Intermolecular vibrational energy transfer via microcavity strong light-matter coupling

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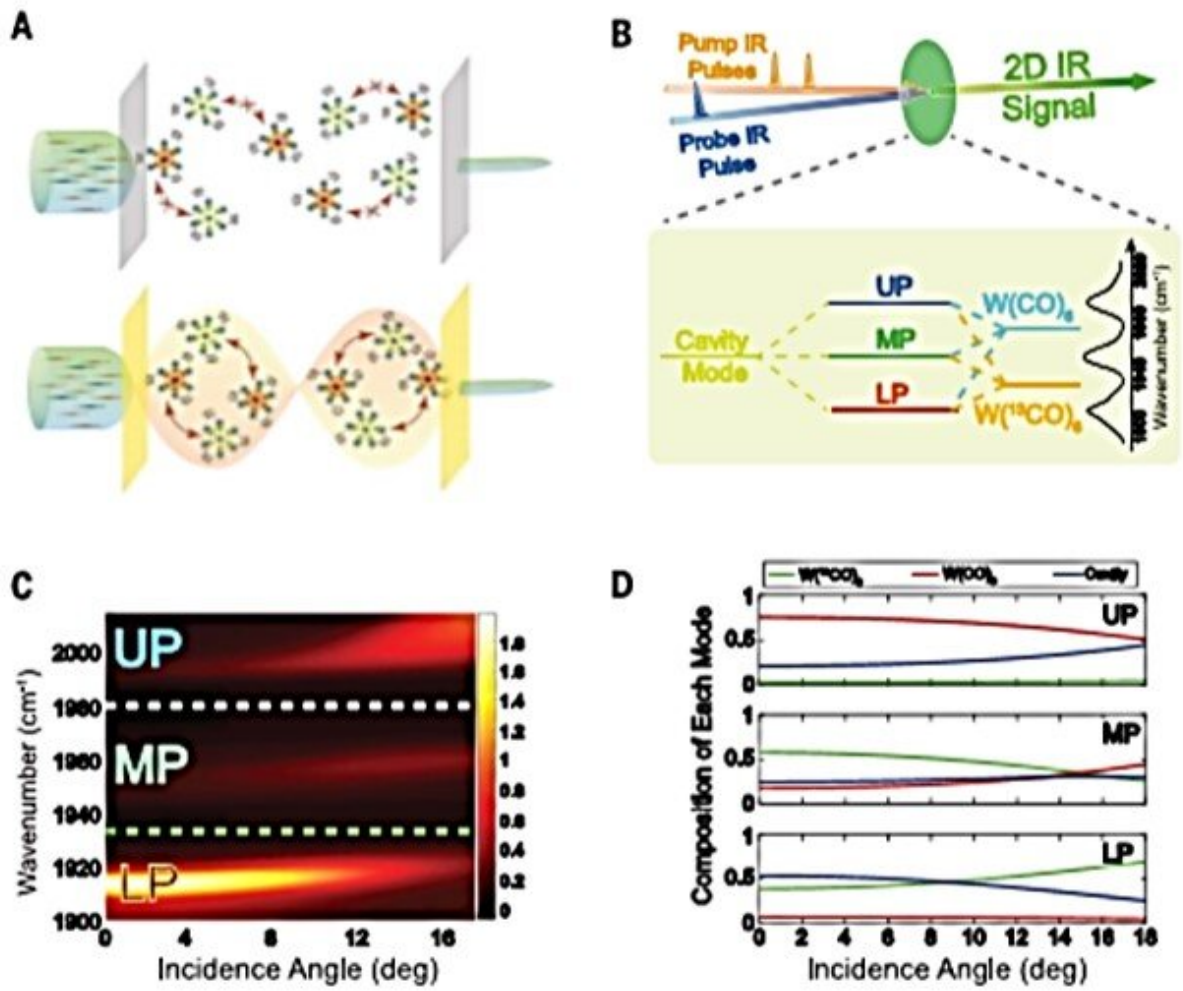


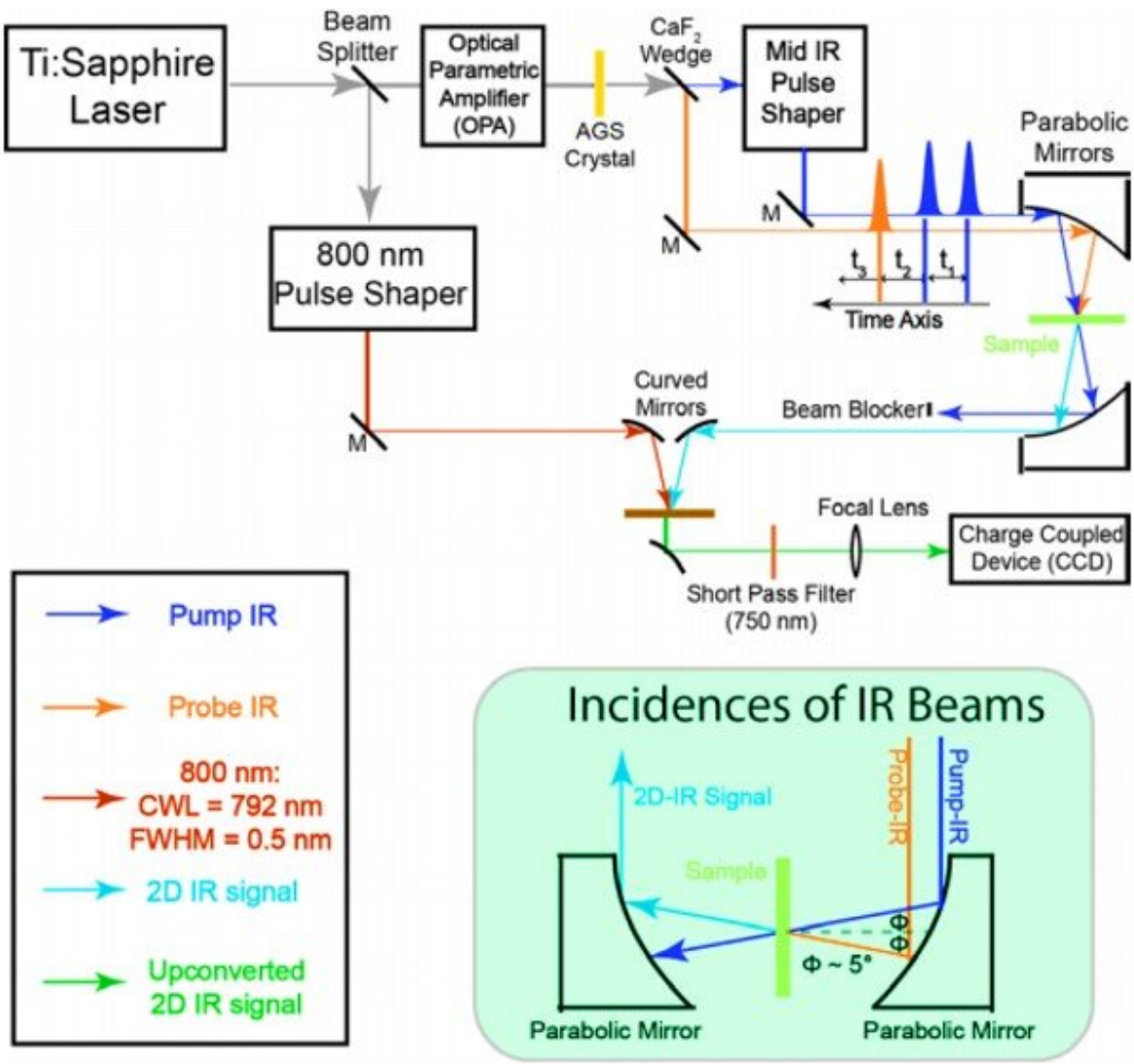
Strongly coupled system between W(CO)6 and W(13CO)6 in a hexane/DCM mixture and a cavity. (A) Schematic illustration showing that VET between vibrational modes of W(CO)6 and W(13CO)6 molecules is unfavorable in solution (top) but is enabled by strong coupling of the molecular system to an

infrared cavity mode (bottom). (B) Diagram of the 2D IR pulse sequence along with the IR spectrum and energy diagram of the system. (C) Transmission spectra of the polaritonic system as a function of incidence angle; white and green dashed lines denote bare W(CO)6 and W(13CO)6 vibrational transitions, respectively. (D) Hopfield coefficients for LP, MP, and UP as a function of incidence angle. Credit: Science, doi: 10.1126/science.aba3544

Strong coupling between cavity photon modes and donor/acceptor molecules can form polaritons (hybrid particles made of a photon strongly coupled to an electric dipole) to facilitate selective vibrational energy transfer between molecules in the liquid phase. The process is typically arduous and hampered by weak intermolecular forces. In a new report now published on *Science*, Bo Xiang, and a team of scientists in materials science, engineering and biochemistry at the University of California, San Diego, U.S., reported a state-of-the-art strategy to engineer strong light-matter coupling. Using pump-probe and two-dimensional (2-D) infrared spectroscopy, Xiang et al. found that strong coupling in the cavity mode enhanced the vibrational energy transfer of two solute molecules. The team increased the energy transfer by increasing the cavity lifetime, suggesting the energy transfer process to be a polaritonic process. This pathway on vibrational energy transfer will open new directions for applications in remote chemistry, vibration polariton condensation and sensing mechanisms.

Vibrational energy transfer (VET) is a universal process ranging from chemical catalysis to biological signal transduction and molecular recognition. Selective intermolecular vibrational energy transfer (VET) from solute-to-solute is relatively rare due to weak intermolecular forces. As a result, intermolecular VET is often unclear in the presence of intramolecular vibrational redistribution (IVR). In this work, Xiang et al. detailed a state-of-the-art method to engineer intermolecular vibrational

interactions via strong light-matter coupling. To accomplish this, they inserted a highly concentrated molecular sample into an optical microcavity or placed it onto a plasmonic nanostructure. The confined electromagnetic modes in the setup then reversibly interacted with collective macroscopic molecular vibrational polarization for hybridized light-matter states known as vibrational polaritons. When the scientists investigated the phenomena under strong light-matter coupling, the intermolecular VET appeared to operate via different mechanisms to those previously established. Since selective intermolecular VET in condensed phases rarely occurs, its polaritonic counterpart introduced a powerful concept capable of altering the course of the ground-state chemistry in solution.



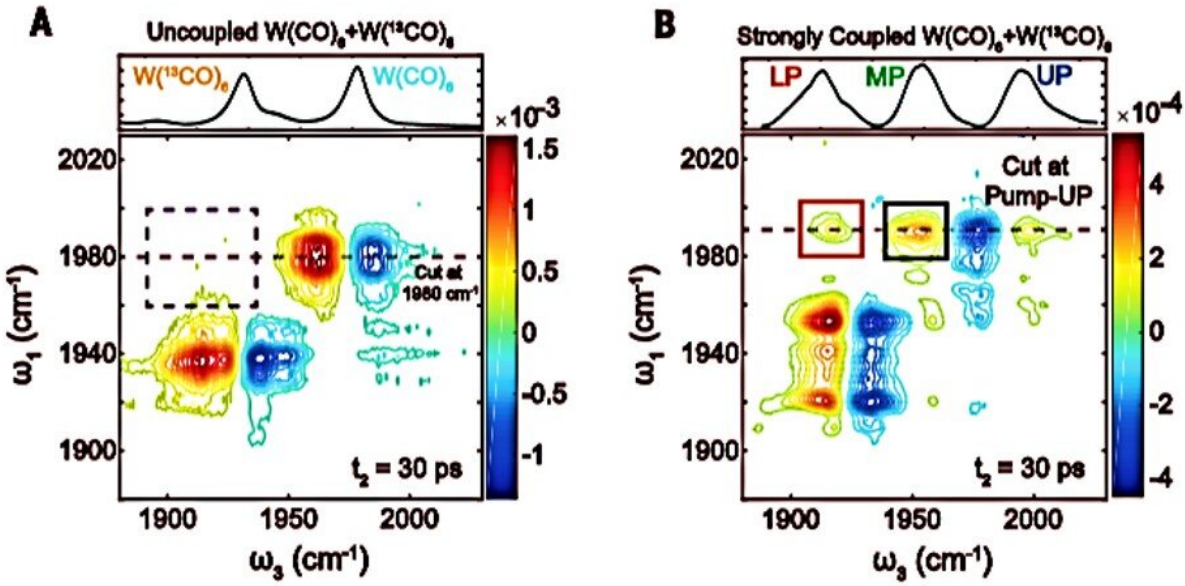
Scheme of two-dimensional infrared experimental setup. The inset shows the incidence of pump and probe IR beams. Credit: Science, doi: 10.1126/science.aba3544

Xiang et al. then designed a strongly coupled system containing a microcavity and ensembles of two vibrational modes from different molecules to study cavity-assisted intermolecular VET. For this, they selected molecules that were ideal for vibrational strong coupling with

degenerate asymmetric stretch modes, high oscillator strengths and narrow linewidths. On each molecular subsystem, the light-matter coupling constant (g) was proportional to the square root of the concentration of the absorbers (√C). Given a large enough concentration, each molecular subsystem satisfied a condition where the light-matter coupling constant (g) was greater than the full width at half maximum of the vibrational and cavity modes.

As a result, the vibrational and cavity modes (also known as basis modes) hybridized and formed new normal modes as upper, middle, and lower polaritons (UP, MP and LP). Each polariton contained a super-position of the basis modes. The scientists could control the polariton resonance frequency and composition by changing the resonance frequency. This information was vital to understand the ability of strong coupling to allow intermolecular vibrational energy transfer.

For the two experimental molecules, Xiang et al. used tungsten hexacarbonyl; $W(CO)_6$ and $W(^{13}CO)_6$ in a solvent within a Fabry-Perot optical microcavity. Using two-dimensional infrared spectroscopy (2-D IR), the scientists showed vibrational energy transfer from $W(CO)_6$ to $W(^{13}CO)_6$ and compared the 2-D IR spectra of the mixture inside and outside the microcavity. The 2-D IR spectrum of the bare $W(CO)_6/W(^{13}CO)_6$ mixture confirmed the absence of energy transfer between vibrational modes. In contrast, the strongly coupled $W(CO)_6$ $/W(^{13}CO)_6$ system showed several cross peaks to indicate cavity-induced intermolecular correlations. Further transitions provided an optical window into the population dynamics of the $W(CO)_6$ and $W(^{13}CO)_6$ reservoir modes.

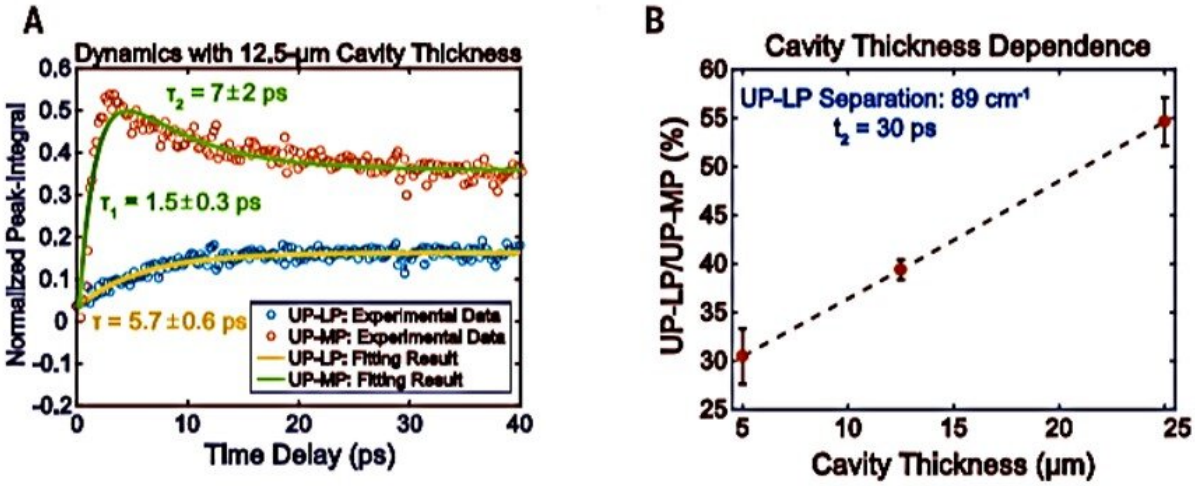


Comparison of 2D IR spectra inside and outside of the microcavity. 2-D IR spectra of (A)uncoupled and (B) strongly coupled W(CO)6/W(13CO)6 with a total concentration of 105 mM in binary solvent (hexane/DCM), along with the corresponding linear spectra of the two systems (top panels).The strongly coupled sample was taken at an incidence angle of 15°,where the cavity resonance is kept at 1961cm−1.The dashed box in(A) indicates the absence of cross peaks. The red and black boxes in (B) indicate the [wUP,wLP] and [wUP,wMP] cross-peaks, respectively. Credit: Science, doi: 10.1126/science.aba3544

The team then used pump-probe spectroscopy to study ultrafast electrodynamics and investigated the VET dynamics when they only excited the upper polariton (UP) population. The intensity of the cross peaks corresponding to the upper and lower polaritons (denoted W_{UP} and W_{LP}) increased with a time constant of 5.7 ± 0.6 ps. In contrast, direct relaxation of the upper polariton to $W(CO)_6$ occurred much faster than vibrational energy transfer with a lifetime of 1.5 ± 0.3 ps. The experimental conditions implied an energy "leakage" from the $W(CO)_6$

mode to the $W(^{13}CO)_6$ mode.

The team then conducted experiments to confirm the importance of cavity modes to facilitate polariton VET by increasing the cavity thickness and noted the efficiency of vibrational energy transfer increase with increasing thickness. Since thicker cavities had longer lifetimes, the dependence suggested that a larger fraction of upper polariton energy collected in $W(^{13}CO)_6$ modes as polariton decay due to slow photon leakage. This feature implied that intermolecular vibrational energy transfer involved polaritonic intermediate states.



Dynamics and cavity-thickness dependence of polariton-enabled intermolecular VET. (A) Dynamics of [wUP, wLP] and [wUP, wUP] peak integrals and the fitting results. The sample was taken at an incidence angle of 15°. (B) Plot of IUP,MP/IUP,LP as a function of cavity thickness at t2 = 30 ps. Error bars represent the SD of three independent scans. Credit: Science, doi: 10.1126/science.aba3544

In contrast to measurements conducted in organic microcavities, the relaxation kinetics of this work were dictated by previously unexplored mechanisms that require further study. Xiang et al. expect possible mechanisms to include polariton-mediated scattering and the interaction of polaritons with other dark modes. The team intend to expand the reported concept to polariton-enabled intermolecular vibrational energy transfer (VET) to selectively promote or suppress vibrational energy transport channels. The described method is key for other practical applications including IR polariton condensation, remote energy transfer and cavity chemistry.

More information: Bo Xiang et al. Intermolecular vibrational energy transfer enabled by microcavity strong light–matter coupling, *Science* (2020). DOI: 10.1126/science.aba3544

Xiaoze Liu et al. Strong light–matter coupling in two-dimensional atomic crystals, *Nature Photonics* (2014). DOI: 10.1038/nphoton.2014.304

David M. Coles et al. Polariton-mediated energy transfer between organic dyes in a strongly coupled optical microcavity, *Nature Materials* (2014). DOI: 10.1038/nmat3950

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