Femtosecond laser-nanostructured substrates for surface enhanced Raman scattering (SERS)

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Motivation

Raman spectroscopy has applications in:

- Pharmaceuticals
- Homeland Security
- Forensics
- Medical diagnostics
- Analytical chemistry

Motivation

However, Raman scattering cross sections are very small (~10^{-30} cm^2)

Trace detection using Raman spectroscopy is insensitive, and not widely used

Motivation

SERS promises to enable the use of Raman spectroscopy in a wide variety of new applications

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SERS promises to enable the use of Raman spectroscopy in a wide variety of new applications

However, a current dearth of inexpensive, reliable, high performance substrates is limiting the application of SERS

Outline

- Raman scattering
- Surface enhancement
- Femtosecond laser-structured substrates
- Experimental results
- Conclusions

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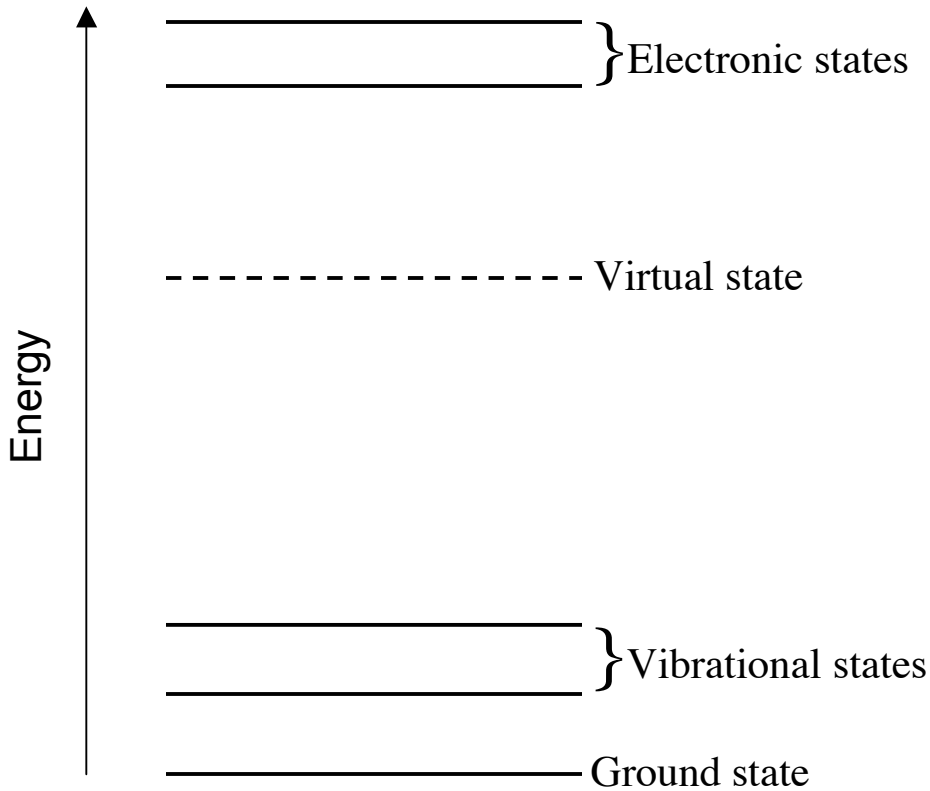
Raman scattering



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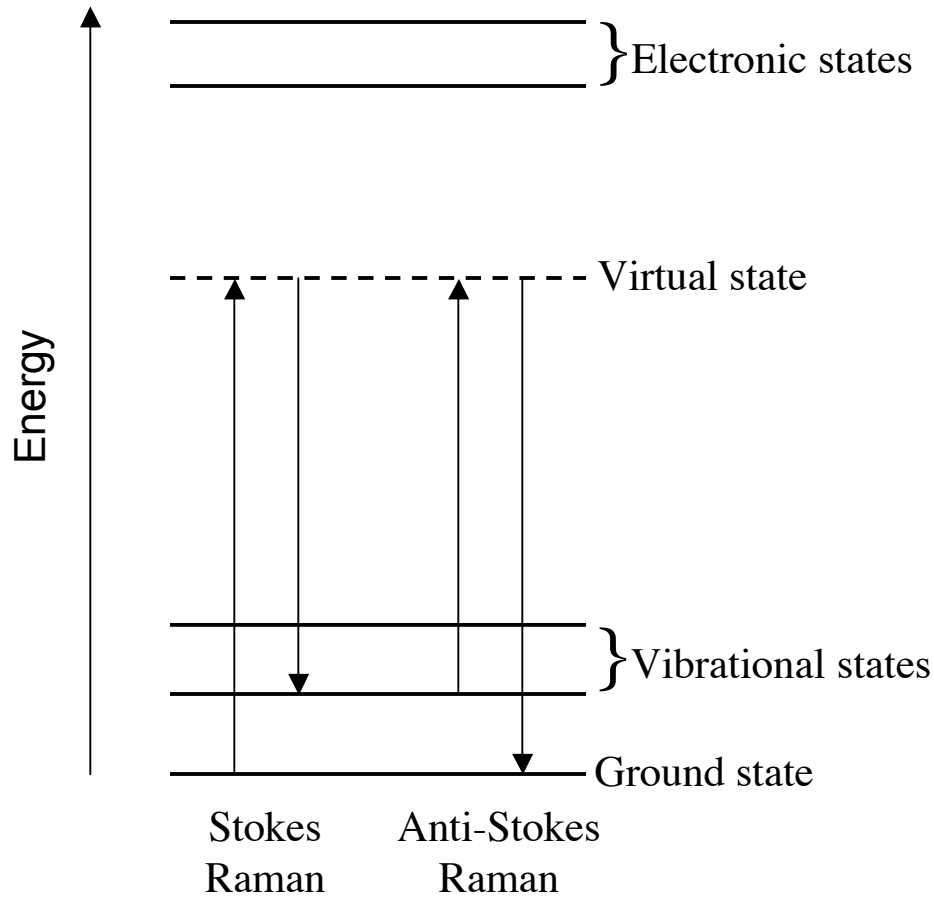

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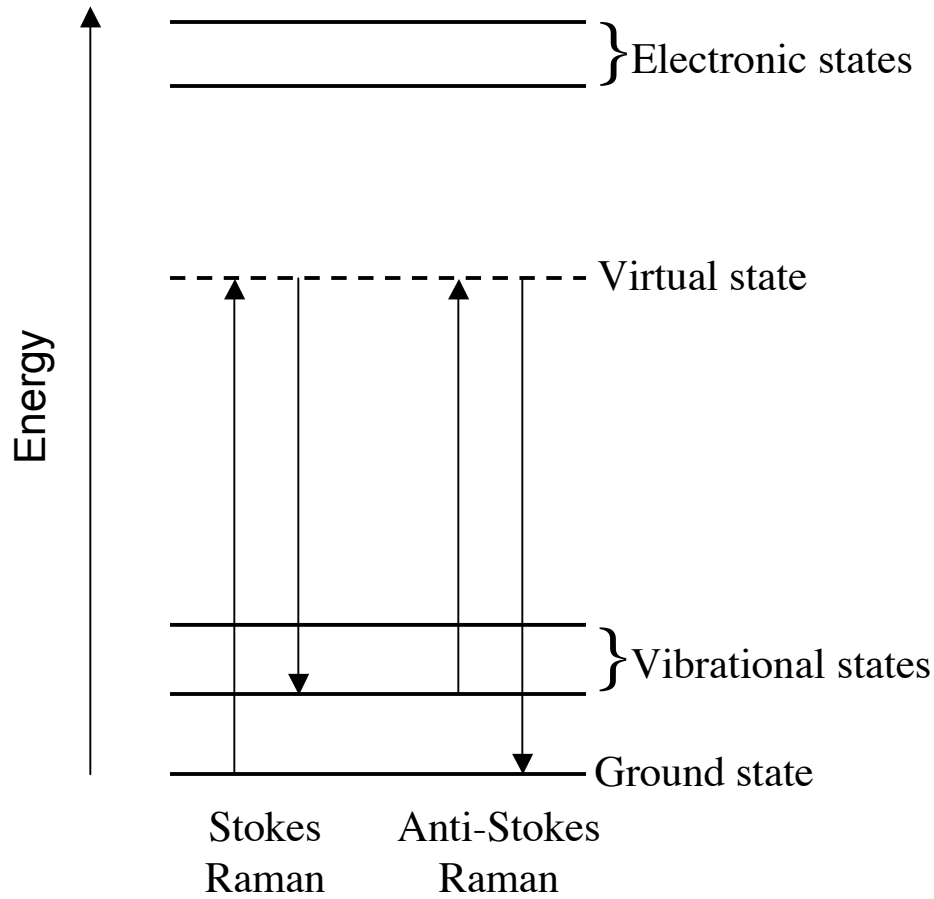

$$\Delta\upsilon = \frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}}$$

Raman scattering: a classical approach

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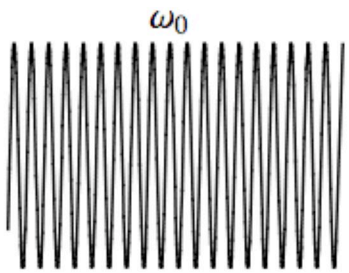
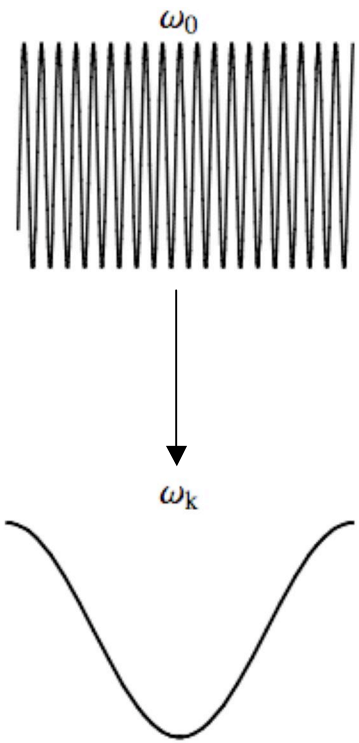
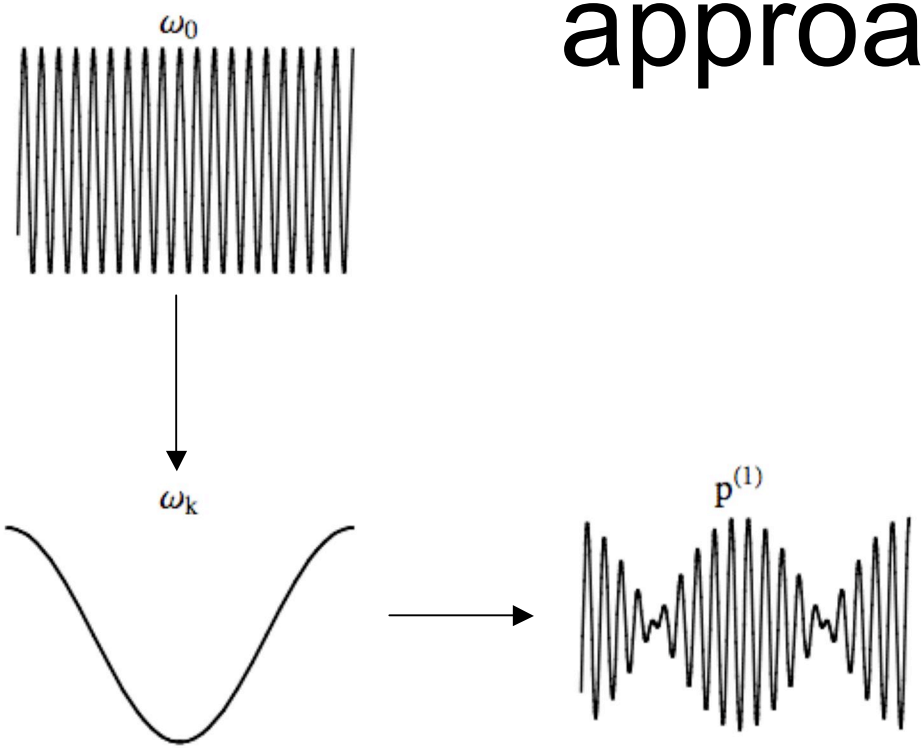


Raman scattering: a classical approach



Raman scattering: a classical approach



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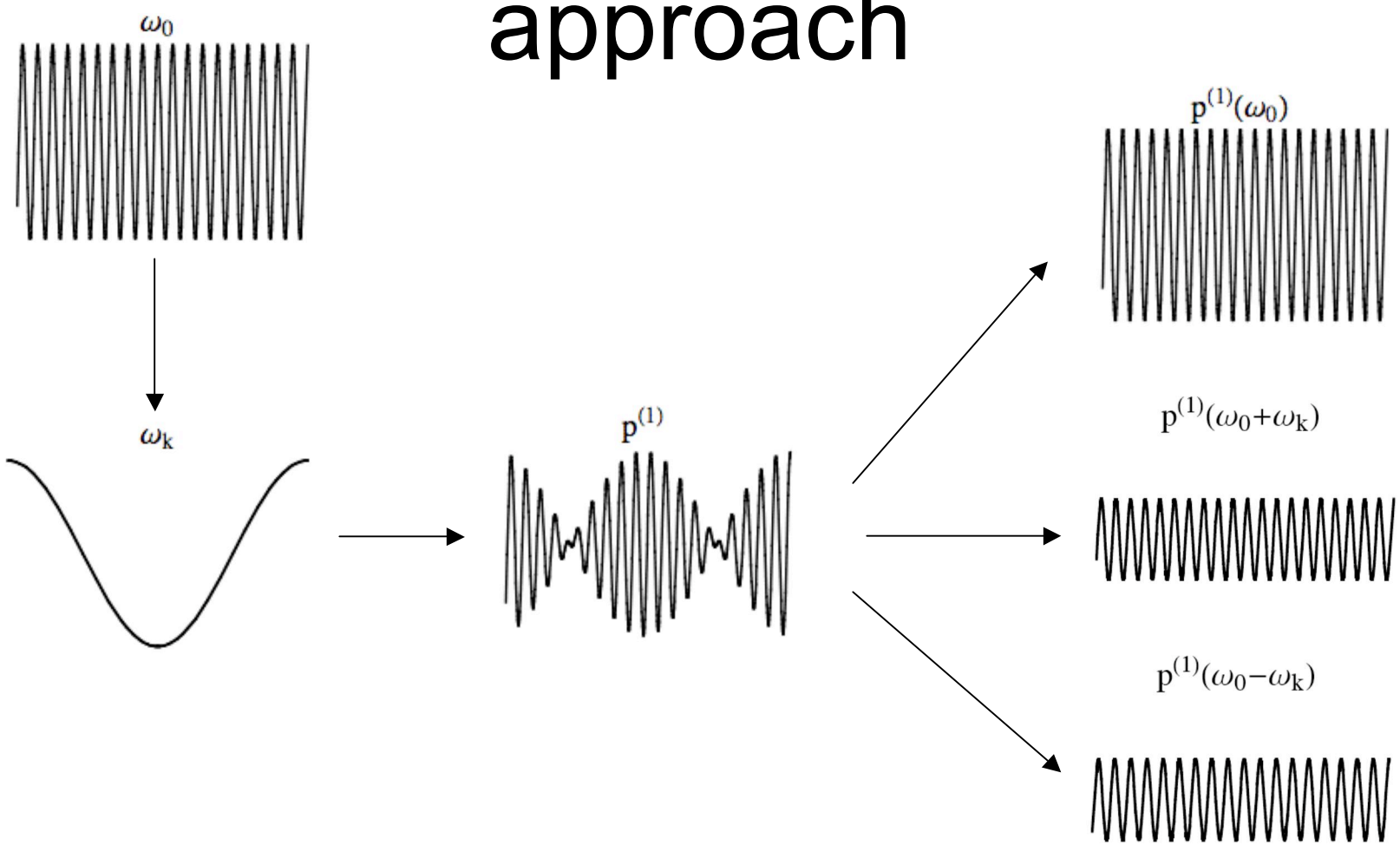

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- ***Surface enhancement***
- Femtosecond laser-structured substrates
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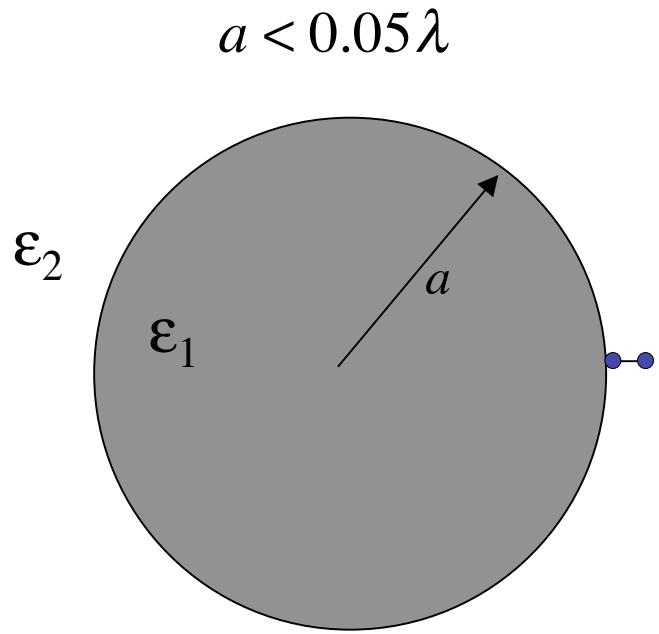
Surface enhancement



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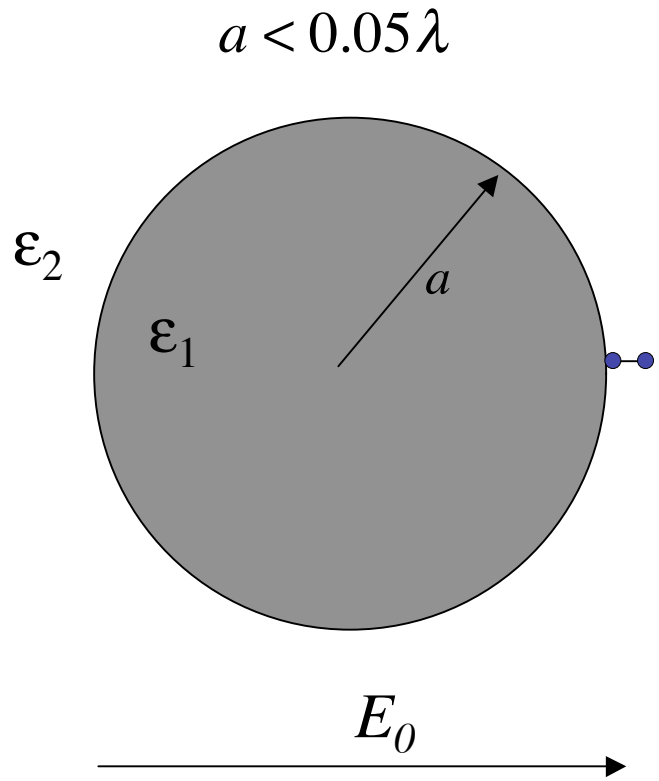
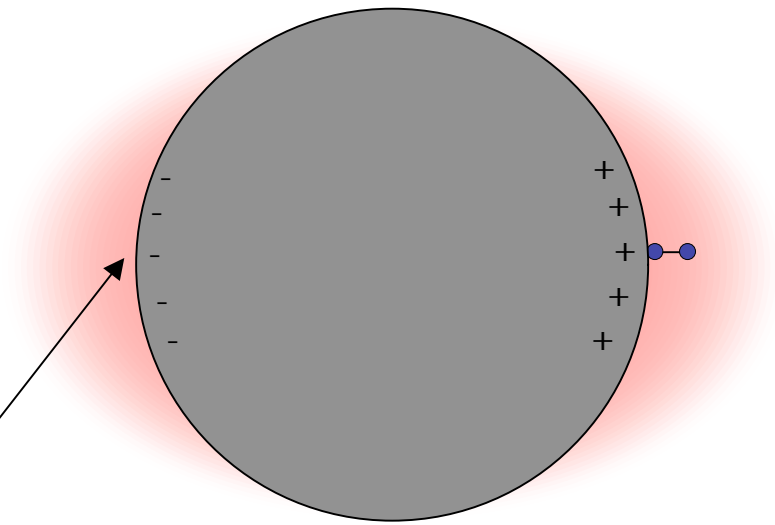


Surface enhancement

1. Near-field scattered electric field enhances polarization of molecules located near surface



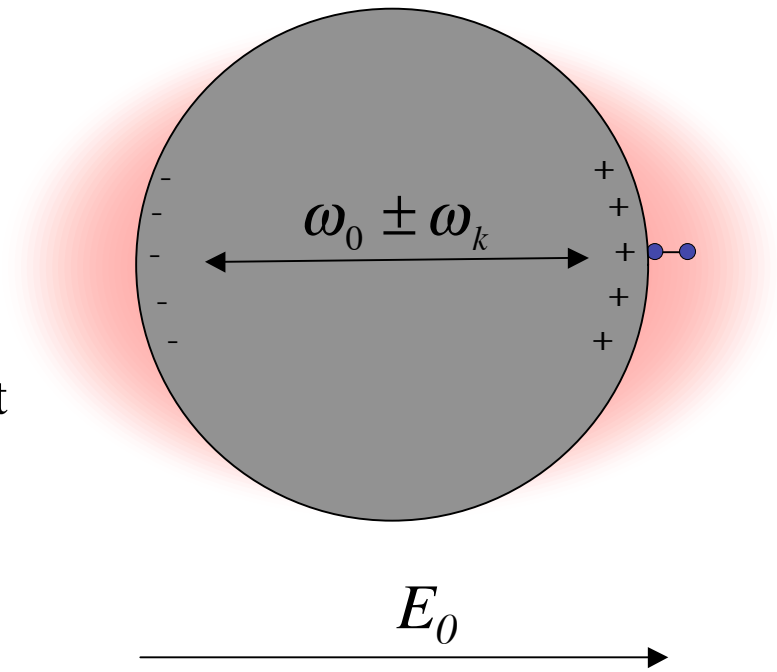
$$\frac{|E_s|}{|E_0|} \propto \frac{\varepsilon_1(\omega) - \varepsilon_2}{\varepsilon_1(\omega) + 2\varepsilon_2}$$

E_0

Surface enhancement

1. Near-field scattered electric field enhances polarization of molecules located near surface

2. Field from molecular polarization generates polarization of surface at Raman frequency



Surface enhancement

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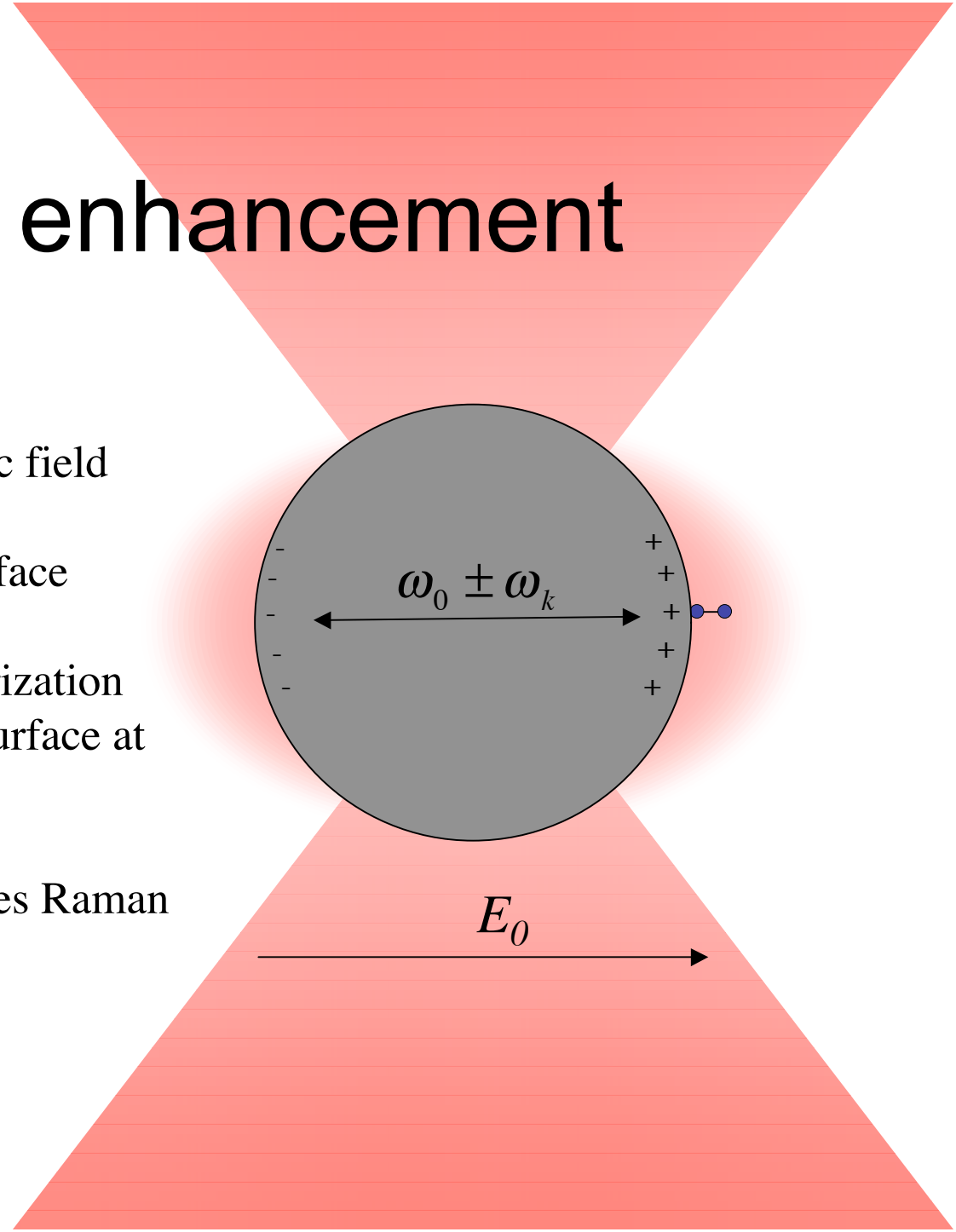
3. Surface polarization radiates Raman field into far field



Surface enhancement

$$SERS \text{ Enhancement Factor} = \frac{I_{\text{SERS}}}{I_{\text{Normal Raman}}} \propto \left(\frac{\left| E_s\left(\omega_0\right) \right|}{\left| E_0\left(\omega_0\right) \right|} \right)^2 \times \left(\frac{\left| E_s\left(\omega_0 - \omega_k\right) \right|}{\left| E_0\left(\omega_0 - \omega_k\right) \right|} \right)^2$$

$$\approx \left(\frac{\left| E_s\left(\omega_0\right) \right|}{\left| E_0\left(\omega_0\right) \right|} \right)^4$$

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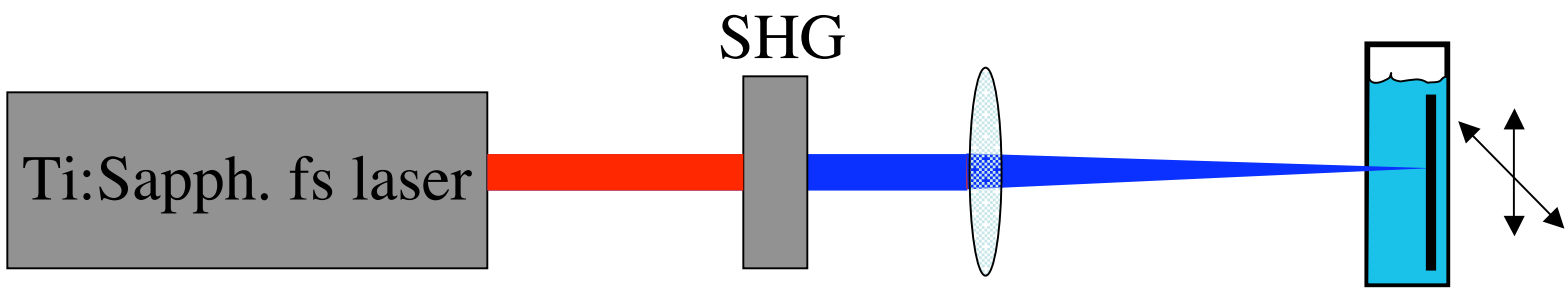
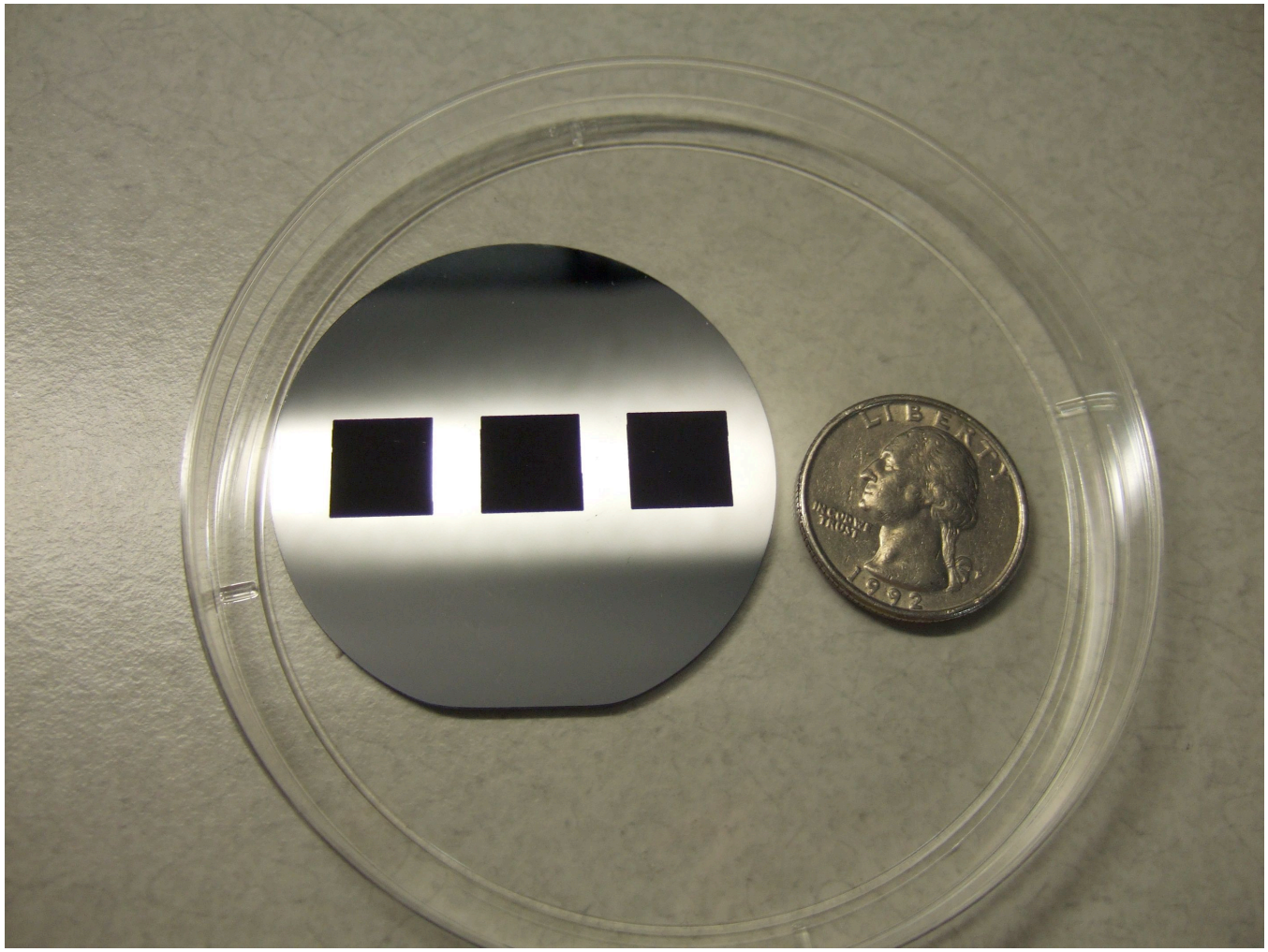
Femtosecond laser-structured substrates



Femtosecond laser-structured substrates



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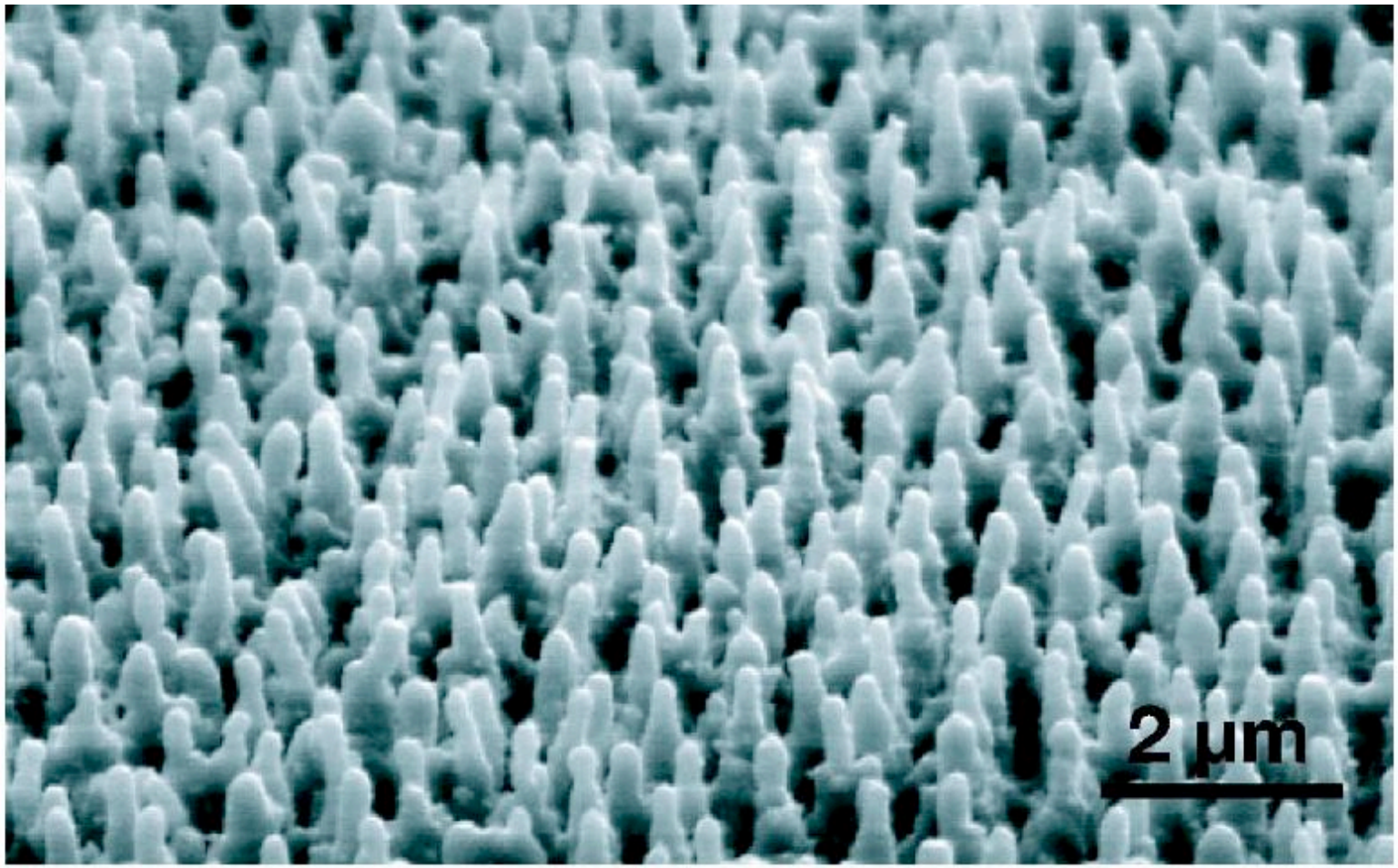
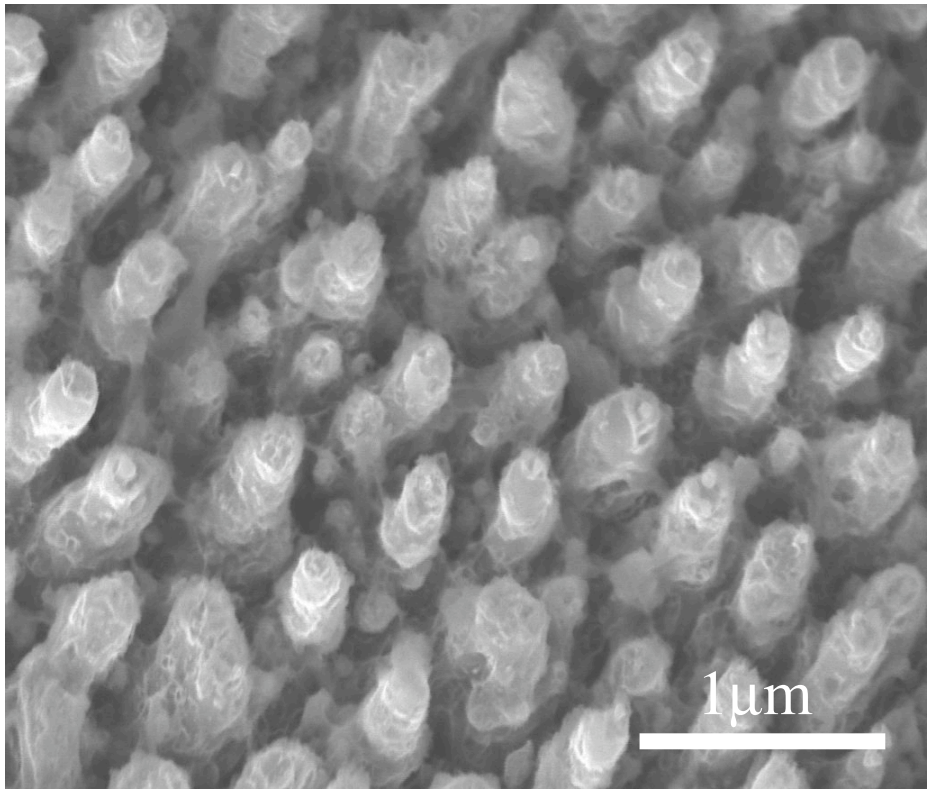
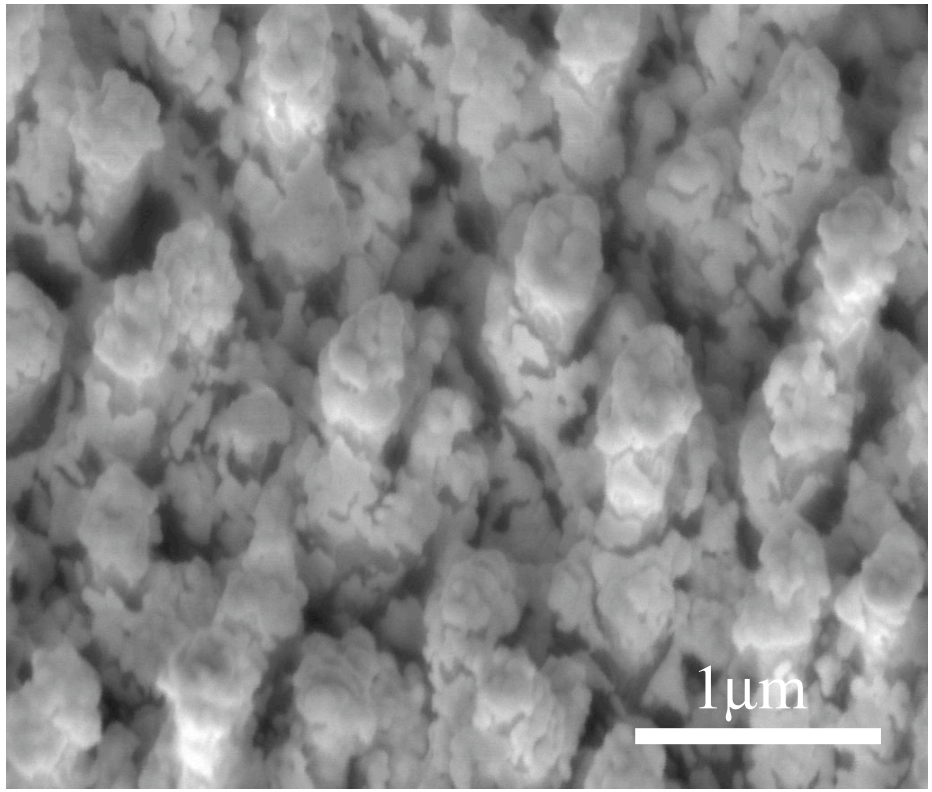


From: M. Shen, C.H. Crouch, J.E. Carey, and E. Mazur, *Appl. Phys. Lett.*, **85**, 5694-5696 (2004)

Femtosecond laser-structured substrates





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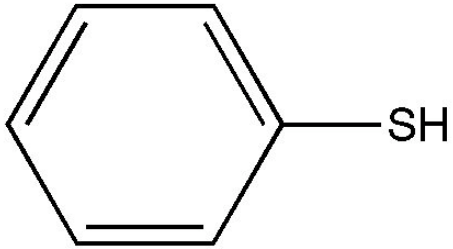
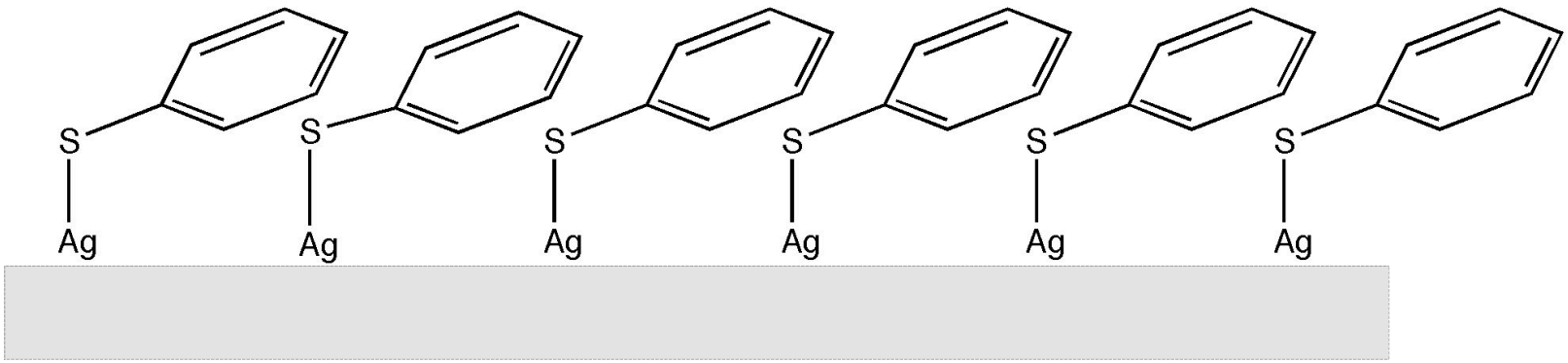
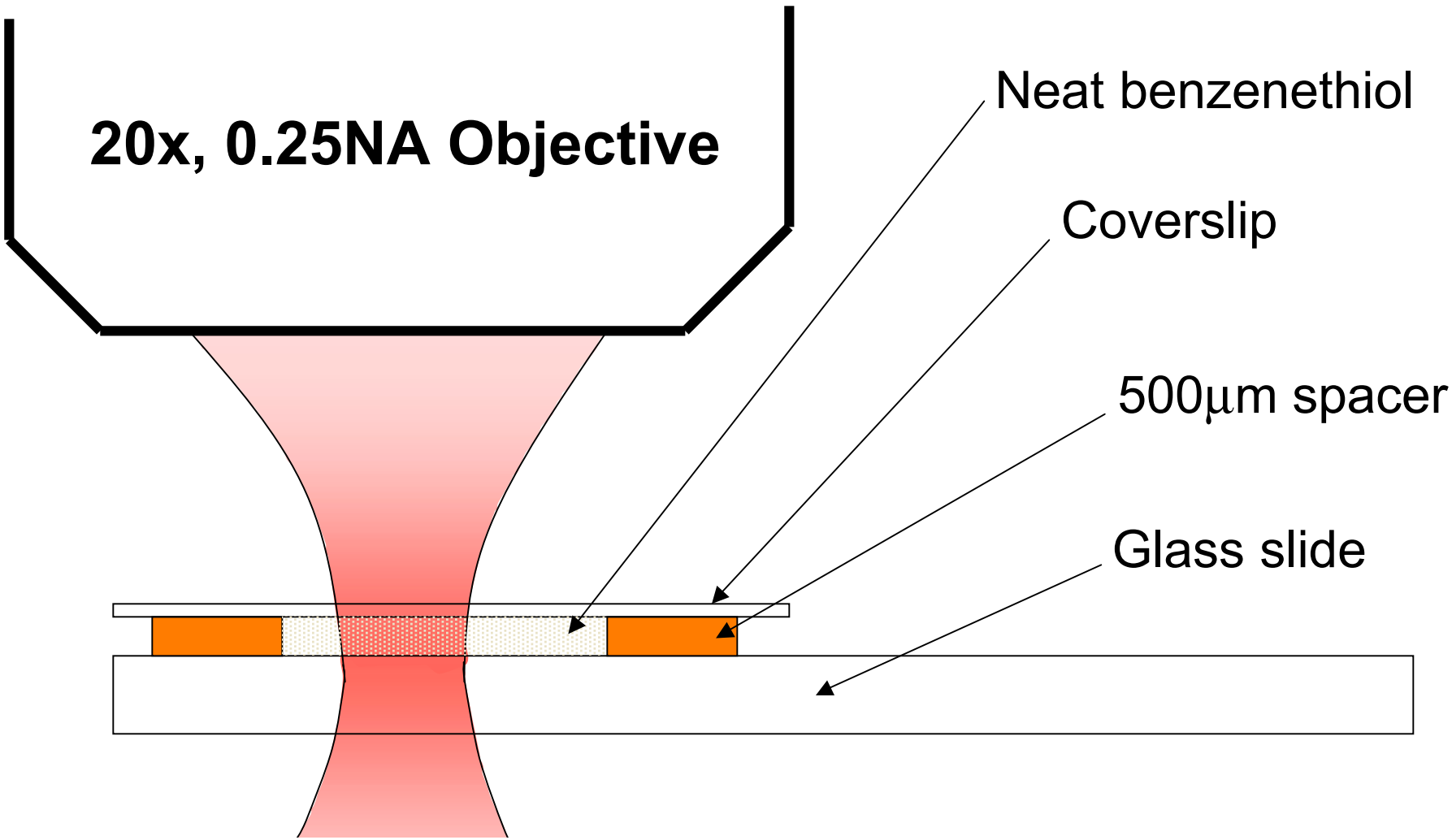
Experimental procedure

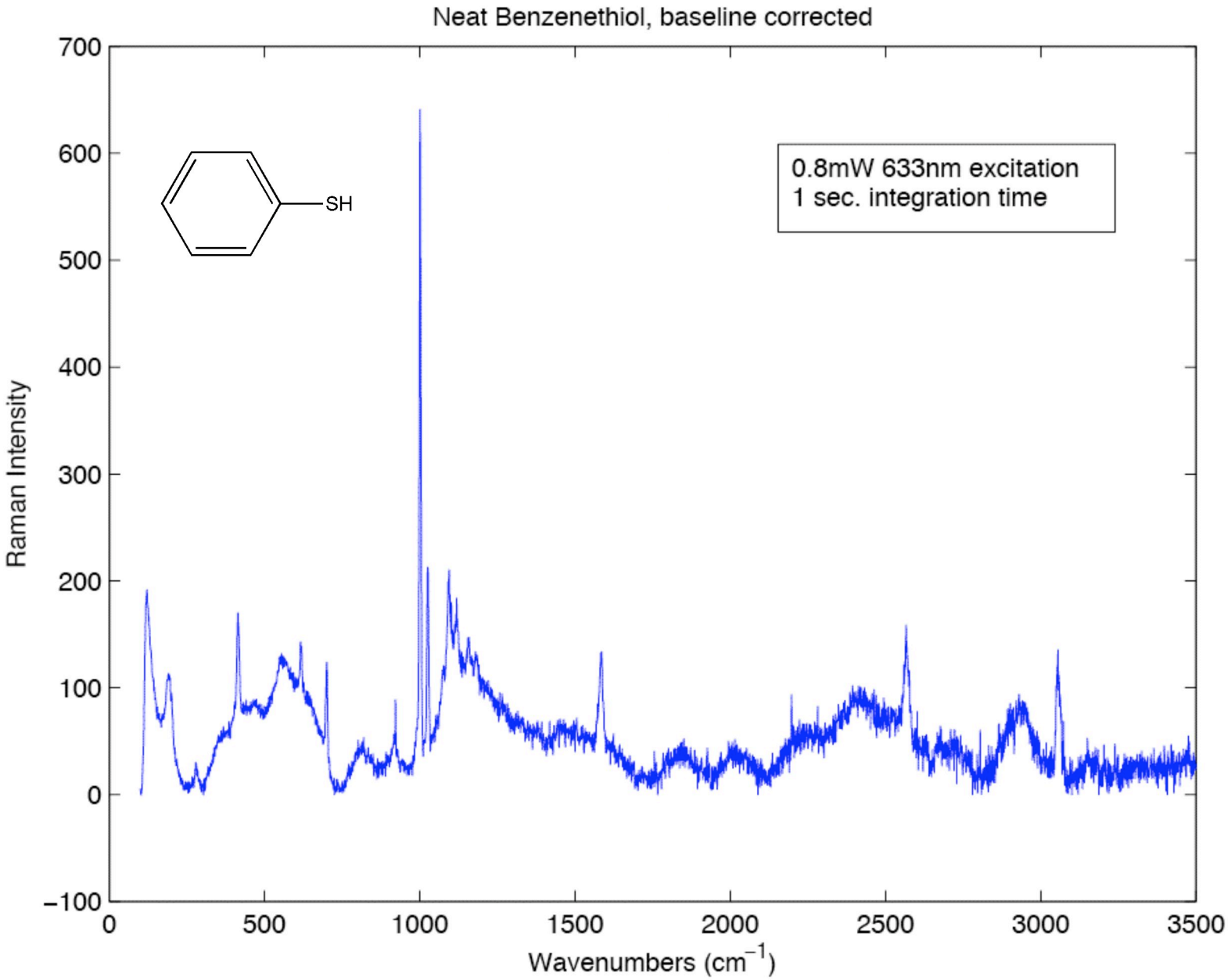
Benzenethiol self-assembled monlayer (SAM)



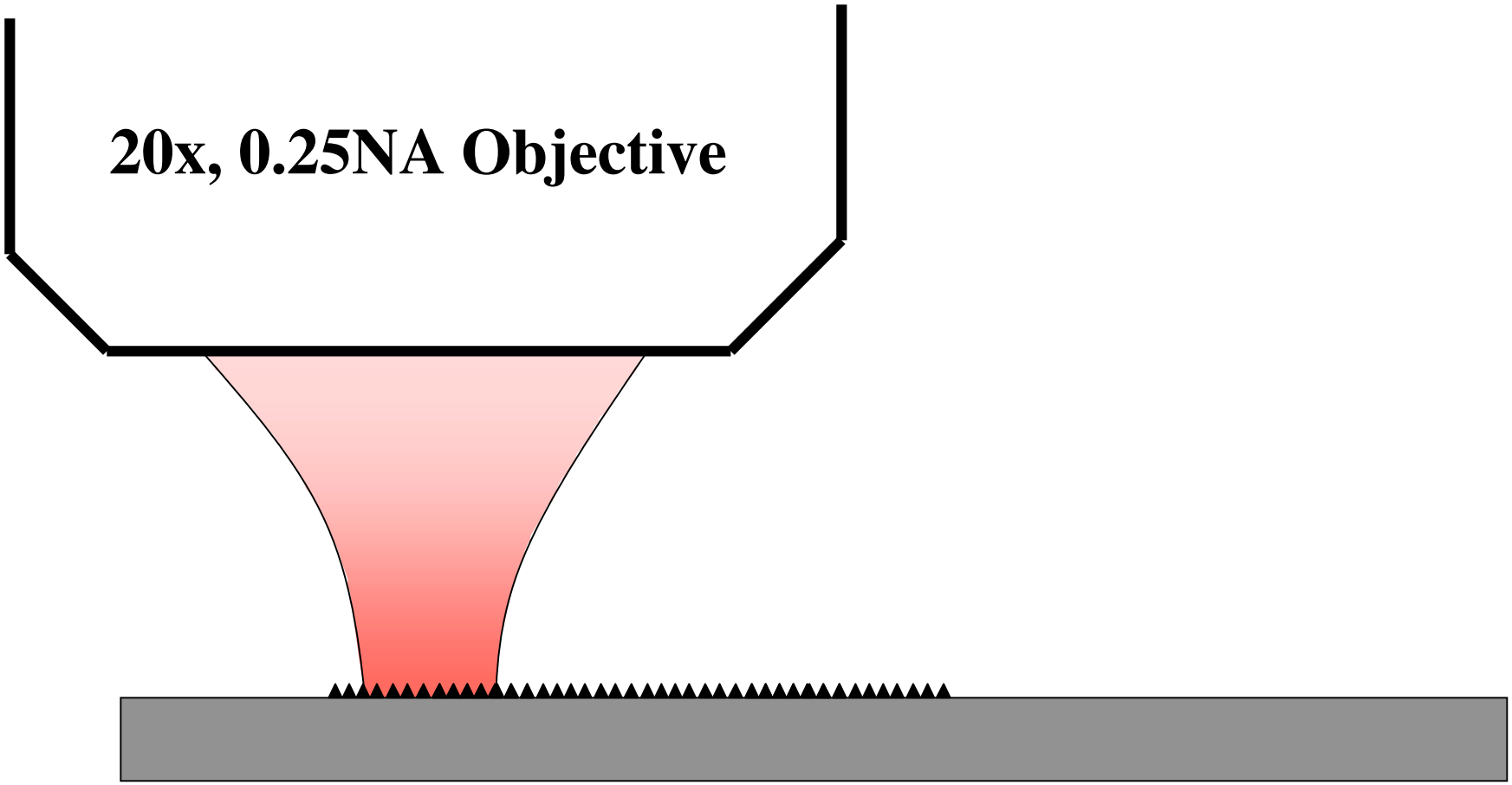


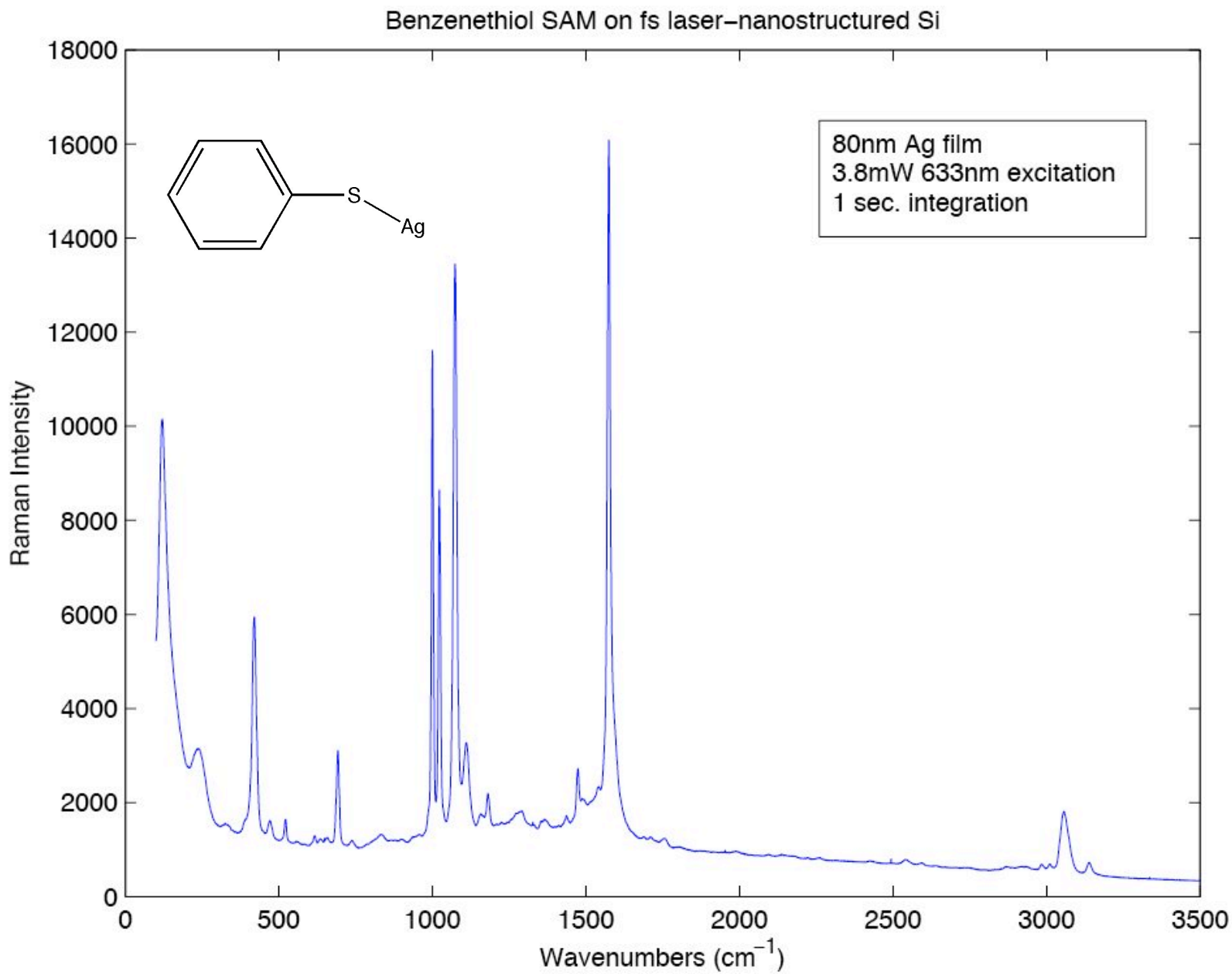
Enhancement factor calculation

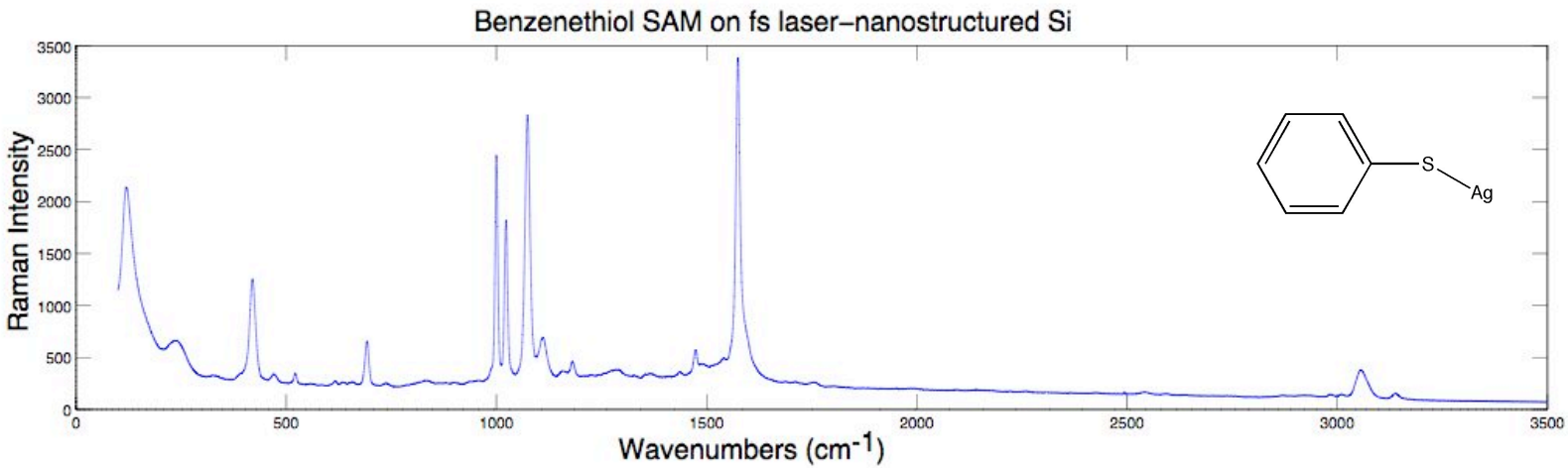


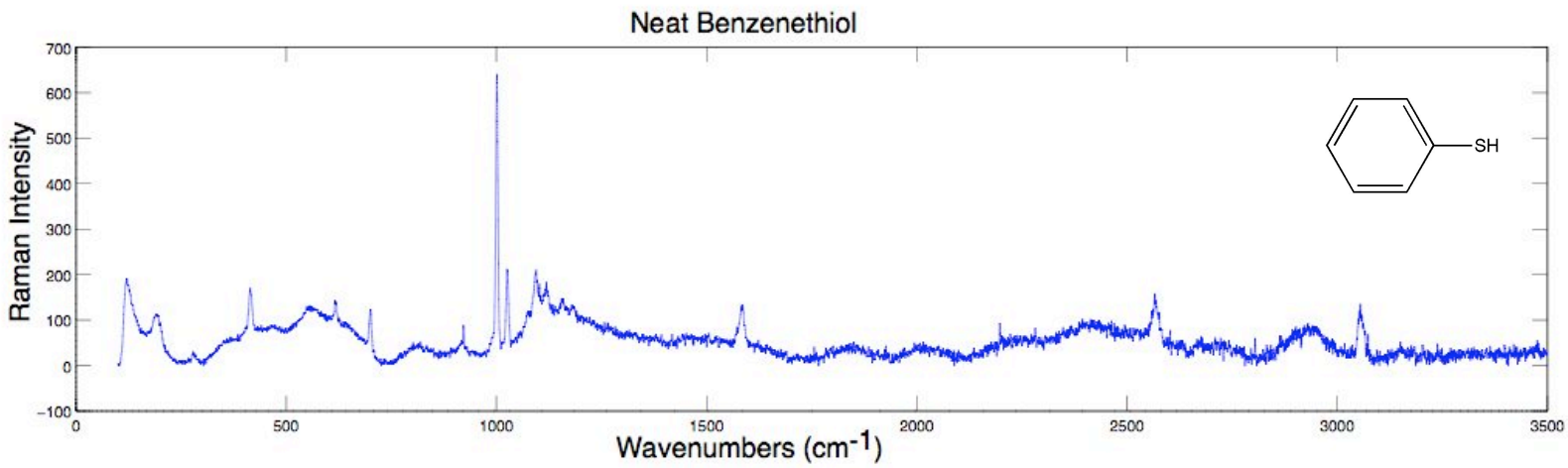

Neat Benzenethiol, baseline corrected
0.8mW 633nm excitation
1 sec. integration time
SH
Raman Intensity
Wavenumbers (cm^{-1})
700
600
500
400
300
200
100
0
−100
0
500
1000
1500
2000
2500
3000
3500

Enhancement factor calculation




Benzenethiol SAM on fs laser−nanostructured Si
80nm Ag film
3.8mW 633nm excitation
1 sec. integration
S
Ag
Raman Intensity
Wavenumbers (cm^{-1})
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
0
500
1000
1500
2000
2500
3000
3500


Benzenethiol SAM on fs laser–nanostructured Si
Raman Intensity
Wavenumbers (cm-1)
S
Ag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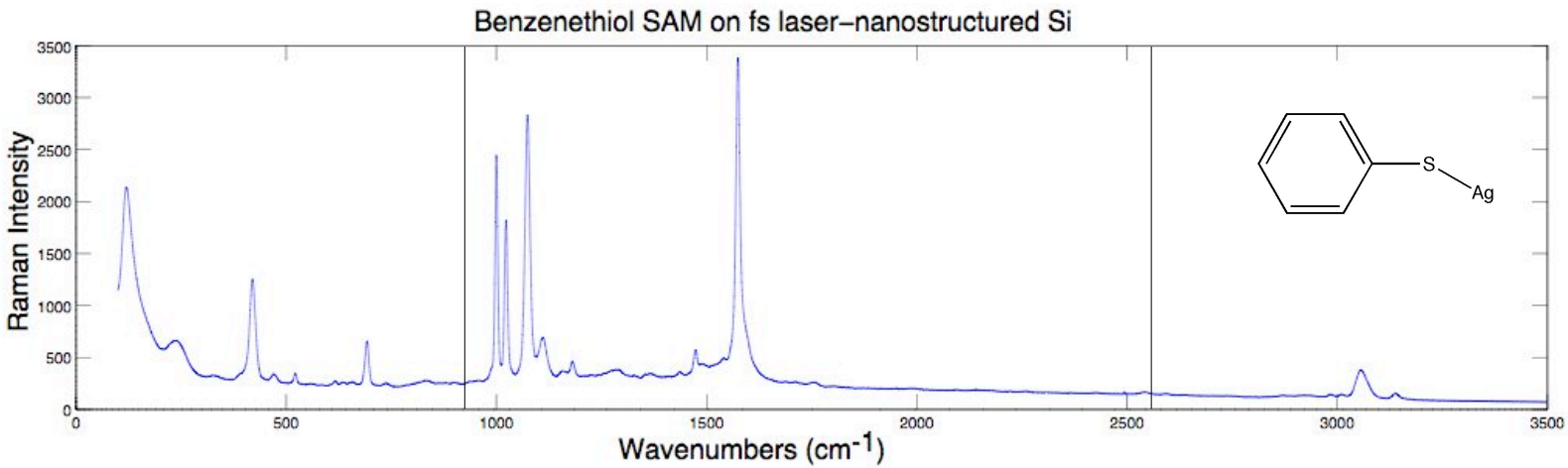
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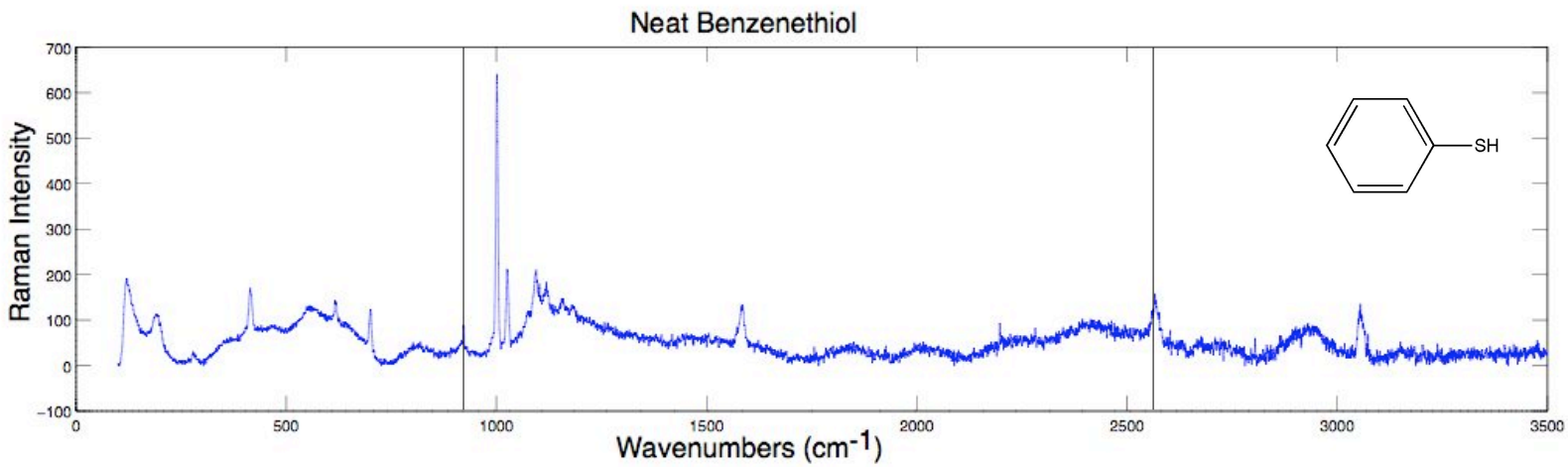
S
Ag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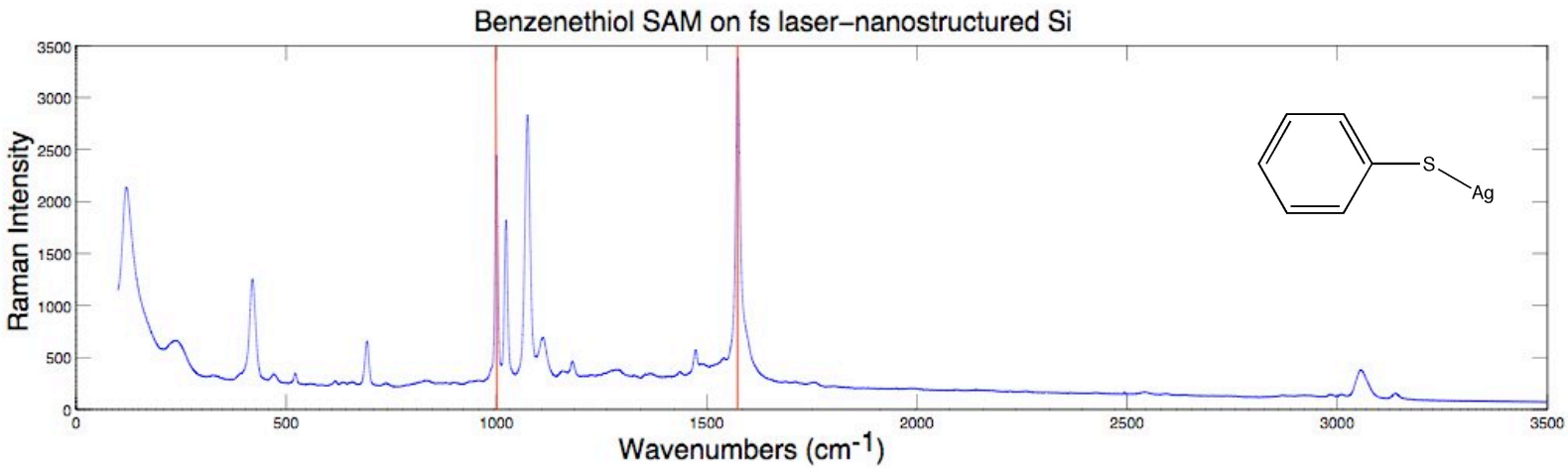
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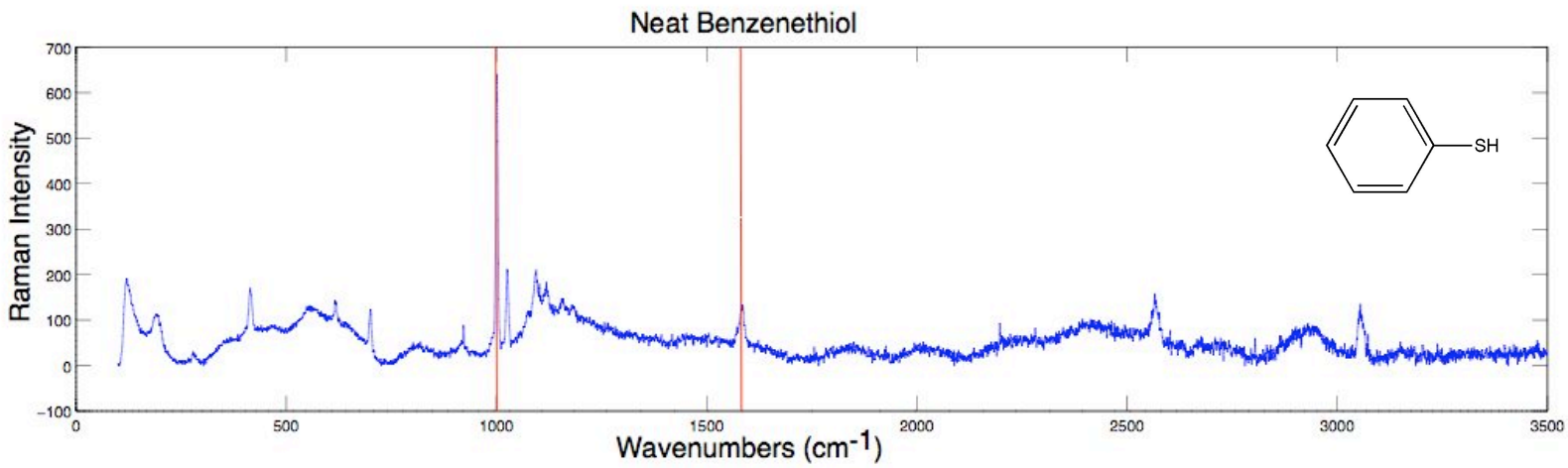
Raman Intensity
Wavenumbers (cm-1)
S
Ag


Neat Benzenethiol
Raman Intensity
Wavenumbers (cm-1)
SH

Enhancement factor calculation

$$SERS \text{ Enhancement Factor} = \left(I_{SERS} / I_{Raman}\right) \times \left(N_{Raman} / N_{SERS}\right)$$

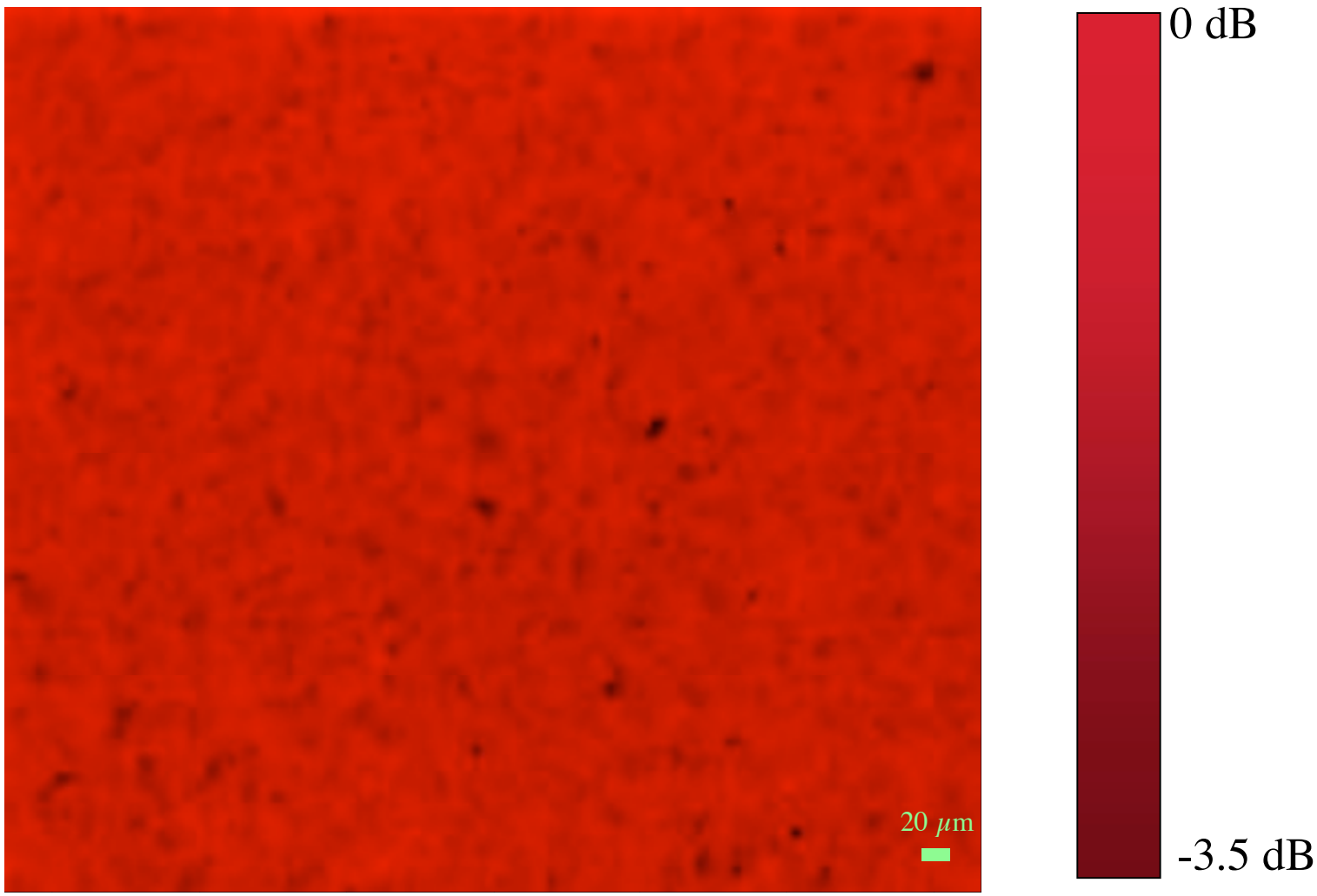
EF (1000 cm^{-1} band)	1.9×10^{10}
EF (1572 cm^{-1} band)	1.5×10^{11}

SERS substrates: important characteristics

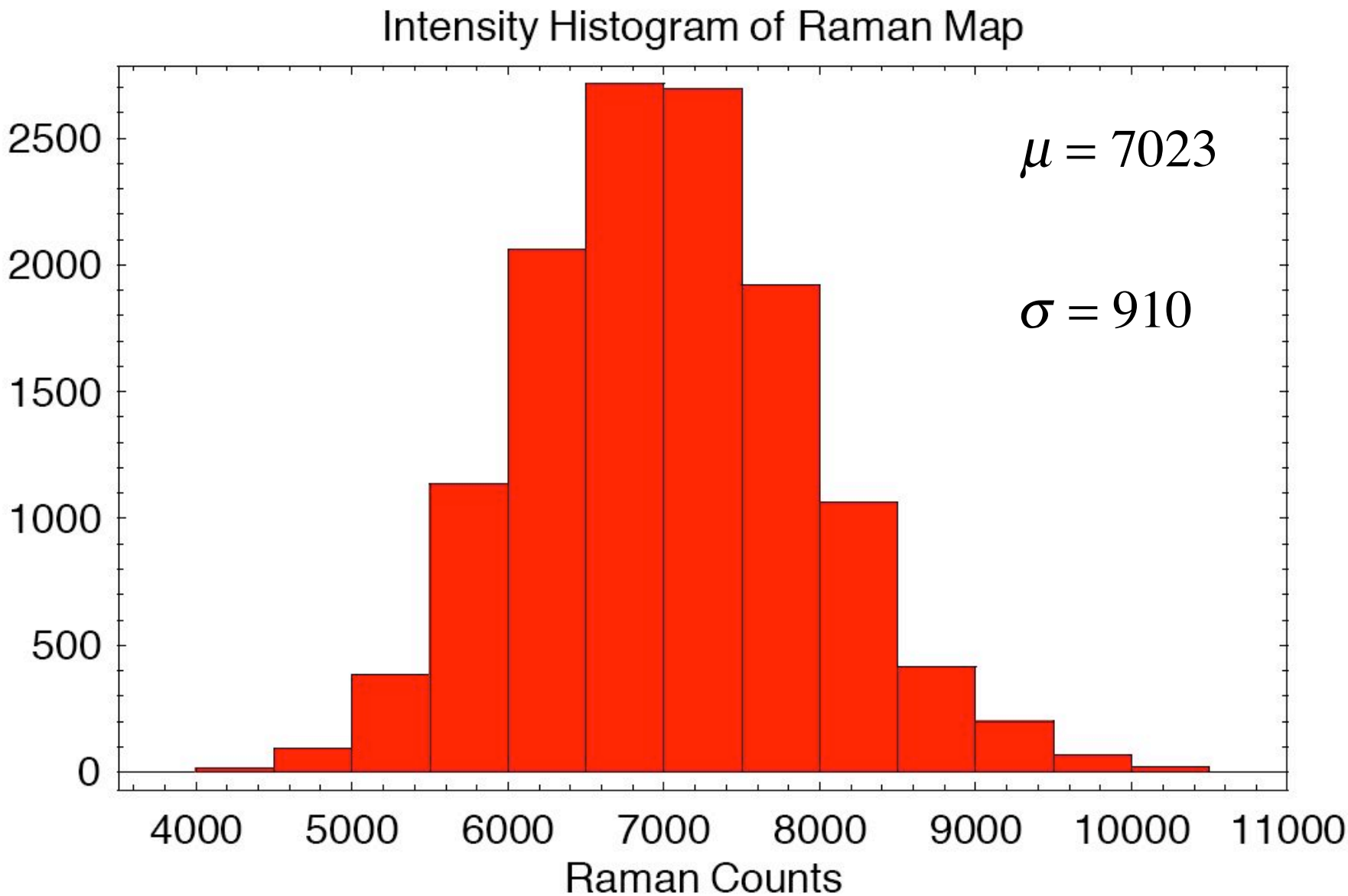
1. Large cross-section enhancement factor

2. Signal is reproducible, uniform across substrates

Signal uniformity



Signal uniformity



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We have demonstrated SERS from laser nanostructured substrates;

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Enhancement mechanism needs to be better understood; future work will focus on understanding operation of substrates

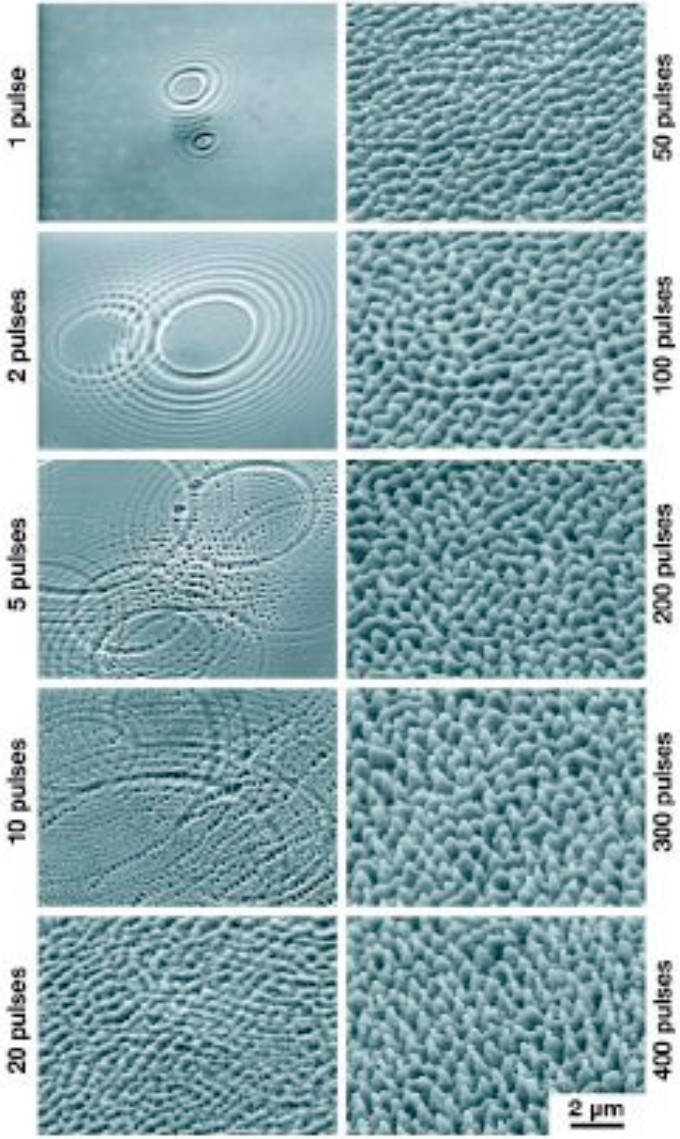
- near field optical profiling, etc.

Thank you!

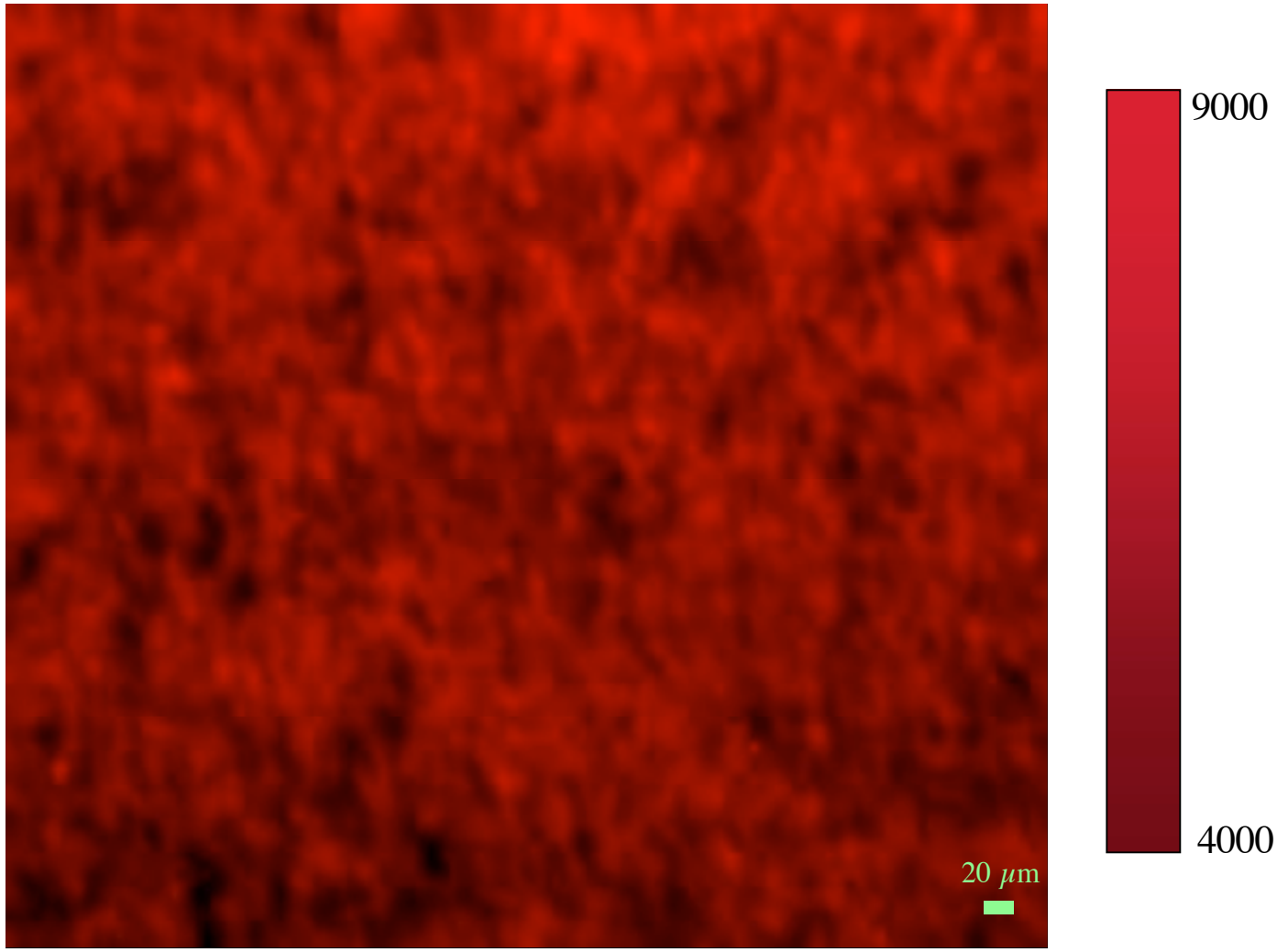
Mazur Group, NDSEG Fellowship, Horiba Jobin Yvon

http://mazur-www.harvard.edu

Femtosecond laser-structured substrates



Signal uniformity (linear scale)



Motivation

1. Raman scattering/spectroscopy reveals the unique vibrational spectrum of a molecule

2. Molecular Raman scattering cross sections are very small: $\sim 10^{-30}$ cm^2: Raman scattering is difficult to detect for spectroscopy applications ($\sim$1 in 10^7 incident photons are Raman scattered from a molecule)

3. Efficient, inexpensive enhancement mechanisms and substrates will enable the use of Raman scattering in a host of new applications

Raman scattering: a classical approach

$$p^{(1)} = \alpha \cdot E$$

$$Q_k(t) = Q_{k0} \cos(\omega_k t + \delta_k)$$

$$E(t) = E_0 \cos(\omega_0 t)$$

$$\alpha \simeq \alpha_0 + \sum_k \left(\frac{\partial \alpha}{\partial Q_k} \right)_0 Q_k + \ldots$$

Raman scattering: a classical approach

$$p^{(1)}(t) = \alpha_0 E_0 \cos(\omega_0 t) + \frac{1}{2}\sum_k \alpha'_{k0} E_0 Q_{k0} [\cos((\omega_0 - \omega_k)t - \delta_k) + \cos((\omega_0 + \omega_k)t + \delta_k)]$$

Rayleigh

Stokes Raman

Anti-Stokes Raman

Polarization at the Raman frequencies is LINEAR in E_0

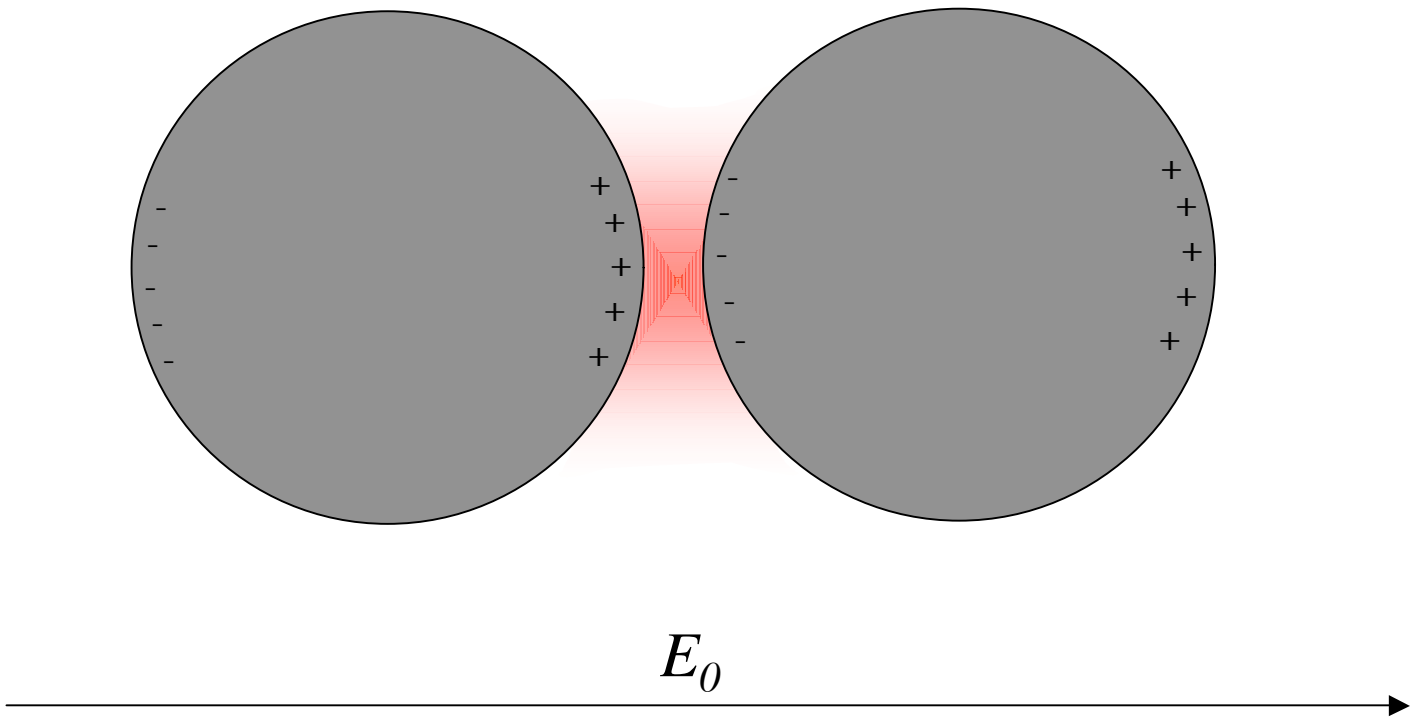
Raman scattering: possibility of enhancement?

$$p^{(1)} = \alpha \cdot E$$

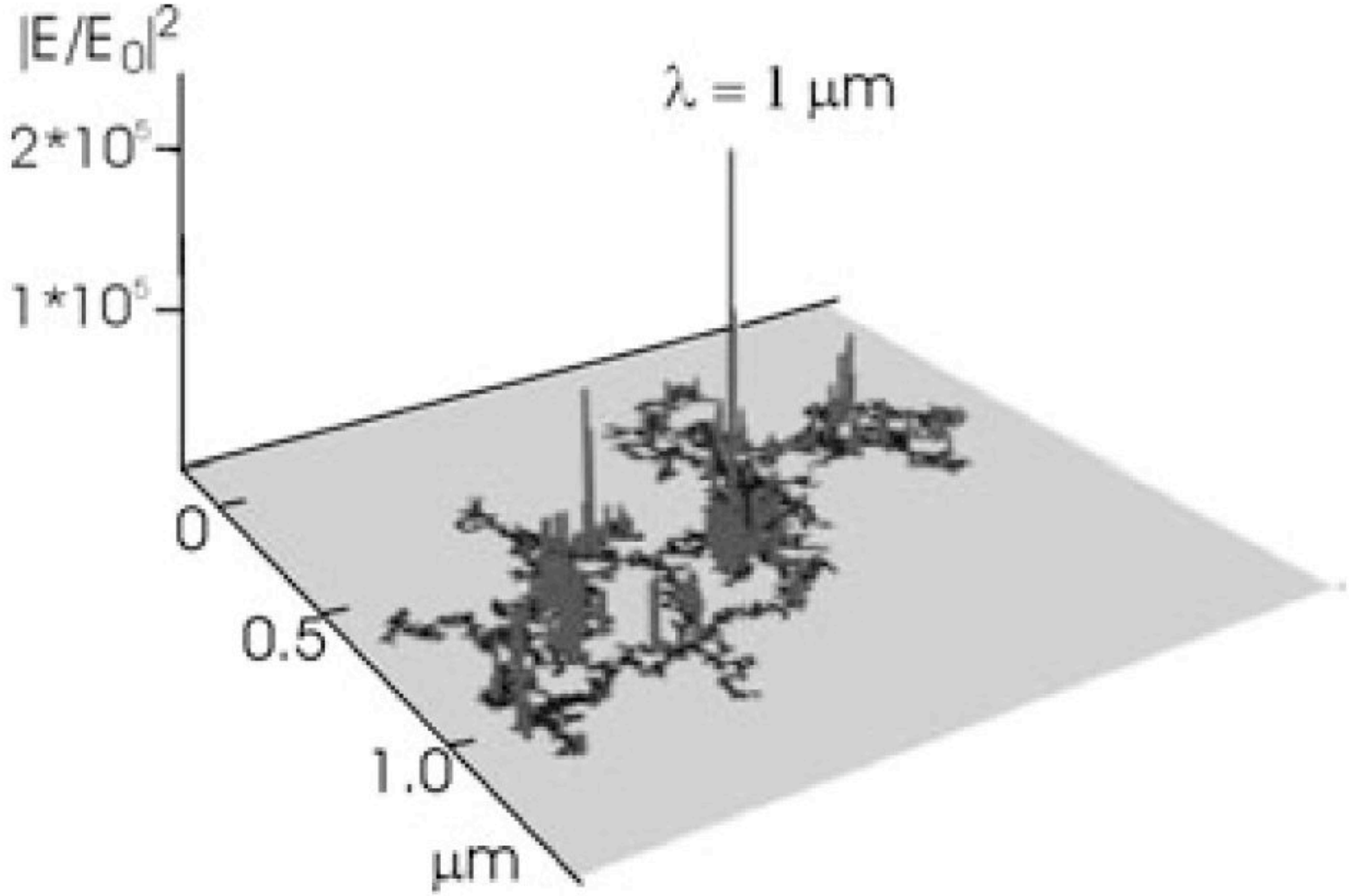
Enhance α, α'_{k0}?

Enhance E?

Surface enhancement

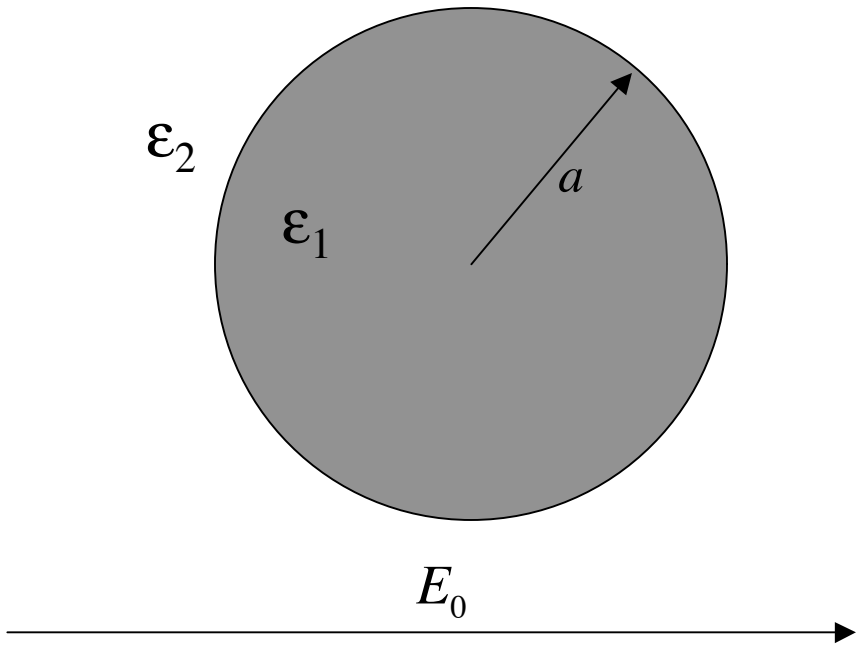


Surface Enhancement



From: K. Kneipp, H. Kneipp, I. Itzkan, R.R. Dasari, and M.S. Feld, *J. Phys.: Condens. Matter* **14** (2002) R567-R624

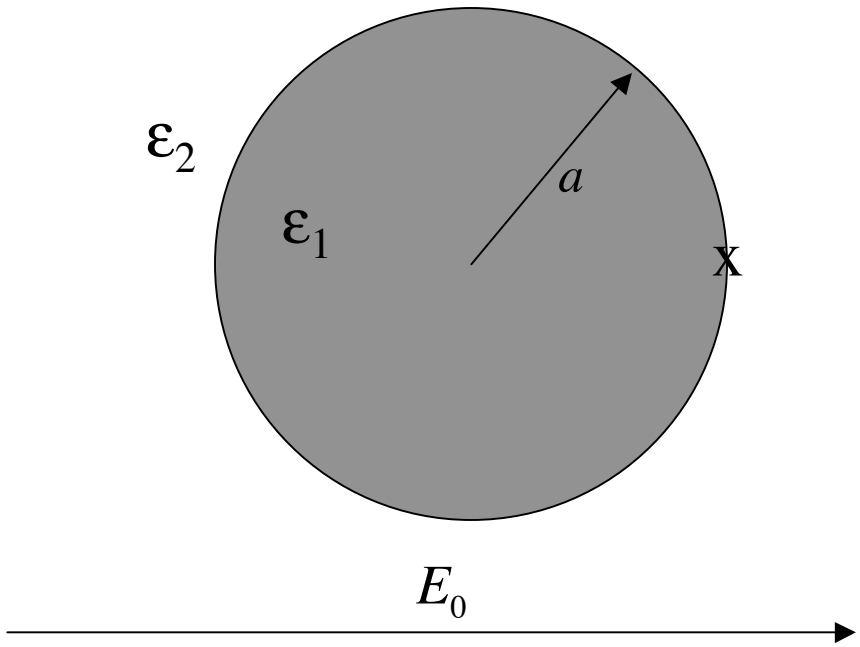
Surface enhancement



Quasi-static approximation
(Rayleigh particle limit)

$$a < 0.05\lambda$$

Surface enhancement



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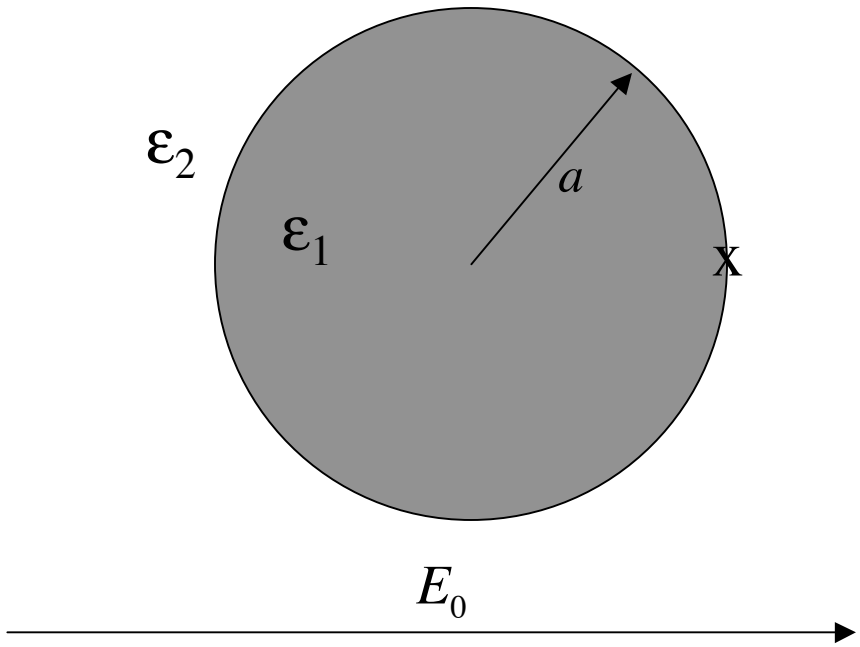
Near-field enhancement factor

$$\frac{|E_s|}{|E_0|} \propto \frac{\varepsilon_1(\omega) - \varepsilon_2}{\varepsilon_1(\omega) + 2\varepsilon_2}$$

Surface enhancement



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For Ag particle on resonance,
$EF \sim 10$