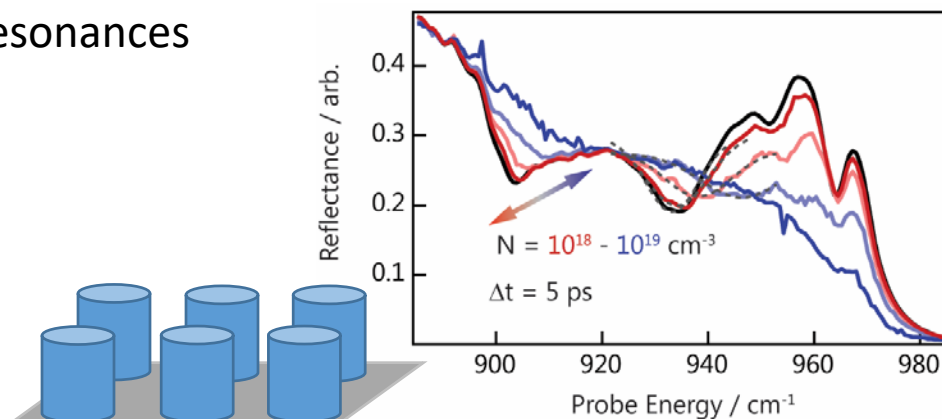
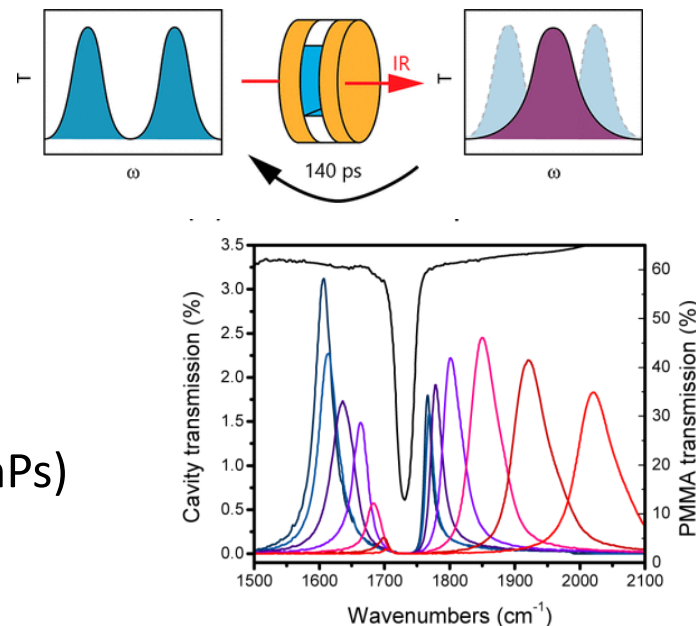




Polariton Enhanced Spectroscopy and Dynamics

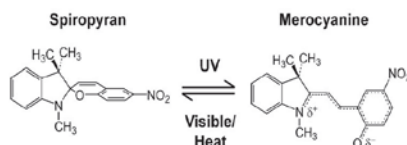
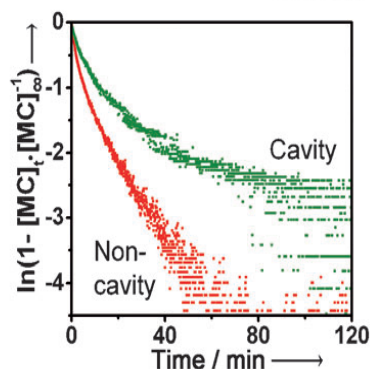
Jeff Owrutsky
Molecular Dynamics Section
Chemistry Division, U.S. Naval Research Laboratory

- Molecular Vibrations and Cavity Optical Modes
 - Recent interest in strong coupling
 - Coupling optical modes to material resonances
 - Frequency domain vibration cavity coupling
 - Dynamics of cavity-coupled $\text{W}(\text{CO})_6$
- Charge Carriers and Surface Phonon Polaritons (SPhPs)
 - Surface phonon polaritons vs plasmons
 - Motivation – tunable infrared resonances
 - Carrier tuning in bulk SiC
 - Active tuning of SiC SPhP resonances



BACKGROUND ON CAVITY COUPLING

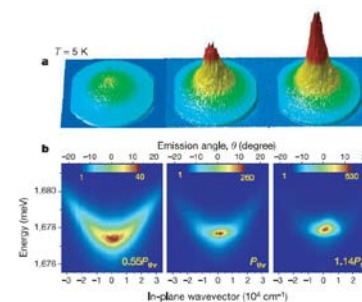
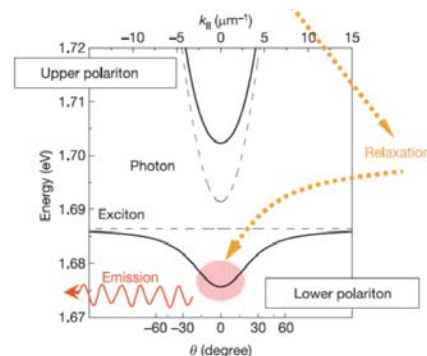
Electronic coupling



Photochemistry

J. Hutchison, et al. Angew. Comm. 2012

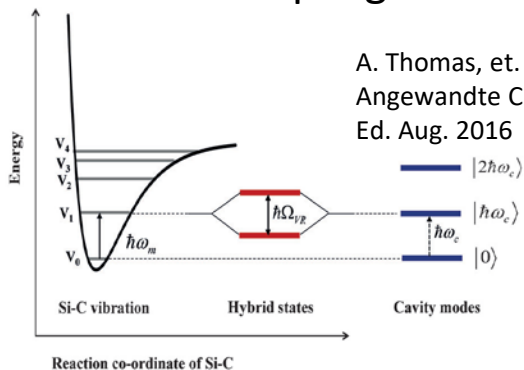
New Condensed Phases



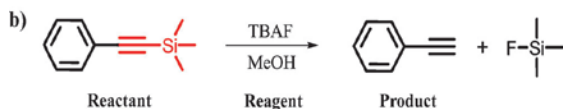
Bose-Einstein condensates

J. Kasprzak, et al. Nature 2006

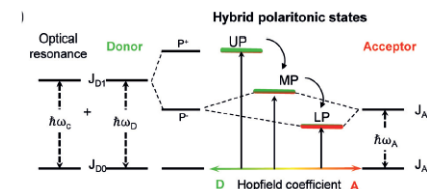
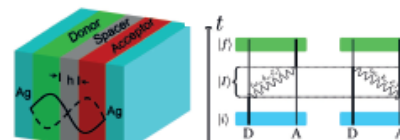
Vibrational coupling



A. Thomas, et. al.
Angewandte Chemie, Int.
Ed. Aug. 2016



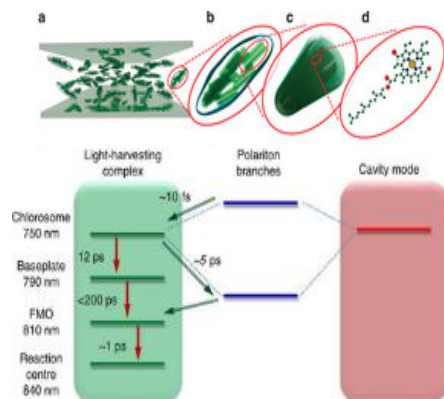
Delocalized Energy Transfer



Zhong et al.
Angew.Chem. Int. Ed. 2017

BACKGROUND ON CAVITY COUPLING

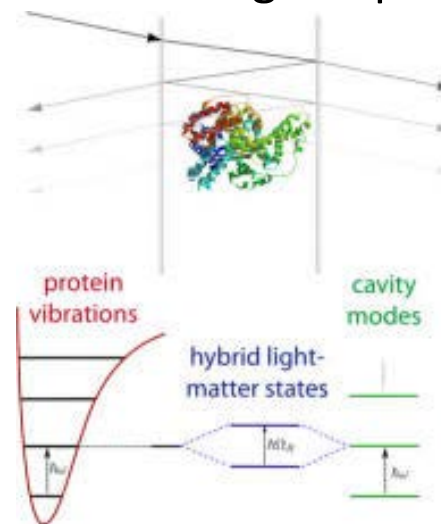
Energy Transfer



Pursuing artificial photosynthesis

Coles, et al, Nat. Comm. 2014

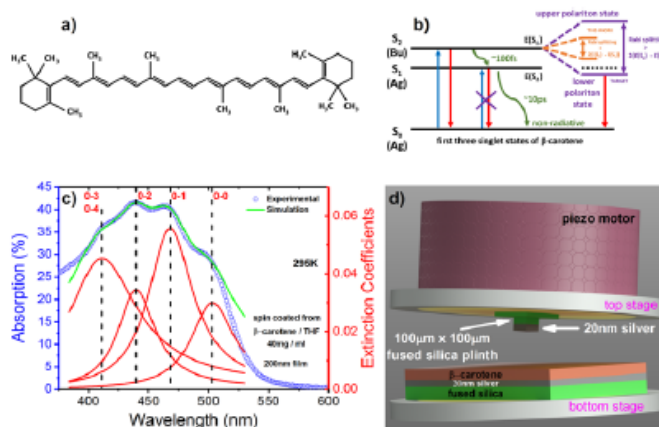
Protein Strong Coupling



Vergauwe et al J. Phys. Chem. Lett. 2016

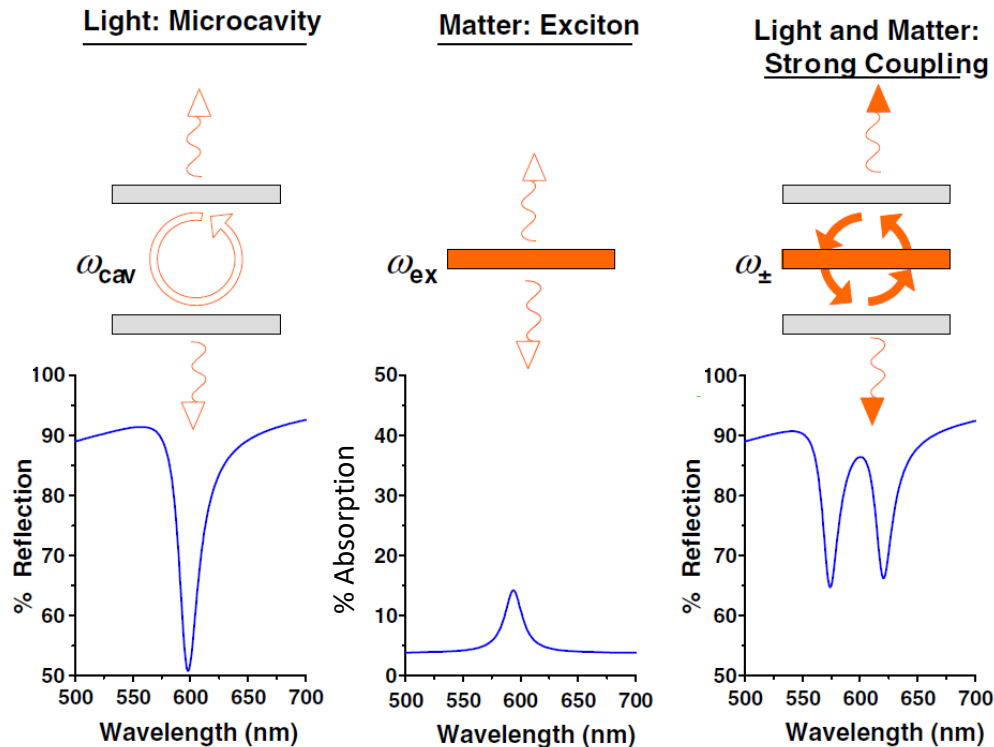
Microcavity Carotene Coupling

Grant et al Optics Express 2018



EXCITONS COUPLE TO CAVITIES

Cavity coherent coupling to electronic transitions:
quantum wells, quantum dots, excitons (J aggs)

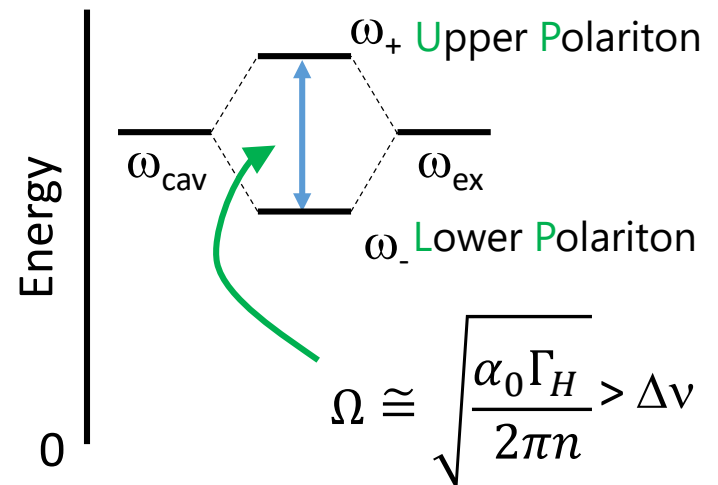


J. R. Tischler, *et al.*, *Org. Elec.*, **8** 94 (2007)
Khitrova, *et al.*, *Rev. Mod. Phys.* 71 1591 (1999)

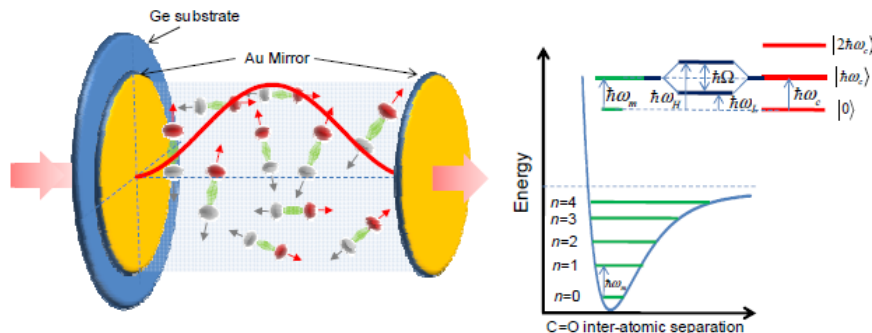
Electronic transitions couple to cavity
modes, creating
exciton-polaritons

“Vacuum Rabi Splitting”

Interaction between quantized light
field of cavity and transition dipole of
material



VIBRATIONAL POLARITONS

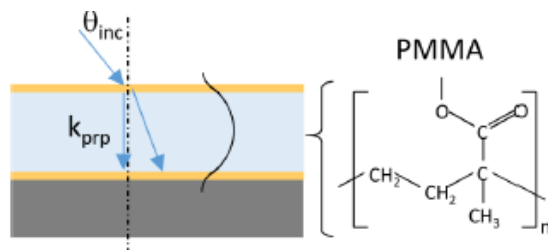


Shalabney, *et al. Nat. Comm.* **6** (2015)
arXiv 2014

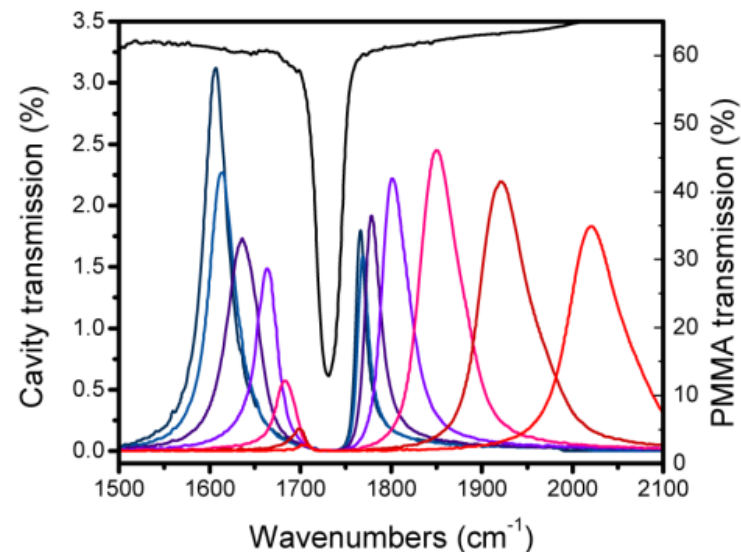
2015 - first vibration-cavity
polaritons

Polymers give control of sample
thickness (~2 mm)

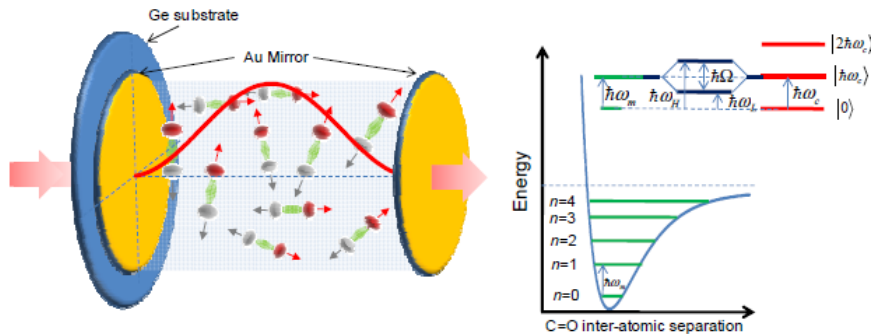
Tuning angle tunes polariton
position – *tunes energy of
vibrational mode!*



Long and Simpkins, *ACS Photonics*, **2** (2015)



VIBRATIONAL POLARITONS

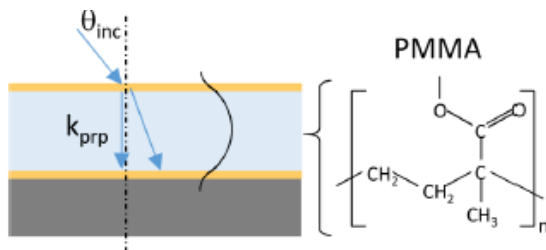


Shalabney, *et al. Nat. Comm.* **6** (2015)
arXiv 2014

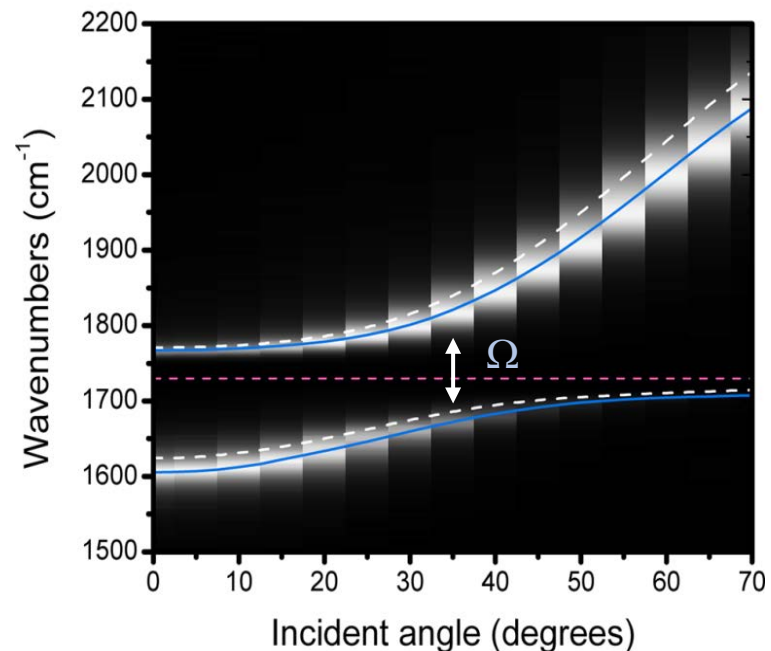
2015 - first vibration-cavity polaritons

Polymers give control of sample thickness (~2 mm)

Tuning angle tunes polariton position – *tunes energy of vibrational mode!*



Long and Simpkins, *ACS Photonics*, **2** (2015)

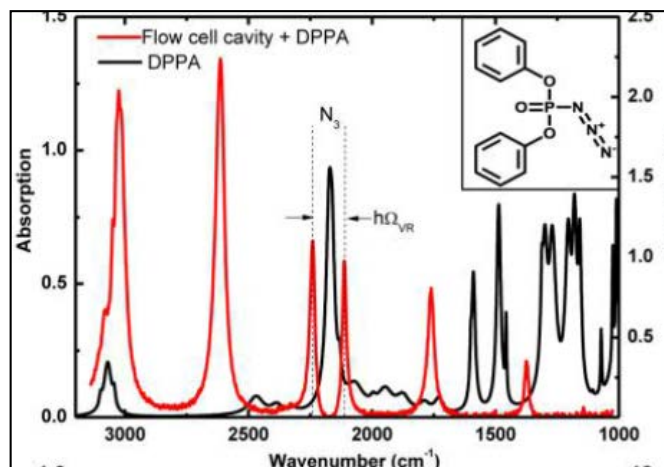


CAVITY-COUPLED LIQUIDS

Extend to liquids & longer pathlengths:

Ebbesen group:

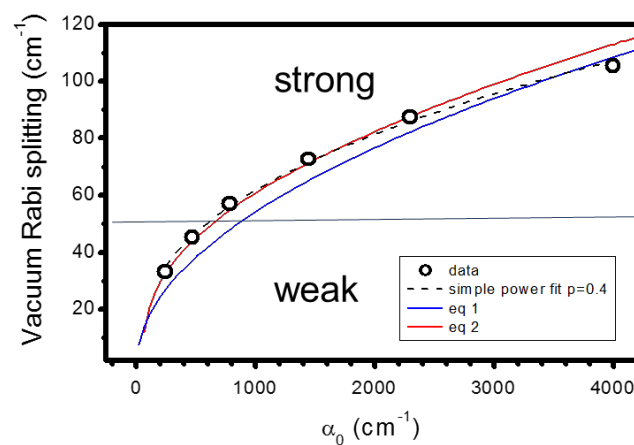
J. Phys. Chem. Lett. 6, 1027 (2015)



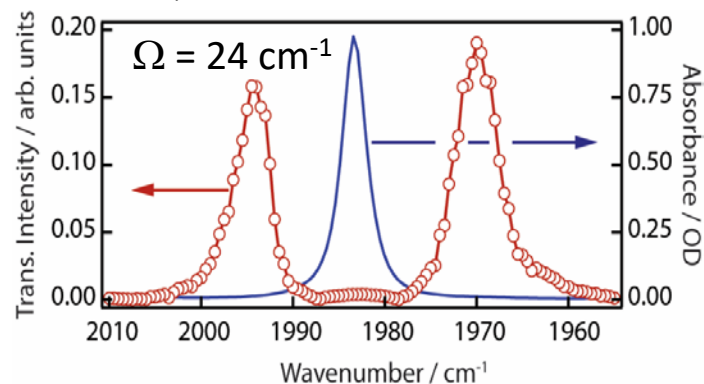
$$\Omega_T = \sqrt{\frac{\alpha_0 \Gamma_H}{2\pi n_B}}$$

Concentration dependence,
dissolved species:

Simpkins, *et al.*: *ACS Photonics* 2 1460 (2016)



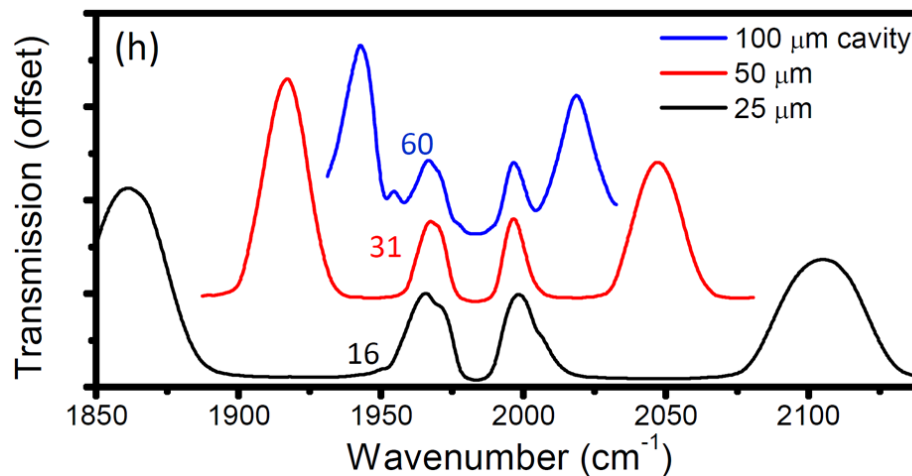
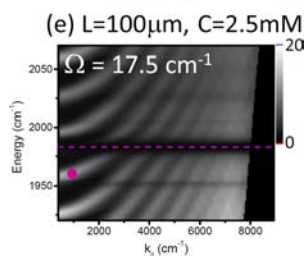
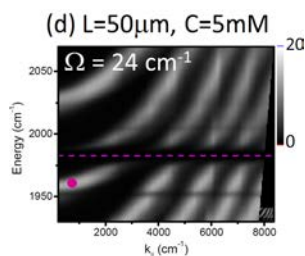
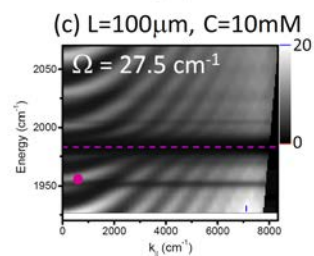
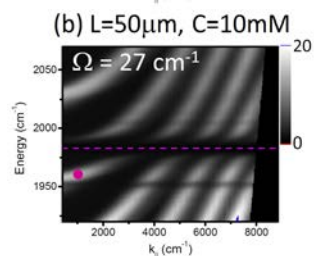
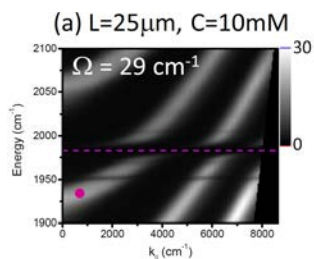
10 mM W(CO)₆ in hexane
25 μm spacer, dielectric mirrors



POLARITONS IN SOLUTION

$W(CO)_6$ in hexane

- Splitting depends on concentration
- **Not pathlength****



$$\Omega \cong \sqrt{\frac{\alpha_0 \Gamma_H}{2\pi n}} \quad \alpha_0 \propto \text{absorber conc.}$$

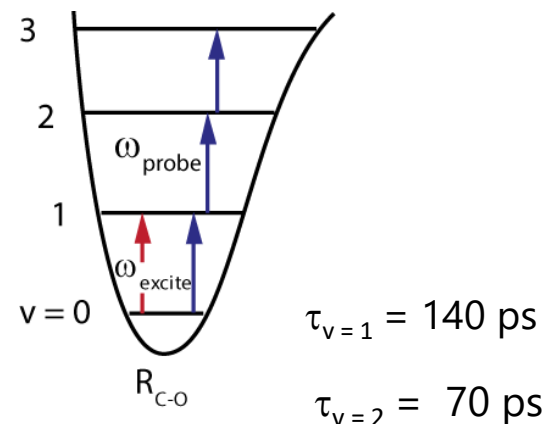
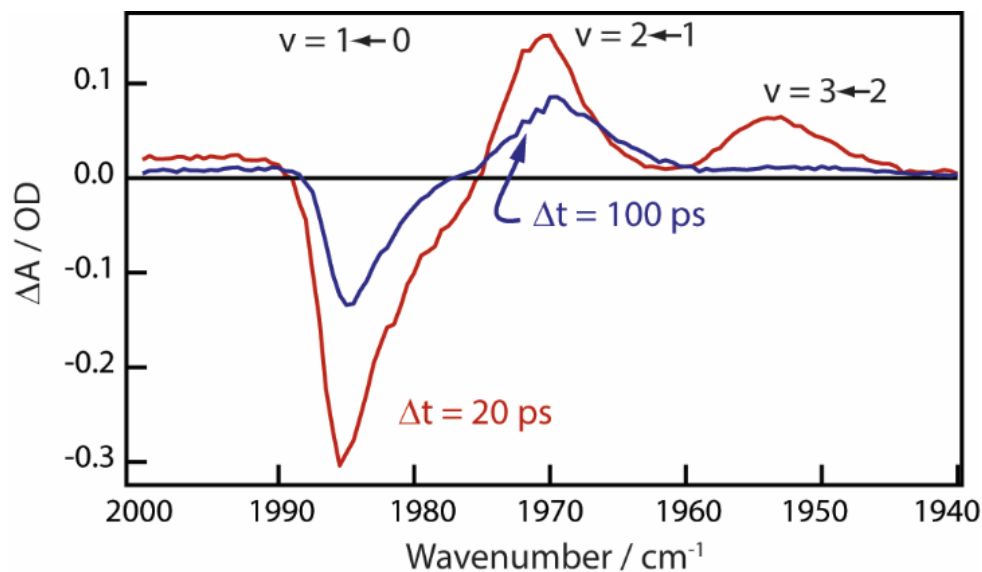
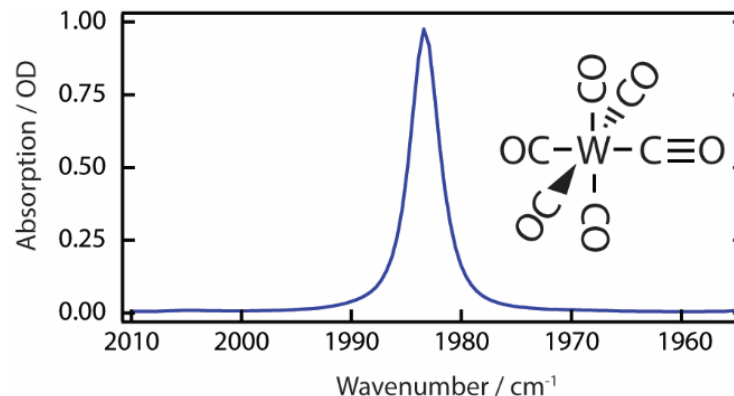
Opportunity:

Modify Vibrational Energy Transfer

W(CO)₆ VIBRATIONAL DYNAMICS

W(CO)₆ in hexane: benchmark vibrational relaxation

- Strong, narrow absorption
- Ground state bleach & excited-state absorptions
- **Amplitudes evolve – NOT SHAPE!**



Dougherty & Heilweil
Chem. Phys. Lett. 227, 19 (1994).

CAVITY-VIBRATION POLARITON DYNAMICS

Measure transient spectra and decays

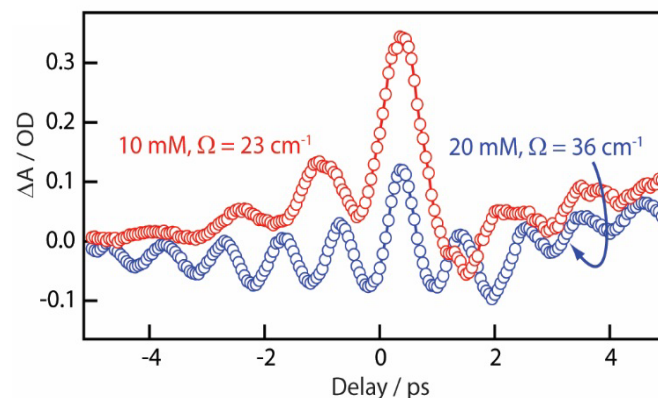
Match spectra to classical cavity model to determine assignment of excited states

Signal only where cavity transmits

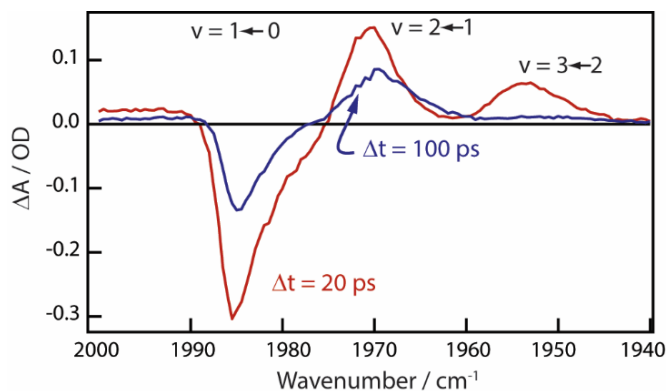
Most response near LP/hot band at 1968 cm^{-1}

Spectra evolve with population changes

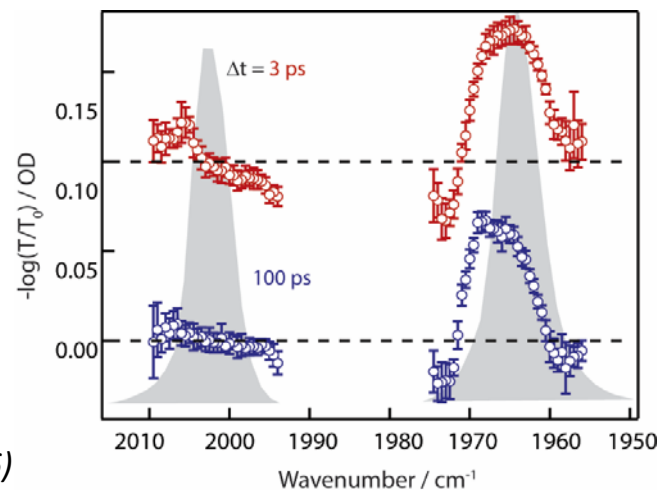
Rabi oscillations at early times



from this – outside cavity

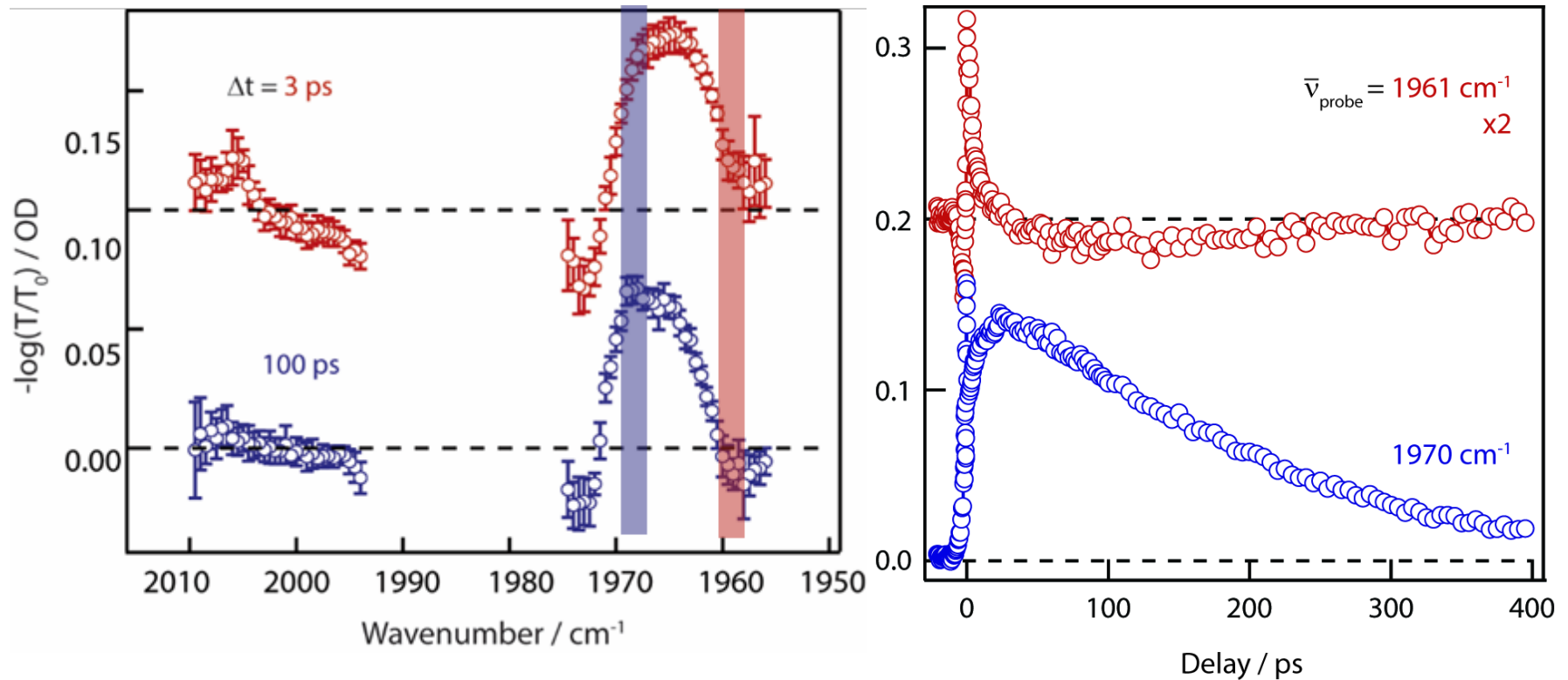


to this – inside

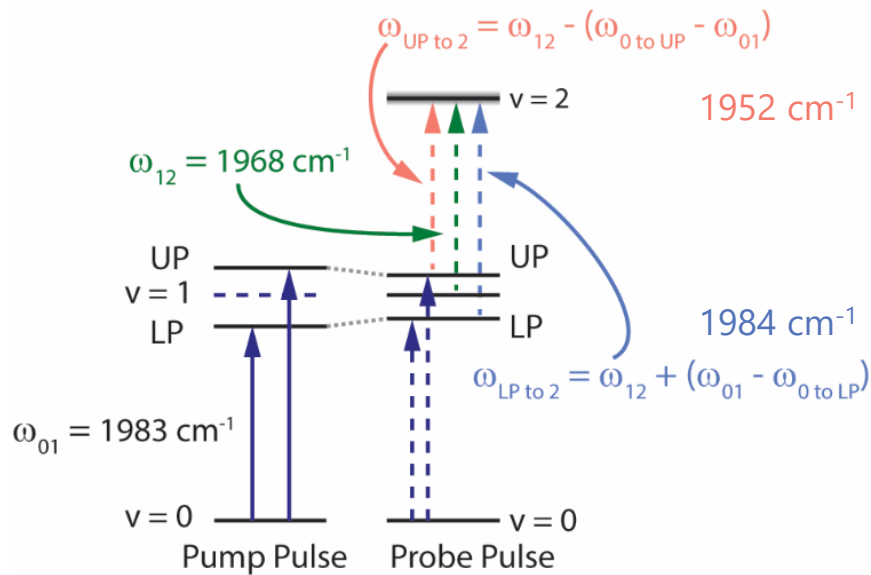


Dunkelberger et al. Nat. Comm., 7, 13504 (2016)

TWO COMPONENTS EVIDENT IN LP



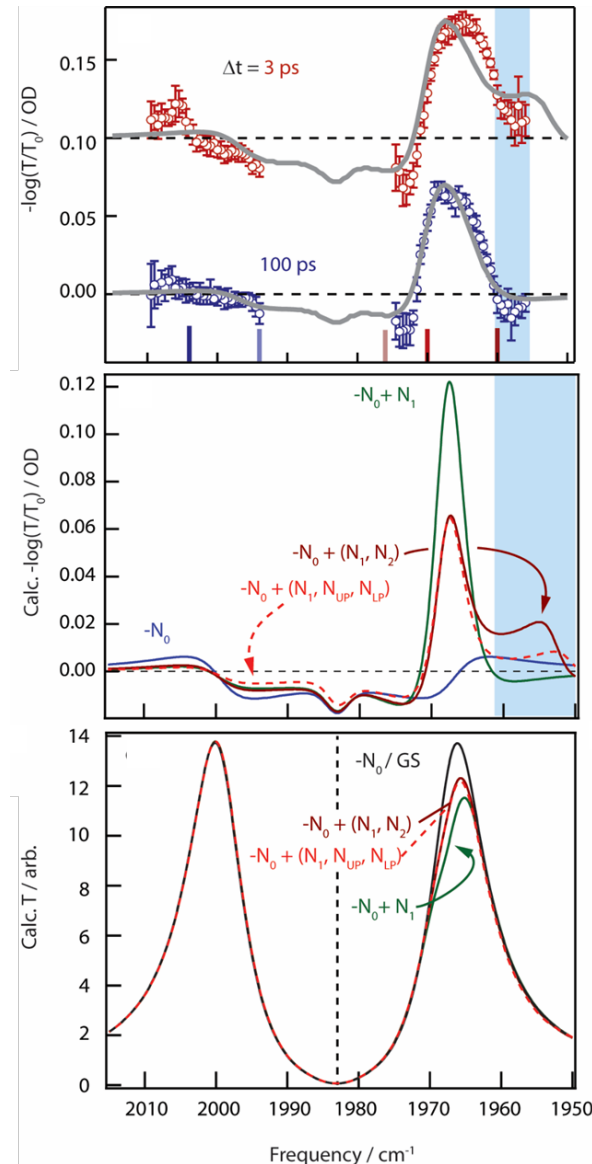
CALCULATE SPECTRA to MATCH OBSERVED



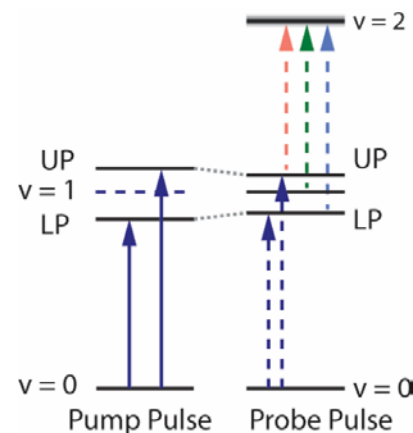
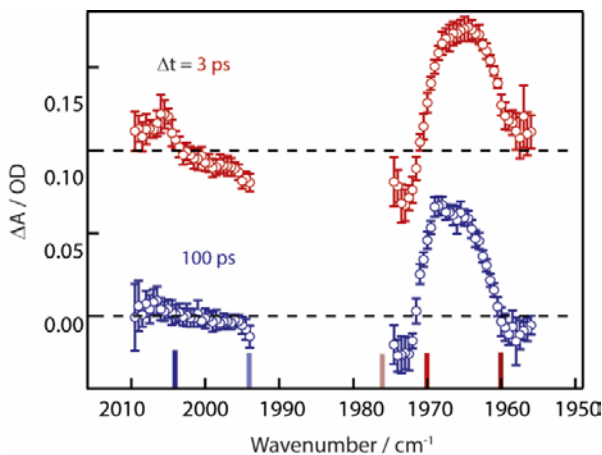
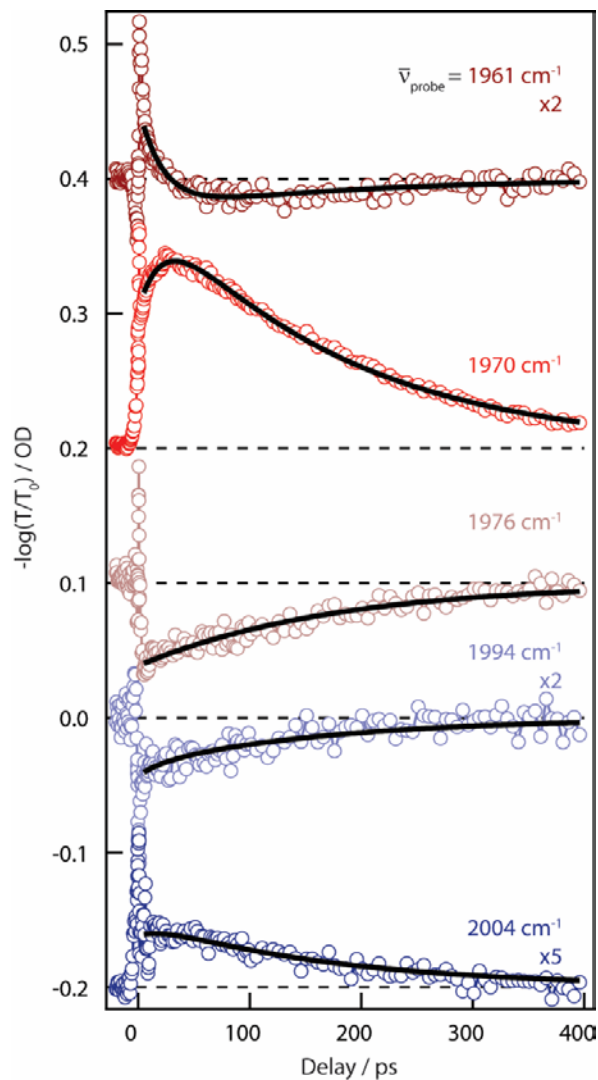
$$T = \frac{t^2 e^{-\alpha L}}{1 + r e^{-2\alpha L} - 2r^2 e^{-\alpha L} \cos(4\pi n L \bar{\nu} + 2\phi)}$$

Calculate cavity transmission analytically:
absorbers determine α and n

Consistent with model in which UP, LP, and
reservoir are populated



POLARITON DECAY DYNAMICS



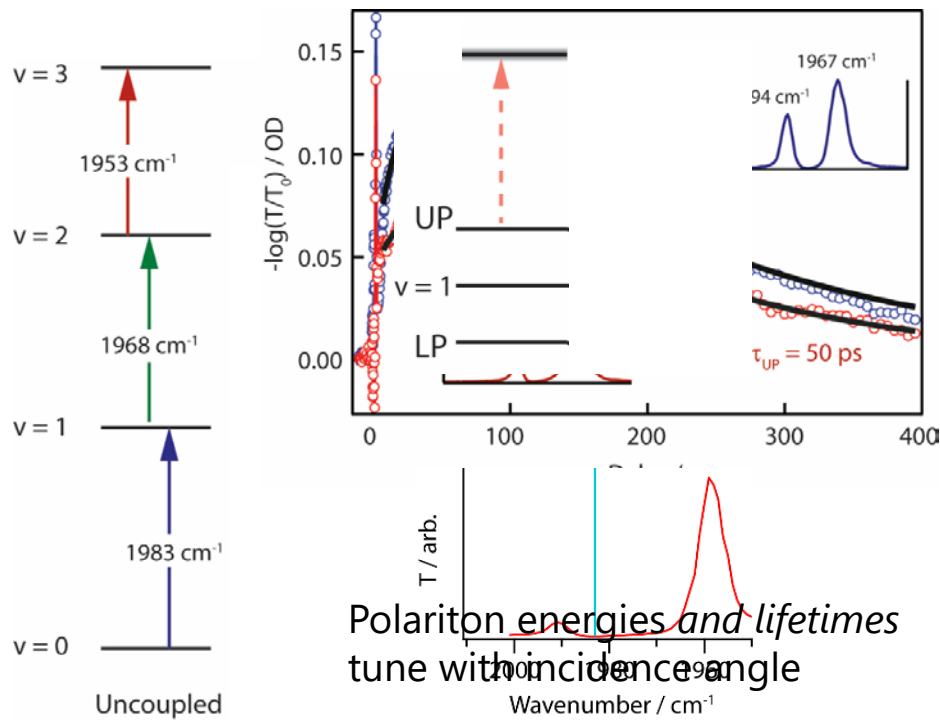
UP decays in 20 ps
Slow component in 170 ps ($\tau_{v=1} = 140 \text{ ps}$)

ω_{01} overlaps $\omega_{\text{LP to } 2}$ – no direct evidence for LP, but likely convoluted with $v = 1$

First report of vibration – cavity polariton relaxation dynamics

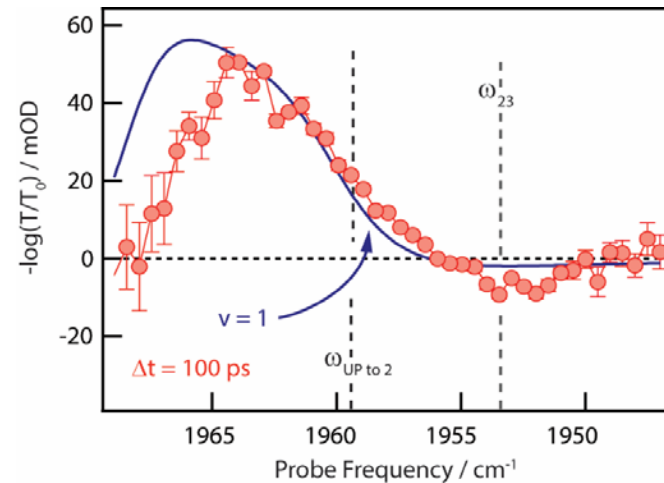
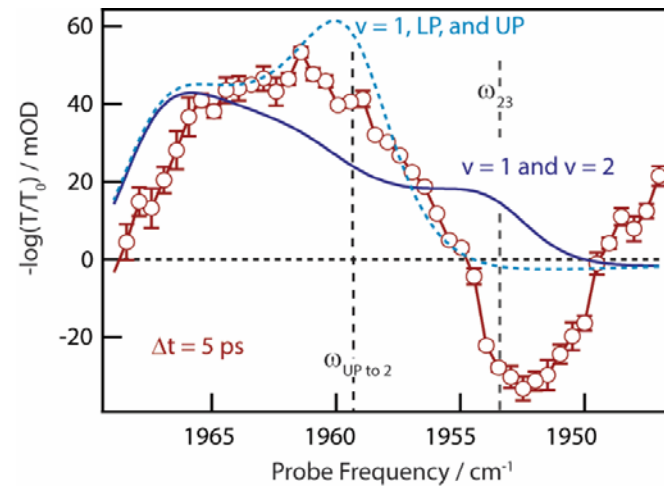
ANGLE TUNING

$\omega_{UP \text{ to } 2}$ overlaps ω_{23}



Polariton energies and lifetimes
tune with incidence angle

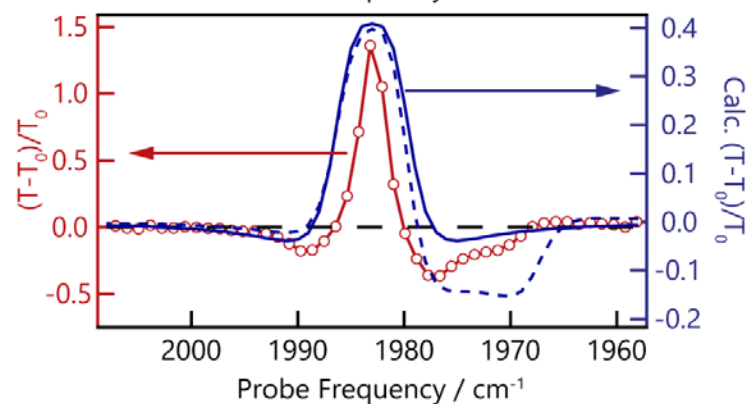
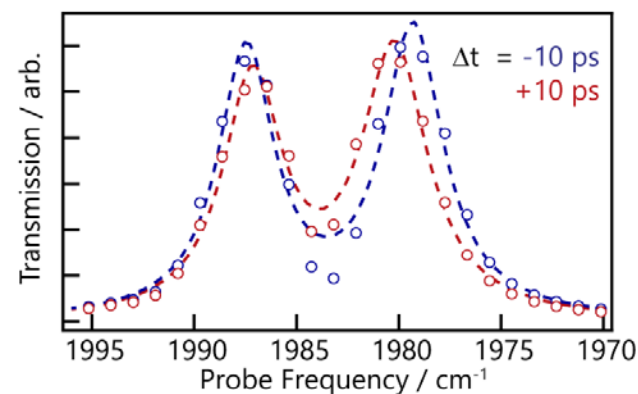
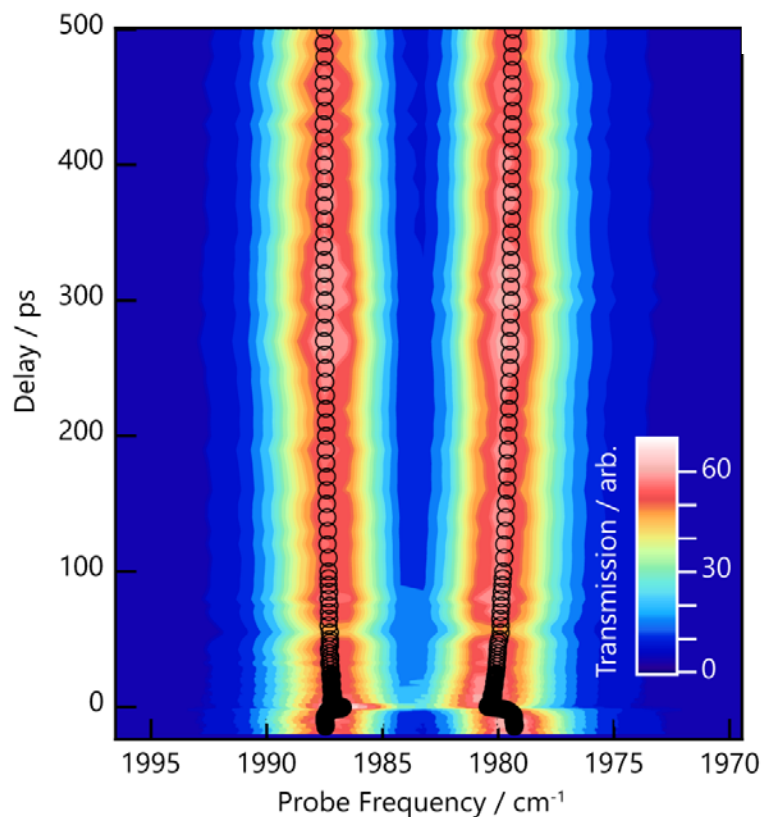
Confirms polariton assignment:
reservoir modes should be not
tune with angle



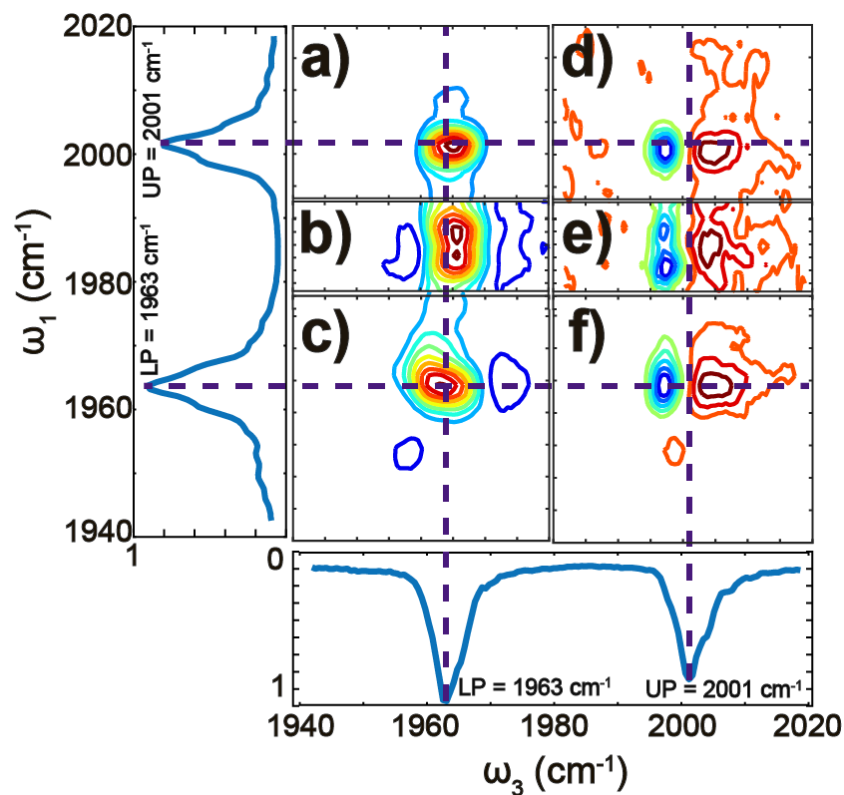
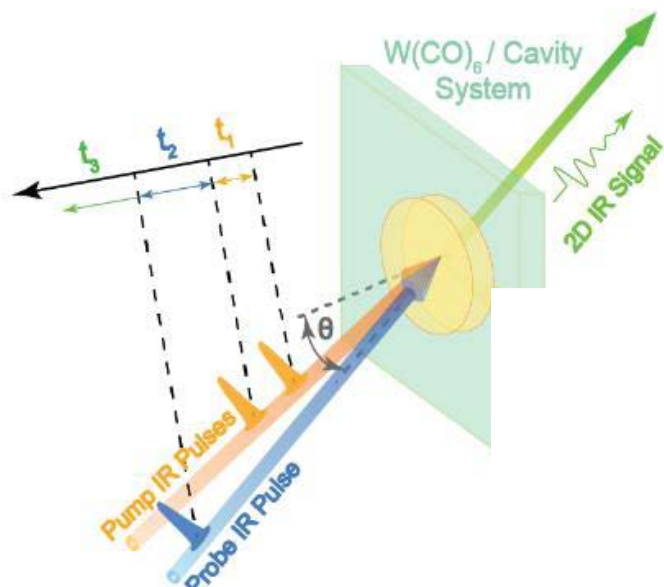
LOW CONCENTRATION

At low concentration (1 mM), cavity not resonant with $v = 1 \rightarrow 2$

Only observe effect of GS **population** decrease that reduces splitting



2DIR of $\text{W}(\text{CO})_6$ VIBRATION POLARITONS



Consistent with pump-probe results

Clear evidence of uncoupled excitation

More rigorous theoretical treatment – calculations match observed data

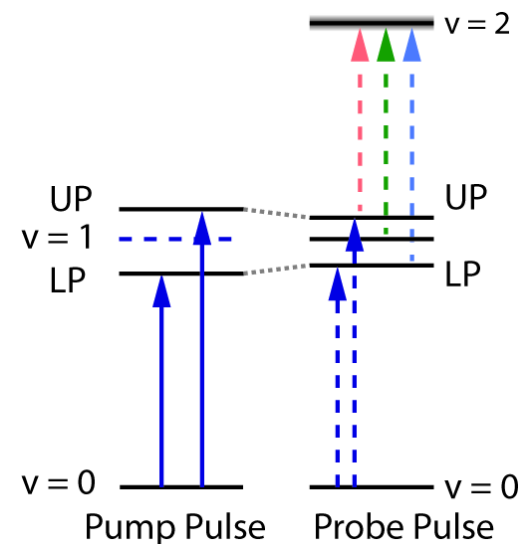
First transient studies of vibration-cavity coupled polaritons

Assignments based on matching observed and calculated spectra

- UP to $v=2$ is fast and angle tunable
- most of signal from reservoir $v=1$
- low concentration results isolate GS/splitting evolution
demonstrates spectral evolution with population changes

2DIR by Wei Xiong and Bo Xiang / UCSD

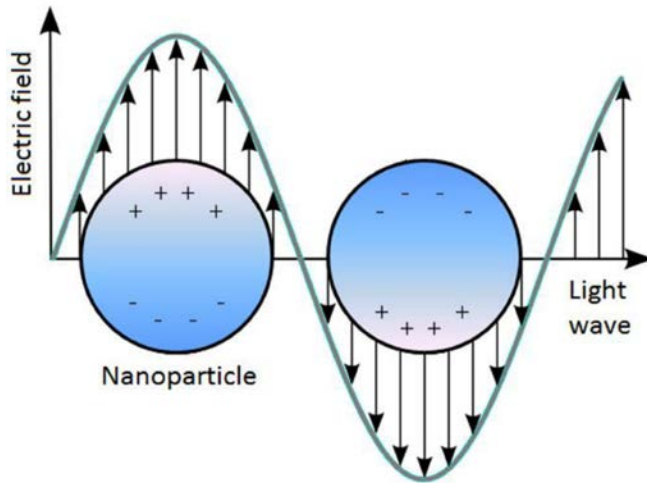
- expand on 1D results
- good agreement, especially at long time (>25 ps)
- strong contribution from reservoir 0-1 absorption



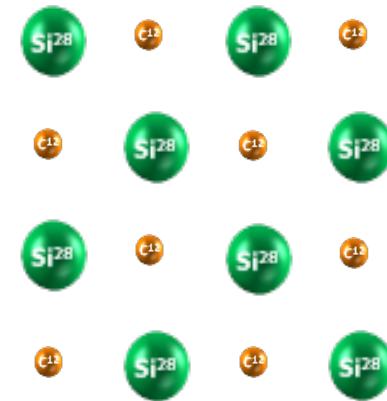
Avenue for altering molecular energy transfer, nonlocal coupling,
modifying chemical and *biochemical* reactions

SURFACE PHONON POLARITONS

Hammond, et al. *Biosensors* 4 (2014)



Plasmons – Collective electron oscillations



$\delta+$

$\delta-$

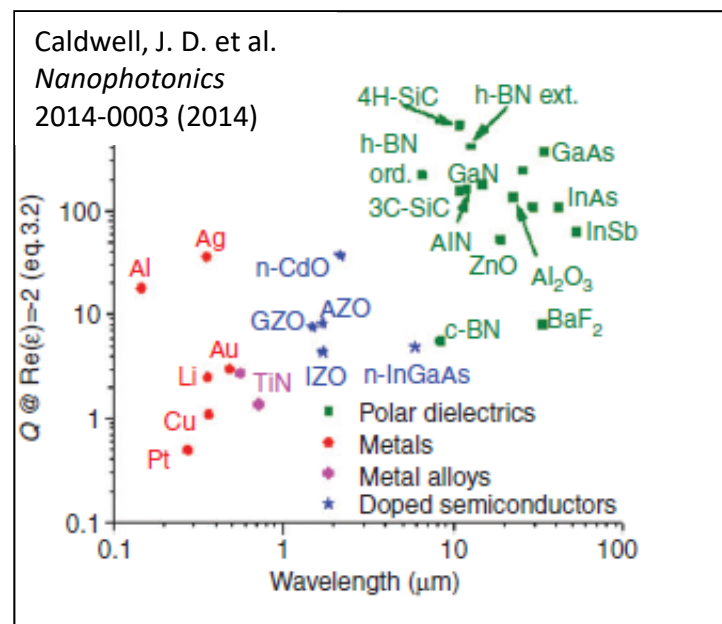
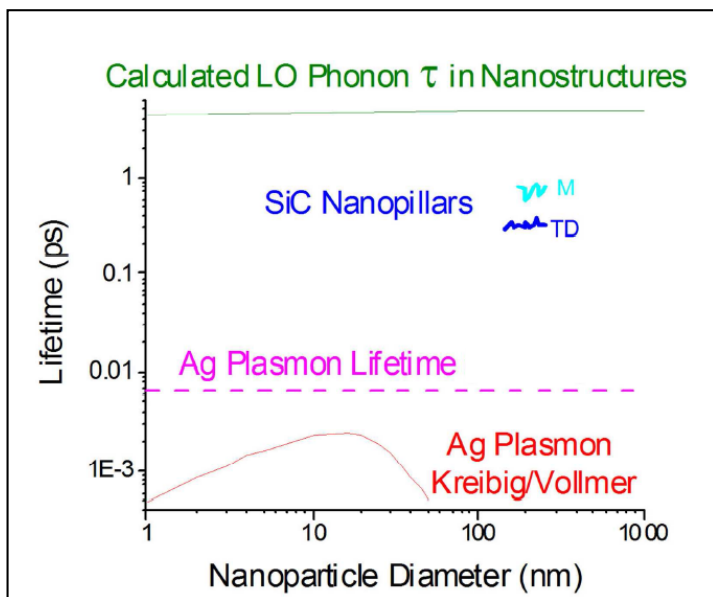
Phonon-polaritons – oscillating nuclear charge

Primary advantage: long lifetimes can lead to narrow resonances

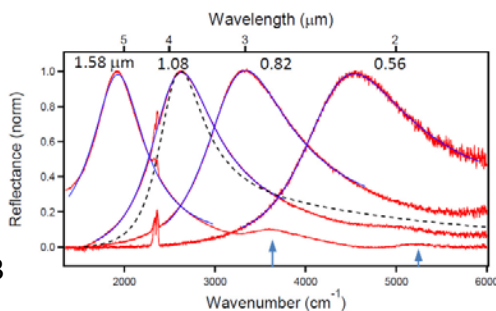
SURFACE PHONON POLARITONS – LOW LOSS ANALOGS OF PLASMONICS

Phonon / vibrational scattering & relaxation:

- much slower than for electrons, evident in linewidths

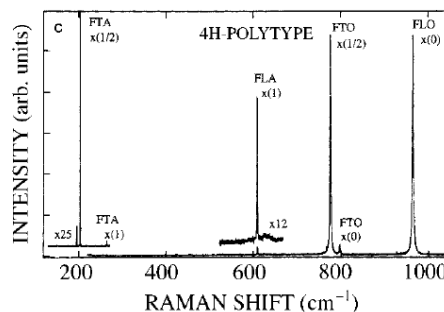


Au nanorods $\Delta\nu \sim 500 \text{ cm}^{-1}$



Simpkins et al,
Opt. Express, 2013

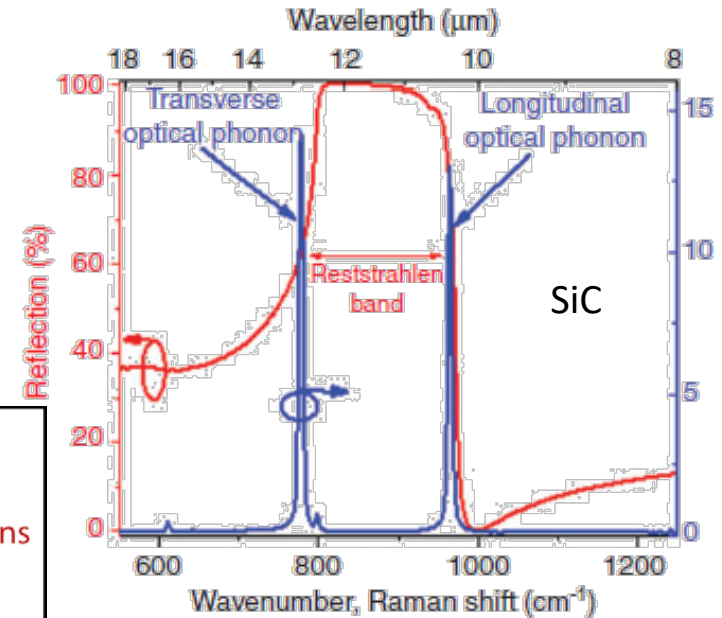
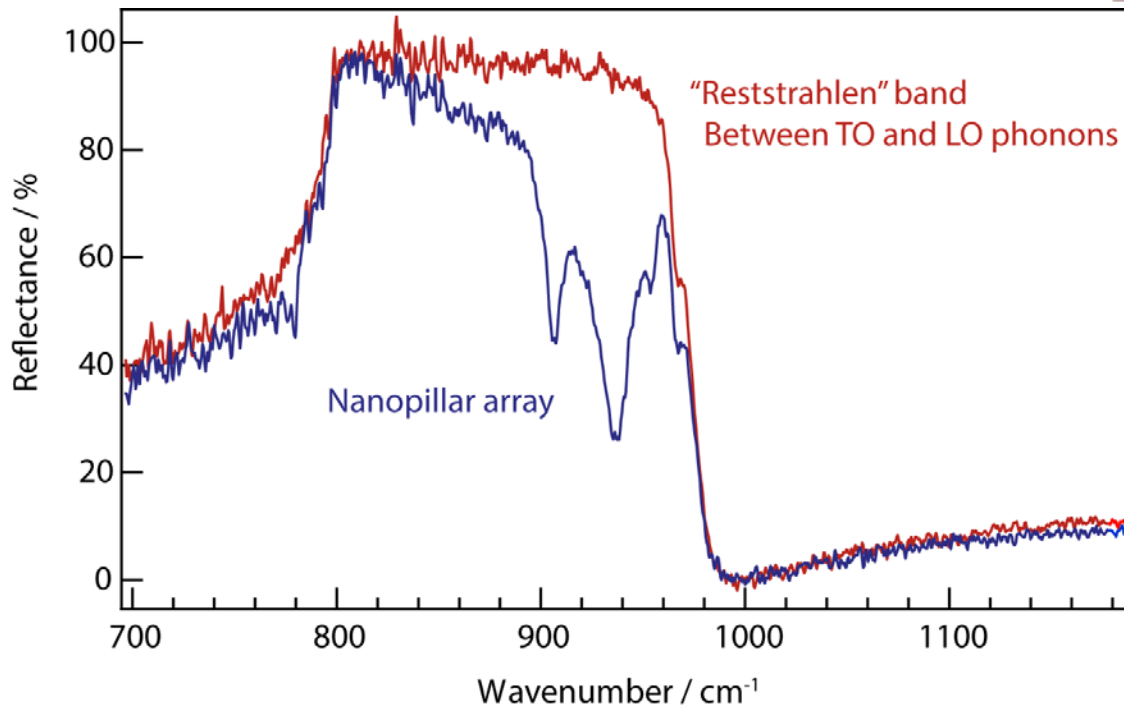
SiC $\Delta\nu \sim 5\text{-}15 \text{ cm}^{-1}$



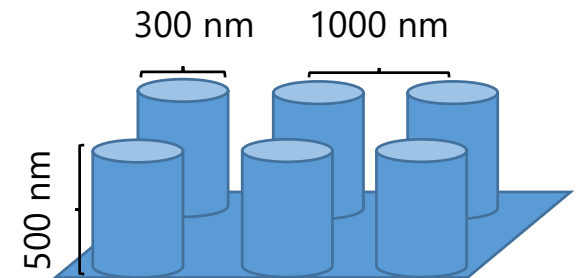
Nakashima and Harima,
Phys. Stat. Sol. A. Appl Res. 1997

SURFACE PHONON POLARITONS

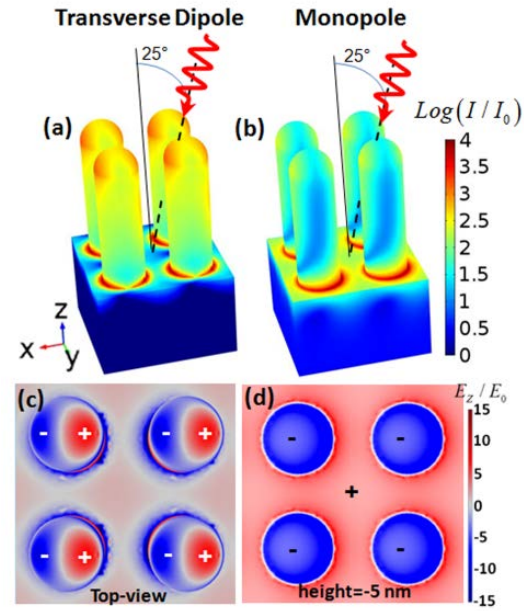
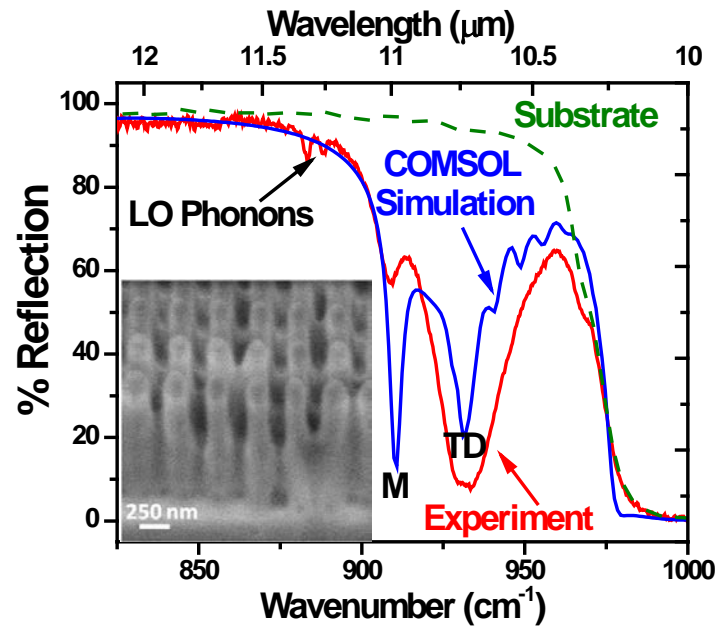
- Polar dielectrics:
- Metallic optical behavior between the TO and LO
- Surface-phonon polariton resonances (SPhPRs)
- Resemble plasmon resonances



Caldwell, et al. *Nanophot.* 4 (2015)



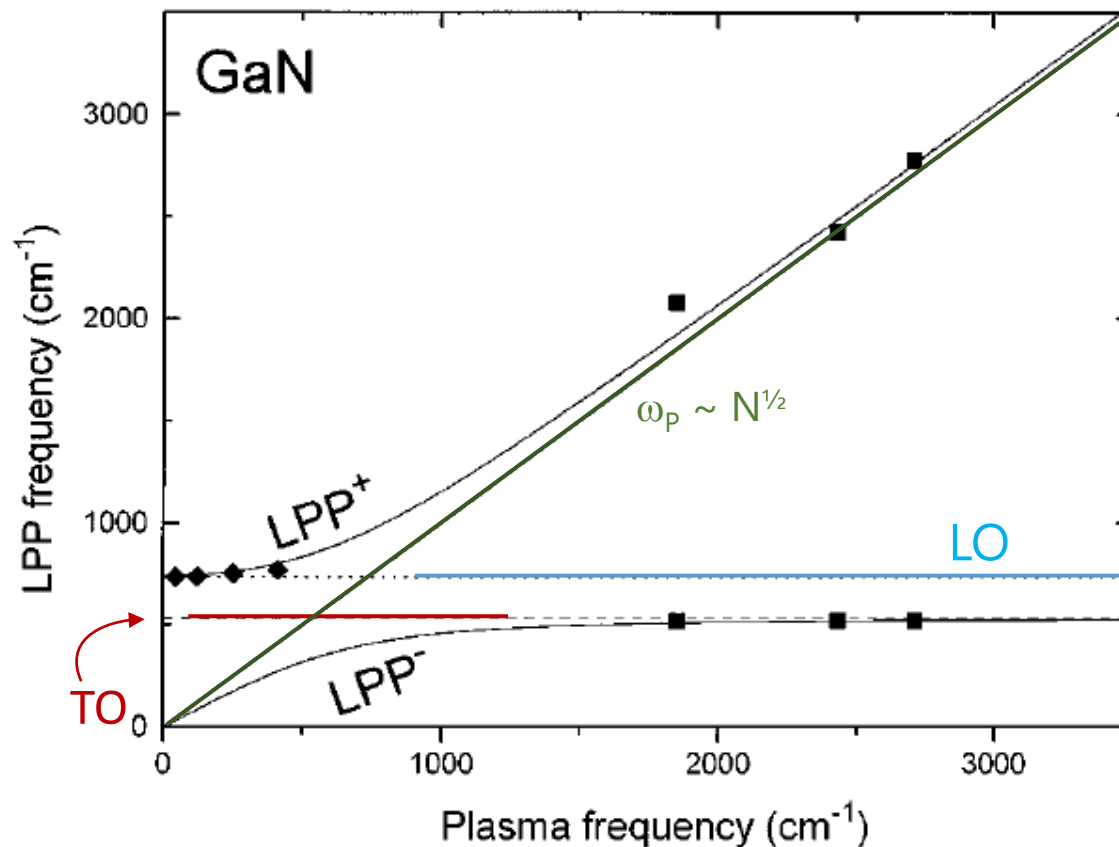
LOCALIZED MODES IN SiC NANOPILLARS



- Good agreement between simulations and experiments
- Observe transverse dipole & *monopole* resonances
- Modal confinements of $\left(\frac{\lambda_{res}^3}{V_{eff}}\right)^{1/3} = 50\text{-}200$ achieved

SURFACE PHONON POLARITONS

- Longitudinal-optical plasmon coupling (LOPC)
- LO tunes with carrier concentration/plasma frequency



Upper phonon-plasmon mode dictates Reststrahlen band edge

Various approaches

- 1) Doping
- 2) Photoinjection

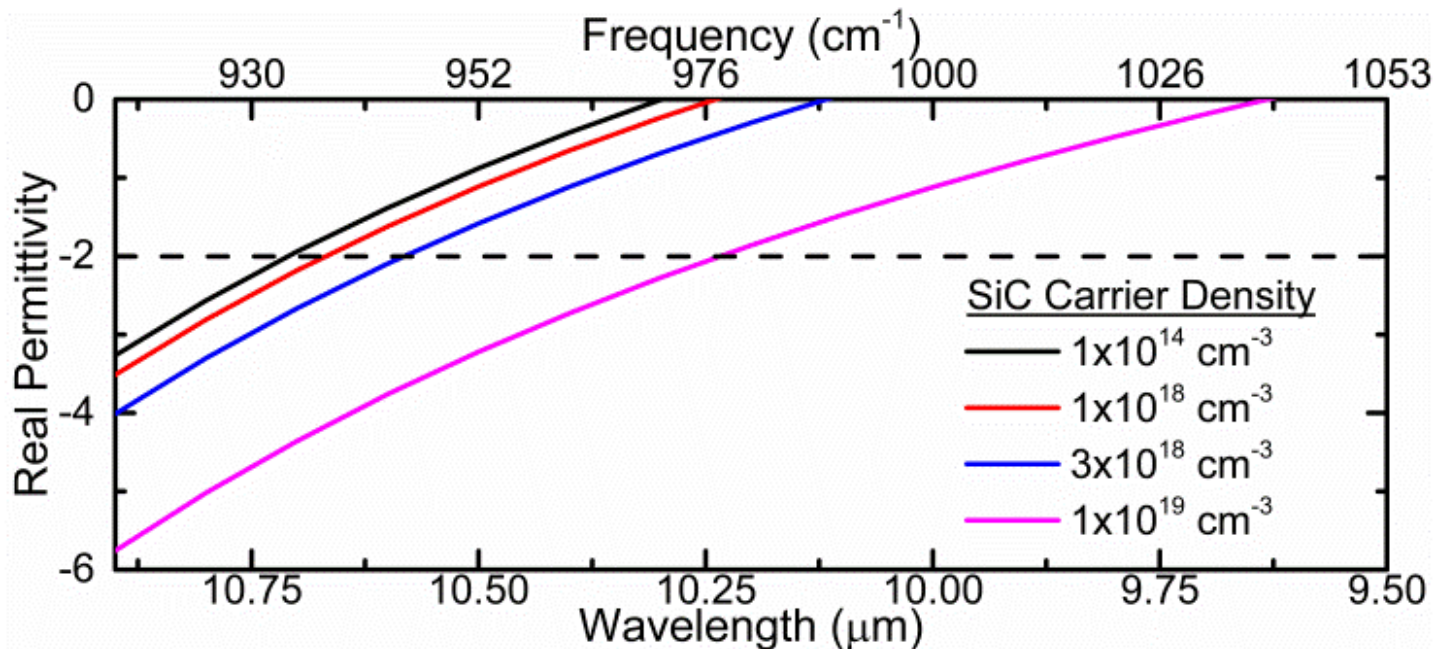
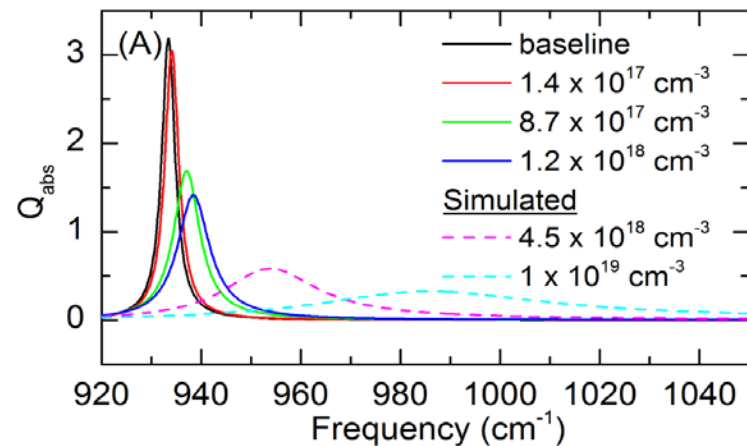
TUNING RESONANCES

For a sphere:

$$Q_{abs} = \frac{24\pi a}{\lambda} \frac{\epsilon_m^{3/2} \epsilon''}{(\epsilon' + 2\epsilon_m)^2 + \epsilon''^2}$$

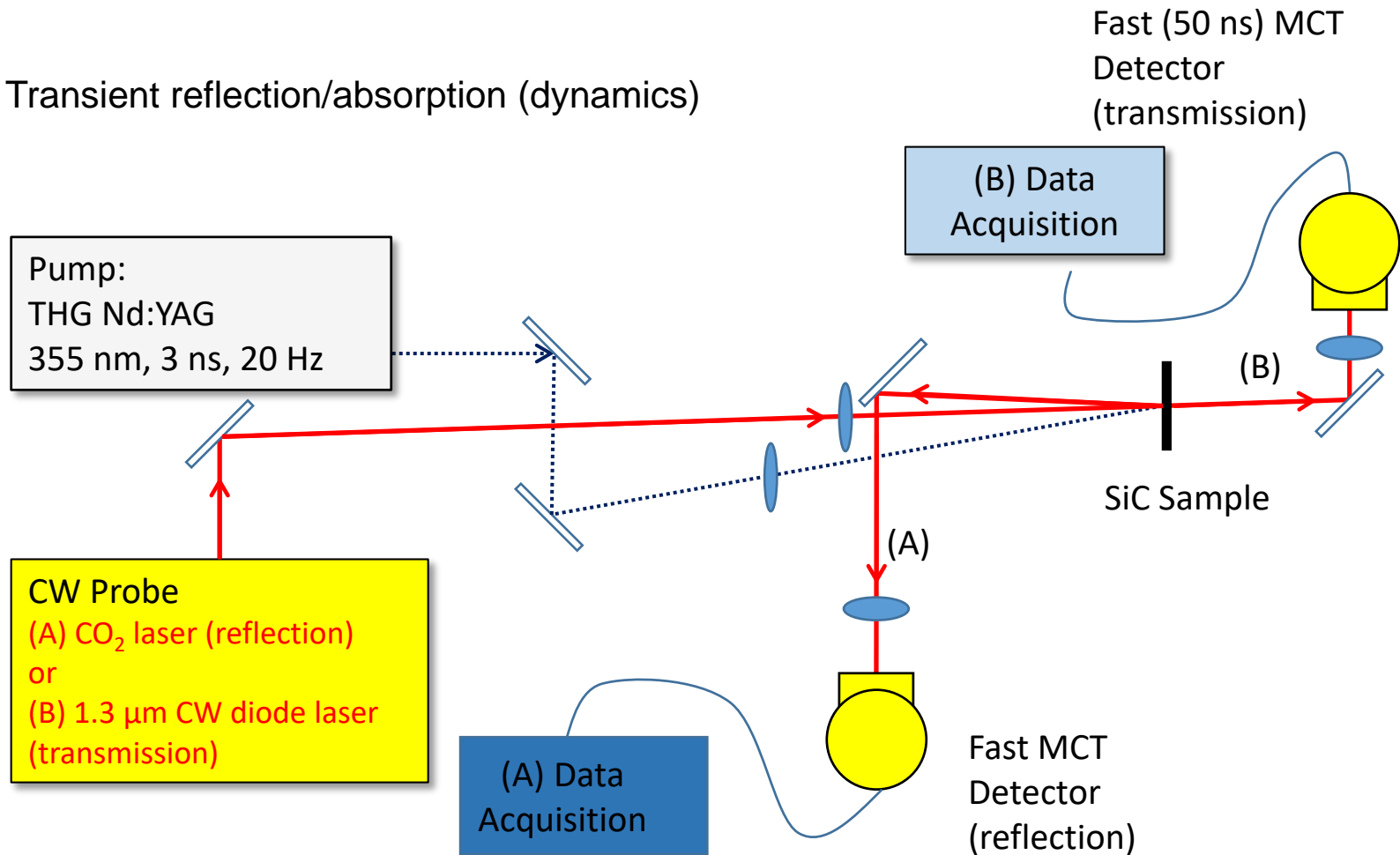
In air, resonance where $\epsilon' = -2$

Increasing N modifies ϵ'

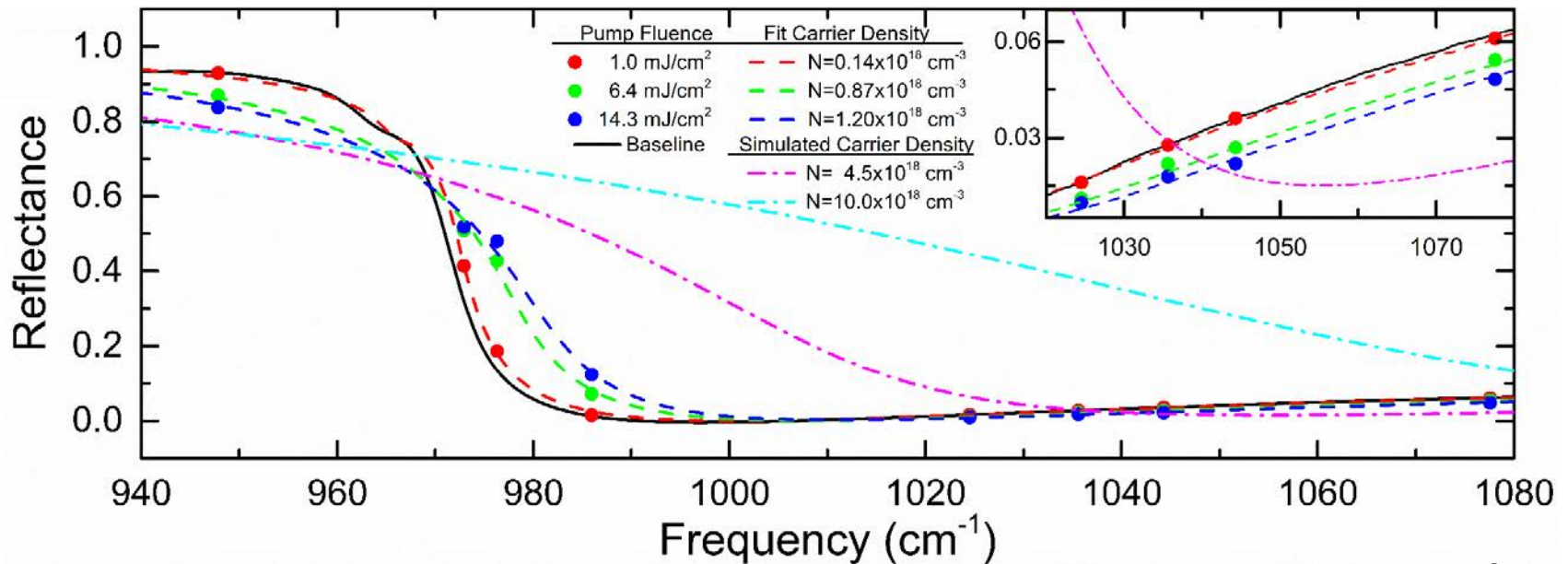


EXPERIMENTAL APPROACH

Transient reflection/absorption (dynamics)



TUNING RESTSTRAHLEN BAND



Spann, et al.
Phys. Rev. B 93 (2016)

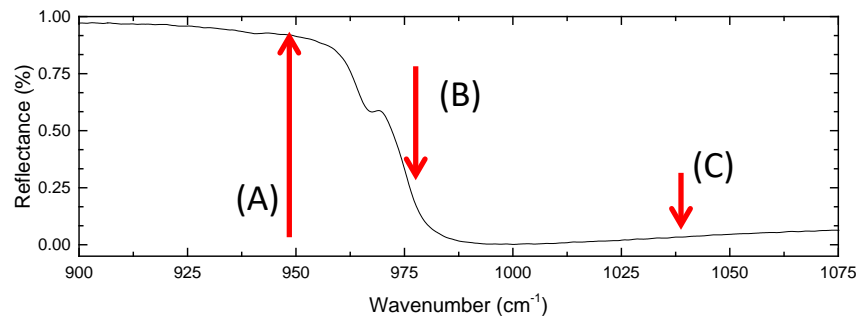
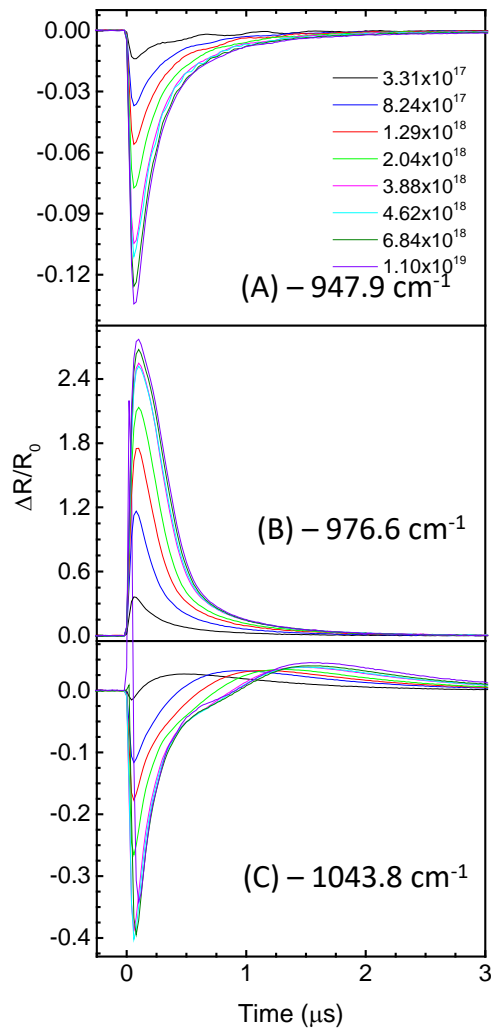
$$\varepsilon(\omega) = \varepsilon_{\infty} \left(1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\omega\gamma} \right) - \sum_{j=e,h} \frac{N_j e^2}{\varepsilon_0 m_j^* m_o} \frac{1}{\omega^2 + i\omega\Gamma}$$

Excite with 355 nm, probe with CO₂ laser

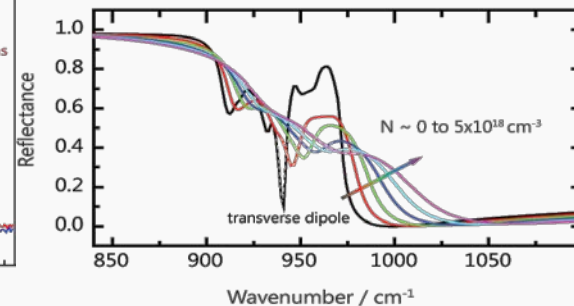
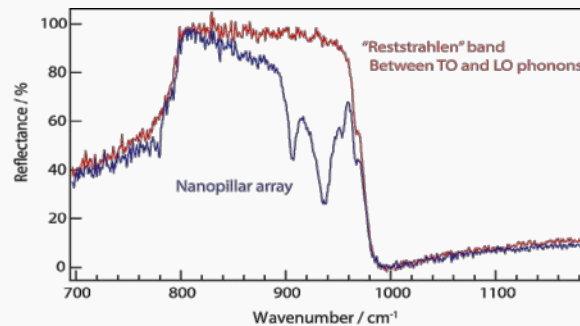
Reststrahlen band “softens” and shifts

Recovers with 700 ns carrier lifetime, but evidence for fast decay component (<100 ns)

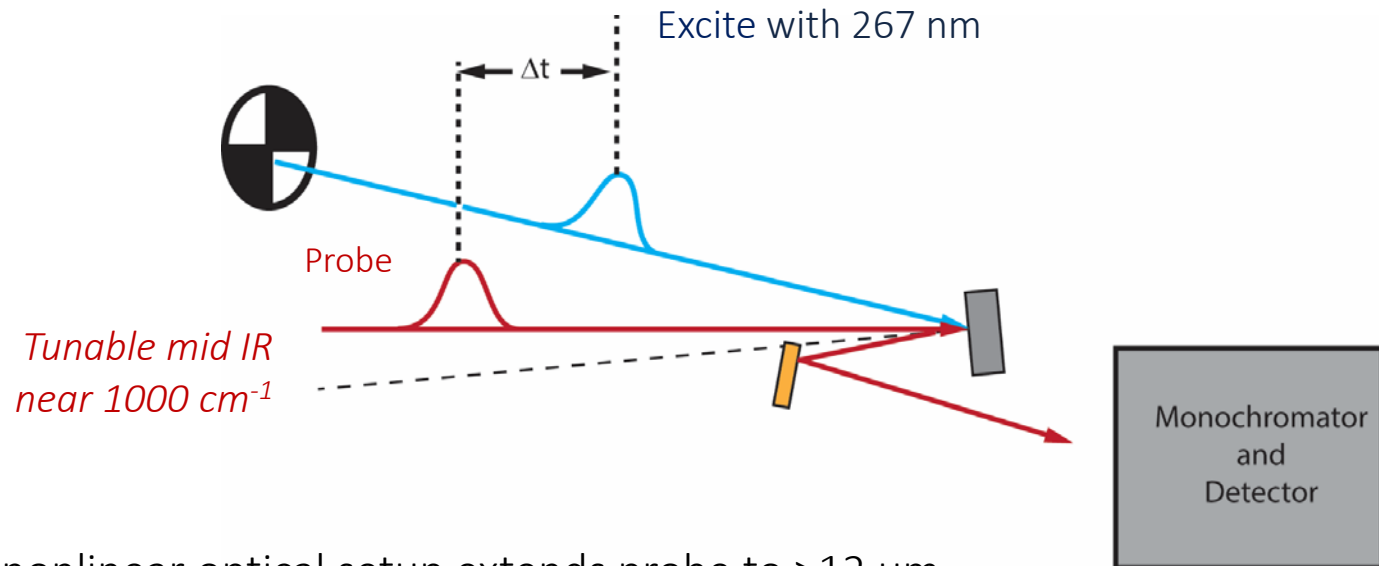
TRANSIENTS SHOW BULK PERMITTIVITY TUNING ON & NEAR RESTSTRAHLEN BAND



Too slow for nanoresonator tuning



ULTRAFAST IR TRANSIENT REFLECTION

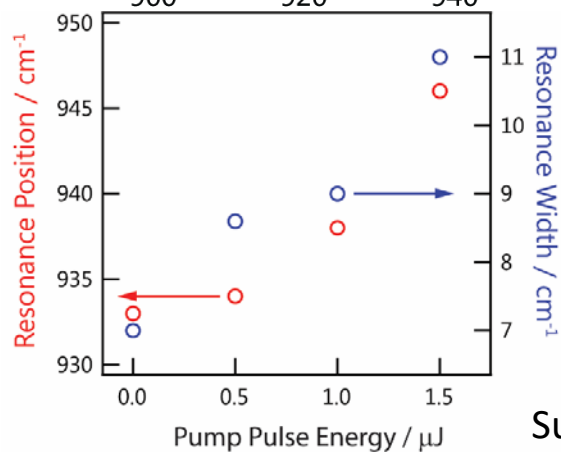
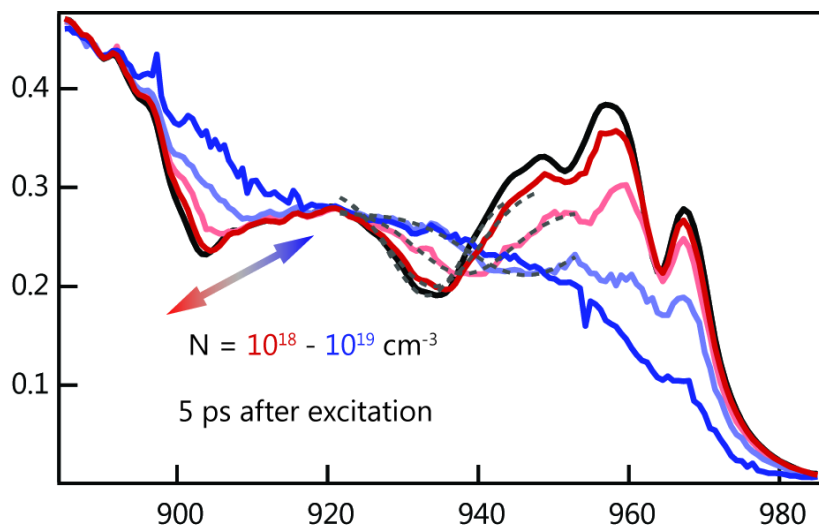


New nonlinear optical setup extends probe to >12 μm

Reflection at small angles is challenging

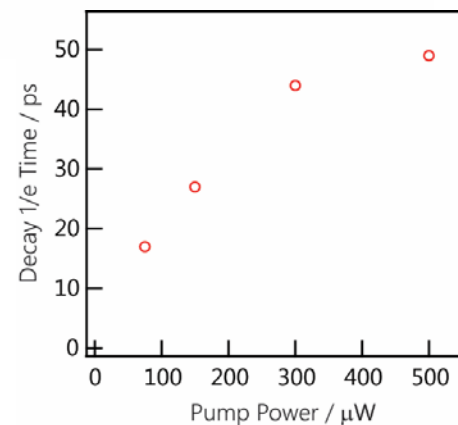
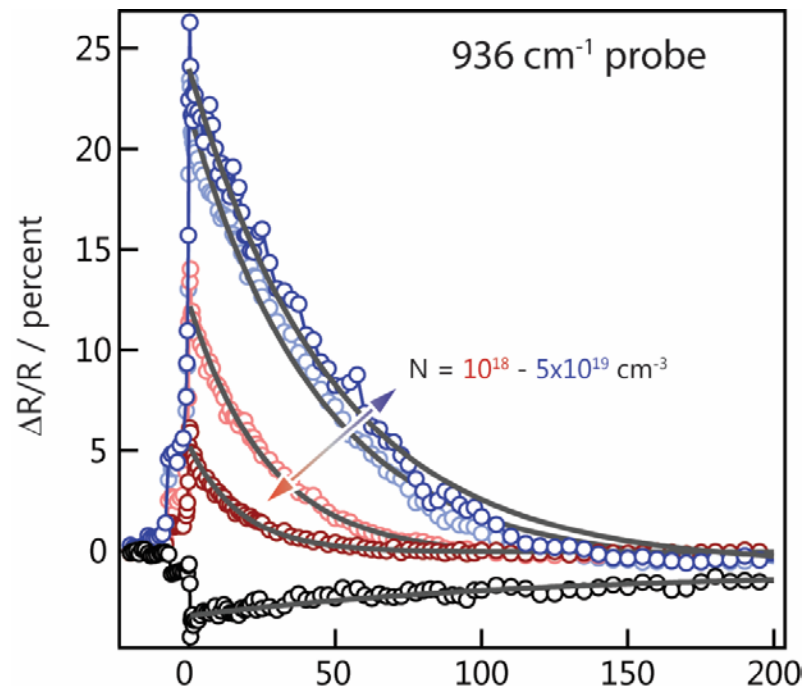
~ 200 fs time resolution

TUNING RESONANCES

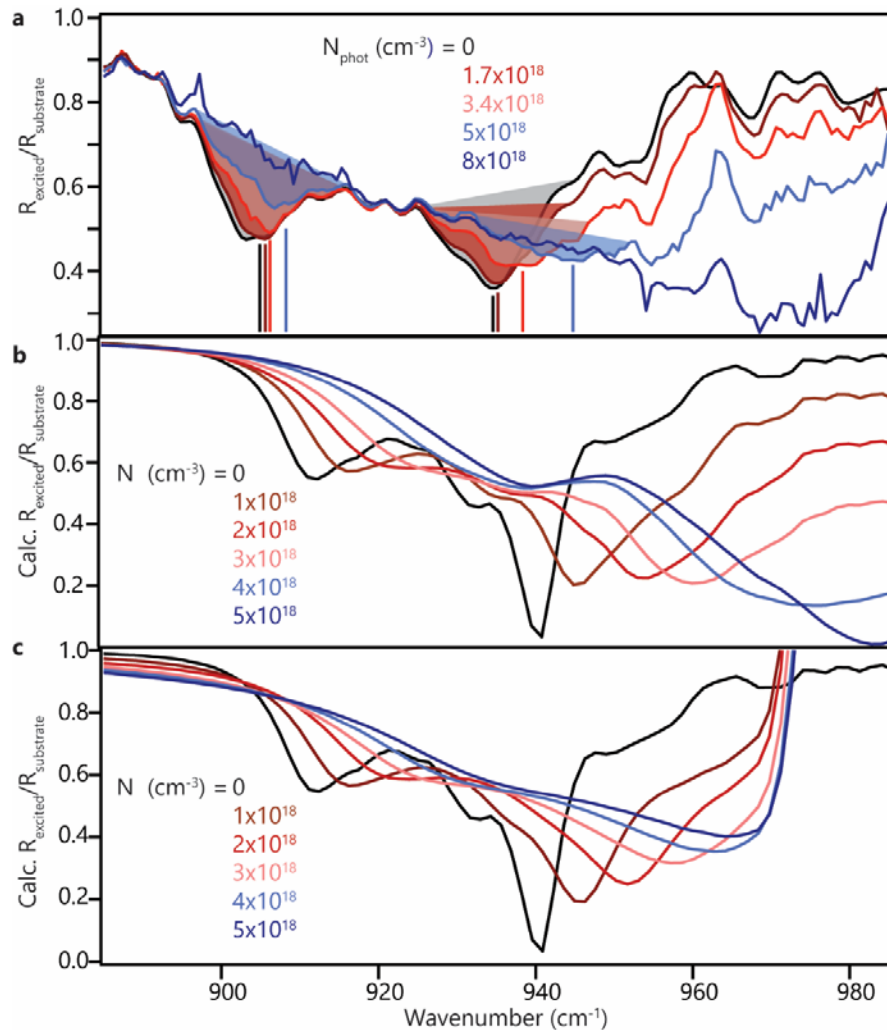


Why the fast decay quickly?
Carrier lifetime is 700 ns
Redistribution from
pillars to bulk?

Successful active tuning!
Modulation depth ($\delta\omega / \Delta\omega$) > 1

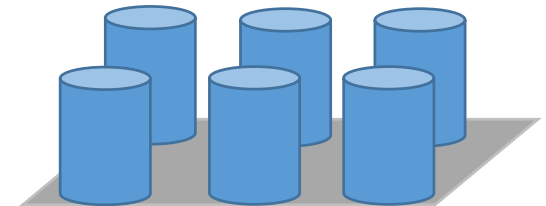


TUNING RESONANCES

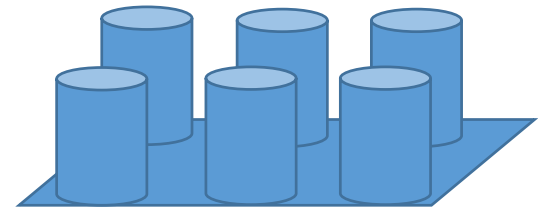


Observed

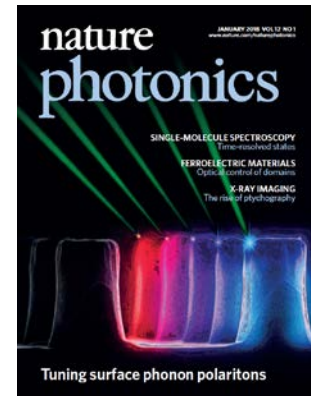
Calculated: carriers only in pillars



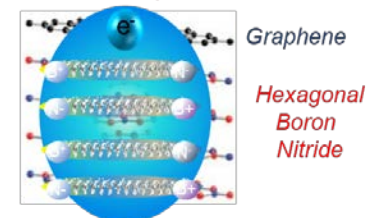
Calculated: carriers in pillars & substrate



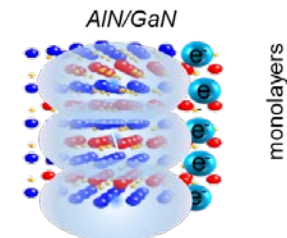
- SPhPs: Narrower Analog of Plasmonics
- Demonstrated active tuning
- Atomic-scale heterostructures for improved tunability in IR
Caldwell et al. Nature Nanotechnology 11, 9–15 (2016)
- Surface enhance infrared spectroscopy (SEIRA)
 - not as well developed as plasmonic SEIRA
 - biosensing
- Expanding to materials beyond semiconductors
 - inorganics
 - bio-related and biomaterials?



Electromagnetic Plasmon-Phonon Hybrids



Crystalline - Mixed Phonon Polaritons



NRL at AFOSR International Meetings

- 2012 AFOSR/ANFF
- 2014 Joint Services and OSD Africa Technical Exchange Meeting



- 2014 AFOSR/NIH/NCR Technical Exchange Meeting
- 2015 Enabling Technologies Technical Exchange Meeting (ANFF)
- 2015 International Basic Research Infrastructure Meeting

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SPhPs in SiC

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