Department of Physics
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Harnessing Shape Effects for Adsorbate Signal Enhancement in Vibrational EELS

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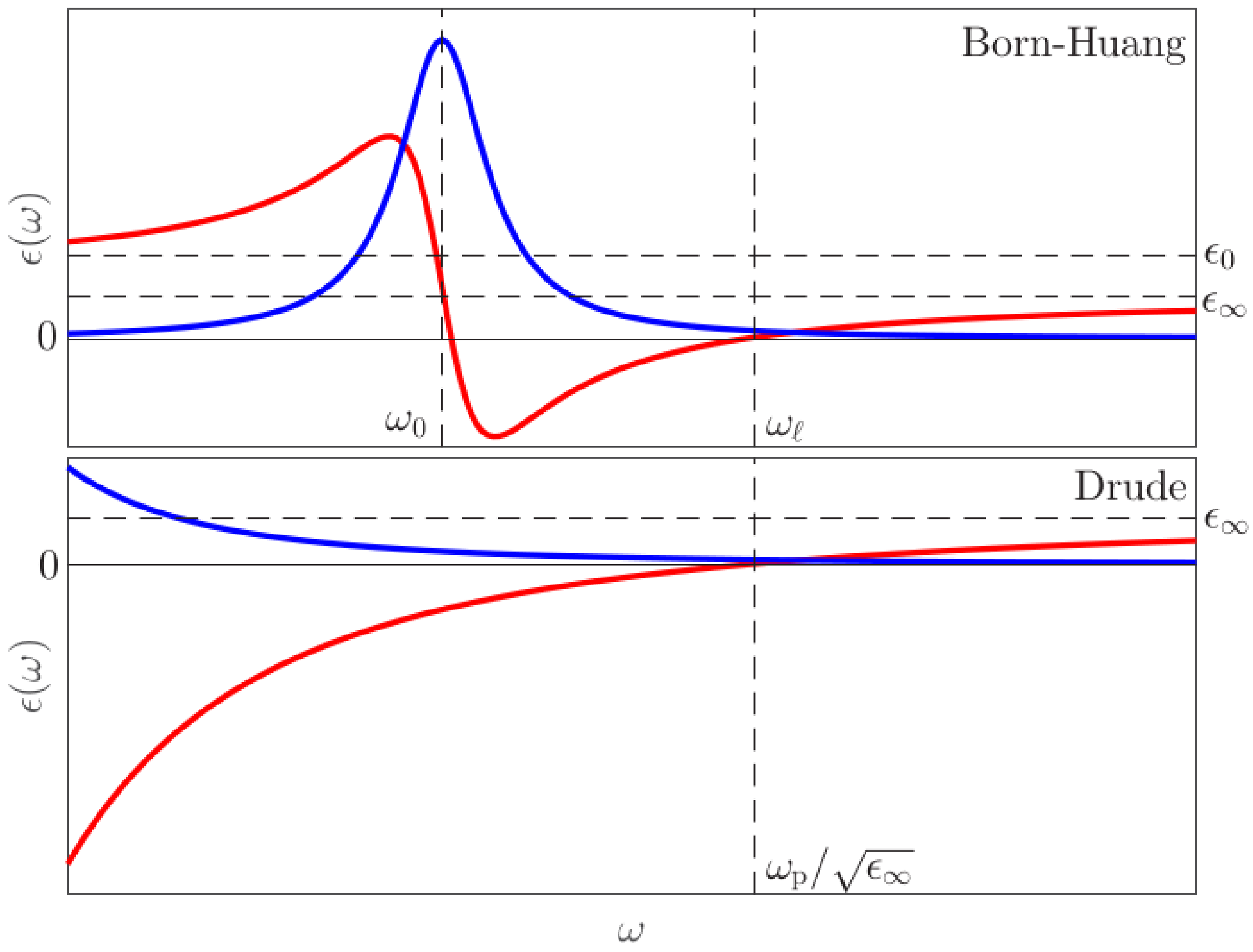
Summary

- Shape effects and surface modes in EELS
- Coupling a surface molecule to surface modes
- Quantifying the molecular signal enhancement
- On- and off-resonance driven molecular signals

Shape effects and surface modes

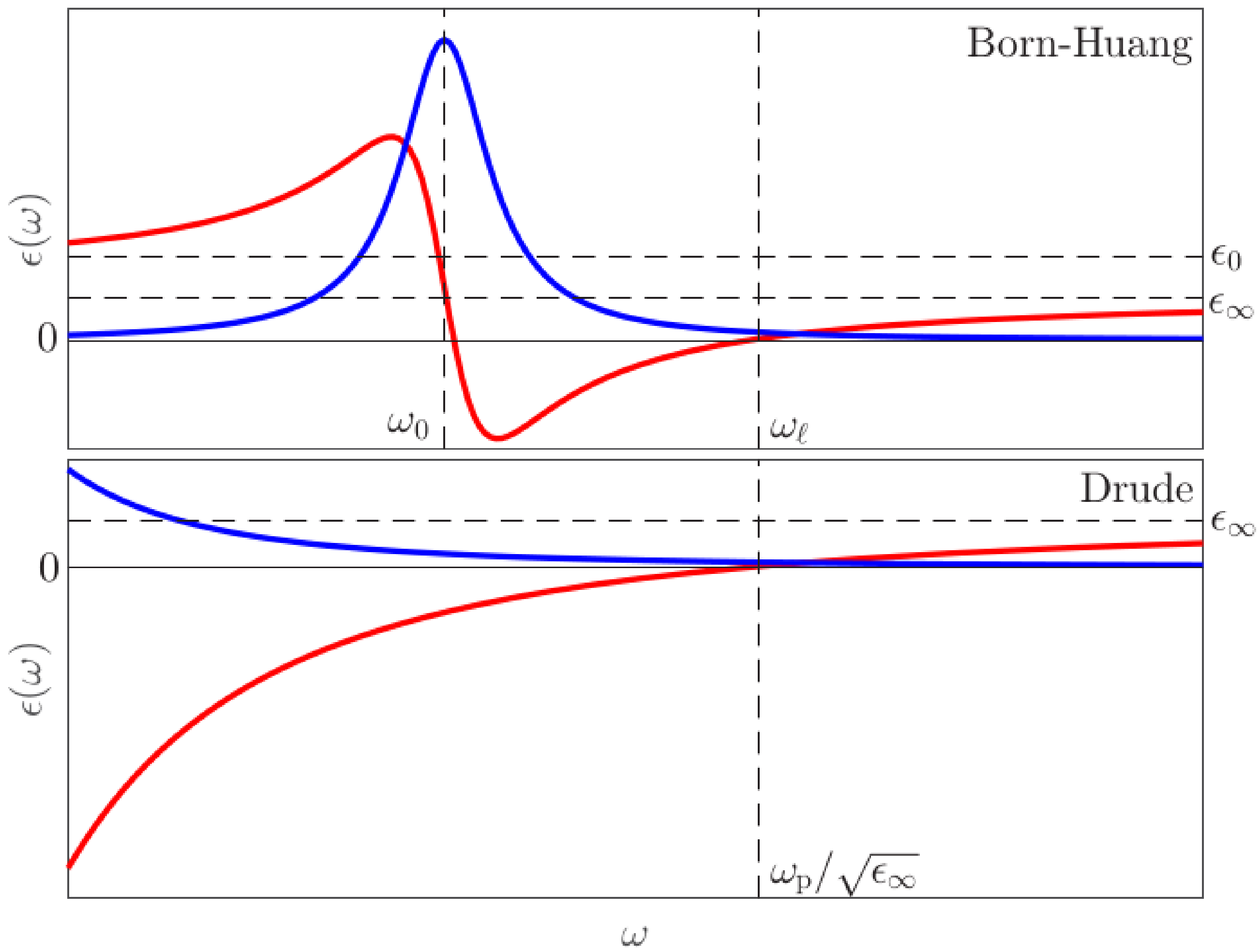
Born-Huang and Drude dielectric functions



***Born-Huang (Lorentz) dielectric function:**

$$\epsilon(\omega) = \epsilon_\infty \frac{\omega(\omega + 2i\eta) - \omega_\ell^2}{\omega(\omega + 2i\eta) - \omega_0^2}$$

Born-Huang and Drude dielectric functions



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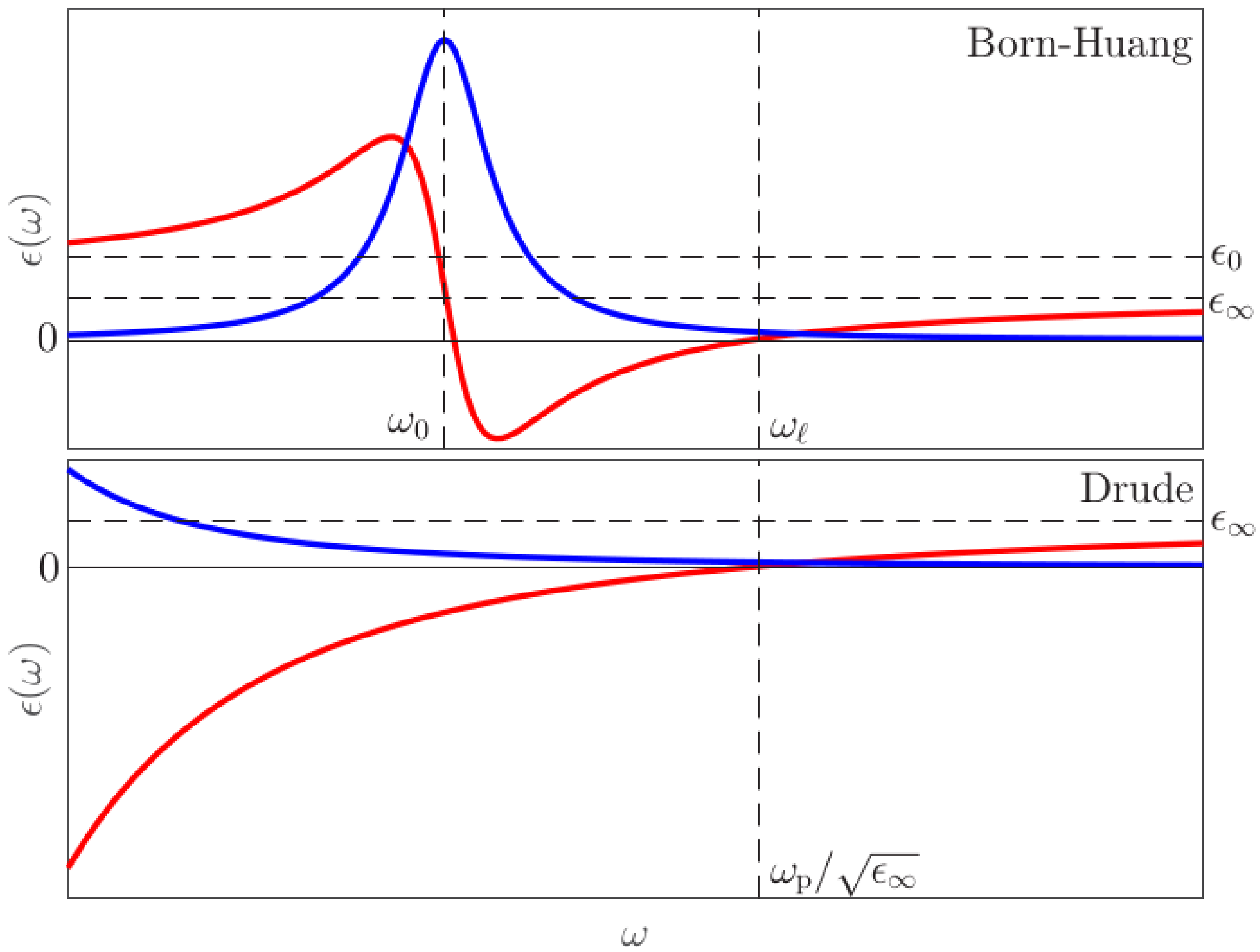

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$$\epsilon_\infty \omega_\ell^2 \to \omega_p, \quad \omega_0 \to 0$$

*For frequencies where the dielectric function is negative, particles can support harmonic modes

$$\ddot{\phi}_h = -\omega_h^2 \phi_h$$

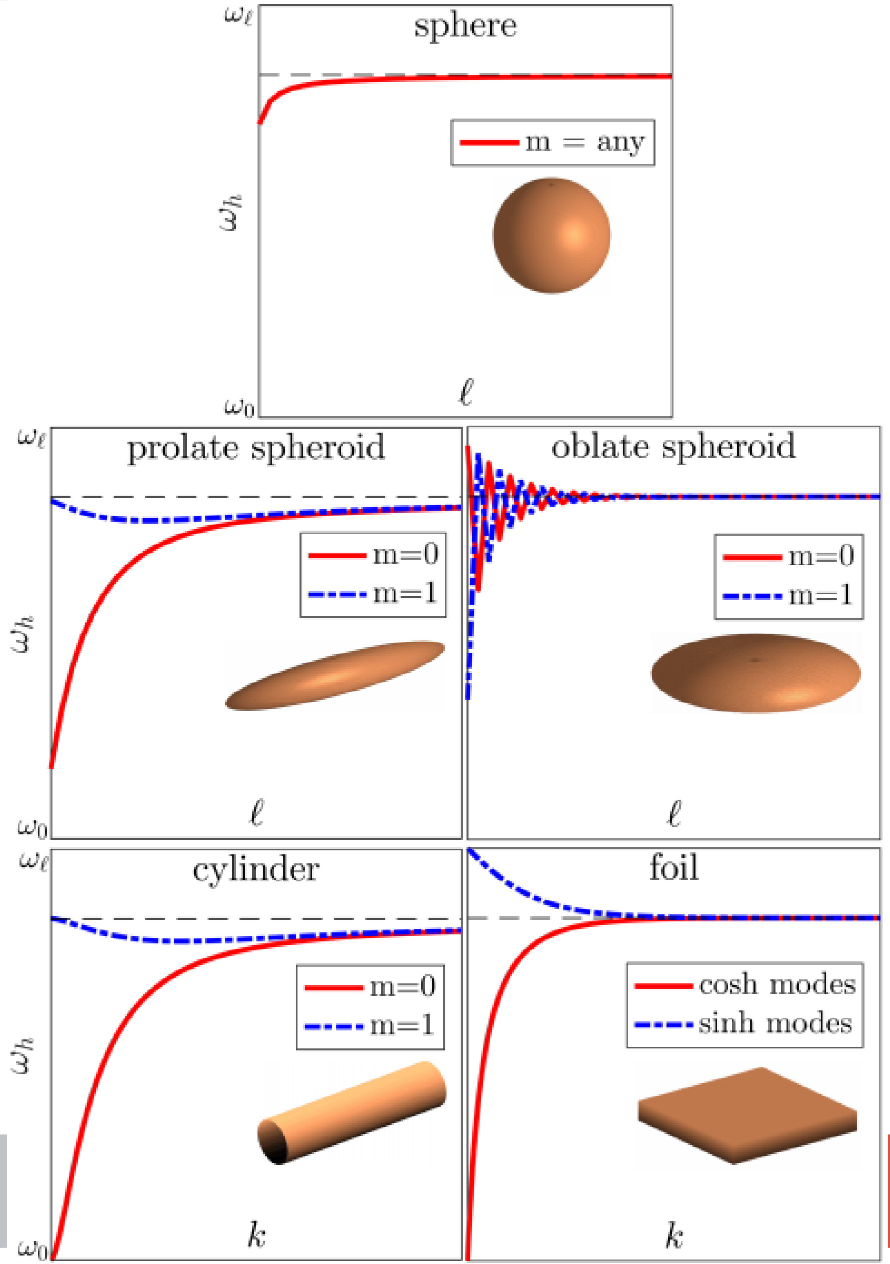
Harmonic frequencies for regular geometries

Simplest example: sphere

1. Scale harmonic functions

$$\phi_{\ell m}^{\text{in}} \propto (r/a)^{\ell} P_\ell^m(\cos\vartheta)\exp(im\varphi)$$

$$\phi_{\ell m}^{\text{out}} \propto (a/r)^{\ell+1} P_\ell^m(\cos\vartheta)\exp(im\varphi)$$



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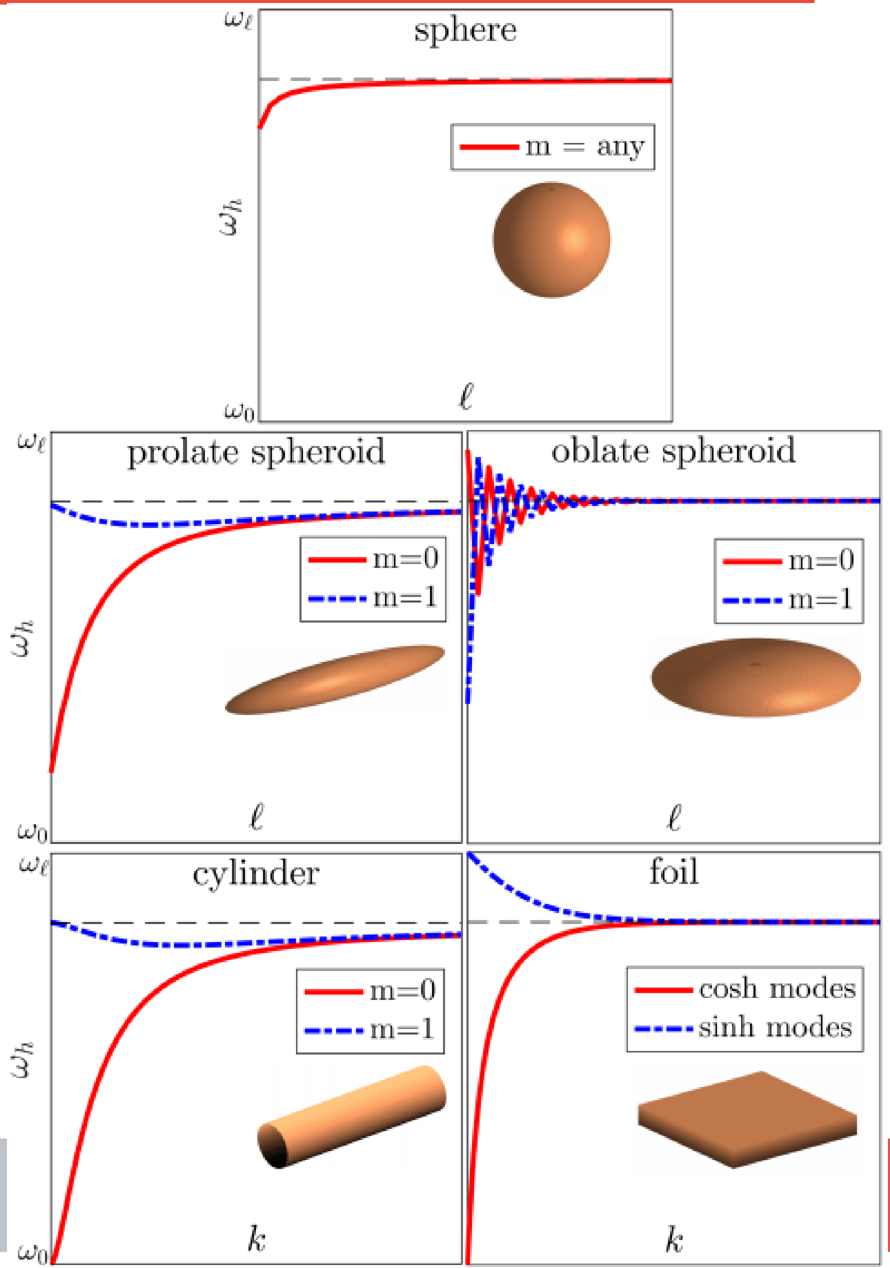
2. Find mode dielectric values

$$\epsilon_h = \left.\frac{\partial_\perp \phi_h^{\text{out}}}{\partial_\perp \phi_h^{\text{in}}}\right|_{\text{surface}} \;\Rightarrow\; \epsilon_{\ell m} = -\frac{\ell+1}{\ell}$$



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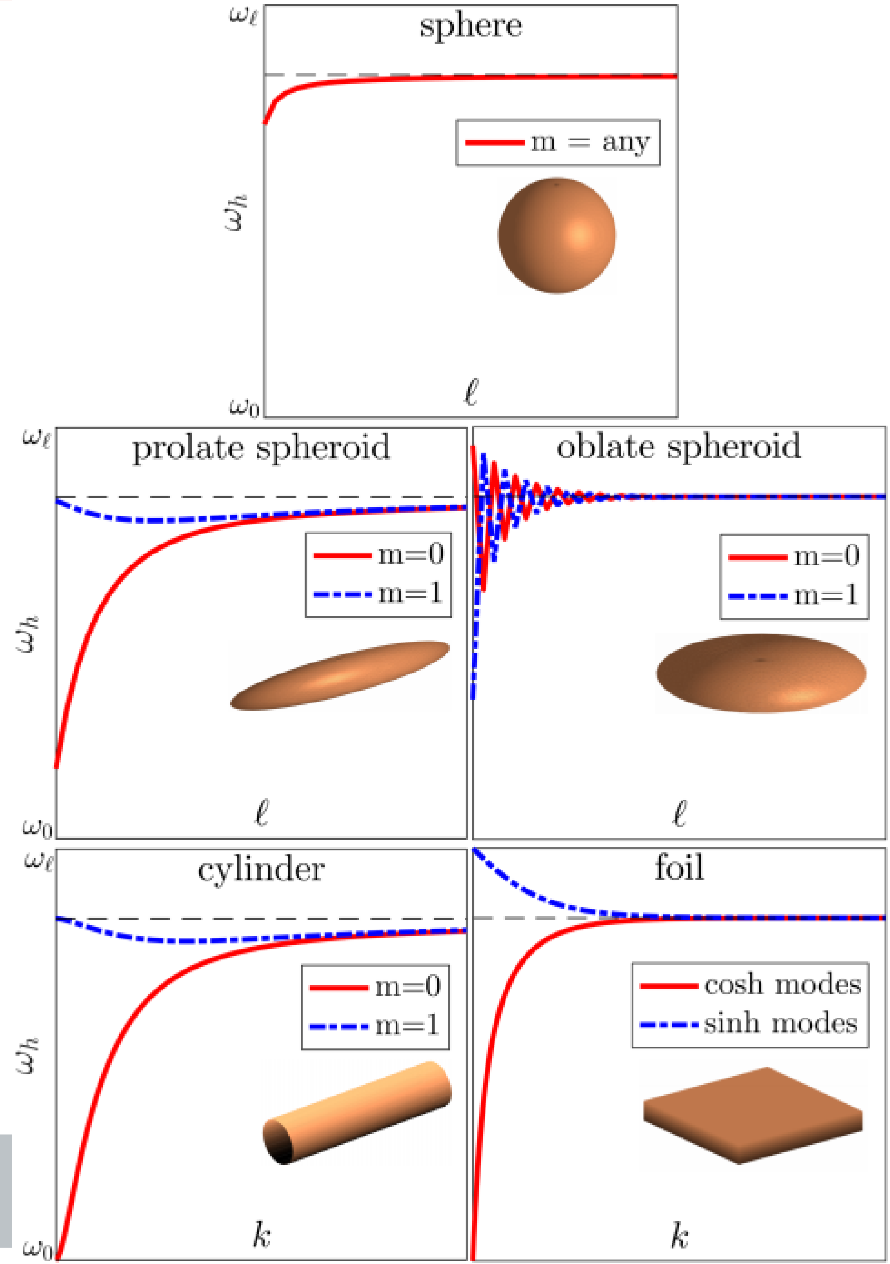
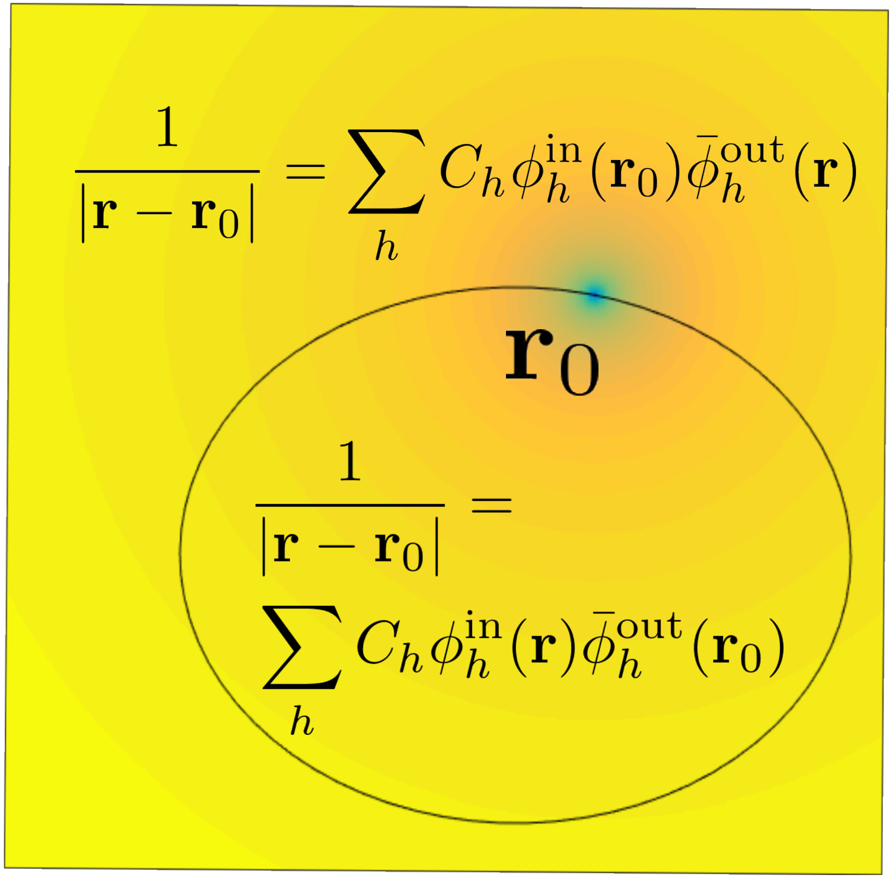
3. Find mode frequencies

$$\epsilon(\omega_h) = \epsilon_h$$

$$\omega_{\ell m}^2 = \frac{\ell\epsilon_\infty\omega_\ell^2 + (\ell+1)\omega_0^2}{\ell\epsilon_\infty + (\ell+1)}$$



Coupling the electron beam to harmonic modes



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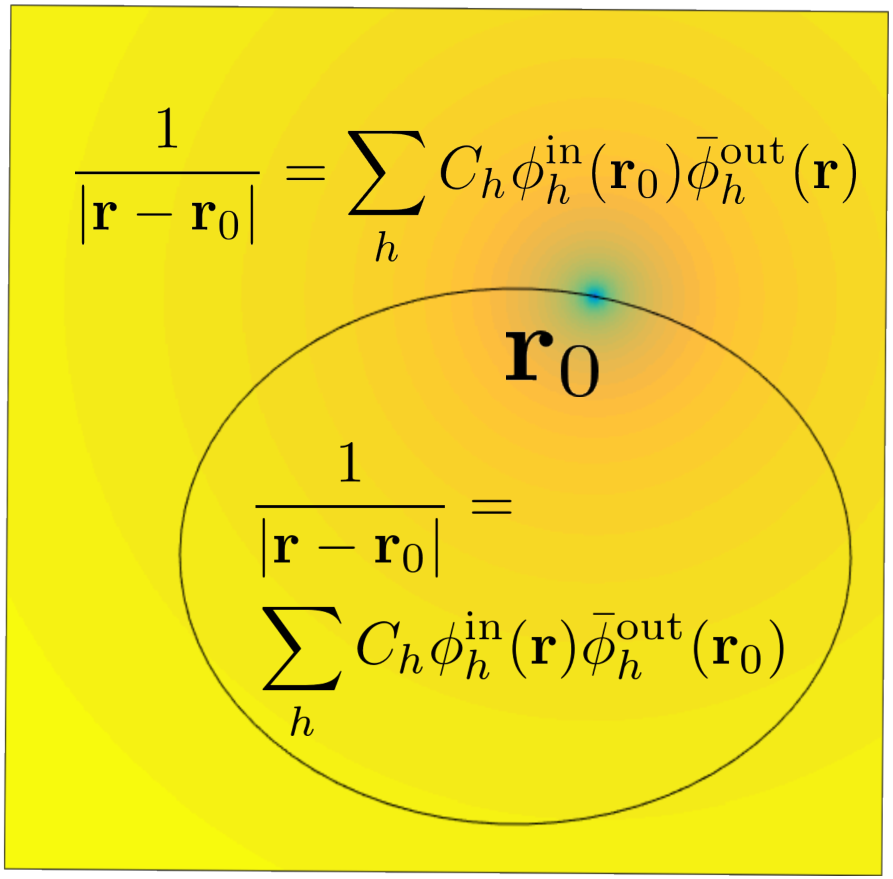

An electron beam following $z = vt$ has the electronic potential

$$\Phi_{\text{e}}(\mathbf{r},\omega) = \sum_h -eC_h \phi_h^{\text{in}}(\mathbf{r}) I_h(\mathbf{x},\omega),$$

where

$$I_h(\mathbf{x},\omega) = \int_{-\infty}^{\infty} \frac{\mathrm{d}z}{v}\, \phi_h^{\text{out}}(\mathbf{x},z)\, e^{i\omega z/v}.$$

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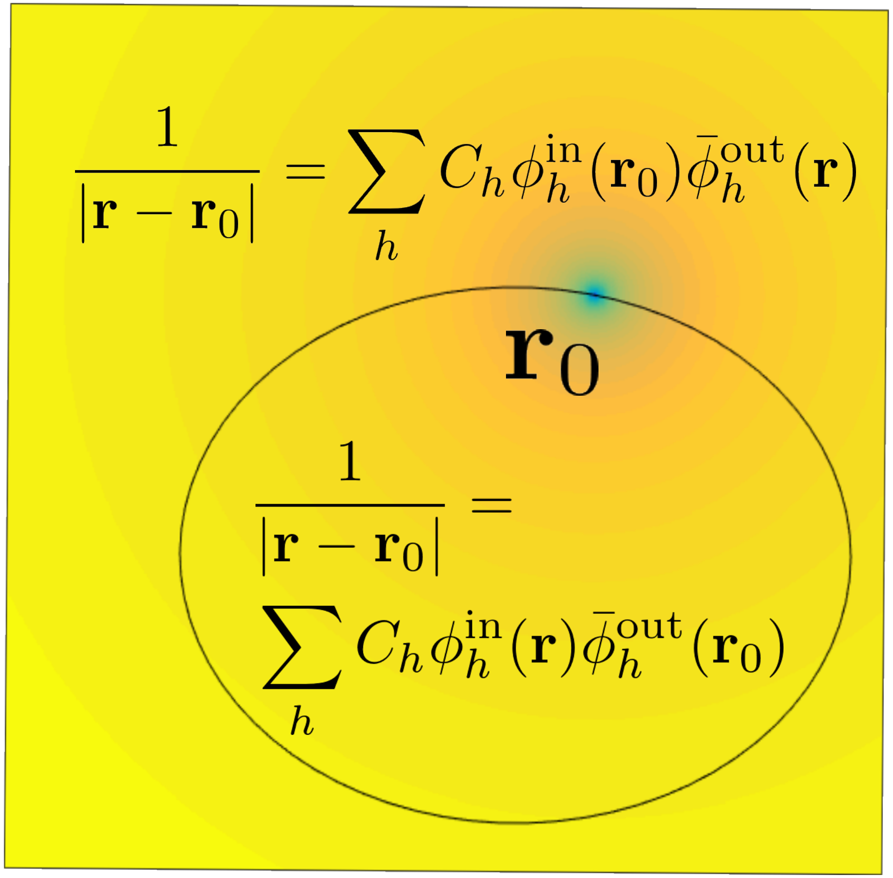

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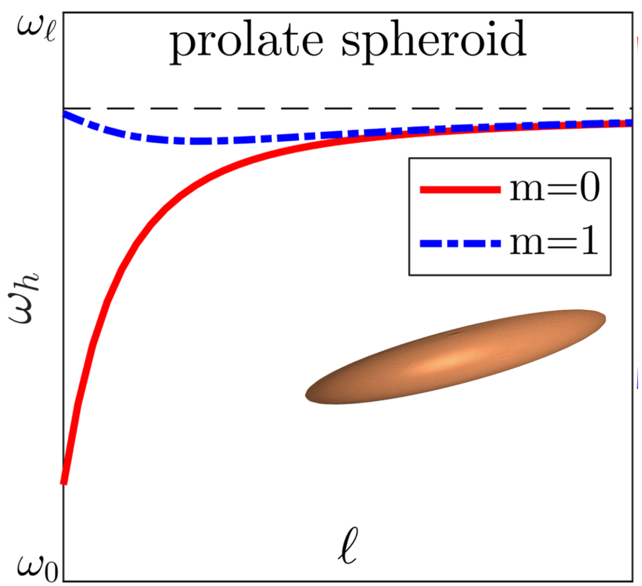
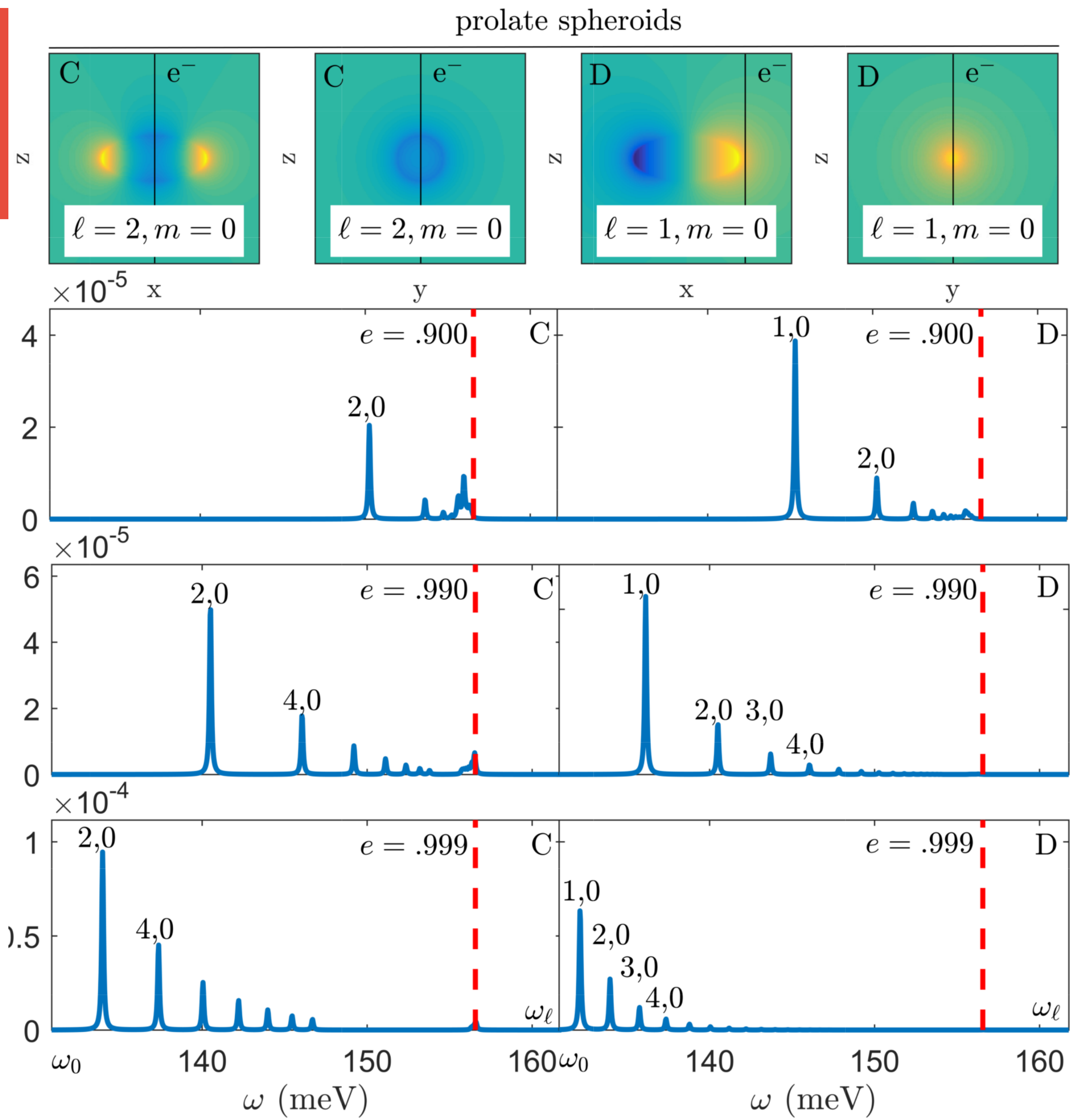
Finding the induced potential of the particle and integrating the work it does on the beam yields the nanoparticle EEL spectrum:

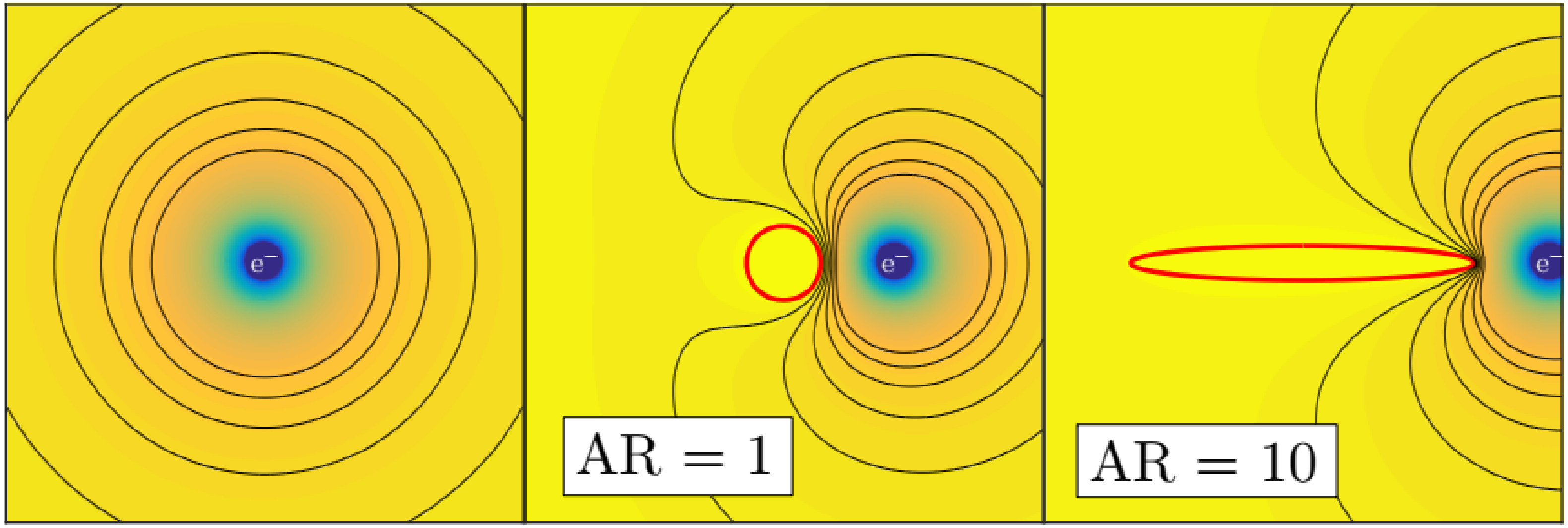
$$\frac{\mathrm{d}P_0}{\mathrm{d}\omega} = \frac{e^2}{\pi\hbar} \sum_h C_h \left|I_h(\mathbf{x},\omega)\right|^2 \mathrm{Im}\left(\alpha_h(\omega)\right), \quad \alpha_h(\omega) = \frac{\epsilon(\omega)-1}{\epsilon(\omega)-\epsilon_h}.$$

Test case: prolate spheroids





Prolate spheroids as "lightning rods"



For long needle-like geometries in the presence of a beam

* from screening, the beam potential is deformed most at the tip → the induced field is largest near the nanoparticle tip

* the internal electric field is weak for modes with charge at tips → harmonic frequencies for these antenna modes are low

Surface molecules and surface modes

Adsorbate as a Born-Huang dipole

We choose to model the adsorbate as a Born-Huang dipole constrained to vibrate along the surface normal:

$$\frac{q^2}{\mu}\hat{\mathbf{n}}\cdot\mathbf{E}(\omega) = \left(\omega_{\mathrm{m}}^2 - \omega(\omega + 2i\gamma)\right) p(\omega)$$

This dipole potential can be expanded in modes:

$$\Phi_{\mathrm{m}}(\mathbf{r},\omega) = \mathbf{p}(\omega)\cdot\nabla_{\mathrm{m}}\frac{1}{|\mathbf{r}-\mathbf{r}_{\mathrm{m}}|}$$

$$\Phi_{\mathrm{m}}^{\mathrm{in}}(\mathbf{r},\omega) = \sum_h C_h p(\omega)\hat{\mathbf{n}}\cdot\bar{\mathbf{u}}_h^{\mathrm{out}}(\mathbf{r}_{\mathrm{m}})\phi_h^{\mathrm{in}}(\mathbf{r})$$

$$\Phi_{\mathrm{m}}^{\mathrm{out}}(\mathbf{r},\omega) = \sum_h C_h p(\omega)\hat{\mathbf{n}}\cdot\bar{\mathbf{u}}_h^{\mathrm{in}}(\mathbf{r}_{\mathrm{m}})\phi_h^{\mathrm{out}}(\mathbf{r})$$

where

$$\nabla\phi_h^{\mathrm{in/out}} = \mathbf{u}_h^{\mathrm{in/out}}$$

Molecular contributions to the EEL spectrum

Self-consistent boundary conditions for the nanoparticle lead to an extra spectrum term, beyond that of the nanoparticle:

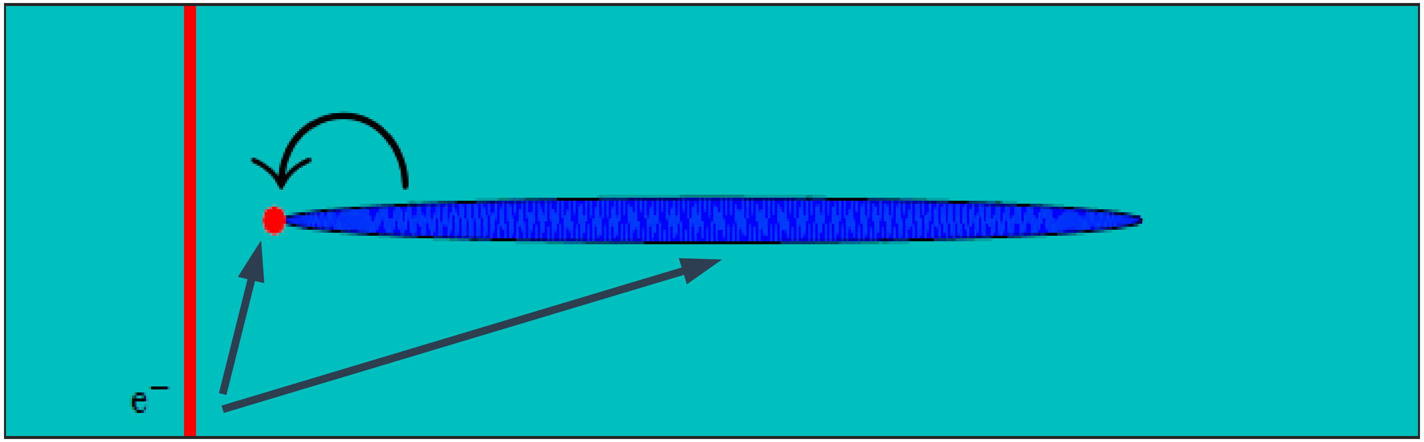
$$\underbrace{\frac{\mathrm{d}P}{\mathrm{d}\omega}}_{\text{full}} = \underbrace{\frac{\mathrm{d}P_0}{\mathrm{d}\omega}}_{\text{bare nanoparticle}} + \underbrace{\frac{\mathrm{d}P_\mathrm{m}}{\mathrm{d}\omega}}_{\text{molecule}}$$

$$\frac{\mathrm{d}P_0}{\mathrm{d}\omega} = \frac{e^2}{\pi\hbar}\sum_h C_h \left|I_h(\mathbf{x},\omega)\right|^2 \mathrm{Im}\left(\alpha_h(\omega)\right)$$

The extra term depends on three ancillary functions, each of which has a clear physical interpretation:

$$\frac{\mathrm{d}P_\mathrm{m}}{\mathrm{d}\omega} = \frac{1}{\mu}\frac{q^2}{\pi\hbar}\mathrm{Im}\left(\frac{E_\mathrm{m}(\omega)E_\mathrm{e}(\omega)}{\omega_\mathrm{m}^2 - \Delta\omega_\mathrm{m}^2(\omega) - \omega(\omega + 2i\gamma)}\right)$$

Physics of the coupled dipole model: excitation



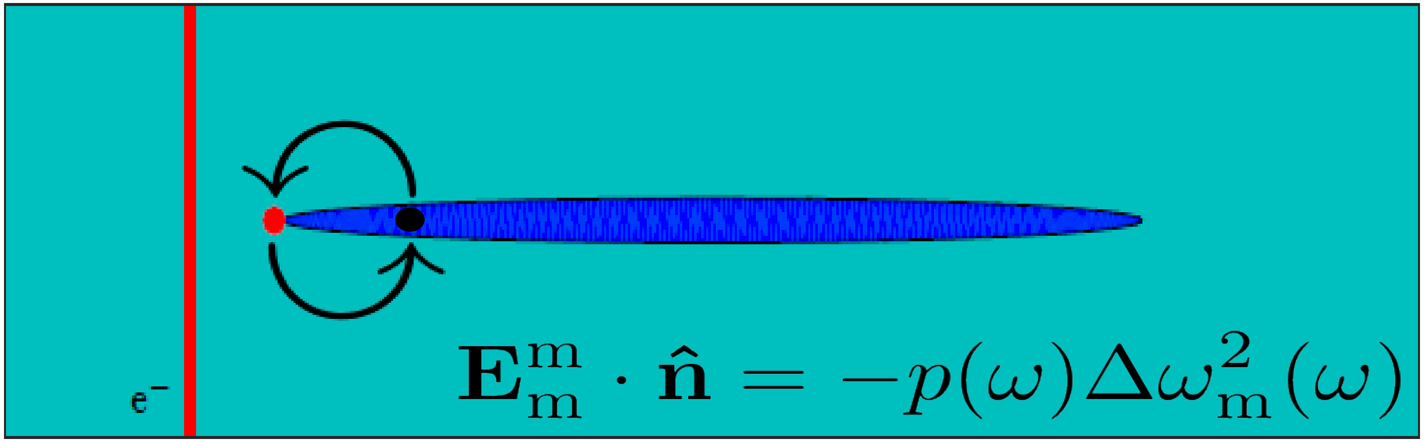
1. The electric field of the beam and the induced electric field from the particle both push on the molecule

$$E_{\mathrm{m}}(\omega) = \sum_h eC_h I_h(\mathbf{x},\omega)\left(\mathbf{u}_h^{\mathrm{in}}(\mathbf{r}_{\mathrm{m}}) - \alpha_h(\omega)\mathbf{u}_h^{\mathrm{out}}(\mathbf{r}_{\mathrm{m}})\right)\cdot\hat{\mathbf{n}}$$

nanoparticle polarizability → $\alpha_h(\omega) = \frac{\epsilon(\omega)-1}{\epsilon(\omega)-\epsilon_h}$

$$\frac{\mathrm{d}P_{\mathrm{m}}}{\mathrm{d}\omega} = \frac{1}{\mu}\frac{q^2}{\pi\hbar}\mathrm{Im}\left(\frac{E_{\mathrm{m}}(\omega)E_{\mathrm{e}}(\omega)}{\omega_{\mathrm{m}}^2 - \Delta\omega_{\mathrm{m}}^2(\omega) - \omega(\omega+2i\gamma)}\right)$$

Physics of the coupled dipole model: redshift

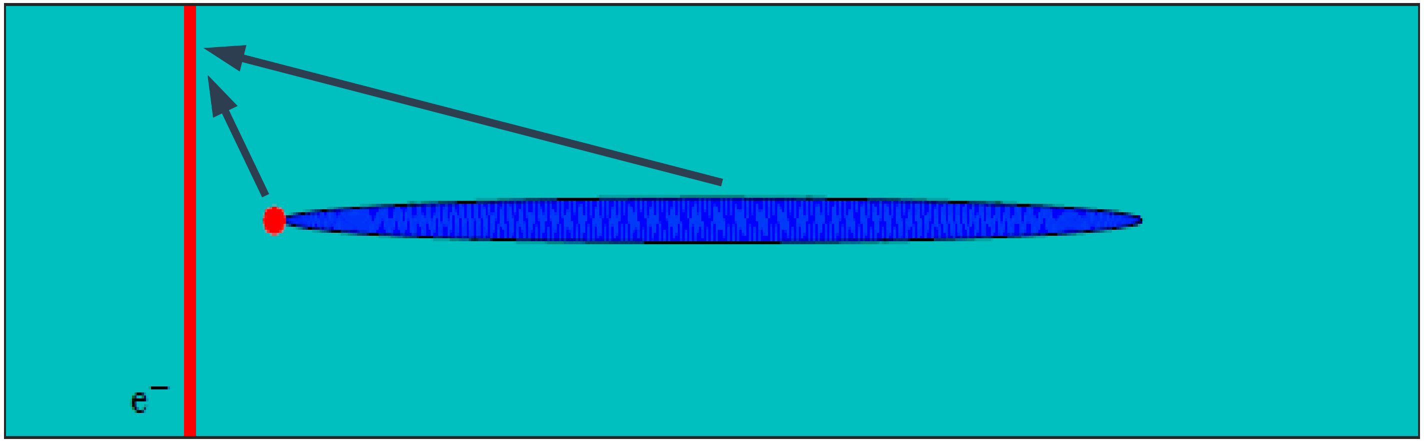


2. The molecular dipole couples to its own image dipole, and this serves to redshift its spectral signal

$$\Delta\omega_{\mathrm{m}}^2(\omega) = \frac{q^2}{\mu} \sum_h C_h \alpha_h(\omega) \left| \mathbf{u}_h^{\mathrm{out}}(\mathbf{r}_{\mathrm{m}}) \cdot \hat{\mathbf{n}} \right|^2$$

$$\frac{\mathrm{d}P_{\mathrm{m}}}{\mathrm{d}\omega} = \frac{1}{\mu} \frac{q^2}{\pi\hbar} \mathrm{Im}\left(\frac{E_{\mathrm{m}}(\omega) E_{\mathrm{e}}(\omega)}{\omega_{\mathrm{m}}^2 - \Delta\omega_{\mathrm{m}}^2(\omega) - \omega(\omega + 2i\gamma)} \right)$$

Physics of the coupled dipole model: EEL signal



3. The electric field of the molecule and the induced electric field from the molecule both pull on the beam

$$E_{\mathrm{e}}(\omega) = \sum_h e C_h \bar{I}_h(,\omega)\left(\bar{\mathbf{u}}_h^{\mathrm{in}}(\mathbf{r}_{\mathrm{m}}) - \alpha_h(\omega)\bar{\mathbf{u}}_h^{\mathrm{out}}(\mathbf{r}_{\mathrm{m}})\right)\cdot\hat{\mathbf{n}}$$

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$$\frac{\mathrm{d}P_{\mathrm{m}}}{\mathrm{d}\omega} = \frac{1}{\mu}\frac{q^2}{\pi\hbar}\mathrm{Im}\left(\frac{E_{\mathrm{m}}(\omega)E_{\mathrm{e}}(\omega)}{\omega_{\mathrm{m}}^2 - \Delta\omega_{\mathrm{m}}^2(\omega) - \omega(\omega + 2i\gamma)}\right)$$

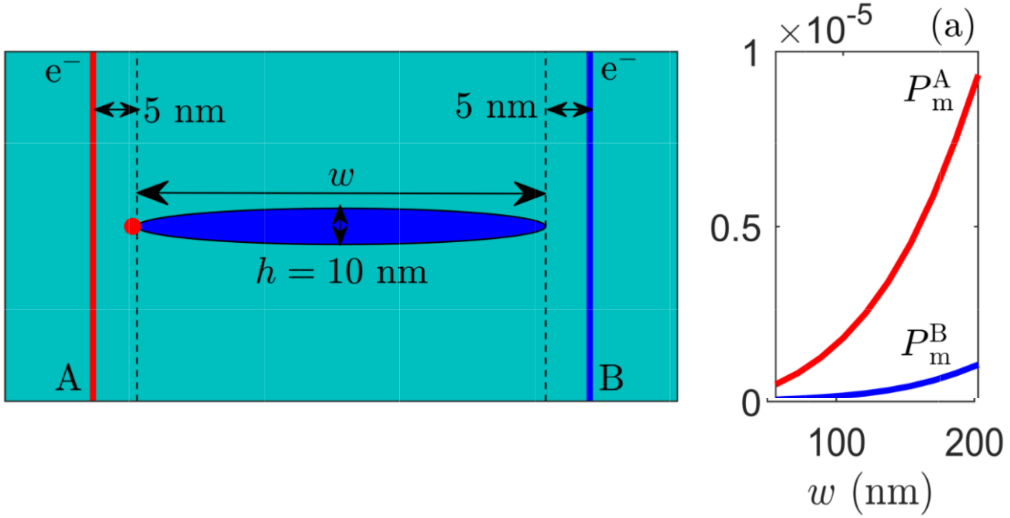
Quantifying the molecular signal

Near and "ultra-remote" probes

The molecular signal depends on the electric field at the surface adsorption site

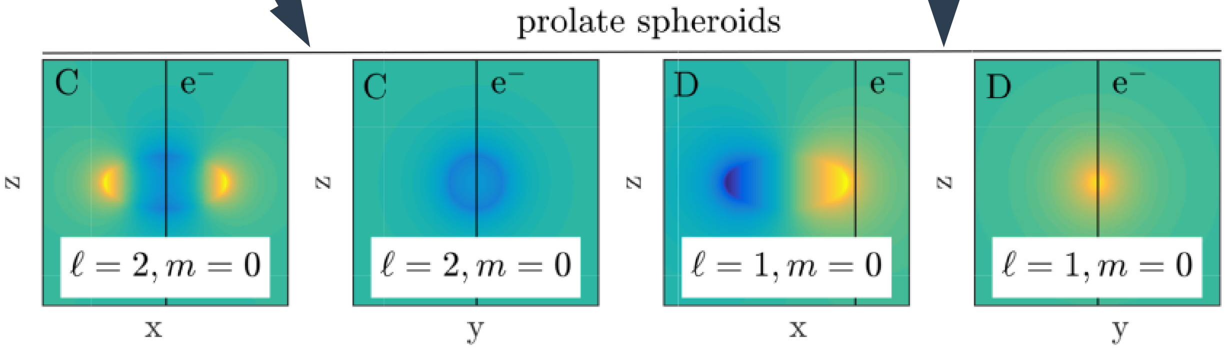
$$P_{\rm m} \approx \frac{q^2}{2\hbar\omega'_{\rm m}\mu}|\mathbf{E}^{\rm out}(\mathbf{r}_{\rm m},\omega'_{\rm m})\cdot\hat{\mathbf{n}}|^2$$

so the beam does not necessarily need to be near the sample to find a molecular signal



Even modes are the same on both sides of spheroid

Odd modes may differ on sides of spheroid by sign



Near and “ultra-remote” probes (2)

The molecular signal depends on the electric field at the surface adsorption site

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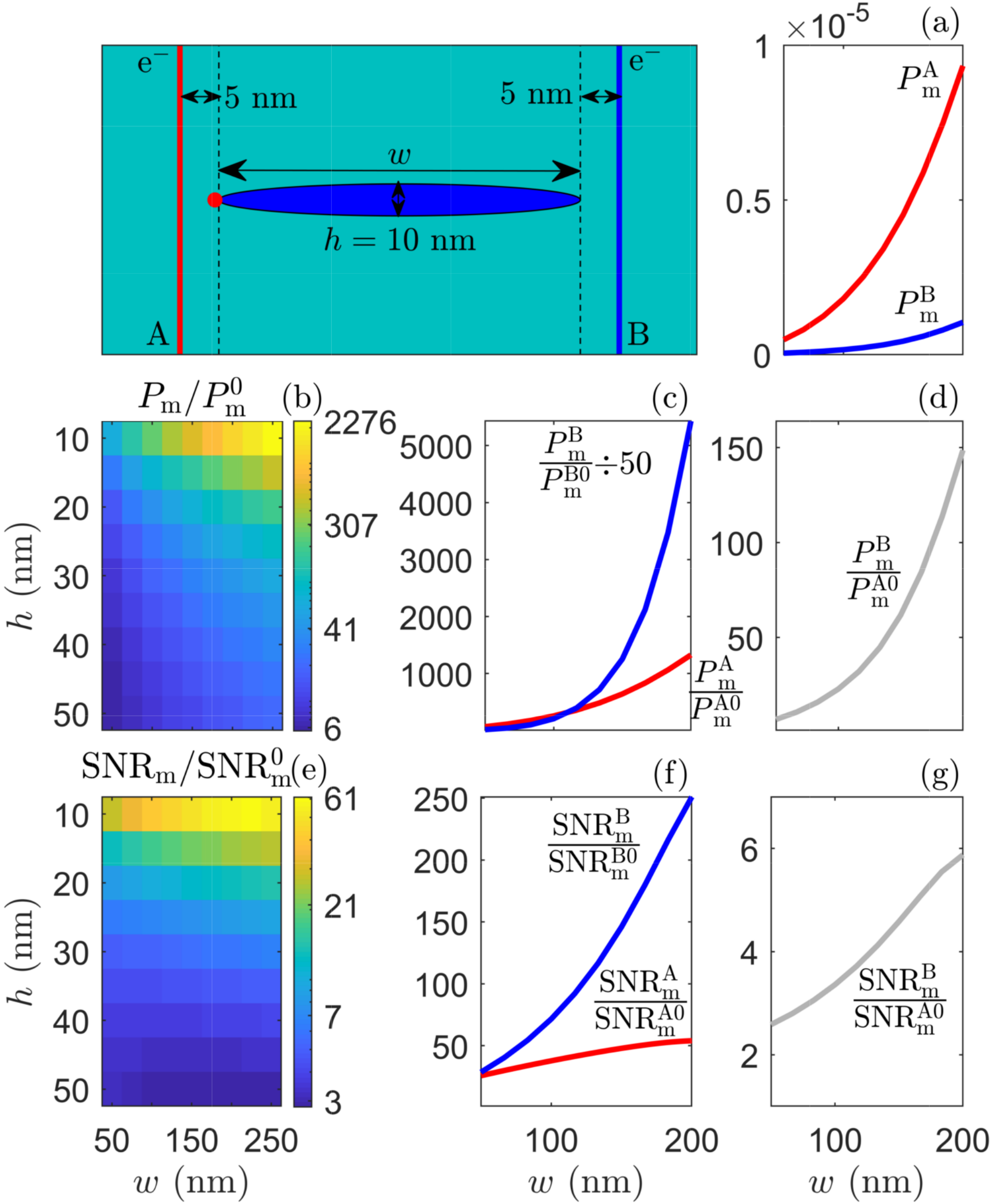

Off- and on-resonant enhancement

Uncovering Fano-type line shapes

In the vicinity of the molecular frequency, use

$$E_{\mathrm{m}}(\omega) \rightarrow |E_{\mathrm{m}}(\omega'_{\mathrm{m}})| \exp(i\theta_{\mathrm{m}})$$
$$E_{\mathrm{e}}(\omega) \rightarrow |E_{\mathrm{e}}(\omega'_{\mathrm{m}})| \exp(i\theta_{\mathrm{e}})$$

$$\delta = \theta_{\mathrm{m}} + \theta_{\mathrm{e}}$$

and expand the molecular contribution to the spectrum

$$\frac{\mathrm{d}P_{\mathrm{m}}}{\mathrm{d}\omega} = \frac{1}{\mu}\frac{q^2}{\pi\hbar}\mathrm{Im}\left(\frac{E_{\mathrm{m}}(\omega)E_{\mathrm{e}}(\omega)}{\omega_{\mathrm{m}}^2 - \Delta\omega_{\mathrm{m}}^2(\omega) - \omega(\omega + 2i\gamma)}\right)$$

around the molecular frequency $\Omega = (\omega - \omega'_{\mathrm{m}})/\gamma'$
to uncover the model's possible Fano-type line shapes

$$\frac{\mathrm{d}P_{\mathrm{m}}}{\mathrm{d}\omega} \approx \frac{1}{\mu}\frac{q^2}{\pi\hbar}\frac{|E_{\mathrm{m}}(\omega'_{\mathrm{m}})E_{\mathrm{e}}(\omega'_{\mathrm{m}})|}{2\omega'_{\mathrm{m}}\gamma'}\left(\frac{\cos(\delta) - \Omega\sin(\delta)}{1 + \Omega^2}\right)$$

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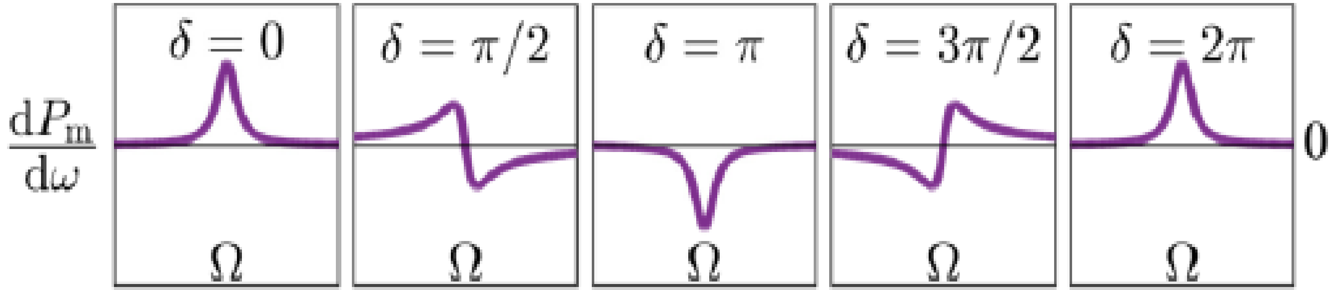
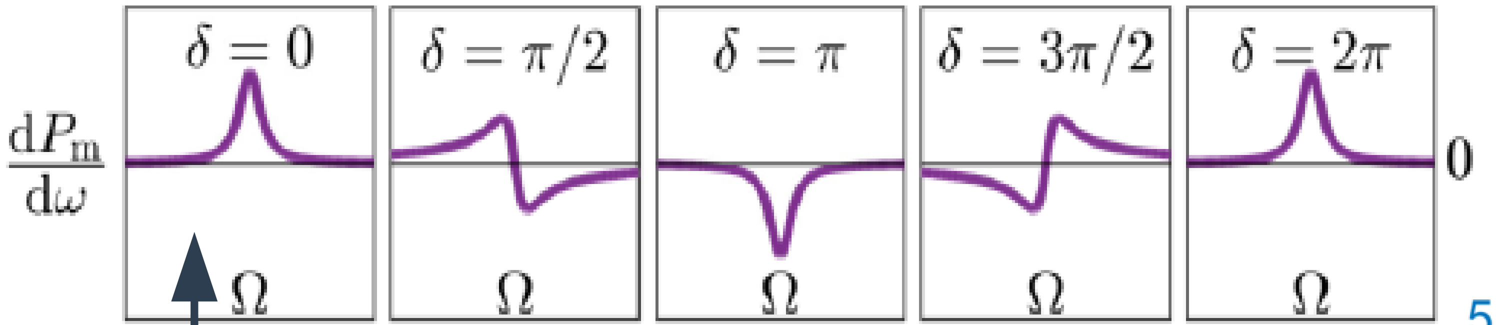
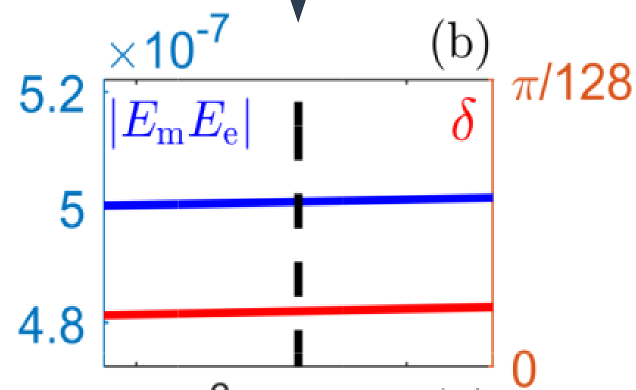


Lineshapes for "off" and "on" resonance (1)

$\delta = \theta_\mathrm{m} + \theta_\mathrm{e}$ $\quad$ $\Omega = (\omega - \omega'_\mathrm{m})/\gamma'$

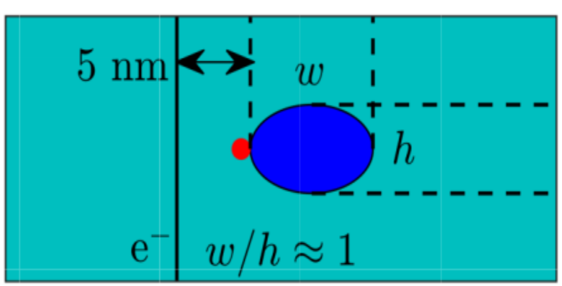
"off resonance"

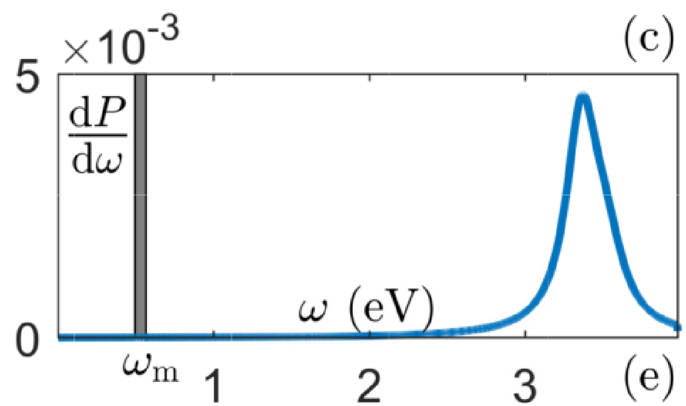


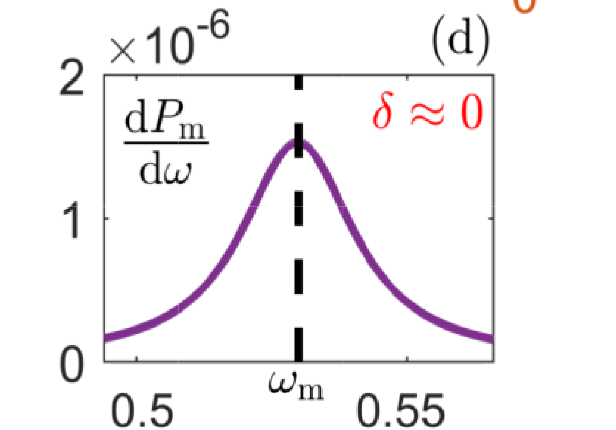


"off resonance"

$$\frac{\mathrm{d}P_\mathrm{m}}{\mathrm{d}\omega} \approx \frac{1}{\mu}\frac{q^2}{\pi\hbar}\frac{|E_\mathrm{m}(\omega'_\mathrm{m})E_\mathrm{e}(\omega'_\mathrm{m})|}{2\omega'_\mathrm{m}\gamma'}\left(\frac{\cos(\delta) - \Omega\sin(\delta)}{1+\Omega^2}\right)$$

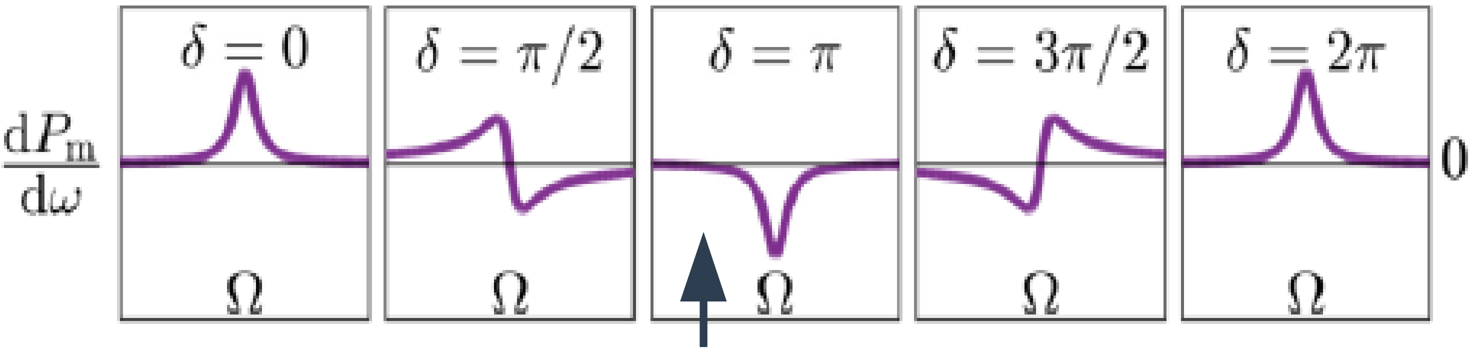






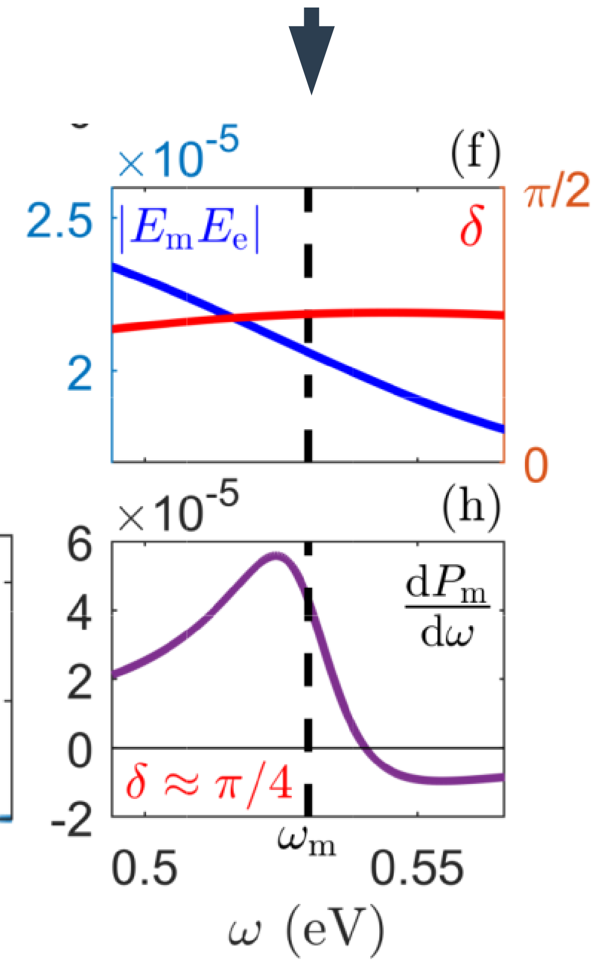
Lineshapes for "off" and "on" resonance (2)

$\delta = \theta_m + \theta_e \qquad \Omega = (\omega - \omega'_m)/\gamma'$

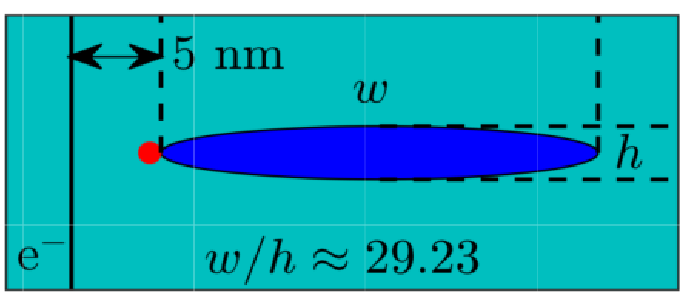


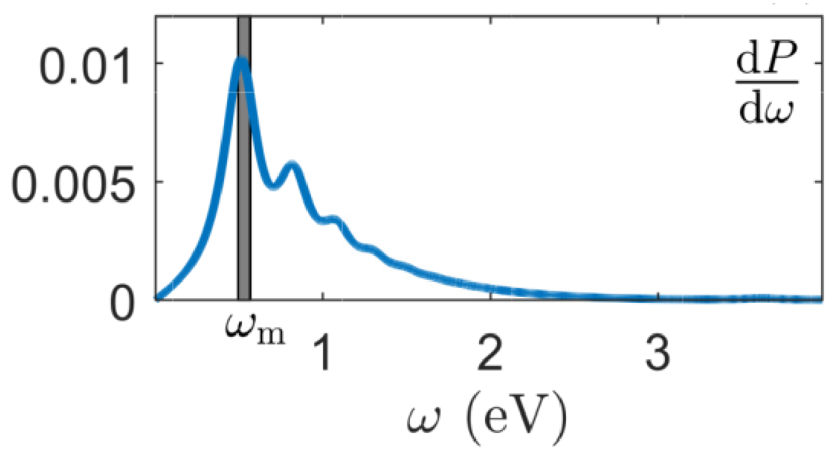
"on resonance" (in theory)

"on resonance" (in practice)

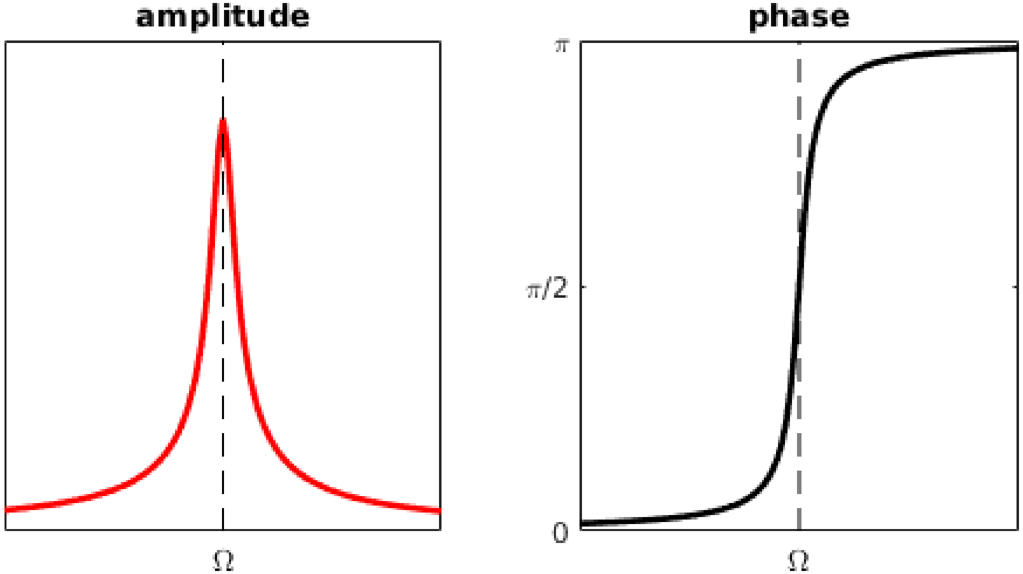


$$\frac{dP_m}{d\omega} \approx \frac{1}{\mu}\frac{q^2}{\pi\hbar}\frac{|E_m(\omega'_m)E_e(\omega'_m)|}{2\omega'_m\gamma'}\left(\frac{\cos(\delta) - \Omega\sin(\delta)}{1+\Omega^2}\right)$$





An analogy: damped oscillators and phase shifts

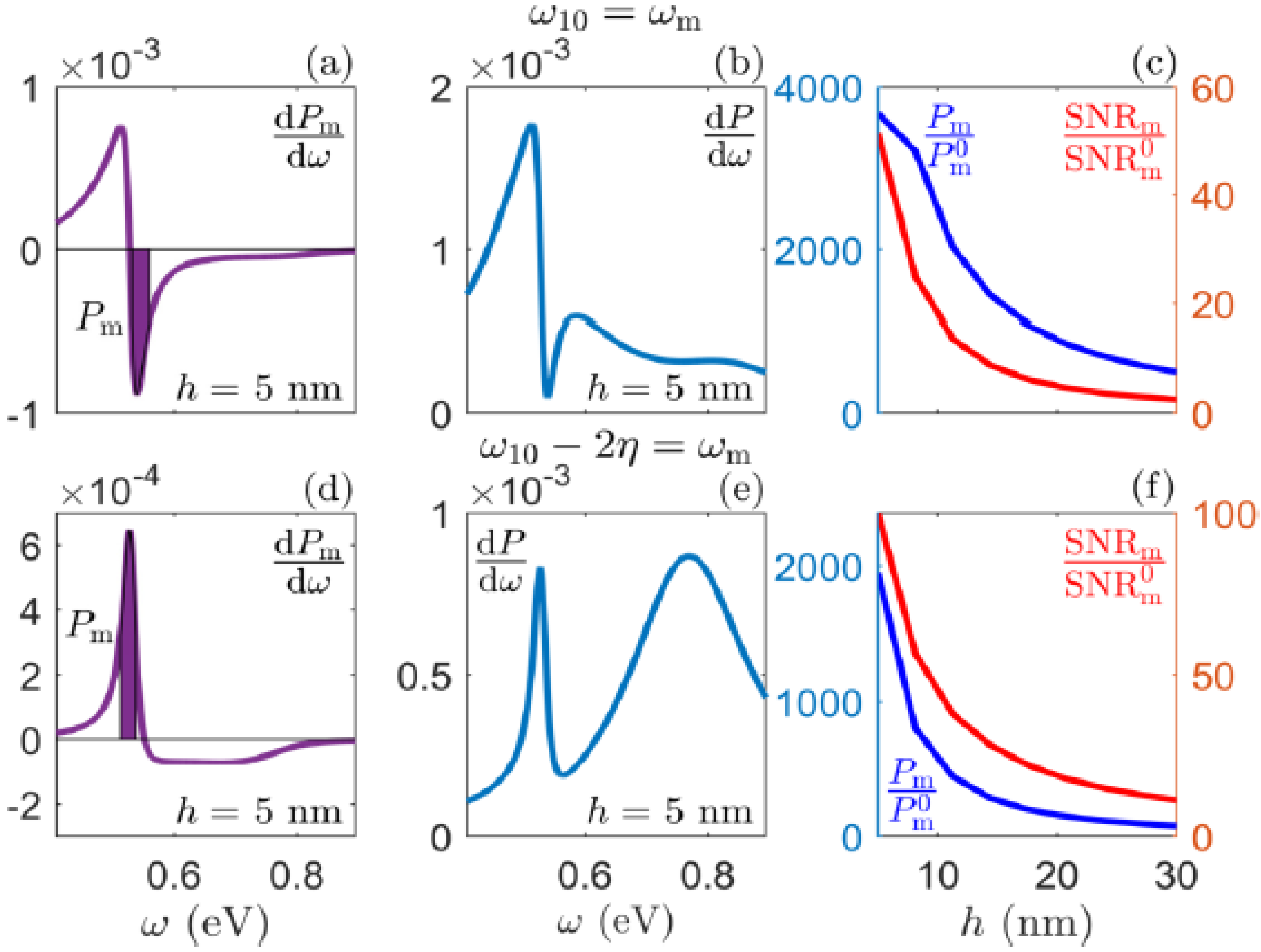


One can picture each mode response as a damped harmonic oscillator—driving another damped harmonic oscillator

* Directly on resonance, a single mode phase shift is $\pi/2 + \pi/2 = \pi$
* Far above or far above the resonance, the phase shift → $0, 2\pi$

Typically, cumulative phase-shift effects make the line shape difficult to predict when all modes are included

Large enhancements for tuned particles—and some different line shapes



When particle surface mode frequencies overlap the vibrational frequency of the adsorbate, we find large signal and SNR enhancements

Conclusion

- We have given a plausible mechanism for the plasmon-enhanced vibrational EELS of adsorbates
- Adsorbate signal enhancement is mediated via the site-specific strength of the electric field ($\propto E^2$)
- Thin, sharp nanoparticles deliver can deliver large electric fields with low background signal, leading to large signal and SNR enhancement for adsorbates
- Surface mode frequencies overlapping the adsorbate vibrational frequencies give signal enhancements of 10^2-10^3