Real-space observation of flat-band ultrastrong coupling between optical phonons and surface plasmon polaritons

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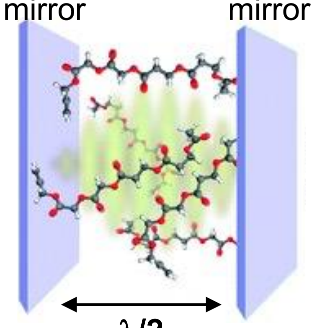
Nanooptics Group

Strong coupling can change chemical reaction rates

Molecules in IR cavity



Tilting a ground-state reactivity landscape by vibrational strong coupling

A. THOMAS, L. LETHUILLIER-KARL, K. NAGARAJAN, R. M. A. VERGAUWE, J. GEORGE, T. CHERVY, A. SHALABNEY, E. DEVAUX, C. GENET, J. MORAI..., AND T. W. EBBESEN fewer Authors Info & Affiliations

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Modification of ground-state chemical reactivity via light–matter coherence in infrared cavities

WONMI AHN, JOHAN F. TRIANA, FELIPE RECABAL, FELIPE HERRERA, AND BLAKE S. SIMPKINS Authors Info & Affiliations

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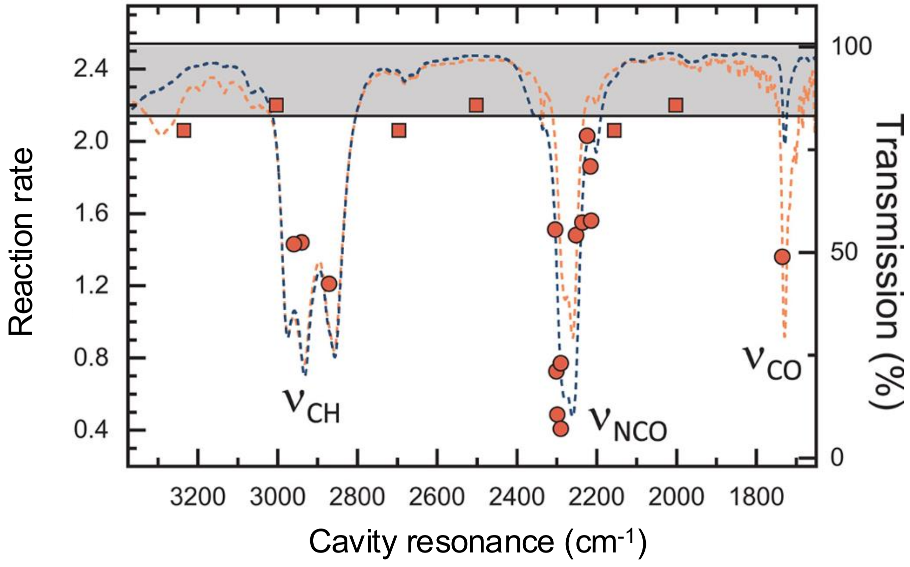

Outline

Introduction

- Strong coupling explained by coupled harmonic oscillators model
- Light dispersion to describe light-matter coupling

Results

- Theoretical prediction of flat-band coupling
- s-SNOM principle and measurements of polariton dispersion
- Experiment validation of flat-band strong coupling
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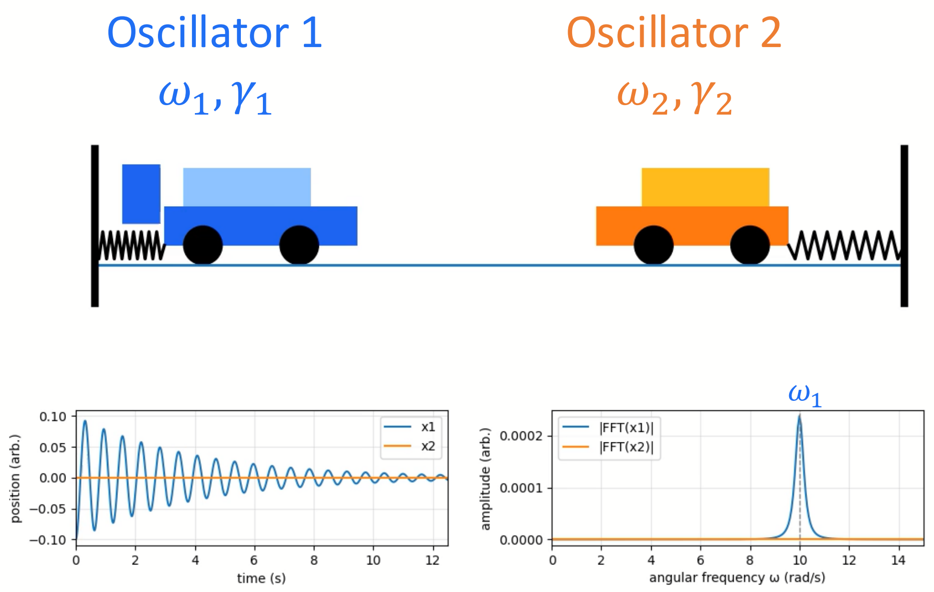
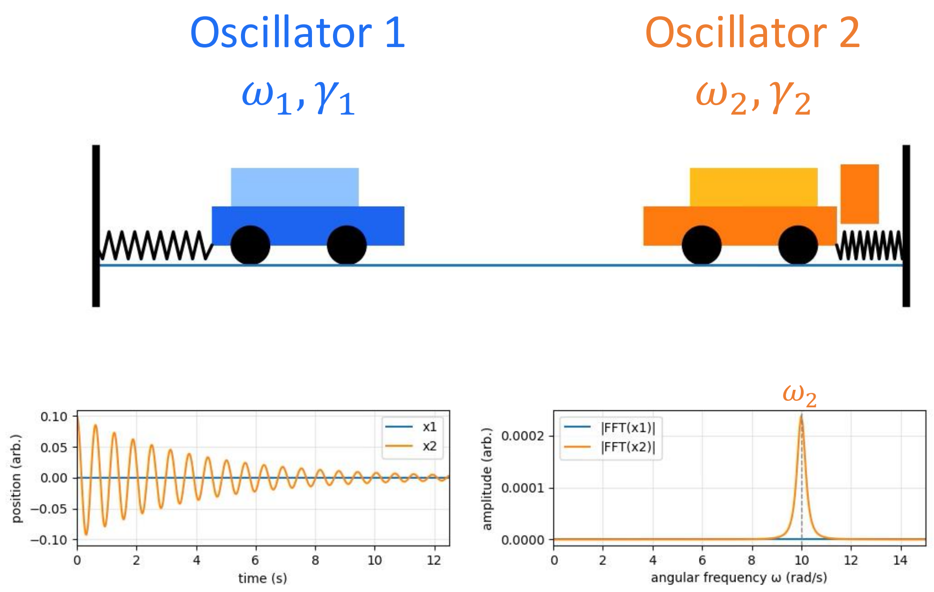
Two harmonic oscillators





Harmonic oscillator 1

$$\ddot{x}_1 + \omega_1^2 x_1 + \gamma_1 \dot{x}_1 = 0$$
$$x_1(t) = Ae^{i(\omega_1 + i\gamma_1)\,t}$$

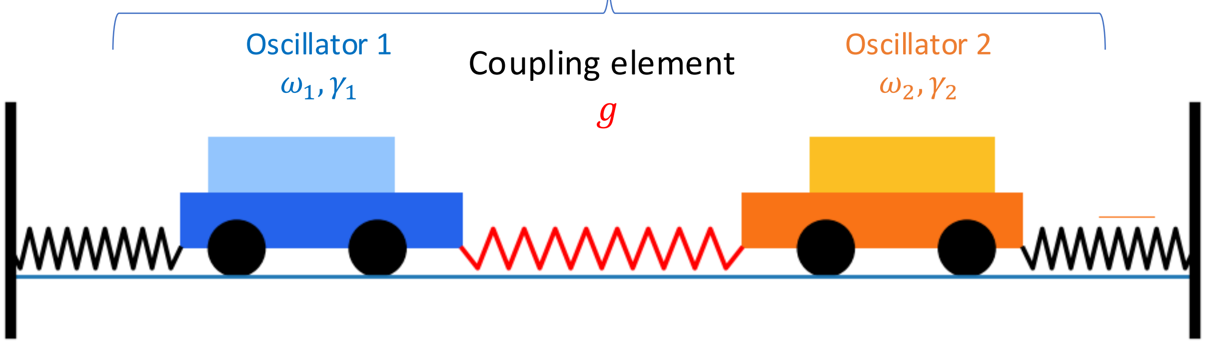
Harmonic oscillator 2

$$\ddot{x}_2 + \omega_2^2 x_2 + \gamma_2 \dot{x}_2 = 0$$
$$x_2(t) = Ae^{i(\omega_2 + i\gamma_2)\,t}$$

Two coupled harmonic oscillators

Hybrid system

$\omega_{\pm}$



Coupled harmonic oscillator model

$$\ddot{x}_1 + \omega_1^2 x_1 + \gamma_1 \dot{x}_1 + 2g\omega_1 x_2 = 0$$
$$\ddot{x}_2 + (\omega_2^2 + 4g^2) x_2 + \gamma_2 \dot{x}_2 + 2g\omega_1 x_1 = 0$$

$$x_1(t) = A_{\pm,1} e^{i(\omega_{\pm} + i\gamma_{\pm})\,t}$$
$$x_2(t) = A_{\pm,2} e^{i(\omega_{\pm} + i\gamma_{\pm})\,t}$$

$$\omega_{\pm}(k) = \frac{1}{\sqrt{2}} \sqrt{(\omega_1^2 + \omega_2^2 + 4g^2) \pm \sqrt{(\omega_1^2 + \omega_2^2 + 4g^2)^2 - 4\omega_1^2\omega_2^2}}$$

Weak coupling:

$$g < \frac{\gamma_1 + \gamma_2}{4}$$

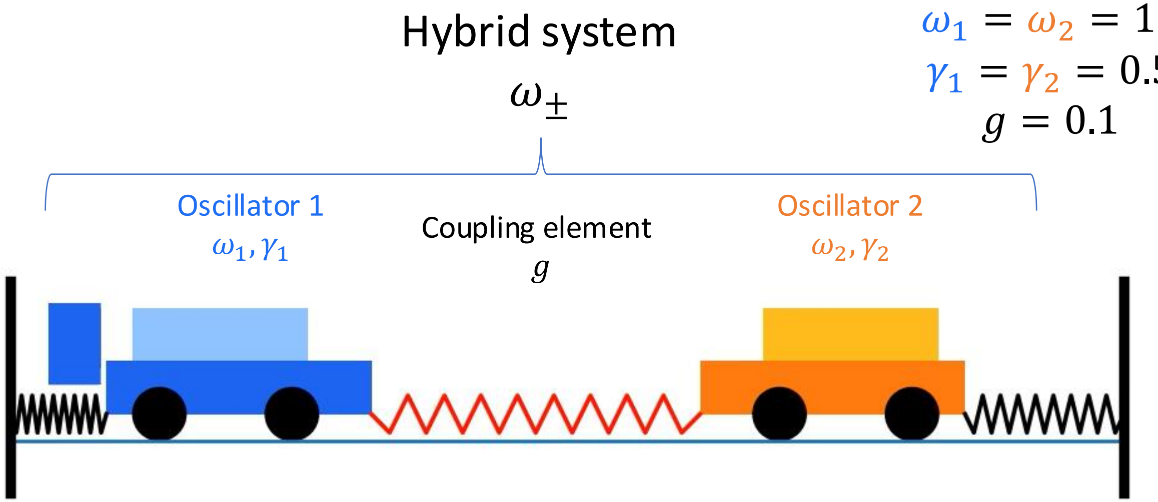
Strong coupling:

$$g > \frac{\gamma_1 + \gamma_2}{4}$$

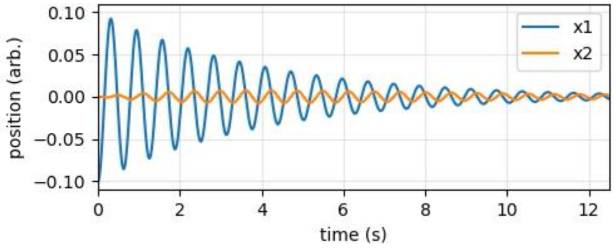
Ultrastrong coupling:

$$g > 0.1\omega_1$$

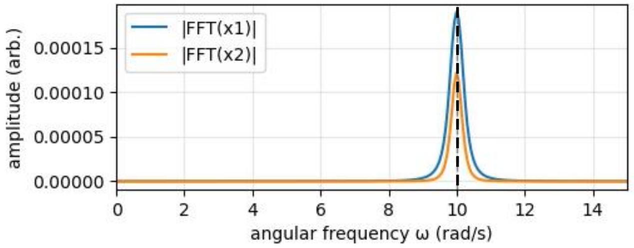
Weak coupling



$$\omega_1 = \omega_2 = 10$$
$$\gamma_1 = \gamma_2 = 0.5$$
$$g = 0.1$$



$\omega_\pm \cong \omega_1 = \omega_2$



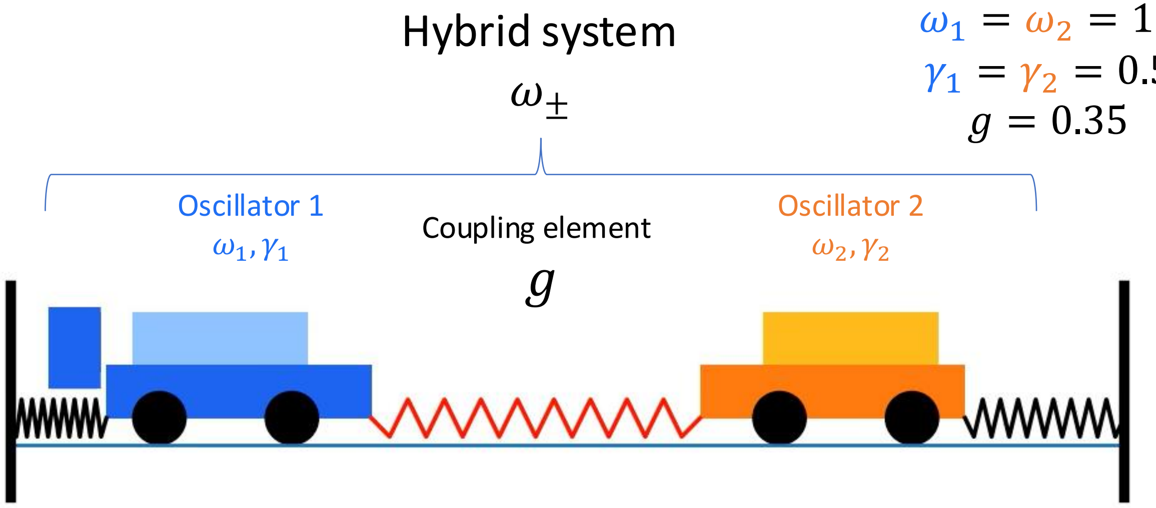
- Line broadening or narrowing
- Intensity changes

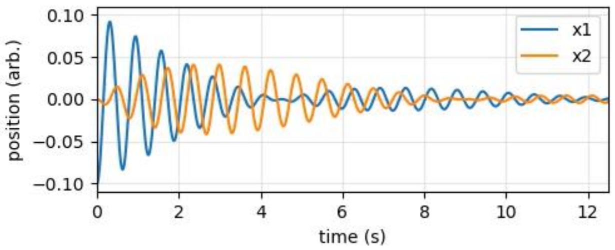
Weak coupling:

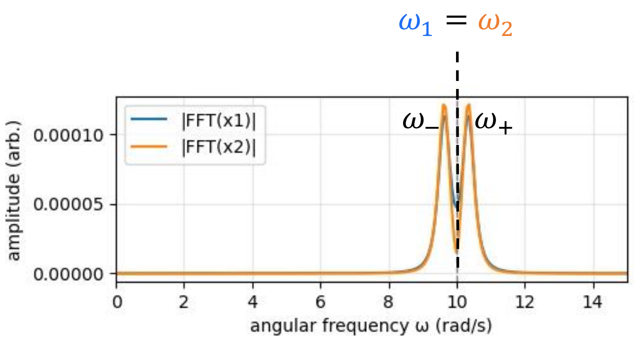
$$g < \frac{\gamma_1 + \gamma_2}{4}$$

Strong coupling

$$\omega_1 = \omega_2 = 10$$
$$\gamma_1 = \gamma_2 = 0.5$$
$$g = 0.35$$







- New hybrid system frequencies
- Frequency splitting

Strong coupling:

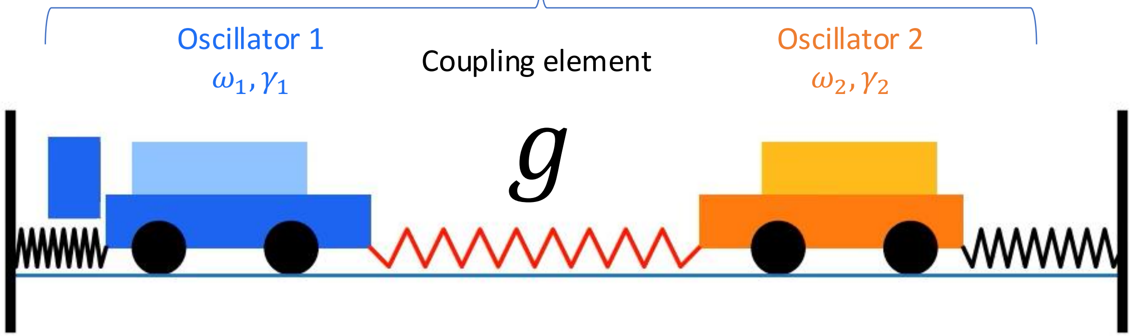
$$g > \frac{\gamma_1 + \gamma_2}{4}$$

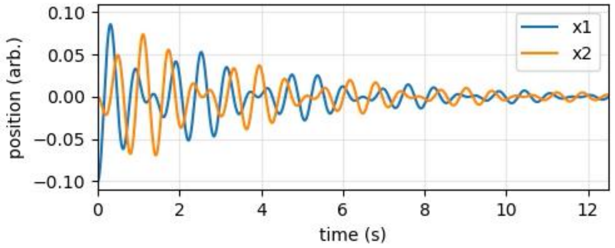
Ultrastrong Coupling

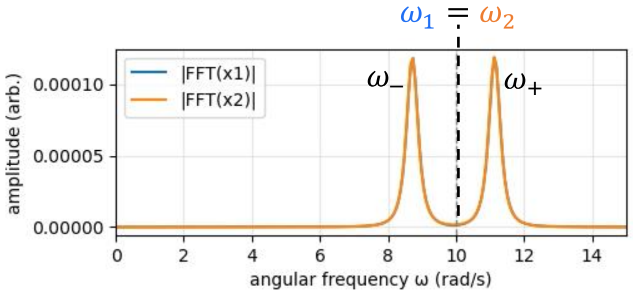
Hybrid system

$\omega_{\pm}$

$$\omega_1 = \omega_2 = 10$$
$$\gamma_1 = \gamma_2 = 0.5$$
$$g = 1$$







- New hybrid system frequencies
- Larger frequency shift

Ultrastrong coupling:

$$g > 0.1\omega_1$$

$\omega_1 \neq \omega_2$

$\omega_1 = 9$
$\omega_2 = 10$
$\gamma_1 = \gamma_2 = 0.5$
$g = 0.35$

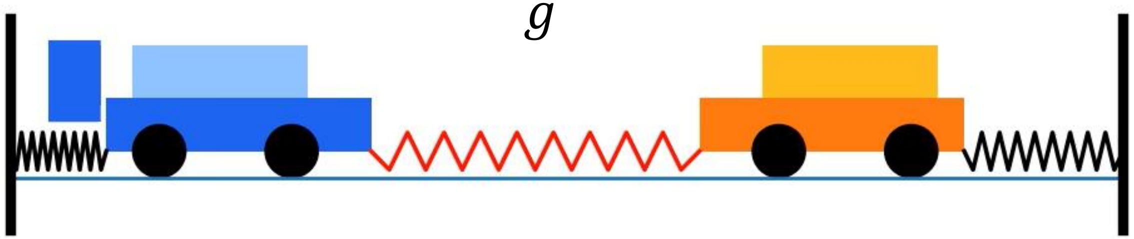
Hybrid system

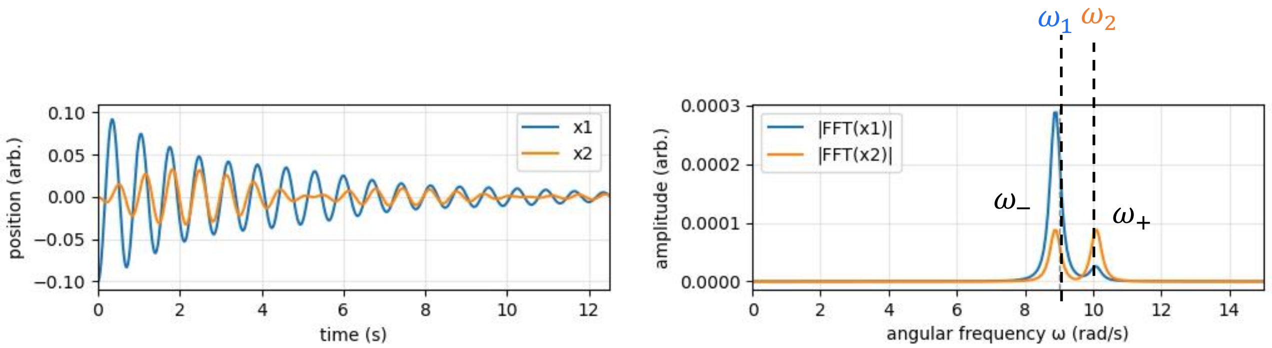
$\omega_\pm$

Oscillator 1
ω_1, γ_1

Coupling element
g

Oscillator 2
ω_2, γ_2

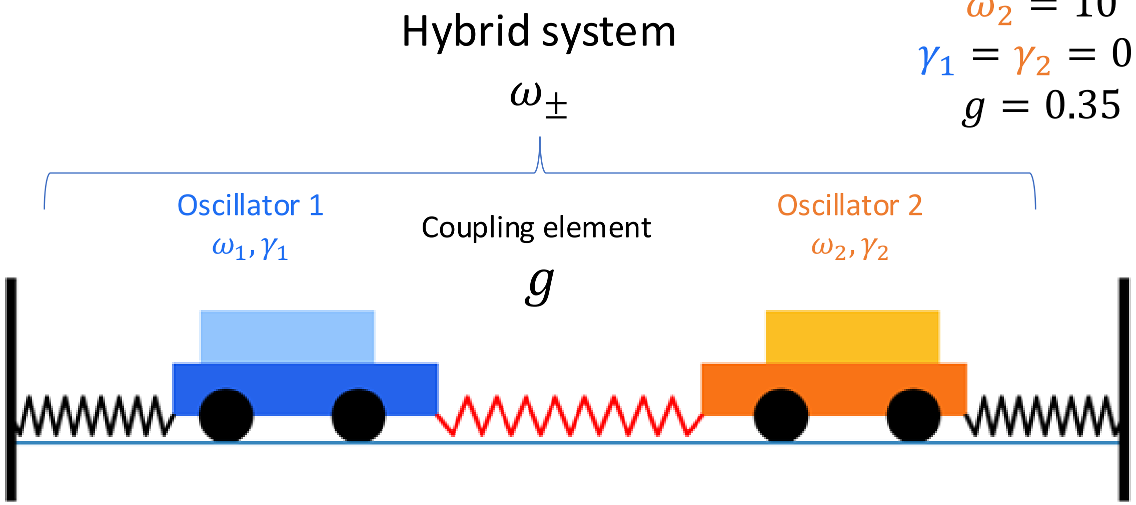


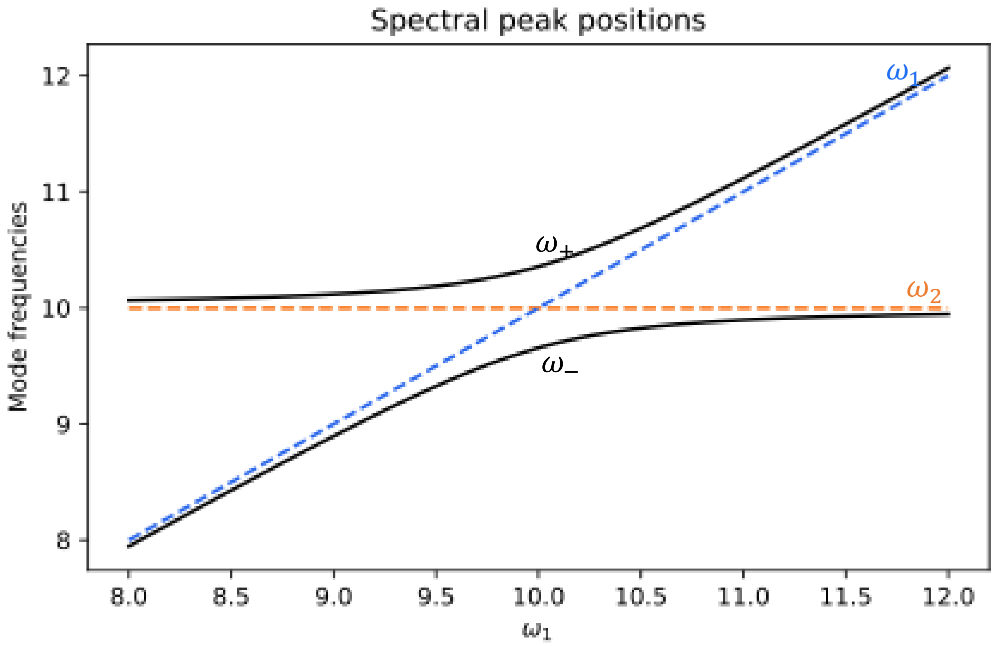


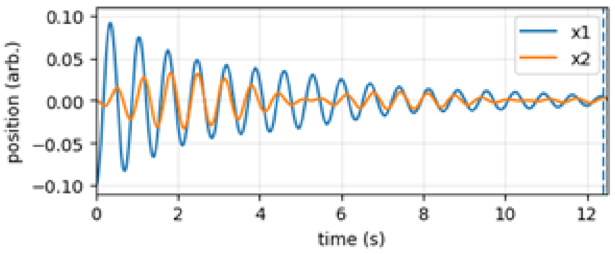
Hybrid system frequencies coincide with isolated system frequencies

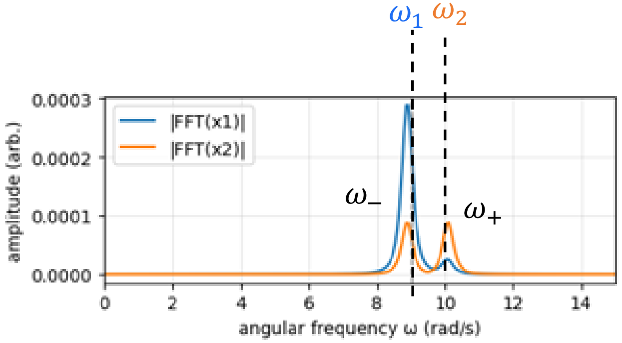
Detuning study

ω_1 varying
$\omega_2 = 10$
$\gamma_1 = \gamma_2 = 0.5$
$g = 0.35$







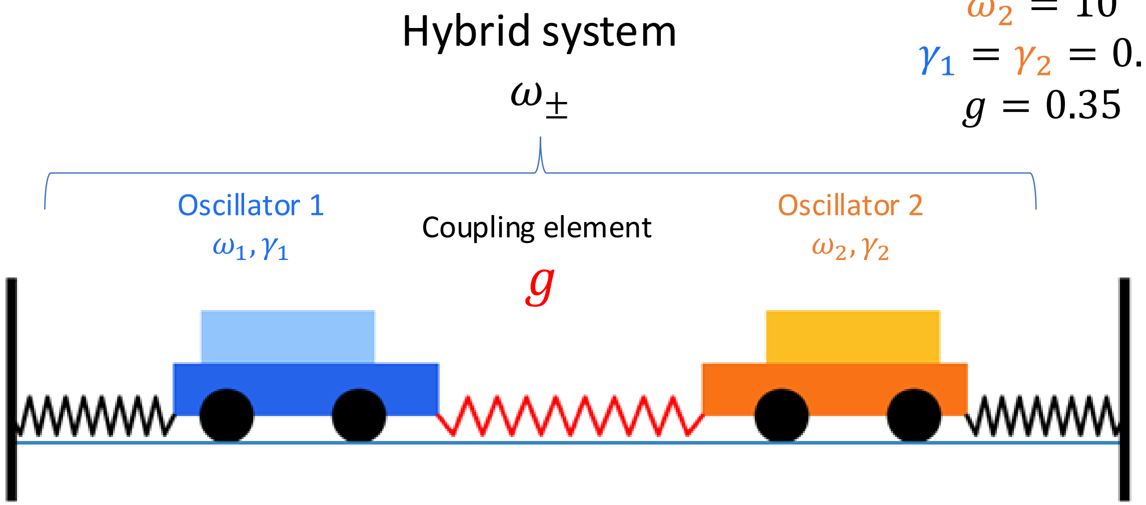


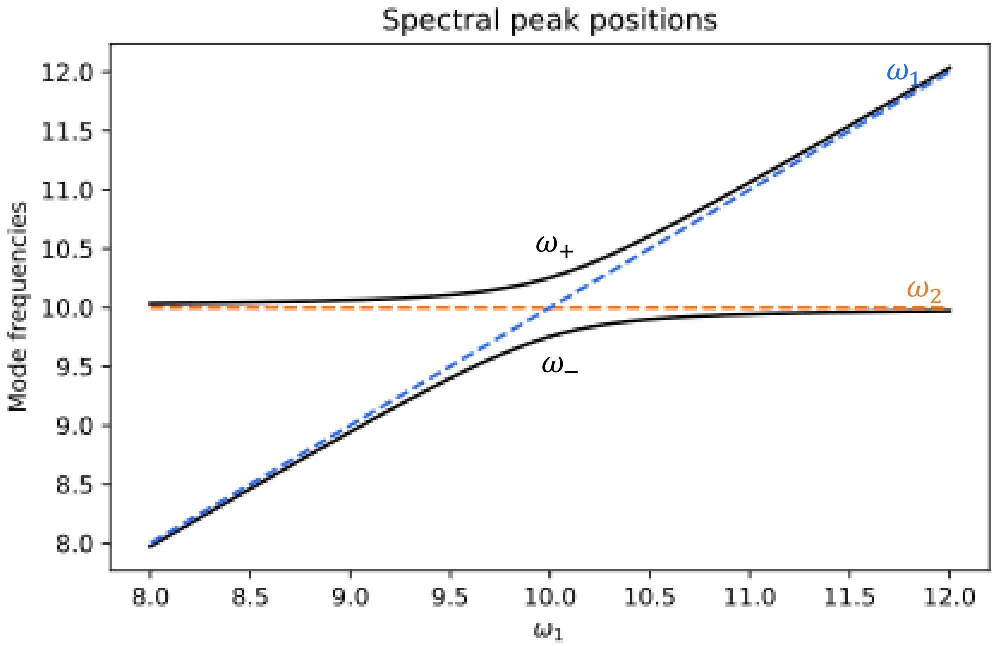
Observations:

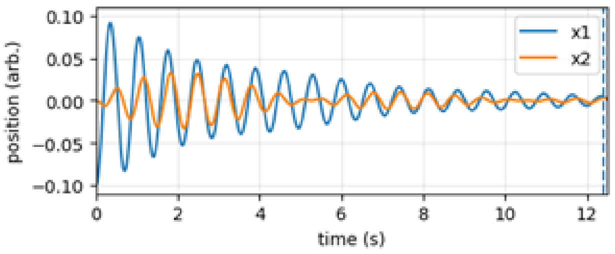
- Anticrossing at $\omega_1 = \omega_2$
- Maximum splitting = $2g$
- At high detuning, hybrid mode light uncoupled modes

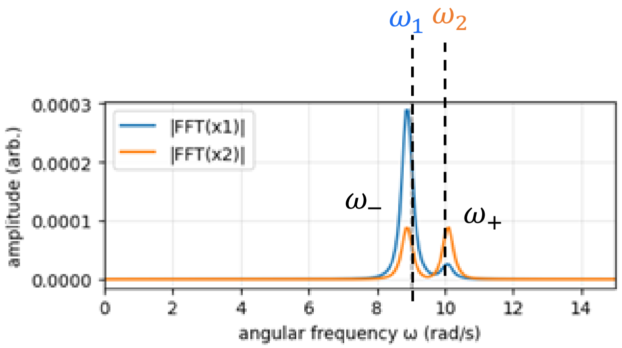
Detuning study

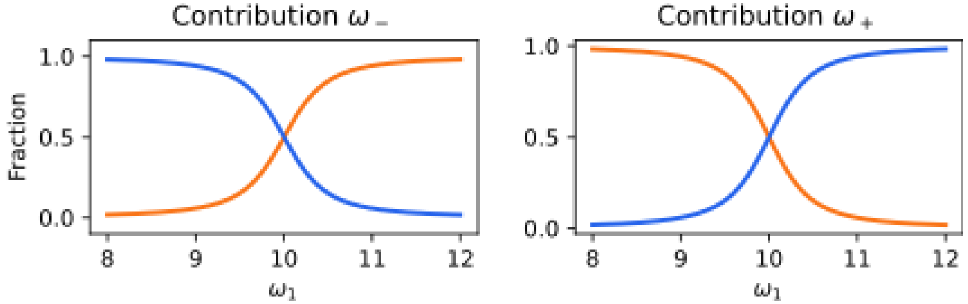
ω_1 varying
$\omega_2 = 10$
$\gamma_1 = \gamma_2 = 0.5$
$g = 0.35$











Contributions

$$\Sigma_1(\omega_+) = \frac{|X_1(\omega_+)|^2}{|X_1(\omega_+)|^2 + |X_2(\omega_+)|^2}$$

$$\Sigma_2(\omega_+) = \frac{|X_2(\omega_+)|^2}{|X_1(\omega_+)|^2 + |X_2(\omega_+)|^2}$$

Spectral peak intensity ratio

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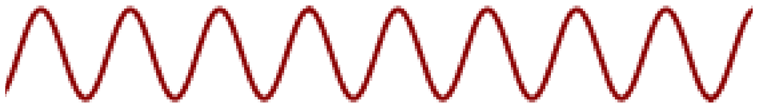
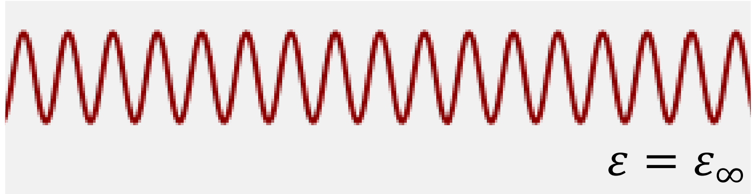
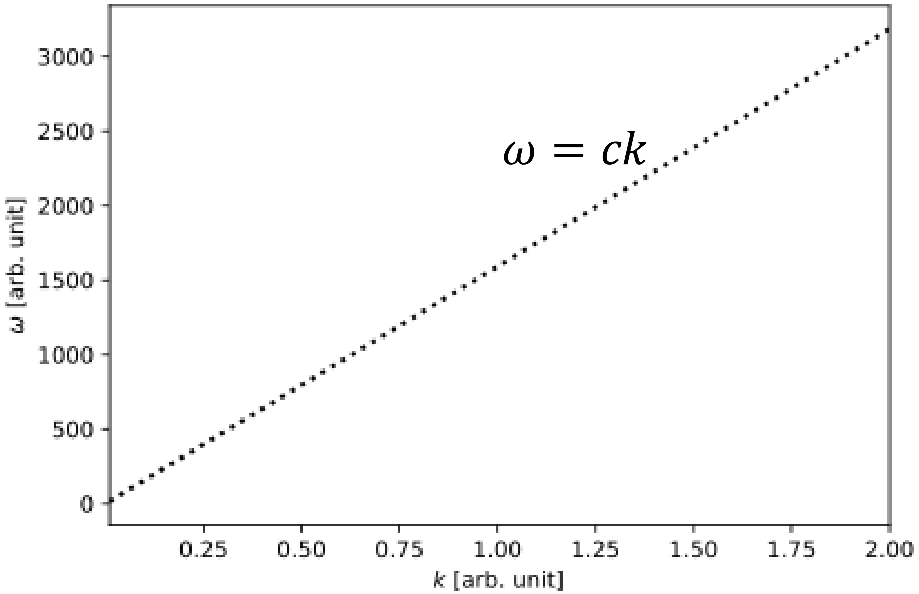
Light dispersion describe how frequency and wavelength are related

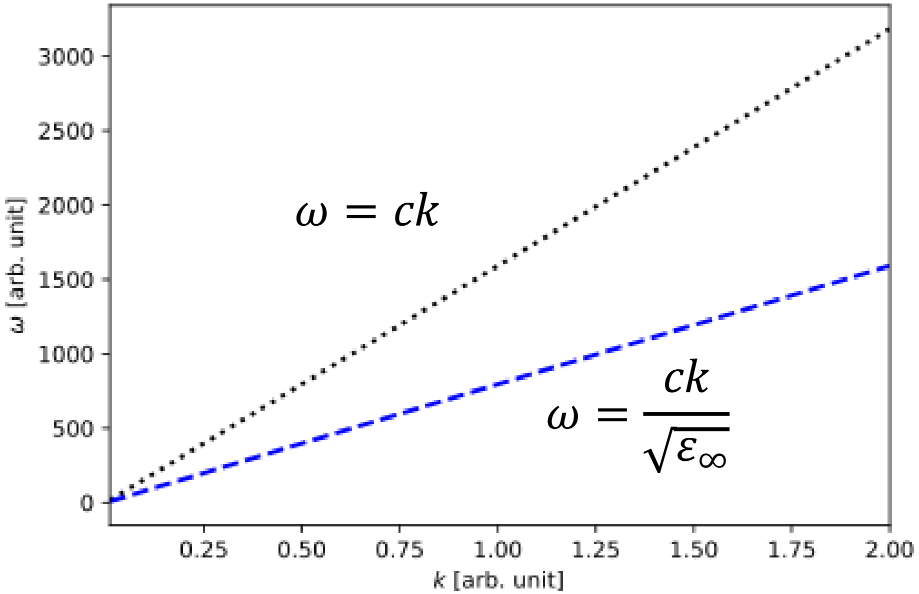




Light dispersion in vacuum



Light dispersion in a dielectric

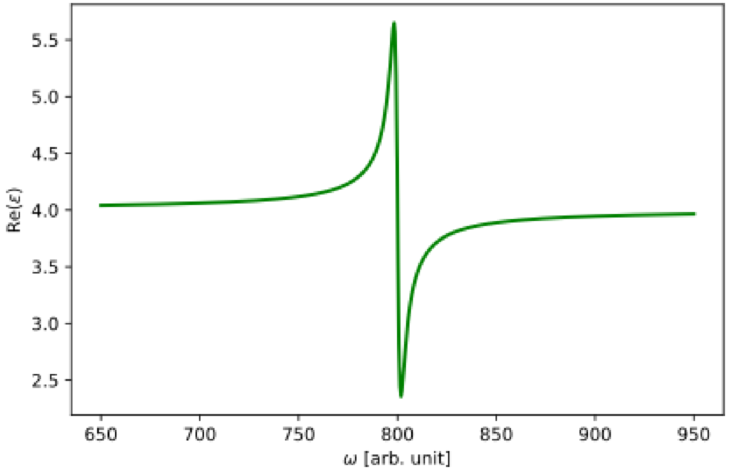


$$\omega = 2\pi f \qquad k = \frac{2\pi}{\lambda}$$

Light dispersion in presence of vibrational mode

dielectric function of a vibration mode

$$\varepsilon(\omega) = \varepsilon_\infty \left(1 + \frac{A^2}{(\omega^2 - \omega_0^2 - i\gamma\omega)}\right)$$



Light dispersion in presence of a vibrational mode

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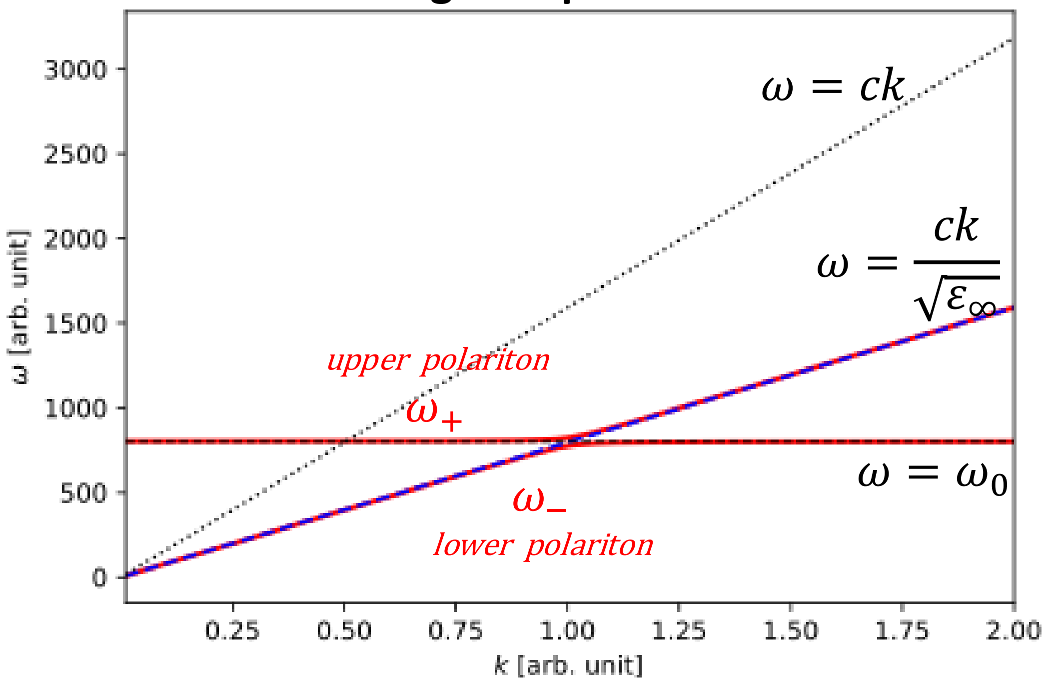
Light dispersion equation

$$\omega = \frac{ck}{\sqrt{\varepsilon(\omega)}}$$

Two solutions
- $\omega_+(k)$: upper polariton
- $\omega_-(k)$: lower polariton

Light dispersion



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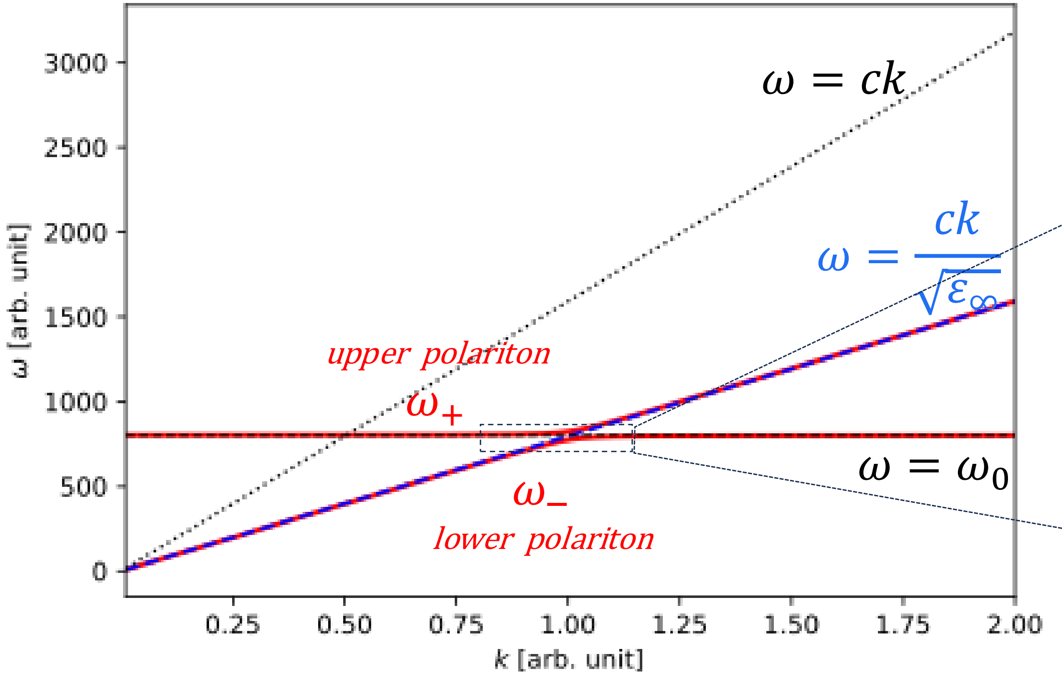

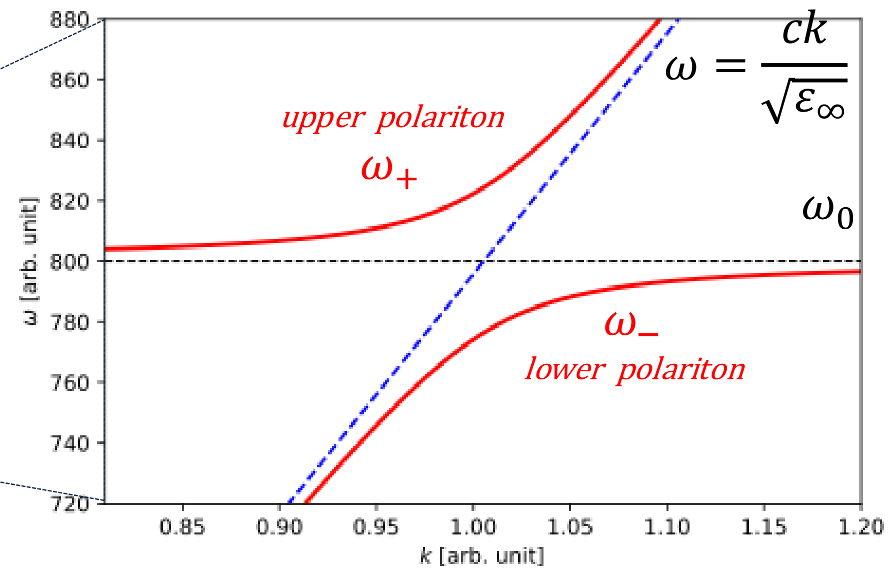

It resemble detuning study of coupled harmonic oscillator

Coupled harmonic oscillators to describe light dispersion in presence of a vibrational mode

Coupled harmonic oscillator model

$$\ddot{x}_1 + \omega_1^2 x_1 + 2g\omega_1 x_{m2} = 0$$
$$\ddot{x}_2 + (\omega_2^2 + 4g^2)x_2 + +\gamma\dot{x}_2 + 2g\omega_1 x_1 = 0$$

$$\omega_\pm(k) = \frac{1}{\sqrt{2}}\sqrt{(\omega_1^2(k) + \omega_2^2 + 4g^2) \pm \sqrt{(\omega_1^2(k) + \omega_2^2 + 4g^2)^2 - 4\omega_1^2(k)\omega_2^2}}$$

$$\omega_1(k) = \frac{ck}{\sqrt{\varepsilon_\infty}}$$

$$\omega_2 = \omega_0$$

$$g = \frac{A}{\sqrt{\varepsilon_\infty}}$$

$\Rightarrow$ $\omega_+(k)$, $\omega_-(k)$

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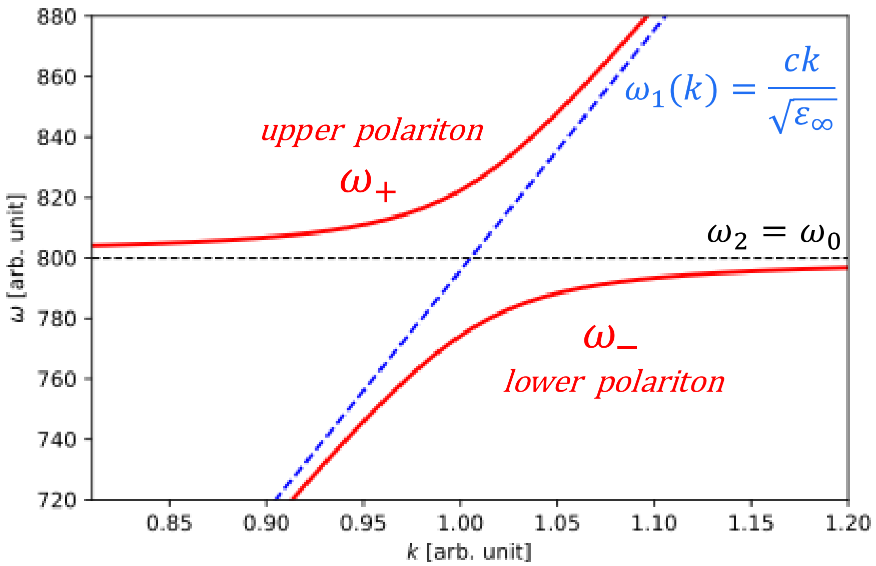
$$g = \frac{A}{\sqrt{\varepsilon_\infty}}$$

$$\omega_+(k)$$

$$\omega_-(k)$$



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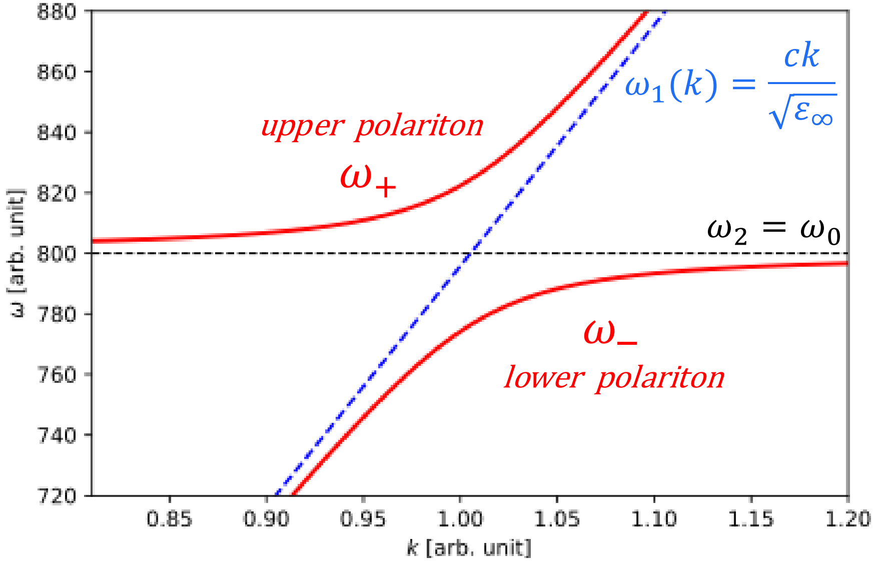
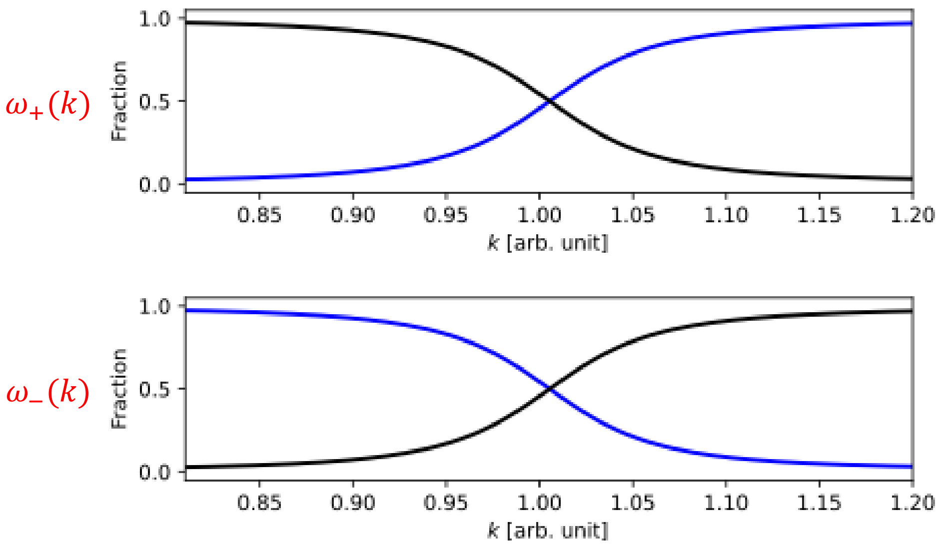


Contributions



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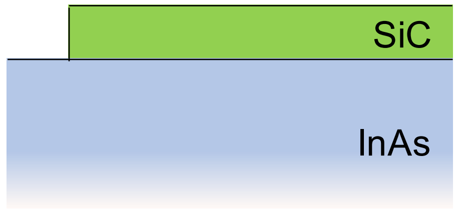
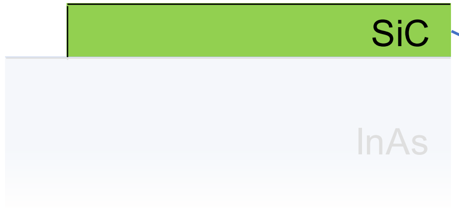
We want to study strong coupling between phonons in SiC and surface plasmon polariton in InAs

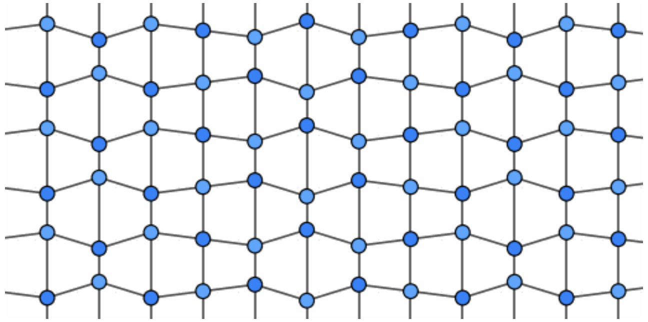


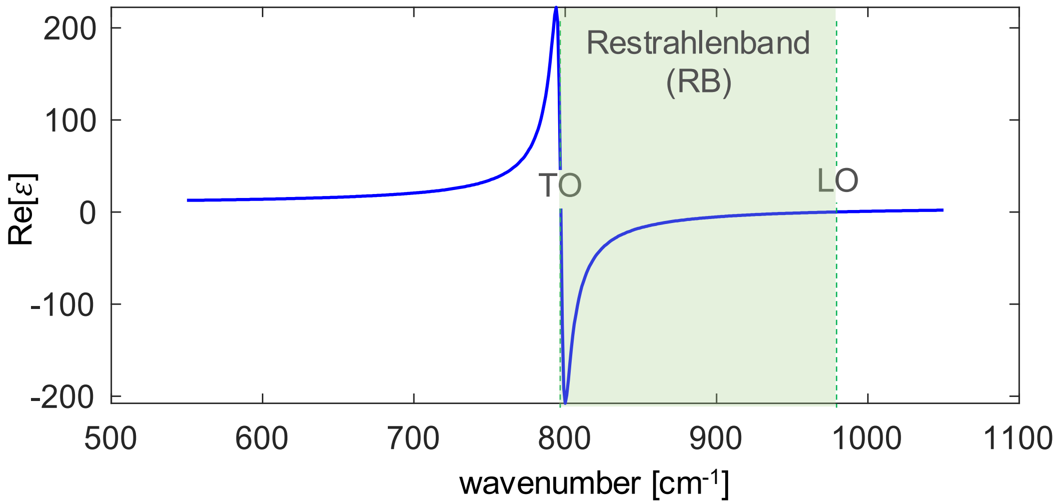
SiC has TO phonons (high oscillator strength)

SiC: polar crystal, supports strong optical phonons at mid-IR frequencies



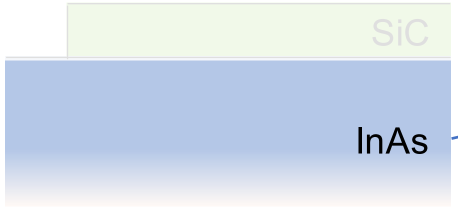
Lattice vibrational mode





TO frequency: 797 cm^{-1}

InAs supports surface plasmon polaritons

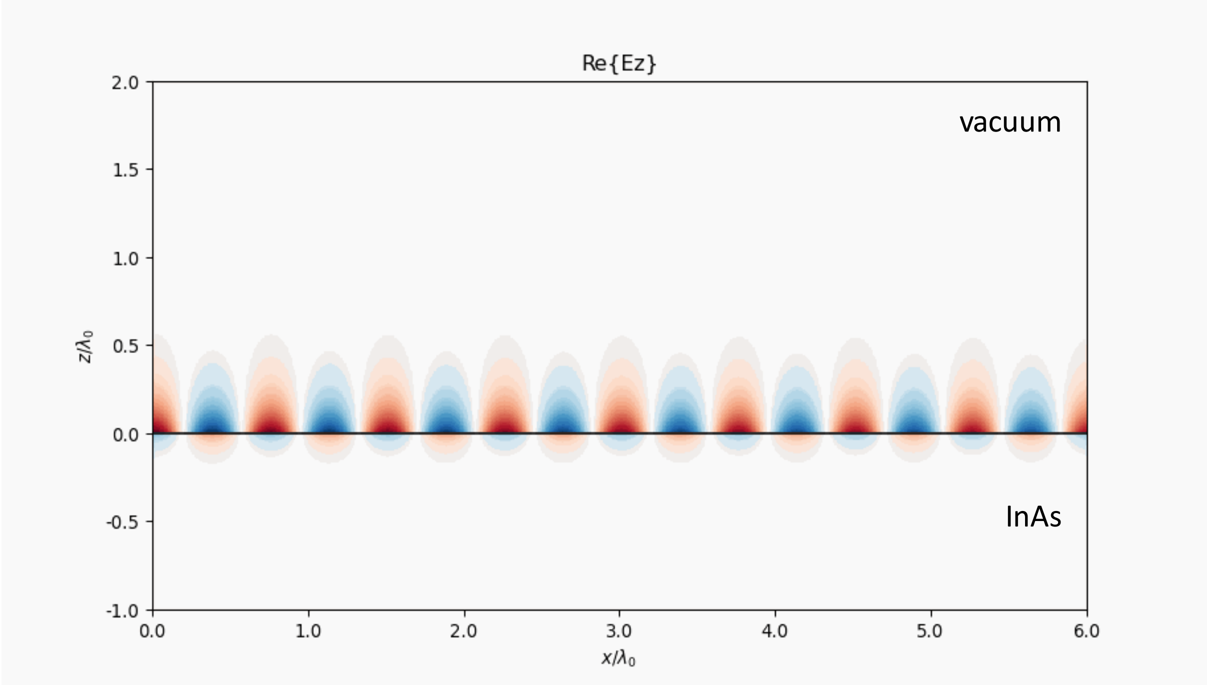


InAs: semiconductor, supports mid-IR SPPs when doped highly enough

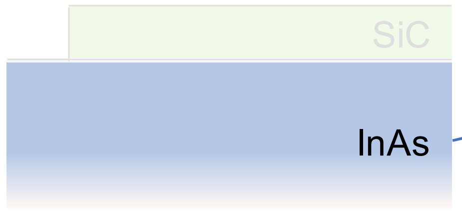
$$\varepsilon(\omega) = \varepsilon_{\infty}\left(1 - \frac{\omega_P^2}{\omega^2 + i\gamma\omega}\right) \qquad \omega_P^2 = \frac{n e^2}{\varepsilon_0 \varepsilon_{\infty} m^* m_0}$$

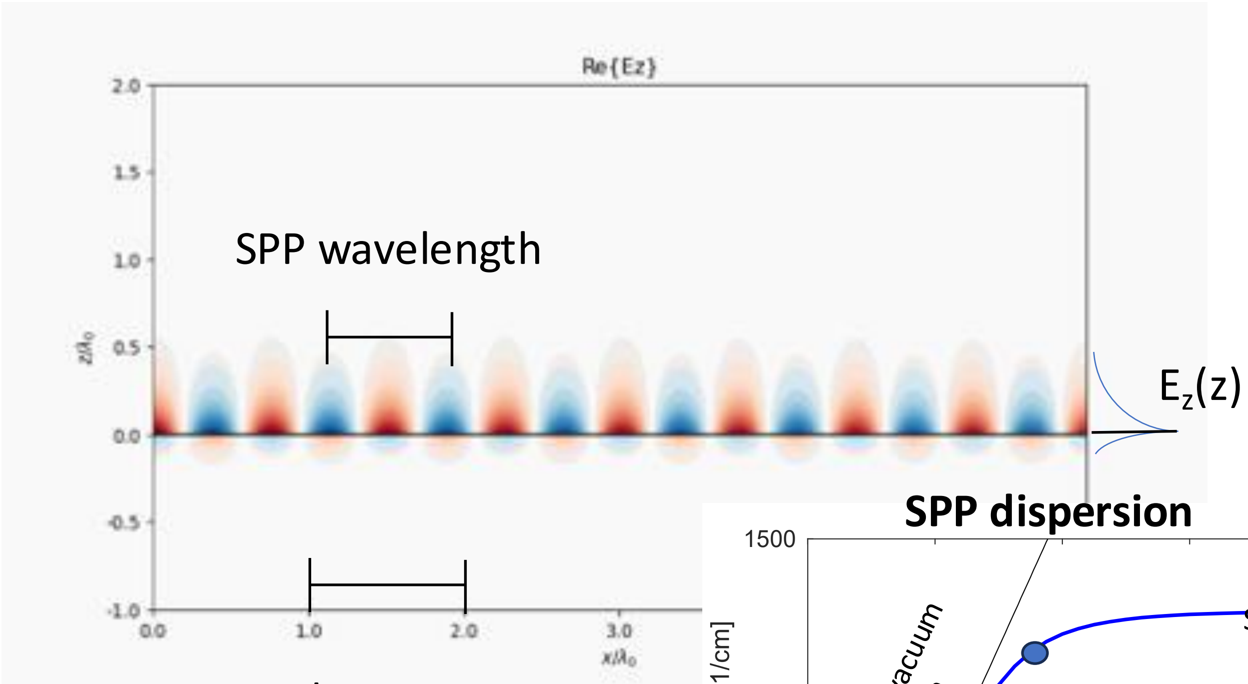
n: carrier concentration

Surface plasmon polariton are surface confined wave between a metal (doped semiconductor) and a dielectric

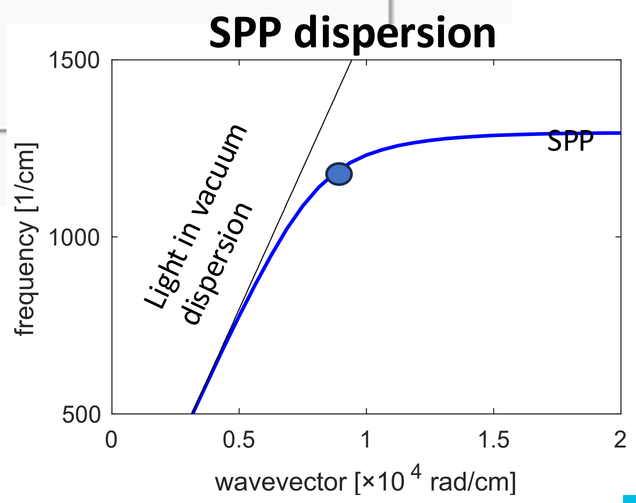


Surface plasmon polariton are confined surface waves with higher wavevector compared to free-space light.





Light in vacuum wavelength



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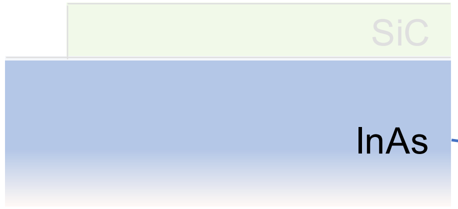
InAs surface plasmon polaritons are tunable by doping

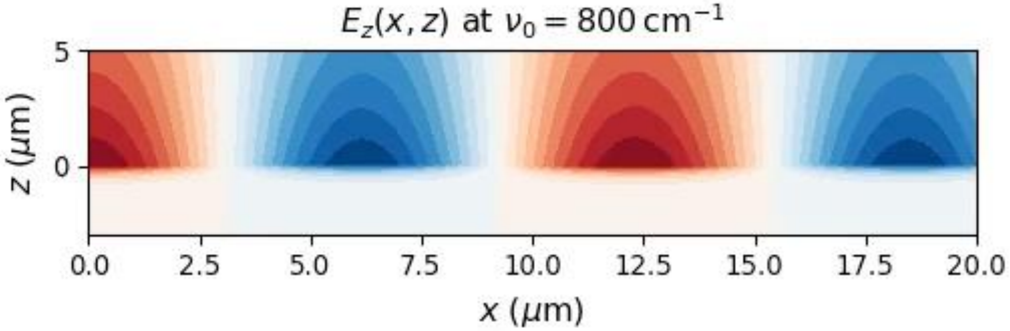


InAs: semiconductor, supports mid-IR SPPs when doped highly enough

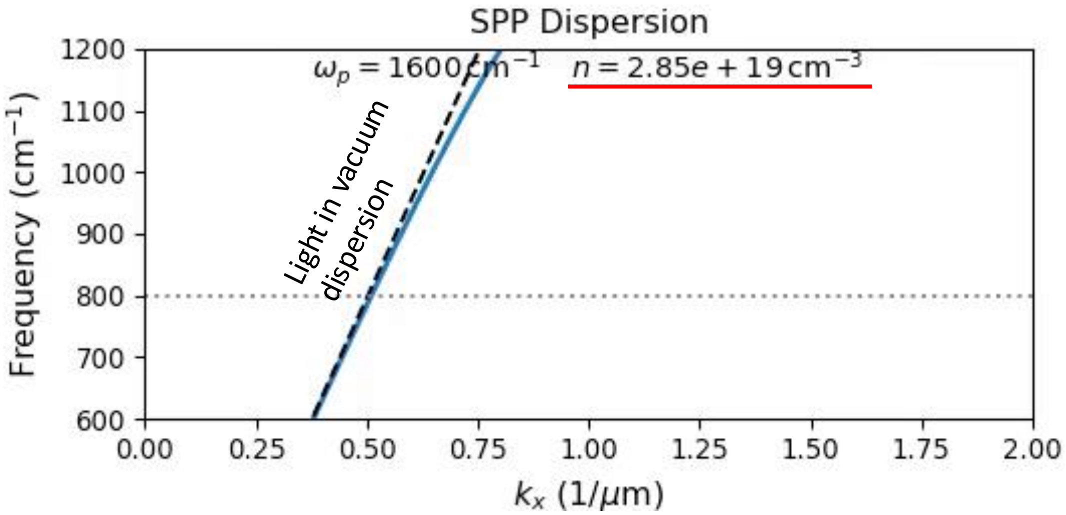
$$\varepsilon(\omega)=\varepsilon_{\infty}\left(1-\frac{\omega_P^2}{\omega^2+i\gamma\omega}\right) \qquad \omega_P^2=\frac{n e^2}{\varepsilon_0\varepsilon_{\infty} m^* m_0}$$

n: carrier concentration

Tunable SPP with carrier concentration



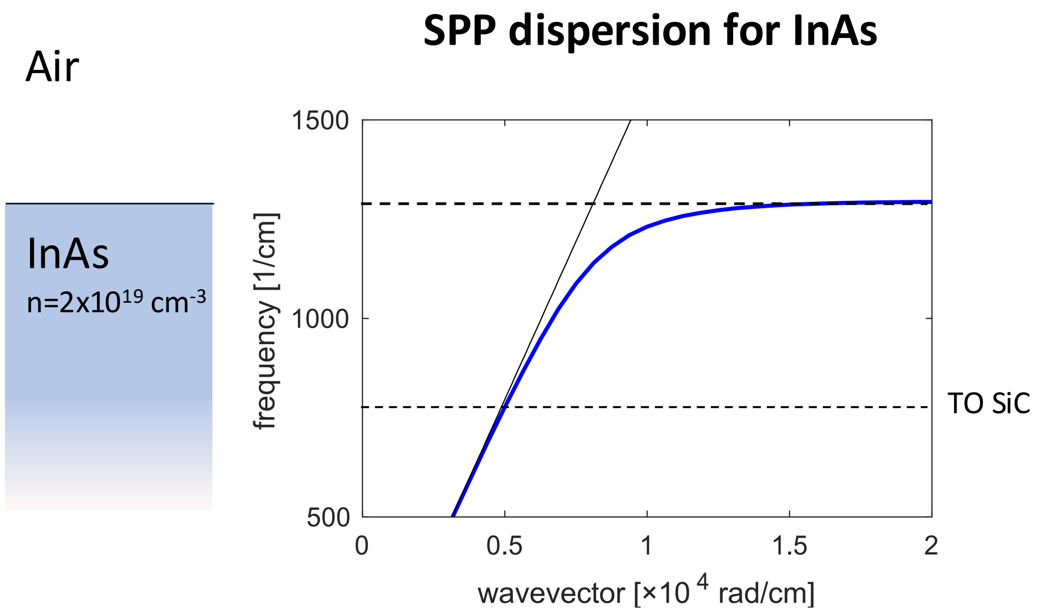
Changing field confinement



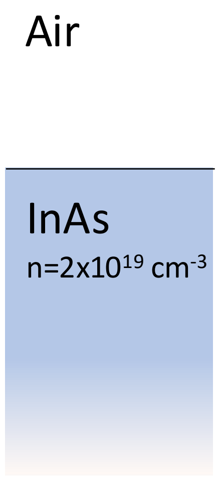
Surface polariton dispersion

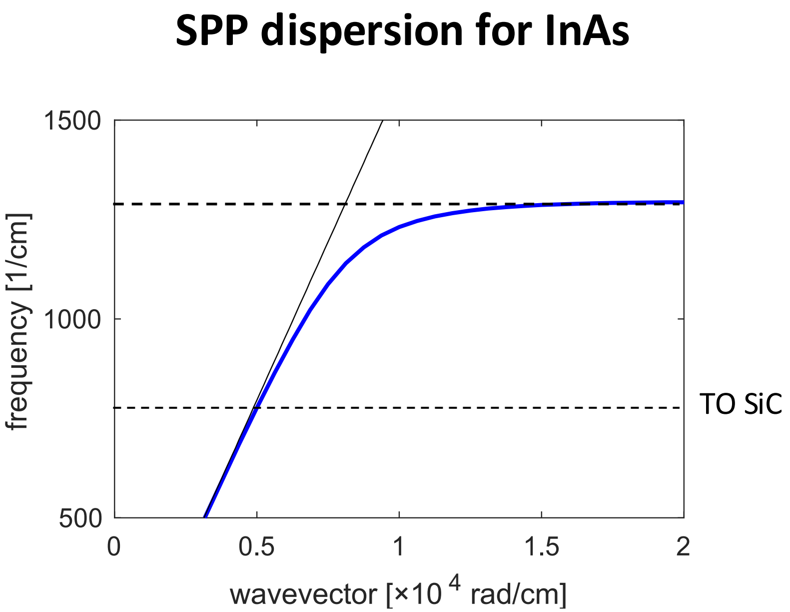
$$\omega = ck\sqrt{\frac{\varepsilon(\omega)}{\varepsilon(\omega)+1}}$$

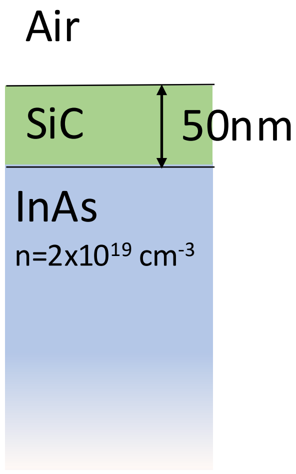
Dispersion calculation of InAs SPP with n = $2x10^{19}$ cm^{-3}



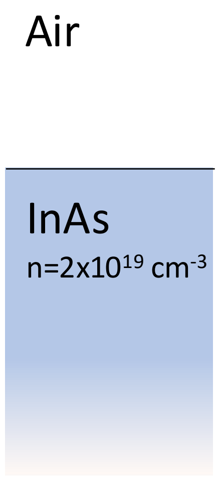
Hybrid polariton dispersion calculation in InAs + SiC layer



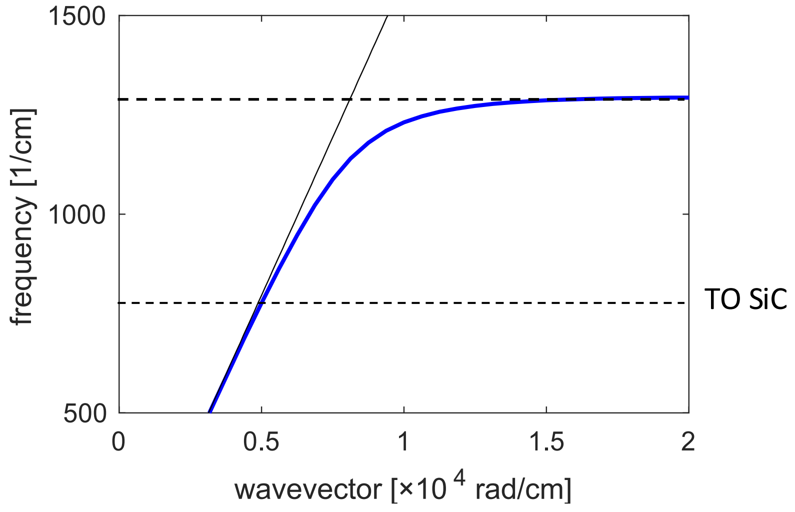


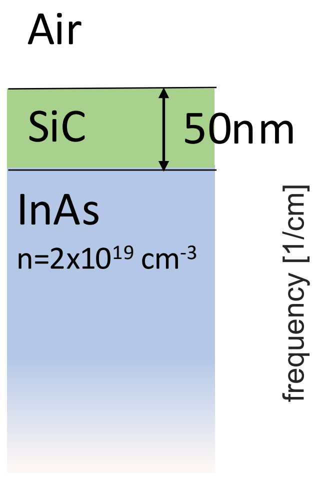


Hybrid polariton dispersion calculation in InAs + SiC layer

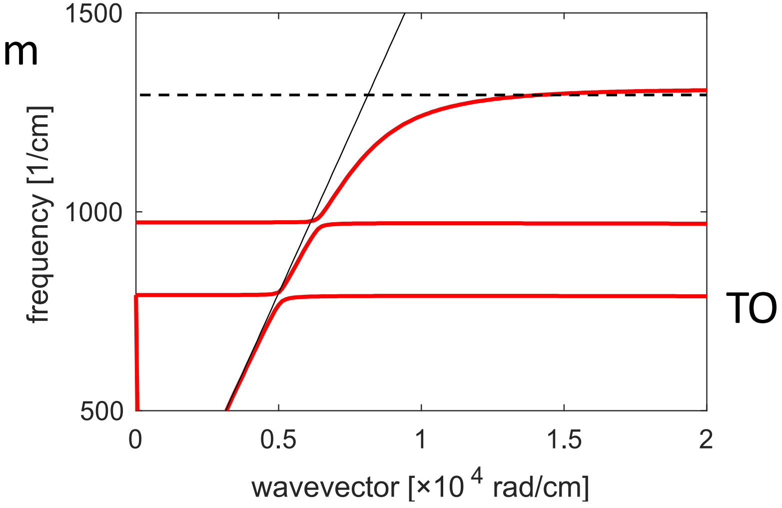


SPP dispersion for InAs

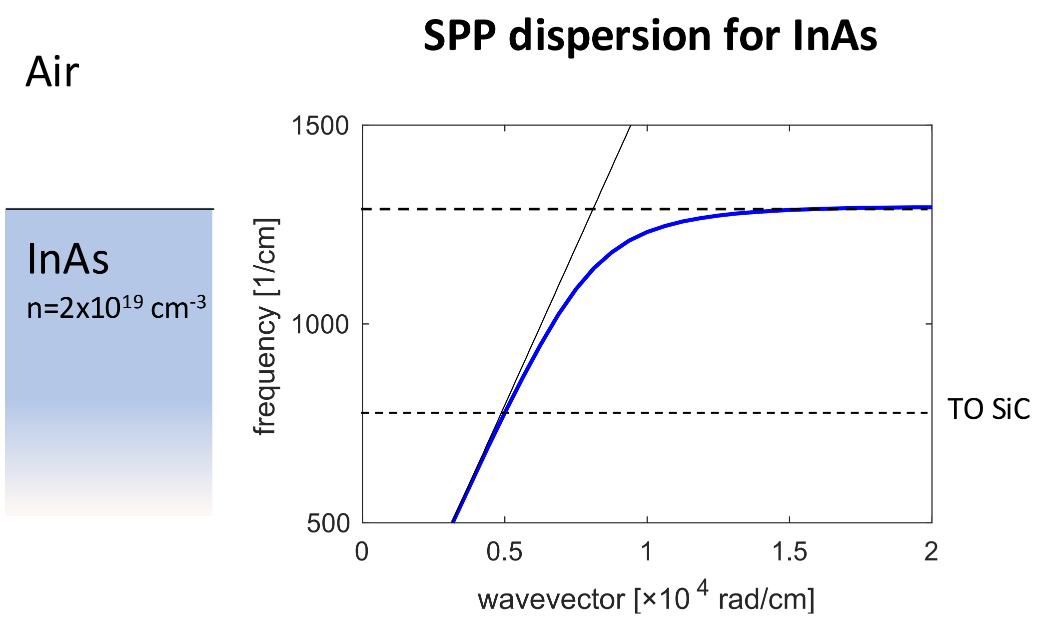


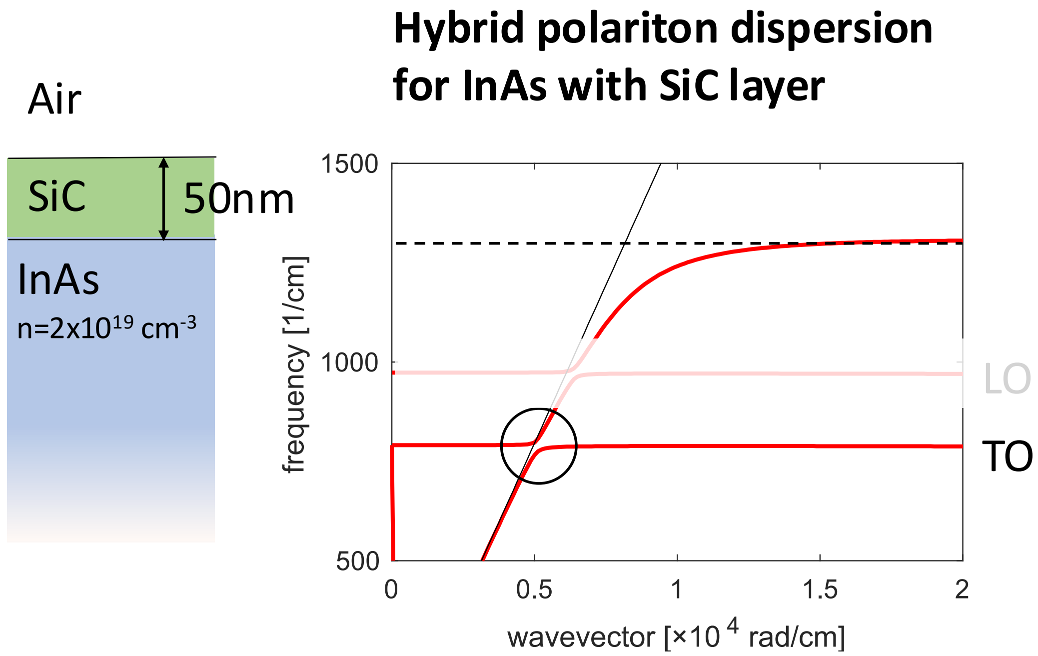


Hybrid polariton dispersion for InAs with SiC layer



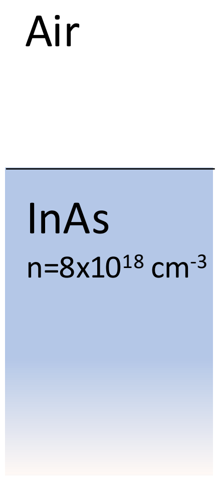
We observe typical anticrossing at TO frequency signature of coupling between SPP and TO phonon

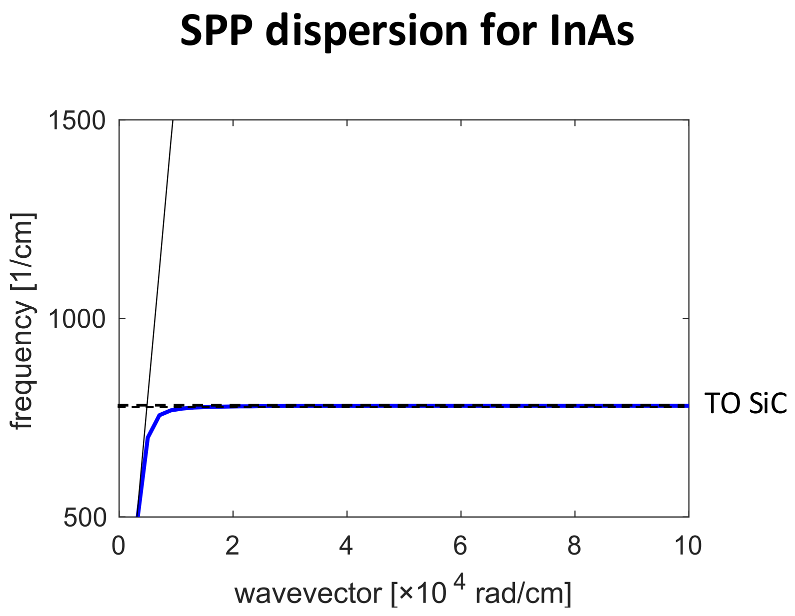




- Anti-crossing at SiC TO phonons frequency.
- Small mode splitting

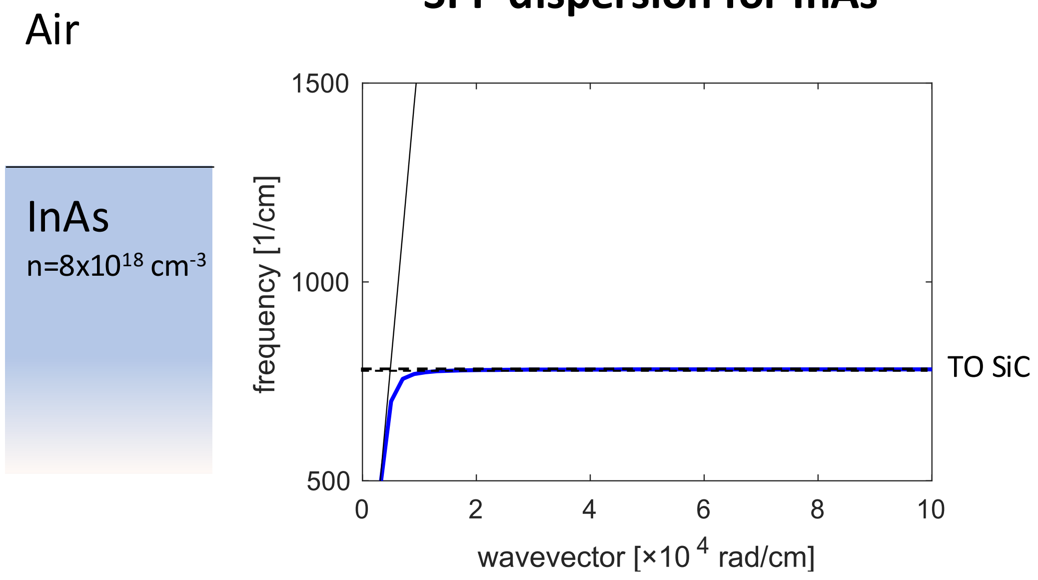
Dispersion calculation of InAs SPP with $n = 8x10^{18}$ cm^{-3}



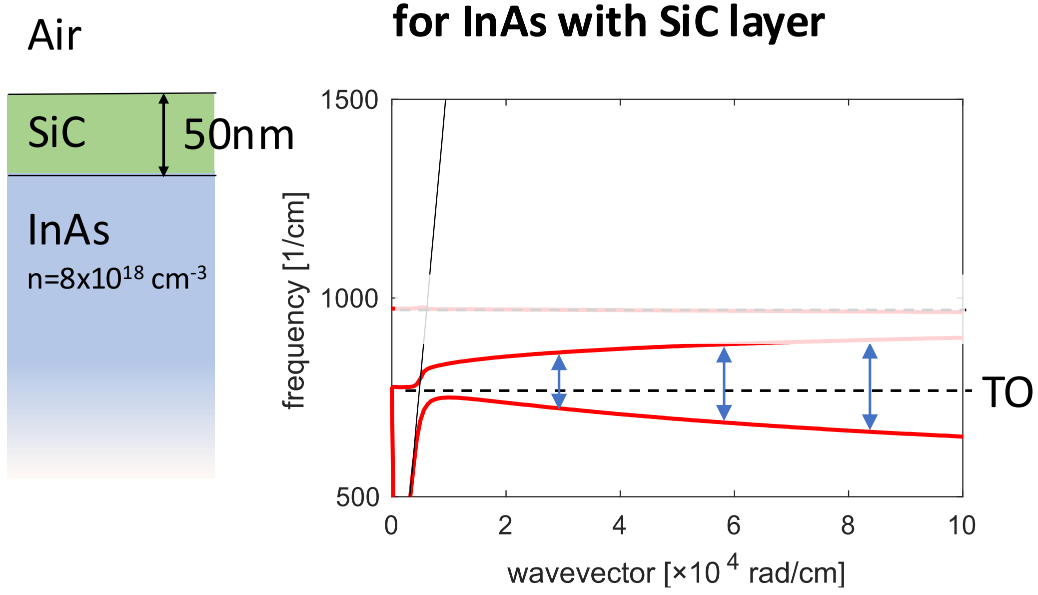


We observe unusual anticrossing at TO frequency

SPP dispersion for InAs



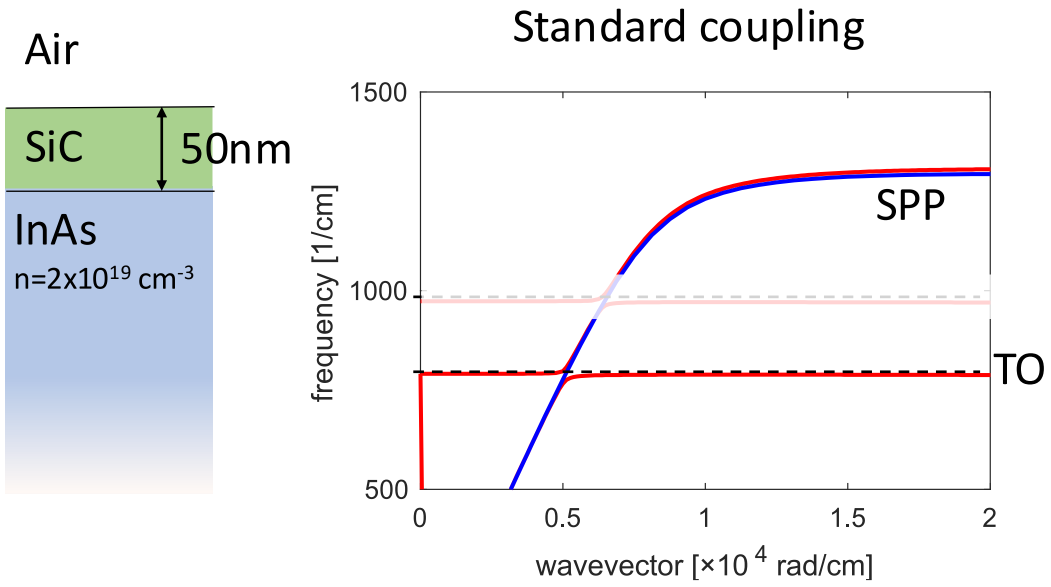
Hybrid polariton dispersion for InAs with SiC layer

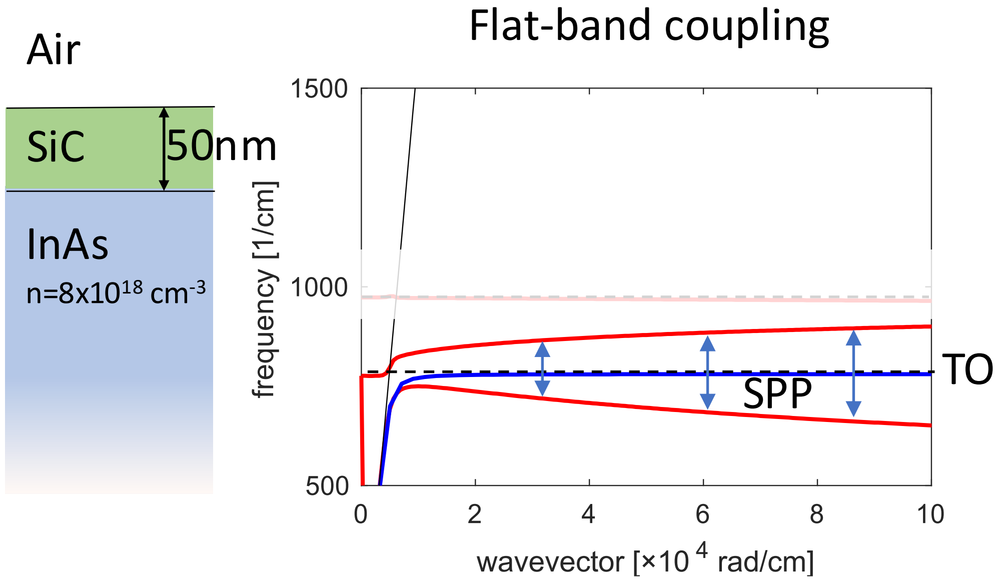


Moving SP to match TO, we observe:

- Anticrossing over an extended momentum range.
- Large mode splitting indicating ultrastrong coupling

Flat-band coupling





We want to experimentally verify this observation.

We need to measure hybrid polariton dispersion at high wavevectors.

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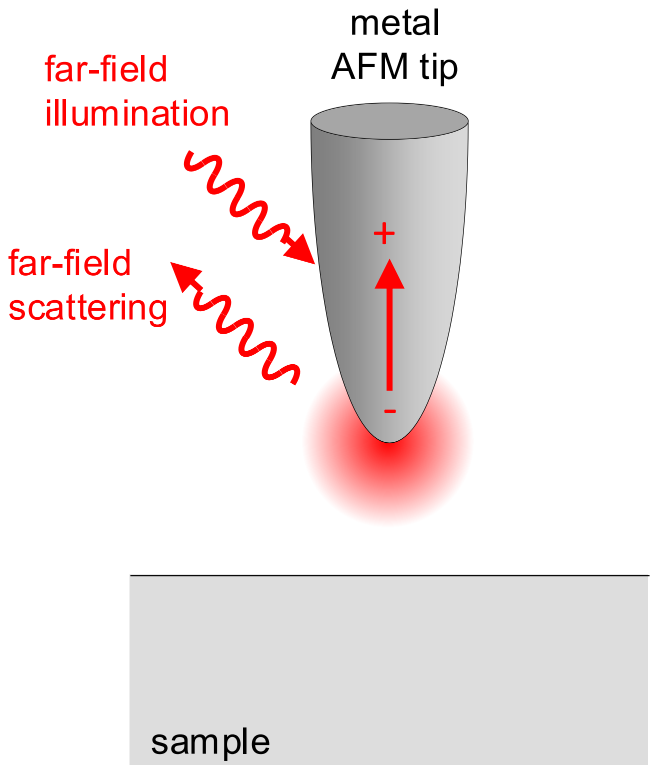
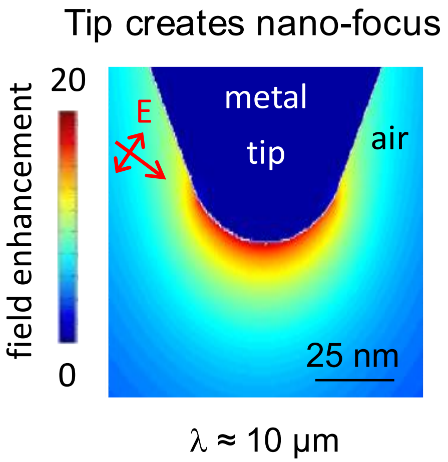
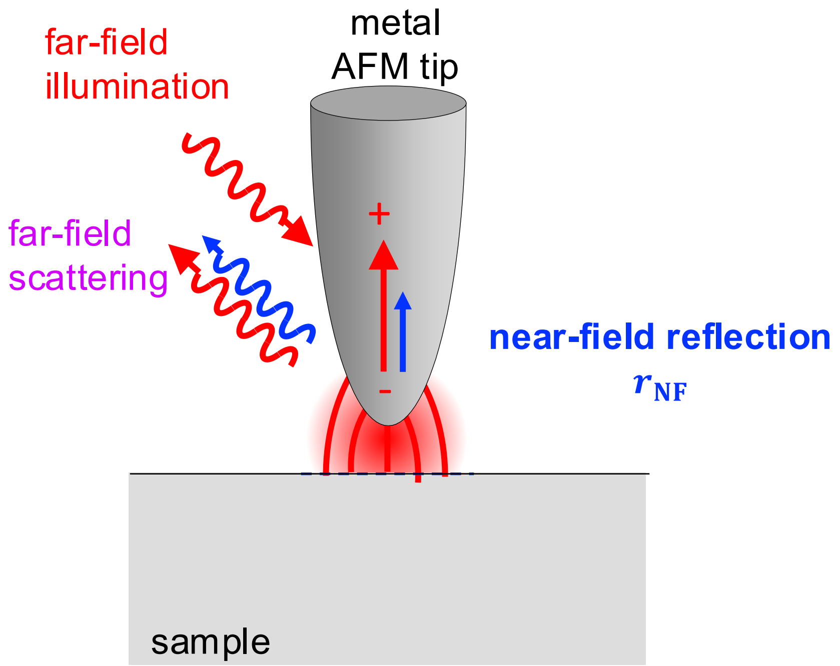
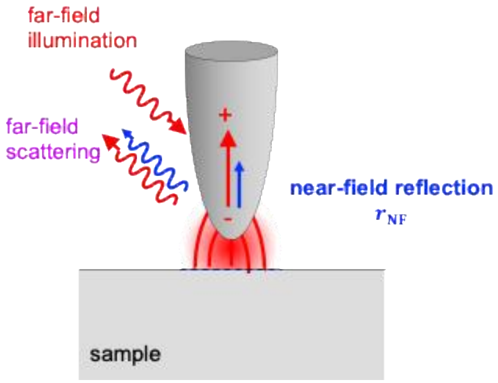
Scattering-scanning near field optical microscopy (s-SNOM)

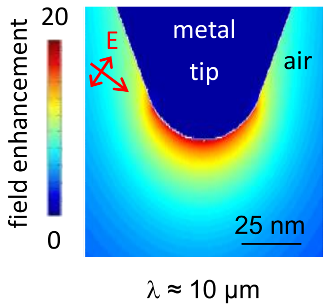




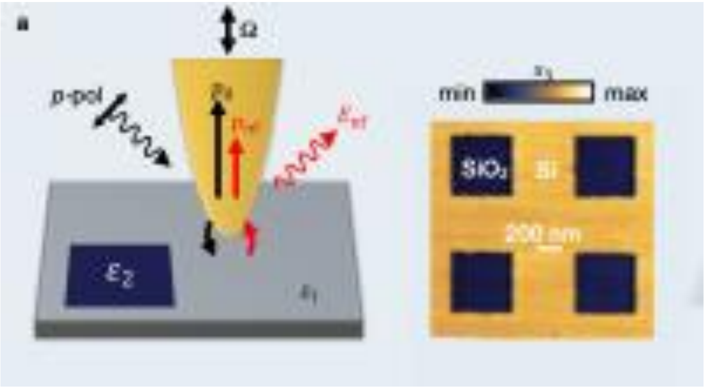


s-SNOM probes …

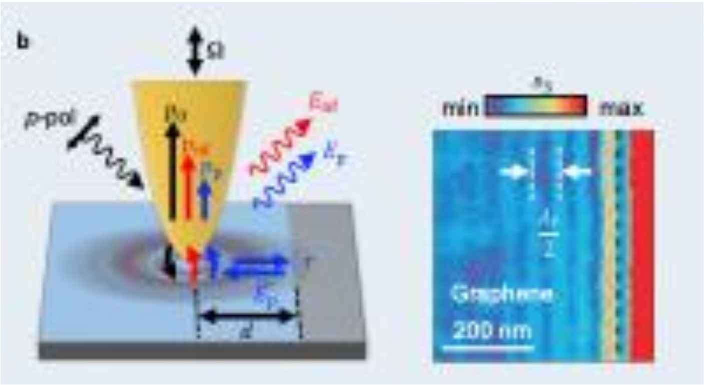




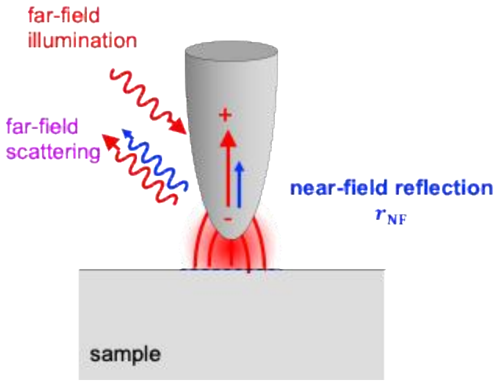
Material contrast mapping

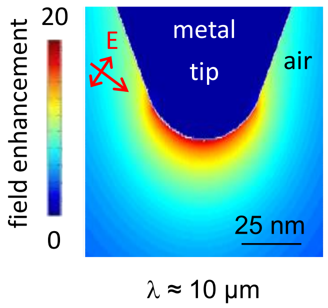


Polariton imaging (Polariton interferometry)



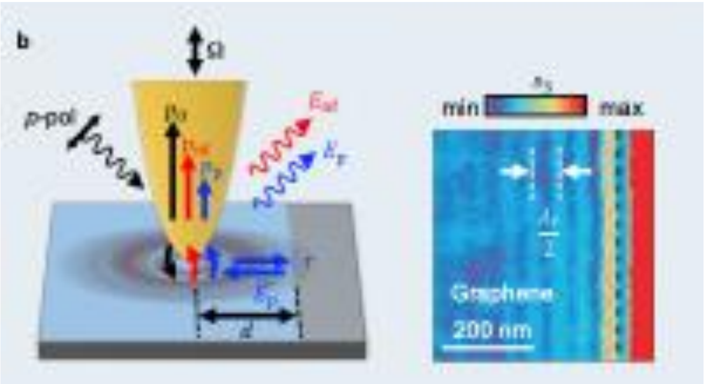
s-SNOM probes …



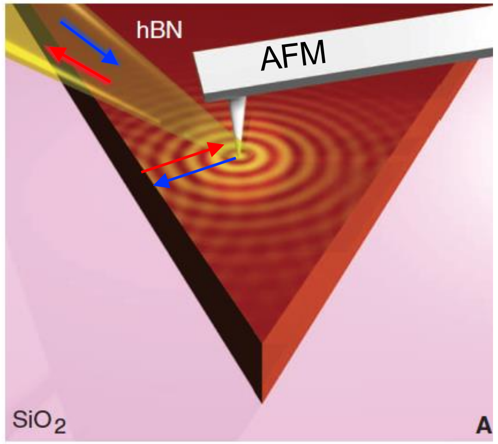


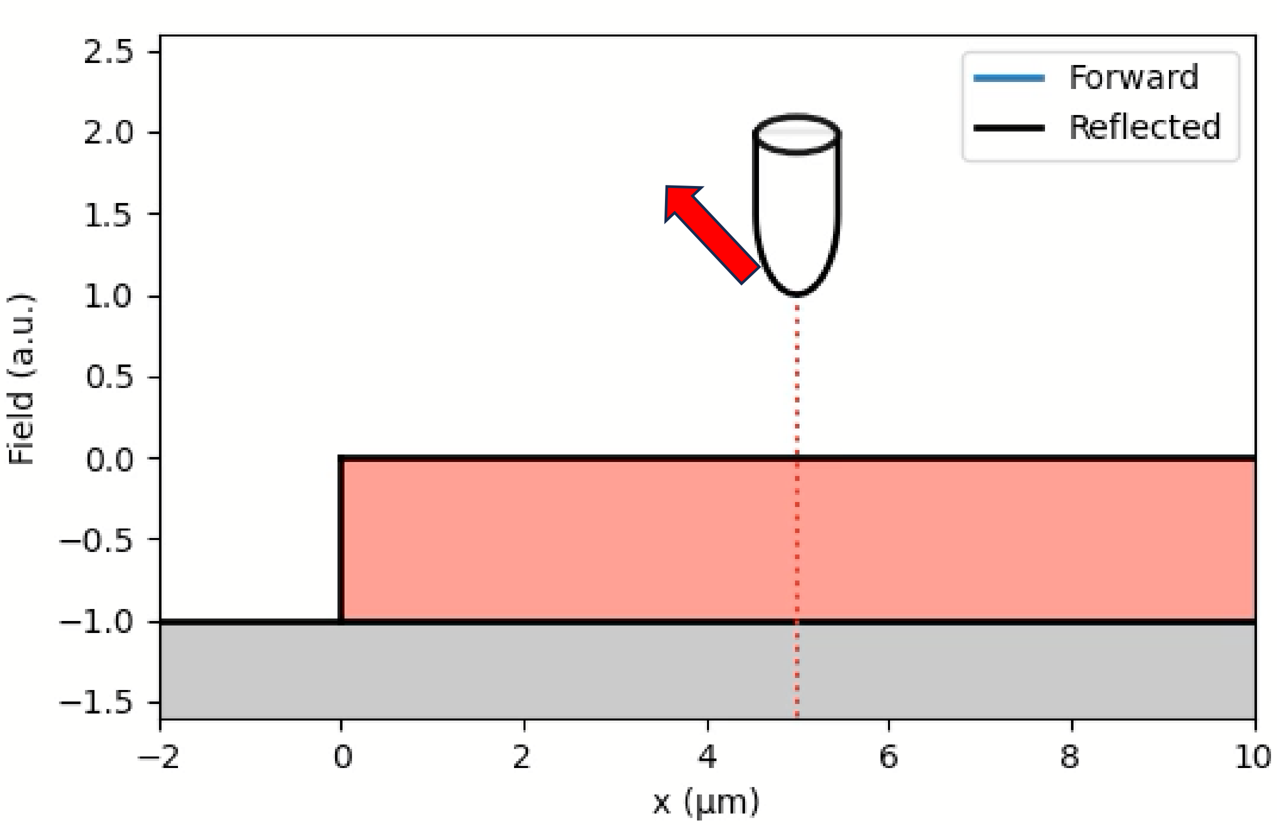
Material contrast mapping

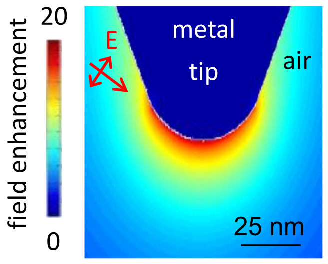
Polariton imaging
(Polariton interferometry)



The tip launches polariton waves which are reflected at the material edge.







$\lambda \approx 10$ µm

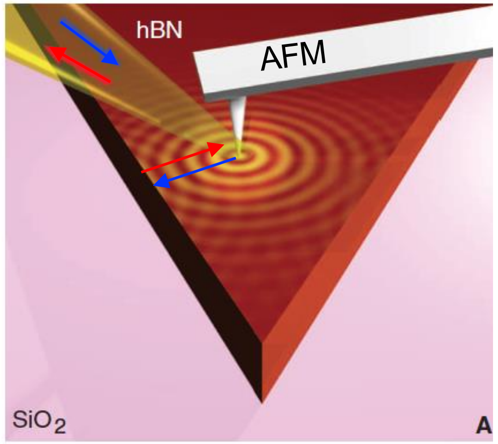
Localized field has high momentum.

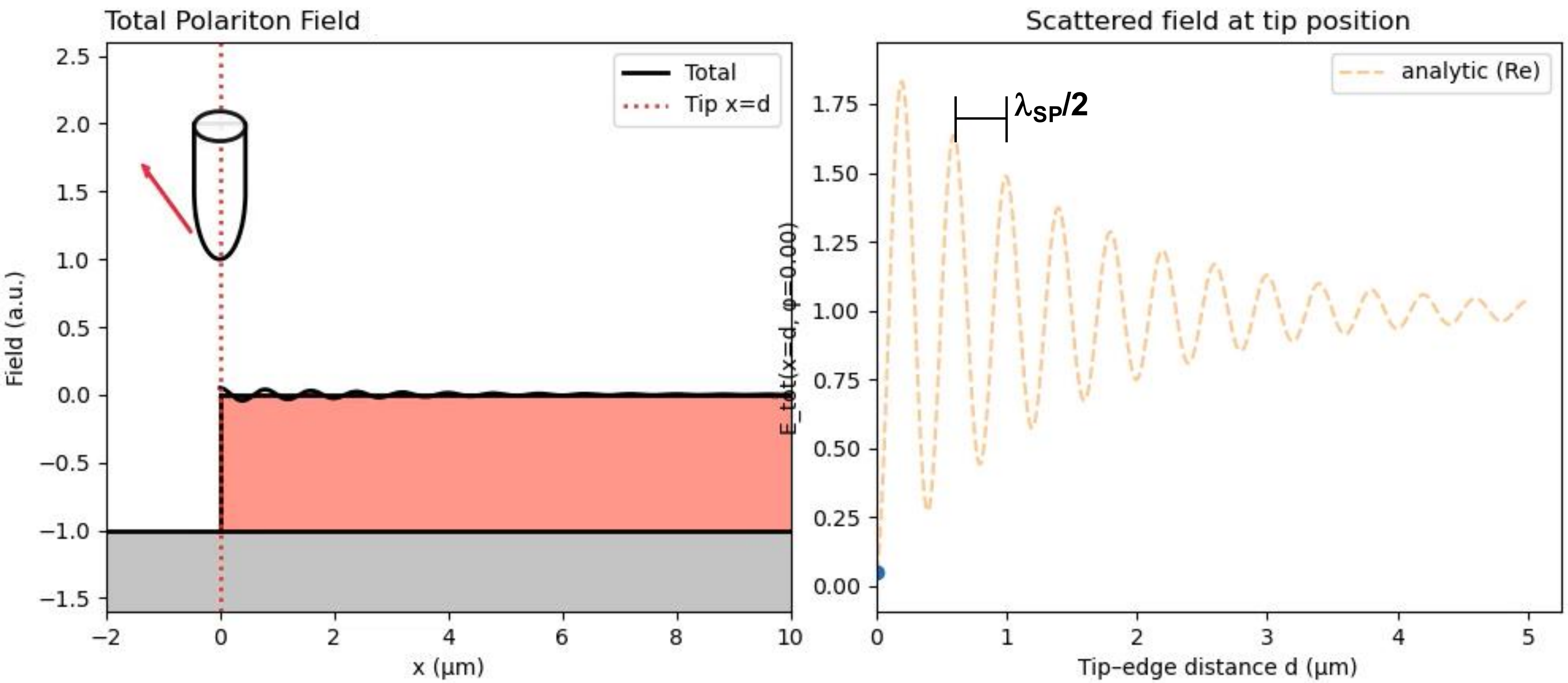
⇩

It can launch surface polariton waves

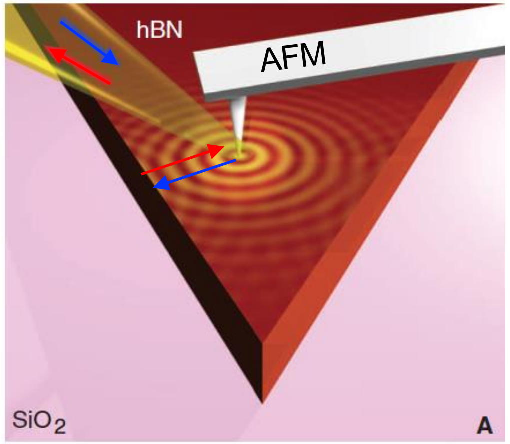
The tip scattered field is proportional to the interference of the reflected wave with the local field at the tip position.

Scanning the tip across the edge allows to record the polariton wave

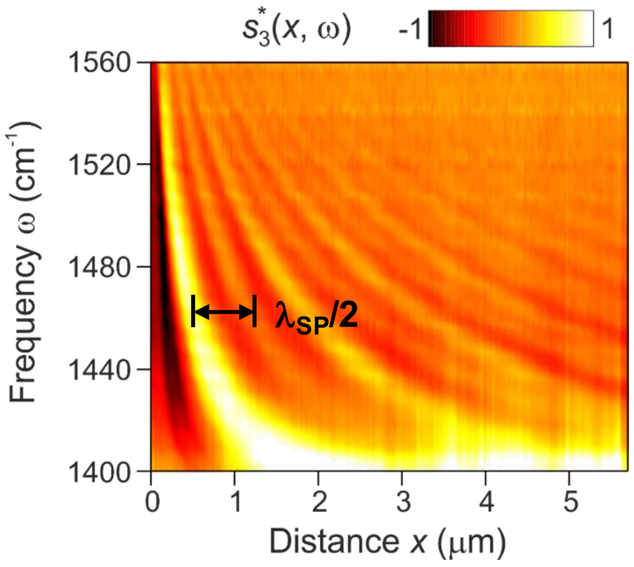




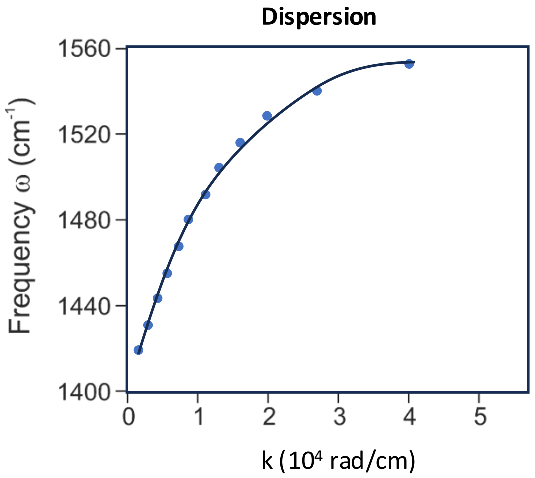
The analysis of the polariton wavelength at different frequencies allows to determine the polariton dispersion



Broadband laser



$$k = \frac{2\pi}{\lambda}$$



A. Bylinkin et al., *Nature Photon.* **15**, 197 (2021)

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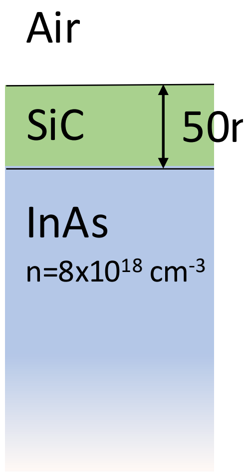
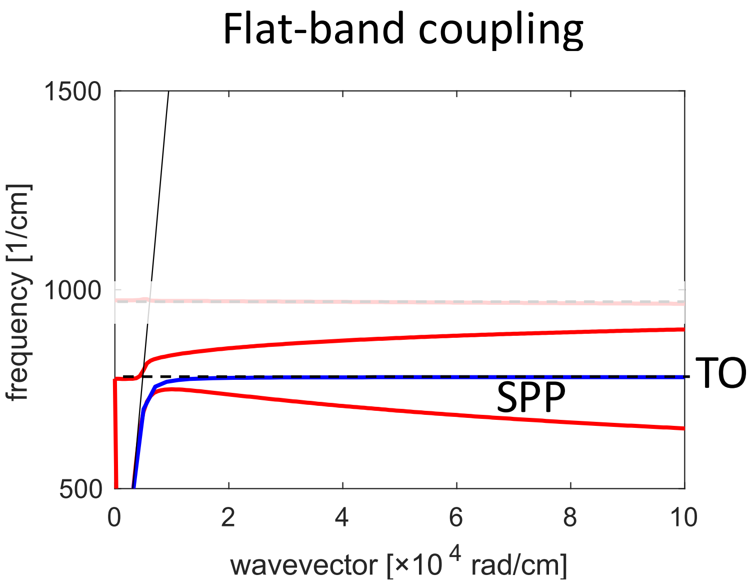
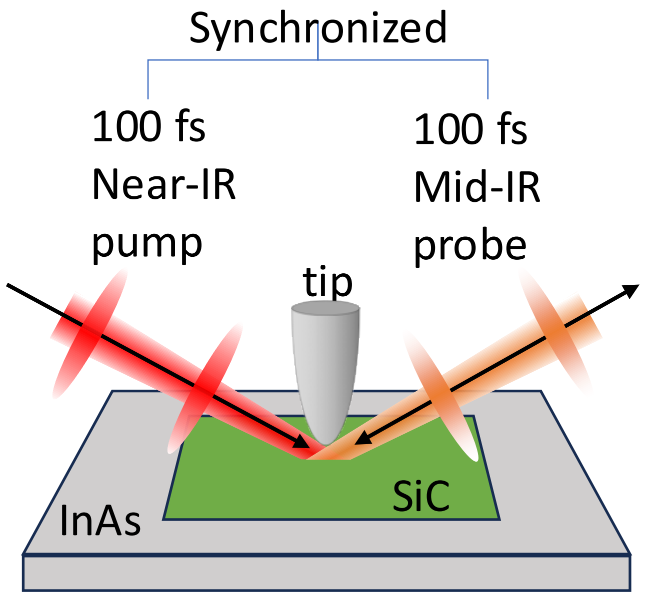
To verify the flat-band coupling we need a specific carrier concentration in InAs

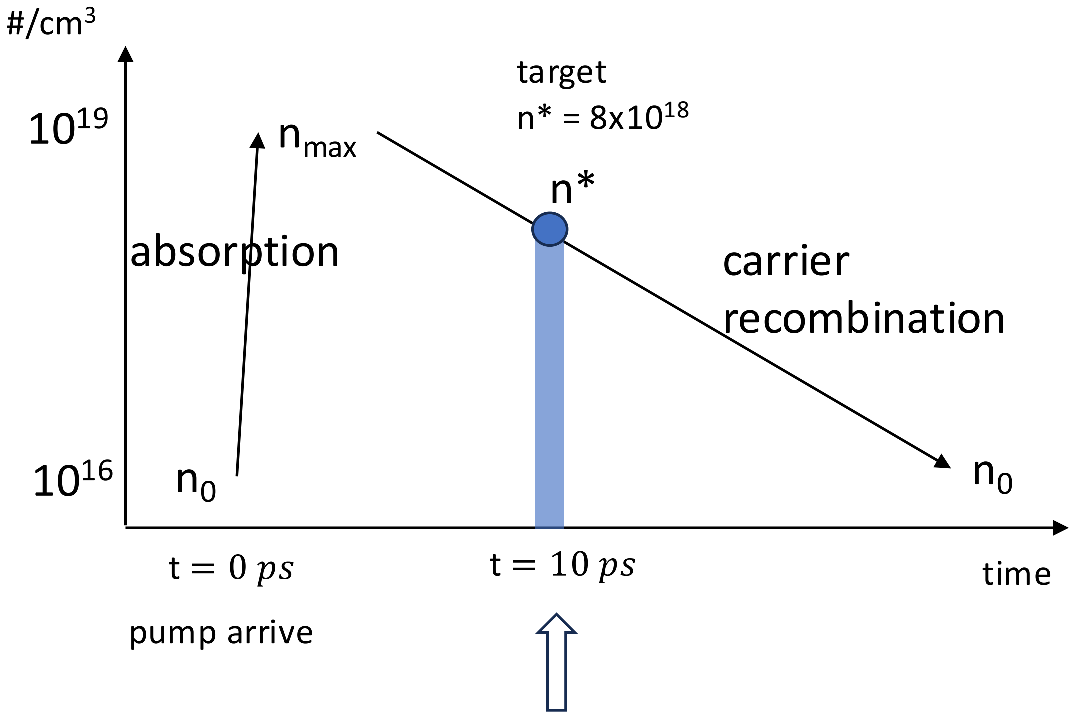
We want n = 8 x10^{18} cm^{-3}





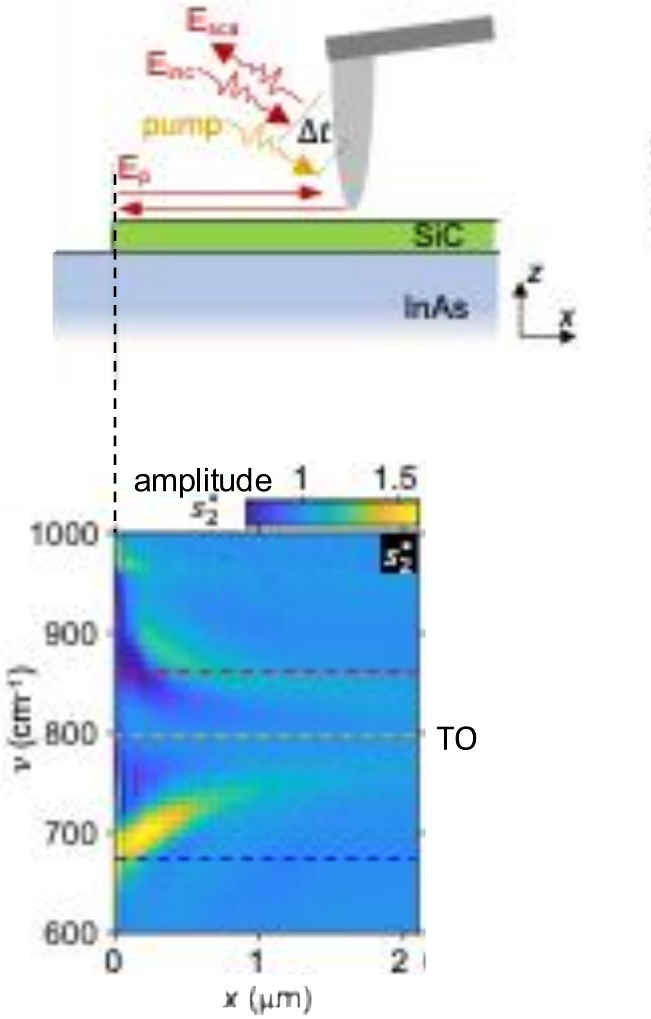
Pump-probe nanospectroscopy to photoexcite carriers in InAs and probe a specific carrier concentration





By selecting the pump-probe delay, we can select the carrier concentration.

Hybrid polariton dispersion is measured by polariton interferometry



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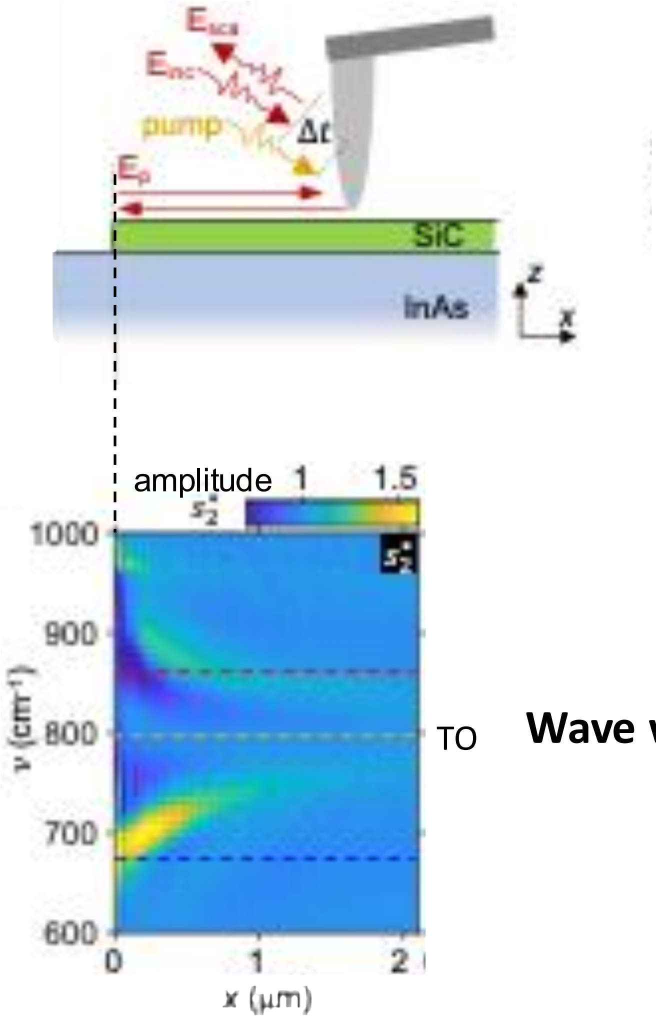
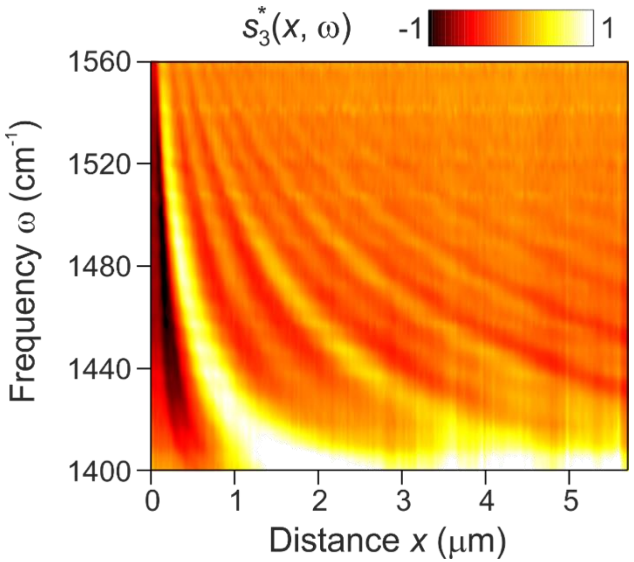
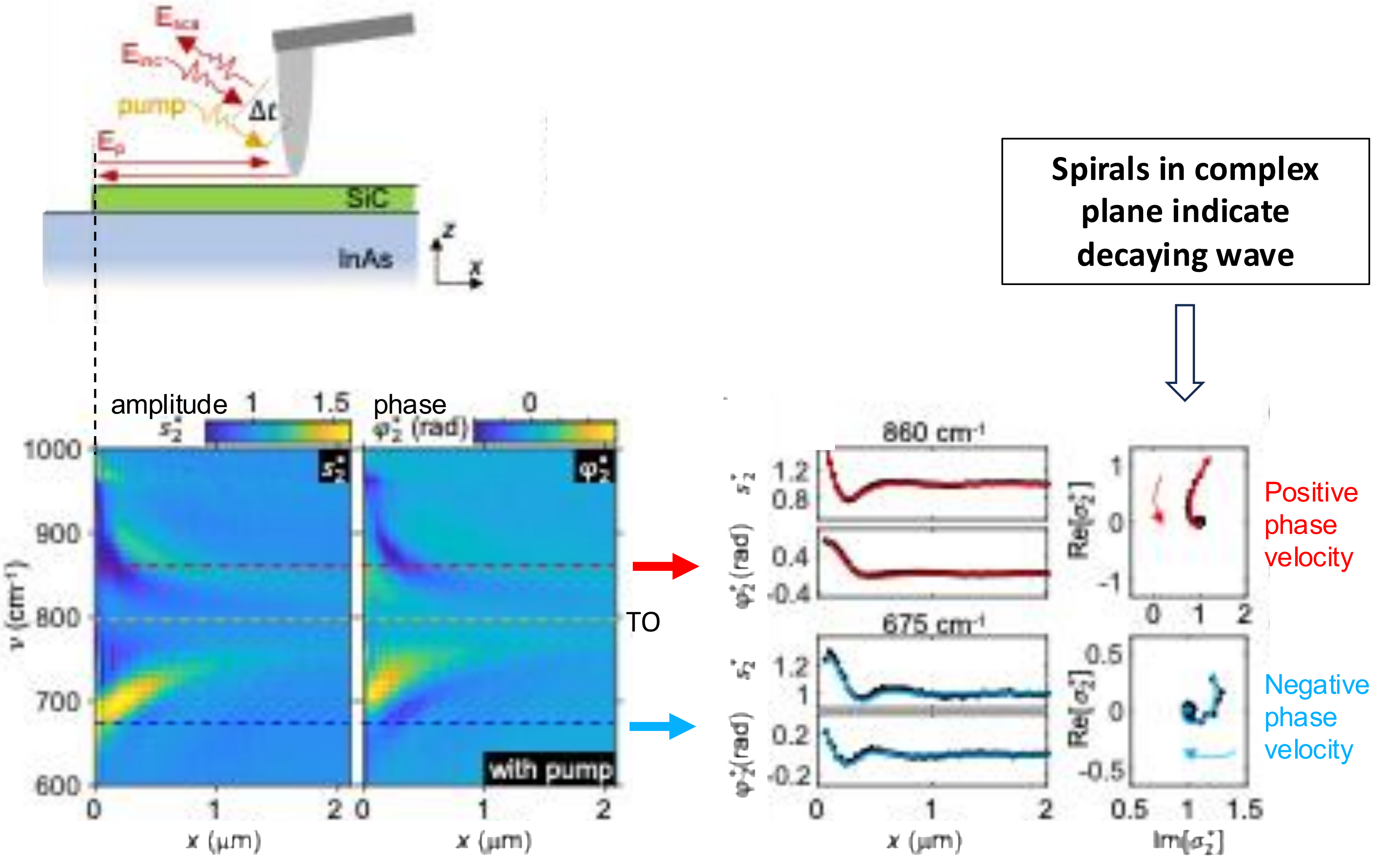


TO

Wave with high damping?



Complex-valued line profiles yield phase velocity



With interferometric detection we measure amplitude and phase.

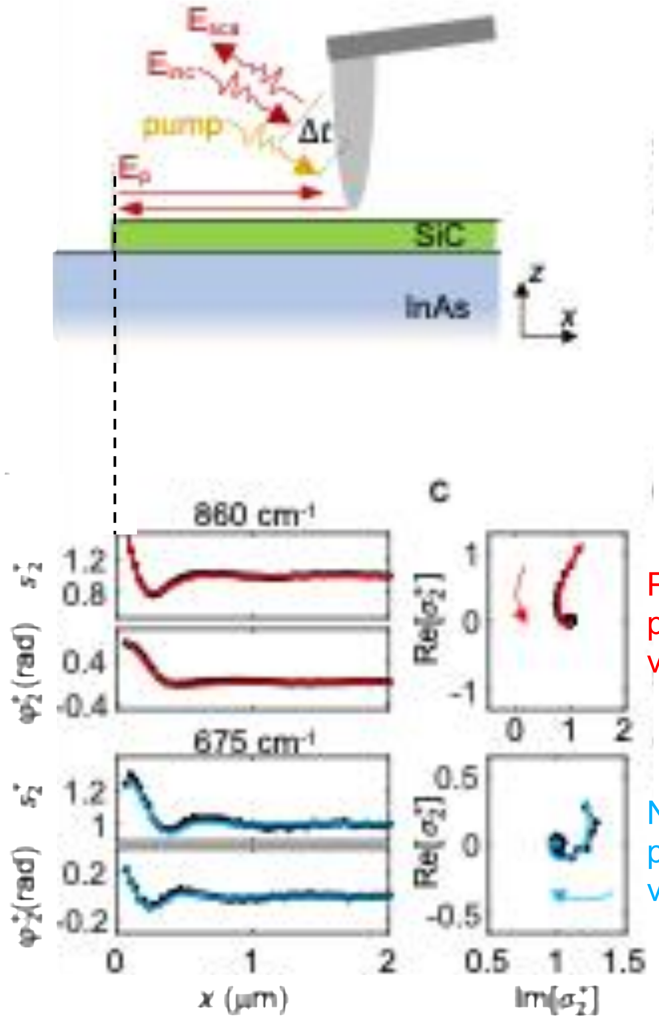
E. Vicentini, et al. *accepted Nat. Mat,*

Line profile fitting yields hybrid polariton wavevector

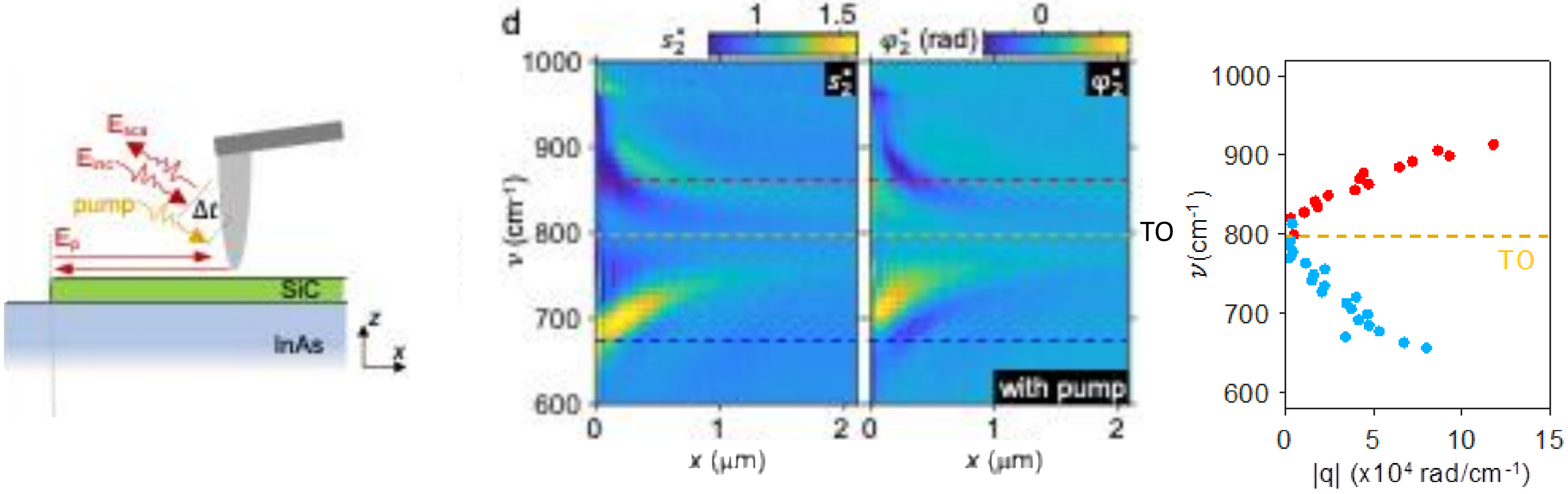
Field of a radially propagating damped wave

$$E_{\mathrm{sca}}(x) = A\frac{e^{i2k_{\mathrm{p}}x}}{\sqrt{x}} + C$$

A – complex amplitude
C – complex offset
k_{p} – complex polariton wavevector



Experimental hybrid polariton dispersion in agreement with dispersion calculations



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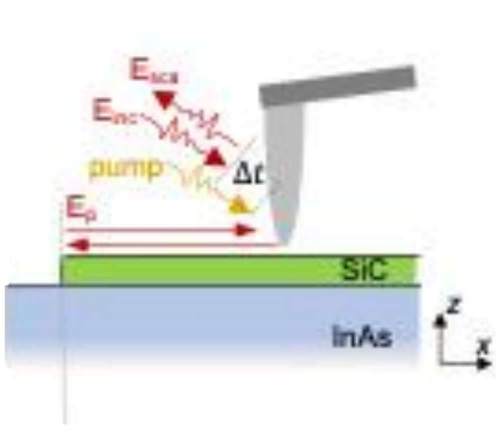

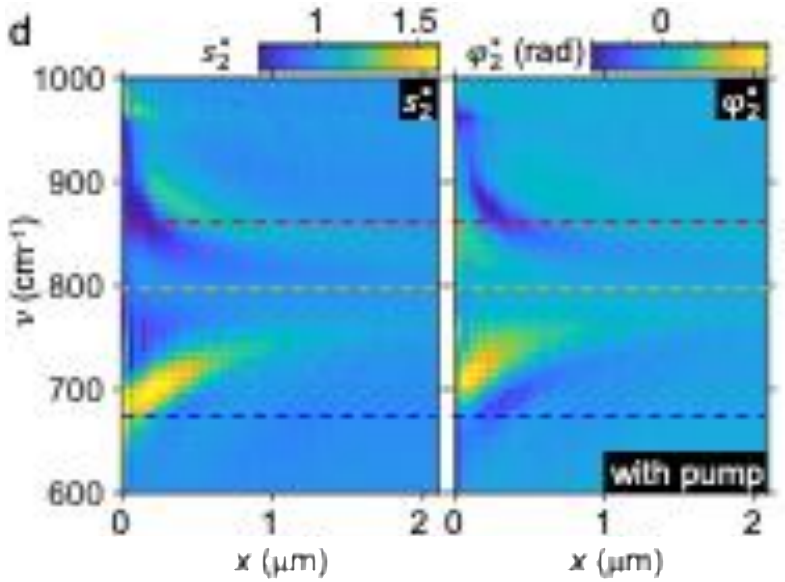

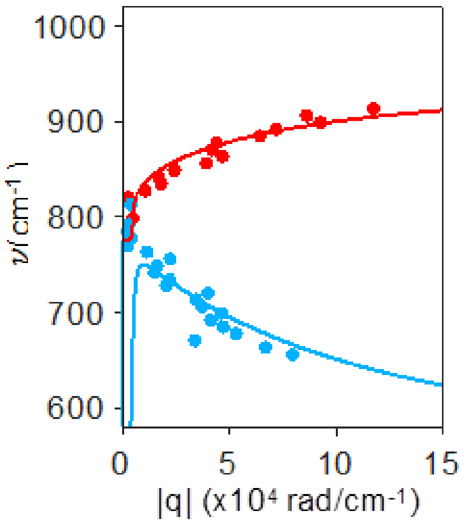

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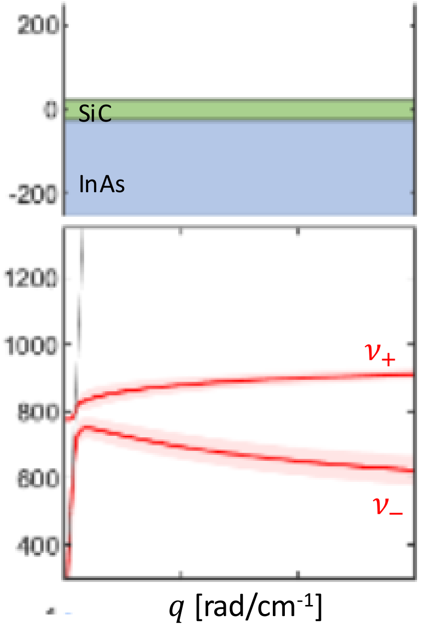
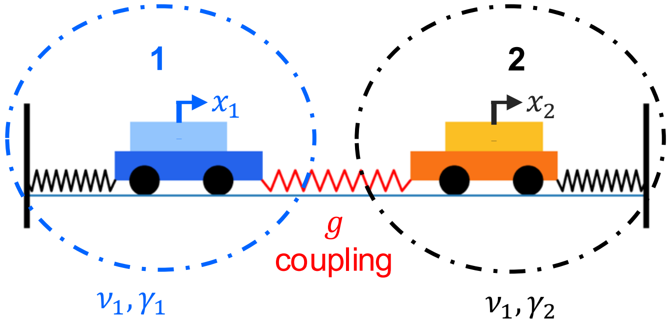
Hybrid modes are analysed with a coupled harmonic oscillator model esablished for the USC regime



Dispersions obtained from fitting the experimental nano-FTIR data

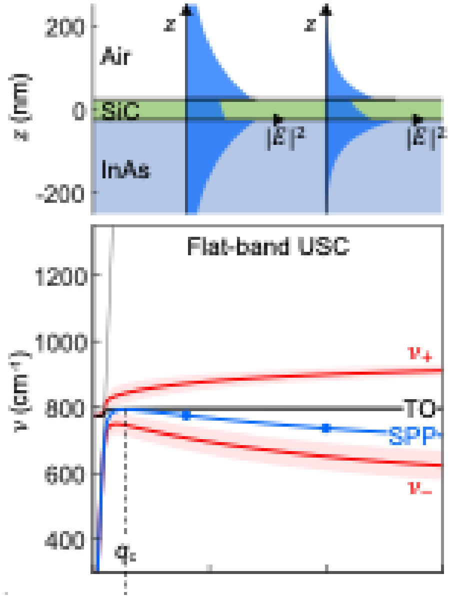
$$\ddot{x}_1 + \nu_1^2 x_1 - 2g\dot{x}_2 = 0$$
$$\ddot{x}_2 + \nu_2^2 x_2 + 2g\dot{x}_1 = 0$$

$$\nu_\pm = \frac{1}{\sqrt{2}}\sqrt{(\nu_1^2 + \nu_2^2 + 4g^2) \pm \sqrt{(\nu_1^2 + \nu_2^2 + 4g^2)^2 - 4\nu_1^2\nu_2^2}}$$



U. Muniain, et al. *Nanophotonics*, 14, 2031(2025)

Hybrid modes are analysed with a coupled harmonic oscillator model esablished for the USC regime

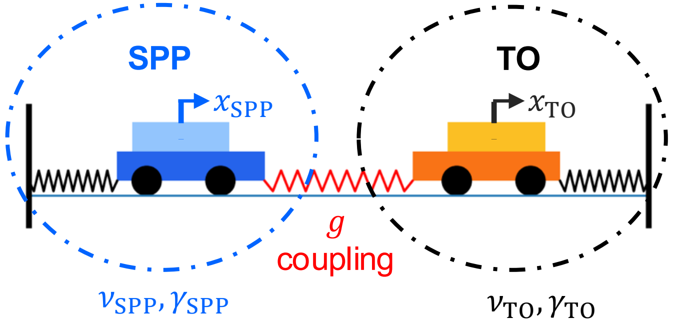


$$\ddot{x}_1 + \omega_{SPP}^2 x_1 - 2g\dot{x}_2 = 0$$
$$\ddot{x}_2 + \omega_E^2 x_2 + 2g\dot{x}_1 = 0$$

$$\nu_\pm = \frac{1}{\sqrt{2}}\sqrt{\left(\nu_{SPP}^2 + \nu_{TO}^2 + 4g^2\right) \pm \sqrt{\left(\nu_{SPP}^2 + \nu_{TO}^2 + 4g^2\right)^2 - 4\nu_{SPP}^2\nu_E^2}}$$

Hybrid modes can be explained by (U)SC of two excitations with flat dispersion:

- TO phonon of SiC
- SPP at dispersion limit



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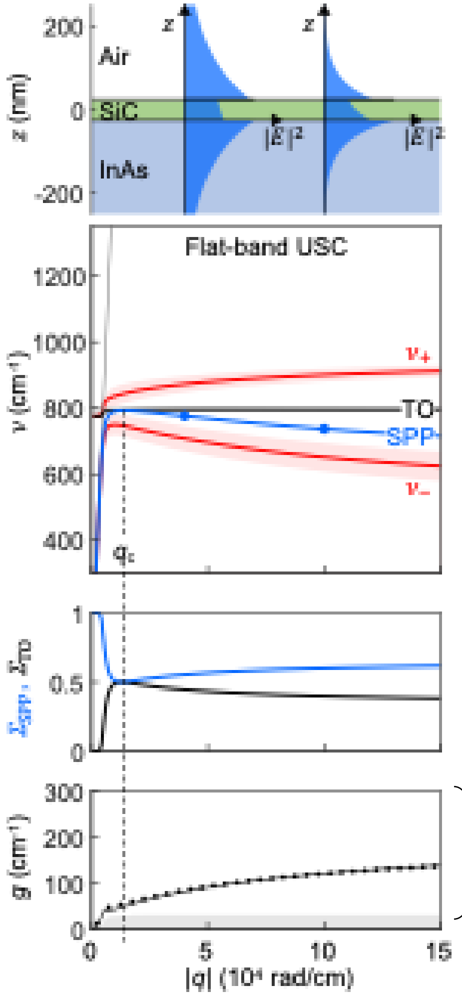
Hybrid modes are analysed with a coupled harmonic oscillator model



$$\ddot{x}_1 + \omega_{SPP}^2 x_1 - 2g\dot{x}_2 = 0$$
$$\ddot{x}_2 + \omega_E^2 x_2 + 2g\dot{x}_1 = 0$$

$$\nu_\pm = \frac{1}{\sqrt{2}}\sqrt{\left(\nu_{SPP}^2 + \nu_{TO}^2 + 4g^2\right) \pm \sqrt{\left(\nu_{SPP}^2 + \nu_{TO}^2 + 4g^2\right)^2 - 4\nu_{SPP}^2\nu_E^2}}$$

Relative contribution of SPP to upper hybrid mode

Relative contribution of TO to upper hybrid mode

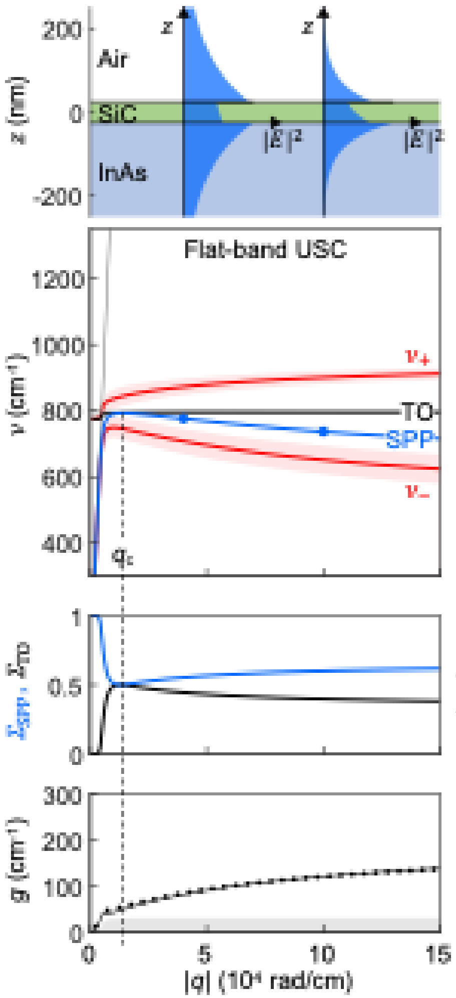
Hybrid modes exist within semi-infinite *q*-range

Coupling strength

$g > \frac{\gamma_{SPP} + \gamma_{TO}}{4}$ fulfills SC criterium

$g > 0.1\nu_{TO}$ fulfills USC criterium

For better understanding, we compare with results obtained for fully SiC filled upper half space



System

Dispersion

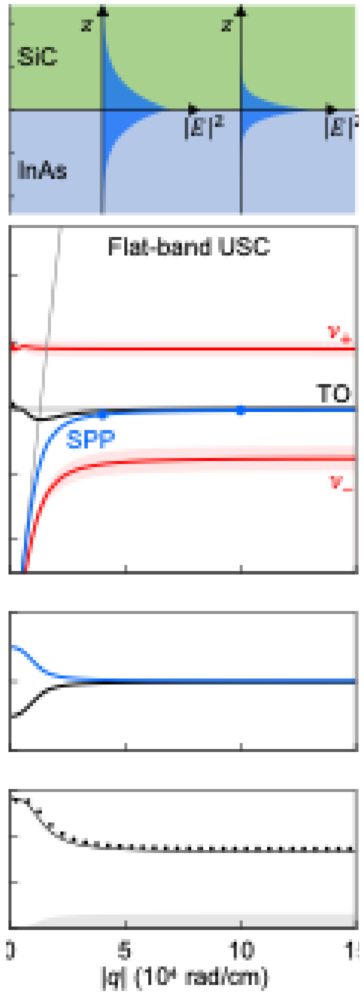
Molecule/SPhP Contribution

65/35 within semi-infinite *q*-range

50/50 within finite *q*-range

Coupling strength *g*

fulfills USC criterium



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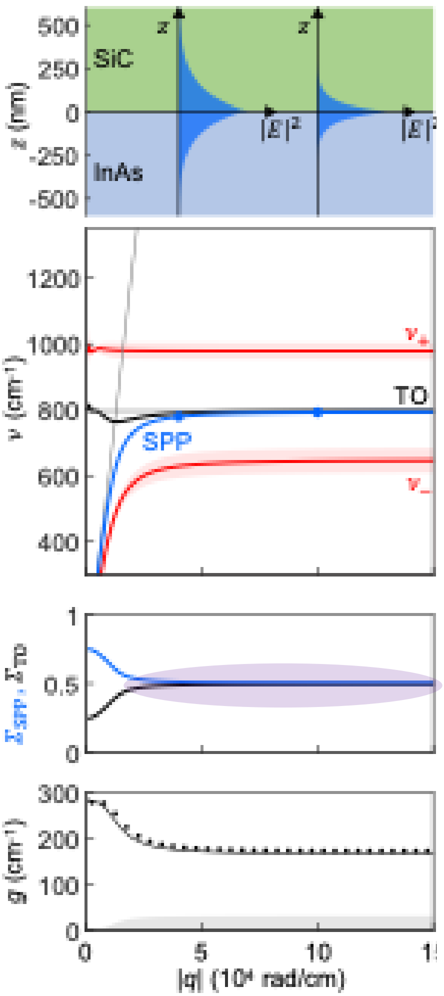
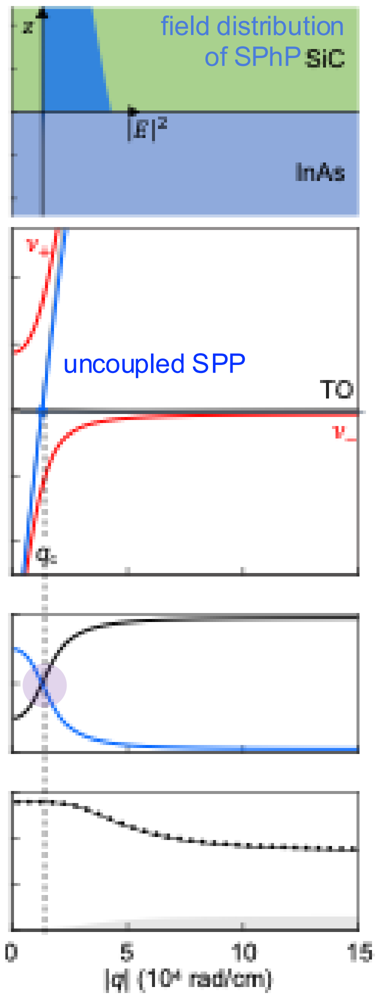
Comparison flat-band vs. conventional USC

Flat-band USC



Conventional USC



Model system

SiC half space
on InAs hosting SPPs

Dispersion

Dispersion limit of
uncoupled SPP

Molecule/SPhP Contribution

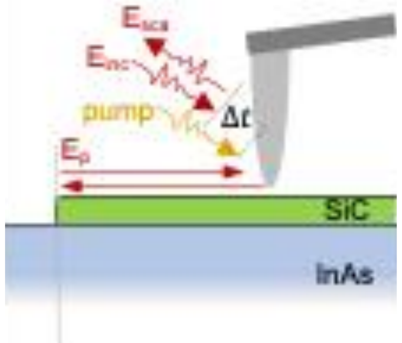
50/50 within
semi-infinite
q-range

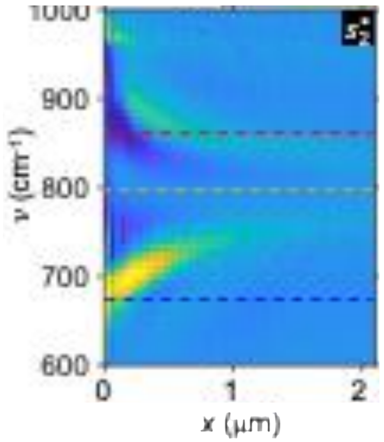
50/50
within finite
q-range

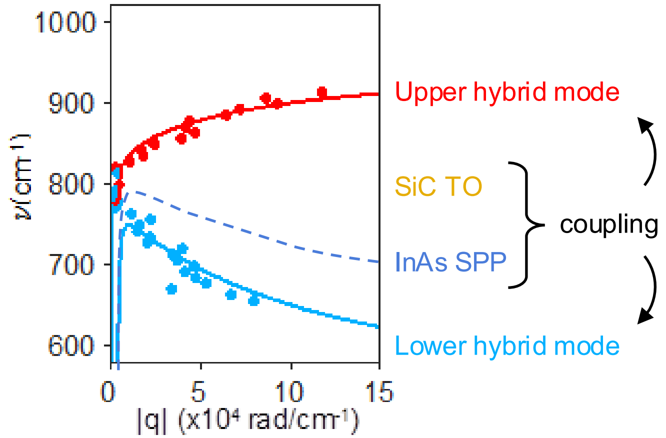
Coupling strength *g*

fulfills USC criterium

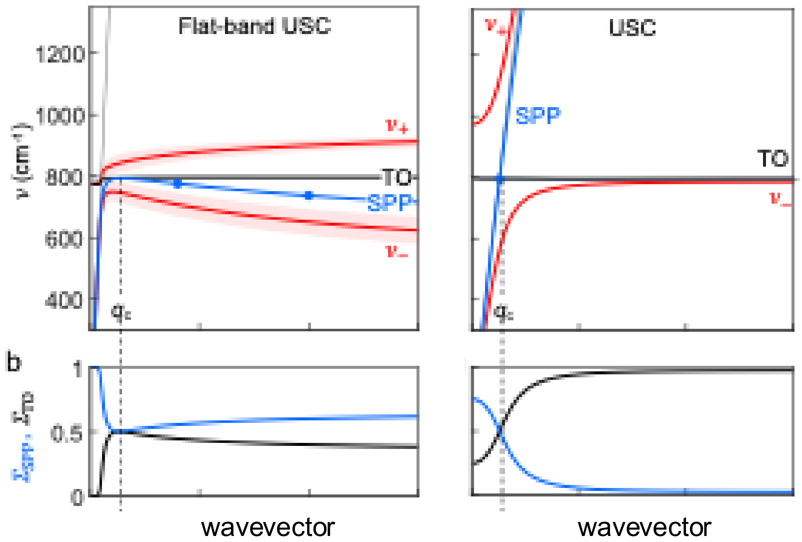
Conclusion







- (U)CS of optical excitations with flat dispersion exhibit hybrid modes in largely extended wavevector range
- Amount of hybrid modes is strongly enhanced compared to that of conventional (U)SC
- Exploit how future how flat-band (U)SC affects (U)SC-mediated matter manipulation



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Nanooptics group

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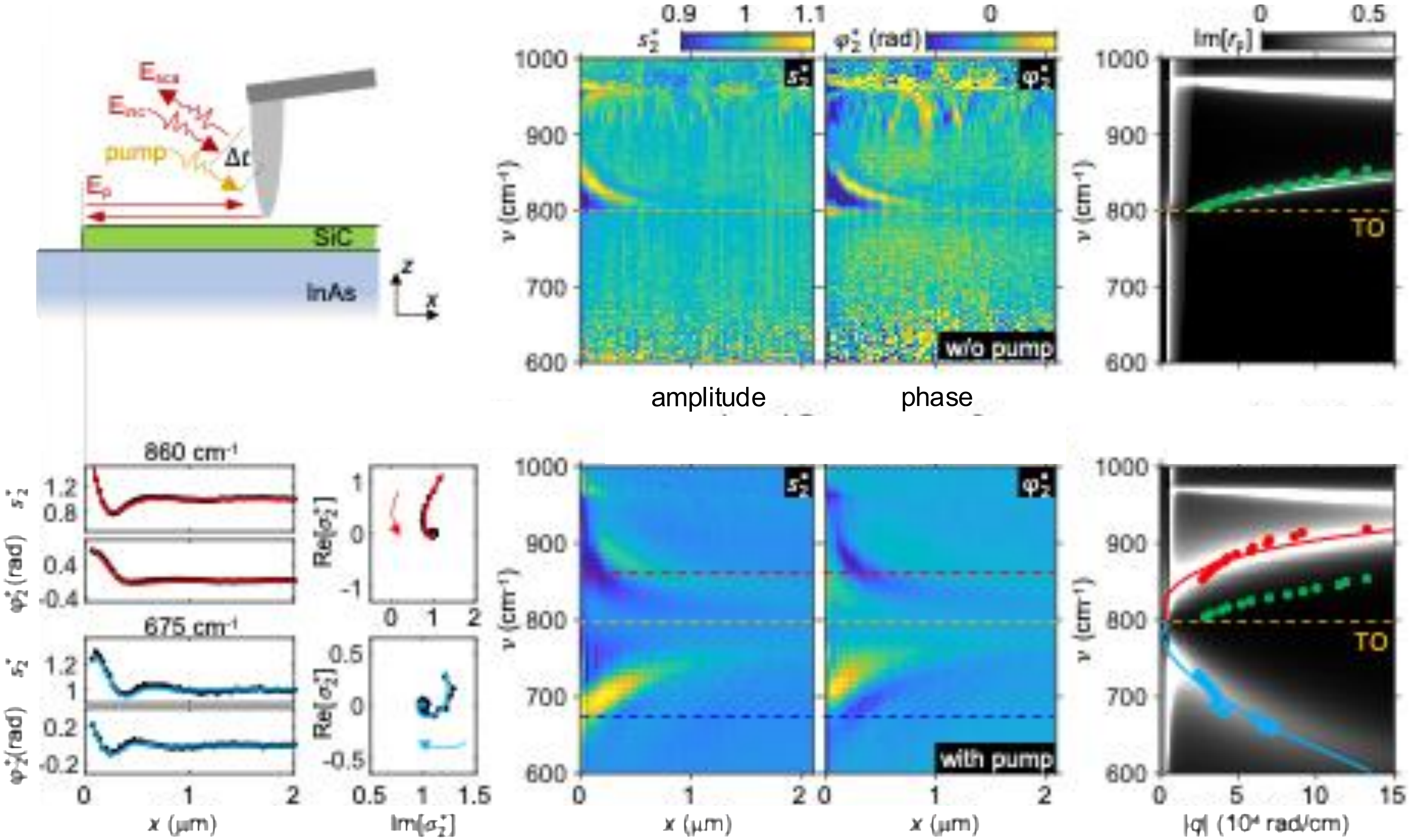
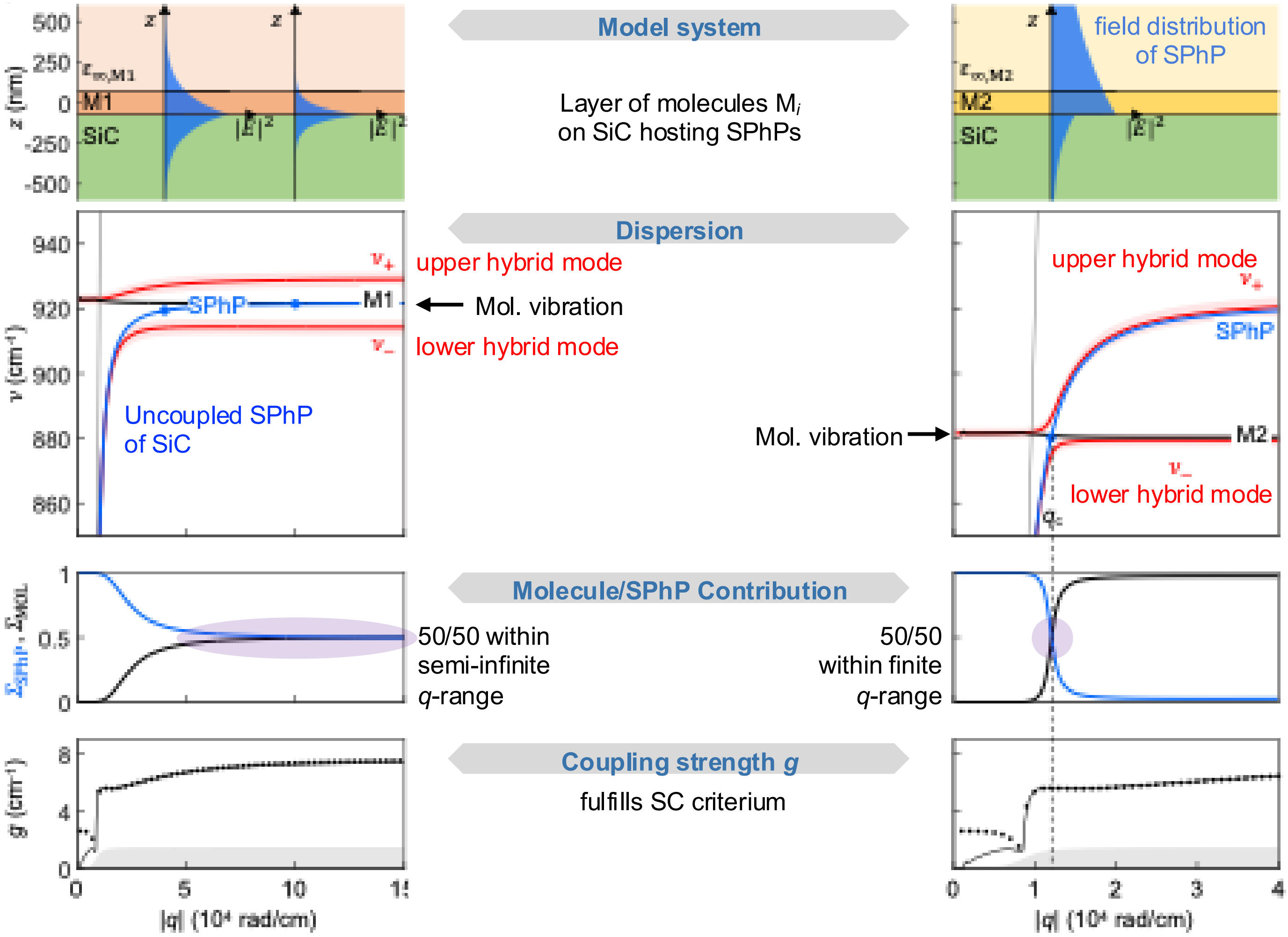
Thank you for the attention

Polariton interferometry of unpumped sample yields SPhP dispersion



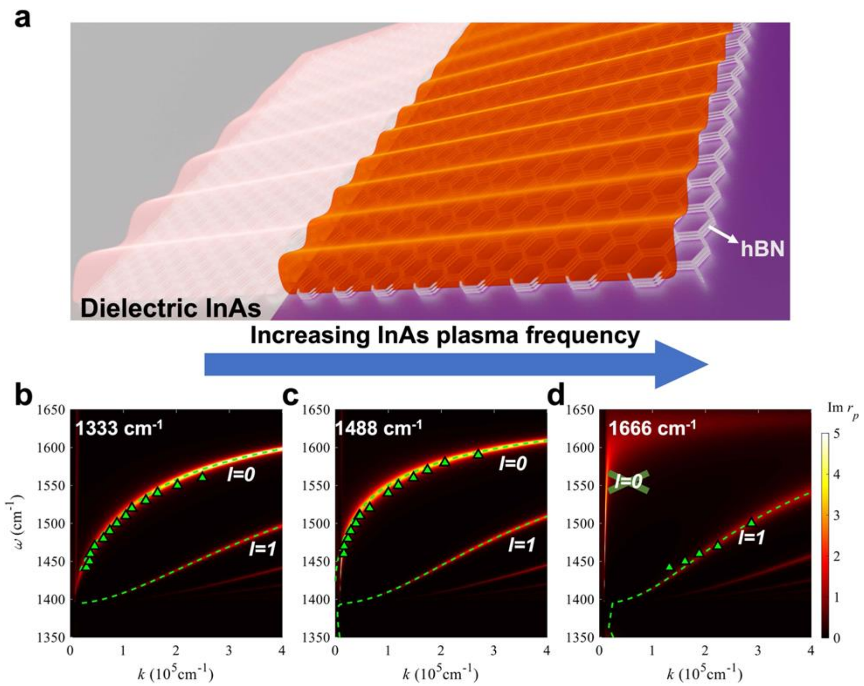
Calculations predict flat-band VSC for molecular vibrations

Flat-band VSC | **Conventional VSC**



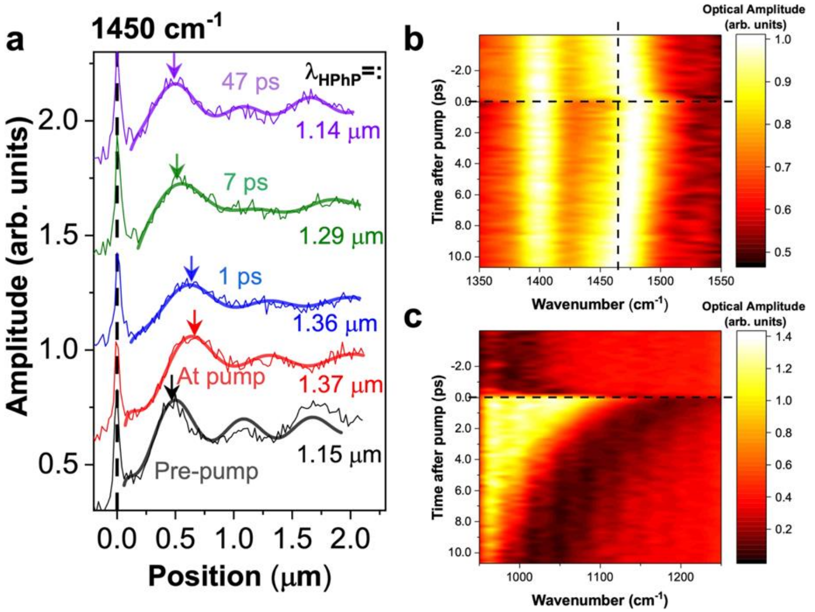
h-BN phonon polariton dispersion can be controlled by mobile carriers in InAs substrate

h-BN on chemically doped InAs



➡ **Static phonon polariton tuning**

h-BN on photo-excited InAs

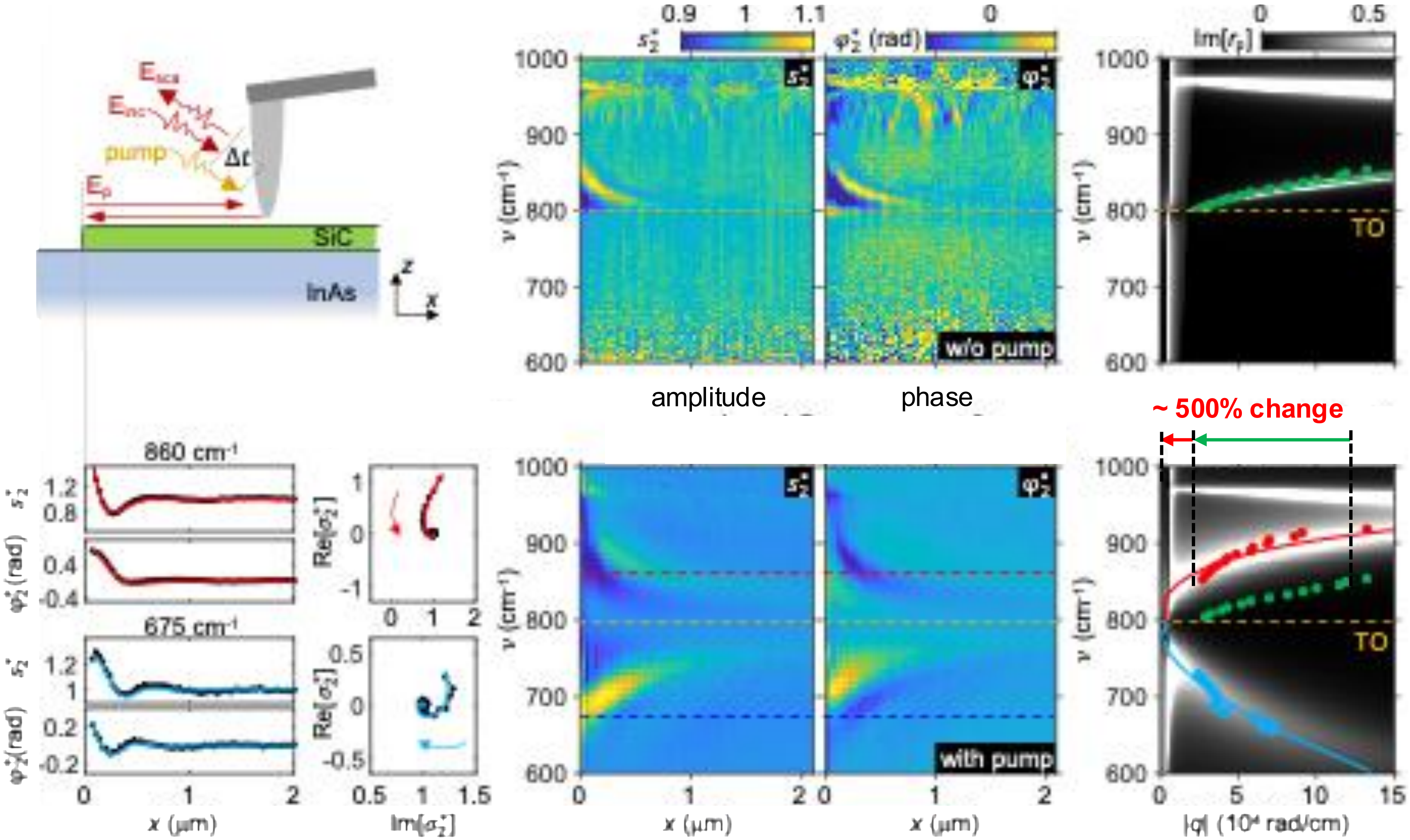


➡ **Ultrafast (ps) phonon polariton tuning**

wavevector change of ~ 20%

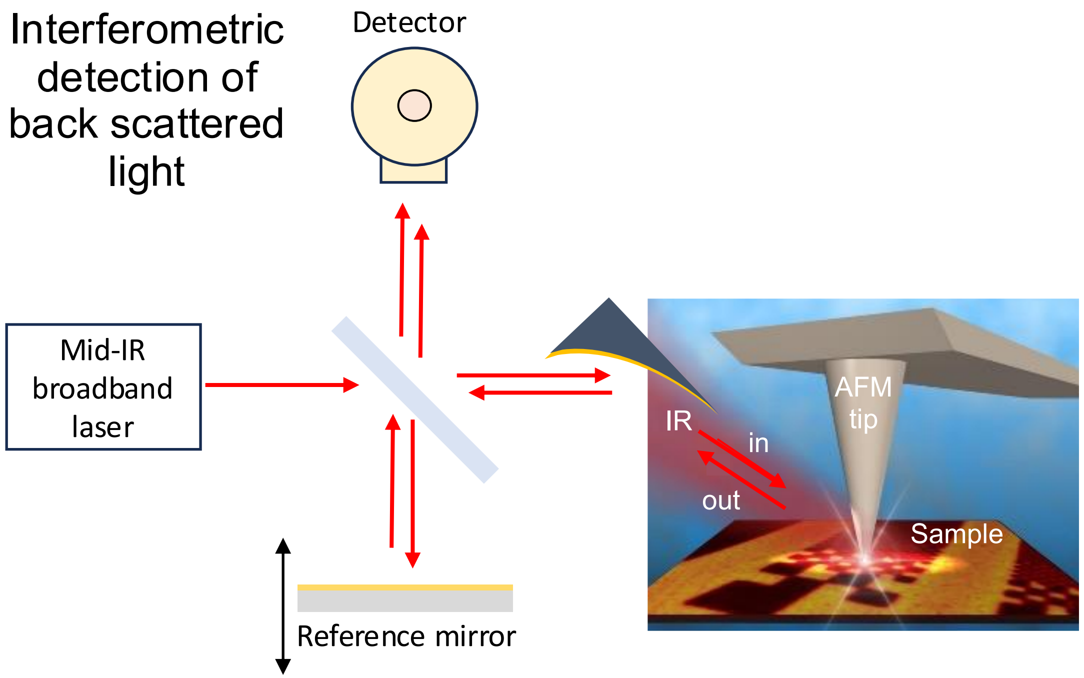
M. He, et al., *Nat. Comm.* **14**, 7965 (2023) (Caldwell Group)

Polariton interferometry of unpumped sample yields SPhP dispersion



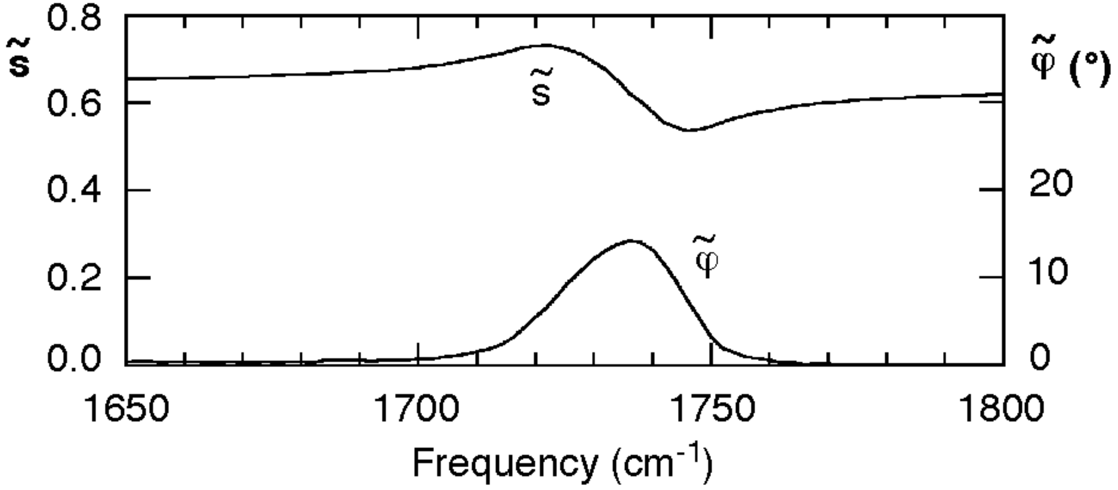
s-SNOM probe optical properties at nanoscale

Interferometric detection of back scattered light



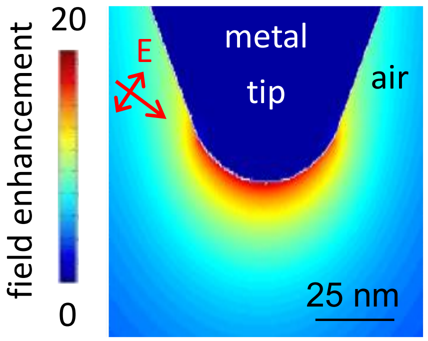
Focused laser beam illuminates AFM tip

s-SNOM amplitude and phese spectra

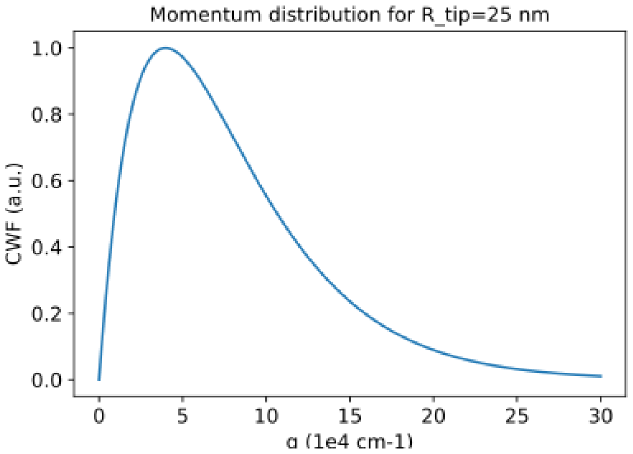


s-SNOM probe a distribution of momentum/wavevectors

Tip momentum



$\lambda \approx 10$ µm



s-SNOM probe a distribution of momentum/wavevectors

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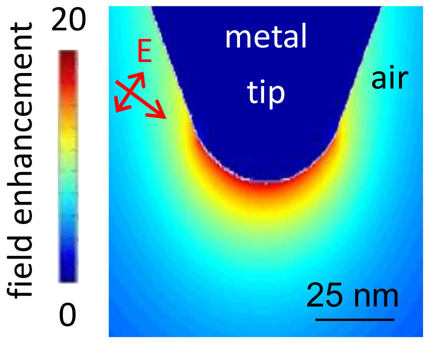
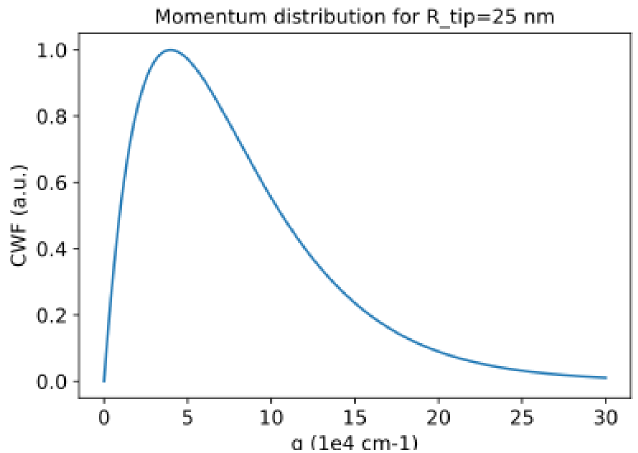
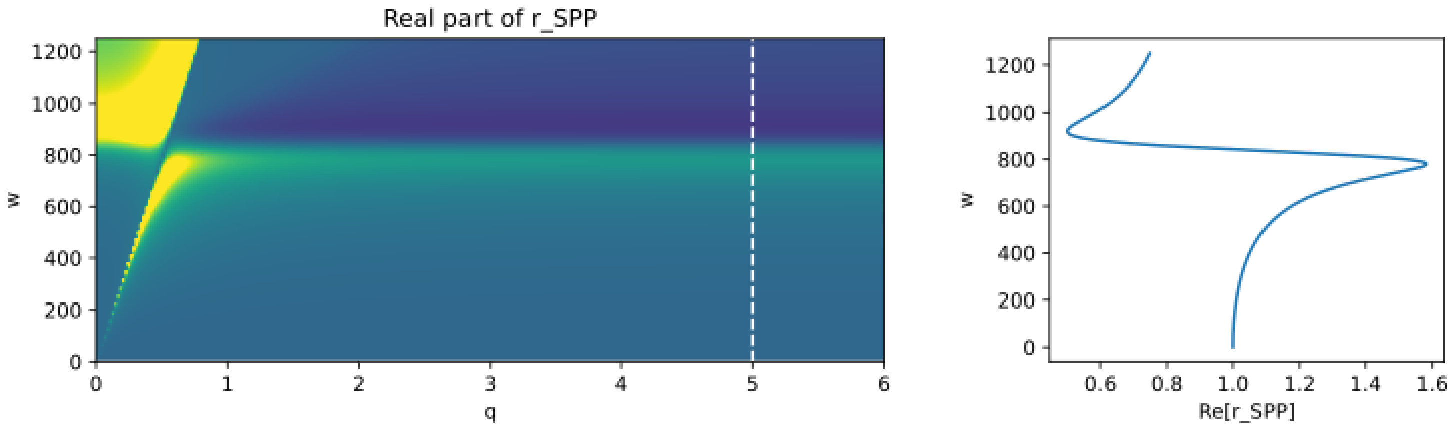
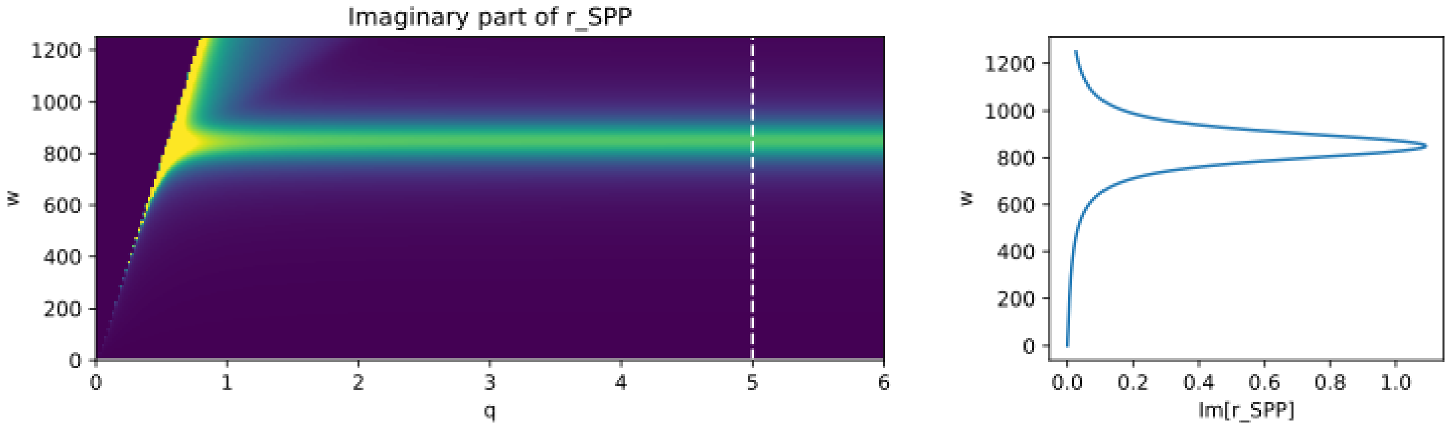


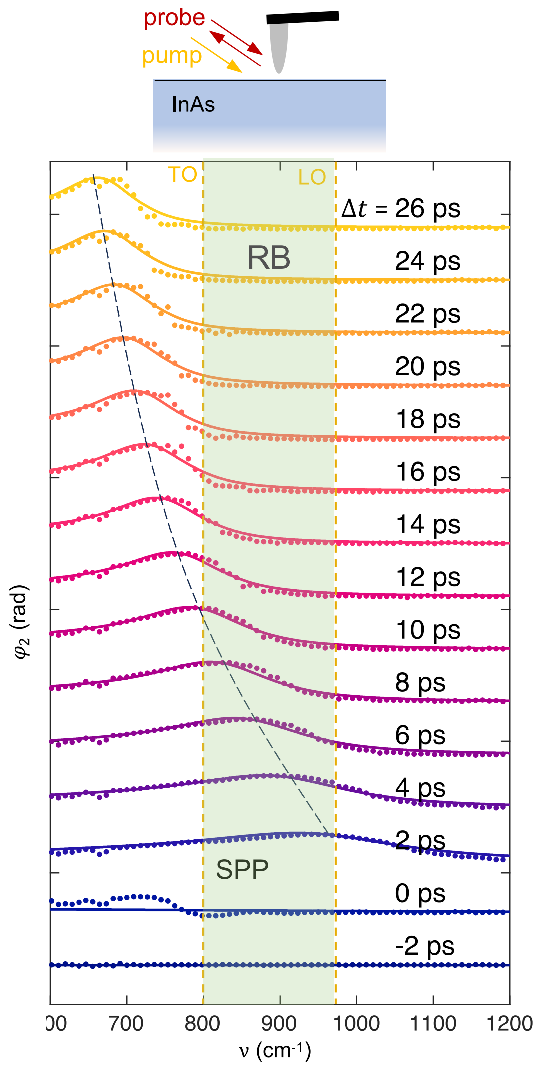
λ ≈ 10 µm





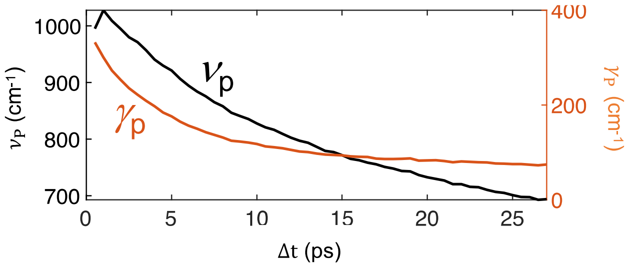


100 fs near-IR pulses photo-excite mobile electrons in InAs and change the SPP frequency

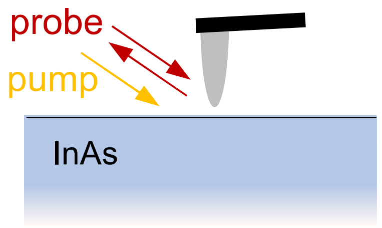


nano-FTIR phase spectra at pump-probe delay time Δt

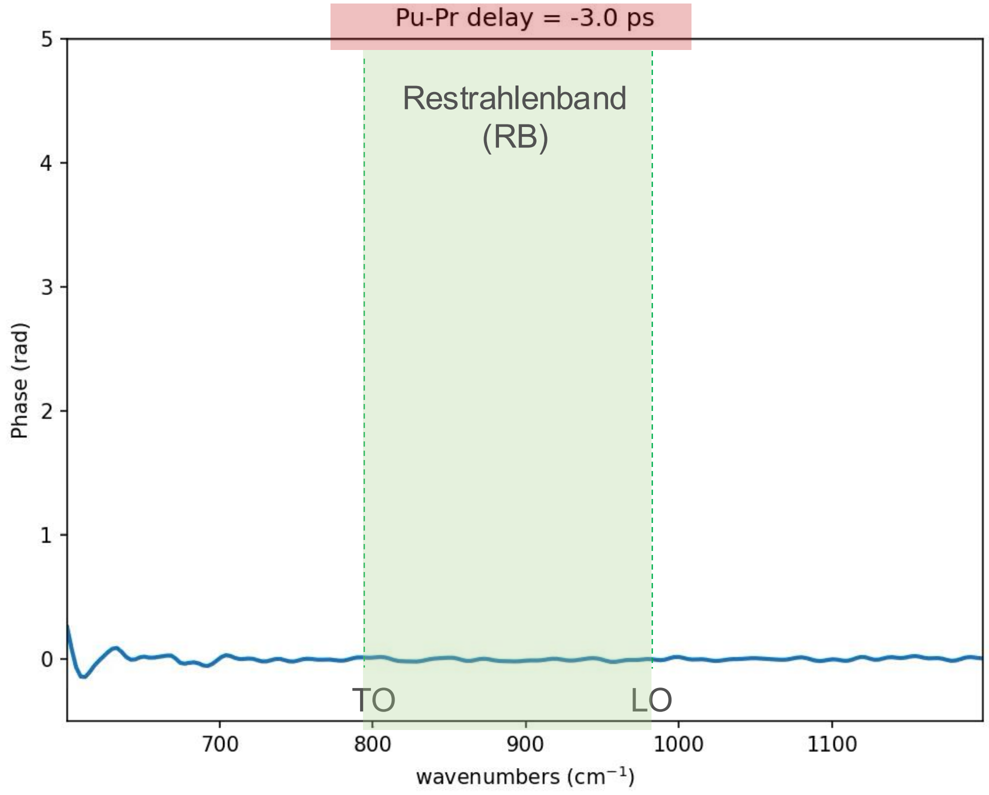
- reveal temporary SPP resonance
- yield plasma frequency ν_p
- yield plasma damping γ_p



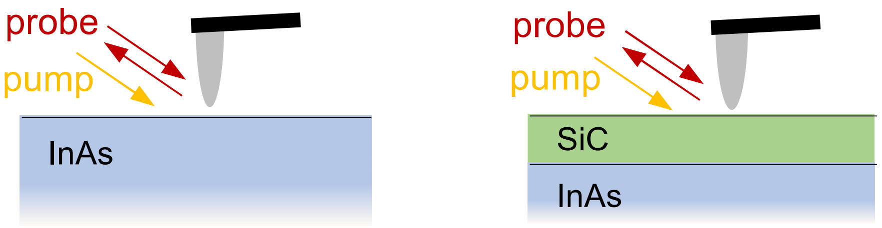
Pump-probe nanospectroscopy of InAs



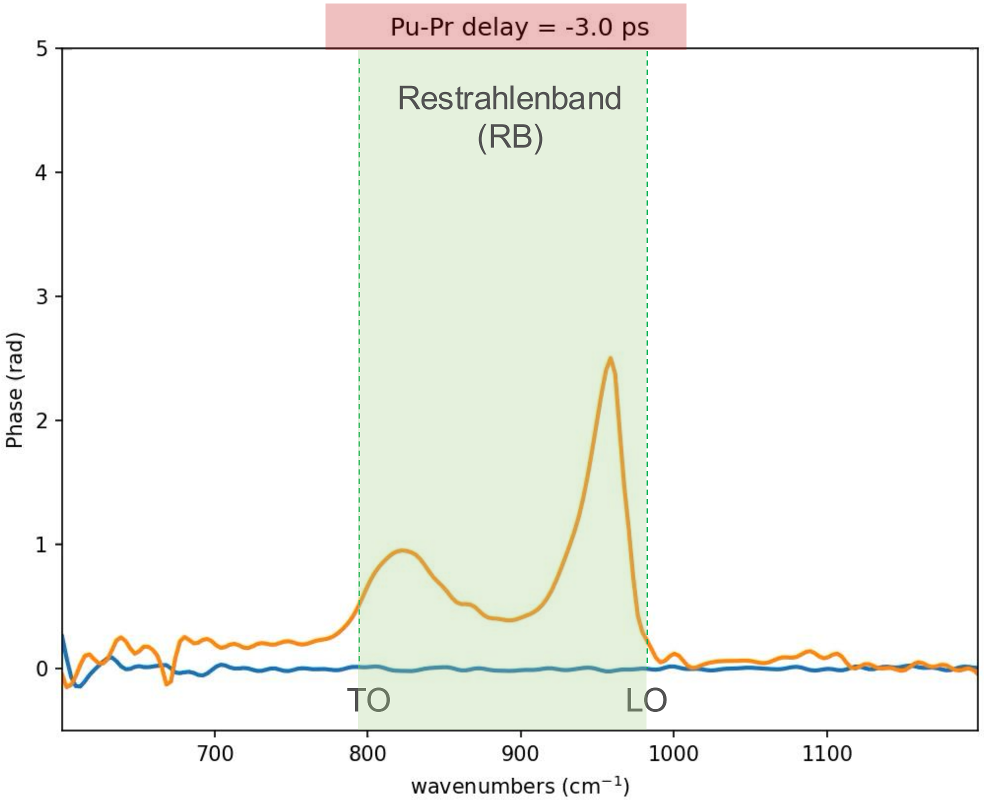
nano-FTIR phase spectra at pump-probe delay time Δt



Pump-probe nanospectroscopy of SiC/InAs

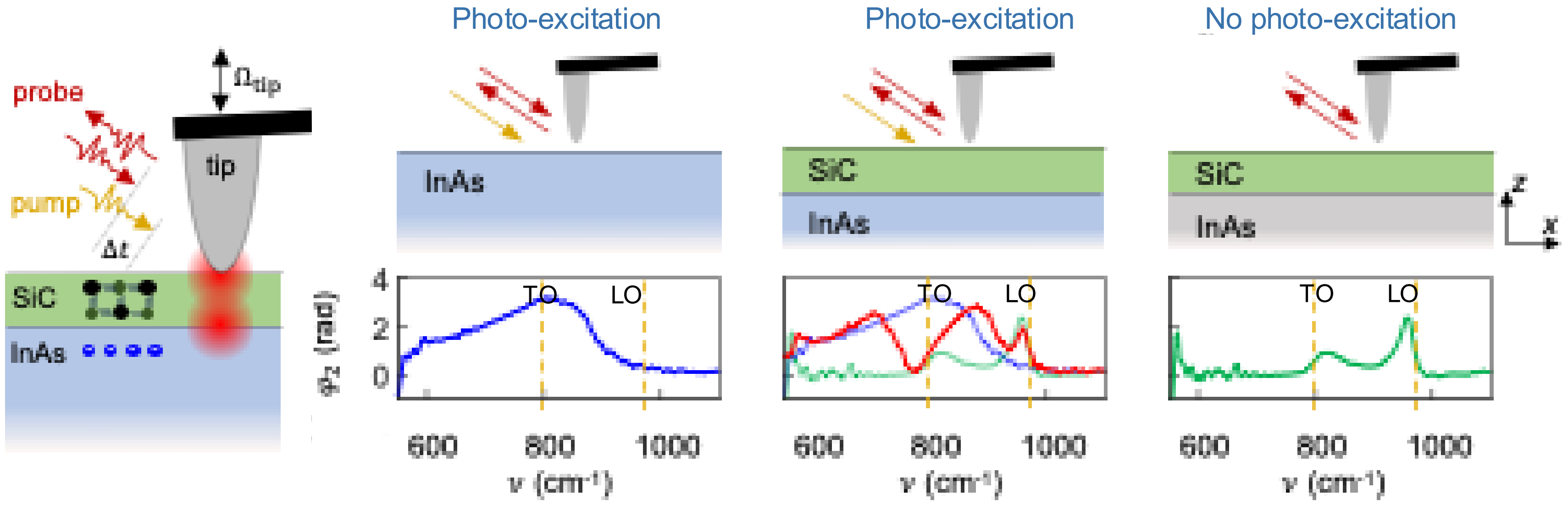


nano-FTIR phase spectra at pump-probe delay time Δt



At time delay $\Delta t \sim 10$ ps the SPP resonance in InAs matches the TO phonon of SiC

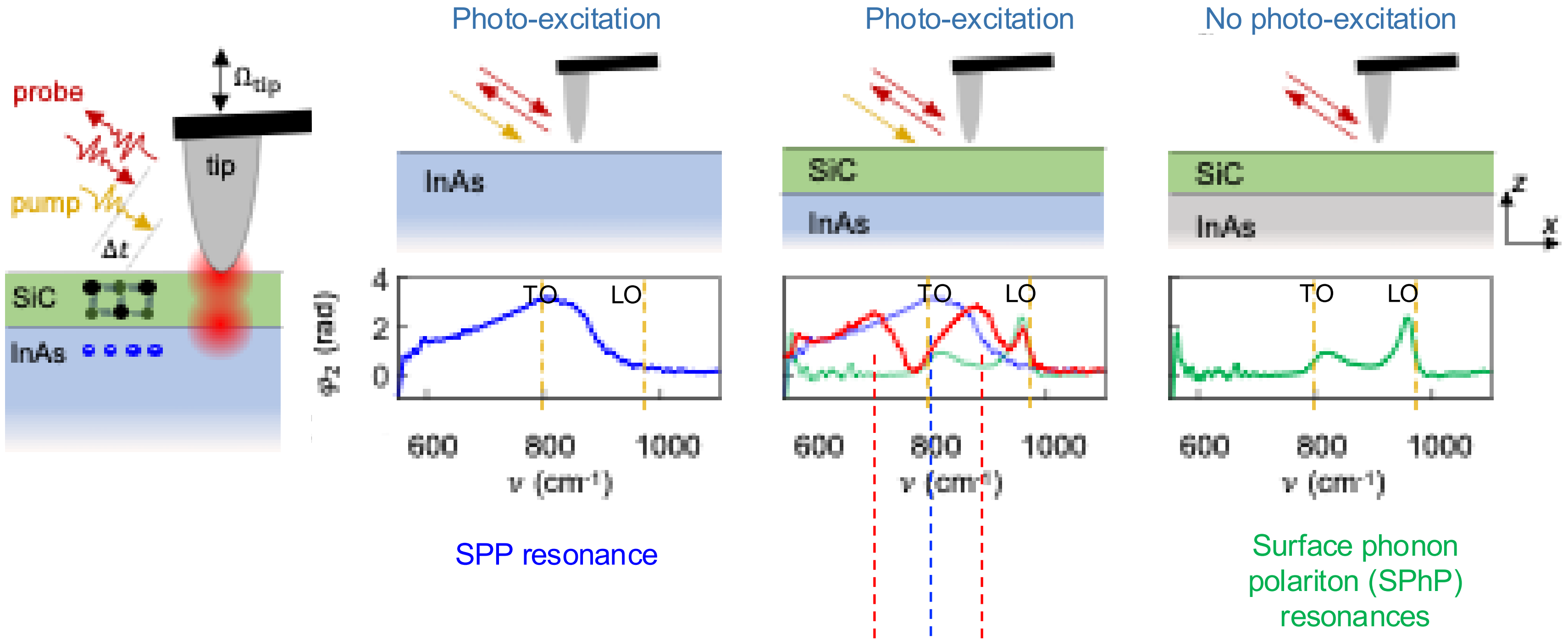
At time delay Δt ~ 10 ps the SPP resonance in InAs matches the TO phonon of SiC



SPP resonance

Surface phonon polariton (SPhP) resonances

When SPP matches TO we observe indication of USC



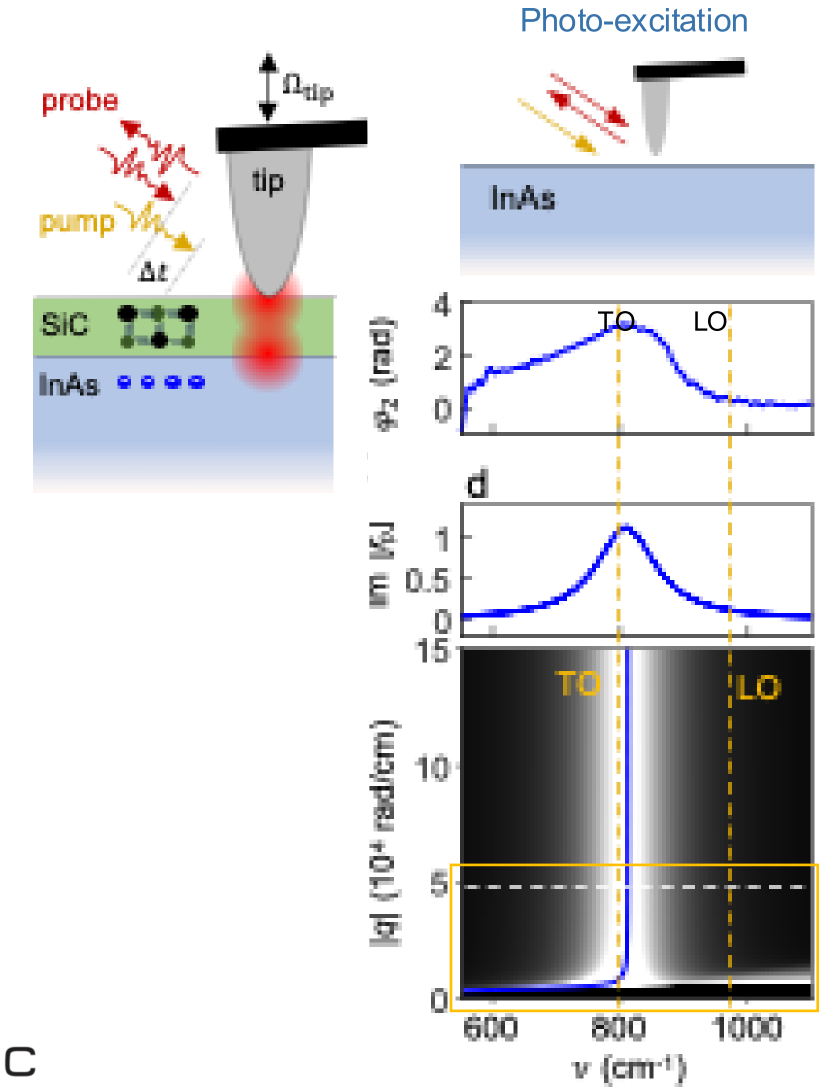
SPP resonance

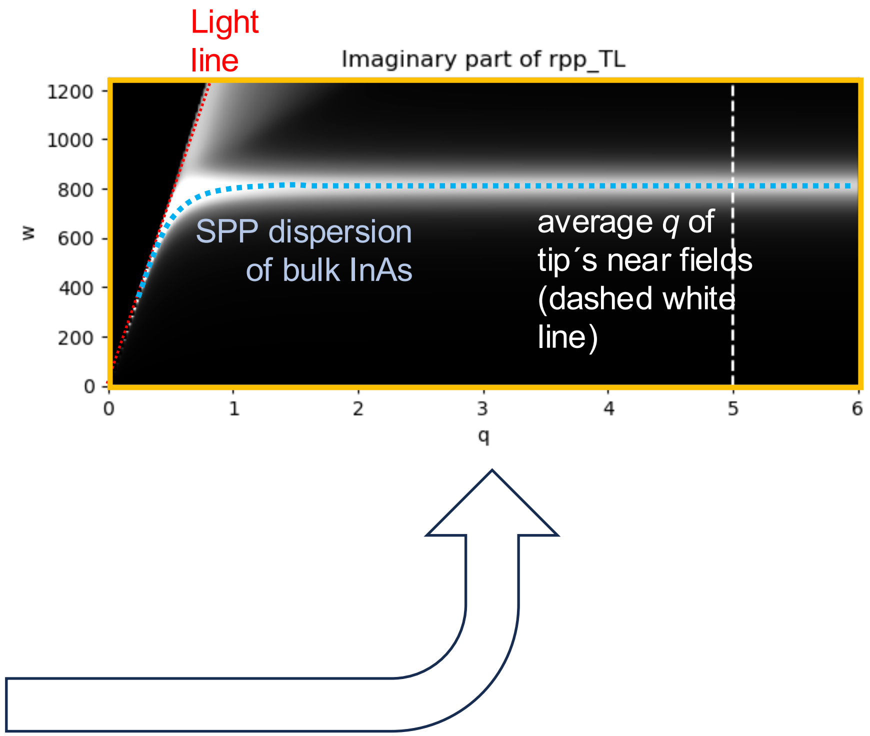
Surface phonon polariton (SPhP) resonances

SPP resonance splitting ~ 20% in presence of SiC

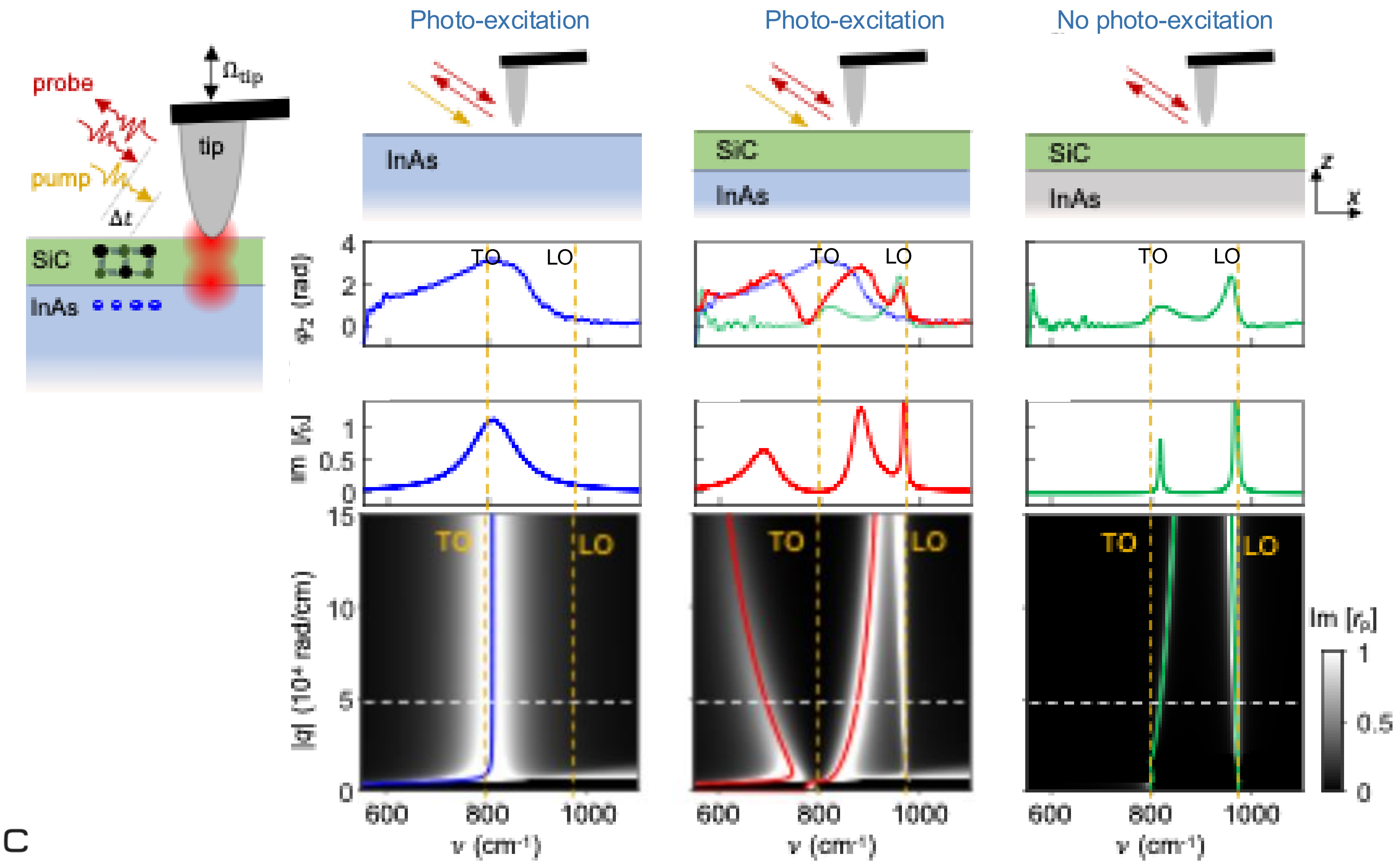
➡ **ultrastrong coupling (USC)**

Multilayer reflectivity confirm the experimental observation



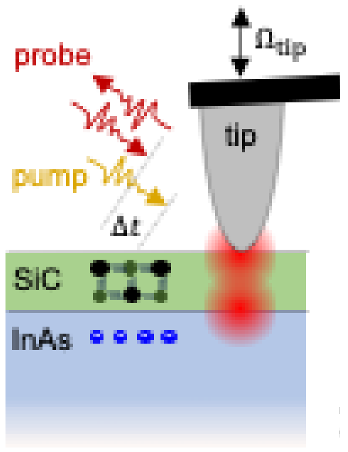


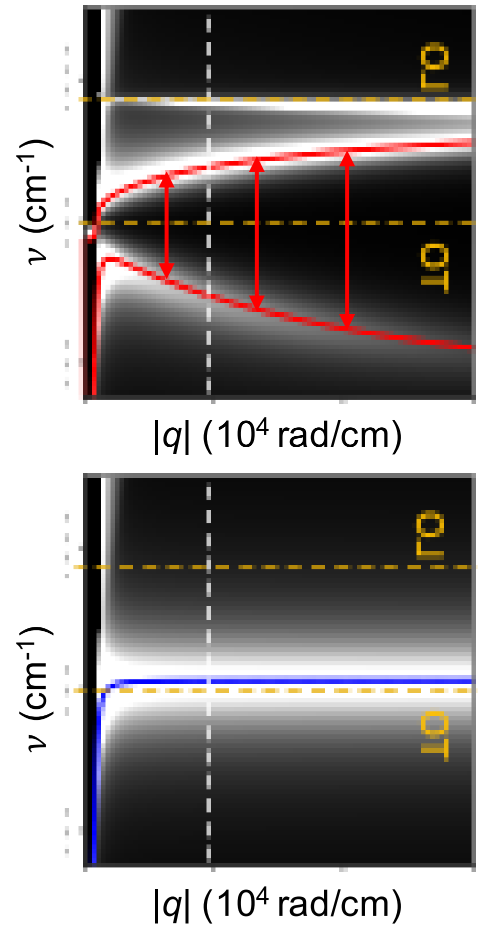
Multilayer reflectivity confirm the experimental observation



Transfer matrix calculations confirm the experimental observation

… and reveal an unusual anti-crossing behaviour





Anti-crossing and hybrid modes extend to q→ ∞,
i.e. they do not approach the uncouple SPP and TO modes