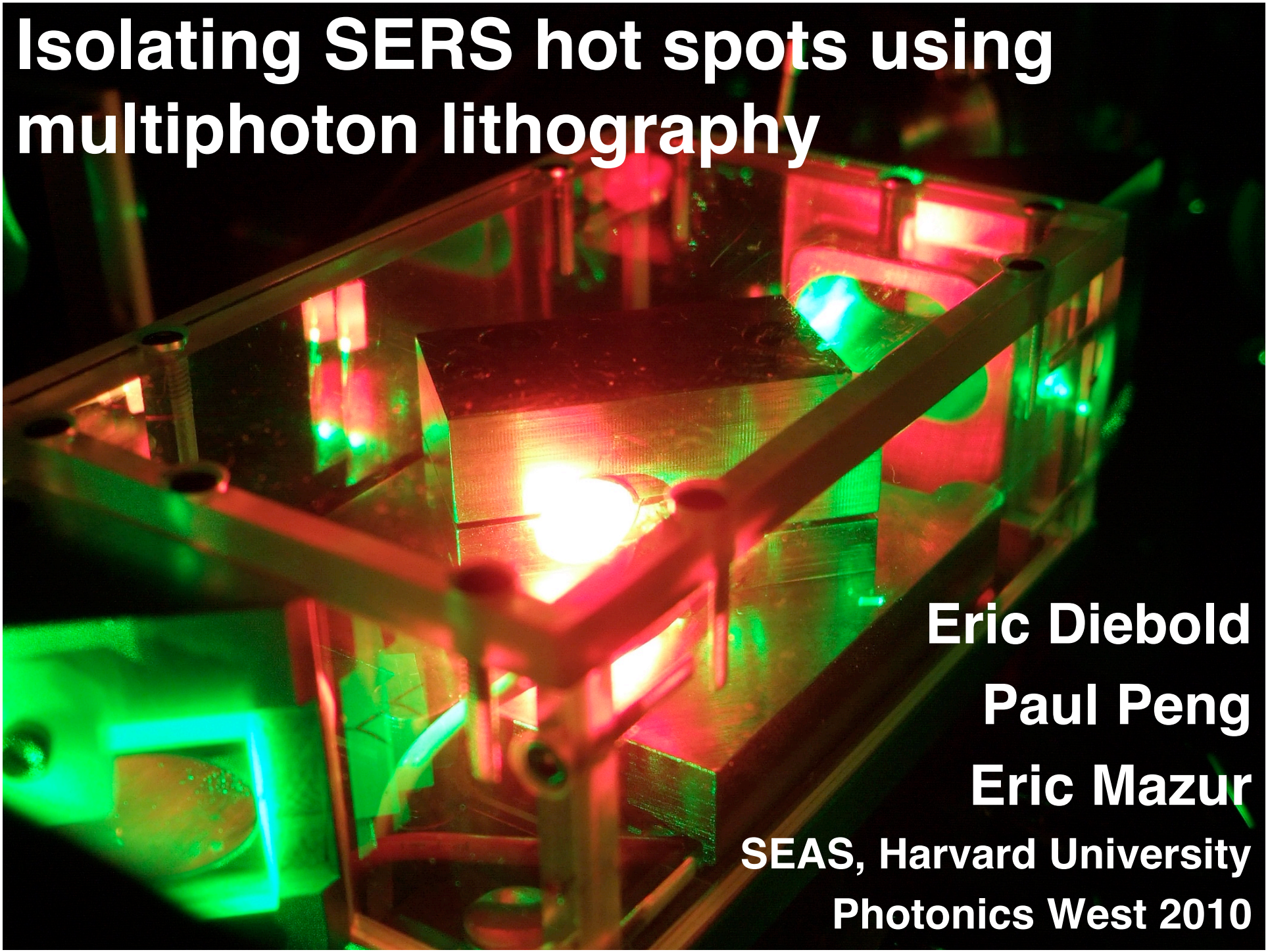
Isolating SERS hot spots using multiphoton lithography



Eric Diebold

Paul Peng

Eric Mazur

SEAS, Harvard University

Photonics West 2010

Outline

Background

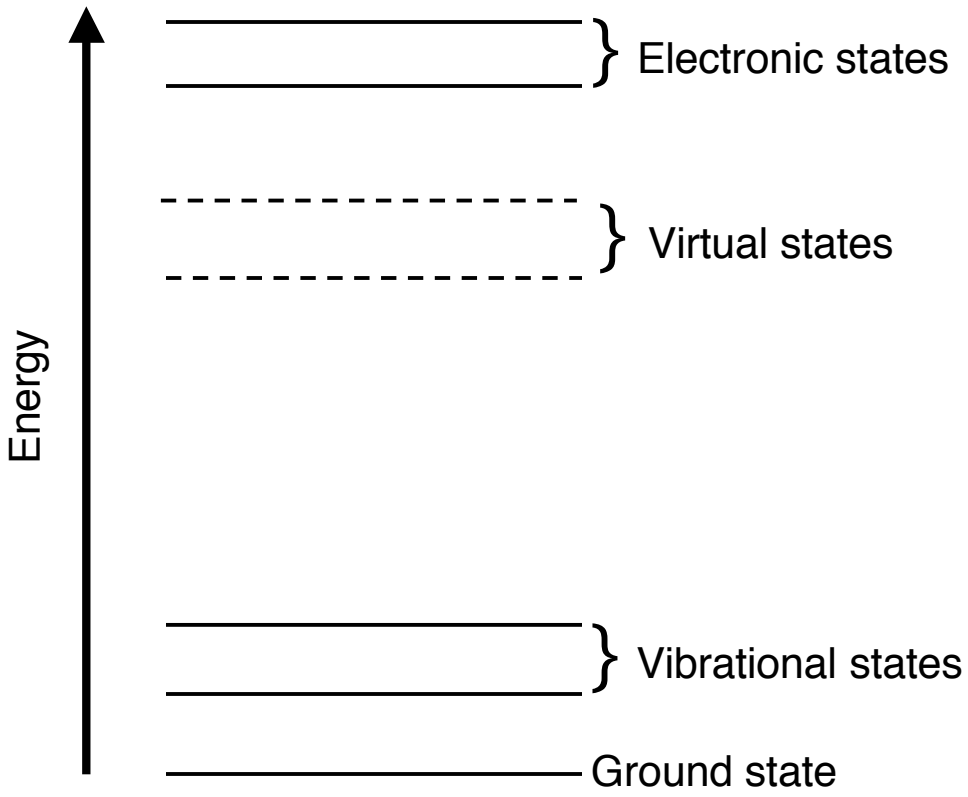
Motivation: hot spot distribution

Hot spot isolation

Conclusion

Background

Raman scattering



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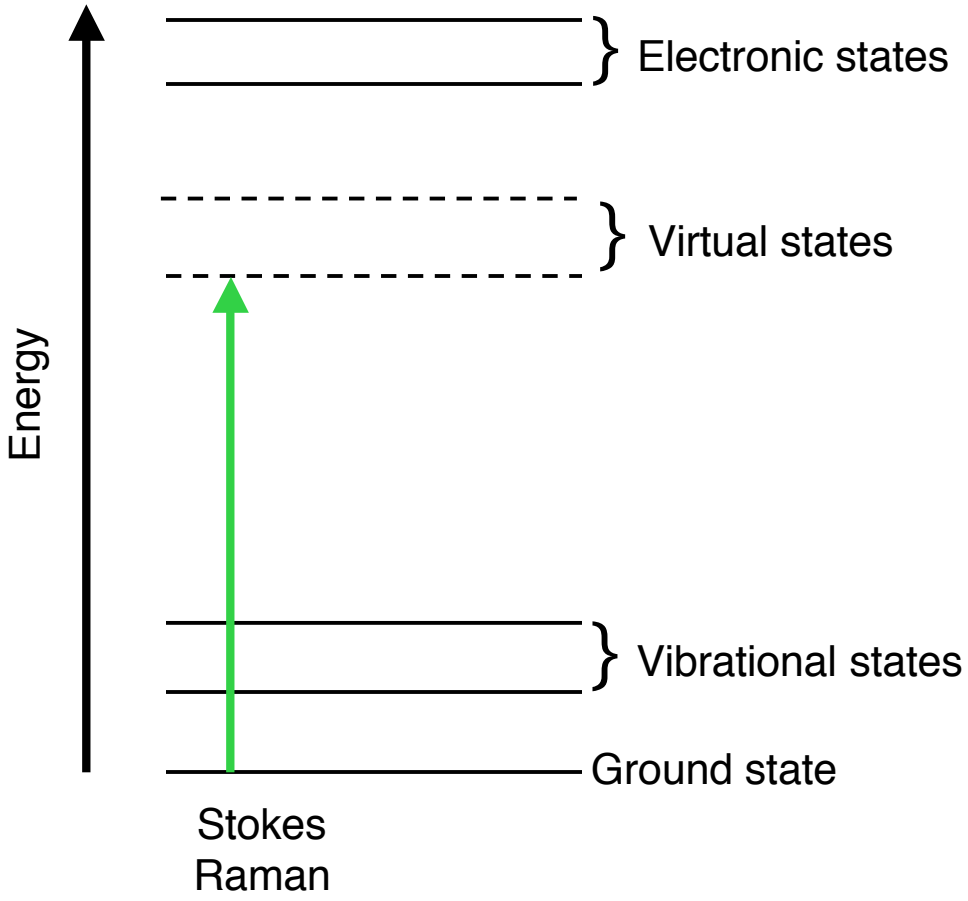

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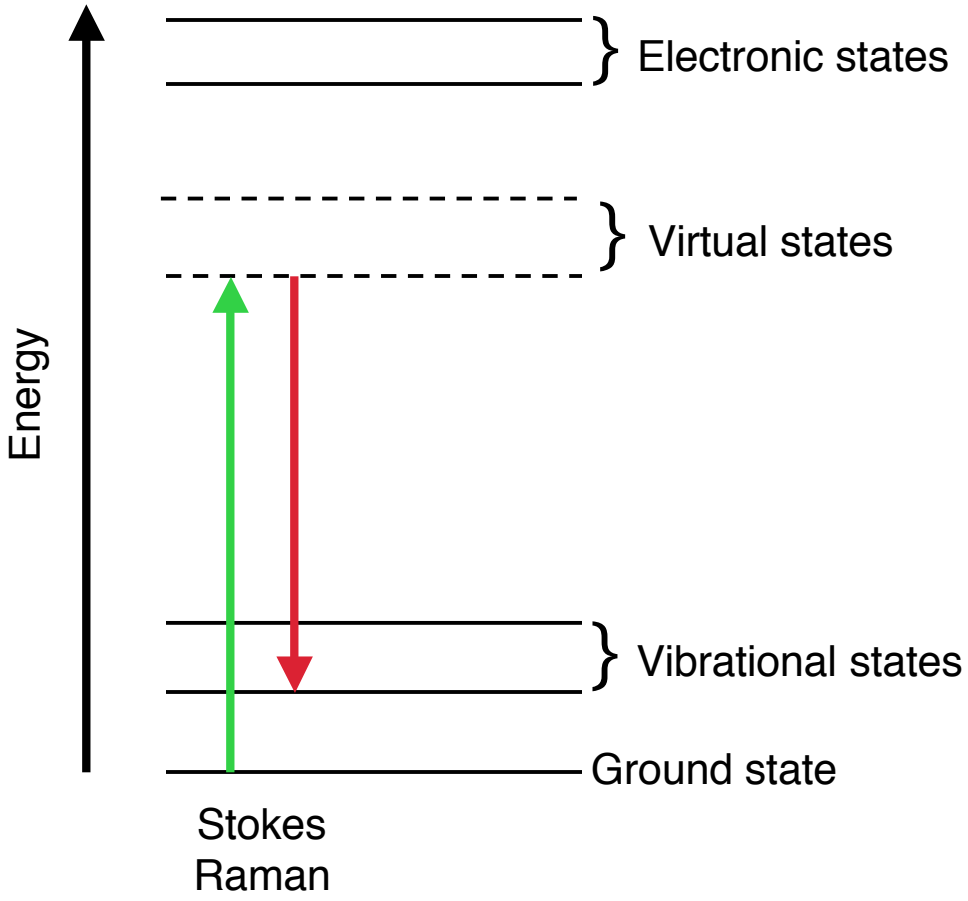

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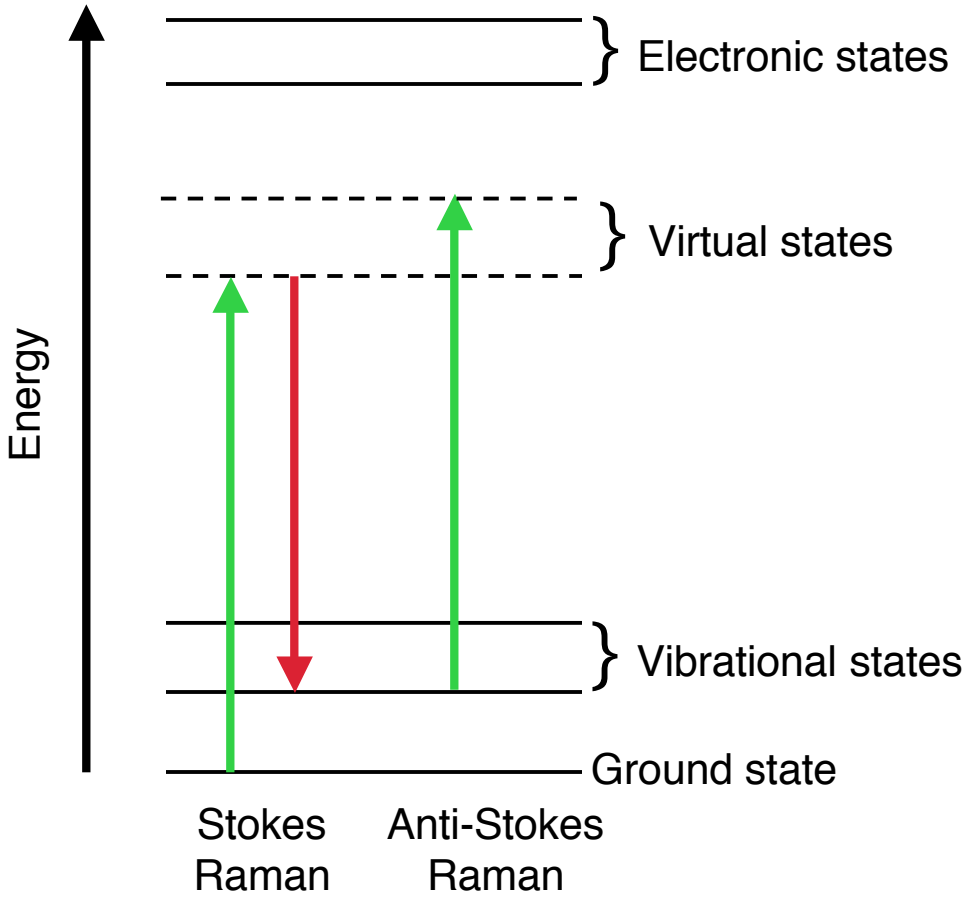

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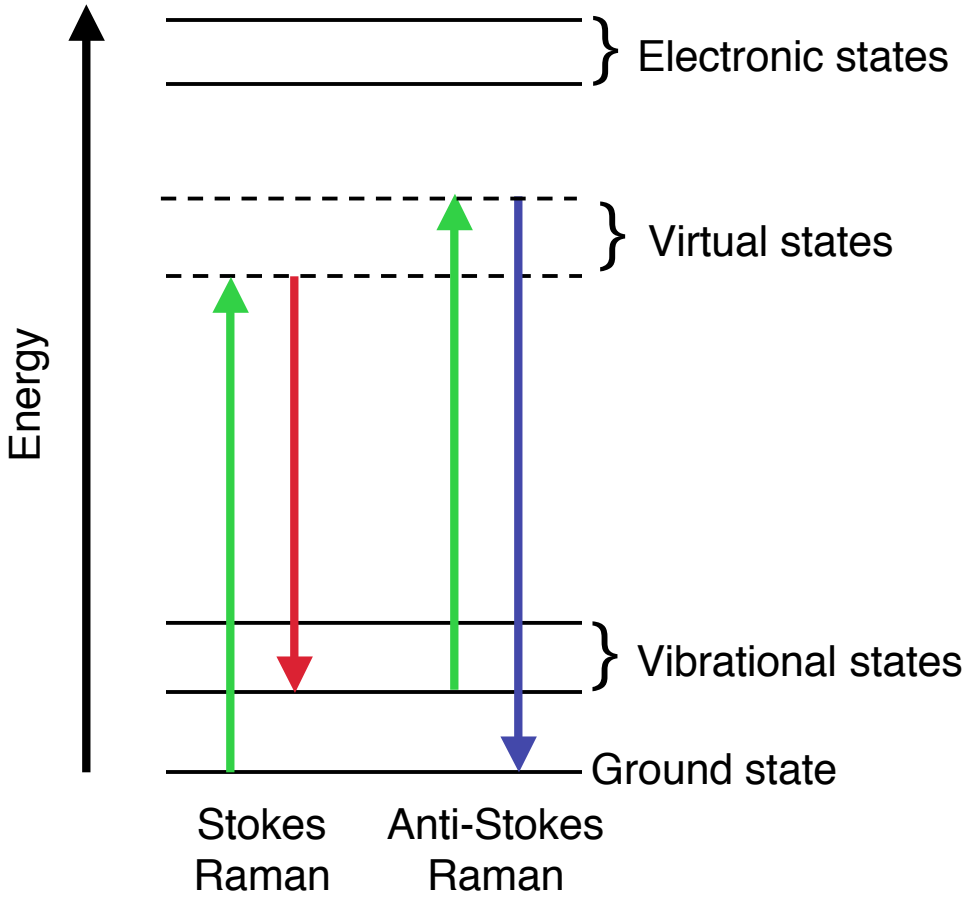
Raman scattering



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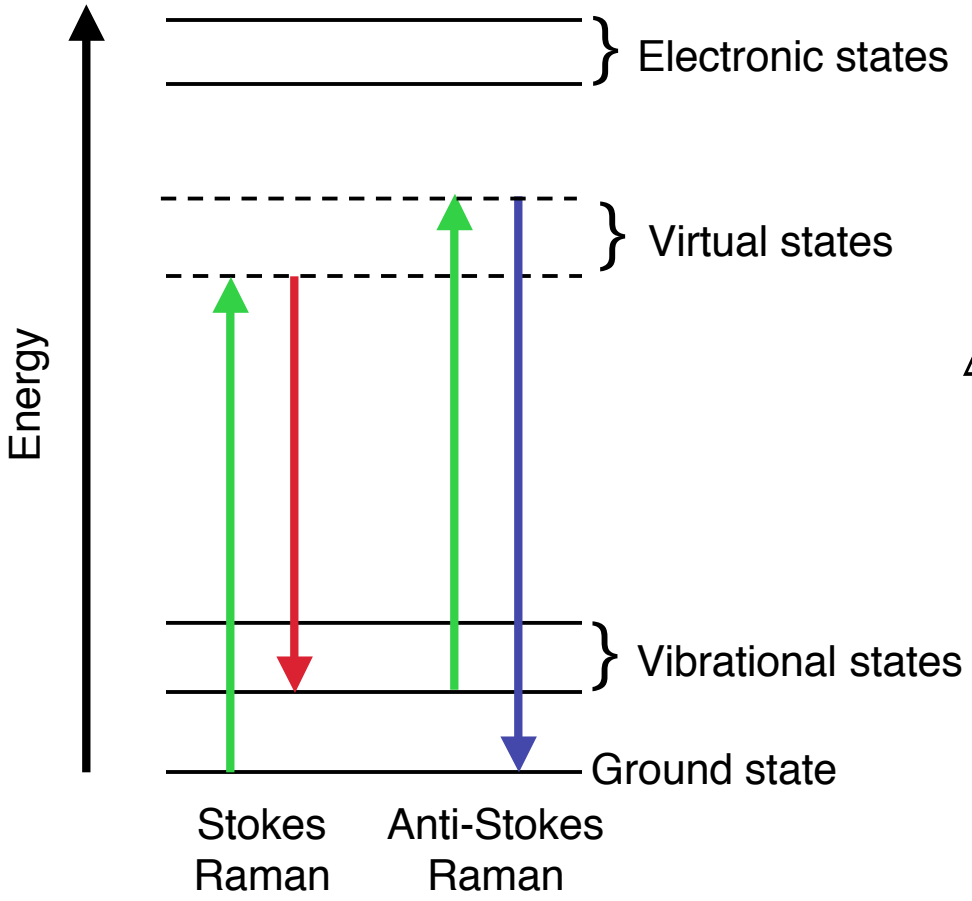
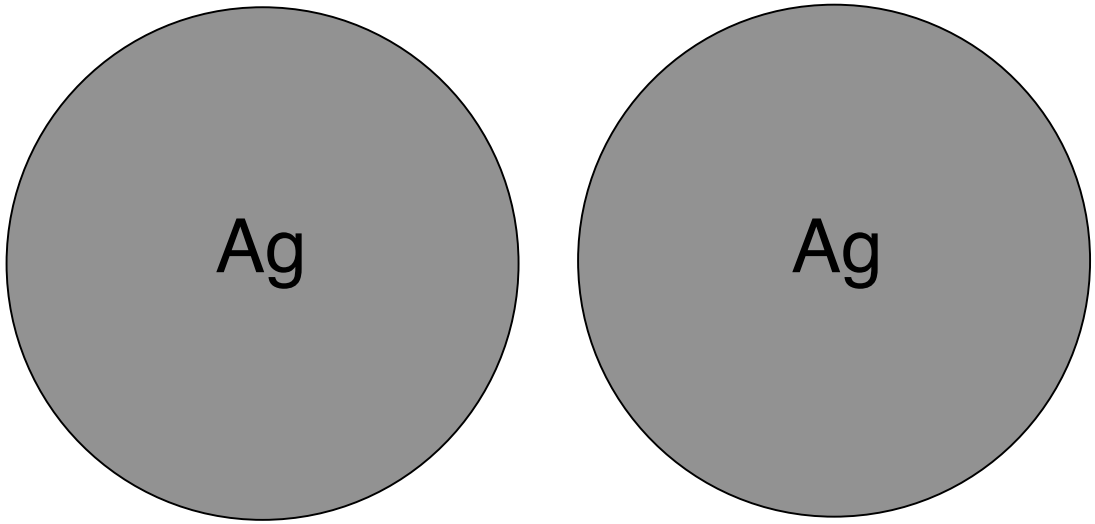


$$\Delta\upsilon = \frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}}$$

Background

Surface enhancement



Background

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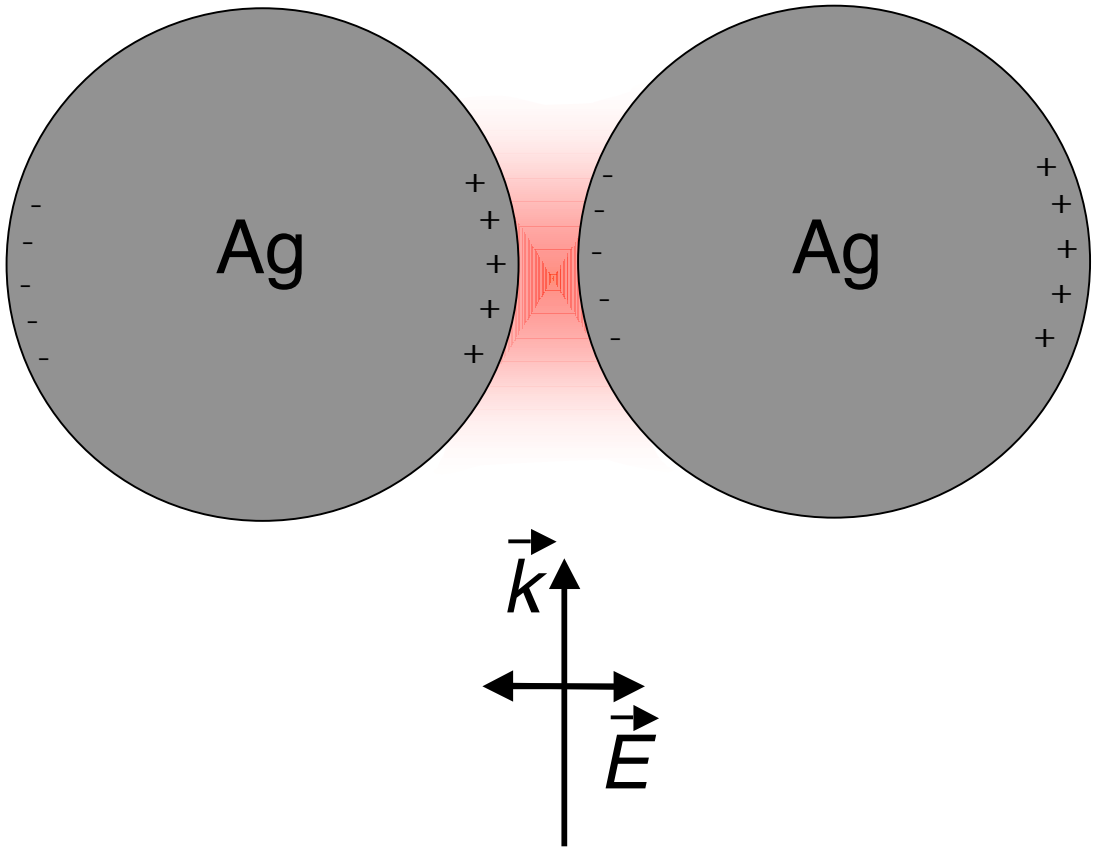

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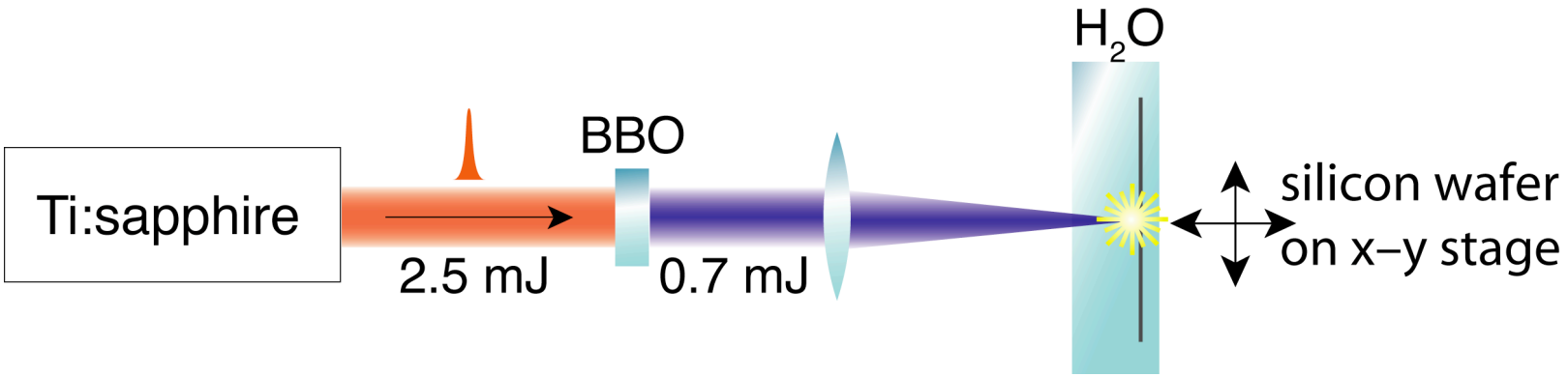
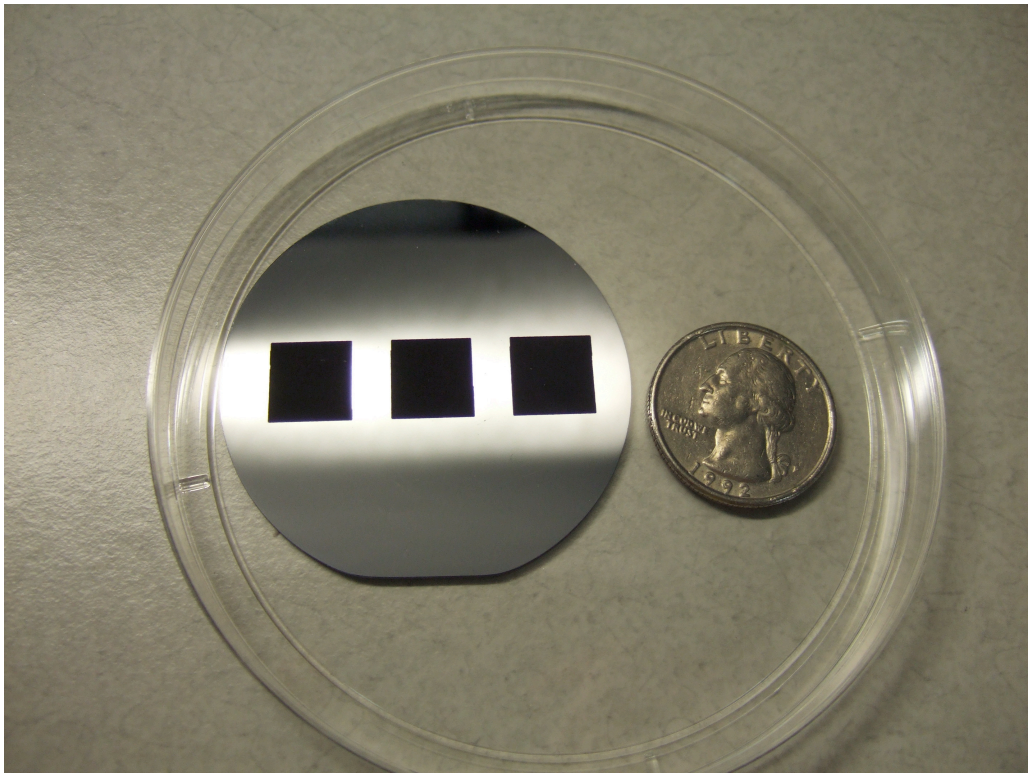
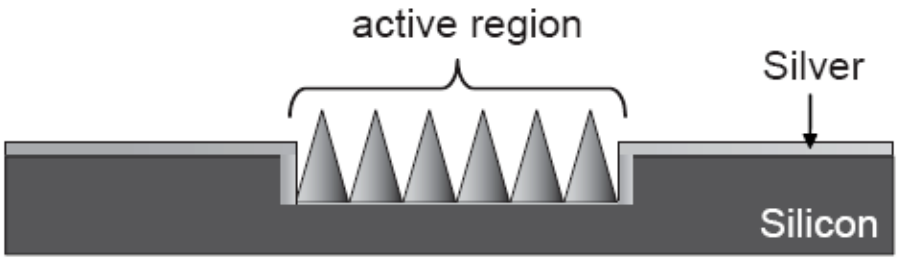




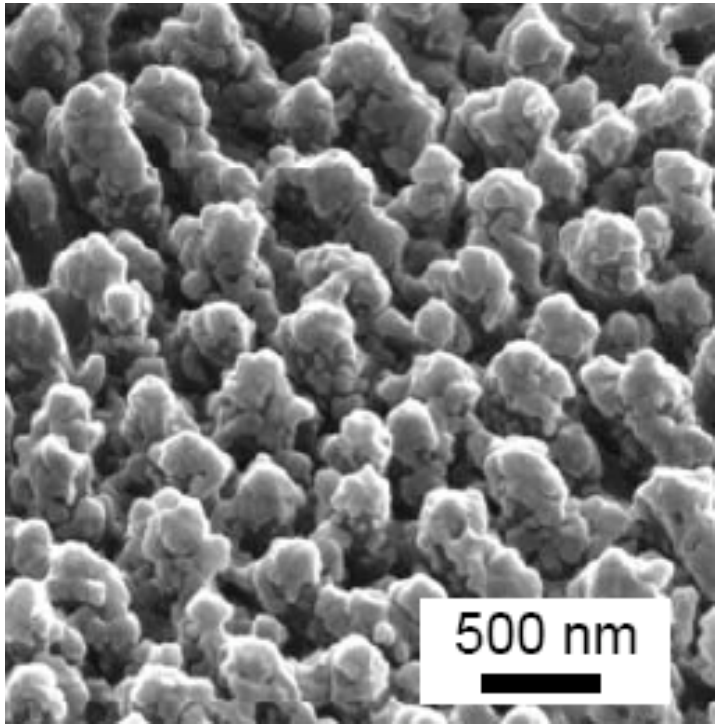
Diebold, et al. *Langmuir* **25**, 1790 (2009)

Background

1. Femtosecond laser structuring
2. Thermal evaporation - 80nm Ag



Active region



Average enhancement factor (benzenethiol) ~ 10^7

Diebold, et al. *Langmuir* **25**, 1790 (2009)

Outline

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Motivation: hot spot distribution

Hot spot isolation

Conclusion

Motivation: hot spot distribution

Measurement of the Distribution of Site Enhancements in Surface-Enhanced Raman Scattering

Ying Fang, Nak-Hyun Seong, Dana D. Dlott

Raman enhancement factor η	Percentage of molecules	Percentage contribution to overall SERS signal
$<2.8 \times 10^4$	0	0
2.8×10^4 to 1×10^5	61%	4%
10^5 to 10^6	33%	11%
10^6 to 10^7	5.1%	16%
10^7 to 10^8	0.7%	22%
10^8 to 10^9	0.08%	23%
10^9 to 10^{10}	0.006%	17%
$>10^{10}$	0.0003%	7%

Fang, et al. *Science* **381**, 288 (2008)

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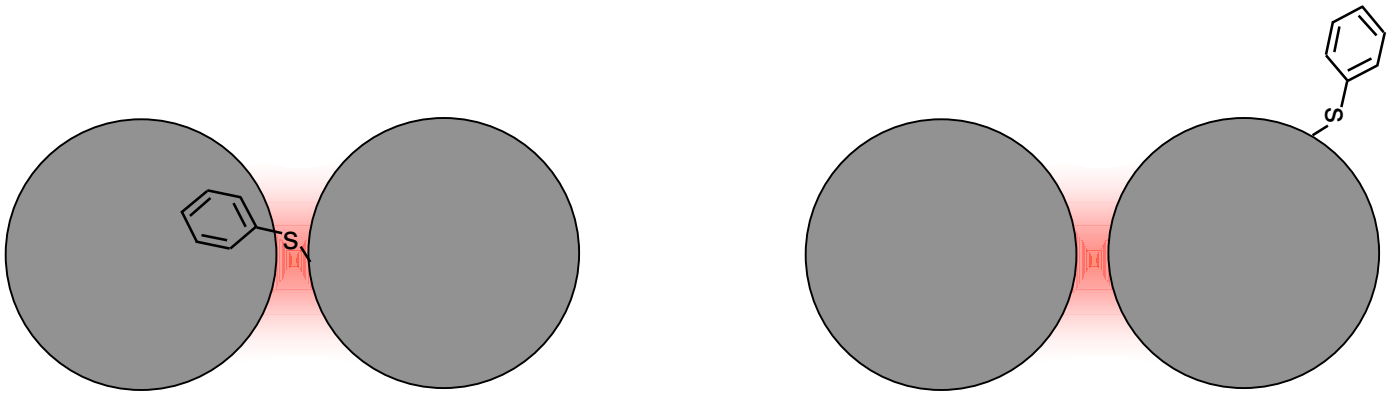
$>10^{10}$	0.0003%	7%

Only **63** out of **1,000,000** sites are "hot spots" (EF > 10^9), yet their contribution to the total SERS signal is 24%!

Fang, et al. *Science* **381**, 288 (2008)

Motivation: hot spot distribution

If $N_{analyte}$ is small, how do we ensure that molecules adsorb only to hot spots?



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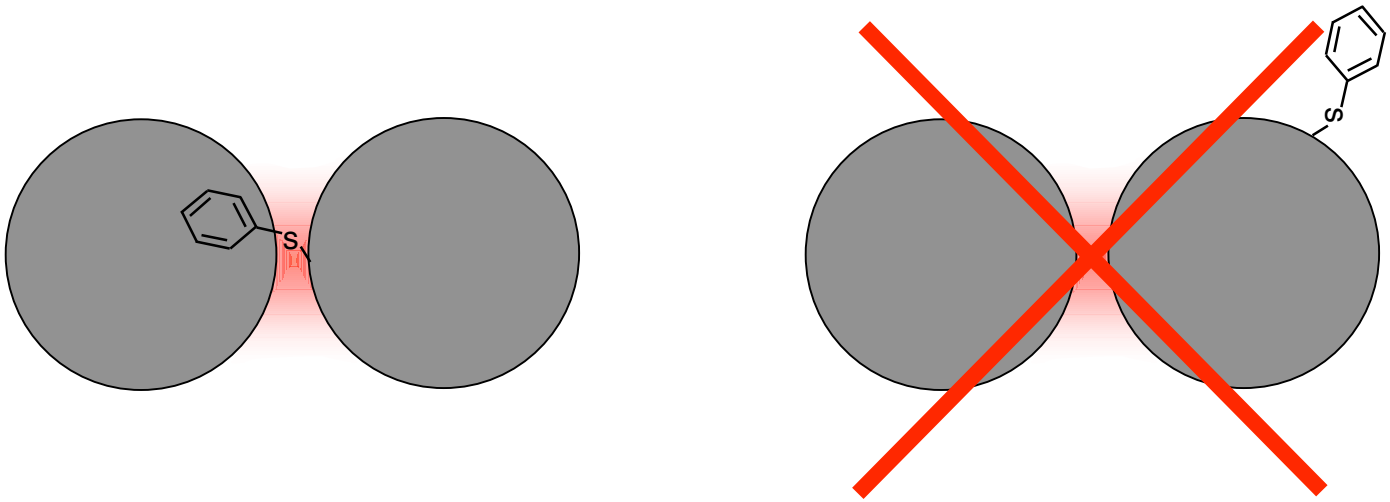
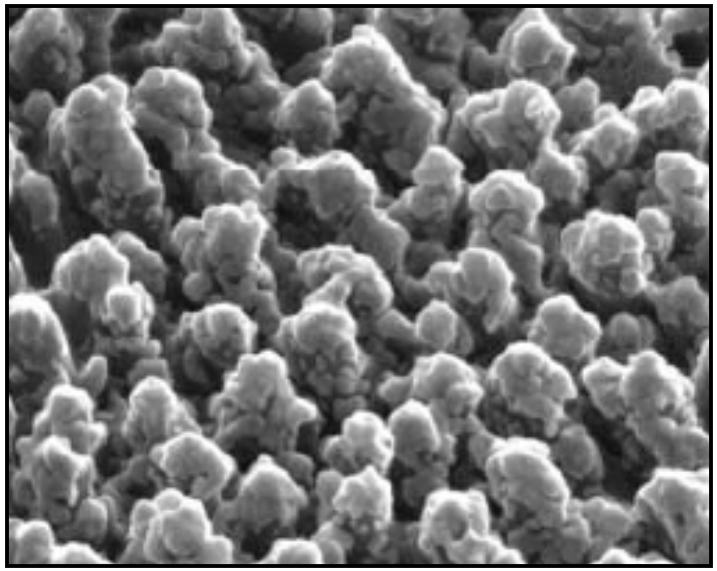
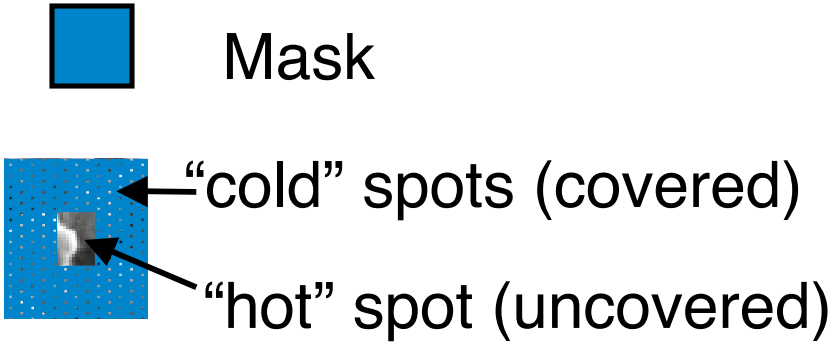


Motivation: hot spot distribution





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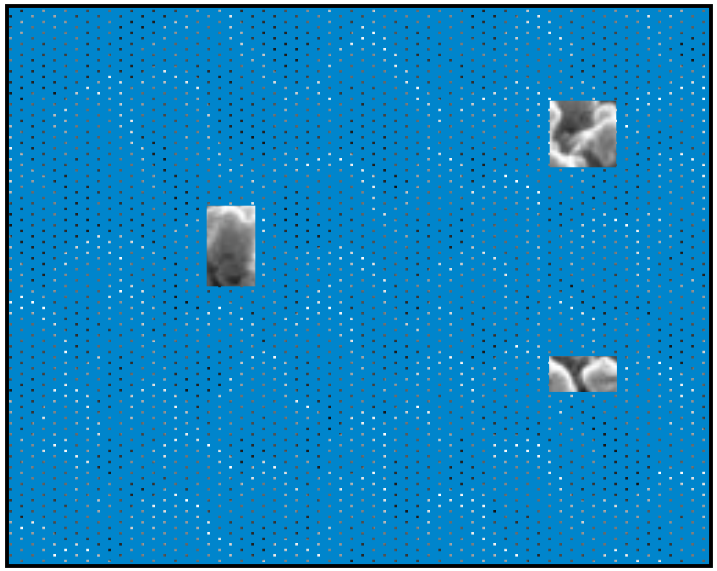
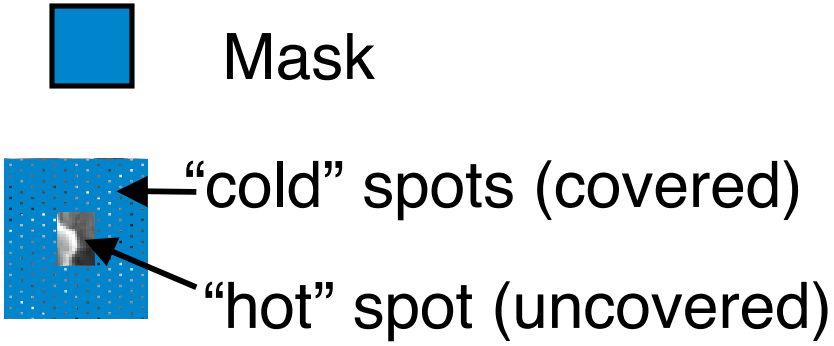




Outline

Background

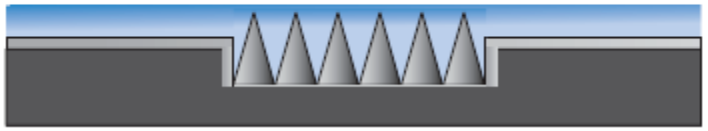
Motivation: hot spot distribution

Hot spot isolation

Conclusion

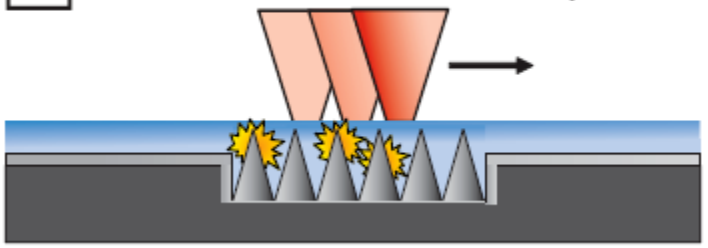
Hot spot isolation

1 Spin coat positive-tone resist



Shipley S1805 photoresist
(~30nm thick layer)

2 Femtosecond-laser exposure



Multiphoton-induced luminescence from Ag hot spots exposes photoresist

3 Development

Developer removes exposed areas, uncovering hot spots

Diebold et al., *J. Am. Chem. Soc.*, **131**, 16356-16357 (2009)

Hot spot isolation

HSI substrates expected to show higher enhancement
under conditions of sub-monolayer coverage.

$$N_{analyte} << N_{adsorption\ sites}$$

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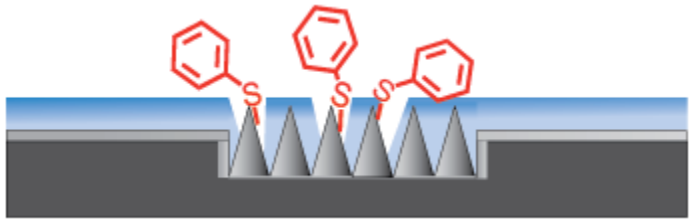
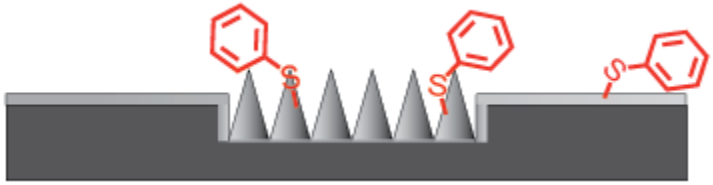


HSI-SERS substrate

Analyte binds exclusively
to exposed hot spots



SERS substrate

Analyte distributed over
both hot and cold spots

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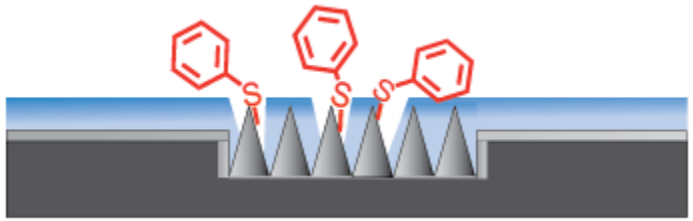

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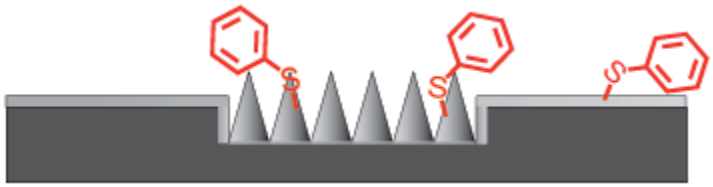

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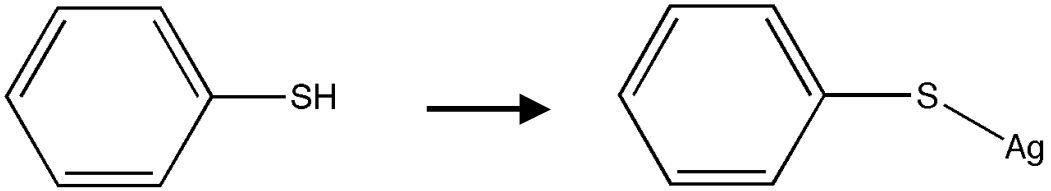
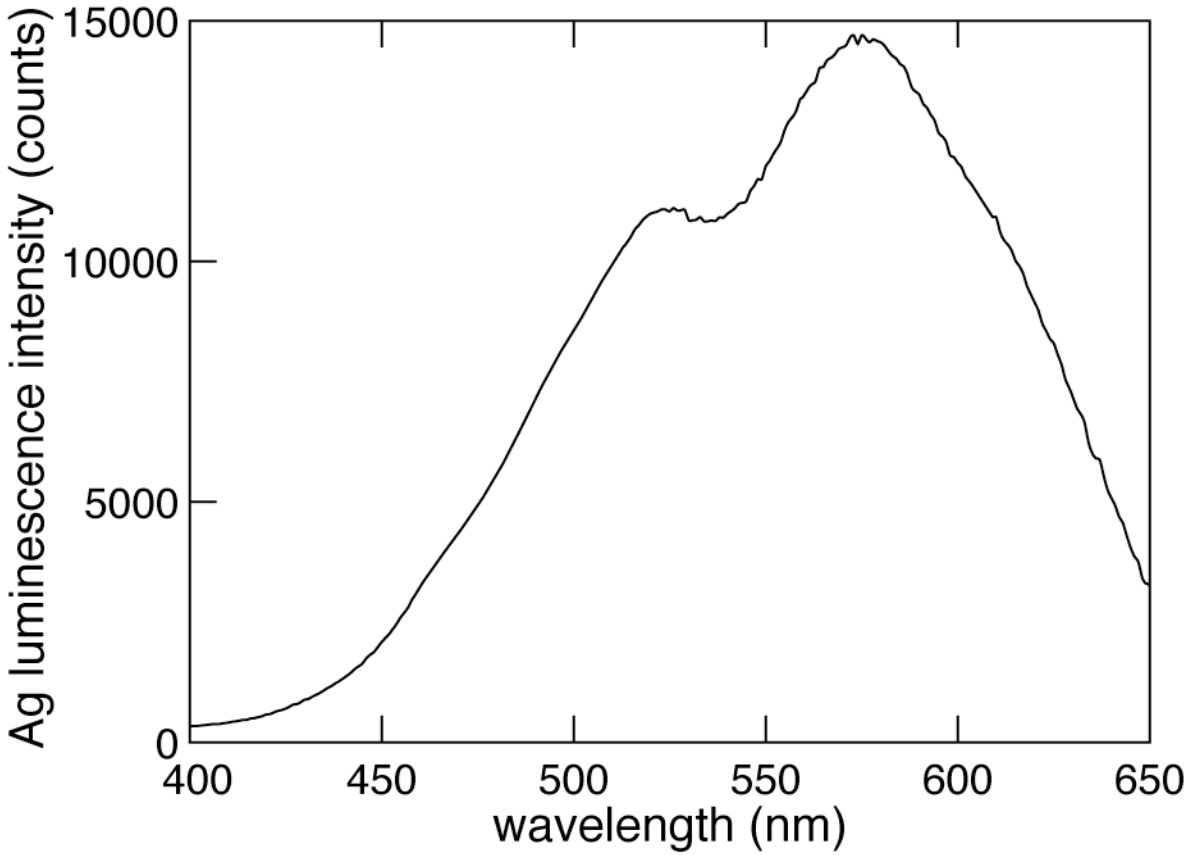


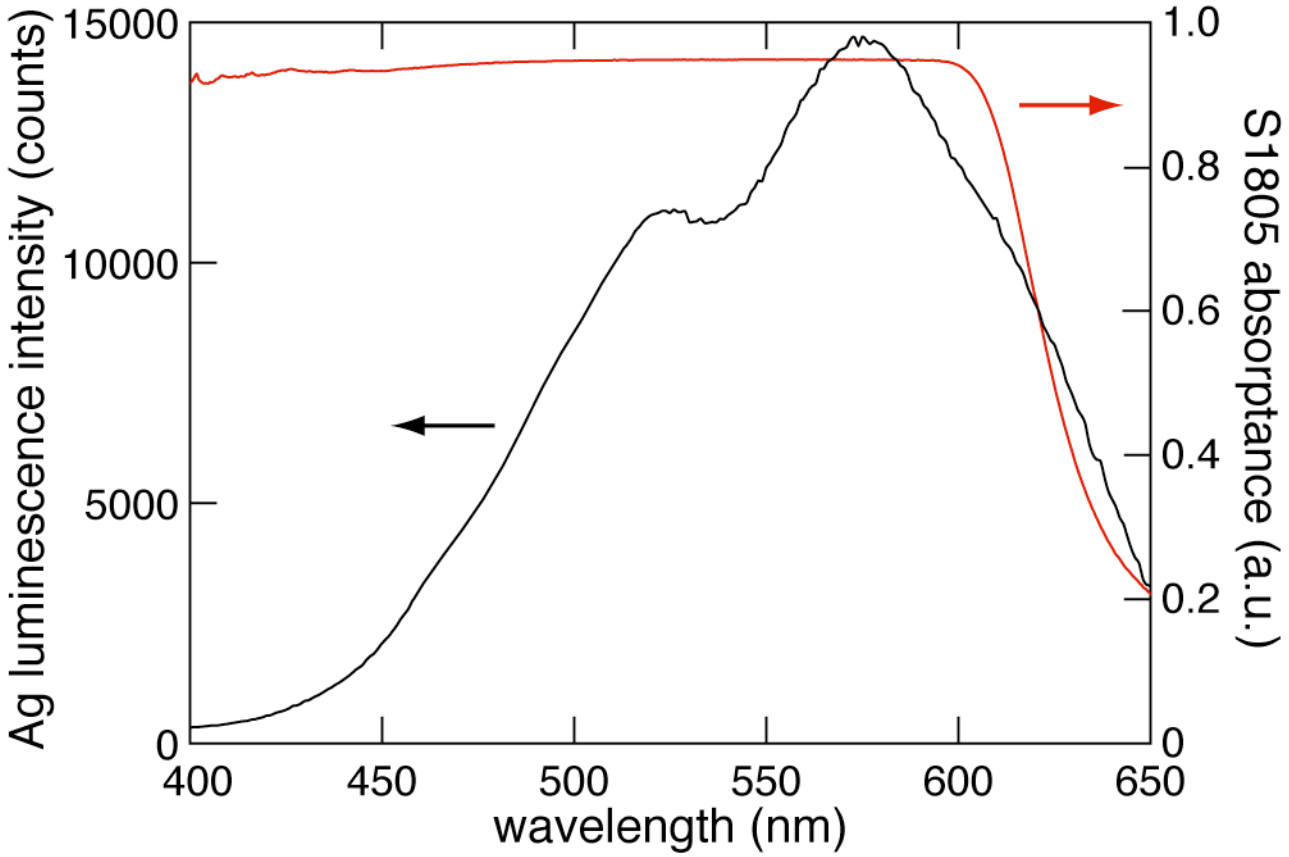
Benzenethiol

Hot spot isolation



λ_{center} = 795nm, τ = 60fs, 100 pulses/spot

Hot spot isolation



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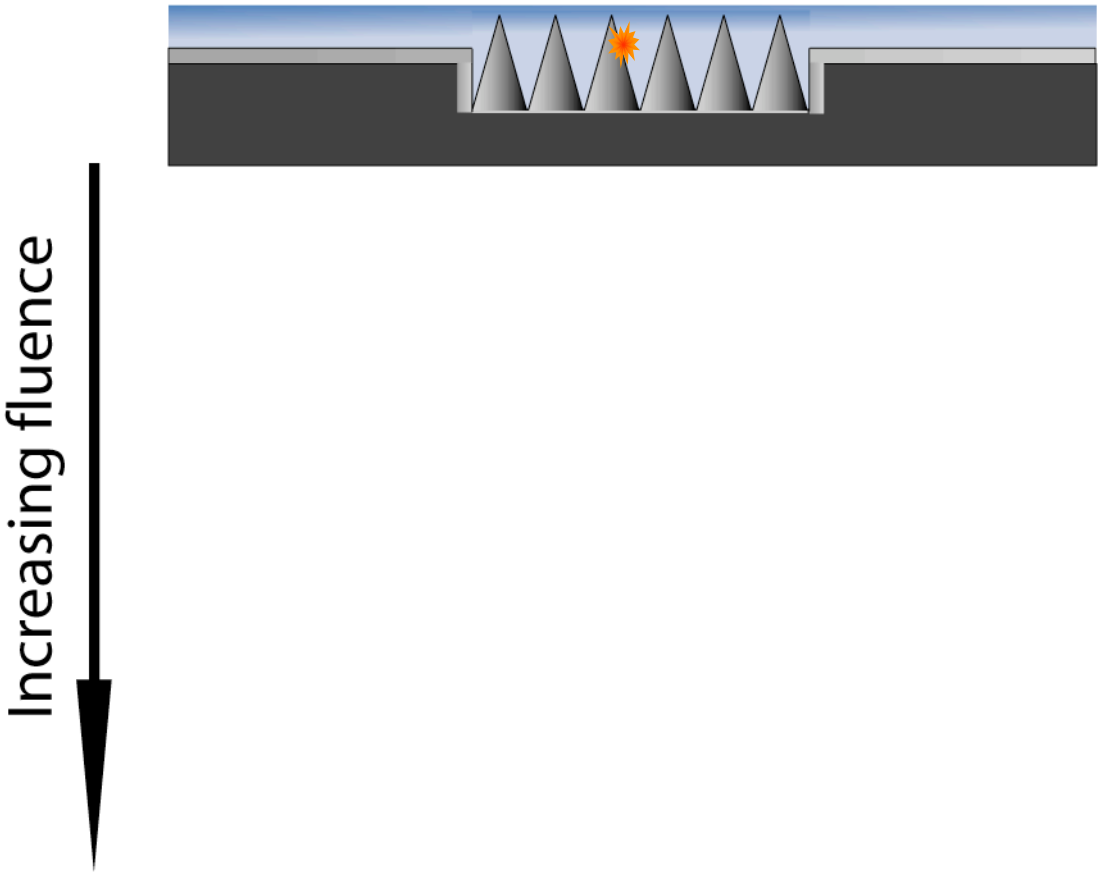

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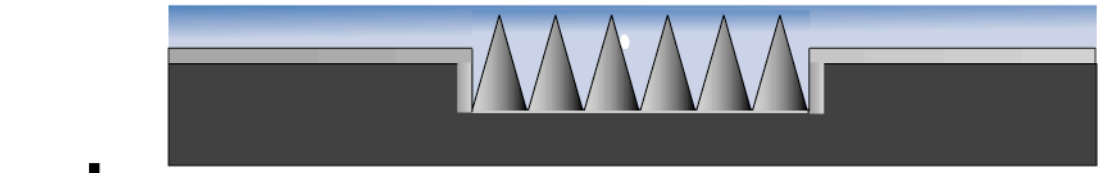

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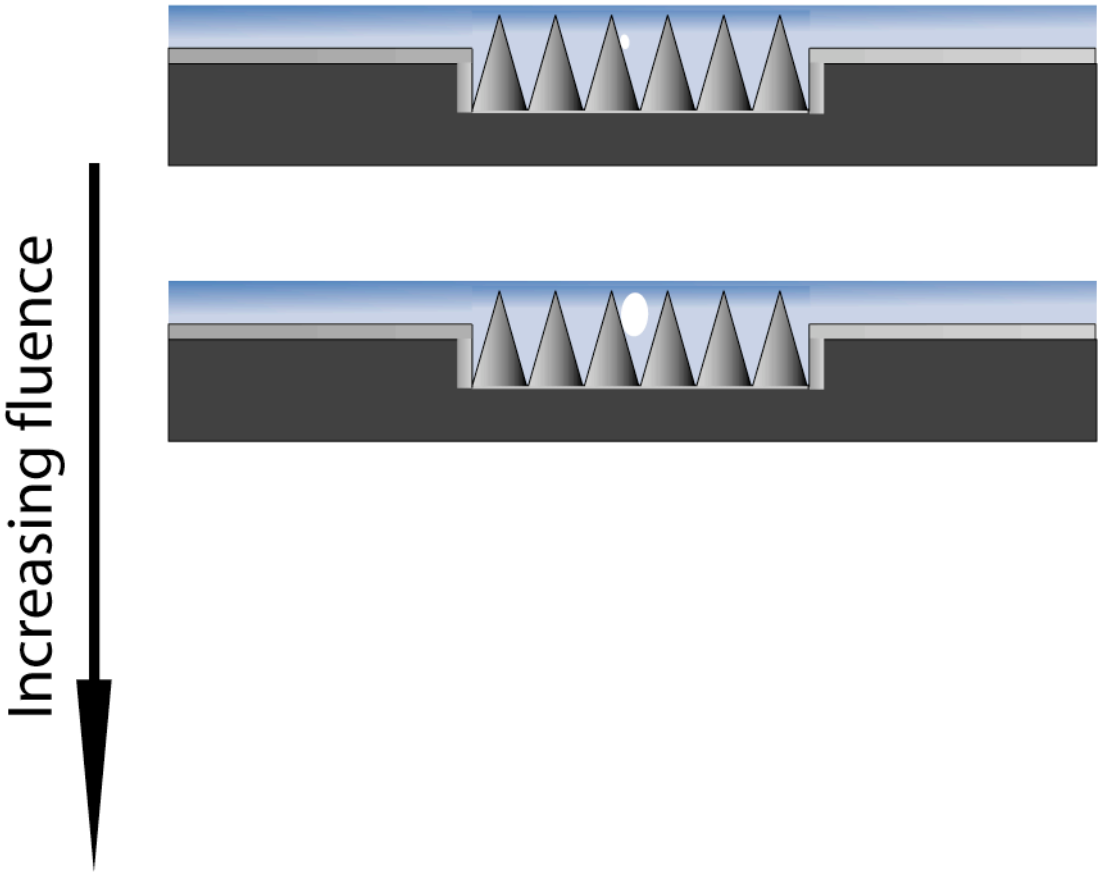

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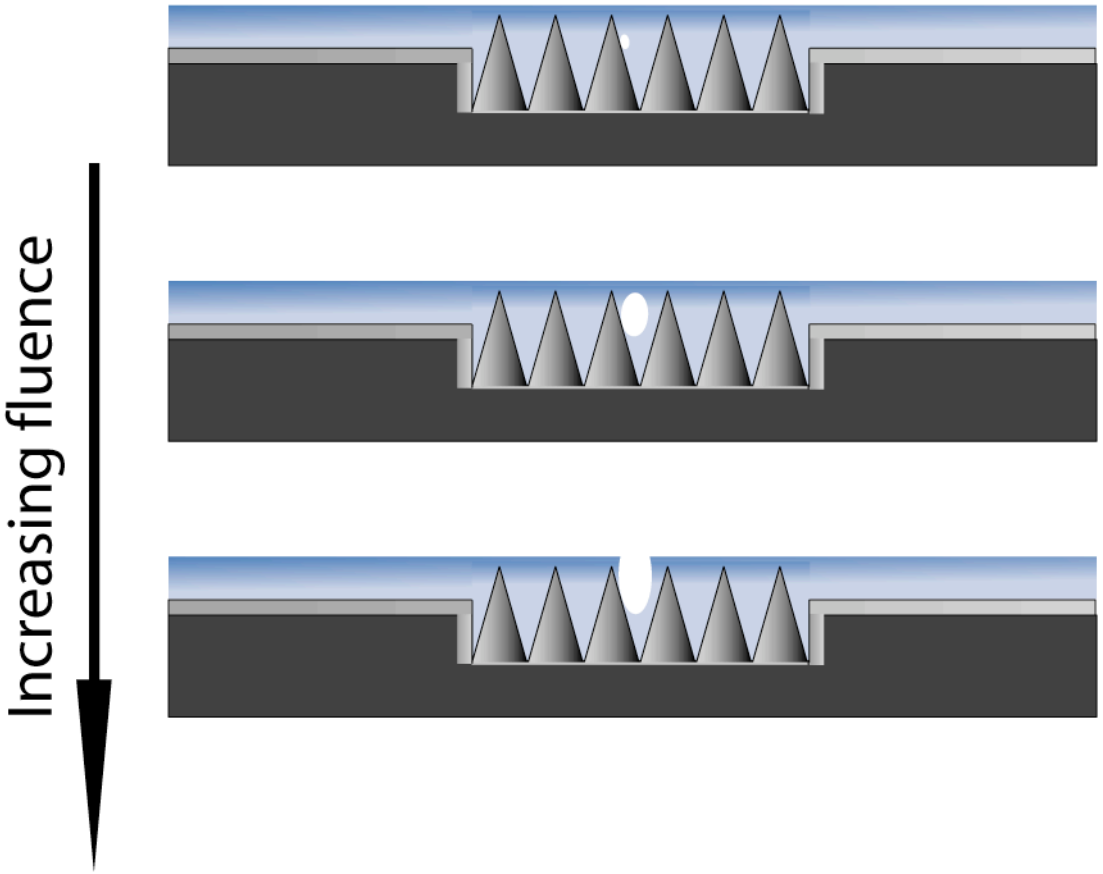

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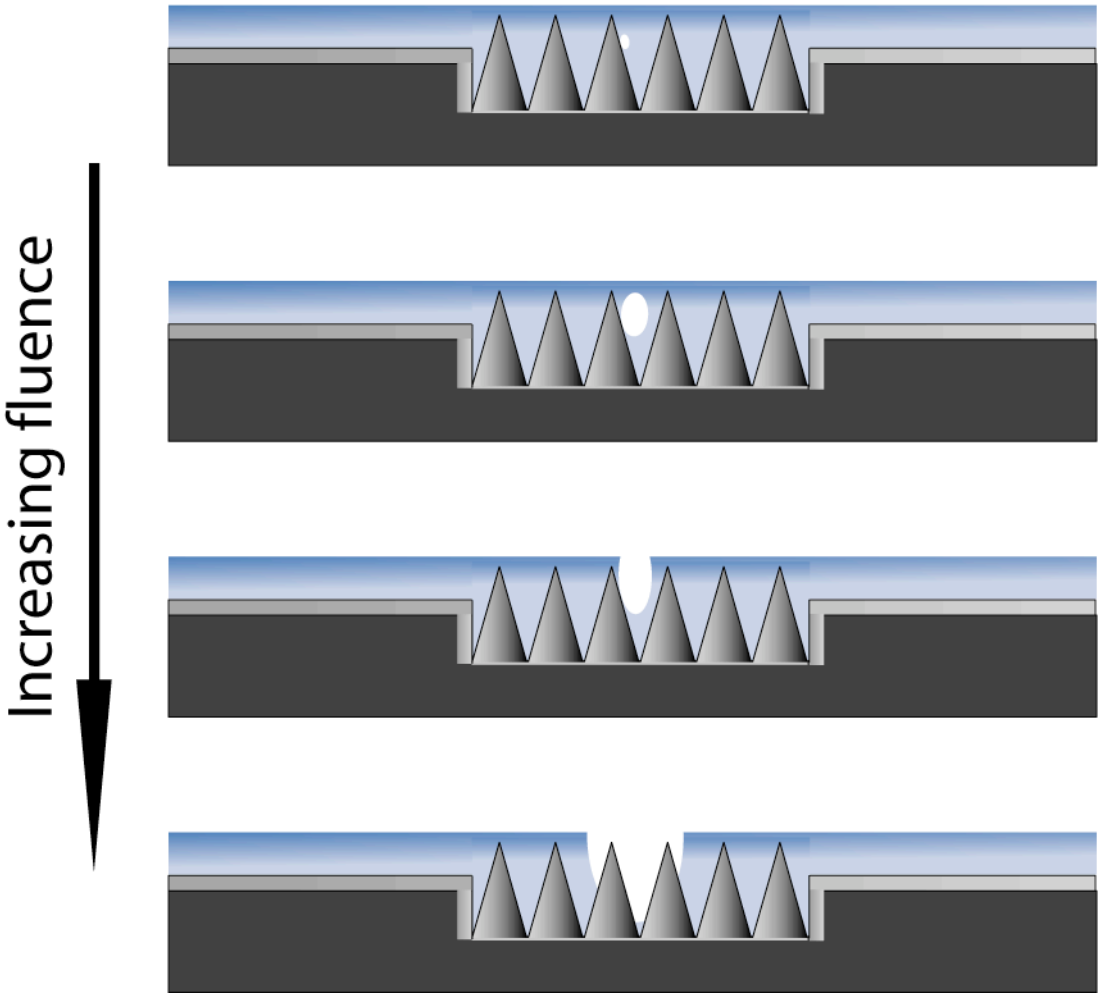

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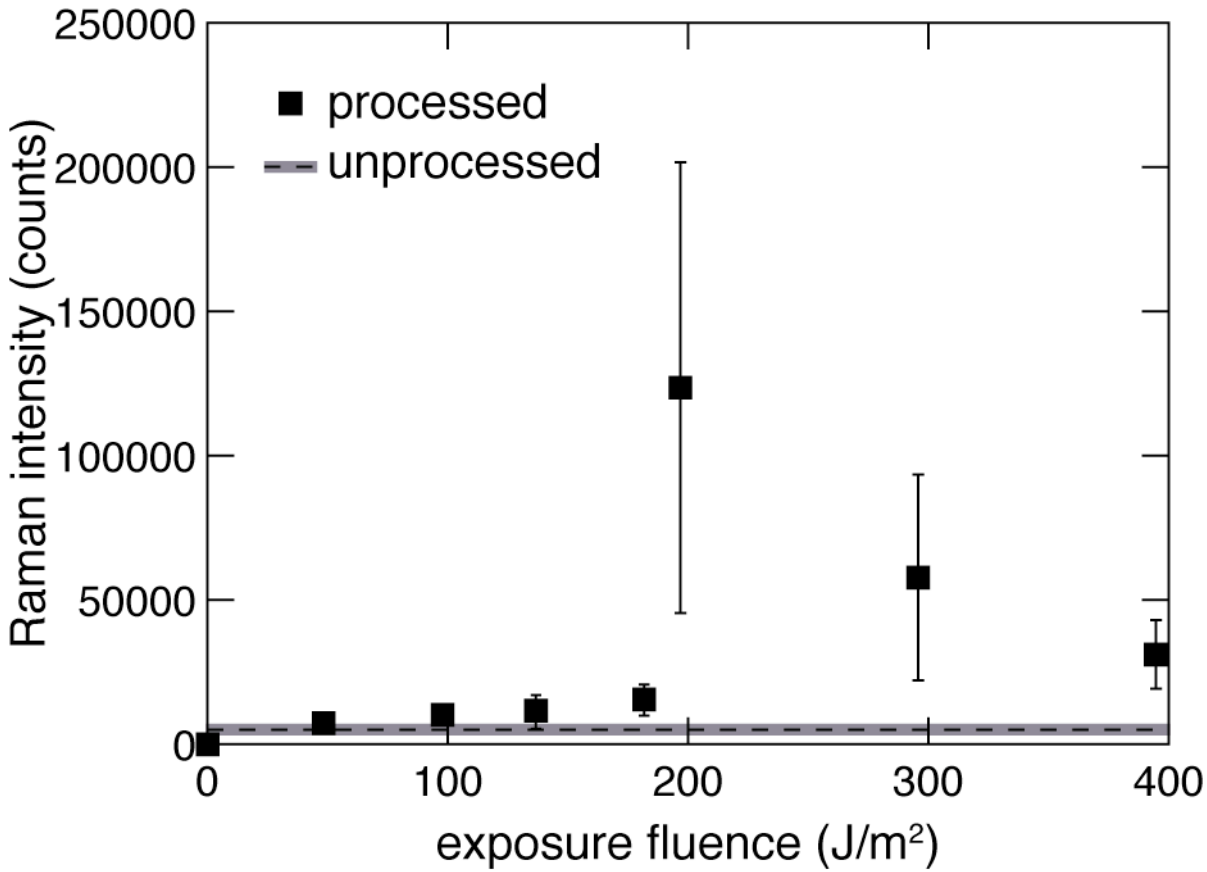
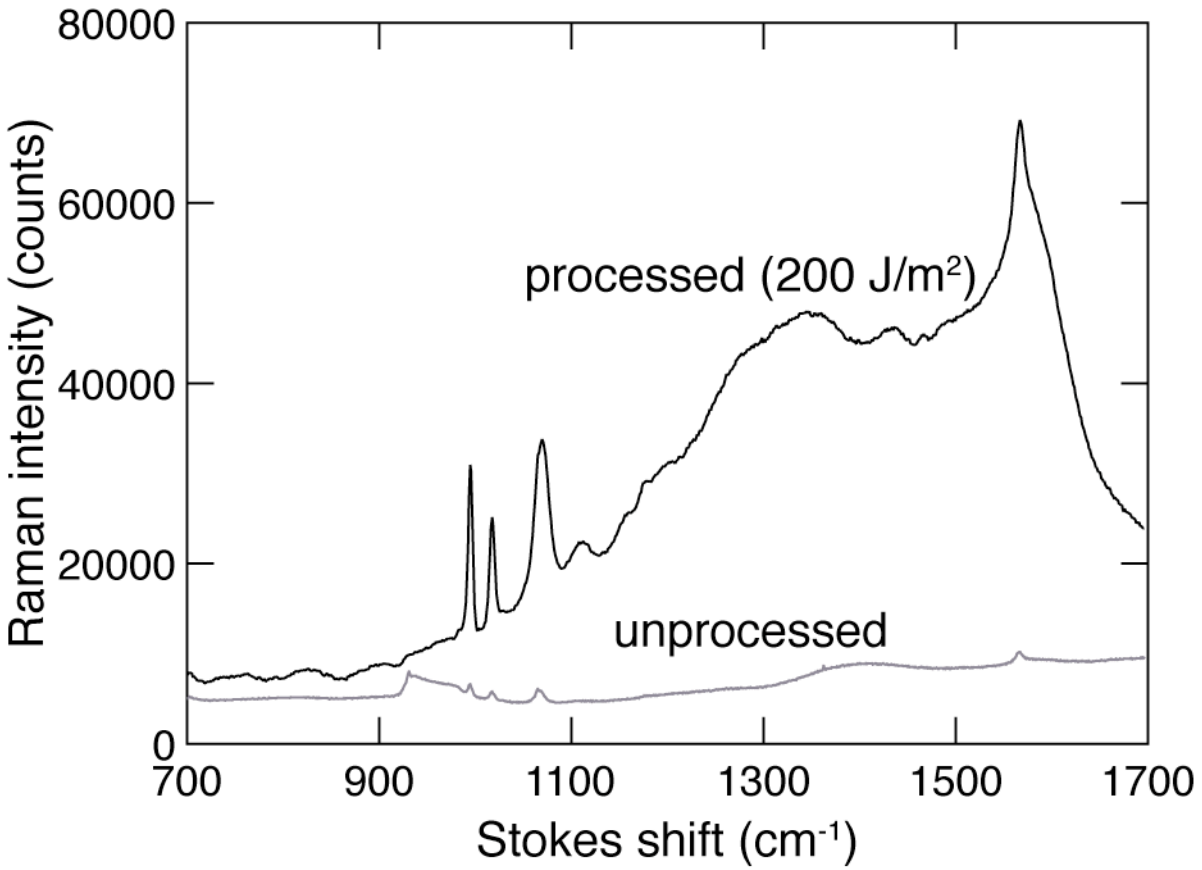


24-hour incubation with 4 femtomoles of benzenethiol
12mW, 785nm excitation, 30s integration, 0.40NA objective

Diebold et al., *J. Am. Chem. Soc.*, **131**, 16356-16357 (2009)

Hot spot isolation



27× times signal improvement (998 cm^{-1} band)

Diebold et al., *J. Am. Chem. Soc.*, **131**, 16356-16357 (2009)

Hot spot isolation

Average enhancement factor:

Submonolayer coverage:

24 hour incubation with 2.4 x 10^9 molecules = 0.001% surface coverage.

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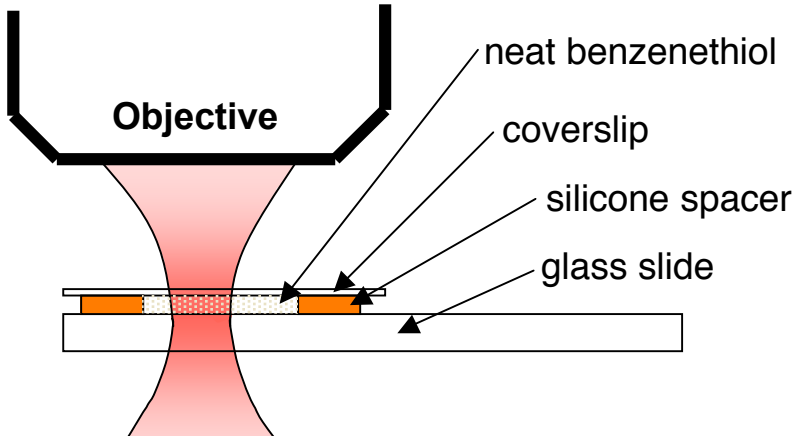
Signal normalized to neat benzenethiol using confocal microscope method.

$$EF = \frac{I_{SERS}}{I_{Neat}} \frac{N_{Neat}}{N_{SERS}}$$



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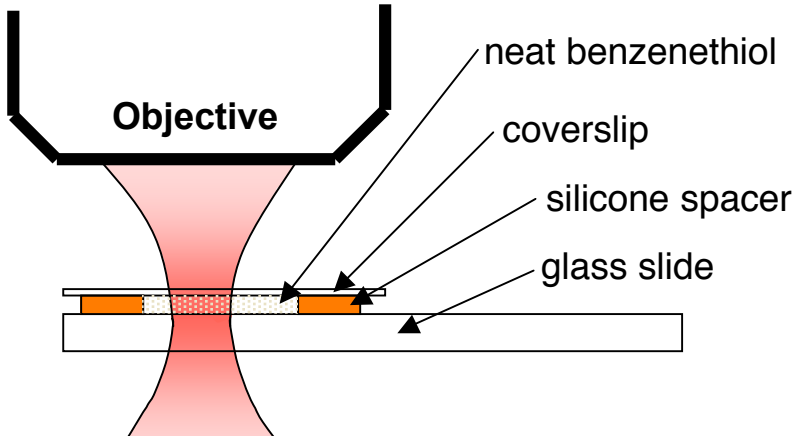


Enhancement factor (998 cm^{-1}) = 3 x 10^9

Outline

Background - laser nanostructured substrates

Motivation: hot spot distribution

Hot spot isolation

Conclusion

Take home message

Hot spot isolation:

1. is generally applicable to noble metal SERS substrates and masks “cold spots,” allowing molecules to bind only to “hot spots.”

Take home message

Hot spot isolation:

1. is generally applicable to noble metal SERS substrates and masks “cold spots,” allowing molecules to bind only to “hot spots.”

2. does not require knowledge of hot spot location or enhancement factor.

Take home message

Hot spot isolation:

1. is generally applicable to noble metal SERS substrates and masks “cold spots,” allowing molecules to bind only to “hot spots.”

2. does not require knowledge of hot spot location or enhancement factor.

3. offers significant SERS signal improvement under sub-monolayer coverage.

Acknowledgements

Mazur group

Center for Nanoscale Systems, Harvard University

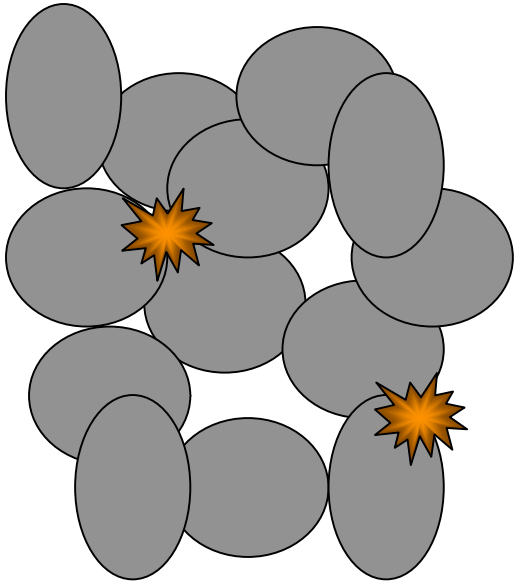
DARPA S&T fundametals program

NDSEG fellowship

Hot spot isolation

Hot spots in random metallic nanoparticle clusters exhibit large spatial dispersion.

785 nm



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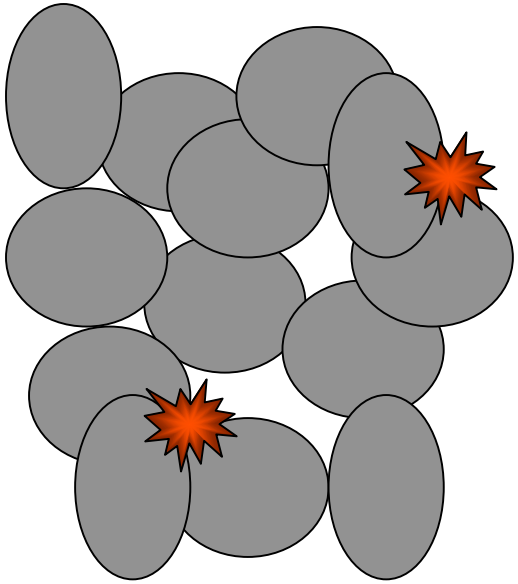
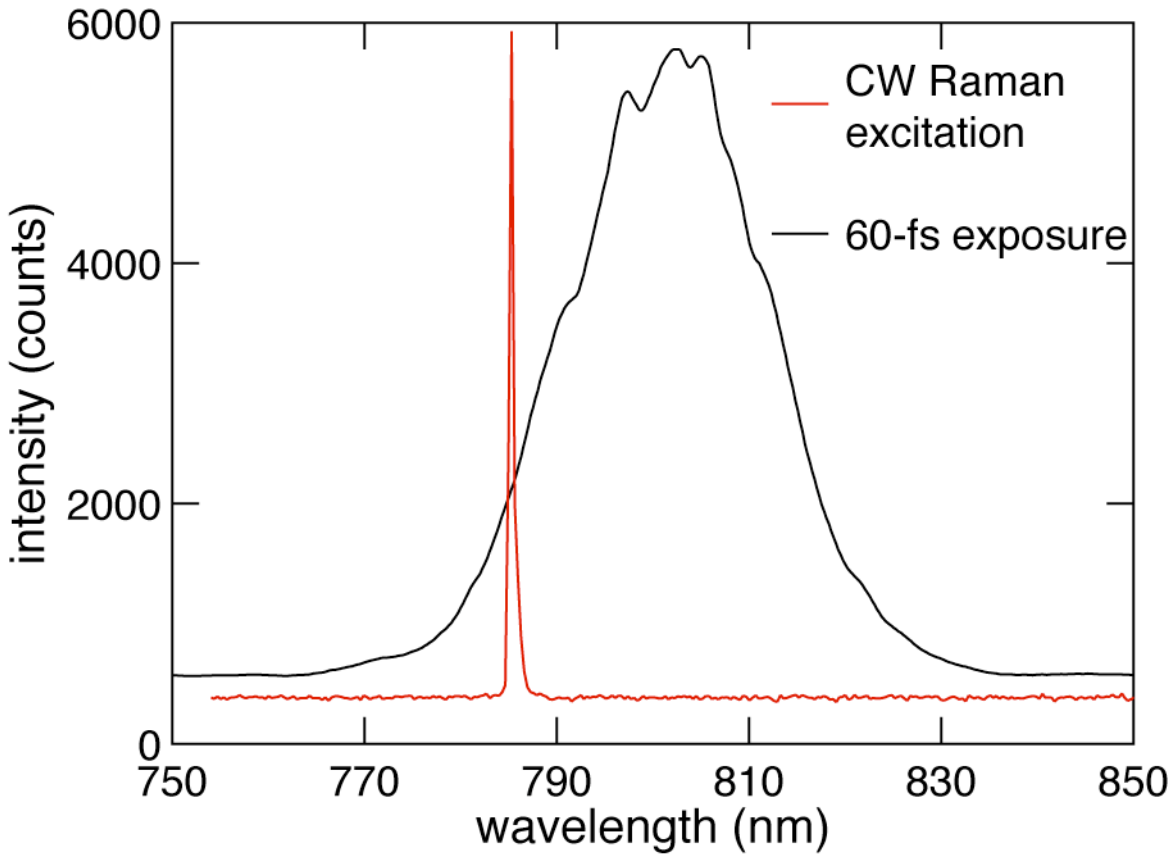


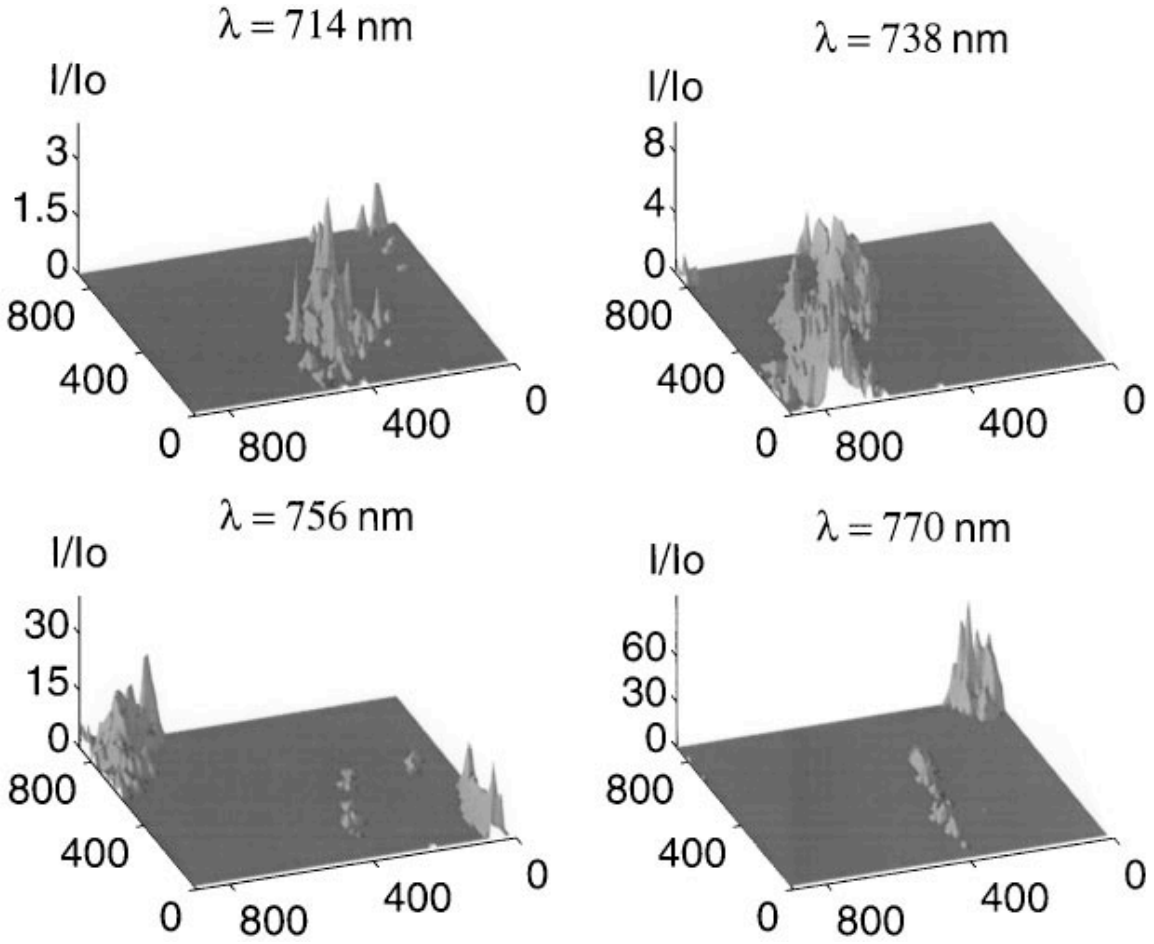
Grésillon et al. *Phys. Rev. Lett.* **82** 4520-4523 (1999)

Hot spot isolation



Hot spot dispersion necessitates overlap of Raman excitation and fs-exposure spectra.

Hot spot isolation



Hot spots in random metallic nanoparticle clusters exhibit large spatial dispersion
(x-y units in nanometers)

Grésillon et al. *Phys. Rev. Lett.* **82** 4520-4523 (1999)