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Tracking Ultrafast Charge Dynamics in Energy Materials with Atomic Specificity

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14. ABSTRACT

In this project, supported by the AFOSR Molecular Dynamics and Theoretical Chemistry Program, we mainly made major achievement.

First, we pioneered a new area of ultrafast dynamics of molecular vibrational polaritons, quasiparticles between photons and molecular vibrations through strong coupling: (1) we demonstrated the first twCrdimensional infrared spectroscopy of molecular vibrational polaritons and developed appropriate theory for the spectra at longer waiting time; (2) we showed that molecular vibrational polaritons can have large, tunable nonlinearities for quantum simulation applications and photonic circuitry; (3) we showed that by selectively exciting lower polaritons, the molecular vibrations can be directly promoted to higher excited states; (4) we enabled intermolecular vibrational energy transfer through molecular vibrational polaritons, as a general way to engineer intermolecular interactions in liquid phase, which was otherwise not available without strong coupling. These findings lay the fundamental understanding of molecular vibrational polariton dynamics and also opens new platform for photonic devices in mid-infrared and quantum simulation using molecular states.

Second, we constructed a time-resolved EUV spectrometer, and used it to probe ultrafast polaron formation at surfaces of a-Fe203 and FeOOH, in the reflective geometry. We found that in addition to the resonant absorption having transient changes, the non-resonant imaginary refractive index was also reduced by the polaron formation. The decrease of non-resonant imaginary refractive index was due to the change of XUV photoemission cross-section upon the formation of a trapped charge-polaron. Using this observation, we compared the trapping depth relatively between Fe203 and FeOOH, which was not discussed in previous publications. Our work showed that the non-resonant index could also be changed during charge excitation and reflect important physical phenomena. This work is important, because it allows future study of element-specific dynamics of surfaces.

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Accomplishment

The major goals of the project are (1) to develop a compact high-harmonic generation based transient EUV spectrometer for element specific charge dynamics at surfaces, and later added (2) understand and control molecular vibrational polariton dynamics, reflecting the surge of research in using molecular vibrational polaritons to control chemistry.

Several important goals were accomplished.

(1) We performed the *first* coherent two-dimensional infrared (2D IR) spectroscopy of molecular vibrational polaritons, a class of emerging quantum coherent light-matter states. Molecular vibrational polaritons are new members of the polariton family, and can be understood as superpositions of light and *molecular vibrations* due to strong coupling between them in optical microcavities. These exotic quasiparticles have high expectations that these can be important in modifying optical properties of molecules, designing high-performance mid-infrared optoelectronic devices, controlling chemical reactions, and mediating long-range excitation energy transfer, which create a broad range opportunities for vibrational-polaritons in physical and photonic science. This work gained the fundamental understanding of molecular vibrational-polaritons, beyond the knowledge revealed by linear spectroscopy[1].

In this work, 2D IR spectroscopy is shown to not only unambiguously resolve optical features due to polaritonic states (Fig.1 a,c,d and f), but also for the first time expose surprising optical response of reservoir modes which are believed to be optically dark (Fig.1 b and e). These 2D IR spectral features indicate hidden ultrafast population transfer pathways between polaritonic and reservoir states that hitherto was unknown. Both a classical and a newly developed quantum mechanical model are used to understand these interactions between polaritons and reservoir modes. It is found that within 25 picoseconds, the majority of polaritons relax and populate reservoir states, which subsequently influence optical response and the effective energy landscape of polaritons. We further show that light-matter hybridization is extremely sensitive to cavity detuning, thus adding a fine-tuned control knob for the composition and physical properties of vibrational-polaritons. This research represents a major step forward in the critical development of a comprehensive understanding of how to achieve novel mid-IR photonic behavior with molecular vibrational-polaritons. We also worked with the Yuen-Zhou group to develop theory for spectroscopy in this condition[2].

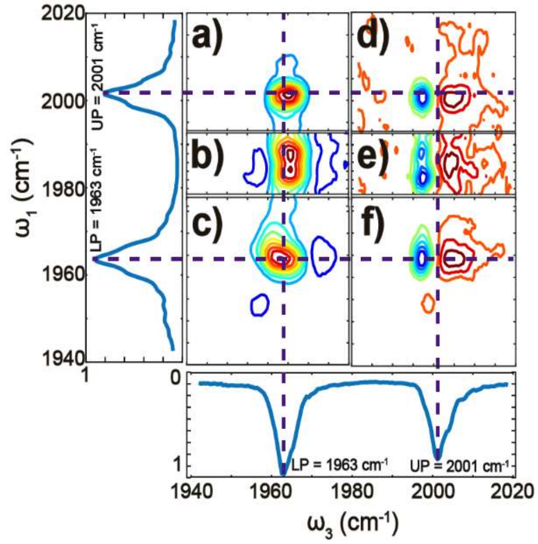

Figure 1. 2D IR spectrum of $W(CO)_6$/cavity polariton system at 25 ps delay with -2 cm^{-1} detuning. Each spectral region is scaled to its own intensity maximum and minimum. Spectra of the pump (ω_1) and probe (ω_3) pulses are shown on their respective axes. (b) and (e) are results of hidden interactions between polariton and dark states

(2) We have used 2D IR spectroscopy to demonstrate a unique properties of molecular vibrational polaritons: macroscopic tunable optical nonlinearity.

We realized control of vibrational polariton coherent nonlinearities by manipulation of macroscopic parameters such as cavity longitudinal length or molecular concentration (Fig.2a). We first find that pump probe spectra of molecular polaritons (Fig.2b and c), under the same condition, can be directly controlled by cavity thickness (longitudinal length), e.g., when the cavity thickness is reduced from 25 to 12 micron, the nonlinearity is increased. This result indicate that optical nonlinearity becomes macroscopic dependent, which used to be a property for microscopic molecular structure. This unique property is because that polaritons integrate both the macroscopic delocalization from photon, and the nonlinearity from microscopic molecules. Further 2D IR investigations reveal that this nonlinearity feature also quantum beats at the Rabi splitting between lower and upper polaritons (Fig.2d), which further reveal that the nonlinear signal is originated from quantum coherence, and from an unconventional nonlinear dephasing dynamics (Fig.2e). The reported phenomena originate from the nonlinear macroscopic polarization stemming from strong coupling between microscopic molecular excitations and a macroscopic photonic cavity mode. This finding enables exclusive control of optical nonlinearity of polaritons[3].

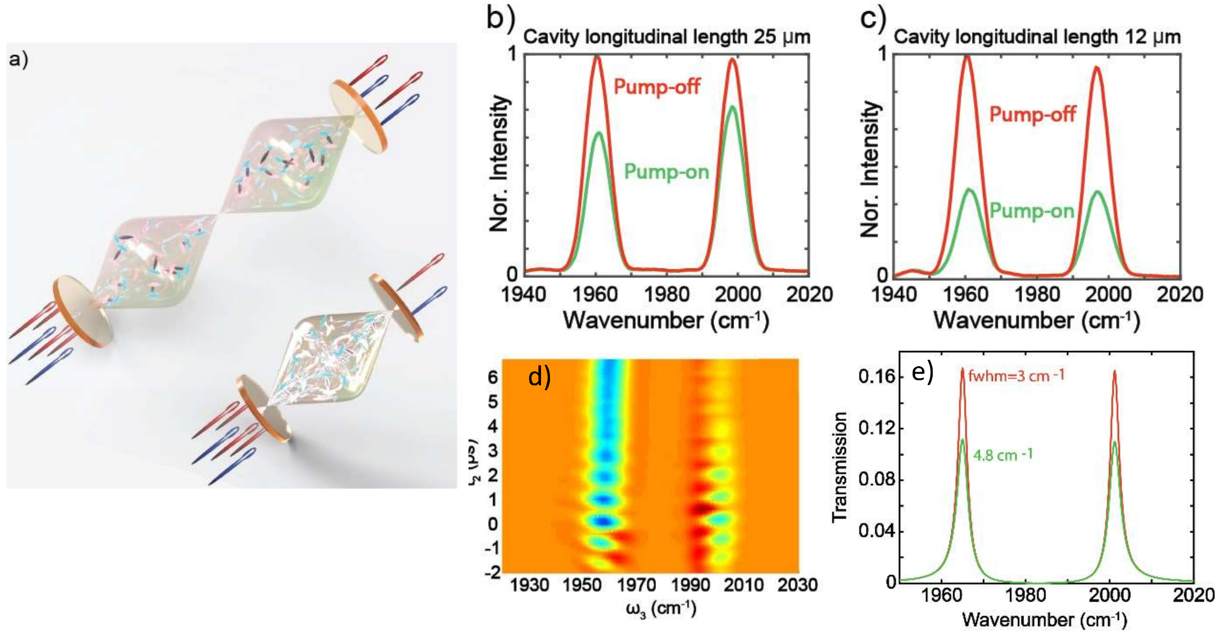

Figure 2. macroscopic dependent nonlinearity from vibrational polaritons. (a) concept to demonstrate the cavity thickness dependence of optical nonlinearity. (b) and (c) probe transmission spectra with IR pump on and off, with 25 and 12 micron spacers. The pump probe signal is larger with 12 micron spacers, when all other parameters remain the same (d) quantum beat dynamics of the nonlinear signal. (e) simulated result to show that the nonlinear signal (transmission reduction in b and c) can be reproduced by changing fwhm and therefore dephasing time of polaritons, indicating nonlinear dephasing dynamics.

(3) We conducted the first, state-resolved dynamics of molecular vibrational polariton relaxation to dark states, which provide the theoretical framework for designing molecular polaritons for cavity-modified chemistry. We found that under certain conditions, polaritons exhibit a relaxation mechanism that highly resembles hot electron dynamics in plasmons: collective polaritons first relax to high-lying hot molecular vibrational states and then subsequently relax to the first excited vibrational state. This mechanistic similarity lays the foundation to directly transfer many principles of plasmon applications to polaritons. For example, hot electrons from plasmons trigger reactions effectively. Similarly, we could expect that it is possible to concentrate polariton energies into specific vibrational modes to promote chemical bond

breaking. This work also studied how population relaxation from polaritons can be controlled by solvents, which could shed light on recent cavity chemistry studies[4].

(4) My lab further demonstrated unprecedented energy transfer pathways between molecular vibrational modes in the liquid phase under strong coupling conditions[5].

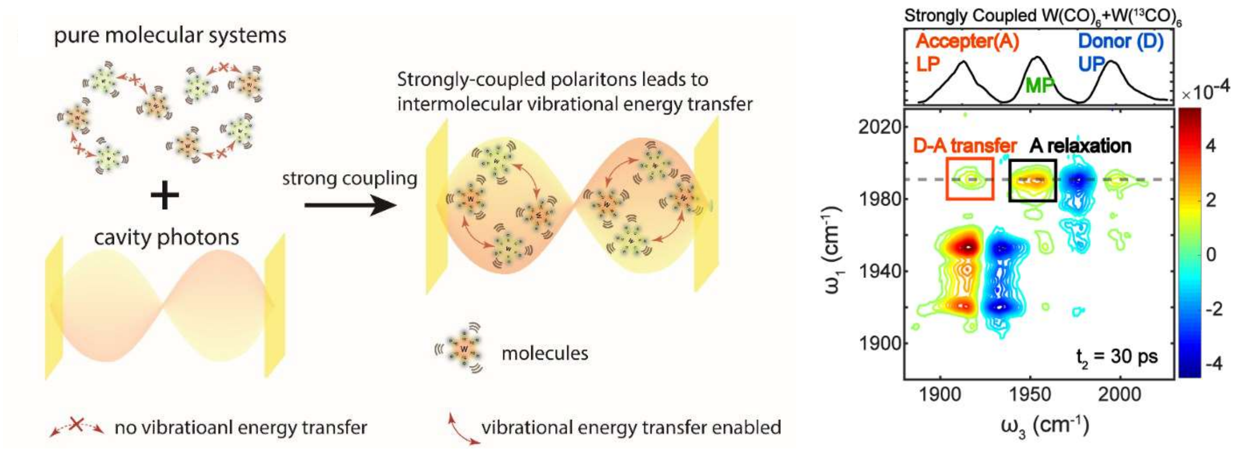

Figure 3. Intermolecular vibrational energy transfer enabled by strong coupling (left). By combining molecular systems with photonic environment, strong coupling led to intermolecular vibrational energy transfer (middle), as evidenced by the cross peak (red rectangular, right) in the 2DIR spectrum.

We developed a new energy-transfer paradigm by forming polaritons and inducing molecules in solution to exchange vibrational energy at room temperature . Energy transfer is a critical step for chemical reactions, biological signal transduction, and energy harvesting processes. However, in nature, the exchange of vibrational energy between molecules is slow (Fig.3, upper left) relative to energy dissipation into the solvent, i.e., heat loss. My lab showed that by forcing vibrational modes of donor and acceptor molecules strongly coupled to the photon mode, vibrational energy is transferred between them (Fig.3, middle and right). We demonstrated methods that can control the amount of energy transfer by changing cavity thickness and coupling strength. By characterizing the energy transfer dynamics, we introduced a broadly applicable way of engineering artificial forces between photons and molecules, a result that opens up entirely new ways to transmit signals among biological molecules or achieve chemical catalysis without direct contact between catalysts and reactants.

(5) Finally, we we constructed a high-harmonic-generation (HHG)-based table top transient XUV reflection-absorption spectrometer and used it to follow polaron formation at Fe_2O_3 and FeOOH surfaces (Figure 4). We found that in addition to the resonant absorption having transient changes, the non-resonant imaginary refractive index was also reduced by the polaron formation. The decrease of non-resonant imaginary refractive index was due to the change of XUV photoemission cross-section upon the formation of a trapped charge-polaron. Using this observation, we compared the trapping depth relatively between Fe_2O_3 and FeOOH. Before our work, the influence of the non-resonant imaginary refractive index was overlooked, as most works focused on the resonant feature. Our work showed that the non-resonant index

could also be changed during charge excitation and reflect important physical phenomena. This work is important, because it allows the study of element-specific dynamics of surfaces[6].

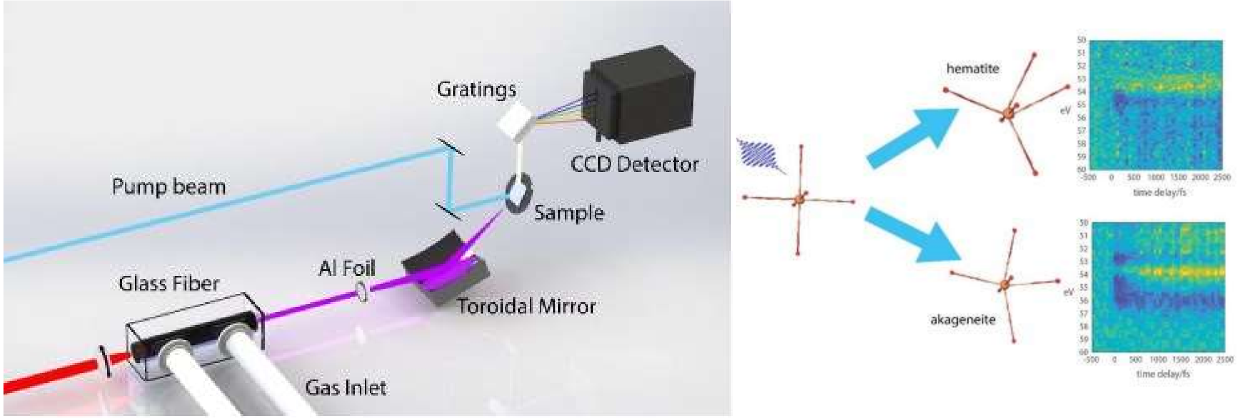

Figure 4. Table-top transient XUV reflection absorption spectrometer. (left) setup; (right) different charge dynamics on the Fe element of Fe2O3(hematite) and FeOOH(akageneite).

This program has also supported graduate students (Dr. Bo Xiang, Wenfan Chen) to pursue their PhD degrees. In particular, Dr. Bo Xiang has been awarded the 2020-21 Carol and George Lattimer Award for Graduate Excellence and moved on to pursue a postdoctoral position and later an academic position,

All results have been published in research journals and presented in academic conferences.

Impact

The impact on the principal disciplines of the project. The polariton dynamics projects opened a new direction for physical chemistry. 2D IR spectroscopy advanced our understanding of molecular vibrational polaritons, and further demonstrates its potential in nonlinear photonics applications and modifying energy transfer and relaxation pathways.

The transient XUV project opens ways to probe element specific dynamics at surfaces and in particular, pointed out the importance of considering the change of non-resonance refractive index in the experiment, which added an additional parameter for gaining insights of surface charge dynamics

The impact on human resources. A PhD degree was awarded under the support of this grant, and the student continued academic career as a postdoctoral scholar in the U.S.

The impact on infrastructures. A compact transient EUV reflection absorption spectrometer was developed on campus and it is the first and only instrument that allows probing element specific dynamics, which can draw collaborations from other departments.

(1) Xiang, B.; Ribeiro, R. F.; Dunkelberger, A. D.; Wang, J.; Li, Y.; Simpkins, B. S.; Owrutsky, J. C.; Yuen-Zhou, J.; Xiong, W. Two-Dimensional Infrared Spectroscopy of Vibrational Polaritons. *Proc. Natl. Acad. Sci.* **2018**, *115* ((19)), 4845–4850. https://doi.org/10.1073/pnas.1722063115.

(2) Ribeiro, R. F.; Dunkelberger, A. D.; Xiang, B.; Xiong, W.; Simpkins, B. S.; Owrutsky, J. C.; Yuen-Zhou, J. Theory for Nonlinear Spectroscopy of Vibrational Polaritons. *J. Phys. Chem. Lett.* **2018**, *9* (13), 3766–3771. https://doi.org/10.1021/acs.jpclett.8b01176.

(3) Xiang, B.; Ribeiro, R. F.; Li, Y.; Dunkelberger, A. D.; Simpkins, B. B.; Yuen-Zhou, J.; Xiong, W.

Manipulating Optical Nonlinearities of Molecular Polaritons by Delocalization. *Sci. Adv.* **2019**, *5* (September), eaax5196.

(4) Xiang, B.; Ribeiro, R. F.; Chen, L.; Wang, J.; Du, M.; Yuen-Zhou, J.; Xiong, W. State-Selective Polariton to Dark State Relaxation Dynamics. *J. Phys. Chem. A* **2019**, *123* (28), 5918–5927. https://doi.org/10.1021/acs.jpca.9b04601.

(5) Xiang, B.; Ribeiro, R. F.; Du, M.; Chen, L.; Yang, Z.; Wang, J.; Yuen-Zhou, J.; Xiong, W. Intermolecular Vibrational Energy Transfer Enabled by Microcavity Strong Light–Matter Coupling. *Science (80-.).* **2020**, *368* (6491), 665–667. https://doi.org/10.1126/science.aba3544.

(6) Chen, W.; Xiong, W. Polaron-Formation Revealed by Transient XUV Imaginary Refractive Index Changes in Different Iron Compounds. *Phys. Chem. Chem. Phys.* **2021**, *23* (8), 4486–4490. https://doi.org/10.1039/d1cp00103e.