Spectroscopic evidence of the existence of angstrom-scale SERS hot-spots

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2018 International Workshop Meta-Optics and Metamaterials

Shin et al, Nano Lett. (2018), 18, 262-271.
Shin et al., TBP (2018).

Unusual Molecular Vibrational Excitations Induced by Gap-Plasmons

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Shin et al, Nano Lett. (2018), 18, 262-271.
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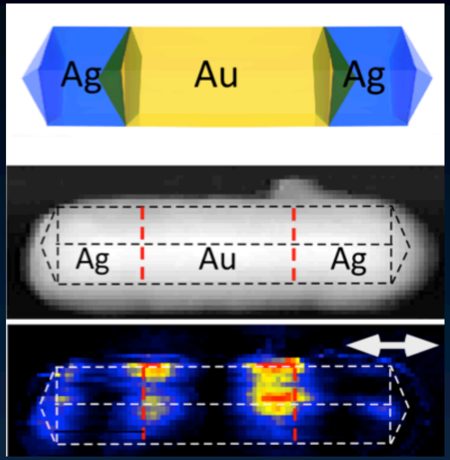
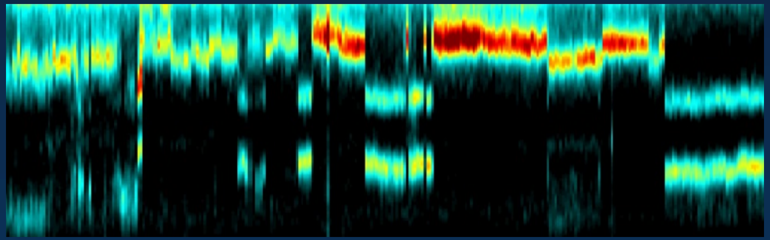
KIM group@SNU

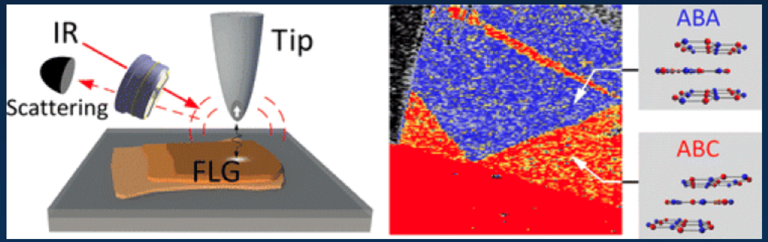
Nanoparticle plasmonics



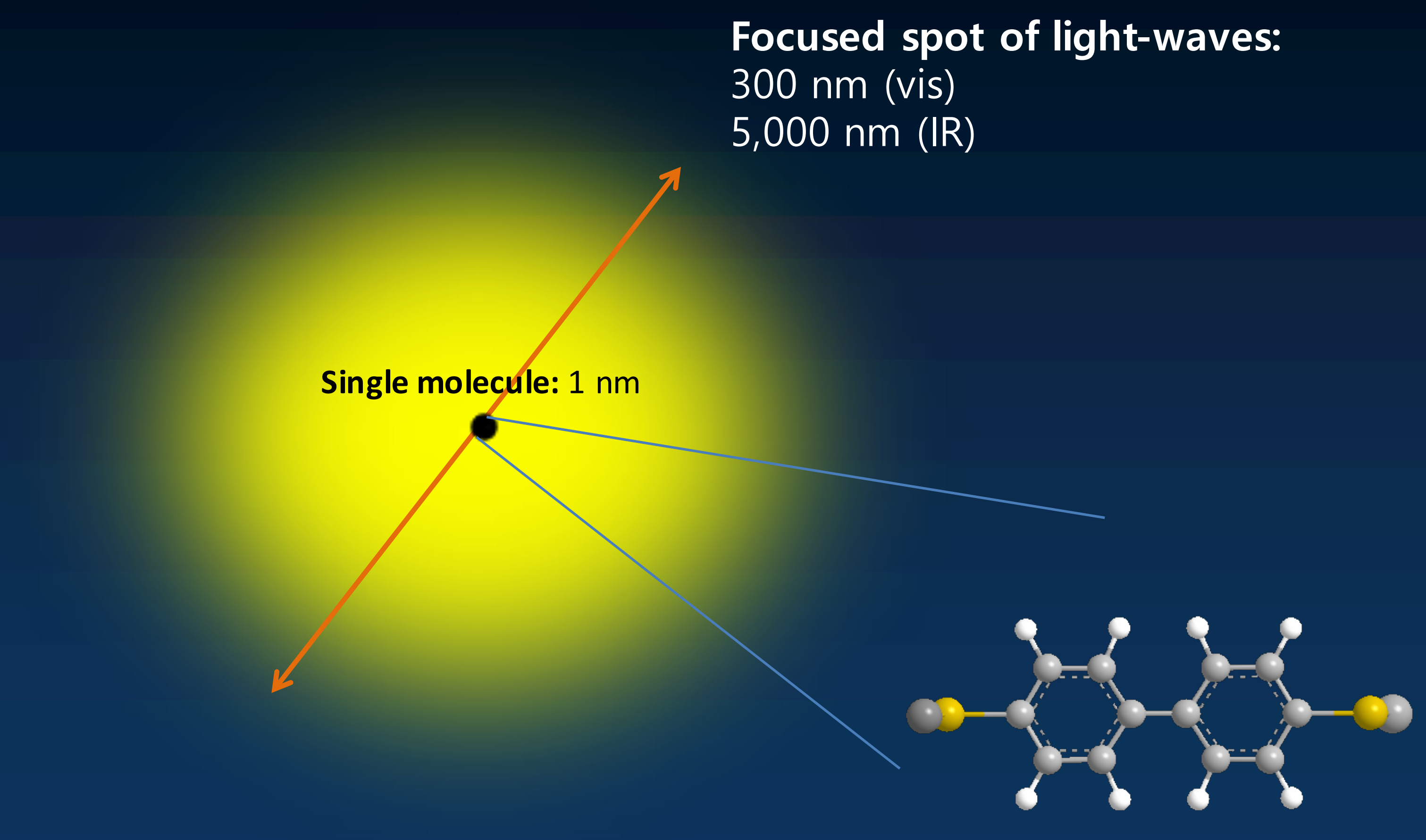
Single-molecule vibrational spectroscopy



Nano (IR, vis) imaging tool development

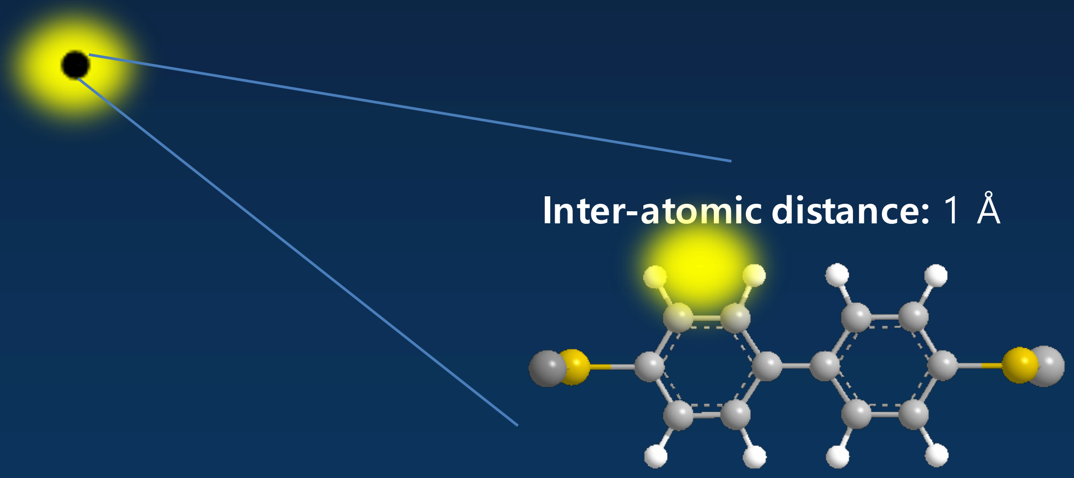


Plasmonics for optical spectroscopy and imaging

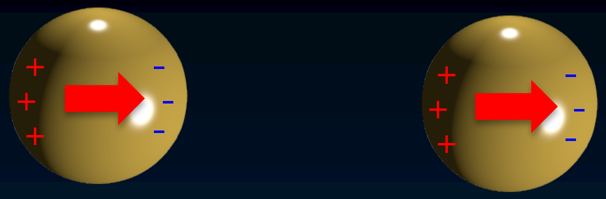


Plasmonics for optical spectroscopy and imaging

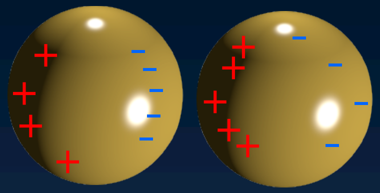
Plasmonics allows us to focus light down to ~10 nm scale



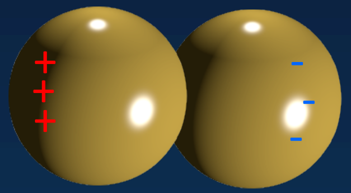
Plasmonic coupling between NPs



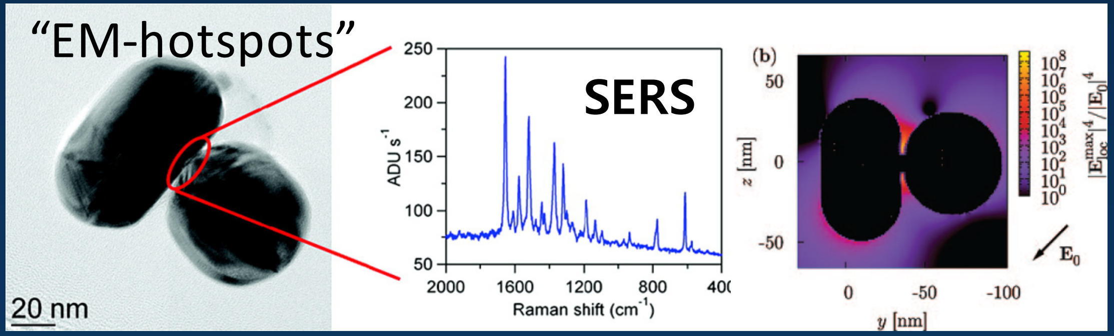
Size << Distance
Dipole-dipole Coupling



Size >> Distance
Capacitive Coupling
(Gap-plasmons)



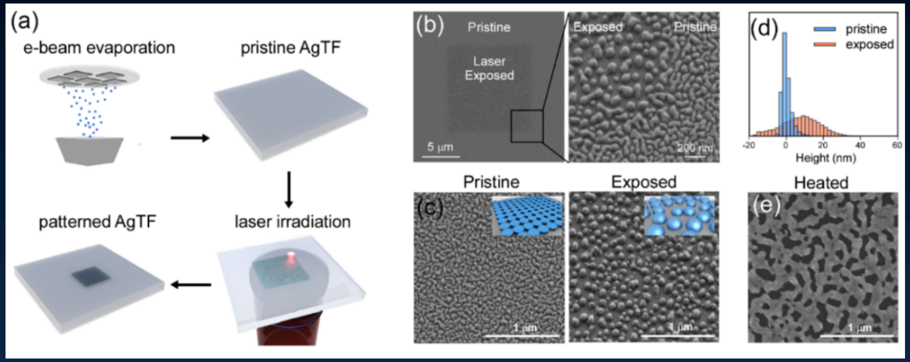
Distance < 0
Conductive Coupling

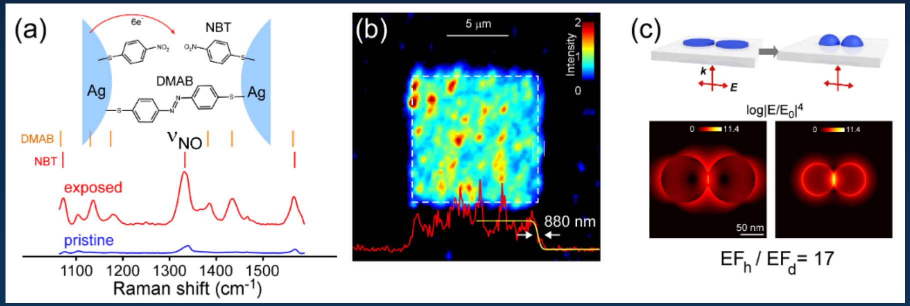


Camden et al., J. Am. Chem. Soc., **2008, 130 (38), 12616.**

Make – Measure – Model of plasmons: more examples

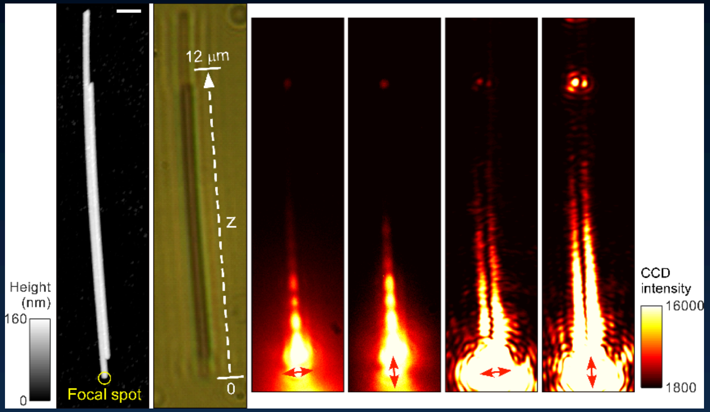
Photo-thermal generation of plasmonic gaps [1]

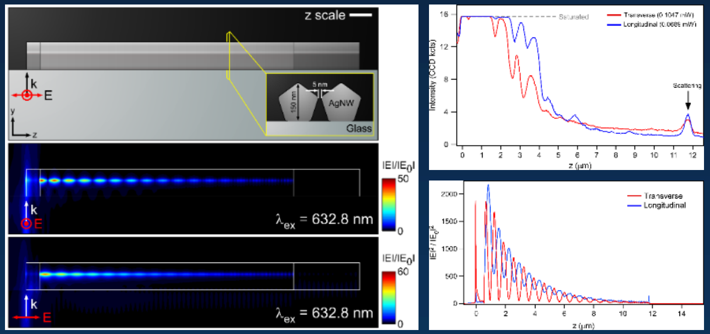




Choi et al. TBP (2018).

Gap-plasmons of NW dimers [2]



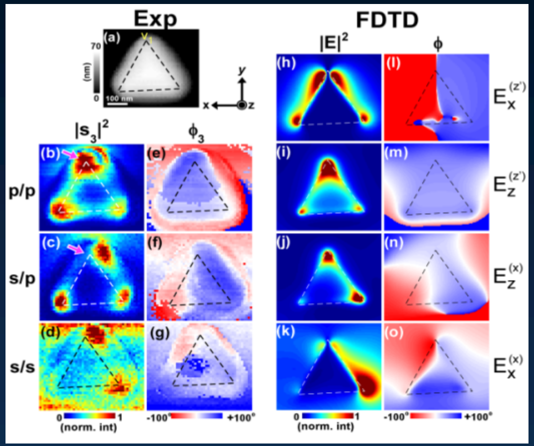


Park et al. TBP (2018).

Make – Measure – Model

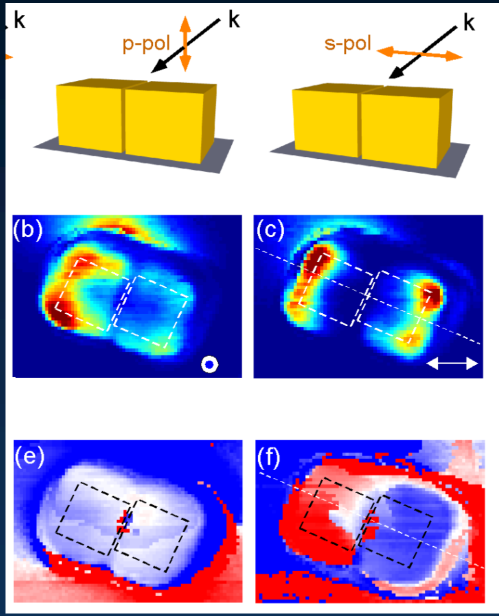
Make: nano-synthesis
Measure: NSOM, EELS, cathodo-luminescence, dark-field scattering
Model: classical electrodynamics with continuum dielectric functions

Monomers



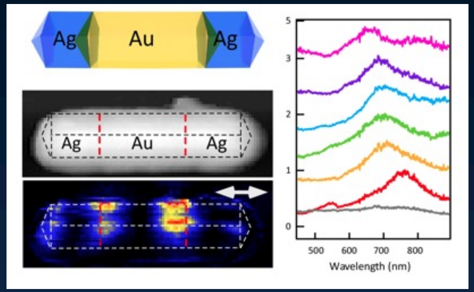
Kim et al., *Opt. Express*, 20, 8689 (2012)

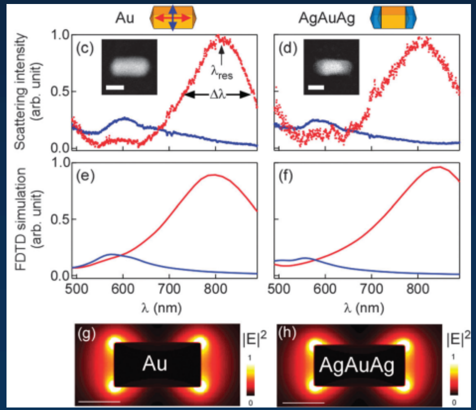
Dimers



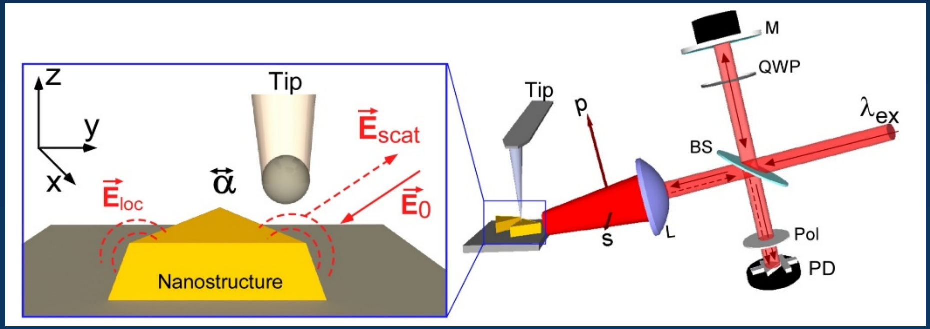
Kim et al., *Nano Lett.* 9, 3619 (2009).

Heterostructures



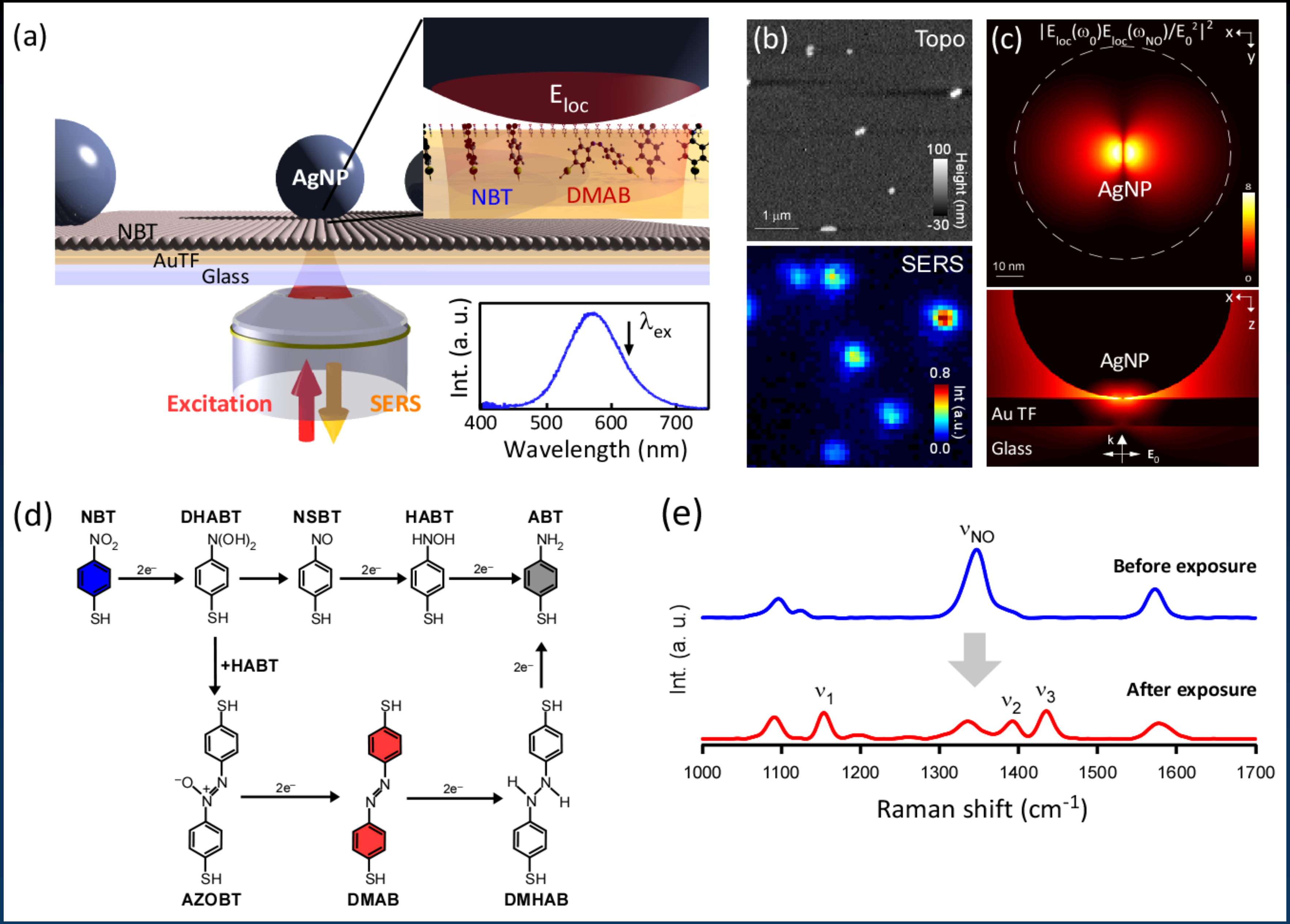


Ahn et al., *Phys. Chem. Chem. Phys.*, 15, 4190 (2013)
Kim et al., *J. Phys. Chem. C.* 120, 21082, (2016)



A success story

Driving and monitoring sm-reaction with a gap-plasmon



Molecular Plasmonics Nanoscopy Lab

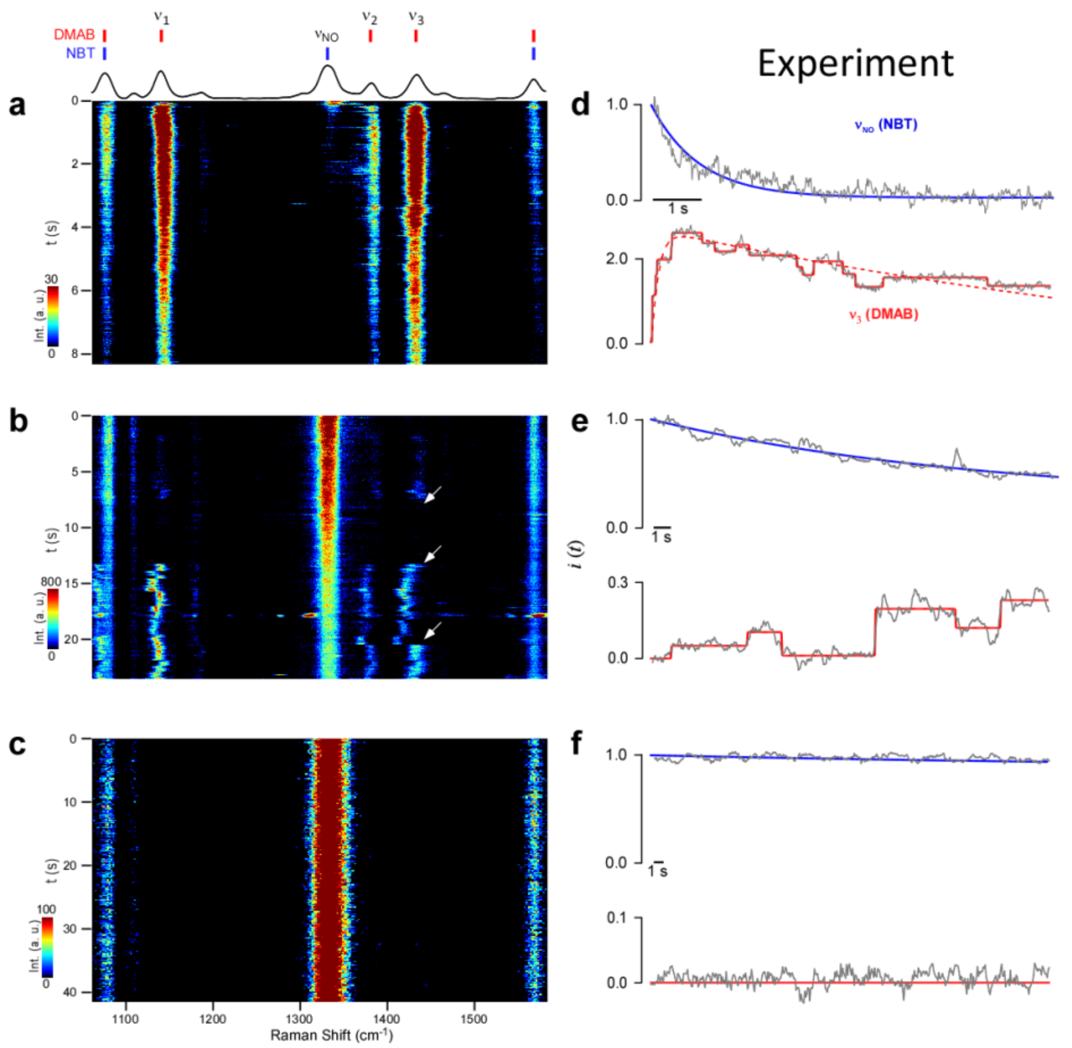
H. Choi et al., J. Phys. Chem. Lett. 2016, 7, 4099-4104.
H. Choi et al, J. Am. Chem. Soc. 2016, 138(13), 4673-4684

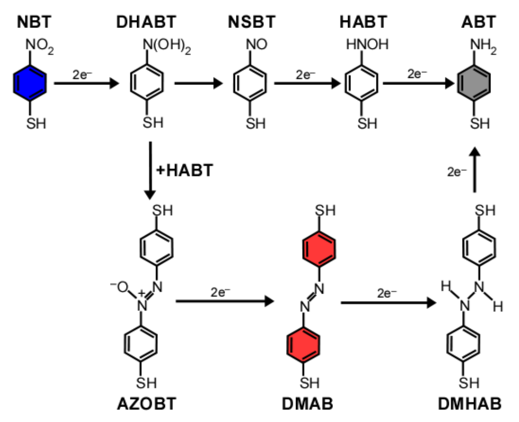
Time-resolved SERS from individual junctions

Hot
(ensemble-like)

Mild
(discrete)

Cold
(no rxn)

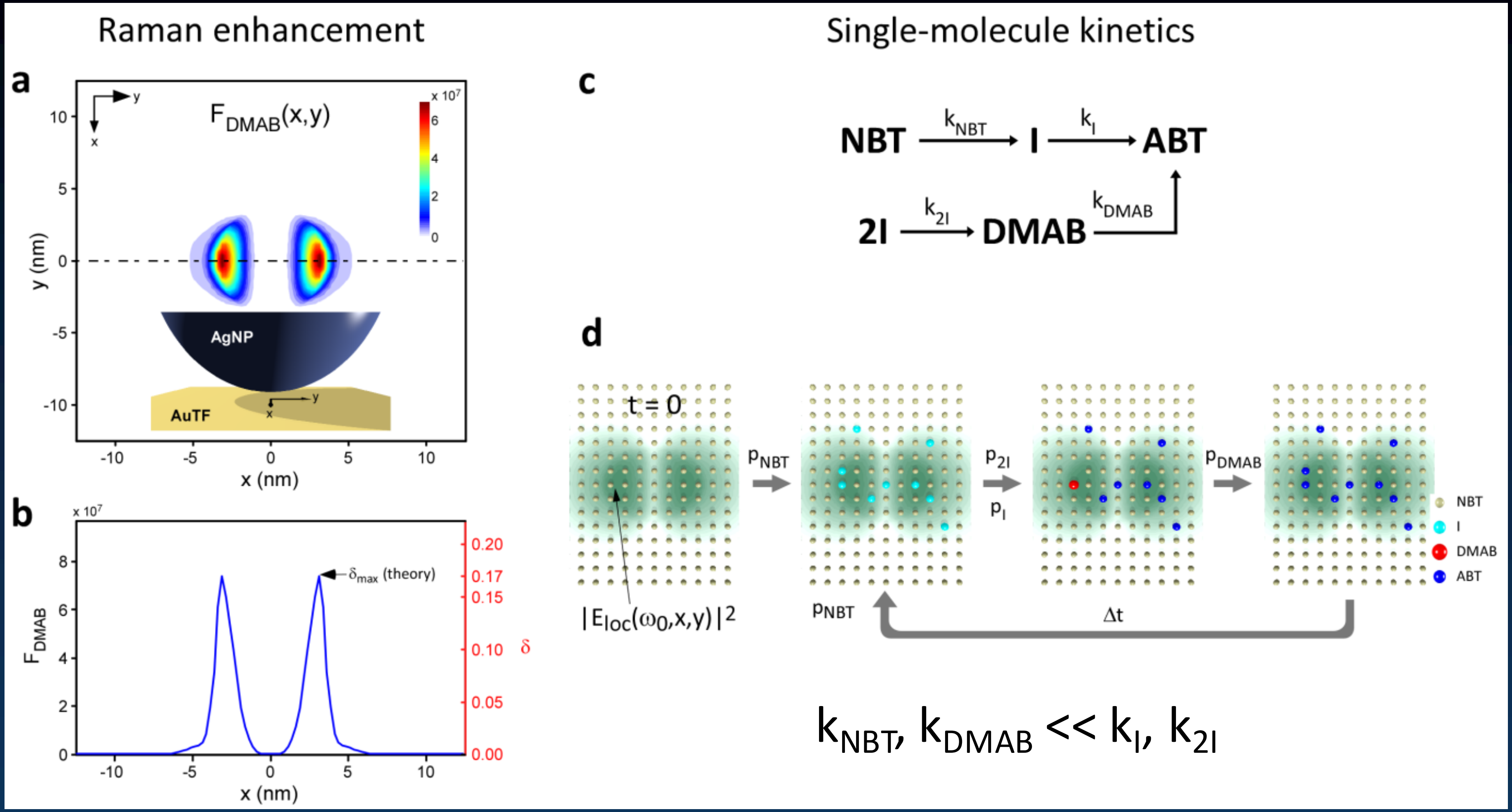




Molecular Plasmonics
Nanoscopy Lab

H. Choi et al, J. Am. Chem. Soc. 2016, 138(13), 4673-4684

Kinetic Monte Carlo simulation of SERS trajectories

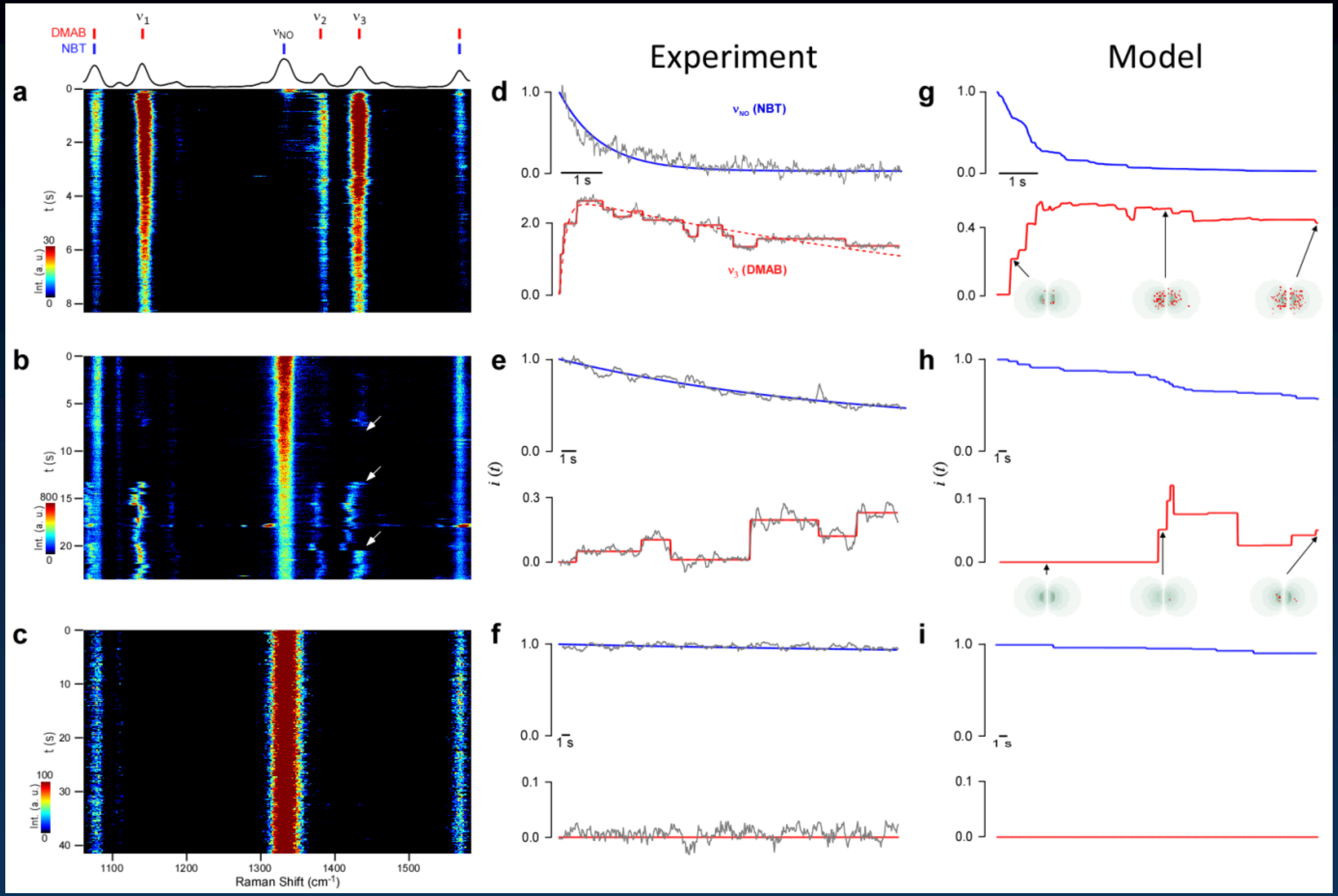


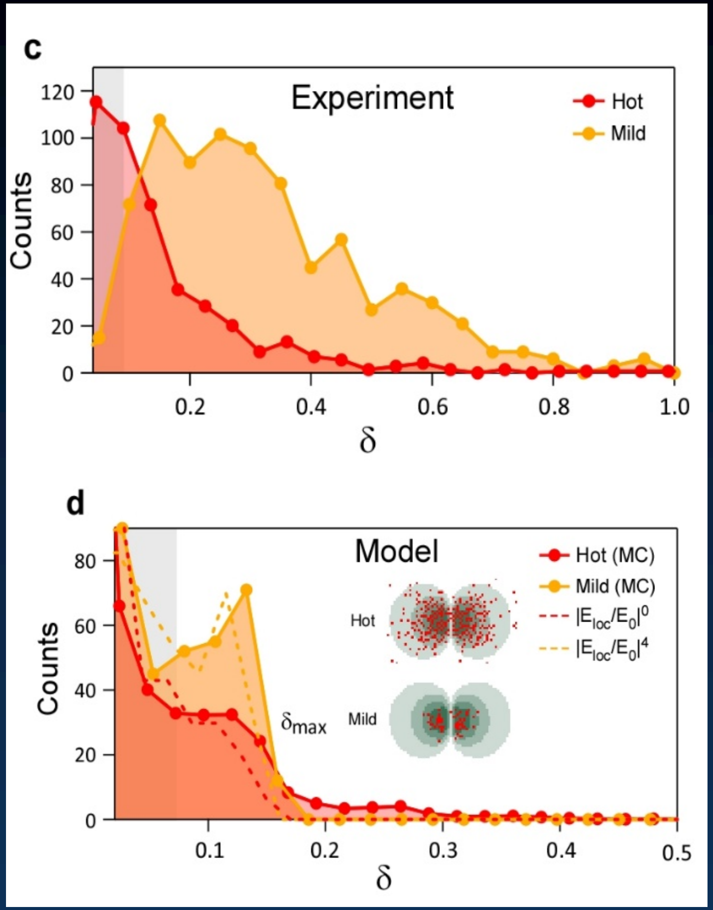
Probability of a single reaction event in a time-interval of Δt

$$p_A = 1 - \exp(-k_A \Delta t)$$

H. Choi et al, J. Am. Chem. Soc. 2016, 138(13), 4673-4684

Time-resolved SERS from a single AgNP-NBT-AuTF

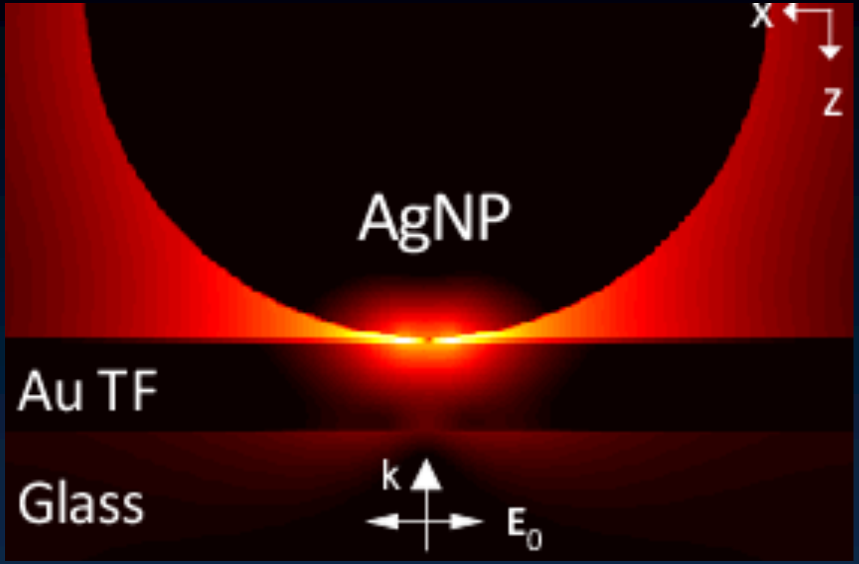


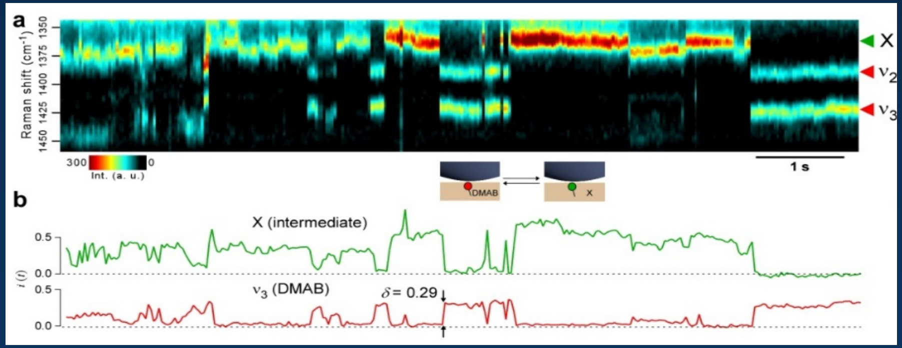


Increasing $|E_{loc}|^2$

H. Choi et al, J. Am. Chem. Soc. 2016, 138(13), 4673-4684

Commonly accepted numbers in "classical plasmonics"





100 nm nanoparticle / 1 nm gap

Lateral width of E_{loc} = 10 nm

$|E_{loc} / E_0|^4 = 10^6 \sim 10^{10}$

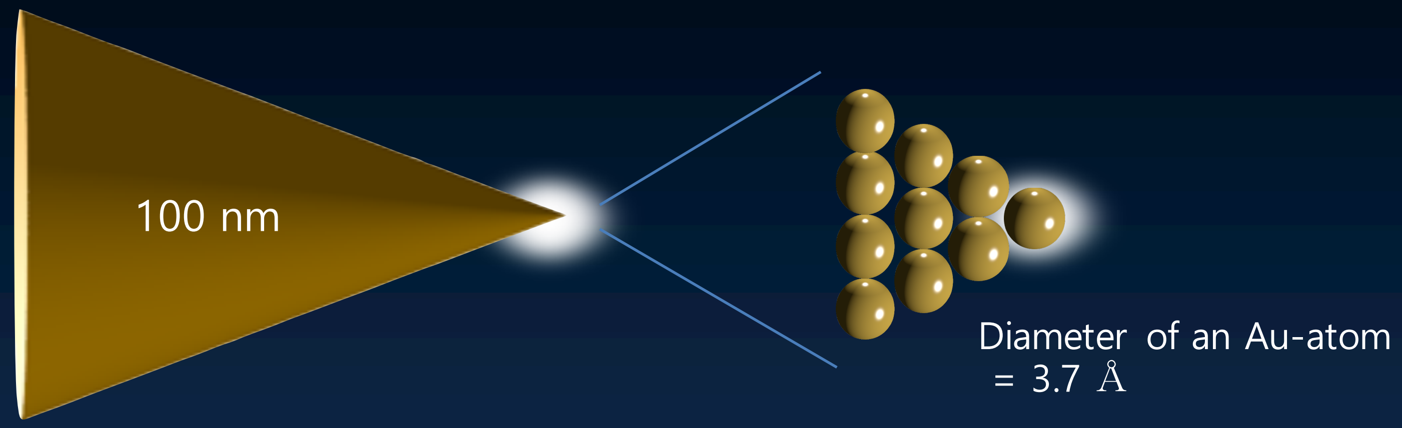
We can make, measure and model the "classical" gap-plasmons

Park et al, Nano Lett. 10, 4040 (2010)
Choi et al, J. Am. Chem. Soc. 2016, 138, 4673-4684

Stochastic vibrational excitation
by angstrom-sized hot-spots (pico-cavities)

Photochemical vibrational excitation
by hot-electrons

Field-confinement below 1 nm ?



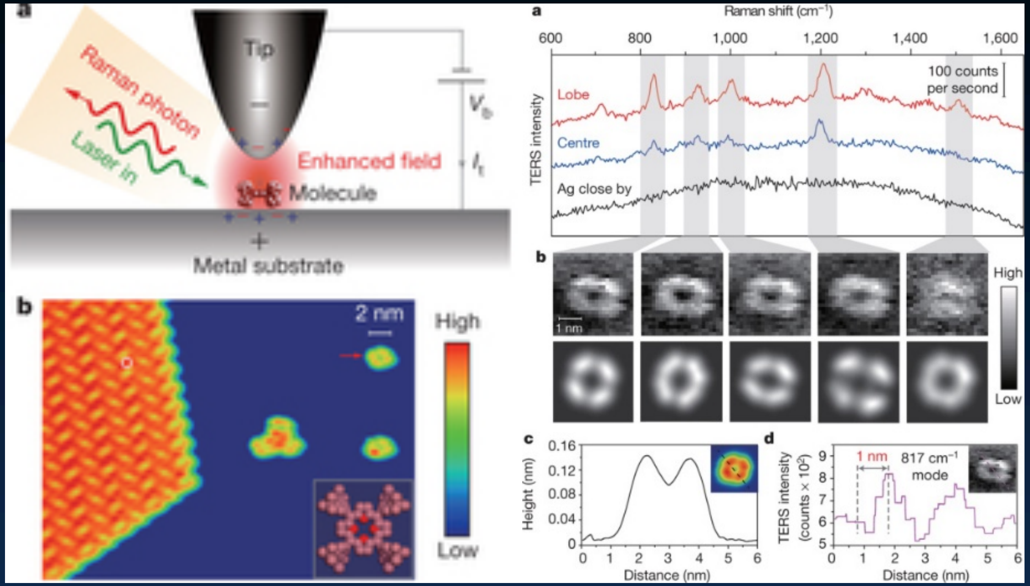
Make
Measure
Model

None of the three is currently possible.

Spectroscopic evidence of angstrom-sized SERS hot-spots

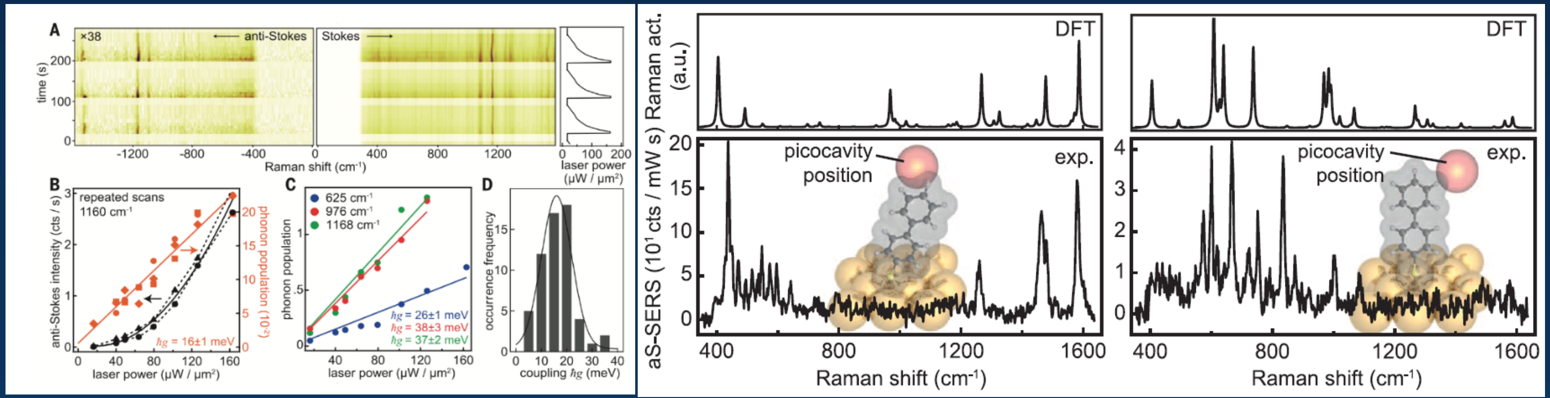
New experimental results

< 1-nm TERS images



Dong; Nature 2013, 498, 82-86
Deckert; Nanoscale 2016, 8, 10229-10239.
Van Duyne; Nano Lett. 2016, 16, 7774- 7778.

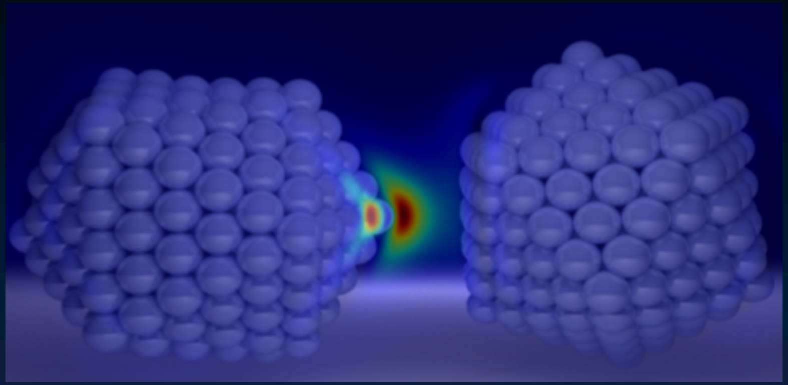
Anti-Stokes anomaly; <1-nm^3 mode-volume



Aizpurua and Baumberg, Science 2016, 354(6313) 726

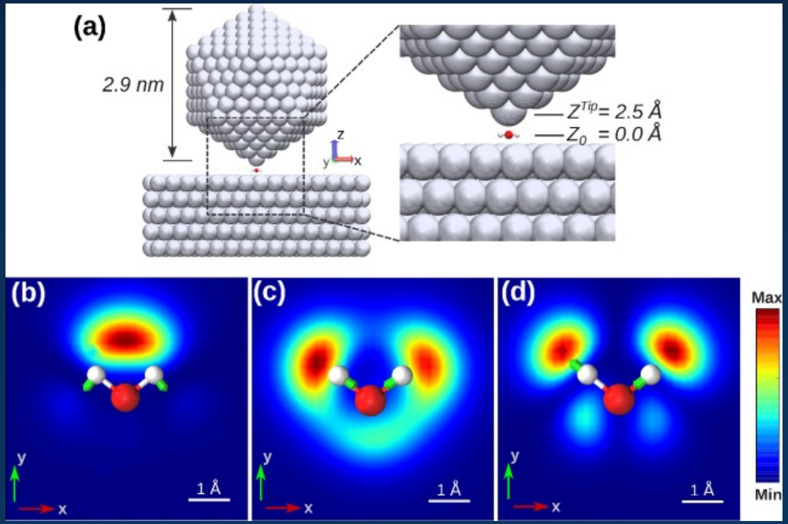
New theoretical calculations

TD-DFT on small (~1 nm) clusters



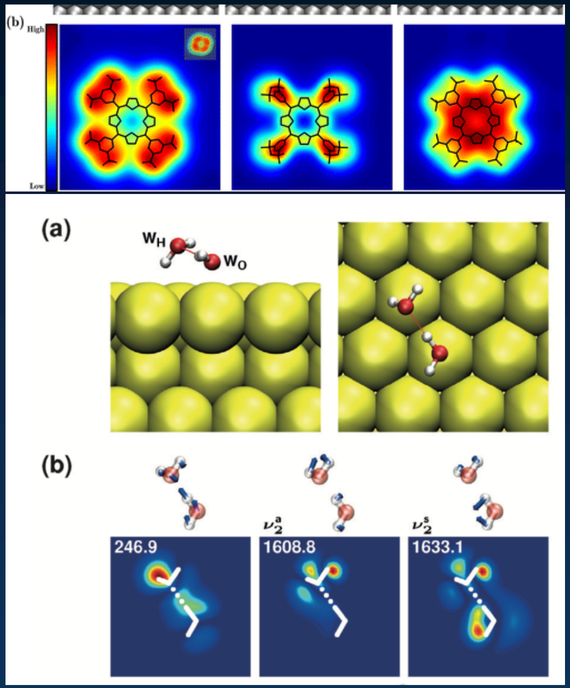
Aizpurua and Sanchez-Portal groups
Barbry et al., Nano Lett. 2015, 15, 3410-3419

Semi-classical EM calculation

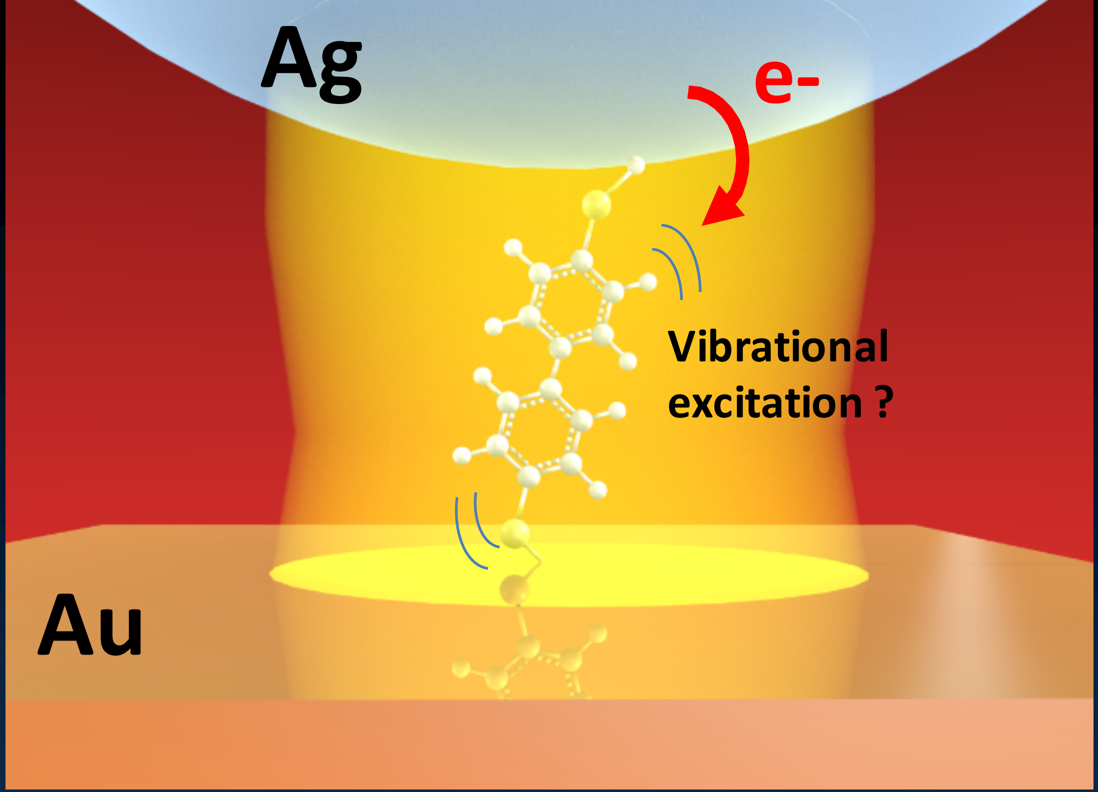


Jensen group:
Liu et al., ACS Nano 11(5), 5094, 2017

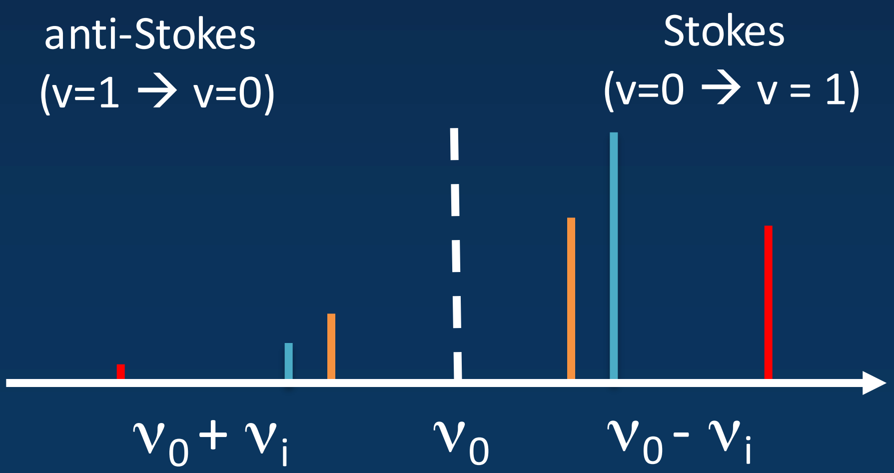
TERS map calculation



Y. Luo group:
J. Am. Chem. Soc., **2015**, *137* (30), pp 9515–9518
Angew. Chem., Int. Ed. 2016, 55, 1041–1045.



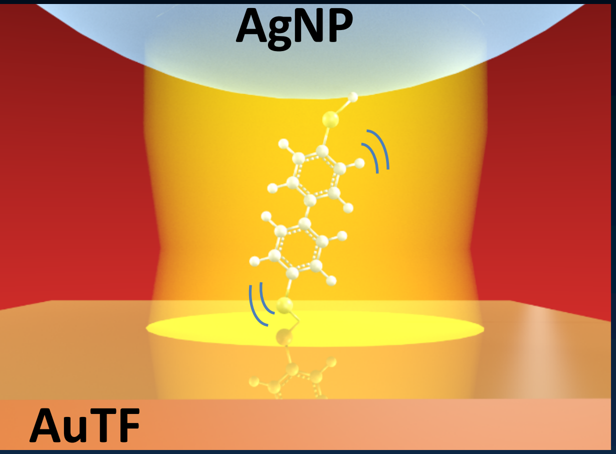
SERS Spectrum



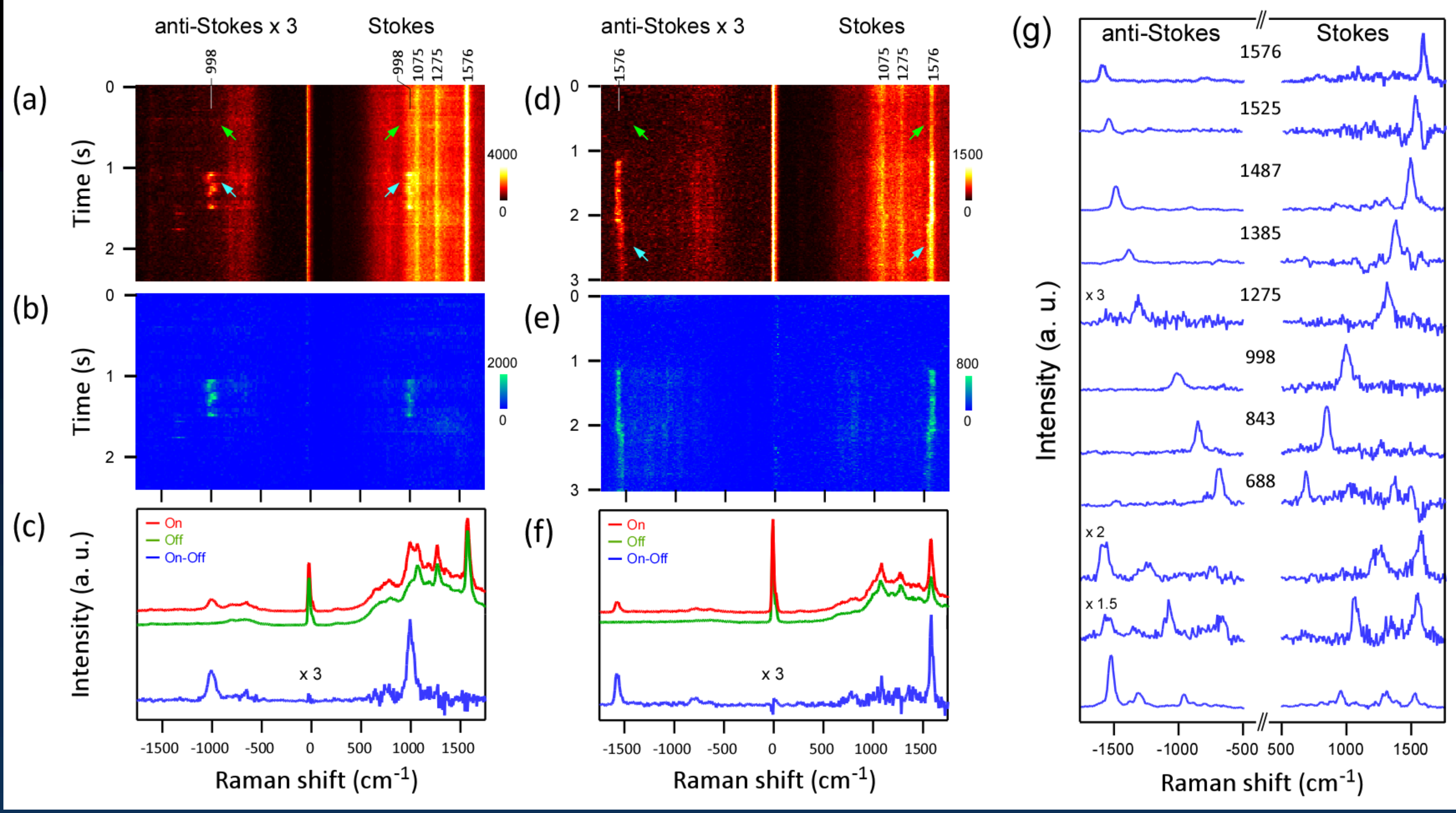
Vibrational population

$$\frac{I_{aS,i}}{I_{S,i}} = A \cdot \frac{(\nu_0 + \nu_i)^4}{(\nu_0 - \nu_i)^4} \cdot \frac{N_{1,i}}{N_{0,i}}$$

Spectrum **Population**



4,4'-biphenyldithiol (BPDT)

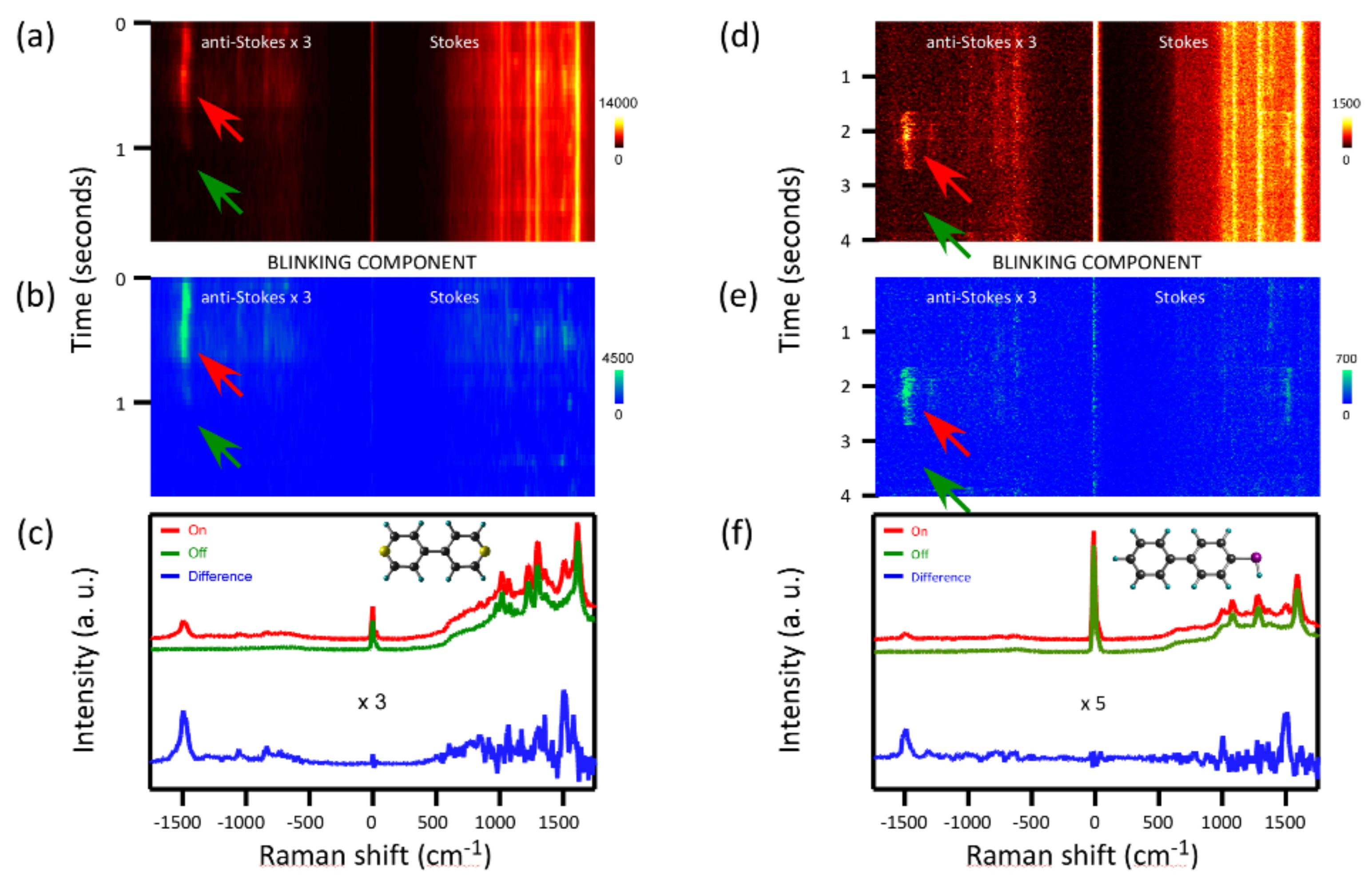


- Blinking of strong anti-Stokes and Stokes peaks
- Raman-forbidden modes
- Single-peak spectra
- Site-specific vibrational selections

Shin et al, Nano Lett. (2018), 18, 262-271.

Shin et al, Nano Lett. (2018), 18, 262-271.

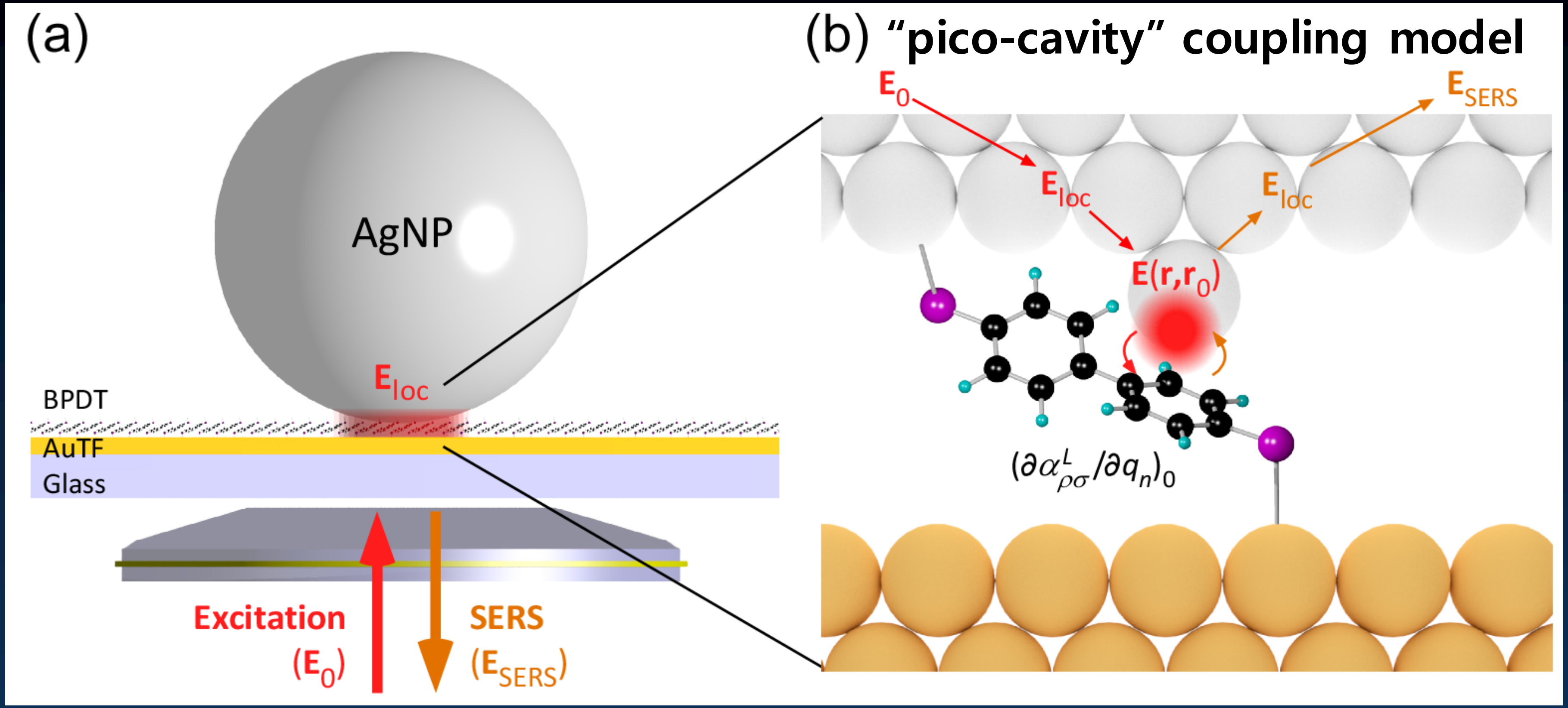
All of the SERS-active molecules show such effect !



Benzenethiol (BT)
Methylbenzenethiol (MBT)
Bipyridine (BPY)
Biphenyl thiol (BPT)
….

Shin et al, Nano Lett. (2018), 18, 262-271.

Actions of sub-nm hotspots in the gap?



Uniform E-field

$$I_k = \left| \sum_{\rho} \sum_{\sigma} E_\rho \cdot \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_k} \right)_0 \cdot E_\sigma \right|^2$$

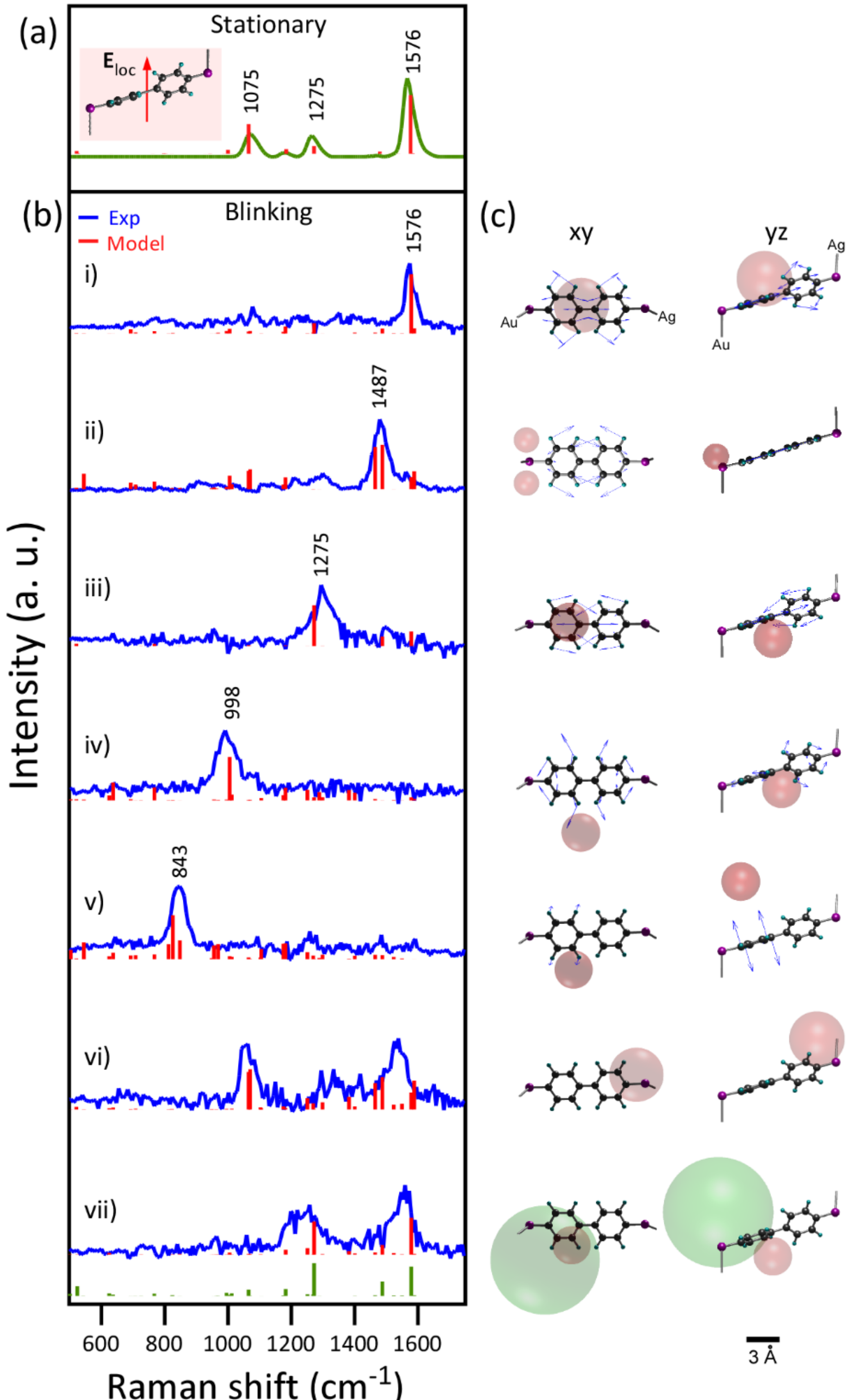
Normal mode coordinate

Heterogeneous field

$$I_k = \left| \sum_{\rho} \sum_{\sigma} \sum_{i=1}^{3N} E_\rho(q_i) \cdot \frac{\varphi_{k,i}}{\sqrt{\mu_k}} \cdot \left(\frac{\partial \alpha_{\rho\sigma}}{\partial q_i} \right)_0 \cdot E_\sigma(q_i) \right|^2$$

Cartesian atomic coordinate

Y. Zhang and J. A. Aizpurua, personal communication 2017



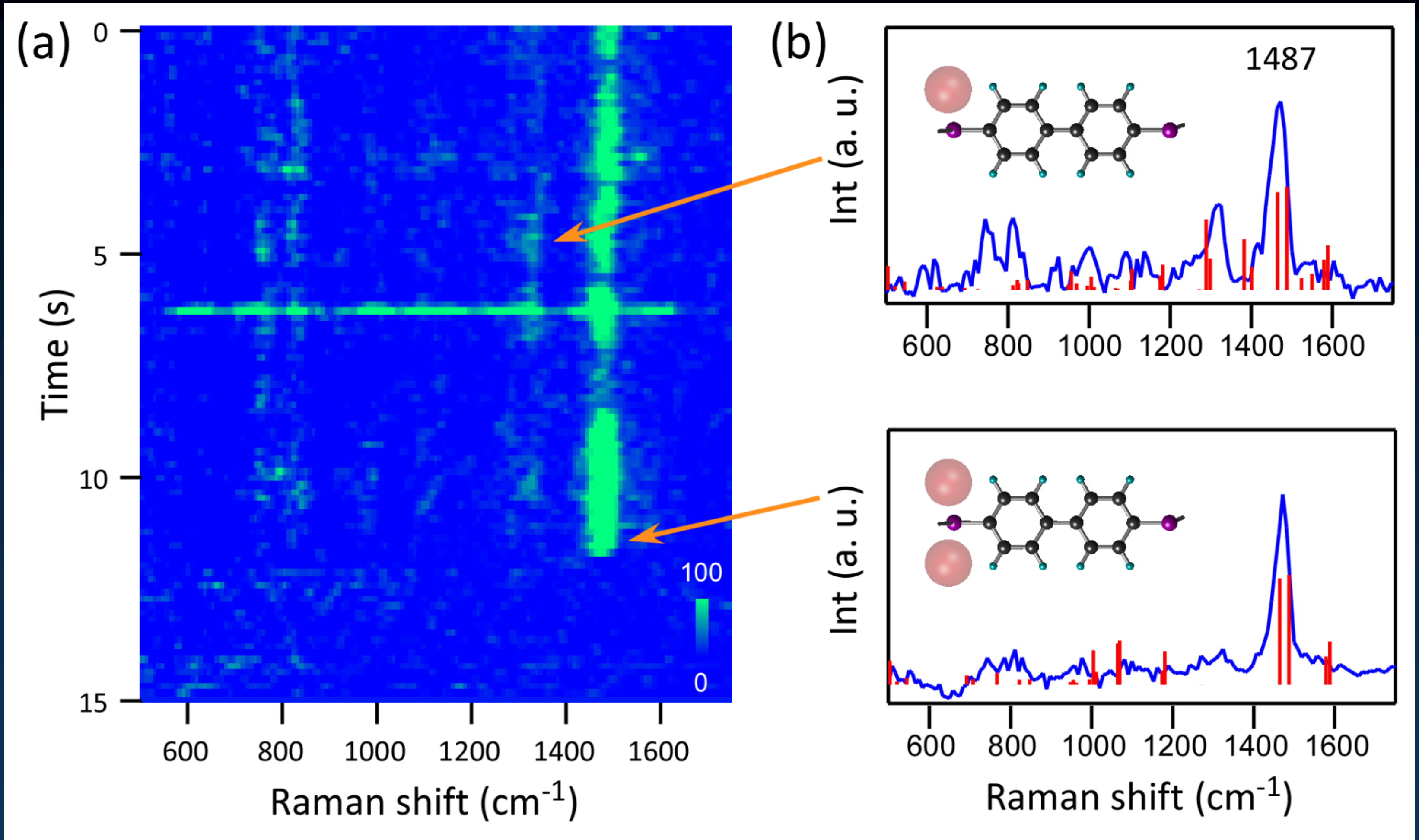
Best fit could be achieved with:

Hotspots with sizes = 3.5 Å
(Upper-limit of 5 Å)

c.f.)
Diameters of Ag and Au = 3.7 Å

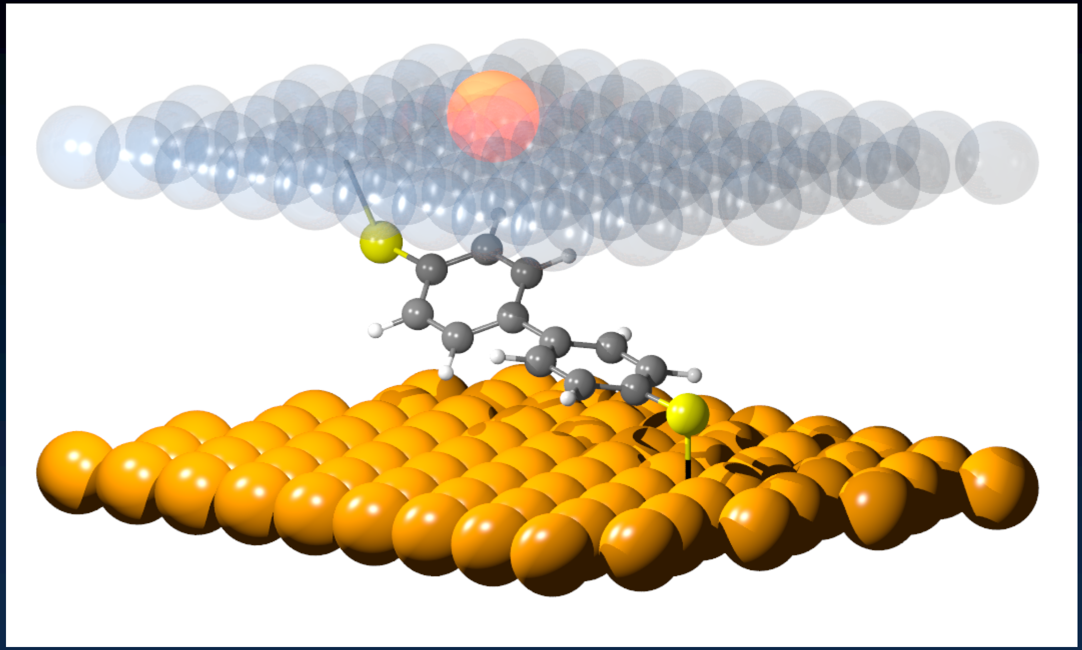
Shin et al, Nano Lett. (2018), 18, 262-271.

Anisotropic or dual hotspots?



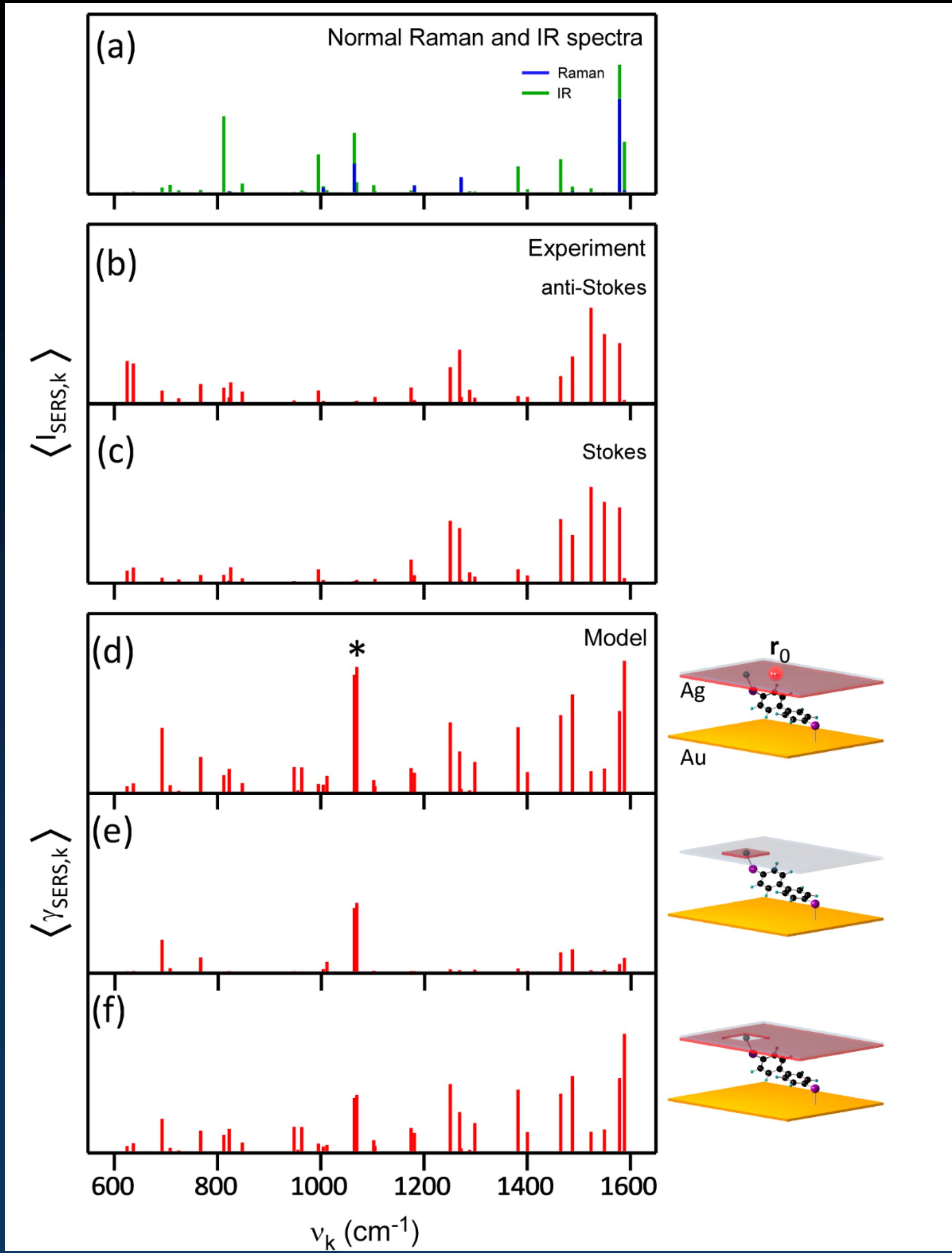
Shin et al, Nano Lett. (2018), 18, 262-271.

Stochastic creation of atomic hotspots



Atomic hotspots should be confined to metallic surfaces…?

Statistically averaged experimental SERS
vs
Spatially averaged model SERS



Ag-surface site is equally active,
except for the Ag-S bonding site.

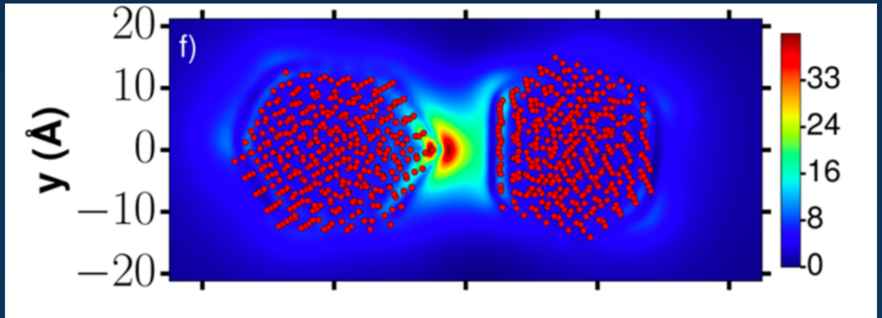
Shin et al, Nano Lett. (2018), 18, 262-271.

What the result reveals:

Electromagnetic field distribution as small as a single-atom

What the result does not reveal:

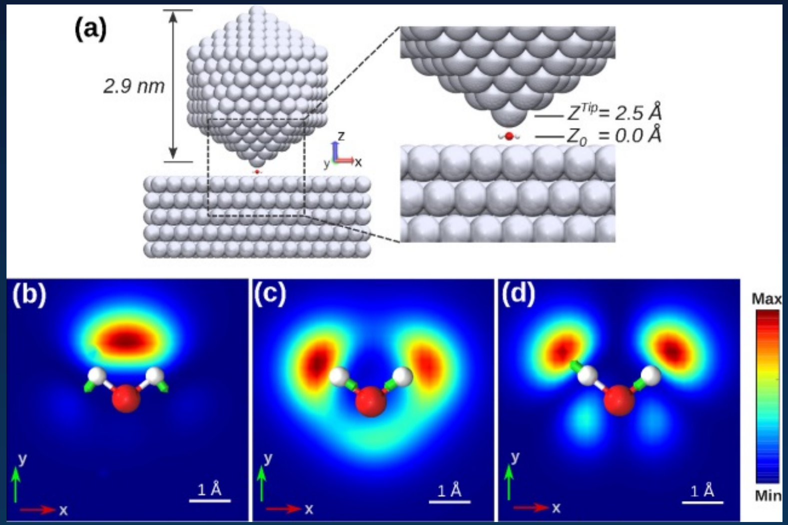
Exact surface structures leading to the atomic-hotspots
Single- adatom defect on surface? (A. Otto)
Possible roles of chemical (vibronic) and quantum effects



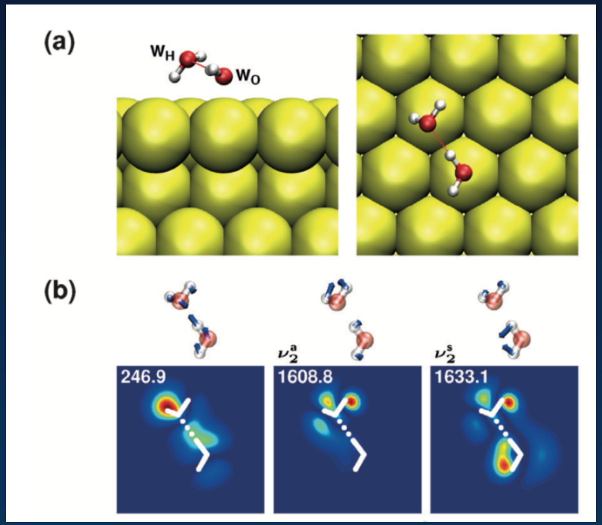
Barbry et al., Nano Lett. 2015, 15, 3410-3419

What does this might do for us ?

Real-space visualization of vibrational modes !



Liu et al., ACS Nano 11(5), 5094, 2017



J. Am. Chem. Soc., **2015**, *137* (30), pp 9515–9518
Angew. Chem., Int. Ed. 2016, 55, 1041–1045.