



Main Manuscript for

Enabling Multiple Intercavity Polariton Coherences by Adding Quantum Confinement to Cavity Molecular Polaritons

Zimo Yang¹, Harsh H. Bhakta², Wei Xiong^{1,2,3}

1 Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA, 92093

2 Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA, 92093

3 Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, CA, 92093

Corresponding author: Wei Xiong

Email: w2xiong@ucsd.edu

Author contributions: Z.Y. and W.X. designed the experiments and analyzed the data. Z.Y. prepared the materials and conducted the experiments. Z.Y. and H.H.B. conducted the simulation. All authors wrote the manuscript. W.X. oversaw the project.

Competing Interest Statement: The authors declare no financial conflicts.

Classification: Physical Sciences

Key words: polaritons, quantum confinement, coherences, 2D IR, quantum simulation.

This PDF file includes:

Main Text

Figures 1 to 5



Main Manuscript for

Enabling Multiple Intercavity Polariton Coherences by Adding Quantum Confinement to Cavity Molecular Polaritons

Zimo Yang¹, Harsh H. Bhakta², Wei Xiong^{1,2,3}

1 Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA, 92093

2 Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA, 92093

3 Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, CA, 92093

Corresponding author: Wei Xiong

Email: w2xiong@ucsd.edu

Author contributions: Z.Y. and W.X. designed the experiments and analyzed the data. Z.Y. prepared the materials and conducted the experiments. Z.Y. and H.H.B. conducted the simulation. All authors wrote the manuscript. W.X. oversaw the project.

Competing Interest Statement: The authors declare no financial conflicts.

Classification: Physical Sciences

Key words: polaritons, quantum confinement, coherences, 2D IR, quantum simulation.

This PDF file includes:

Main Text

Figures 1 to 5

Abstract

In this study, the “particle-in-a-box” idea, which was broadly developed in semiconductor quantum dot research, is extended into mid-Infrared (IR) cavity modes by applying lateral confinement in an optical cavity. The discrete cavity modes hybridize with molecular vibrational modes, resulting in a quartet of polariton states that can support multiple coherence states in the IR regime. We applied tailored pump pulse sequences to selectively prepare these coherences and verified the multi-coherence existence. The simulation based on Lindblad equation shows that because the quartet of polariton states reside in the same cavity, they were specifically robust towards decoherence caused by fluctuations in space. The multiple robust coherences pave the way for entangled states and coherent interactions between cavity polaritons, which is critical for advancing polariton-based quantum information technology.

Significance Statement

A new microcavity infrastructure, with lateral confinements, was designed and built for molecular vibrational polaritons, which are hybrid half-light, half-matter quasi-particles. The newly implemented photonic confinement to the Fabry-Perot cavity created additional “quantized” cavity modes and enabled the formation of a polaritonic multi-qubit systems, also called qudits. This new photonic structure enabled multiple coherences that were robust against environmental fluctuations, addressing a critical limitation in applying molecular polaritons for quantum technology. This work not only serve as an important step for developing molecular vibrational polaritons for quantum information technology, such as simulating light harvesting complex, but also has significant implications in realizing novel topological polariton systems and quantum light spectroscopy for molecular systems.

Main Text

Introduction

Molecular vibrational polaritons^{1–18} are half-matter, half-light quasiparticles that possess unique abilities to change chemical reactions^{3,10,12,15,17,19–22}, modify energy transfer pathways^{7,14,23,24}, and have the potential to be an alternative platform for quantum simulation.^{9,25–32} When the collective dipole coupling between cavity photon modes and molecular vibrational modes are so strong that the two modes exchange energy at a rate faster than the lifetimes of either mode, the upper and lower polaritons (UP and LP) are formed and the systems reach the so-called vibrational strong coupling (VSC) regime^{31–33}. Up to now, the majority of molecular vibrational polaritons are formed in Fabry-Perot (FP) cavity, which has one corresponding cavity photon mode for each specific in-plane momentum. These modes at different in-plane momentum form a continuous parabolic dispersion curve. As such, an FP cavity can support only one pair of UP and LP at a specific in-plane momentum, and thereby, have one coherence³⁰ (i.e., off-diagonal density matrix elements), namely $|UP\rangle\langle LP|$ (or its complex conjugate, Fig. 1A). Thus, UP and LP can be treated as one polariton qubit system at ambient conditions.^{28,29,34}

The molecular vibrational polariton based qubits is a potential platform for quantum simulation with several advantages, such as operating at ambient temperature, ease of tunability of cavities, and the customizable “designer” vibrational chromophores^{35–37}. Although similar efforts have been made on exciton polaritons, the single qubit property of the FP cavity has limited the scalability of molecular vibrational polaritons for advancing quantum simulation³⁴. One way to overcome the limitations is to form multi-qubit systems, also called qudits, using multi-cavity polariton systems. Early work from our group extended the FP cavity into two pairs of polaritons in spatially neighboring cavities^{9,26}, which we termed as dual cavity system herein (Fig.1B). However, the high frequency coherences composed of polaritons from different cavity modes (referred as intercavity coherences) cannot survive due to decoherence, because polaritons reside in

different spatial locations. To address this limitation, a *novel cavity structure is needed to multiplex polariton coherences for simulating complex quantum phenomena.*

In this work, we overcome the FP cavity limitations and create two cavity modes with distinct energies by applying an orthogonal confinement in FP cavity system. This confinement effect is similar to “particle in a box,” which is widely applied in semiconductor materials^{38–45}, including quantum dots and wells. Simply put, when the dimensions of a system are close to the wavelength of the particles, only certain wavefunctions can survive the boundary condition of the spatial confinement, leading to distinct quantum states and tunable energy gaps. However, compared to the confinement effect in semiconductor materials, this phenomenon has not been heavily explored in the IR regime. Here, we implemented confinement to IR cavities to create two photonic modes at a specific in-plane momentum, and we showed that the confined cavity has a discrete dispersion relation with respect to in-plane momentum. We further demonstrated that under VSC conditions, a quadruplet of polaritons (polaritonic qudits) was created which formed coherences between any pairs of polaritons (Fig. 1C). Thus, introducing confinement in a single cavity creates a foundation for generating qudits with complex coherence states or even entanglements in the future^{46–48}. This advance can create a potential platform for quantum light spectroscopy and other quantum science and technology^{49,50}. Therefore, this is a valuable step for molecular polaritonic quantum information technology.

Results

Discrete Dispersion Curve of the Confined Cavity.

To create the confinement effects to the cavity, we fabricated a trench on a distributed Bragg reflector (DBR) optics, and pair it with another flat DBR window to form a cavity (Fig. 1C). The trench had a depth of 1 μm , a width of 25 μm and a length of 7 mm (Fig. 1D) (see Methods for fabrication details). The two DBR mirrors were then separated by a Teflon spacer of thickness 12 μm to form the cavity, such that the trenched area has a 13 μm cavity thickness (illustrated in Fig. 1C. Note: the vertical dimension is drawn to illustrate the confinement effect and is not to scale). The IR transmission spectra of the cavity showed well-resolved peaks at 1971, 1995, and 2099 cm^{-1} (Fig. 1E). As the IR laser beam was scanned away from the trench, the doublet peak (1971 and 1995 cm^{-1}) intensity decreased, and the single peak (2099 cm^{-1}) intensity increased (Fig.S1B). Thus, the double peaks were from the trenched area, whereas the isolated peak was from outside of trench area.

Considering that the confined cavity system is formed with bi-planar mirrors, we might think that it also has two cavity modes corresponding to the different cavity longitudinal lengths. However, the appearance of the three peaks can be explained by the “particle in a box” model confined by a finite potential^{44,51,52}, by considering the confinement in the orthogonal direction in the trenched area. Under the condition of $k_{\parallel} \ll k_{\perp}$, cavity modes have energy dispersion relationship described as

$$E_{cav} = E_{cav}(k_{\parallel} = 0) + \frac{\hbar^2 k_{\parallel}^2}{2m_{cav}} \quad (1)$$

$$E_{cav}(k_{\parallel} = 0) = \frac{\hbar c}{n_c} k_{\perp} \quad (2)$$

where E_{cav} is the energy of the cavity modes, $k_{\parallel} = \frac{\pi n}{L_{\parallel}}$ is the in-plane momentum, $k_{\perp} = \frac{\pi n}{L_{\perp}}$ is the normal momentum, $\hbar$ is the reduced Planck's constant, $m_{cav} = \frac{E_{cav}(k_{\parallel}=0)}{\frac{c^2}{n_c^2}}$ is the effective mass of the cavity, n_c is refractive index of the media inside the cavity, $L_{\parallel}$ and $L_{\perp}$ are the width and height of the cavity, and n is an integer.³¹

When the orthogonal dimension is unconfined, like in FP cavity, $L_{\parallel}$ is infinite and $k_{\parallel}$ is continuously defined. Thus, the dispersion curve is continuous (Fig. 2A). However, when $L_{\parallel}$ is finite and on the order of λ , the wavevector $k_{\parallel}$ changes discretely with step-size of $\pm \frac{\pi}{L_{\parallel}}$, due to the interferences imposed to meet the

boundary conditions. In the trenched cavity, when $L_{\parallel} = 25 \mu\text{m}$, the even modes are observable with $k_{\parallel}$ being $0, \pm \frac{2\pi}{25}$, and $\pm \frac{4\pi}{25}$, beyond which, the corresponding cavity energy would be above the energy of an unconfined cavity (Fig. 2A). On the other hand, the odd modes could not be resolved well under current experimental conditions (See SI.2). Therefore, the two trenched-area peaks in the linear spectra should correspond to the two lowest-energy even modes resulting from the orthogonal confinement of electromagnetic waves inside the trenches. From equation (1), the energy separation between cavity modes depends on the trench width ($L_{\parallel}$) and depth ($L_{\perp}$), and refractive index of the media inside of the cavity (n_c , through the effective mass). We verified the “particle in a box” model by modifying $L_{\parallel}$ and n_c , and showed that the experimental peak separation agreed well with the model prediction (see SI.2). We also found that the optimal condition for resolving the polariton coherence experimentally was a trench with a width of $25 \mu\text{m}$ and depth of $1 \mu\text{m}$, and a cavity of thickness $12 \mu\text{m}$, which will be the cavity parameters used in experiments below.

The discrete dispersion, a character for the “particle in a box” cavity modes, was experimentally confirmed by scanning the linear spectra of the trenches in the confined and unconfined dimensions (Fig. 2B). When the beam incidence angle was adjusted in the plane perpendicular to the long axis of the trench (confined dimension, θ_1), the dispersion curve showed discrete states. Specifically, the frequency of the cavity mode did not change as a function of incident angle (or in-plane momentum), but the relative intensity of the states did. Within a certain angle range, two cavity modes could be resolved well (Fig. 2C). In contrast, when the incidence angle was tuned in a plane parallel to the long axis of the trench (unconfined dimension, θ_2), two continuous dispersion curve of a classical FP cavity was obtained (Fig. 2D), because of the two discrete states that resulted from confinements in the other dimension.

The “particle in a box” model qualitatively described the cavity mode characteristics and provides intuition for understanding the system. A more complete description of the system was obtained by solving the Maxwell's equations²⁶ in two-dimensions, with geometry of the cavity mirrors as the boundary conditions (see SI.1). The frequencies of cavity photon modes and their respective electromagnetic (EM) field distributions were obtained as the solution of the Maxwell's equations. They were subsequently used to calculate linear spectra, where the intensities of cavity modes were determined by the convolution of the corresponding EM field distributions and the gaussian laser beam profile. The calculated spectrum reproduced the experimental measurement well (Fig.1E), so did the calculated discrete dispersion curve (Fig.2E) and the spatial dependence of the peak intensities (Fig S1C). We noted the confined cavity mode could also be described similar to Gaussian TEM mode of FP cavity with spherical mirrors but with different boundary conditions⁵³.

The additional information from the simulation was the EM field intensity distribution (Fig. 2F) for the two trench-cavity modes (1971 and 1995 cm^{-1}). The lowest energy bright mode (S mode) had zero node, whereas the next “visible” mode (D mode) had two nodes. The mode with one node (P mode) was not visible experimentally and from simulation (Fig. 1E). Its invisibility was a net result of a convolution of the mode field distribution with Gaussian beam profile. To see the P mode, it required a tightly focused IR beam ($\sim 20 \mu\text{m}$) that were narrower than the mode spatial distribution and other strenuous conditions (see details in SI.2), which were beyond our experimental limit. Because the two modes (S and D) were eigenvectors (EM field distributions), they were orthogonal with and should not interact with each other. However, later we would show that when polaritons are formed among them, they do interact nonlinearly by sharing the matter components in the same spatial area.

Quadruplet Polaritons in Confined Cavities and Their Nonlinear Interactions.

The double modes in the confined cavity presented an opportunity to create multiple polariton states in one cavity. To achieve this, we filled the system with saturated $\text{W}(\text{CO})_6$ in hexane (red curve in Fig.3A for the spectrum) to form polaritons. Because the cavity modes were discrete in momentum space, we measured the dispersion curve by changing the cavity thickness instead of angle. Near zero detuning, VSC led to four polaritons (Fig. 3A), named UP_D , UP_S , LP_D , and LP_S , from high frequency to low frequency. When away from zero detuning, some polaritons could not be well-resolved from each other since those modes are too close in frequency, and therefore the systems appeared to have three peaks (Fig. 3B). This system was modeled by a 4×4 Hamiltonian, in which two cavity modes coupled to two sub ensembles of vibrational

modes separately (See SI, Sec.3). The modeled dispersion curve (solid lines in Fig. 3B) followed the experimental trend well, giving a collective coupling strength of 21 cm^{-1} for both cavity mode S and D, respectively. Thus, VSC in the confined cavity led to a quadruplet polariton system (Fig.3C). The decoupling between the two cavity modes was not completely surprising, because the two modes were orthogonal to each other^{54,55}.

However, it is still possible that the molecular vibrational modes strongly coupled to one cavity mode, and, at the same time, weakly coupled to the other mode. This type of coupling scheme could facilitate the nonlinear interactions between polaritons. We demonstrated this point by conducting 2D IR spectroscopy of this quadruplet polariton system. In 2D IR, an IR pulse excites the systems into a coherence, oscillating during t_1 , which is transferred by the second IR pulse to a coherence or population state, evolving in t_2 . Then, a third IR pulse transfers the systems into another coherence, resulting in a macroscopic polarization that emits an IR signal^{4,30,56–59} (Fig. 3D). Thus, 2D IR can reveal nonlinear interactions between coherences created by the pulses, which appear as cross peaks.

At $t_2 = 30 \text{ ps}$, the 2D IR spectra resolved all four polariton modes along the diagonal and showed cross peaks among all polaritons (Fig. 3E). These cross peaks were either due to Rabi splitting contraction or absorptive features from excited-state absorption of dark states, as described in previous works by us and Owrutsky et al.^{4,16,27} In brief, at $t_2 = 30 \text{ ps}$, excited polaritons already relaxed to the 1st excited state of the dark modes, which reduced the concentration of molecular absorbers being strongly coupled to the cavity modes, and caused a decrease of the Rabi splitting. The contraction of Rabi splitting led to the derivative spectral features on the $\omega_3 = \omega_{UP}$ region; on the $\omega_3 = \omega_{LP}$ side, the Rabi splitting contraction was overwhelmed by the absorption of the 1st excited state of dark modes, due to its anharmonicity.^{4,16,60} Thus, similar to what we learned from the dual cavity polariton systems²⁶, these cross peaks were caused by the polaritons sharing the same dark modes, indicating all polaritons were interacting with each other at long time delay (e.g., 30 ps).

Preparing Arbitrary Polariton Coherences and Comparison with the Dual Cavity Polaritons.

Next, because the polaritons in the confined cavity had strong nonlinear interactions, we examined whether the coherences in the confined cavity could be more robust to fluctuations than the ones in a dual cavity system. In the dual cavity polariton system, as shown in Figure 4A, if the coherences were created from polaritons residing in two spatially separate cavities, and the coherence frequency was large (e.g., 30 cm^{-1}), the coherences could not survive environmental fluctuations²⁶. This is shown in Figure 4B, where there is no clear coherence oscillation in the time domain, and the corresponding Fourier transform along t_2 resulted in unclear peaks. In the confined cavity polaritons, all polariton states were in the same cavity physically, which could possibly lead to more robust coherences.

To examine whether any arbitrary coherence could be created in confined-cavity polaritons, we tailored the first two IR pulses of 2D IR using a mid-IR pulse shaper (PhaseTech Spectroscopy, Inc.) to create targeted coherences. For example, we shaped the first pump pulse to be centered at ω_{UP_S} to excite the system to $|UP_S\rangle\langle 0|$, and the second pulse to be centered at ω_{LP_S} to initiate the coherence $|UP_S\rangle\langle LP_S|$ (Fig. 4C)^{25,61}. To characterize this coherence, we then took the corresponding 2D IR spectra while scanning t_2 . The 2D IR signal oscillated at the frequency of $\omega_{UP_S} - \omega_{LP_S}$ during t_2 (Fig. 4D, right), indicating the coherence $|UP_S\rangle\langle LP_S|$ is prepared. To better visualize the coherence, we Fourier transformed the 2D IR spectra along the t_2 axis, to plot 2D spectra of ω_2 and ω_3 at specific ω_1 ⁶². For example, when coherence $|UP_S\rangle\langle LP_S|$ was prepared, the spectra cut at $\omega_1 = \omega_{UP_S}$ (Fig. 4D, left) clearly showed a peak of 34 cm^{-1} along ω_2 axis, agreeing with $\omega_{UP_S} - \omega_{LP_S} = 34 \text{ cm}^{-1}$, and demonstrating that this coherence existed.

While it was not surprising to prepare coherences between polaritons from the same cavity modes, referred to as intracavity coherences, the real challenge was to prepare coherences between polaritons from different cavity modes, such as S and D modes, e.g., intercavity coherences. It was a challenge because these polaritons could be subject to different fluctuations²⁶, and it was also where the dual cavity polaritons failed to achieve coherence. As shown in Fig. 4E-F, coherence such as $|UP_S\rangle\langle LP_D|$ can, indeed, be prepared and were robust against environmental fluctuations, as indicated by the peak at $\omega_2 = 29 \text{ cm}^{-1}$. Similarly, coherences of $|UP_D\rangle\langle LP_D|$ and $|UP_D\rangle\langle LP_S|$ could be prepared (See fig S5). The highest frequency of these intercavity mode coherences was 40 cm^{-1} . This is in sharp contrast to the dual cavity systems, which did not support intercavity coherences beyond 10 cm^{-1} , limiting coherences that could be created²⁶ (Fig. 4 A-

B). We note that there were also peaks at lower ω_2 frequency, which could be due to coherence transfer^{63,64}, a topic beyond the scope of the current work.

Origin of Coherence Robustness

Although energy fluctuations due to thermal-activated solvent motions act as a source of decoherence in both the confined cavity and dual cavity systems, the difference between them is that the polaritons in the dual cavity reside in two different physical locations, whereas all polaritons are located in the same physical location in the confined cavity. Thus, we hypothesized that the origin of the more robust coherences in the confined cavity versus the dual cavity is the lack of solvent fluctuations between cavities in different spaces (in short, spatial fluctuations). As a result, the intercavity coherence of the dual-cavity polariton suffers both energy and spatial fluctuations, making it difficult to create.

To model the decoherence, we simulated the coherence signal using Lindblad equation:

$$i\partial_t \rho = \mathcal{L}[\rho] \equiv [H, \rho] + i \sum_a \left(F_a \rho F_a^\dagger - \frac{1}{2} \{F_a^\dagger F_a, \rho\} \right) \quad (3)$$

Where ρ was the time-dependent density matrix, H was the Hamiltonian of the system, and F_a was the Lindblad operators phenomenologically indicating different sources of decoherence. For the polaritons in both cavity systems, the ubiquitous source of decoherence is from energy measurement, described as

$$F_1 = \gamma_1 H = \gamma_1 \begin{pmatrix} E_{UPB} & 0 & 0 & 0 \\ 0 & E_{UPA} & 0 & 0 \\ 0 & 0 & E_{LPB} & 0 \\ 0 & 0 & 0 & E_{LPA} \end{pmatrix}, \text{ where } E_i \text{ is the eigen energy of polariton } i. \text{ In the dual cavity}$$

polariton, an additional source of decoherence is the spatial measurement, $F_2 = \gamma_2 \begin{pmatrix} x_B & 0 & 0 & 0 \\ 0 & x_A & 0 & 0 \\ 0 & 0 & x_B & 0 \\ 0 & 0 & 0 & x_A \end{pmatrix}$,

where x_j is the position of cavity j .

We analytically solved the Lindblad equation and found polariton coherences can be summarized in two categories: for coherence from same cavity region, such as $|UP_A\rangle\langle LP_A| = e^{(i(E_{UPA}-E_{LPA})-\gamma_1^2(E_{UPA}-E_{LPA})^2)t}$, which only have decoherence from energy fluctuations; and for the coherence from different cavity regions, such as $|UP_A\rangle\langle LP_B| = e^{(i(E_{UPA}-E_{LPB})-\gamma_1^2(E_{UPA}-E_{LPB})^2-\gamma_2^2(x_A-x_B)^2)t}$, which have decoherence from both energy and spatial fluctuations. The analytical results agreed with our intuitions.

The numerical simulation based on the equations above suggests that the polariton coherences in the confined cavity are more robust to decoherence than coherences in the dual cavity system. While coherences with larger frequencies have smaller amplitude (i.e., faster decoherence) in the confined cavity system (Fig. 5A), coherences from any polariton combination can be created – even if coherences are prepared from polaritons from different cavity modes. In contrast, the intracavity coherences ($|UP_A\rangle\langle LP_A|$) in the dual cavity system (Fig. 5B) remained strong because of lack of spatial-led decoherence. However, the intercavity coherences $|UP_B\rangle\langle LP_A|$ deteriorated significantly, becoming barely distinguishable from the noise level due to the joint effects of energy and spatial-led decoherences. We emphasize that although the intercavity coherence $|UP_B\rangle\langle LP_A|$ had smaller coherence frequency than $|UP_A\rangle\langle LP_A|$, the overall decoherence was still faster because of the extra spatial fluctuation. However, for certain intercavity coherences, such as $|UP_A\rangle\langle UP_B|$, decoherence due to energy fluctuations was slow because of the small coherence frequency. Therefore, only spatial fluctuation significantly contributes to decoherence and this coherence peak could still be measured (Fig. 5B). Thus, this simulation indicates that the lack of spatial fluctuations mitigates the decoherences of confined-cavity polaritons comparing to those of dual-cavity polaritons. More advanced theory will need to be developed to quantitatively model the decoherence which is out of the scope of the current work.

Discussion

Using the concept of “particle in a box”, we realized multi-cavity modes by applying confinement to the lateral dimension of a trenched geometry cavity. The multiple cavity modes were simulated by solving Maxwell’s equations. By VSC, the confined cavity supported a quadruplet polariton qudit system with multiple coherences. We showed that, unlike previously reported dual cavities, confined cavity polaritons can prepare multiple coherences that are robust to decoherence from energy and spatial fluctuations. Based on Lindblad dynamics⁶⁵, we showed that the tolerance to environments was because polaritons in confined cavities did not suffer from spatial fluctuation the way polaritons did in a dual cavity. With deeper trenches, we expect to see more resolved localized modes mimicking atoms but with a small effective mass, thereby achieving phenomena that are difficult to achieve by atoms or molecules in nature. Furthermore, as “particle in a box” is the most basic concept in semiconductor nanomaterials, its implementation to cavity polaritons warrants more investigation on integrating existing advanced nanomaterial designing principles to polaritonics.

The presented quadruplet polariton states and associated coherence in the confined cavity delivered new opportunities for polariton coherences. Hosting multiple coherences in the same cavity region could lead to entanglements. If two of the confined cavities are brought together with a properly designed potential barrier, it would be possible for the D state polaritons to form bonding and antibonding orbitals, whereas the S states remain at the core level. This design could simulate molecules or other coupled systems, such as light harvesting complexes⁶⁶, and realize topological systems^{67,68} for future investigations. One barrier towards quantum simulation is the fast decoherence, which could be further alleviated by lower the system temperature (but still much higher than cryotemperature) to freeze solvent motions. The confined cavity polaritons also provide new platforms for realizing cavity-based entangled photon sources and entangled photon spectroscopies^{49,50}. Furthermore, in the polariton chemistry community, it was reported that polariton-modified chemical reaction depends on the detuning, i.e. the energy differences between vibrational modes and cavity modes at zero in-plane momentum^{19,69}. However, comprehensive understanding of detuning dependence is complicated by the continuous cavity modes, because many modes at non-zero in-plane momentum can also couple to the molecular modes. Yet, cavity modes at zero in-plane momentum appeared to have greater influence on polariton chemistry than those other modes. The discrete dispersion curve of the confined cavity provides a unique opportunity in resolving this question, because a single discrete cavity mode can be designed such that molecular vibrations essentially only couple to it and not to other modes at non-zero in-plane momentum. Thus, the confined cavity could avoid complications caused by coupling to the continuous cavity modes at higher momentum and provide a clear system for understanding detuning dependence in polariton chemistry.

Materials and Methods

Confined cavity fabrications. To generate confined cavity mode, two cavity mirrors were needed. One mirror is a flat CaF_2 window with 92% reflectivity DBR dielectric coating (Thin Film Corp.) around 5 μm wavelength. For the other mirror, a trench was designed using AutoCAD, where the width and length were specified. The cavity mirror with a trench was then fabricated on a CaF_2 substrate through a lithography process. We first spin coated the negative photoresist on substrate and exposed designed trench area with 375nm laser (Heidelberg MLA150). Then we used developer solution RD-6 to remove the photoresist at all but the trenched area. The entire optics was then deposited with 1 μm ZnO (the depth of the trench) using Denton Discovery 18 Sputter system. Later, the ZnO on photoresist at the trenched area was lifted off using acetone. Thus, all areas were covered by 1 μm ZnO layer, except the lifted off area, forming the trench geometry. Then, the DBR material was deposited on the top. The DBR layers were 4 pairs of alternative layers of Ge and ZnO with thickness of 420 nm and 340 nm, respectively. The resulted DBR mirror had a reflectivity of 96% around 5 μm . Two mirrors were put into Harrick IR spectra cell and separated by a 12 μm Teflon spacer to form the confined cavity mode.

2D IR spectroscopy. 2D IR spectroscopy was applied to investigate the light-matter interaction of a confined polariton system (more detailed 2D IR setup and data acquisition are described in section SI.4). A 800-nm laser pulses (~35 fs, ~5 W, 1 kHz) generated by an ultrafast Ti:Sapphire regenerative amplifier (Astrella, Coherent) were sent into an optical parametric amplifier (OPA) (TOPAS, Light Conversion) which outputs tunable frequency near-IR pulses. Then the mid-IR beams are temporarily and spatially overlapped on a DFG crystal (a type II AgGaS₂ crystal, Eksma) to generate mid-IR around 5 μm . A CaF_2 wedge separates the beam into pump (95% power) and probe (5% power) parts. The pump beam was sent into a Ge-Acoustic

Optical Modulator based mid-IR pulse shaper (QuickShape, PhaseTech) and was shaped into double pulses with tunable time separation t_1 . The double pump pulses and a probe pulse were arranged in a pump-probe geometry to conduct 2D IR measurements. The coherent vibrational states were generated during t_1 and t_3 , respectively. The first coherence was characterized by scanning t_1 , whereas the second coherence during t_3 created a macroscopic polarization that emitted IR signals. The IR pump probe signals were directly measured along ω_3 (probe frequency) at specific t_1 and t_2 using the spectrograph and the MCT detector (PhaseTech). A series pump probe spectra of various t_1 was Fourier transformed to the frequency domain as ω_1 (pump frequency), and to obtain the 2D IR spectra. Delay time between the second pump and probe pulses, t_2 , was scanned, using a motorized translation stage, to characterize population or coherence dynamics. All data were collected using a home-written LabView program.

EM simulation. The wave equation for the photon mode on the cavity lattice is solved by discretizing the Laplacian operator on a 1×400 grid in a unit cell along the confinement dimension. This can be treated as a one-dimension problem because the length of the trench is around 7 mm, which can be seen as infinity when compared to the diameter of the IR beam (around 50 μm). After finding the eigen photon modes, the S-wave mode and D-wave mode were selected as cavity modes. The intensity of cavity modes was calculated by the convolution between the corresponding eigen function and the Gaussian beam profile with a size of 50 μm . Refer to SI for more details.

Acknowledgements

The authors thank the insightful discussion about theory and simulation with Prof. Yi-Zhuang. You. We also acknowledge Dr. Mason Valentine's careful proofreading of this manuscript, the help of Li Chen from Prof. Z. Liu's group in the design of the DBR optics, the discussion with Dr. Chang Yan on manuscript writing, the assistance of Garret Wiesehan on the goniometer and discussion on the experiment, and Jackson Wagner's contribution to Figure 3A. W.X. is grateful for the support from the Alfred P. Sloan Foundation (FG-2020-12845). Z. Y. is supported by the National Science Foundation (DMR-1948215), and H.H.B is supported by the Department of Energy (DE-SC0022134). This work was performed, in part, at the San Diego Nanotechnology Infrastructure (SDNI) of UCSD, a member of the National Nanotechnology Coordinated Infrastructure, which is supported by the National Science Foundation (Grant ECCS-2025752).

References

1. Shalabney, A. *et al.* Coherent coupling of molecular resonators with a microcavity mode. *Nat. Commun.* **6**, 5981 (2015).
2. Ribeiro, R. F. *et al.* Polariton chemistry: controlling molecular dynamics with optical cavities. *Chem. Sci.* **9**, 6325–6339 (2018).
3. Thomas, A. *et al.* Ground-State Chemical Reactivity under Vibrational Coupling to the Vacuum Electromagnetic Field. *Angew. Chemie Int. Ed.* **55**, 11462–11466 (2016).
4. Xiang, B. *et al.* Two-dimensional infrared spectroscopy of vibrational polaritons. *Proc. Natl. Acad. Sci. U. S. A.* **115**, 4845–4850 (2018).
5. Avramenko, A. G. & Rury, A. S. Interrogating the Structure of Molecular Cavity Polaritons with Resonance Raman Scattering: An Experimentally Motivated Theoretical Description. *J. Phys. Chem. C* **123**, 30551–30561 (2019).
6. Brawley, Z. T., Storm, S. D., Contreras Mora, D. A., Pelton, M. & Sheldon, M. Angle-independent plasmonic substrates for multi-mode vibrational strong coupling with molecular thin films. *J. Chem. Phys.* **154**, 104305 (2021).
7. Li, T. E., Nitzan, A. & Subotnik, J. E. Cavity molecular dynamics simulations of vibrational polariton-enhanced molecular nonlinear absorption. *J. Chem. Phys.* **154**, 094124 (2021).
8. Dunkelberger, A. D., Simpkins, B. S., Vurgaftman, I. & Owrutsky, J. C. Vibration-Cavity Polariton Chemistry and Dynamics. *Annu. Rev. Phys. Chem.* **73**, (2022).

9. Xiang, B., Wang, J., Yang, Z. & Xiong, W. Nonlinear infrared polaritonic interaction between cavities mediated by molecular vibrations at ultrafast time scale. *Sci. Adv.* **7**, (2021).
10. Chen, T.-T., Du, M., Yang, Z., Yuen-Zhou, J. & Xiong, W. Cavity-enabled enhancement of ultrafast intramolecular vibrational redistribution over pseudorotation. *Science* (80-.). **378**, 790–794 (2022).
11. Wang, D. S. & Yelin, S. F. A Roadmap Toward the Theory of Vibrational Polariton Chemistry. *ACS Photonics* **8**, 2818–2826 (2021).
12. Nagarajan, K., Thomas, A. & Ebbesen, T. W. Chemistry under Vibrational Strong Coupling. *J. Am. Chem. Soc.* **143**, 16877–16889 (2021).
13. Herrera, F. & Owrutsky, J. Molecular polaritons for controlling chemistry with quantum optics. *J. Chem. Phys.* **152**, 100902 (2020).
14. Xiang, B. *et al.* Intermolecular vibrational energy transfer enabled by microcavity strong light-matter coupling. *Science* **368**, 665–667 (2020).
15. Ebbesen, T. W. Hybrid Light–Matter States in a Molecular and Material Science Perspective. *Acc. Chem. Res.* **49**, 2403–2412 (2016).
16. Dunkelberger, A. D., Spann, B. T., Fears, K. P., Simpkins, B. S. & Owrutsky, J. C. Modified relaxation dynamics and coherent energy exchange in coupled vibration-cavity polaritons. *Nat. Commun.* **7**, 13504 (2016).
17. Garcia-Vidal, F. J., Ciuti, C. & Ebbesen, T. W. Manipulating matter by strong coupling to vacuum fields. *Science* (80-.). **373**, (2021).
18. Long, J. P. & Simpkins, B. S. Coherent Coupling between a Molecular Vibration and Fabry–Perot Optical Cavity to Give Hybridized States in the Strong Coupling Limit. *ACS Photonics* **2**, 130–136 (2015).
19. Thomas, A. *et al.* Tilting a ground-state reactivity landscape by vibrational strong coupling. *Science* (80-.). **363**, 615–619 (2019).
20. Imperatore, M. V., Asbury, J. B. & Giebink, N. C. Reproducibility of cavity-enhanced chemical reaction rates in the vibrational strong coupling regime. *J. Chem. Phys.* **154**, 191103 (2021).
21. Yuen-Zhou, J. & Menon, V. M. Polariton chemistry: Thinking inside the (photon) box. *Proc. Natl. Acad. Sci.* **116**, 5214–5216 (2019).
22. Wiesehan, G. D. & Xiong, W. Negligible rate enhancement from reported cooperative vibrational strong coupling catalysis. *J. Chem. Phys.* **155**, 241103 (2021).
23. Zhong, X. *et al.* Energy Transfer between Spatially Separated Entangled Molecules. *Angew. Chem. Int. Ed. Engl.* **56**, 9034 (2017).
24. Coles, D. M. *et al.* Polariton-mediated energy transfer between organic dyes in a strongly coupled optical microcavity. *Nat. Mater.* **13**, 712–719 (2014).
25. Yang, Z., Xiang, B. & Xiong, W. Controlling Quantum Pathways in Molecular Vibrational Polaritons. *ACS Photonics* **7**, 919–924 (2020).
26. Xiang, B., Yang, Z., You, Y. Z. & Xiong, W. Ultrafast Coherence Delocalization in Real Space Simulated by Polaritons. *Adv. Opt. Mater.* **10**, 2102237 (2022).
27. Xiang, B. & Xiong, W. Molecular vibrational polariton: Its dynamics and potentials in novel chemistry and quantum technology. *J. Chem. Phys.* **155**, 050901 (2021).
28. Ghosh, S. & Liew, T. C. H. Quantum computing with exciton-polariton condensates. *npj Quantum Inf.* **6**, 16 (2020).
29. Demirchyan, S. S., Chestnov, I. Y., Alodjants, A. P., Glazov, M. M. & Kavokin, A. V. Qubits Based on Polariton Rabi Oscillators. *Phys. Rev. Lett.* **112**, 196403 (2014).
30. Xiang, B. *et al.* Manipulating optical nonlinearities of molecular polaritons by delocalization. *Sci. Adv.*

5, (2019).

31. Deng, H., Haug, H. & Yamamoto, Y. Exciton-polariton Bose-Einstein condensation. *Rev. Mod. Phys.* **82**, 1489–1537 (2010).
32. Törmä, P., Barnes, W. L., Törmö, P. & Barnes, W. L. Strong coupling between surface plasmon polaritons and emitters: a review. *Reports Prog. Phys.* **78**, 013901 (2015).
33. Khitrova, G., Gibbs, H. M., Jahnke, F., Kira, M. & Koch, S. W. Nonlinear optics of normal-mode-coupling semiconductor microcavities. *Rev. Mod. Phys.* **71**, 1591–1639 (1999).
34. Yang, Z. & Xiong, W. Molecular Vibrational Polaritons Towards Quantum Technologies. *Adv. Quantum Technol.* **5**, 2100163 (2022).
35. Tesch, C. M. & de Vivie-Riedle, R. Quantum Computation with Vibrationally Excited Molecules. *Phys. Rev. Lett.* **89**, 157901 (2002).
36. Gollub, C., Hoff, P. V. Den, Kowalewski, M., Troppmann, U. & Vivie-Riedle, R. De. Vibrational Energy Transfer Through Molecular Chains: An Approach Toward Scalable Information Processing. in 371–402 (2014). doi:10.1002/9781118742631.ch13.
37. Korff, B. M. R., Troppmann, U., Kompa, K. L. & de Vivie-Riedle, R. Manganese pentacarbonyl bromide as candidate for a molecular qubit system operated in the infrared regime. *J. Chem. Phys.* **123**, 244509 (2005).
38. Nozik, A. J. *et al.* Semiconductor Quantum Dots and Quantum Dot Arrays and Applications of Multiple Exciton Generation to Third-Generation Photovoltaic Solar Cells. *Chem. Rev.* **110**, 6873–6890 (2010).
39. Keuleyan, S., Lhuillier, E., Brajuskovic, V. & Guyot-Sionnest, P. Mid-infrared HgTe colloidal quantum dot photodetectors. *Nat. Photonics* **5**, 489–493 (2011).
40. Steckel, J. S., Coe-Sullivan, S., Bulović, V. & Bawendi, M. G. 1.3 μ m to 1.55 μ m Tunable Electroluminescence from PbSe Quantum Dots Embedded within an Organic Device. *Adv. Mater.* **15**, 1862–1866 (2003).
41. Dai, X. *et al.* Solution-processed, high-performance light-emitting diodes based on quantum dots. *Nature* **515**, 96–99 (2014).
42. Sun, Q. *et al.* Bright, multicoloured light-emitting diodes based on quantum dots. *Nat. Photonics* **1**, 717–722 (2007).
43. Konstantatos, G. *et al.* Ultrasensitive solution-cast quantum dot photodetectors. *Nature* **442**, 180–183 (2006).
44. Yoffe, A. D. Semiconductor quantum dots and related systems: Electronic, optical, luminescence and related properties of low dimensional systems. *Adv. Phys.* **50**, 1–208 (2001).
45. Nozik, A. J. Spectroscopy and Hot Electron Relaxation Dynamics in Semiconductor Quantum Wells and Quantum Dots. *Annu. Rev. Phys. Chem.* **52**, 193–231 (2001).
46. Cuevas, Á. *et al.* First observation of the quantized exciton-polariton field and effect of interactions on a single polariton. *Sci. Adv.* **4**, (2018).
47. Ming, Y. *et al.* Quantum entanglement based on surface phonon polaritons in condensed matter systems. *AIP Adv.* **3**, 042122 (2013).
48. Lüders, C. *et al.* Quantifying Quantum Coherence in Polariton Condensates. *PRX Quantum* **2**, 030320 (2021).
49. Zhang, Z., Saurabh, P., Dorfman, K. E., Debnath, A. & Mukamel, S. Monitoring polariton dynamics in the LHClI photosynthetic antenna in a microcavity by two-photon coincidence counting. *J. Chem. Phys.* **148**, 074302 (2018).
50. Dorfman, K. E. & Mukamel, S. Multidimensional photon correlation spectroscopy of cavity polaritons.

- Proc. Natl. Acad. Sci.* **115**, 1451–1456 (2018).
51. Jayaprakash, R. *et al.* Two-Dimensional Organic-Exciton Polariton Lattice Fabricated Using Laser Patterning. *ACS Photonics* **7**, 2273–2281 (2020).
 52. Zhang, L. *et al.* Van der Waals heterostructure polaritons with moiré-induced nonlinearity. *Nature* **591**, 61–65 (2021).
 53. Nöckel, J. U. Modified Gouy phase in optical resonators with mixed boundary conditions, via the Born-Oppenheimer method. *Opt. Express* **15**, 5761 (2007).
 54. Balasubrahmaniam, M., Genet, C. & Schwartz, T. Coupling and decoupling of polaritonic states in multimode cavities. *Phys. Rev. B* **103**, L241407 (2021).
 55. Georgiou, K., McGhee, K. E., Jayaprakash, R. & Lidzey, D. G. Observation of photon-mode decoupling in a strongly coupled multimode microcavity. *J. Chem. Phys.* **154**, 124309 (2021).
 56. Hamm, P. & Zanni, M. *Concepts and Methods of 2D Infrared Spectroscopy. Concepts and Methods of 2D Infrared Spectroscopy* vol. 9781107000 (Cambridge University Press, 2011).
 57. Kiefer, L. M. & Kubarych, K. J. NOESY-Like 2D-IR Spectroscopy Reveals Non-Gaussian Dynamics. *J. Phys. Chem. Lett.* **7**, 3819–3824 (2016).
 58. Saurabh, P. & Mukamel, S. Two-dimensional infrared spectroscopy of vibrational polaritons of molecules in an optical cavity. *J. Chem. Phys.* **144**, 124115 (2016).
 59. Porter, T. M. *et al.* Direct observation of the intermediate in an ultrafast isomerization. *Chem. Sci.* **10**, 113–117 (2019).
 60. F. Ribeiro, R. *et al.* Theory for Nonlinear Spectroscopy of Vibrational Polaritons. *J. Phys. Chem. Lett.* **9**, 3766–3771 (2018).
 61. Grafton, A. B. *et al.* Excited-state vibration-polariton transitions and dynamics in nitroprusside. *Nat. Commun.* **12**, 214 (2021).
 62. Li, Y., Wang, J., Clark, M. L., Kubiak, C. P. & Xiong, W. Characterizing interstate vibrational coherent dynamics of surface adsorbed catalysts by fourth-order 3D SFG spectroscopy. *Chem. Phys. Lett.* **650**, 1–6 (2016).
 63. Khalil, M., Demirdöven, N. & Tokmakoff, A. Vibrational coherence transfer characterized with Fourier-transform 2D IR spectroscopy. *J. Chem. Phys.* **121**, 362 (2004).
 64. Eckert, P. A. & Kubarych, K. J. Vibrational coherence transfer illuminates dark modes in models of the FeFe hydrogenase active site. *J. Chem. Phys.* **151**, 054307 (2019).
 65. Lindblad, G. On the generators of quantum dynamical semigroups. *Commun. Math. Phys.* **48**, 119–130 (1976).
 66. Law, C. J. *et al.* The structure and function of bacterial light-harvesting complexes (Review). *Mol. Membr. Biol.* **21**, 183–191 (2004).
 67. Karzig, T., Bardyn, C.-E., Lindner, N. H. & Refael, G. Topological Polaritons. *Phys. Rev. X* **5**, 031001 (2015).
 68. Klemmt, S. *et al.* Exciton-polariton topological insulator. *Nature* **562**, 552–556 (2018).
 69. Pannir-Sivajothi, S., Campos-Gonzalez-Angulo, J. A., Martínez-Martínez, L. A., Sinha, S. & Yuen-Zhou, J. Driving chemical reactions with polariton condensates. *Nat. Commun.* **13**, 1645 (2022).

Figures and Tables

Figure 1. Challenges of creating multiple coherences in cavity polaritons. (A) In an FP cavity composed by two flat mirrors, one pair of UP and LP are supported and thereby can only form one coherence $|UP\rangle\langle LP|$

and its conjugate. (B) In the dual cavity, two cavity modes are supported due to the longitudinal cavity thickness difference along the lateral dimension. This cavity can support two pairs of UP and LP and enrich the varieties of coherences. However, coherences such as $|UP_B\rangle\langle LP_A|$ cannot survive the fluctuations between cavities. (C) In this work, we demonstrated the confined cavity by implementing the “particle in a box” concept. In this way, two cavity modes and two pairs of polariton modes are supported in the same spatial location, enabling the creation of coherences among any pairs of polaritons. To clearly show the confinement in the illustration, the vertical dimension was exaggerated. (D) A close view of the confined cavity pattern obtained by optical profilometer. The lateral dimension of the cavity (the short side of the trench) is $25\ \mu\text{m}$. The depth of the trench is $1\ \mu\text{m}$. (E) The linear transmission spectra obtained by focusing IR beams center at trench area on the sample. Two peaks at $1971\ \text{cm}^{-1}$ and $1995\ \text{cm}^{-1}$ are from the confined cavity, whereas the peak at $2099\ \text{cm}^{-1}$ is from the unconfined region. The dash line is simulation result.

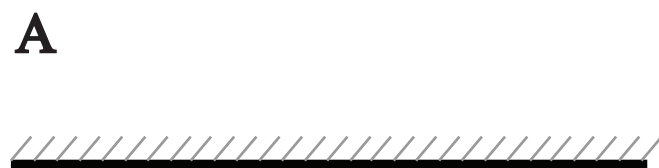
Figure 2. Dispersion curves and electromagnetic wave distributions of the confined cavity modes. (A) The dispersion curve of a free particle. When confined in a box, the particles only allow discrete momentum, labeled by vertical dashed lines, allowing only modes with specific momentums to be created (indicated by cross points of dashed lines of the same colors). (B) Illustration of changing the incidence angles along confined (θ_1) and unconfined (θ_2) dimensions. The corresponding normalized experimental dispersion curves along (C) the confined dimension and (D) the unconfined dimension agree with the particle-in-a-box model: along the confined dimension, the modes are discrete whereas the unconfined dimension has continuous dispersion curves. (E) The simulated dispersion curve along the dimension of confinement. (F) The simulated E-field spatial distribution of cavity modes S and D. The D mode has more nodes, but both modes reside in the same region.

Figure 3. Confined polaritons and the interactions between polaritons. (A) Absorption spectrum of $W(\text{CO})_6$ and transmission linear spectrum of polaritons with confined cavity modes around zero detuning. Four peaks are observed for four polariton modes. (B) Dispersion curve of the confined polariton system and calculated polariton mode dispersion curve using the 4x4 Hamiltonian (solid line). (C) Energy diagram of confined polariton modes summarizing the 4x4 Hamiltonian. S and D modes hybridize with the vibrational modes of $W(\text{CO})_6$ respectively to form two pairs of polariton states. The cavity and vibrational modes are color coded, and the gradient color of polariton modes suggests their approximate compositions (blue for D mode, cyan for S mode, red for molecular vibrational modes). (D) Illustration of the 2D IR pulse sequence, geometry used to vary the angle of incidence. Inset: The incident angle was varied by the goniometer along the confined dimension. (E) 2D IR spectra of polariton in the confined cavity at $t_2 = 30\text{ps}$. The cross peaks (highlighted in boxes) indicate nonlinear interactions between polariton modes.

Figure 4. Energy diagrams of coherence in dual and confined cavity polariton systems, and the corresponding coherence signals. Coherence between UP_B and LP_A (A) originated from the different cavity modes that are spatially separated is not observed in (B). While the coherence between UP_S and LP_S (C) originated from the same cavity modes of the confined cavity shows strong coherence in (D). In (E), the coherence is between UP_S and LP_D . While the composing polaritons are from different cavity modes, they still reside in the same physical locations. As a result, it also shows strong coherence signals in (F). Regardless of the coherences were from the same or different cavity modes, they can be created in the confined cavity systems, and decoherence was on the same time scales. This comparison suggests the intercavity polariton coherences were more robust against fluctuations in confined cavities than the ones in dual cavities.

Figure 5. Simulation of decoherence in confined- and dual-cavity systems. (A) and (B) are corresponding simulation results of confined cavity (Fig. 1C) and dual cavity (Fig. 1B). The largest difference is that the intercavity mode coherence $|UP_S\rangle\langle LP_D|$ in (A) is stronger than coherence $|UP_B\rangle\langle LP_A|$ in (B). This result suggests that the phase fluctuations experienced by polaritons residing in different locations accelerates decoherences. Thus, coherence is more robust in confined cavities than in dual cavities.

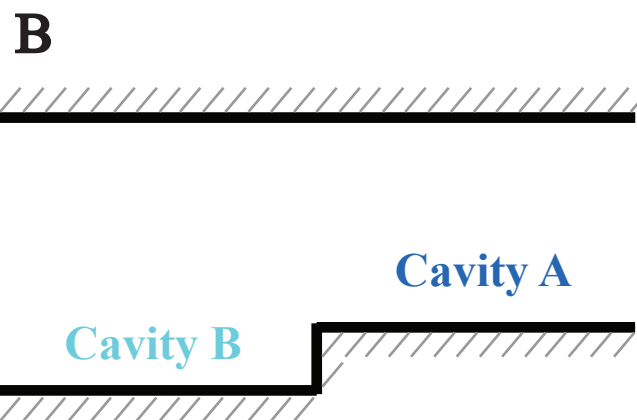
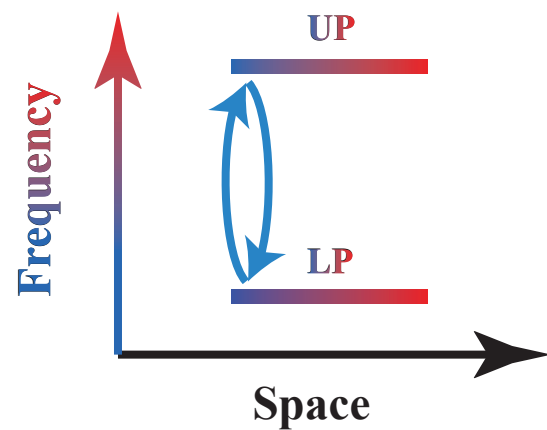
Cavity mirror



FP Cavity

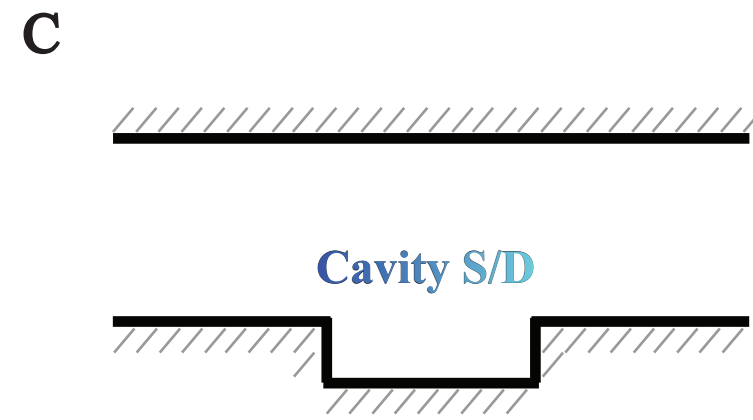
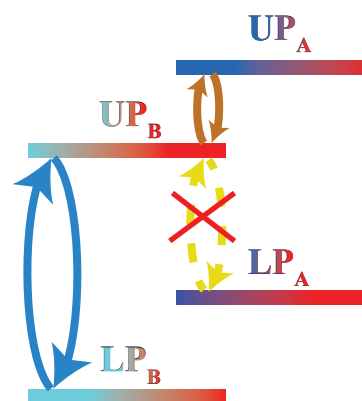


Polariton energy diagram

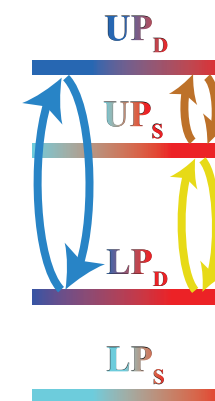


Cavity B

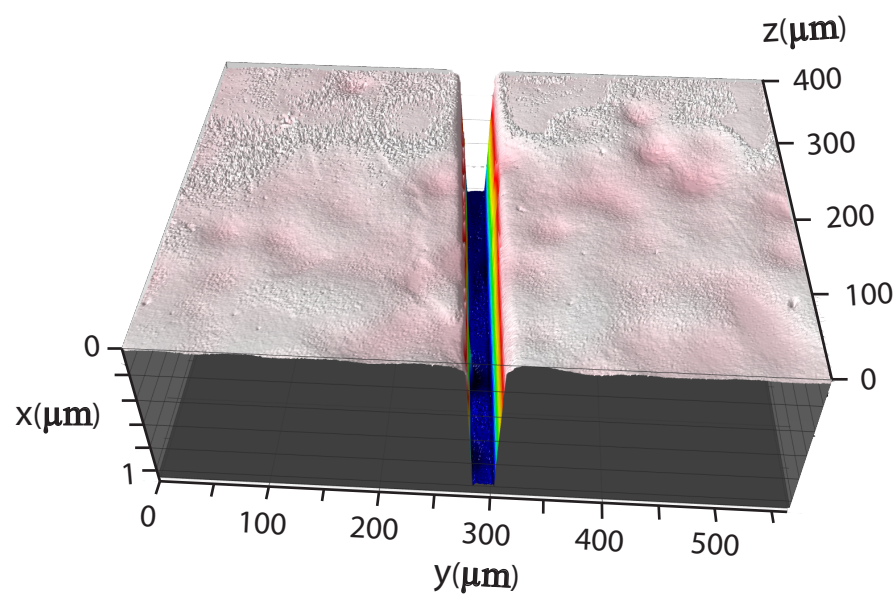
Cavity A



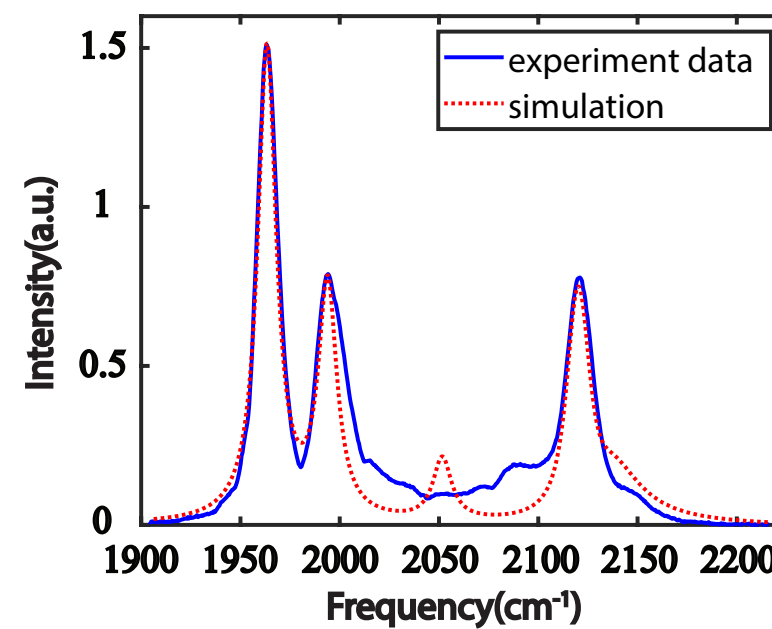
Cavity S/D

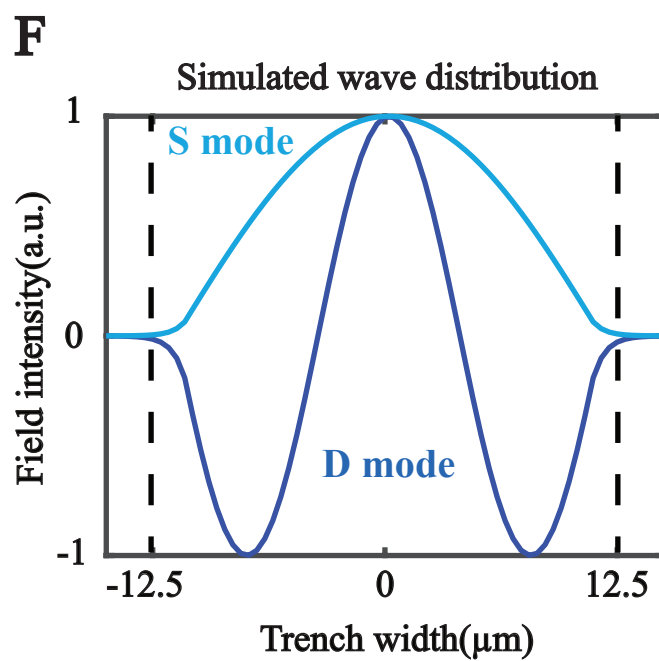
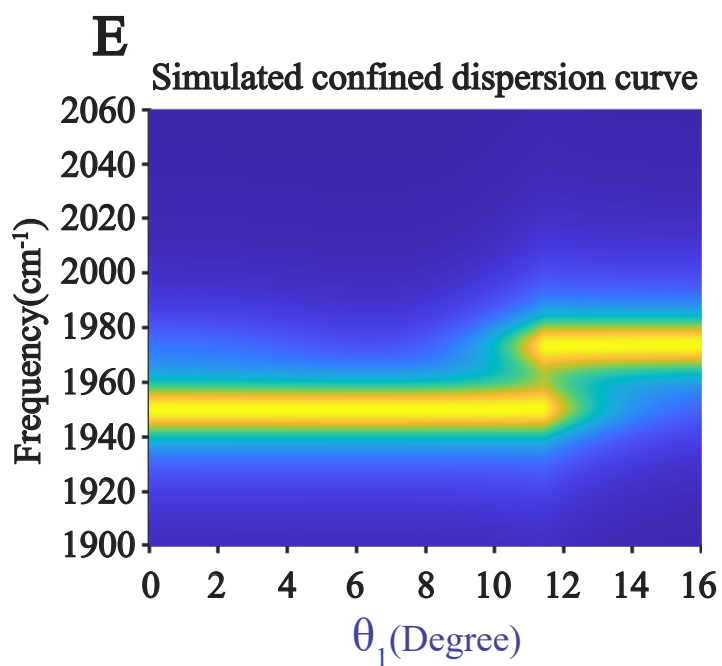
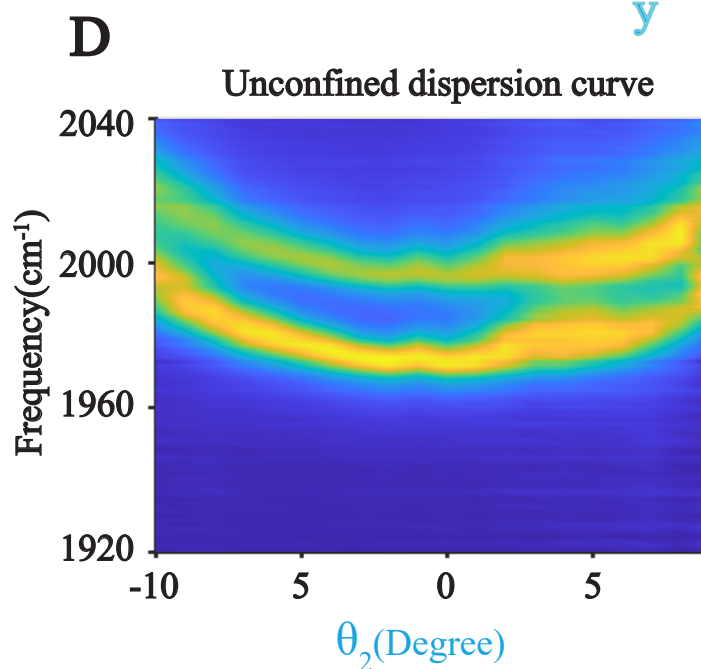
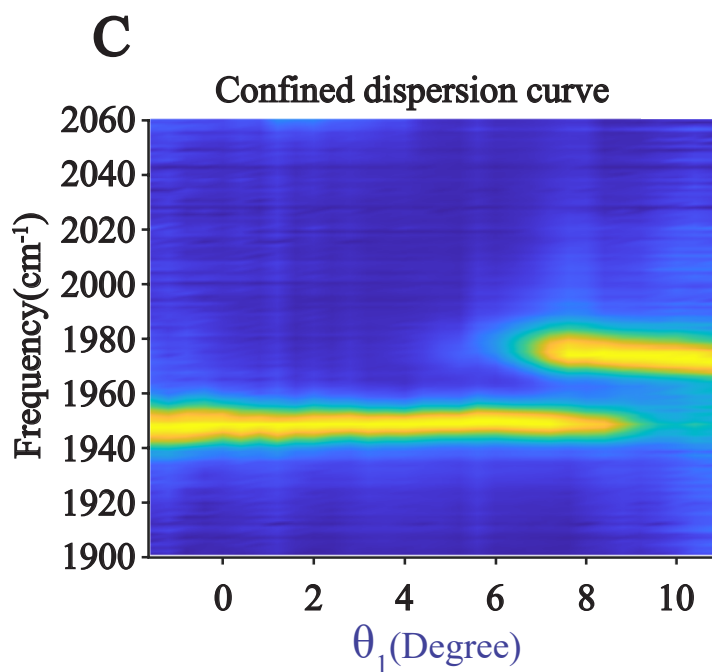
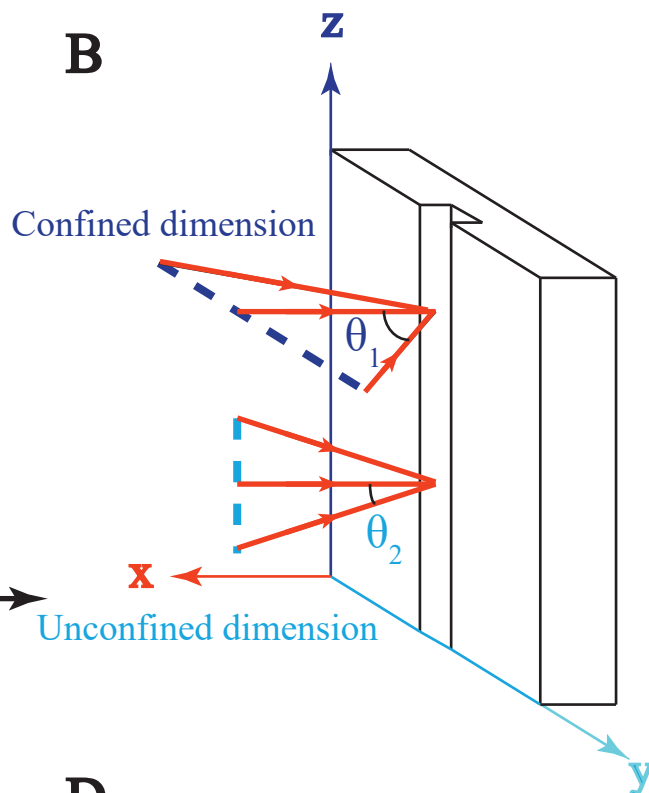
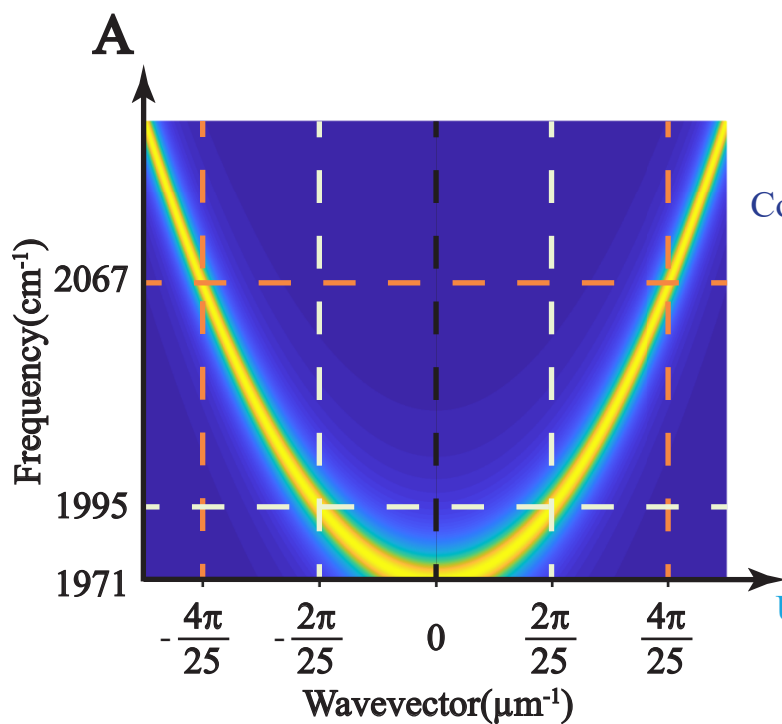


D

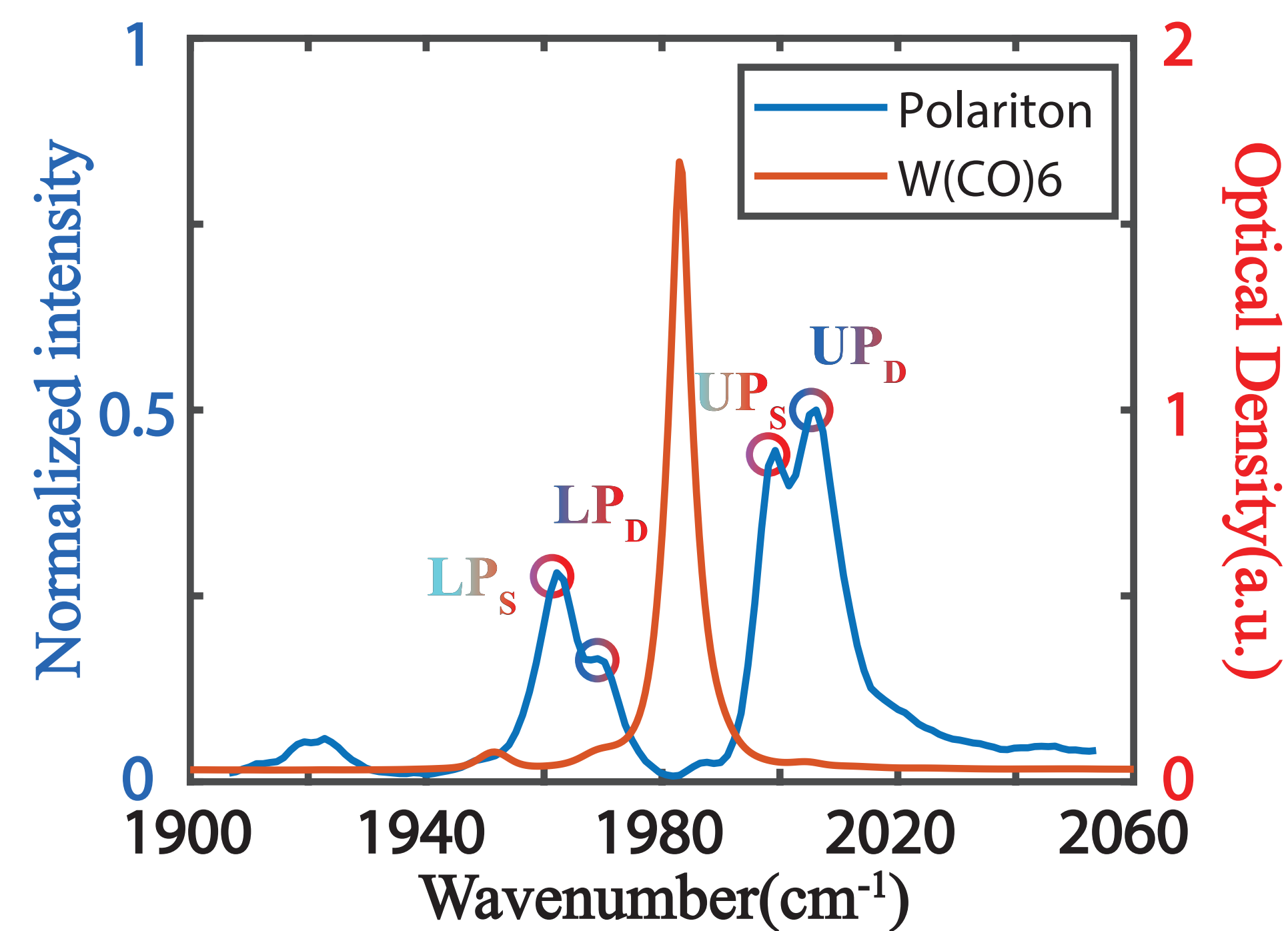


E

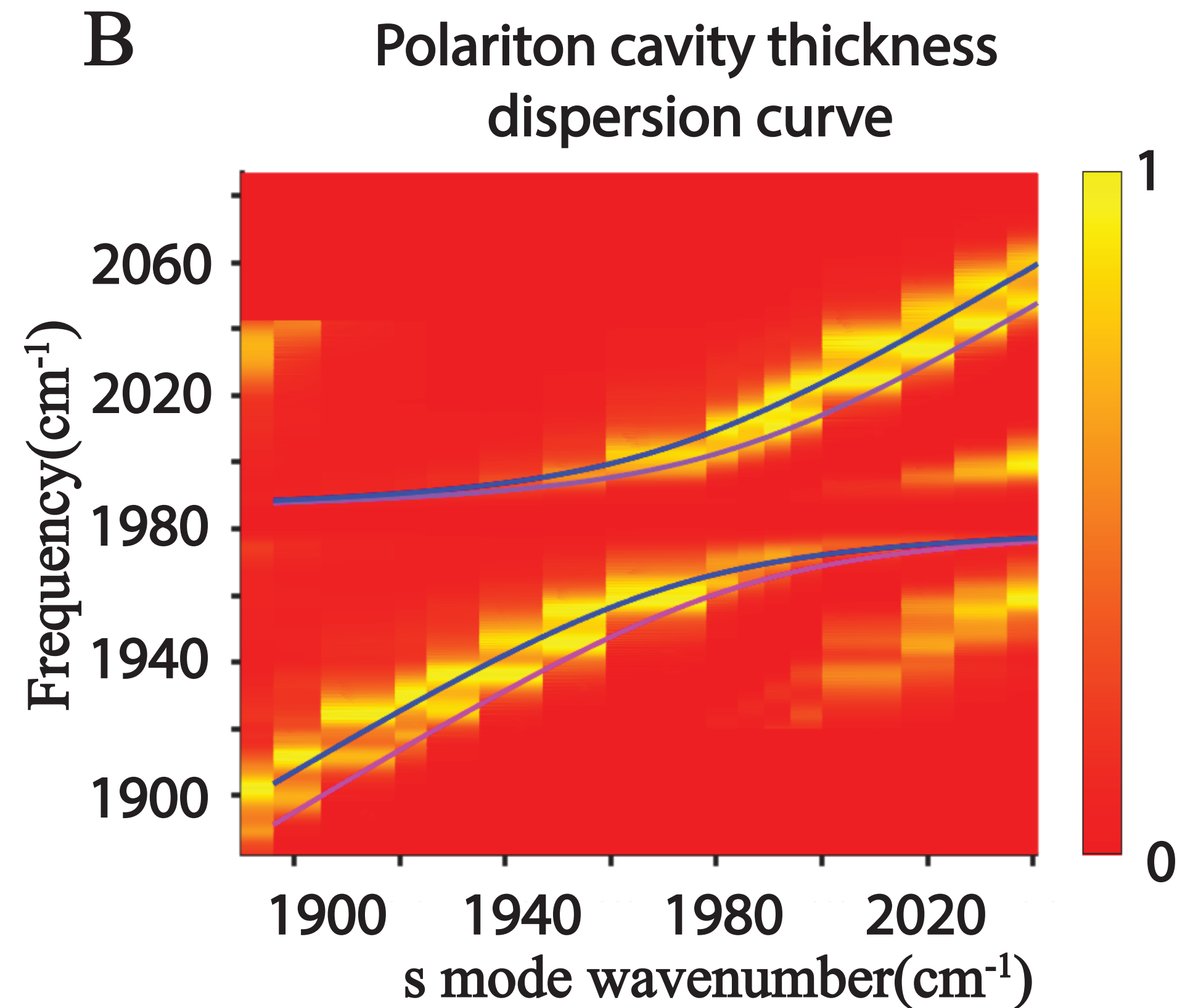




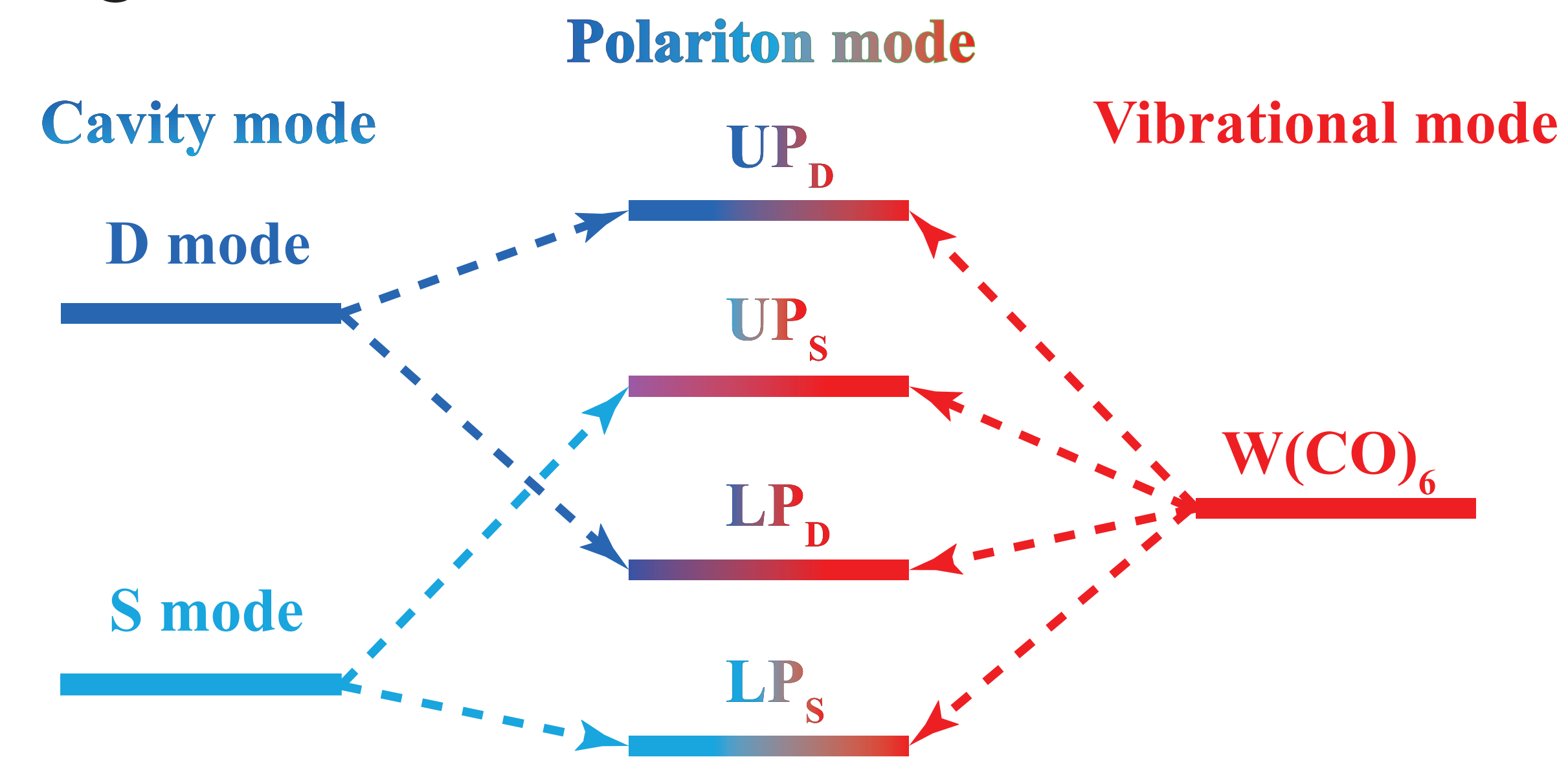
A



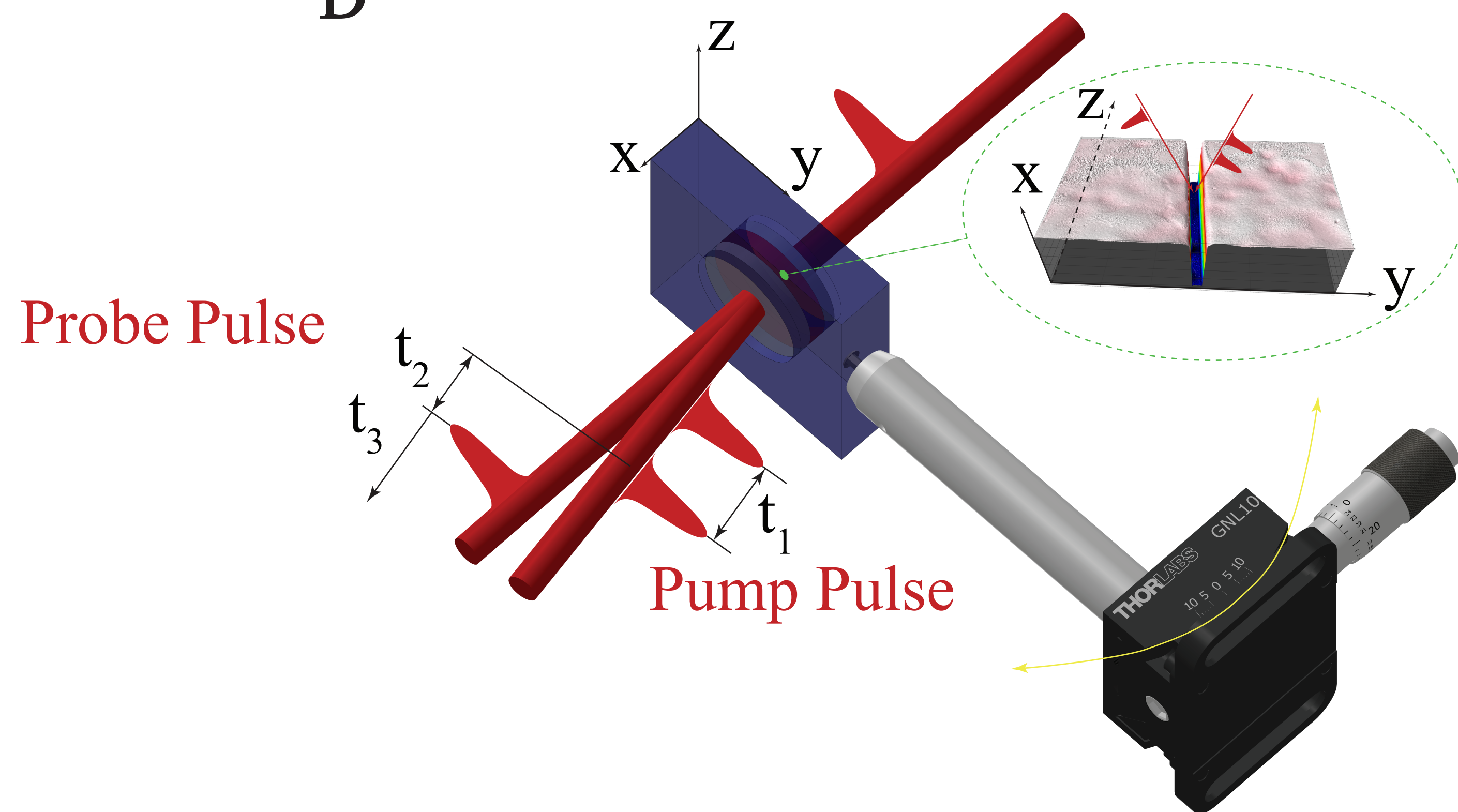
B



C

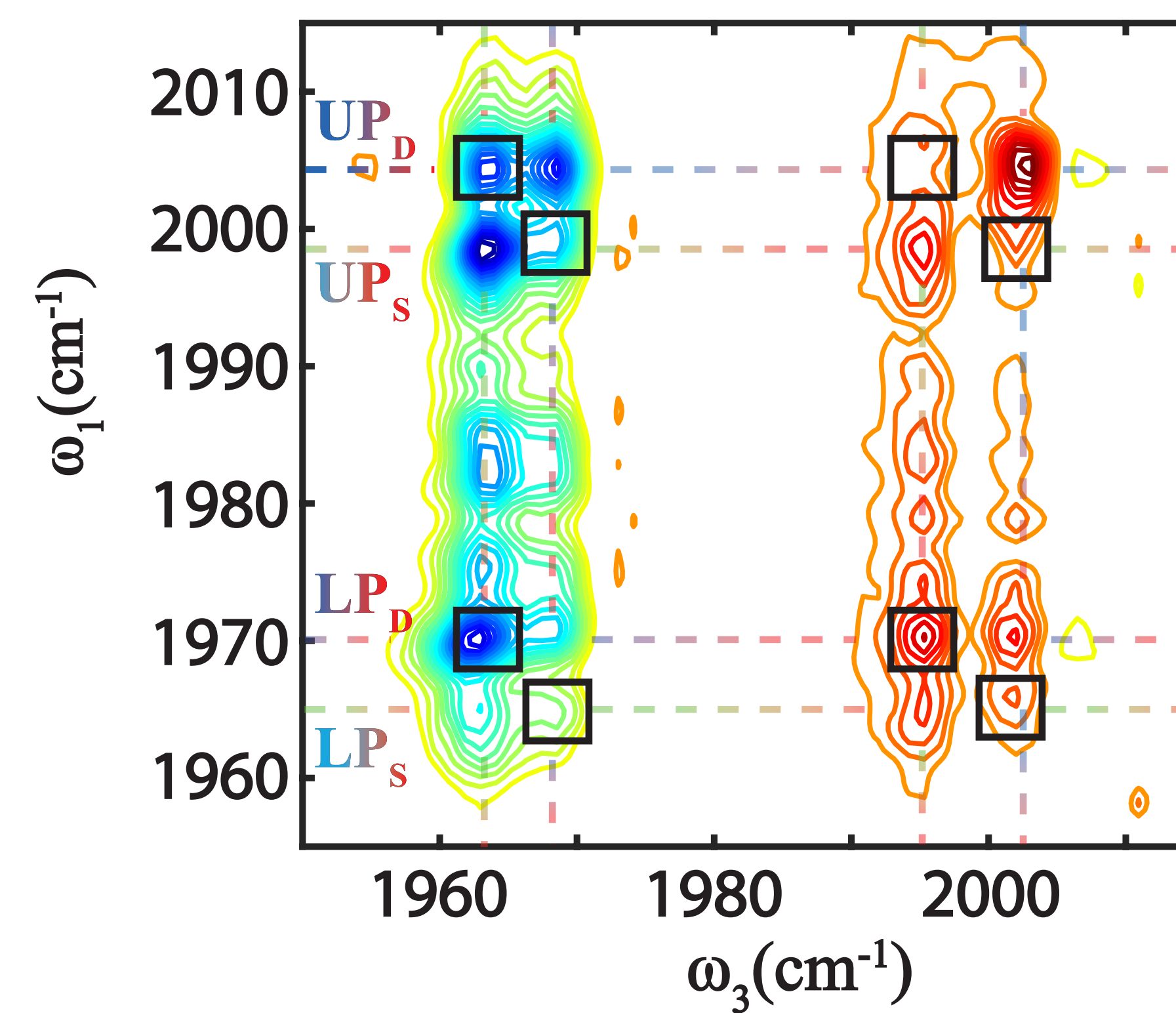


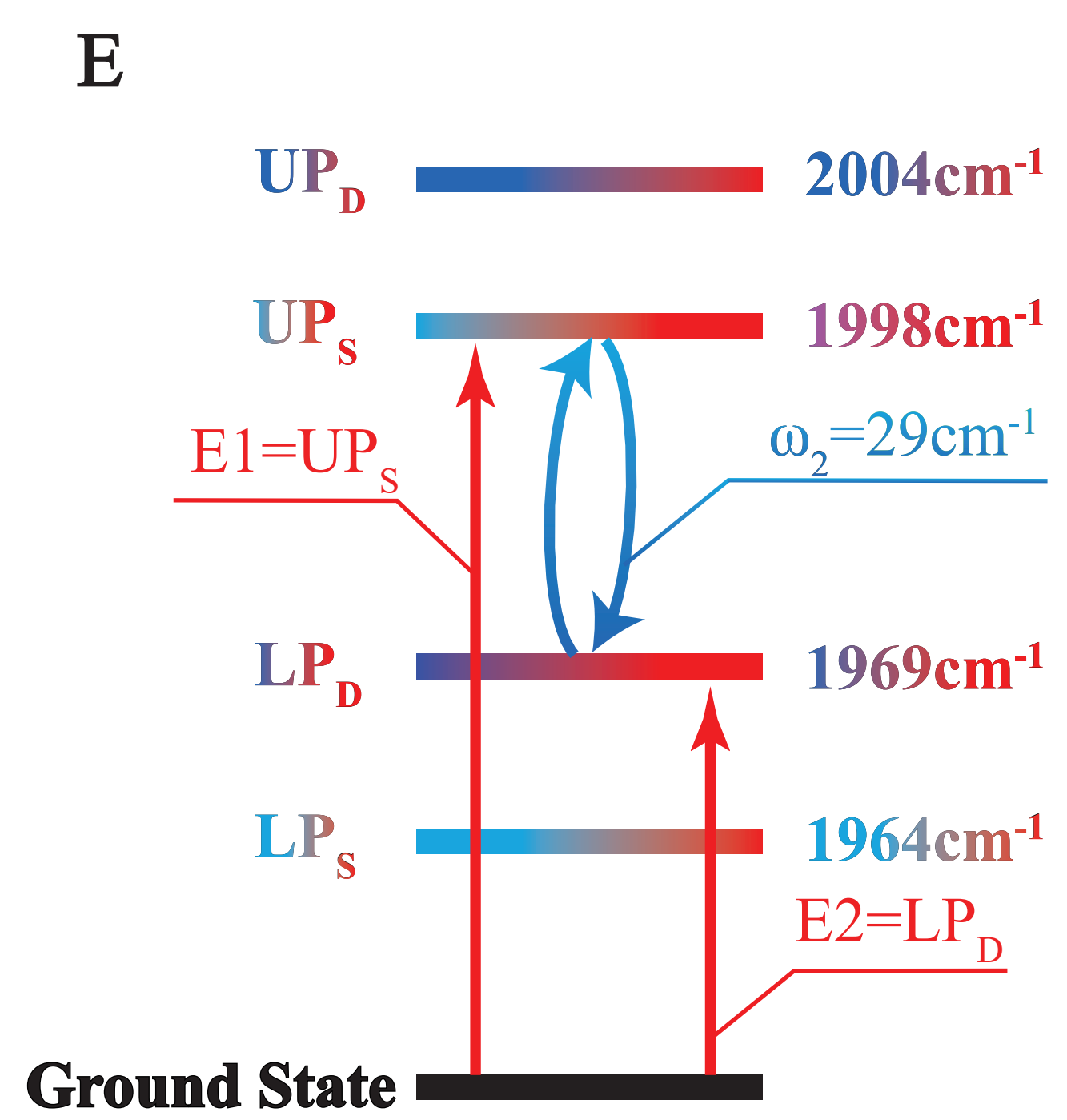
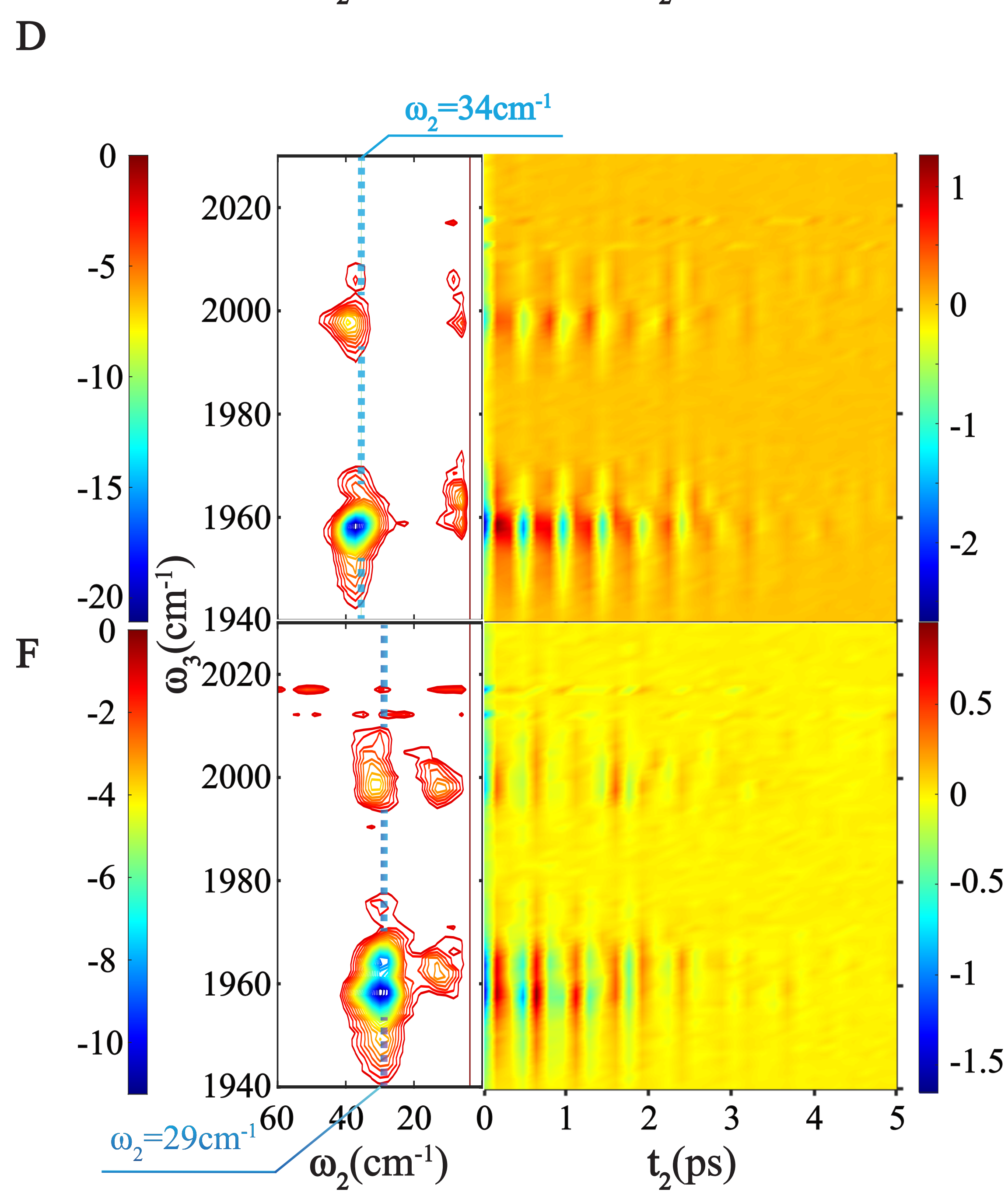
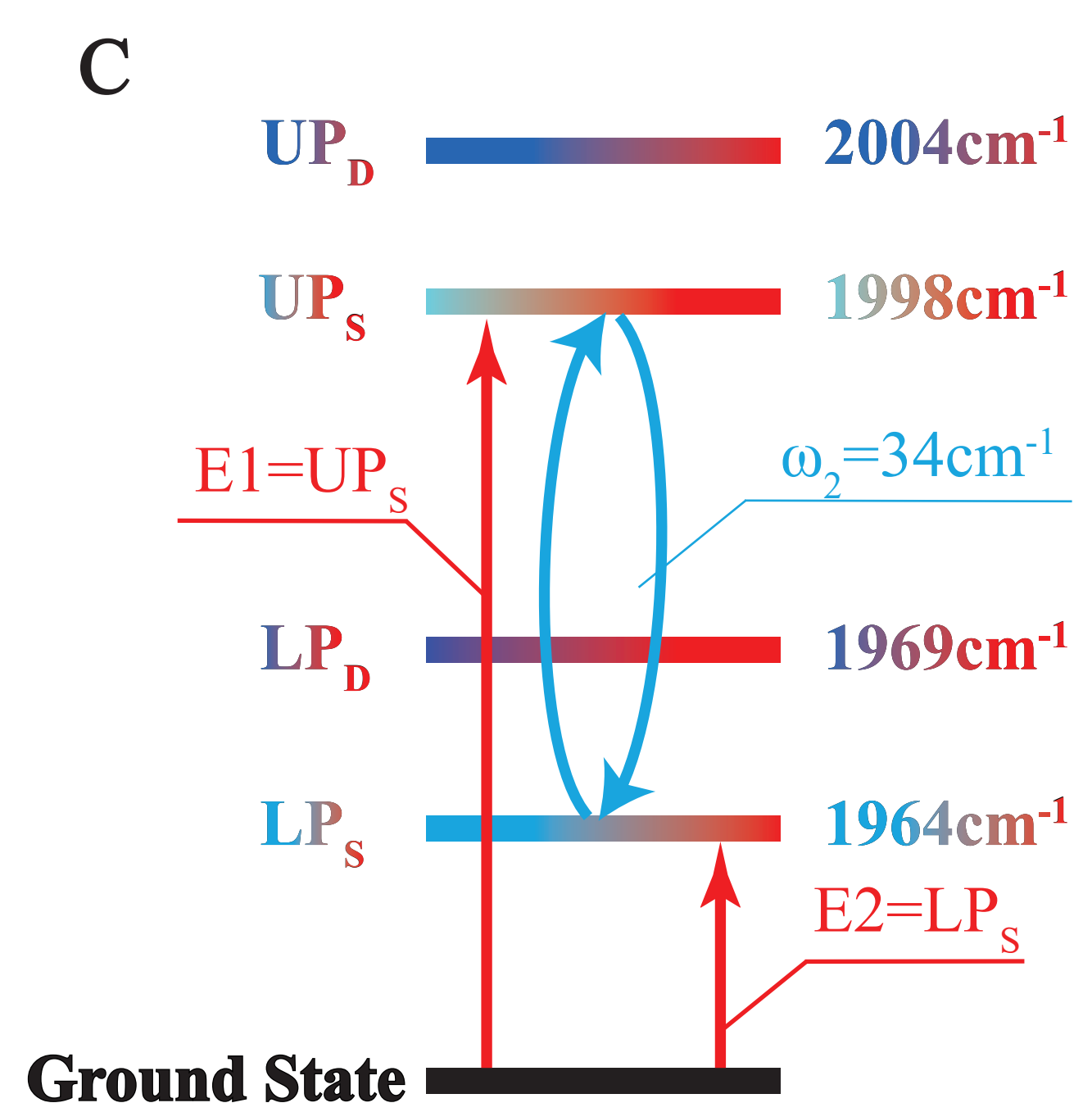
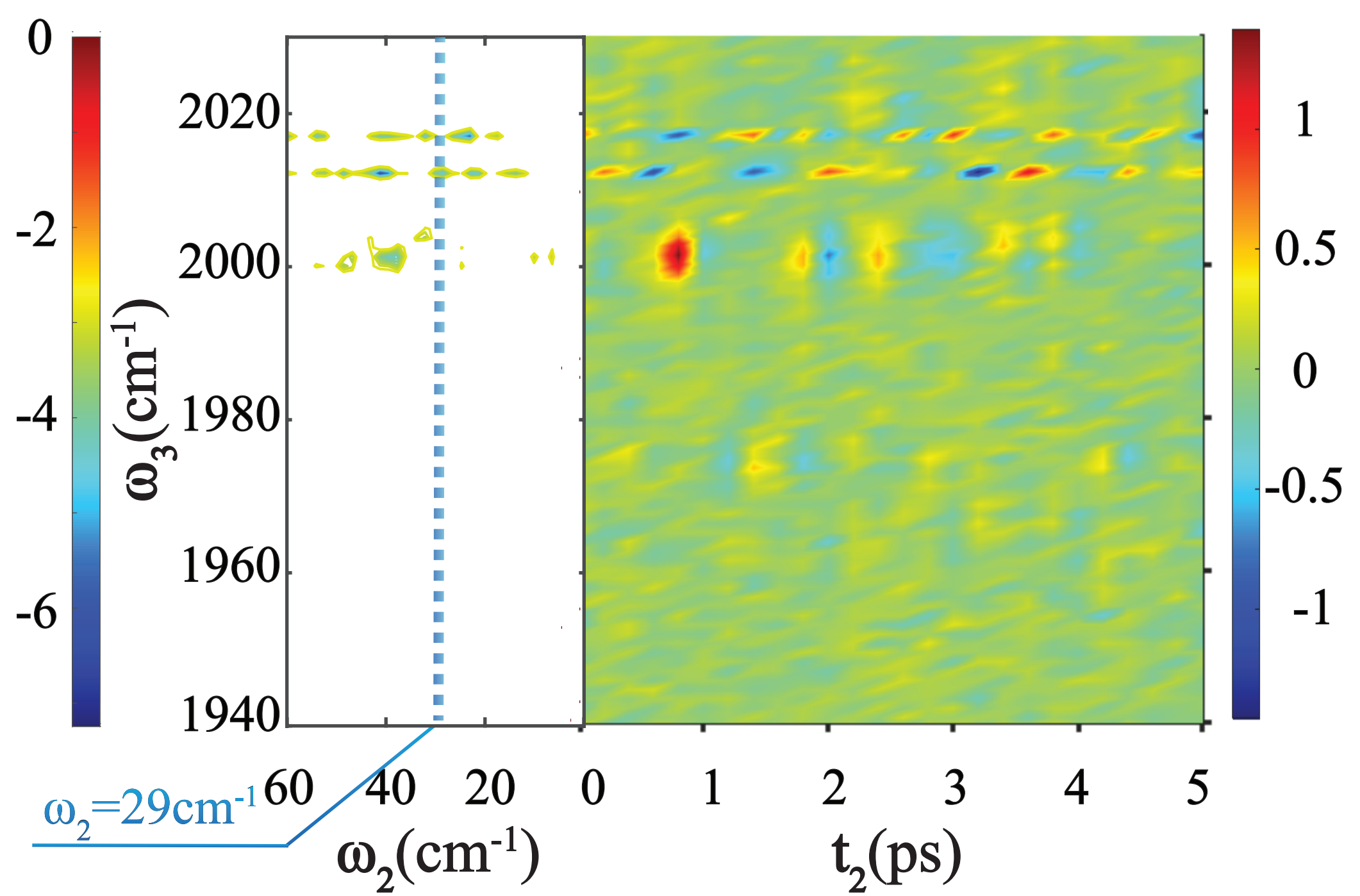
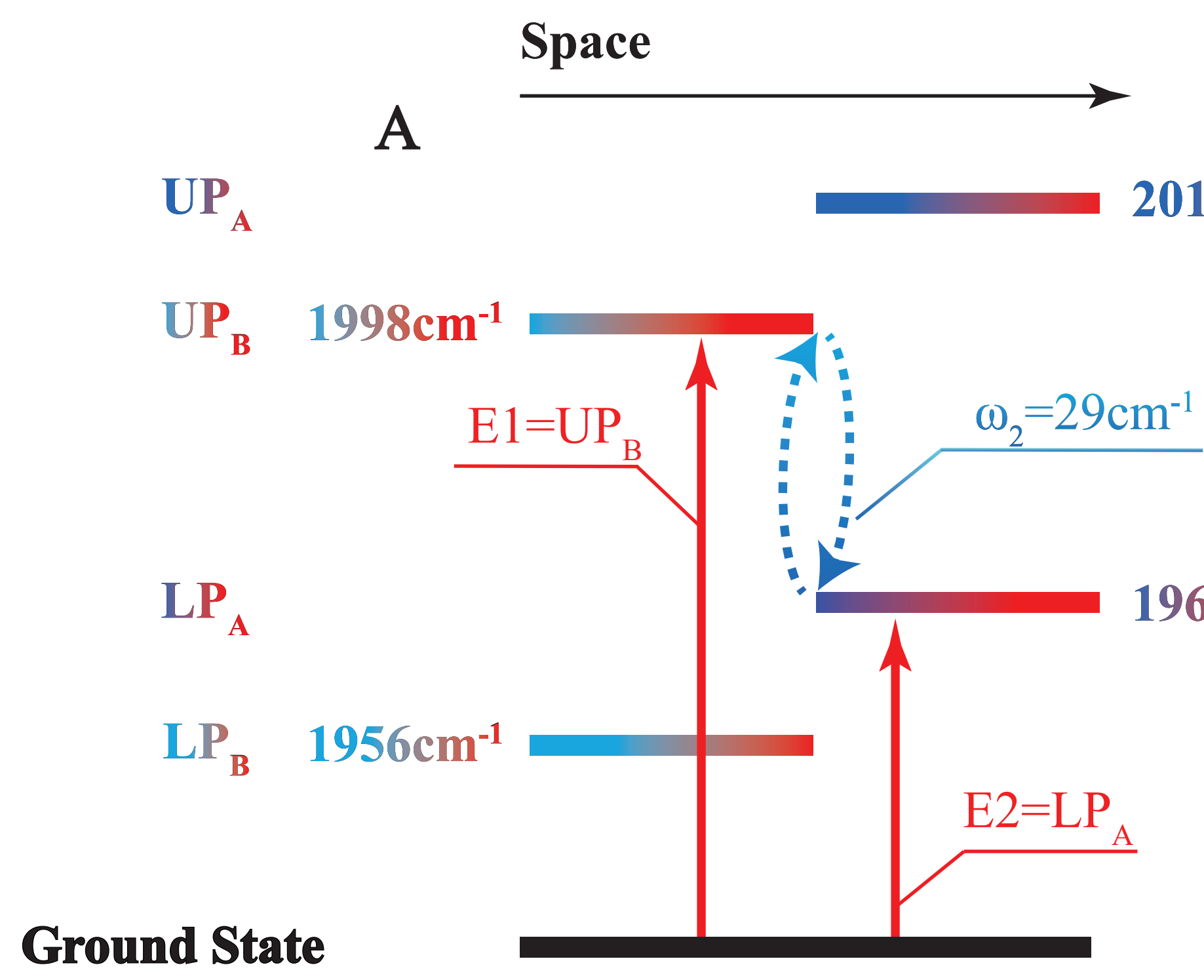
D

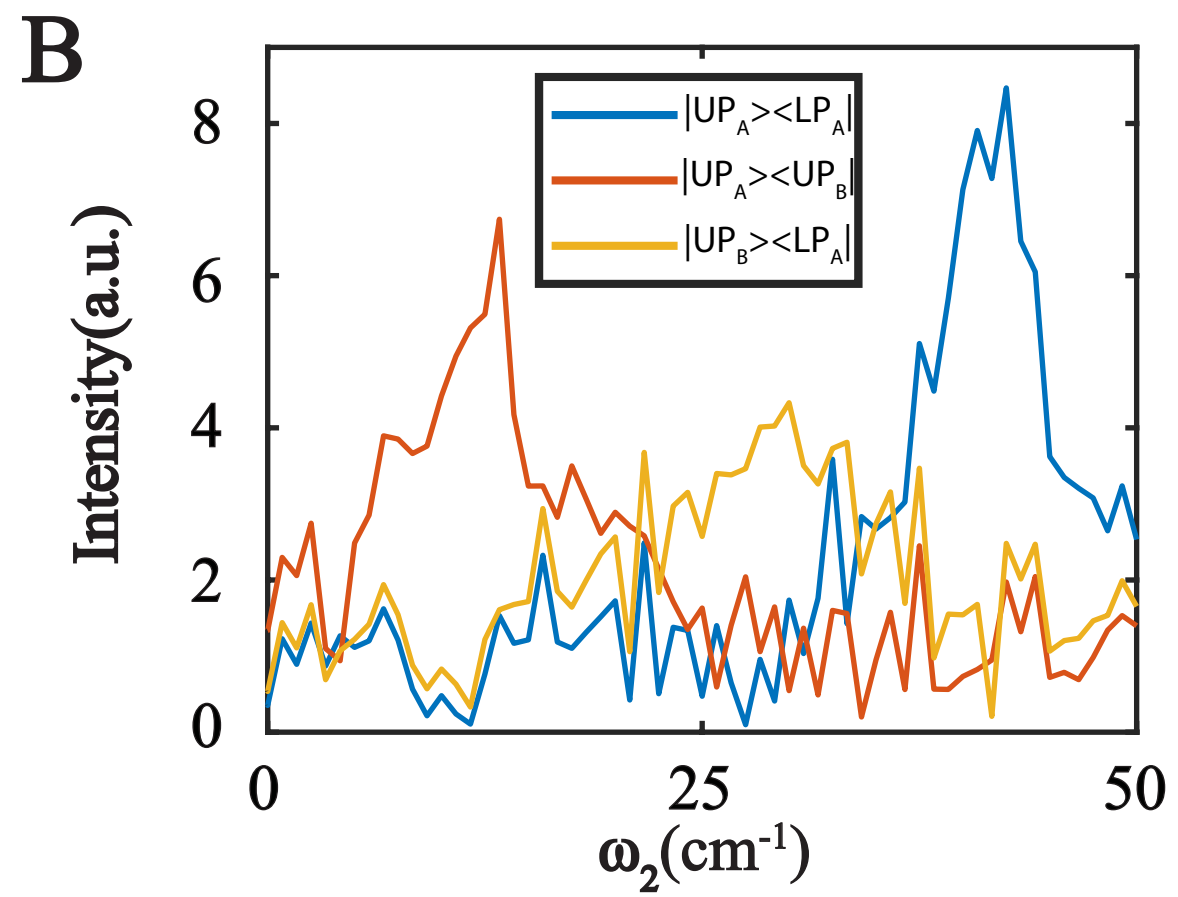
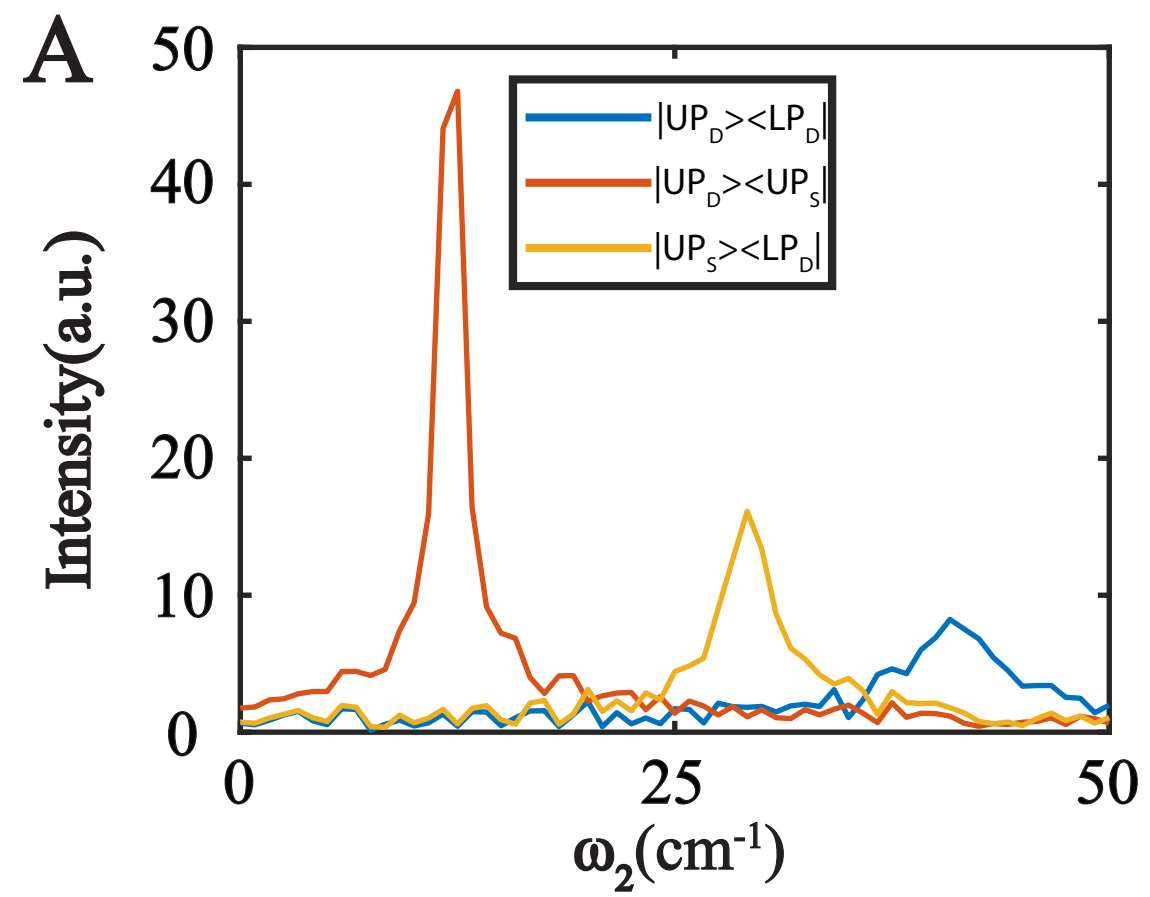


E

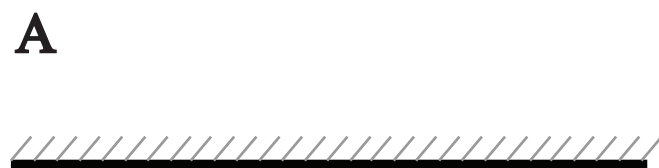
2DIR spectra of polariton system at 30ps







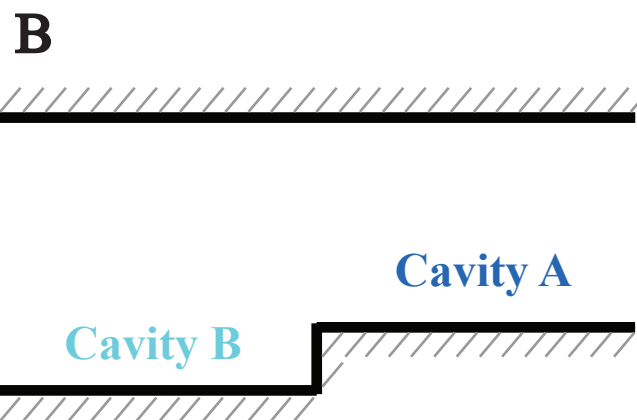
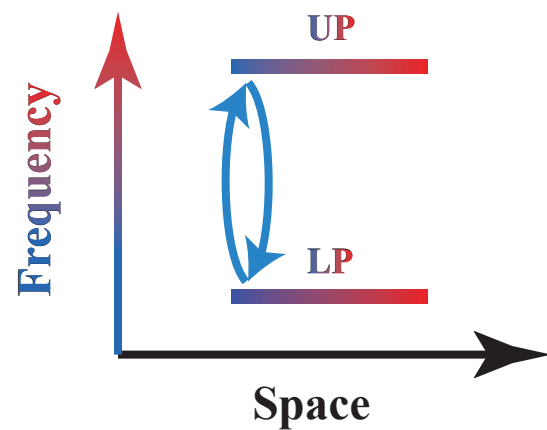
Cavity mirror



FP Cavity

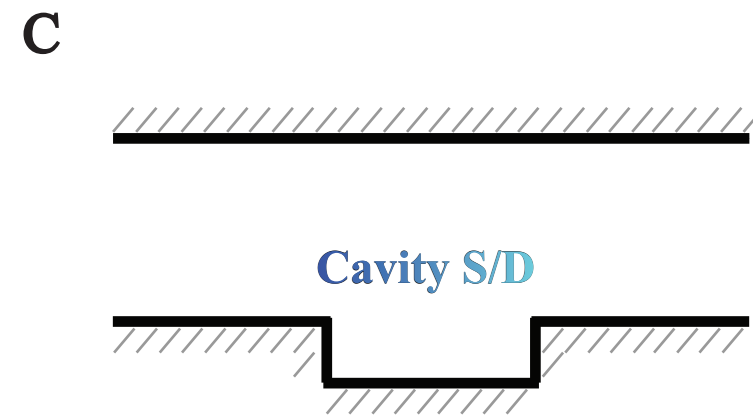
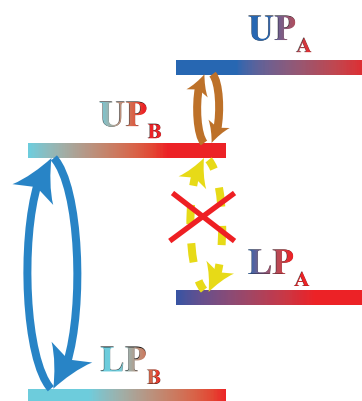


Polariton energy diagram

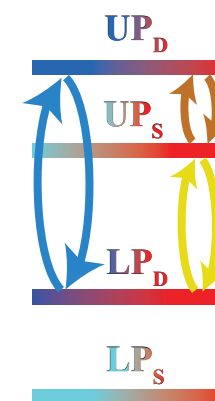


Cavity B

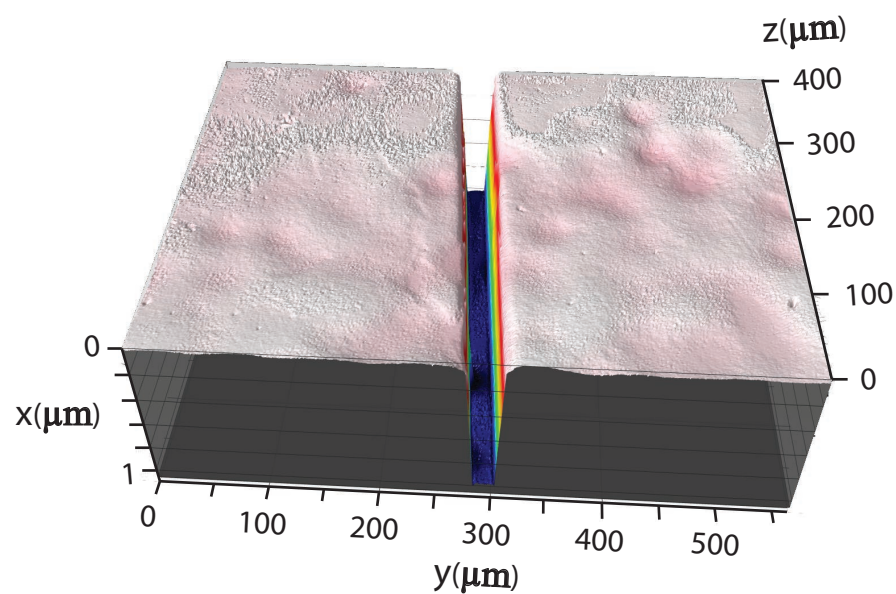
Cavity A



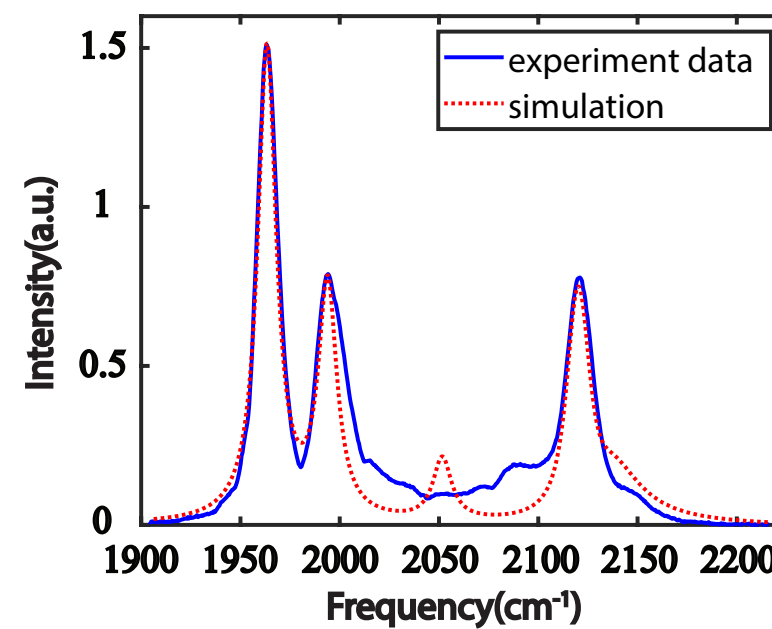
Cavity S/D



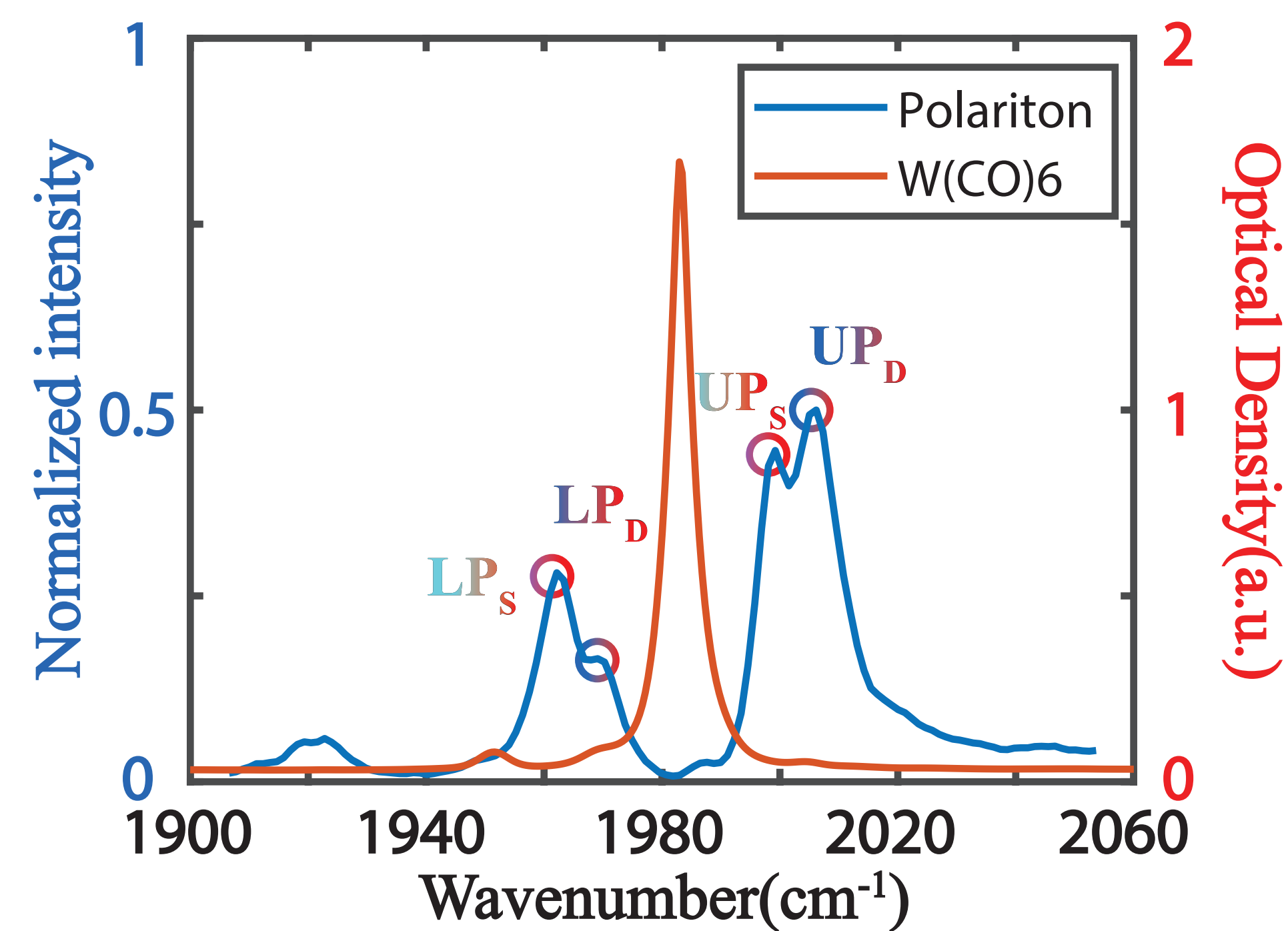
D



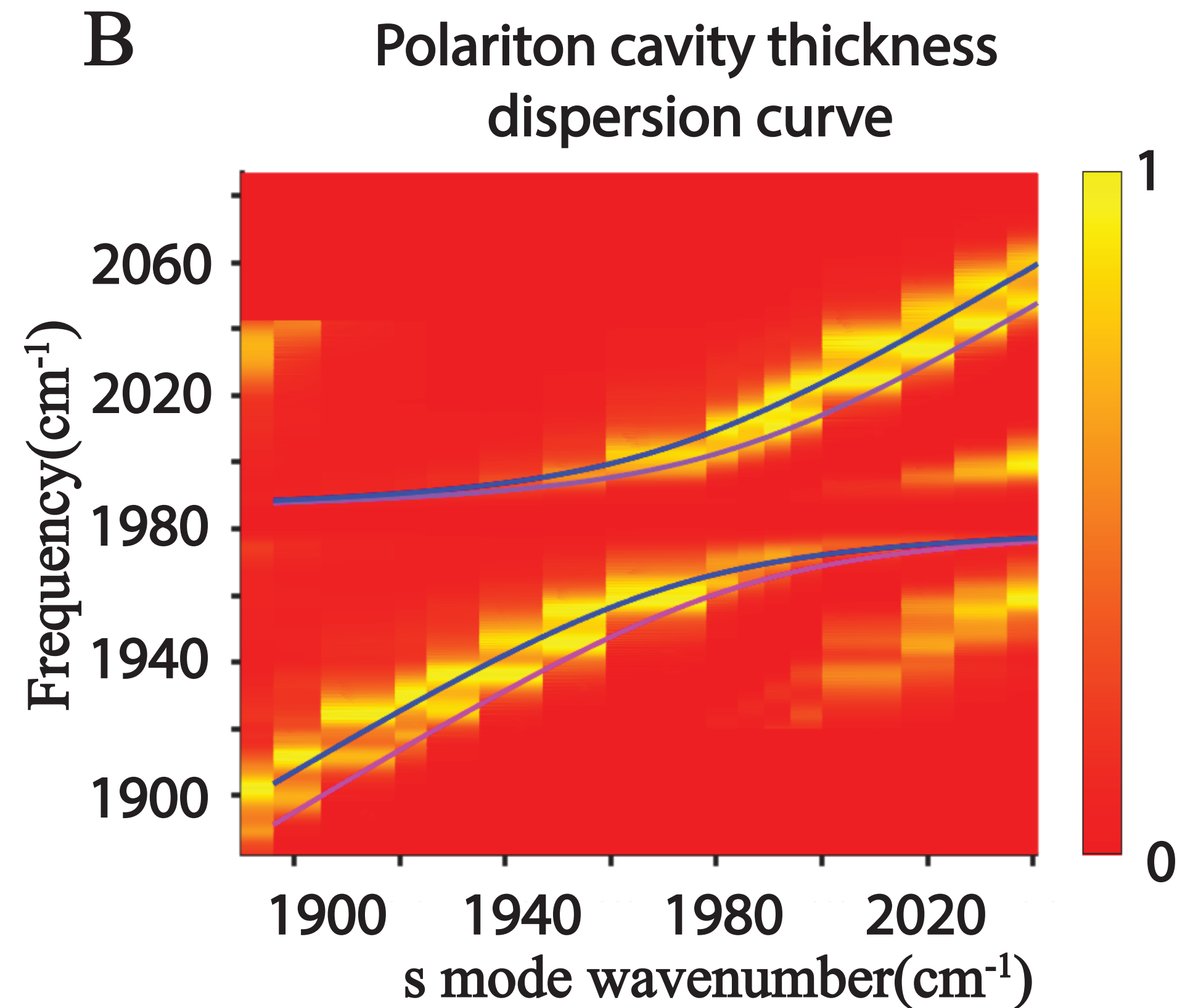
E



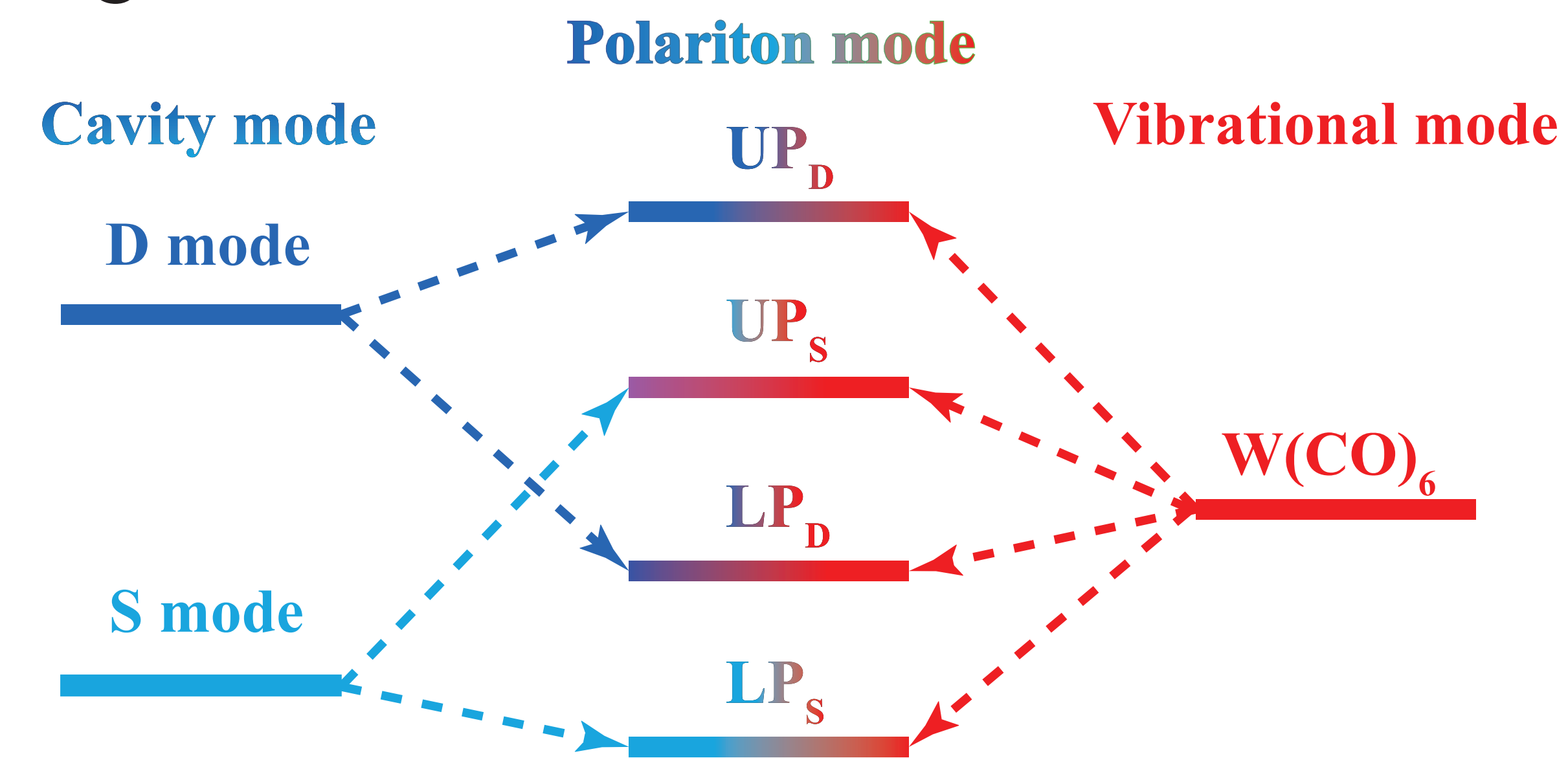
A



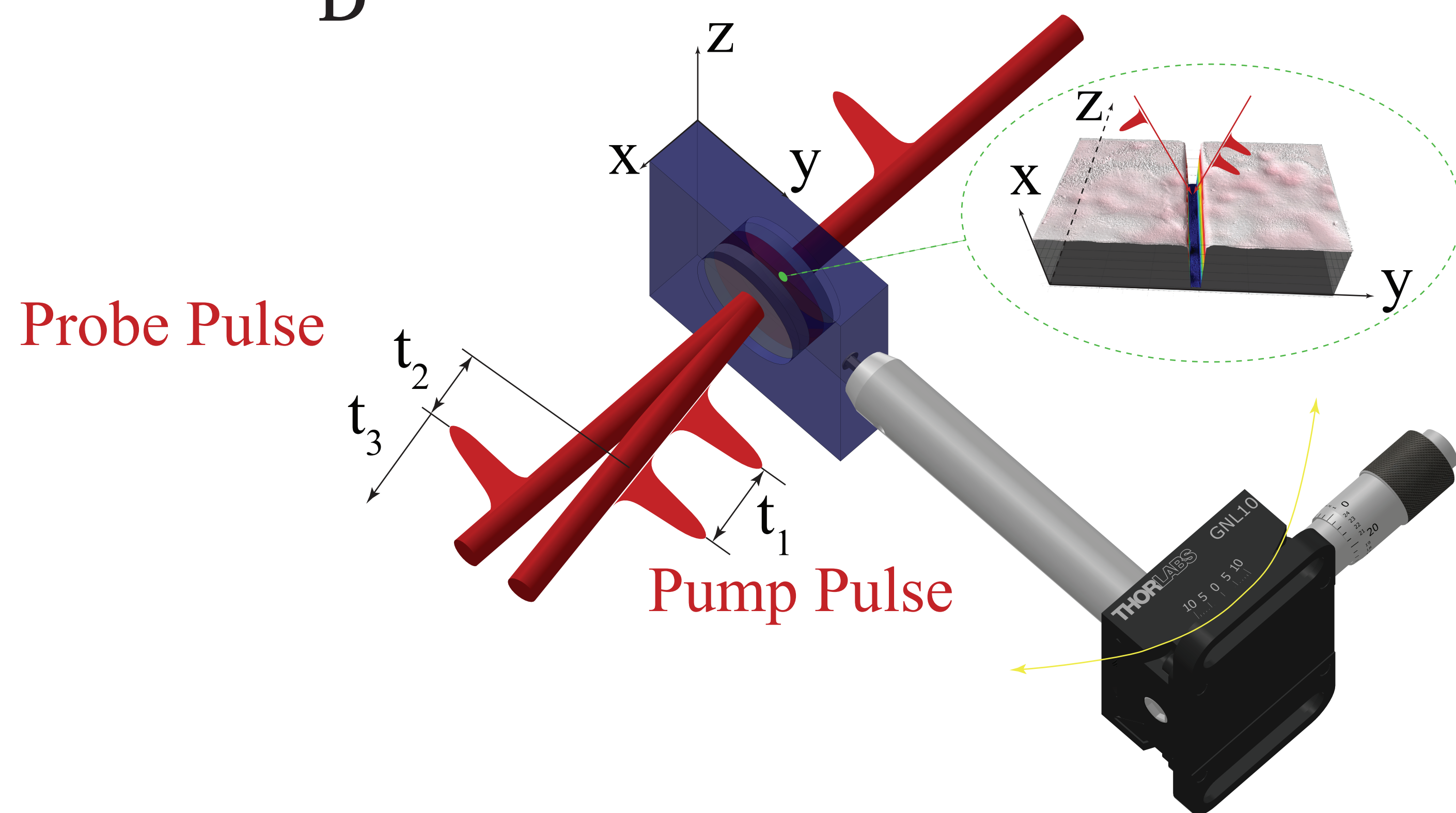
B



C



D



E

2DIR spectra of polariton system at 30ps

