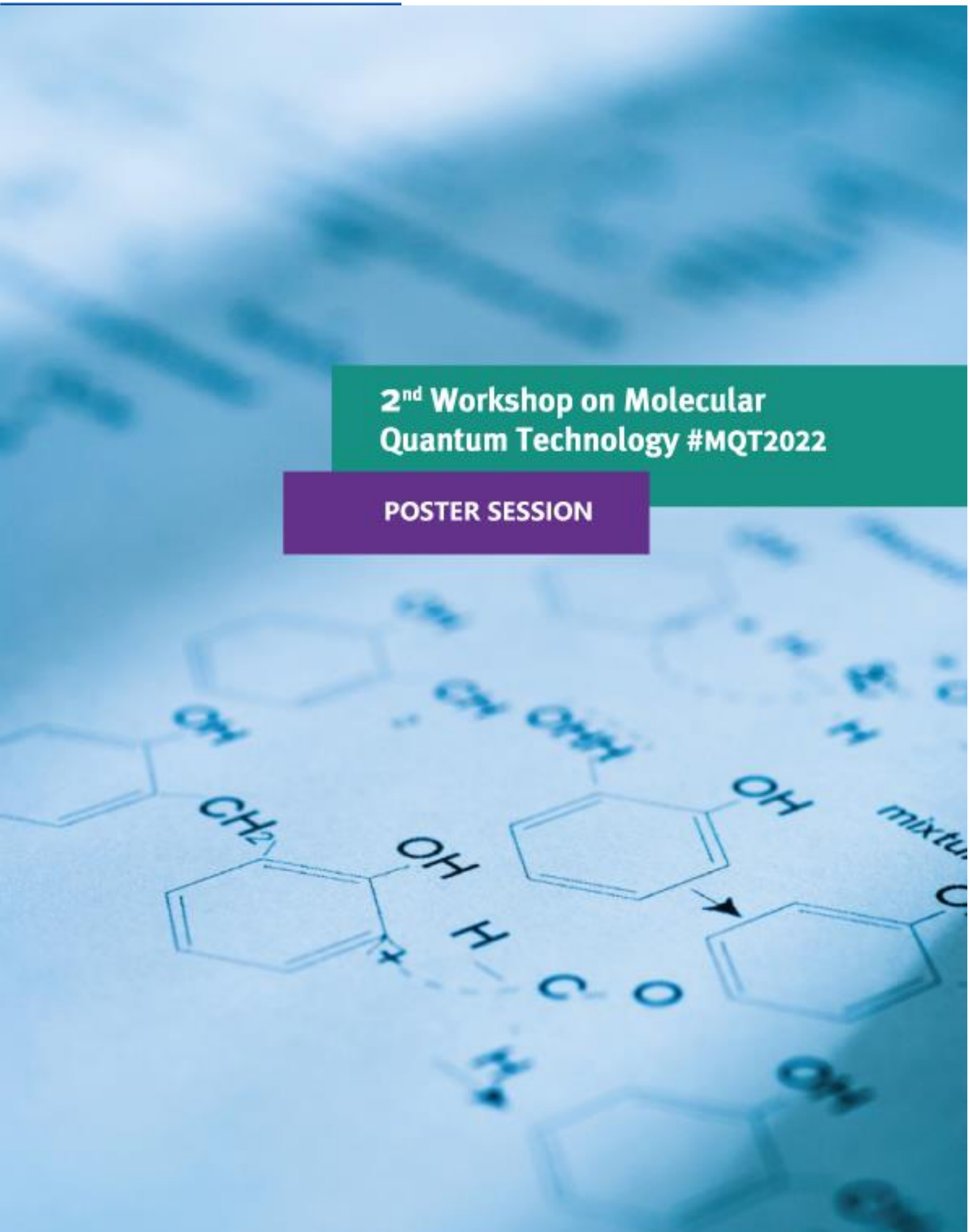
POSTER SESSION



POSTER SESSION

1) Mauricio Arias, Universidad de Santiago de Chile

Nanocavity QED with molecular vibrations in the mid-infrared

J. F. Triana[1], **M. Arias[2]**, J. Nishida[3], E. A. Muller[4], R. Wilcken[3], S. C. Johnson[3], A. Delgado[2.5], M. B. Raschke[3], and F. Herrera[1,5]

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We show a versatile semi-empirical quantum optics approach to describe light-matter interaction in a system driven by mid-IR femtosecond laser pulses. This model is not limited to describe observable dynamics of the coupled system but also provides physical insight for the implementation of coherent phase rotations and anharmonic intensity-dependent phase shifts, suggesting novel applications in the development of weak and strongly coupled infrared nanophotonics hardware for quantum control and quantum information processing [1].

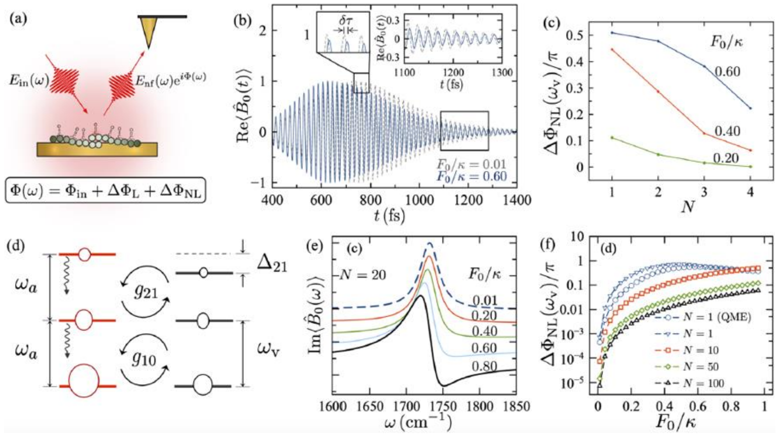

Figure 1. Power-dependent phase rotation of the vibrational coherence. (a) Schematic picture of coherently scattered fields in molecule-coupled resonators. (b) Evolution of the collective coherence. (c) Nonlinear phase as a function of the molecule number N, obtained from exact solutions of the quantum master equation. (d) Level scheme. (e) Imaginary part of the FID signal in the frequency domain for anharmonic oscillators. (f) Nonlinear phase predicted by the nonlinear chirping model

[1] J. F. Triana, M. Arias, J. Nishida, E. A. Muller, R. Wilcken, S. C. Johnson, A. Delgado, M. B. Raschke, and F. Herrera, The Journal of Chemical Physics 156, 124110 (2022), https://doi.org/10.1063/5.0075894

2) Maria Bancerek, University of Warsaw

Strong coupling effects in plasmonic-molecular systems

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Strong light-matter interaction in the system offers the possibility of modifying its properties through the emergence of new, hybridized cavity-exciton eigenmodes, called polaritons [1]. Among various systems used to study strong coupling plasmonic-molecular systems gain attention as one of the simplest yet capable of reaching the strong coupling regime, owing to the small mode volumes of the plasmonic nanostructures and plasmonic resonance tunability [2, 3]. Given the spectral overlap of the plasmonic resonance and the molecular transition and their spatial proximity, one can observe Rabi splitting in the absorption spectrum of the system, indicating the formation of so-called lower and upper plexcitonic branches. Employing TDDFT calculations, we numerically study metallic nanoparticles and aromatic molecules assemblies in order to underpin the atomic-scale changes induced by the strong coupling. We investigate how the coupling changes with the nanoparticle-molecule separation, leading to changes in the absorption spectrum of the system. We show how intensity of molecular transitions increases when placing a molecule closer to the nanoparticle up to a certain distance (~5 Å) at which molecular transitions couple to the variety of nanoparticle states, resulting in mixed metallic-molecular transitions between hybridized states. We investigate how studied effects influence hot carrier generation and show carrier transfer between two subparts of the system, i.e., direct hot electron transfer from the molecule to the nanoparticle and the modified energy landscape of generated holes and electrons.

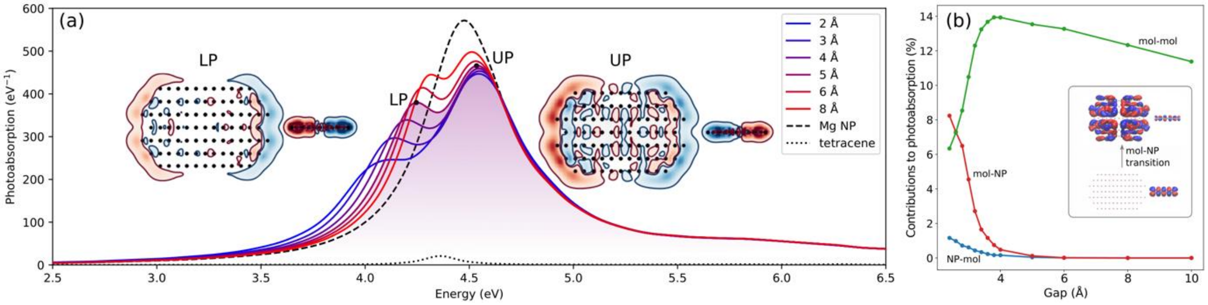

Figure 1. Photoabsorption spectra for a Mg nanoparticle – tetracene coupled system for various gaps and induced electron density for gap = 5 Å at frequencies corresponding to lower and upper polaritons (LP, UP) (a). Molecular/mixed transitions contributions to photoabsorption for LP (b); inset shows wavefunctions of states constituting an exemplary mixed transition at gap = 3 Å.

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3) Edgar Barriga, Universidad de Chile

Non-adiabatic transitions in a diatomic molecule under a bichromatic laser field

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Degeneracies in molecular systems have been studied extensively in the last decades. This kind of singularity has profound impacts on the dynamics since non-adiabatic effects arise due to the coupling between the electronic and nuclear motion [1]. For a N-state system the non-crossing rule requires a (N-1)(N+2)/2 conditions over internal coordinates to achieve a degeneracy point in configuration space. Despite this seemingly strong restriction conical intersections of more than two states have shown to be not just a curiosity but the rule [2]. The existence of degeneracies is not restricted to the field-free case. It has been shown that they can be created by external means [3,4].

In this work we show that by using a bichromatic radiation field a three-state degeneracy can be created in diatomic molecules. This situation is forbidden for field-free diatomic molecules due to the non-crossing rule. The threefold degeneracy comes along with novels kind of two-state intersections (also forbidden for field-free diatomic molecules). We study the effects of the polarization of the lasers in these different induced intersections between the potential energy surfaces. The system chosen is the Cs$_2$ molecule.

The time-dependent Hamiltonian is treated with the Many Mode Floquet Theory (MMFT) [5]. We use the MMFT formalism to calculate the long-time averaged transition probabilities. We found a non-trivial dependence of the relative phase in this observable. Our results establish a way that can be implemented experimentally to control the non-adiabatic dynamics in molecular systems through the relative phase.

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4) Rubén Fritz, Universidad de Santiago de Chile

IRMOF-1 for chemical sensing based in optical fibers

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Materials with optical properties suitable for portable, reusable, and non-destructive chemical sensors with high specificity are of great interest for the development of technology to monitor and detect chemical compounds of interest. Metal-organic frameworks (MOFs) are a promising material for optical sensing, the porous allows the adsorption of molecules, and upon loading their optical properties such as dielectric function change can be exploited for sensing purposes [1–3]. Metal-organic frameworks are extraordinary crystalline materials with an extensive list of properties and applications in several sciences. Their structure is formed by organics molecules as linkers and metal as nodes, in a modular way creating a network that in some cases generates pores that can adsorb other chemical compounds. The combinatorial ensemble of structures from their constitutive parts creates almost an infinite number of possible combinations and a very rich chemical space, that is extremely difficult to explore solely by experiments. Here we present a computational approach to study the changes in the optical properties of the IRMOF-1 upon loading of methane. The aim of this work is to set the basis for a computational filter and characterization of MOFs for chemical sensing purposes.

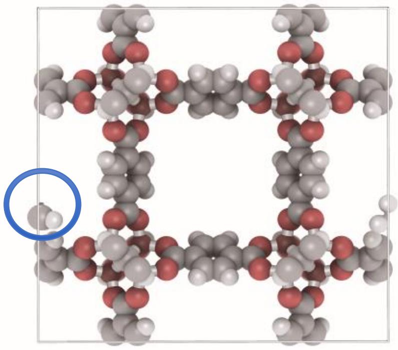

Figure 1. IRMOF-1 structure, a methane molecule inside the pore (blue circle).

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5) Rosario González-Feréz, Universidad de Granada

Polyatomic ultralong range Rydberg molecules

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In cold and ultracold mixtures of atoms and molecules, Rydberg interactions with surrounding atoms or molecules may, under certain conditions, lead to the formation of special long-range Rydberg molecules [1,2,3]. These exotic molecules provide an excellent toolkit for manipulation and control of interatomic and atom-molecule interactions, with applications in ultracold chemistry, quantum information processing and many-body quantum physics. In this poster, we discuss ultralong-range polyatomic Rydberg molecules formed when a heteronuclear diatomic molecule is bound to a Rydberg atom [3,4]. The binding mechanism appears due to anisotropic scattering of the Rydberg electron from the permanent electric dipole moment of the polar molecule. We propose an experimentally realizable scheme to produce these triatomic ultralong-range Rydberg molecules in ultracold KRb traps, which might use the excitation of potassium or rubidium [5]. By exploiting the Rydberg electron-molecule anisotropic dipole interaction, we induce a near resonant coupling of the non-zero quantum defect Rydberg levels with the KRb molecule in an excited rotational level. This coupling enhances the binding of the triatomic ultralong-range Rydberg molecule and produces favorable Franck-Condon factors. Another type of ultralong-range Rydberg molecule is formed in collisions between polar molecules in cold and ultracold settings [6]. The interaction of Λ-doublet nitric oxide (NO) with long-lived Rydberg NO molecules forms ultralong-range Rydberg bimolecules with GHz energies and kilo-Debye permanent electric dipole moments. The description includes both the anisotropic charge-molecular dipole interaction and the electron-NO scattering. The rotational constant for the Rydberg bimolecules is in the MHz range, allowing for microwave spectroscopy of rotational transitions in Rydberg bimolecules. The Rydberg molecules described here hold promise for studies of a special class of long-range bimolecular interactions.

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6) Burak Gürlek, Max Planck Institute for the Science of Light

Quantum optics with organic molecules: cavity QED, optomechanics, and cooperativity

Michael, Becker, Burak Gürlek, Siwei Luo, Masoud Mirzaei, Luis Morales, Mohammad Musavinezhad, Jahangir Nobakht, André Pscherer, Dominik Rattenbacher, Alexey Shkarin, Johannes Zirkelbach, Jan Renger, Tobias Utikal, Stephan Götzinger, Vahid Sandoghdar

Max Planck Institute for the Science of Light, Erlangen, Germany

Laboratory manipulation of single quantum emitters and single photons has matured to a routine procedure over the past two decades [1]. These activities have led to new emerging topics such as optomechanical functionalities and coherent cooperative interactions among several quantum emitters. In this presentation, we discuss our efforts of the last decade in coupling molecules to high-finesse Fabry-Perot cavities [2] and nanoscopic waveguides on a chip [3], demonstrating dipole-induced transparency, strong coupling and single-photon nonlinearity. Moreover, we present data on precision spectroscopy of the vibronic transitions in single molecules and related coherent effects [4]. We also show the latest results on the coupling of two or molecules to each other via a common mode of a micro-resonator.

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7) Felipe Herrera, Universidad de Santiago de Chile

Self-dissociation of polar molecules in a confined infrared vacuum

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Coherent light-matter interaction of molecular media in infrared (IR) cavities is a promising tool for manipulating and controlling chemical reactivity and light emission. We study the wavepacket dynamics of an individual hydrogen fluoride (HF) molecule in strongly-confined electromagnetic environments and show that in the absence of additional thermal or coherent external sources, a single-mode cavity vacuum can efficiently dissociate the molecule, when this is suddenly prepared in the vibrational ground level. We predict dissociation probabilities of up to 20% in less than 200 fs for a bare vacuum field that is resonant with the fundamental vibration frequency at the onset of the ultrastrong coupling regime. Further enhancements of the dissociation probability can be expected for a cavity with thermal excitations and multiple modes. We develop an analytical model for understanding these results using polaron transformation techniques on the multi-level quantum Rabi model of vibrational polaritons. The model highlights the importance of Bloch-Seigert shifts of the vibrational levels and the role permanent dipole moments in the light-matter coupling process. This work highlights the fundamental differences that can be expected for reactive dynamics in infrared cavities and plasmonic nanostructures in comparison with free space chemistry.

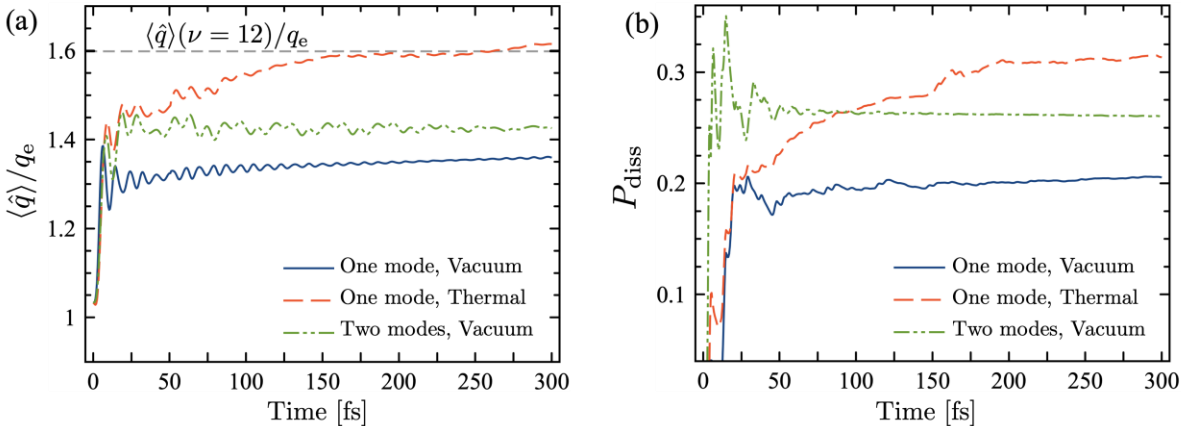

Figure 1. (a) Evolution of the mean hydrogen fluoride (HF) bond distance for different cavity states; (b) Dissociation probability for the same conditions in (a).

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8) Tomohiro Ishii, Polytechnique Montreal

Exciton-Polariton Condensation in Organic Microcavities: Polariton Relaxation and Polariton Dephasing Dynamics

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[f] International Institute for Carbon Neutral Energy Research, Kyushu University, Japan

Exciton-polaritons, in which the electronic state of an excited organic molecule and a photonic state are strongly coupled, can form a Bose-Einstein condensate (BEC) at room temperature [1]. However, so far, the reported thresholds of organic polariton BECs under optical excitation are in the range of $P_{\mathrm{th}} \sim 2.2 - 500\ \mu\mathrm{J\ cm^{-2}}$. One route towards lowering the condensation threshold is to increase the polariton relaxation rate (W_{ep}) [2, 3, 4], but the relationship of W_{ep} with a condensation threshold has not been fully explored.

In this study, we demonstrate a room-temperature polariton condensate at a threshold pump fluence of $9.7 \pm 0.1\ \mu\mathrm{J\ cm^{-2}}$, in a microcavity containing 4,4'-bis((*E*)-4-(3,6-bis(2-ethylhexyl)-(9*H*-carbazol-9-yl))styryl)-1,1'-biphenyl (BSBCz-EH). Notably, this class of organic materials is the only one which has demonstrated the possibility of electrically-pumped lasing. By using a semiclassical model to describe the polariton kinetics, we reveal that the low polariton BEC threshold results from the rapid relaxation rate from the dark exciton reservoir to the set of the lower polariton states forming the condensate, indicating that accelerating polariton relaxation is an important factor for realizing low-threshold polariton condensates (Fig. 1) [3]. In addition, we reveal that polariton dephasing reduces the efficiency of the polariton relaxation, which prevents the low threshold polariton BEC.

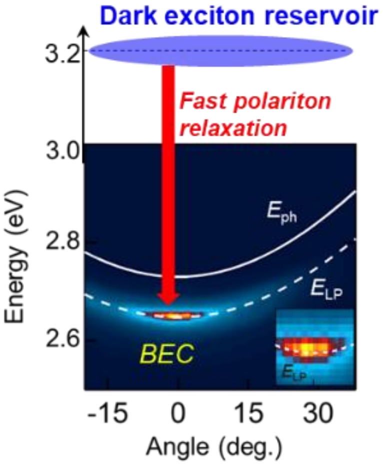

Figure 1. The angle-resolved PL of the microcavity. The threshold is observed at $P_{\mathrm{th}} = 9.7\ \mu\mathrm{Jcm^{-2}}$.

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9) Kyle Kairys, Emory University

Quantum Energy Diffusion in Polaritonic Wires

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Long-range intermolecular energy transport has been observed in optical microcavities. In this work, coherent energy transfer dynamics was probed for exciton wave packets in organic microcavities. This investigation implemented a microscopically detailed computational photonic wire model that evaluates spacetime resolved wave packet evolution under strong light-matter interaction conditions. Simulations were performed for variable light-matter coupling strength, total system size, and molecular excited-state energy fluctuations. This allowed us to elucidate their impact on the intermolecular energy transport in a multimode polaritonic system.

We observed ultrafast ballistic, diffusive and subdiffusive (Anderson Localization) transport depending on the initial state and microscopic parameters. Our investigation has thus determined that, not only polariton transport, but also exciton wave packet propagation is controllable in optical microcavities and likely plays a previously overlooked role in enhancing intermolecular transport in polaritonic materials.

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10) Francesco Mattiotti, University of Strasbourg

Multifractality and localization in the disordered interacting Tavis-Cummings model

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When quantum emitters and a cavity mode coherently exchange energy at a rate faster than their decay, hybrid light-matter states emerge. Such hybrid states are superpositions composed of "bright" emitter modes and cavity photons, while numerous remaining emitter states have no photon contribution, i.e., remain "dark" [1]. The hybridization of N emitters with a single cavity mode is well captured by the Tavis-Cummings (TC) model. Recently, an extensive study of the single-excitation TC model has shown multifractality of all the eigenfunctions for any strength of the light-matter coupling [2]. Multifractality is well known to be a meaningful feature of critical wave functions at Anderson transitions, with a multifractal spectrum that characterizes the universality class of the transition. Here we show that multifractality in the TC model is not limited to single-excitation, analyzing the system at half filling [3]. While multifractality suggests delocalization of the eigenfunctions and, thus, good conductivity, we found that the energies can show Poissonian or Wigner-Dyson-like statistics, related respectively to insulators and conductors. Interestingly, a Poissonian level statistics can coexist with multifractality. Moreover, the average single-spin observables are always localized, in agreement with the Richardson-Gaudin model [4].

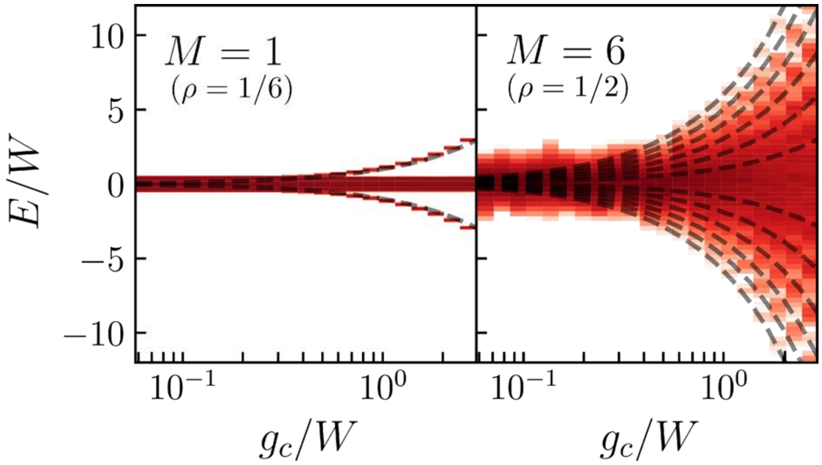

Figure. Density of states of the TC model for *M* excitations in *N* emitters. Single-excitation (left) and half-filling case (right) shown for *N*=12.

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11) Felipe Recabal, Universidad de Santiago de Chile

Driven-dissipative change transport in small networks: negative conductance and light-induced currents

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Nanojunction experiments with single molecules or quantum dots placed between macroscopic leads allow the exploration of quantum transport at the nanoscale [1]. We model these systems adopting a Markovian open-quantum system approach to compute the current-voltage response of small-size networks of interacting two-level conducting sites that are coupled to leads, and radiative and non-radiative reservoirs. We model the phenomenon of light-induced current, reported theoretically [2] and experimentally [3]. We validate our Markovian model by reproducing the experimental results on negative conductance [3] of single-molecule junctions with a two-site model in the absence of electromagnetic driving (Fig. 1). We show that Coulomb blocking of current can be neglected with an external electromagnetic driving source and non-radiative decay. At zero bias voltage, the photocurrent induced by the electromagnetic driving source has a direction that depends on the delocalized orbital. We finally extend these results by treating electron transport under vibrational strong coupling in an infrared cavity (Fig. 1c) and discuss possible verifications of our predictions in current experiments [5].

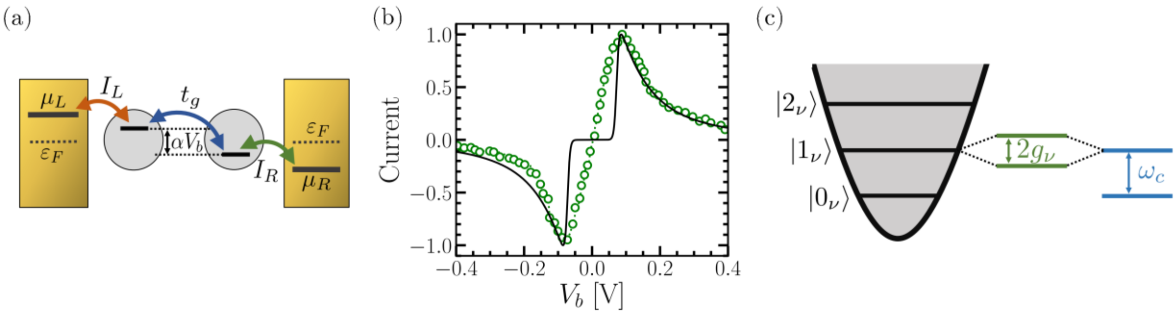

Figure 1. (a) Dimer model. (b) Modelled (solid line) y experimental (dotted line) current-voltage curve of the molecule. (c) Splitting of vibrational levels by a cavity. Experimental data extracted from [5].

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Computational Macroscopic QED Framework for Vibrational Polaritons

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Near-resonant molecule-field interactions have attracted significant attention in chemical physics and quantum optics [1,2]. We study the quantum dynamics of a molecular vibration coupled to near-field modes of an infrared nanoresonator using macroscopic quantum electrodynamics (QED). Nanophotonic structures vary in geometry and material properties, which makes the calculations of interaction dynamics challenging [3]. We use the electromagnetic Green's tensor of the nanophotonic structure to construct frequency and position dependent interaction Hamiltonians in macroscopic QED that are used to derive and numerically solve the system of non-Markovian integro-differential equations (IDE) that describe the dynamics of vibrational and photonic degrees of freedom in strong coupling. The material and dipole parameters are encoded in the structure of the kernel function of the IDE. We solve for photonic and vibrational observables for a single non-polar anharmonic vibration in a resonant infrared nanocavity and compare the results with recent phenomenological Markovian models developed for vibrational polaritons [4], to better understand the reach and limitations of reduced Markovian quantum optics models to describe currently available experiments.

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