Problems of Modern Physics

Lecture 8

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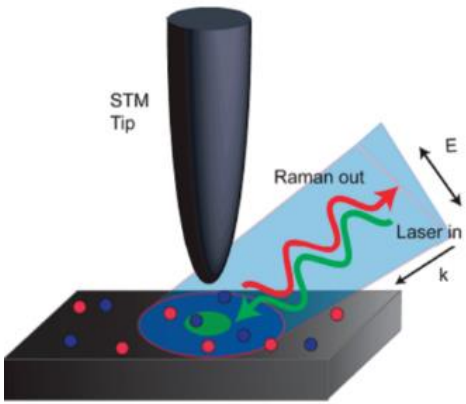
Surface-enhanced spectroscopy

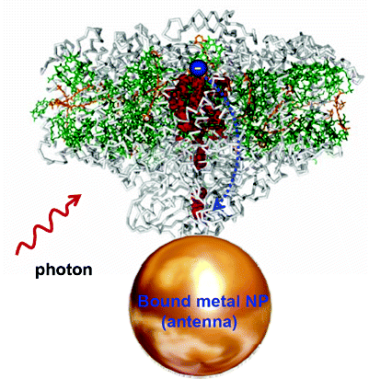
Near field spectroscopy

Single-molecule surface and tip enhanced Raman spectroscopy



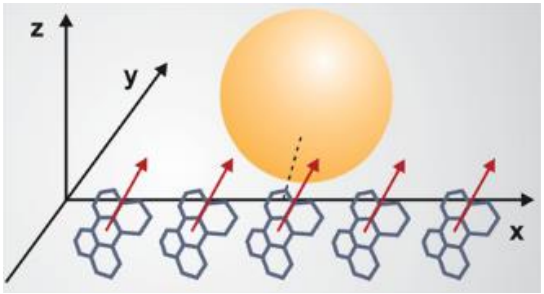
M. T. Sonntag, et. al. J. Phys. Chem. C 116, 478 (2012)

Plasmon enhancement of light absorption and transfer in LHC



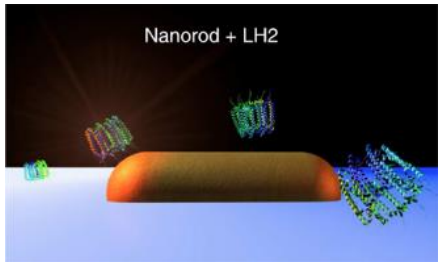
A.O. Govorov and I. Carmeli. Nano Lett. 7, 620 (2007)

Redistribution of absorption and emission spectra of aggregates



Y. Zelinskyy and V. May. Chem. Phys. Lett. 511, 372 (2011)

Plasmon enhanced fluorescence of LHC



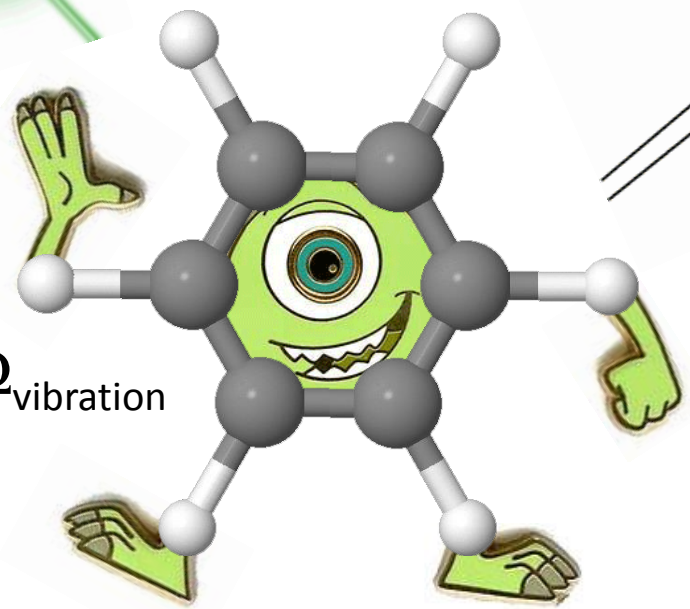
E. Wientjes, et. al. Nat. Commun. 5, 4236 (2014)

Fingerprinting molecules

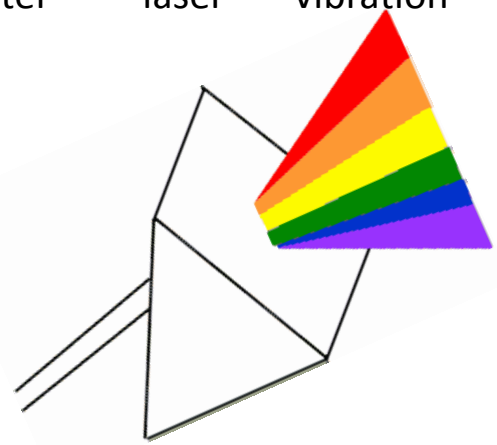
Raman scattering 101

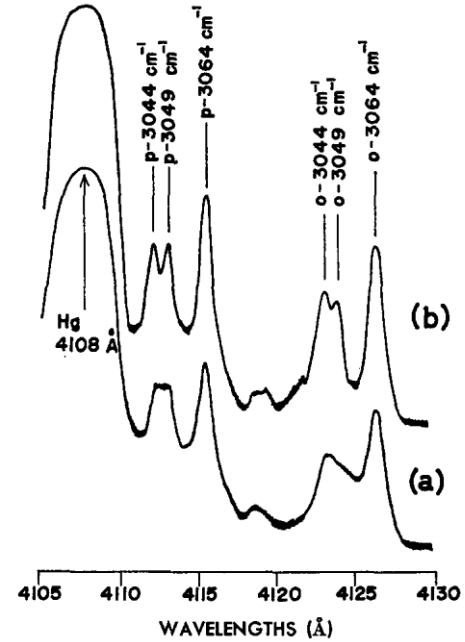
$\omega_{scatter} = \omega_{laser} - \Omega_{vibration}$

ω_{laser}



$\Omega_{vibration}$





M. Ito, *J. Chem. Phys.* 42, 2841-2848 (1964)

- Molecules can be characterized by a specific pattern of lines in Raman spectra

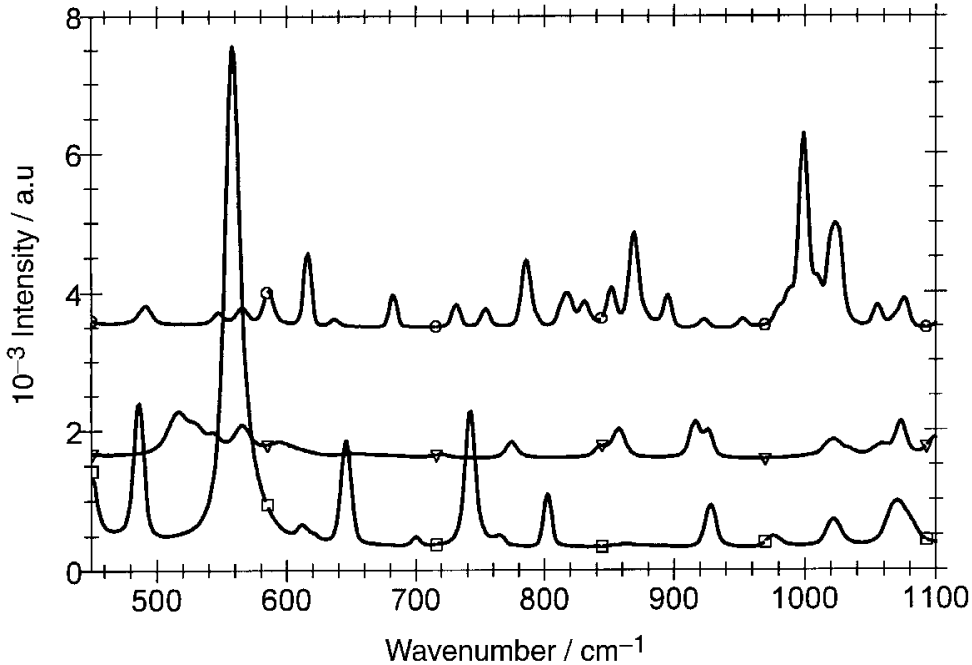
Fingerprinting molecules

Raman spectra

Cocaine

Glucose

Caffeine



A. G. Ryder, G. M. O'Connor and Th. J. Glynn
J. Raman Spectrosc. **31**, 221–227 (2000)

- Can be used to separate good molecules from bad molecules

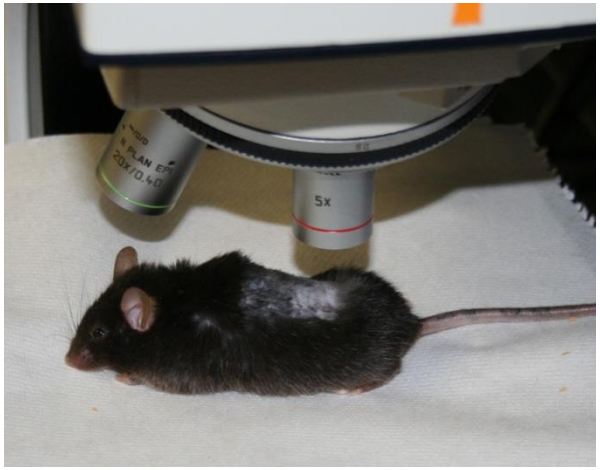
Fingerprinting molecules

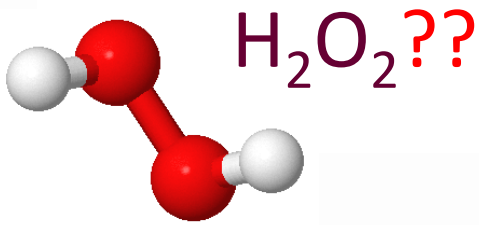
The FASEB Journal • Research Communication

Senile hair graying: H_2O_2-mediated oxidative stress affects human hair color by blunting methionine sulfoxide repair

J. M. Wood,*,†,1 H. Decker,‡ H. Hartmann,‡ B. Chavan,* H.
J. D. Spencer,*,† S. Hasse,*,† M. J. Thornton,* M. Shalbaf,*
and K. U. Schallreuter*,2

*Department of Biomedical Sciences, Clinical and Experimental Derr
Pigmentary Disorders, University of Bradford, Bradford, UK; ‡Institut
University of Mainz, Mainz, Germany; §Department of Dermatology, U
Germany; and ‖University of Manchester, Manchester, UK





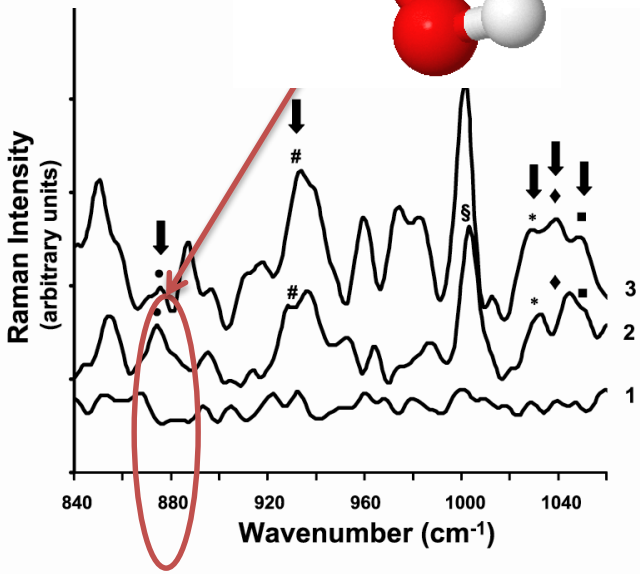


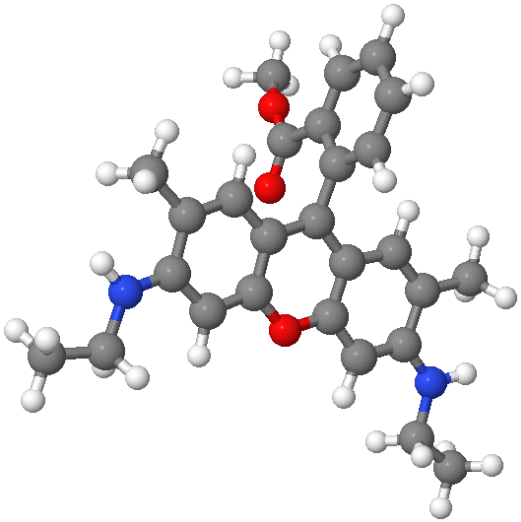
Figure 1. FT-Raman spectroscopy identifies *in vivo* millimolar amounts of H_2O_2 and its oxidation products in gray and white hair shafts. Peaks are assigned accordingly: ●, H_2O_2 at 875 cm^{-1}; §, phenylalanine at 1004 cm^{-1}; *, Met-S=O at 1030 cm^{-1}; #, 5-OH Trp at 930 cm^{-1}; ■ *N*-formylkynurenine/kynurenine at 1050 cm^{-1}; ♦, cysteic acid at 1040 cm^{-1}). Spectrum 1, brown hair; spectrum 2, gray hair; spectrum 3, white hair. Note that no evidence for H_2O_2 or any oxidation products was found in brown hair.

- Can be used to explore unknown structures and phenomena

Raman scattering in molecules

How efficient it is?

Rhodamine 6G

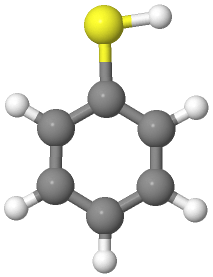


Resonance excitation

Raman cross-section @ 532nm: $\sigma \approx 10^{-22}$ cm^2

To observe a single Raman scattered photon from the molecule with the laser intensity 50 mW/cm^{-2} $\approx 10^{17}$ ph/s/cm^2 one has to wait about 70 days!

Benzenethiol



Lowest electron transition in UV

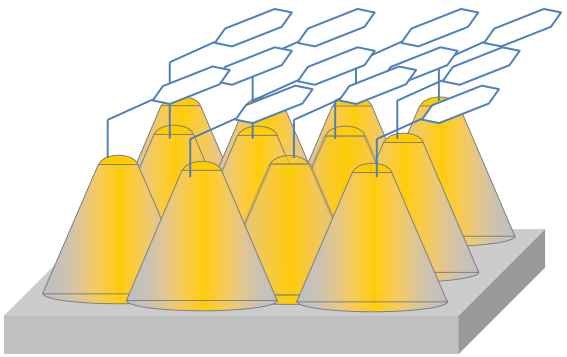
Raman cross-section @ 785 nm: $\sigma \approx 10^{-29}$ cm^2

The waiting time extends to 2 million years

Surface-enhanced Raman scattering

Molecules on nano-structured noble metal surface

Single-molecule Raman spectroscopy is possible



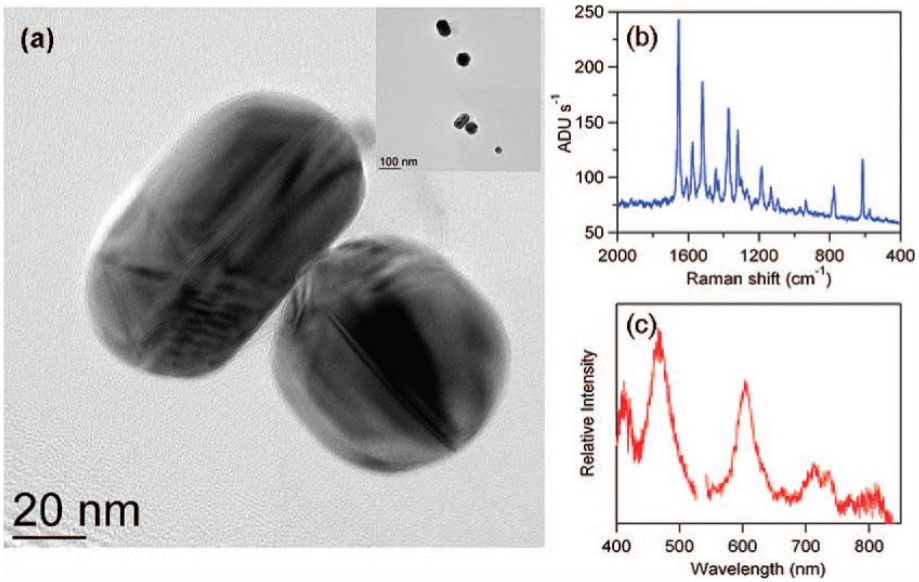


Figure 2. Correlated TEM (a), Raman scattering (b), and dark field scattering spectrum (c) of a single-molecule SERS active structure.

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

SERS Specifics

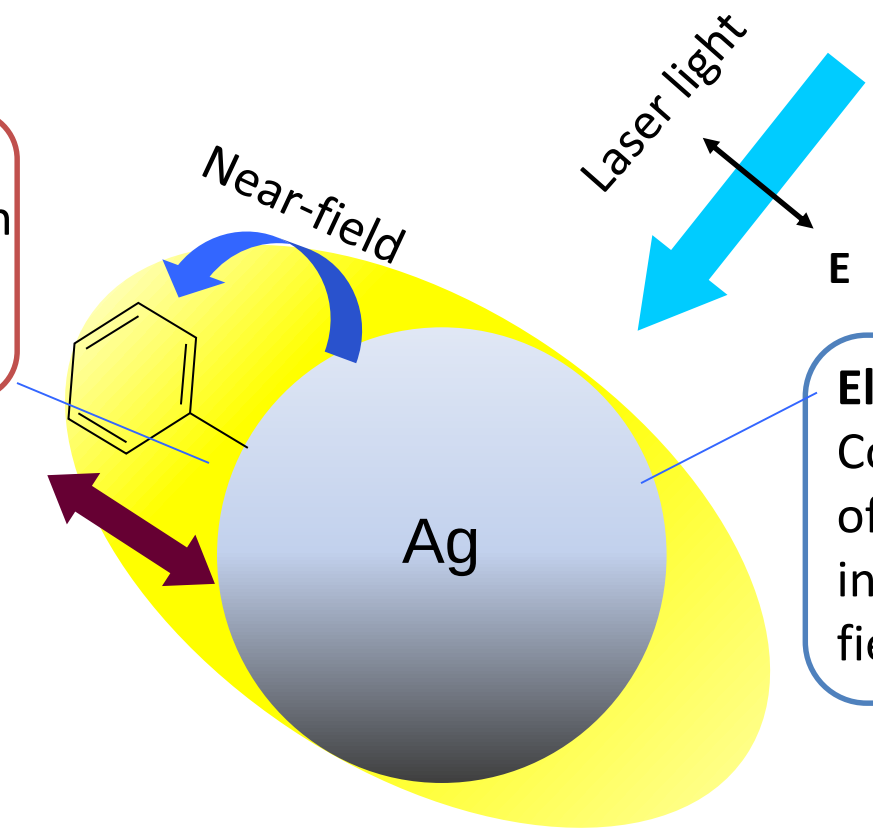
- Lines are enhanced differently
- Some lines appear/disappear
- Continuum background
- Blinking at low concentrations

$$\text{Intensity}_{\text{SERS}}\ /\text{molecule} \approx 10^{7}\text{-}10^{9}\ \text{Intensity}_{\text{Neat}}\ /\text{molecule}$$

Surface-enhanced Raman scattering

How it works?

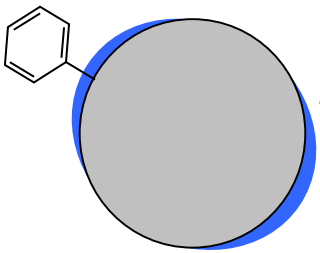
Chemical:
Charge transfer between the molecule and metal modifies the response



Electromagnetic:
Collective oscillations of electrons in metal induce strong near-fields at the molecule

Total enhancement = Electromagnetic enhancement × Chemical enhancement

Quantum model of SERS



$$H_{el} = \sum_i \left\{ \frac{\left(p_i - eA(r_i)\right)^2}{2m_e} - \frac{1}{4\pi\varepsilon_0} \sum_{k\in P} \frac{eq_k}{|r_i - R_k|} - \frac{1}{4\pi\varepsilon_0} \sum_{k\in M} \frac{eq_k}{|r_i - R_k|} \right\} + \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{ij} \frac{e^2}{|r_i - r_j|}$$

$$H_{el} = \underbrace{H_1 + V_{el-ph}}_{\text{single-el. terms}} + \underbrace{H_2' + H_2'' + H_2'''}_{\text{two-el. terms}}$$

$$H_1 = \sum_m E_m a_m^+ a_m + \sum_n \mathrm{E}_n b_n^+ b_n + \sum_{m\neq n} V_{mn}^M a_m^+ a_n + \sum_{m\neq n} V_{mn}^P b_m^+ b_n + \sum_{m,n} \left(T_{mn} a_m^+ b_n + T_{nm}^* b_n^+ a_m \right)$$

single-electron energies

scattering by external nuclear potential

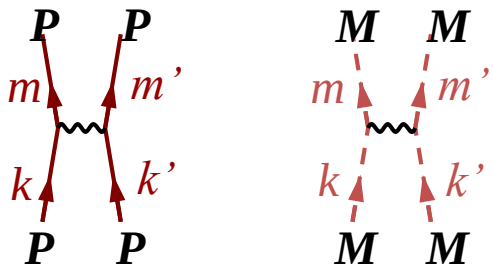
tunneling

Electron-photon interaction: $V_{el-ph} = \sum_{m,m'} \left\{ F_{mm'}^{PP} a_m^+ a_{m'} + F_{mm'}^{MM} b_m^+ b_{m'} + F_{mm'}^{MP} b_m^+ a_{m'} + F_{mm'}^{PM} a_m^+ b_{m'} \right\}$

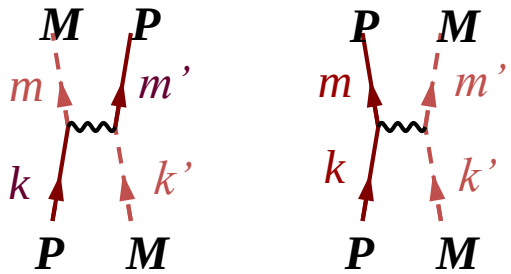
Charge-transfer single-electron excitations

Coulomb interaction

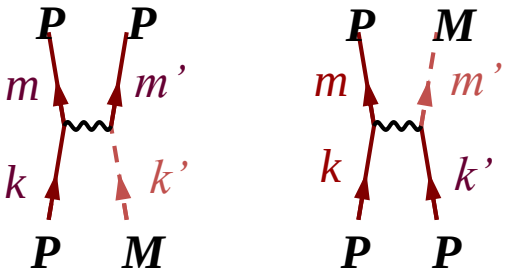
Interaction within a subsystem: $H_2' = \frac{1}{2}\sum_{m,m',k,k'}\left\{V^{PPPP}_{m'mkk'}a^+_{m'}a^+_m a_k a_{k'} + V^{MMMM}_{m'mkk'}b^+_{m'}b^+_m b_k b_{k'}\right\}$



State renormalization, Förster and Dexter terms: $H_2'' = \frac{1}{2}\sum_{m,m',k,k'}\left\{V^{MPMP}_{m'mkk'}b^+_{m'}a^+_m b_k a_{k'} + V^{MPPM}_{m'mkk'}b^+_{m'}a^+_m a_k b_{k'}\right\}$



Coulomb-assisted charge transfer: $H_2''' = \frac{1}{2}\sum_{m,m',k,k'}\left\{V^{PPPM}_{m'mkk'}a^+_{m'}a^+_m a_k b_{k'} + V^{MPPP}_{m'mkk'}b^+_{m'}a^+_m a_k a_{k'} + \ldots\right\}$



Collective modes

Electrons in the metal: $H^P = \sum_i E_i a_i^+ a_i + \frac{1}{2} \sum_{m,m',k,k'} V_{m'mkk'}^{PPPP} a_{m'}^+ a_m^+ a_k a_{k'}$

FT ⇓

$$H^P = \sum_i E_i a_i^+ a_i + \frac{1}{2} \sum_{\mathbf{k}\neq 0} v_{\mathbf{k}} v_{-\mathbf{k}} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \frac{1}{2} \sum_{\mathbf{k}\neq 0,n} v_{\mathbf{k}} v_{-\mathbf{k}} a_n^+ a_n$$

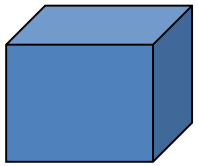
FT electron density $\rho_{\mathbf{k}} = \sum_{m,n} \langle \varphi_m | e^{i\mathbf{kr}} | \varphi_n \rangle a_m^+ a_n$

Canonical coordinates ⇓

$P_{\mathbf{k}} \quad Q_{\mathbf{k}}$

3D: bulk plasmons

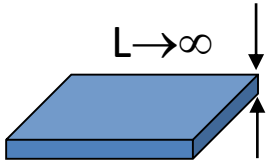
L→∞



$$v_{\mathbf{k}} = \sqrt{\frac{e^2}{\varepsilon_0 \tau |\mathbf{k}|^2}}$$

2D: surface plasmons

L→∞



D

$$v_{\mathbf{k}} \approx \sqrt{\frac{e^2}{\varepsilon_0 \tau |\mathbf{k}|^2} \left(1 - e^{-|\mathbf{k}_\parallel| D - i k_z D}\right)}$$

$$H^P = \sum_i E_i a_i^+ a_i + \frac{1}{2} \sum_{\mathbf{k}<\mathbf{k}_c} \left\{ \omega_P^2 Q_{\mathbf{k}} Q_{\mathbf{k}}^* + P_{\mathbf{k}} P_{\mathbf{k}}^* \right\} - \frac{1}{2} \sum_{\mathbf{k}\neq 0,n} v_{\mathbf{k}} v_{-\mathbf{k}} a_n^+ a_n + \frac{1}{2} \sum_{\mathbf{k}>\mathbf{k}_c} v_{\mathbf{k}} v_{-\mathbf{k}} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + V_{pl-el}$$

plasmons — self-interaction — screened Coulomb term — plasmon-electron scattering

Subsidiary condition: $(P_{\mathbf{k}} - i v_{\mathbf{k}} \rho_{\mathbf{k}}) | \Psi_{\mathrm{pl}} \rangle = 0$

D. Bohm & D. Pines, Phys. Rev. **92**, 609 (1953)

Molecule-environment coupling

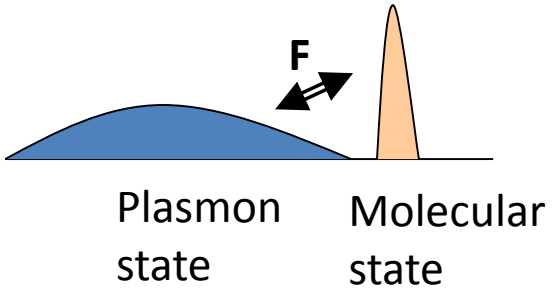
The Förster term: $H_{\mathrm{F}} = \frac{1}{2} \sum_{m,m',k,k'} V^{MPPM}_{m'mkk'} b^{+}_{m'} a^{+}_{m} a_{k} b_{k'}$

$$\Downarrow$$

$$H_{\mathrm{F}} \approx \underbrace{\sum_{\mathbf{k}<\mathbf{k}_c,i} \alpha_i(\mathbf{k}) P_{\mathbf{k}} \cdot \hat{d}_i + \sum_{\mathbf{k}<\mathbf{k}_c,i,j} \beta_{ij}(\mathbf{k}) P_{\mathbf{k}} \cdot \hat{q}_{ij}} + H_{\mathrm{F}}^{\mathrm{SE}}$$

Molecular dipole and quadrupole coupled to the plasmonic modes

Molecular transitions Coupled to single-electron Excitations in the metal

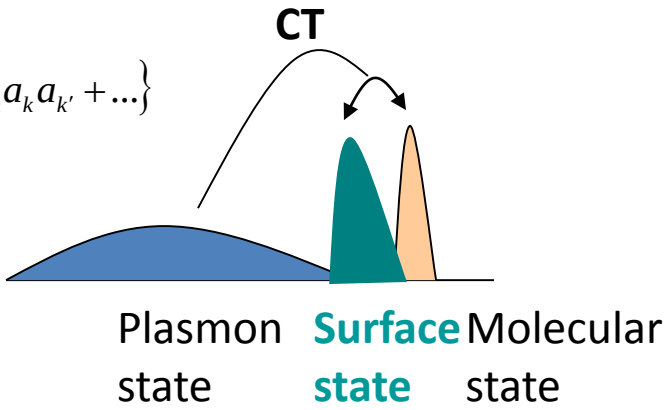


The charge transfer term: $H_{\mathrm{CT}} = \frac{1}{2} \sum_{m,m',k,k'} \left\{ V^{PPPM}_{m'mkk'} a^{+}_{m'} a^{+}_{m} a_{k} b_{k'} + V^{MPPP}_{m'mkk'} b^{+}_{m'} a^{+}_{m} a_{k} a_{k'} + \ldots \right\}$

$$\Downarrow$$

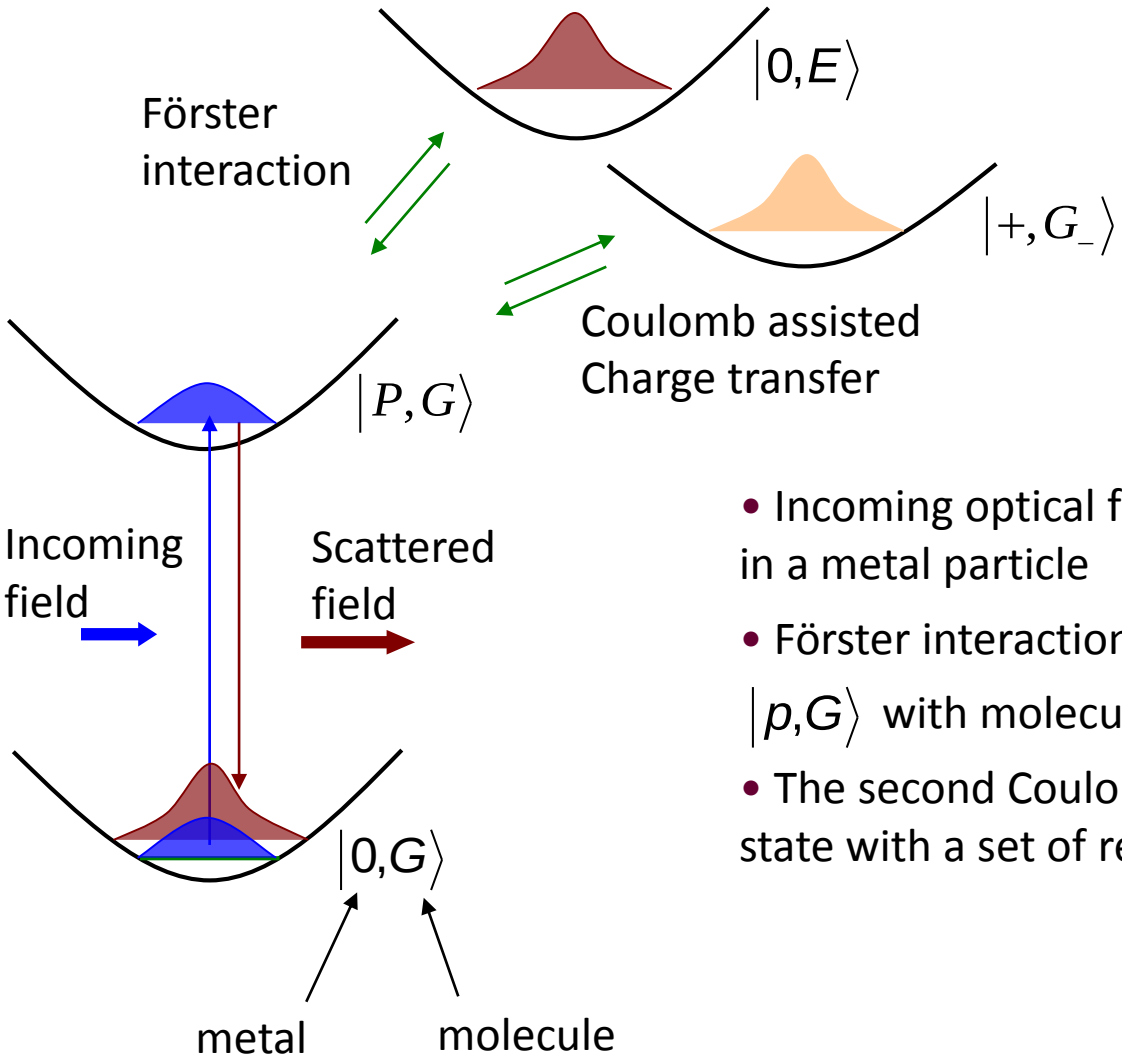
$$H_{\mathrm{CT}} \approx \sum_{m,k,\mathbf{k}<\mathbf{k}_c} \left\{ \gamma_{mk}(\mathbf{k}) P_{\mathbf{k}} a^{+}_{m} b_{k} + \mathrm{c.c.} \right\}$$

Plasmon-induced charge transfer



B. N. J. Persson, Chem. Phys. Lett. **82**, 561 (1981)

Molecule-environment coupling



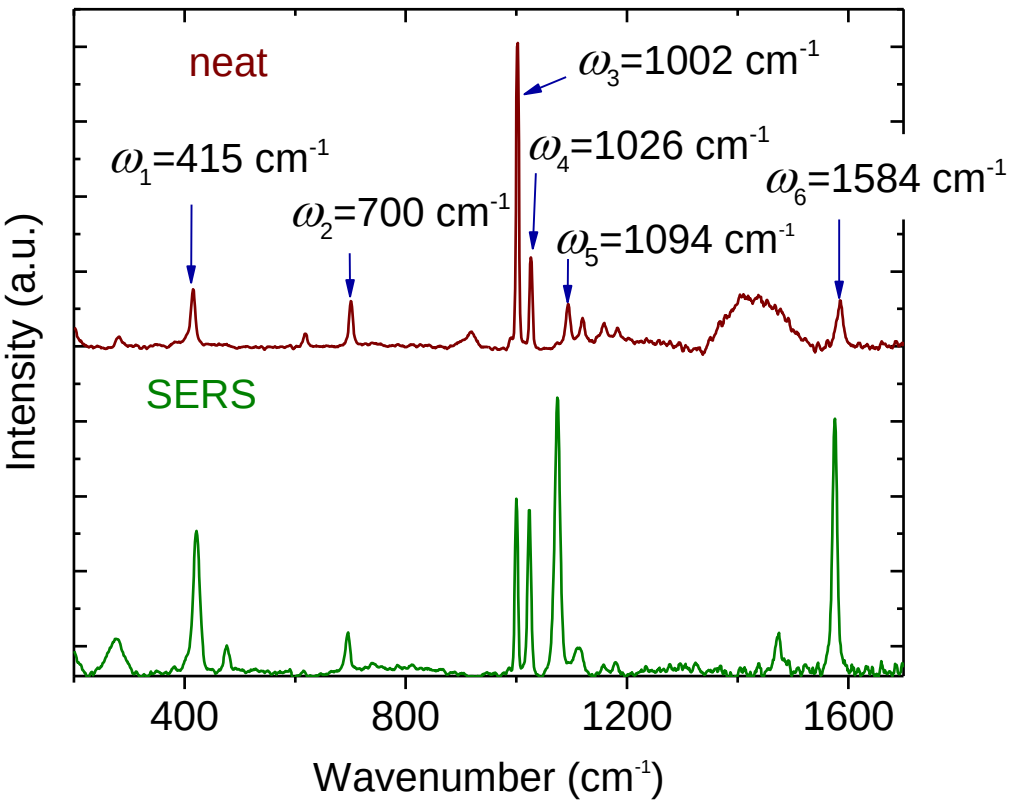
- Incoming optical field excites a resonant transition in a metal particle
- Förster interaction couples the plasmon state $|p,G\rangle$ with molecular excited states $|0,E\rangle$
- The second Coulomb term couples the plasmon state with a set of redox molecular states

Chemical effects &
Raman spectra modification

Raman spectra modification

SERS vs. Raman

Benzenethiol on Au substrate

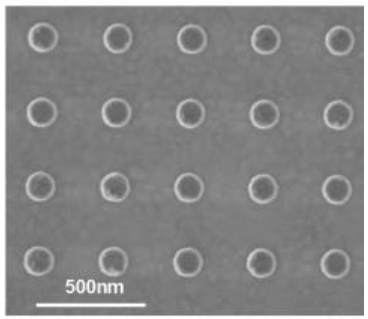


- Lines are enhanced differently
- Vibrational modes are shifted
- Some lines appear/disappear

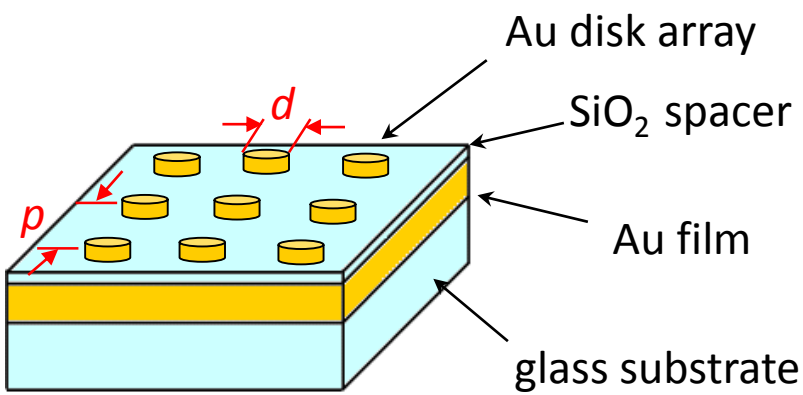
S. K. Saikin, Y. Chu, D. Rappoport, K. B. Crozier, and A. Aspuru-Guzik, *J. Phys. Chem. Lett.* **1**, 2740 (2010)

Double-resonance plasmonic structure

SEM image



Schematic picture

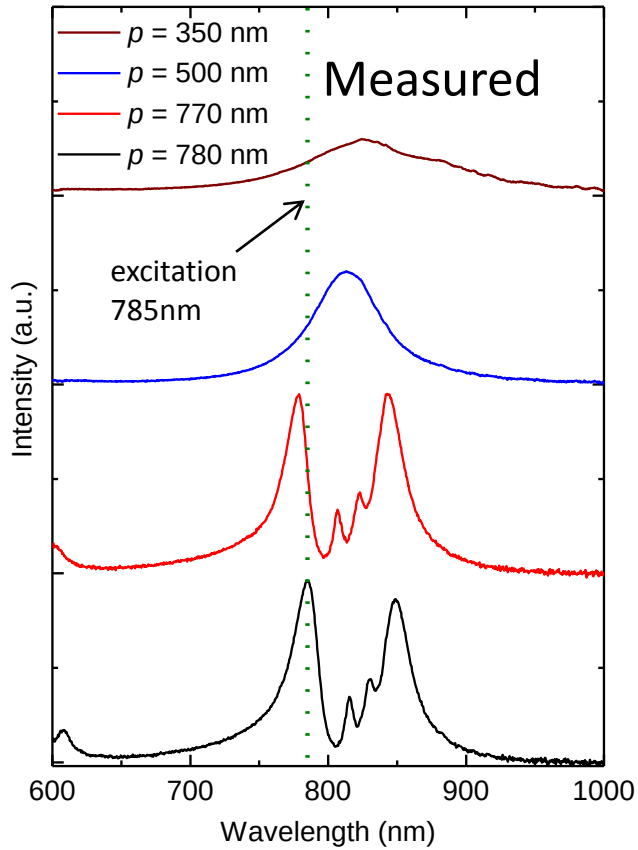


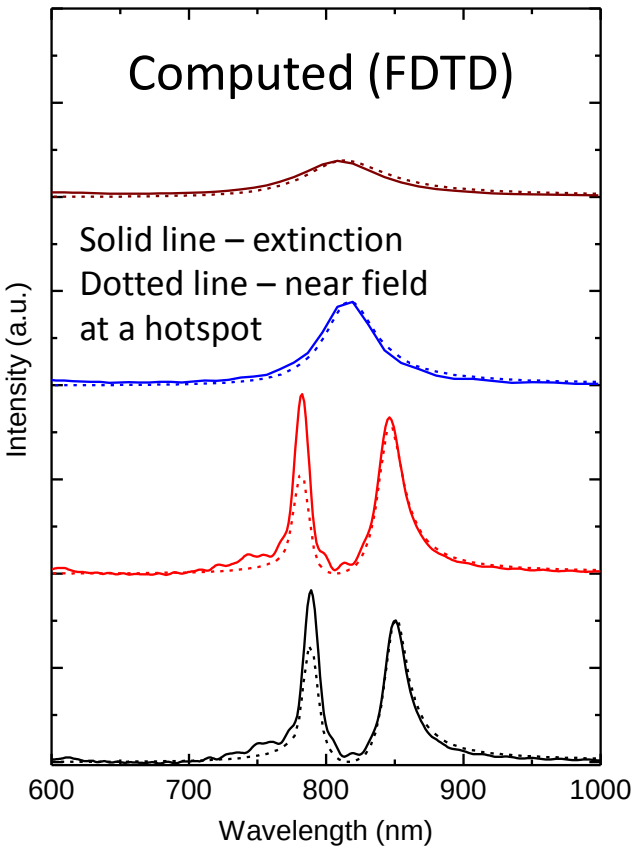
- The disk diameter *d* determines the localized plasmon resonance frequency
- The period of the disk array *p* determines the coupling between the localized and propagating plasmons

Chu, Y.; Banaee, M. G.; Crozier, K. B. *ACS Nano* **4**, 2804 (2010)
Chu, Y.; Crozier, K. B. *Opt. Lett*. **34**, 244 (2008)

Electromagnetic enhancement

Extinction spectra & near fields

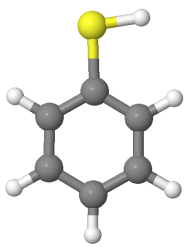




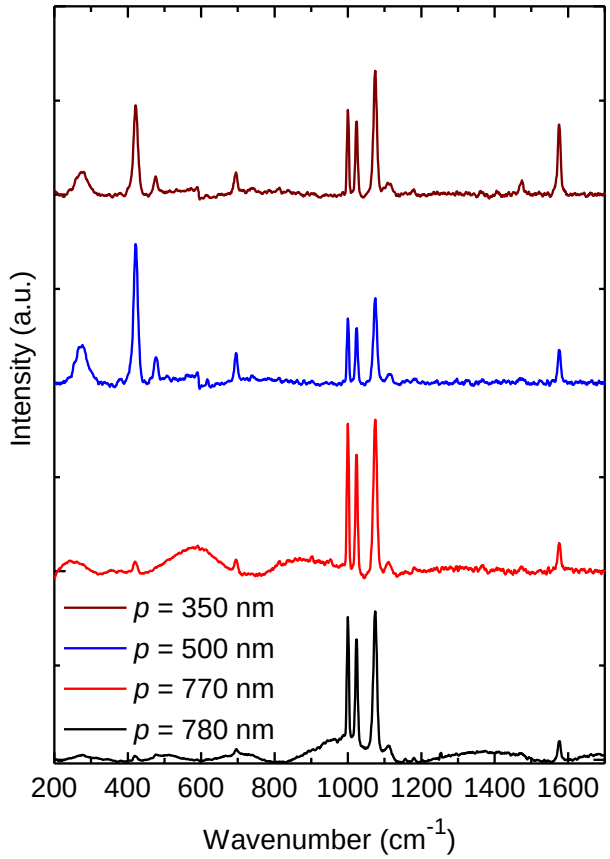
- Computed extinction spectra agree with the measured spectra
- Near-field profiles computed at hotspots are similar to the extinction spectra

Corrections for plasmonic profiles

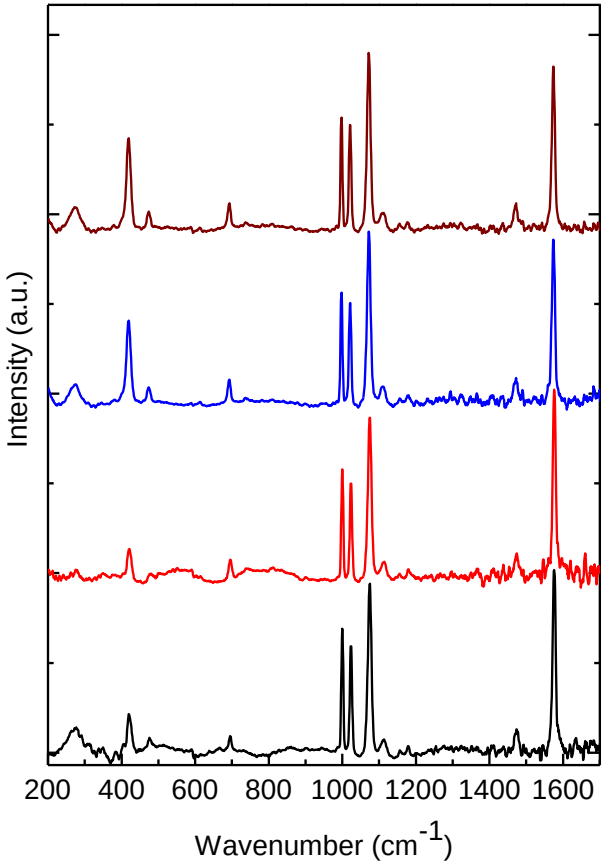
Benzenethiol
PhSH



SERS spectra



Corrected SERS spectra

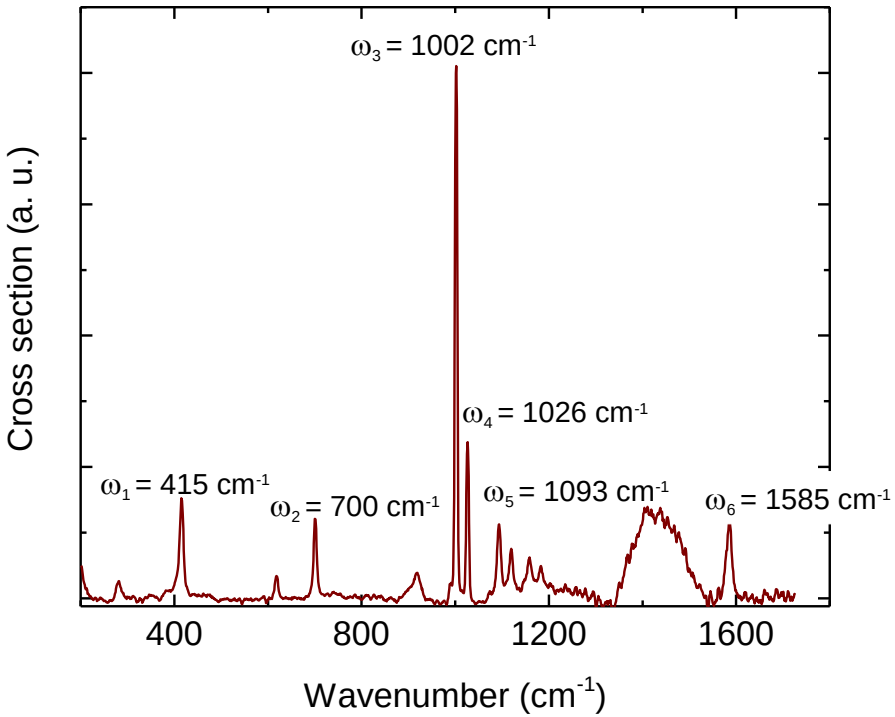


- Spectra corrected for plasmonic enhancement are reproducible for different substrates

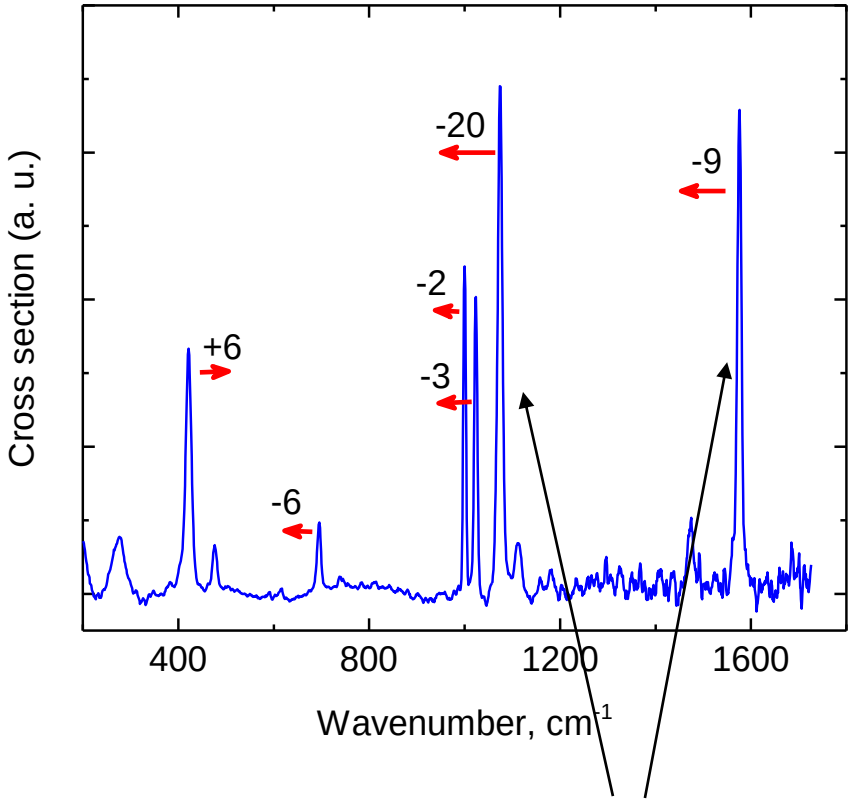
Adsorption effects

Measured data

Neat sample



SERS



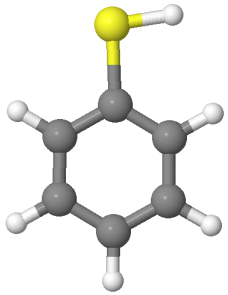
Strongest enhancement

- Lines are enhanced differently

- Vibrational modes are shifted

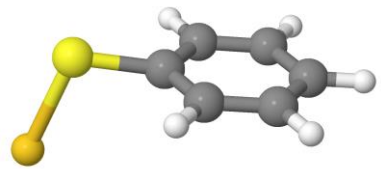
Chemical adsorption effects

Model structures



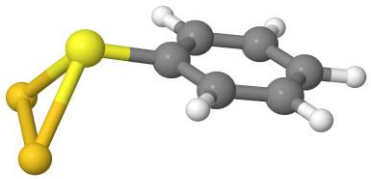
PhSH

Isolated molecule



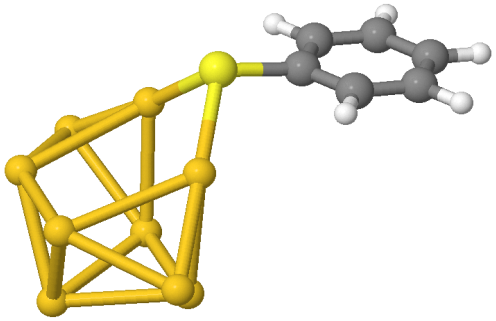
PhS-Au_1

on-top binding motif

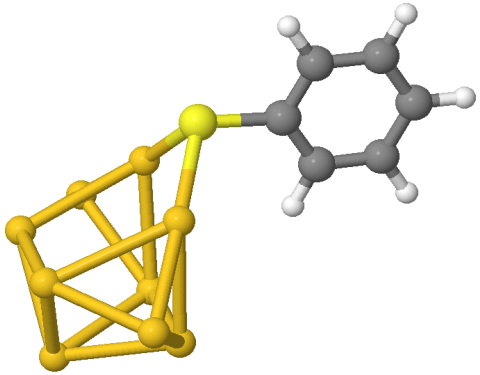


PhS-Au_2

bridge binding motif
small structure

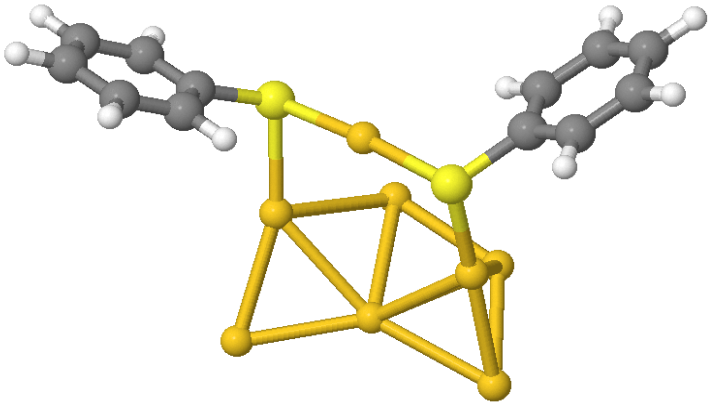


PhS-Au_9 (I)



PhS-Au_9 (II)

bridge binding motif
larger structures



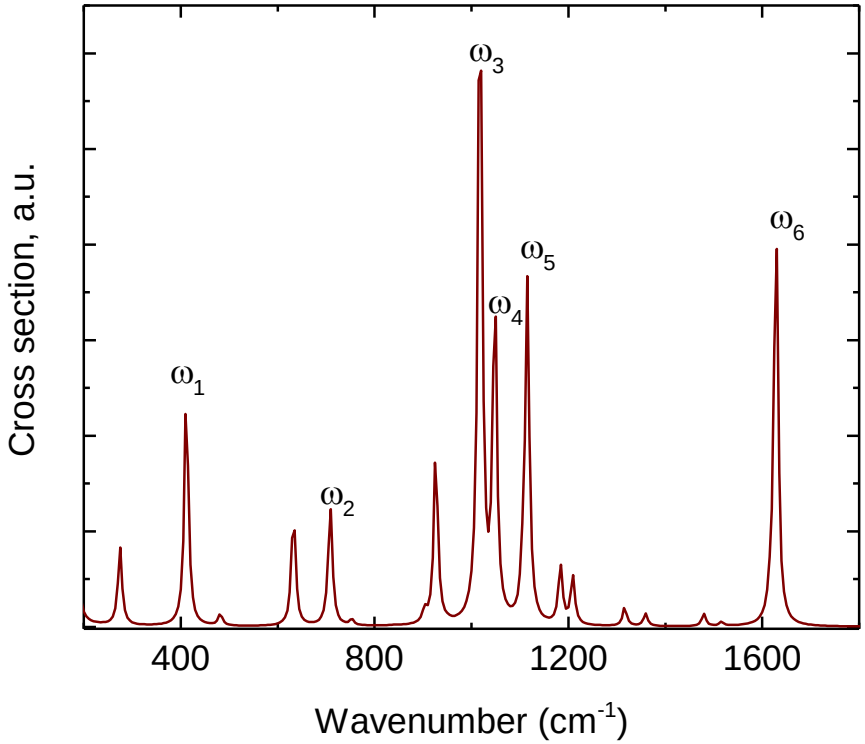
$(PhS)_2$-Au_8

staple binding motif

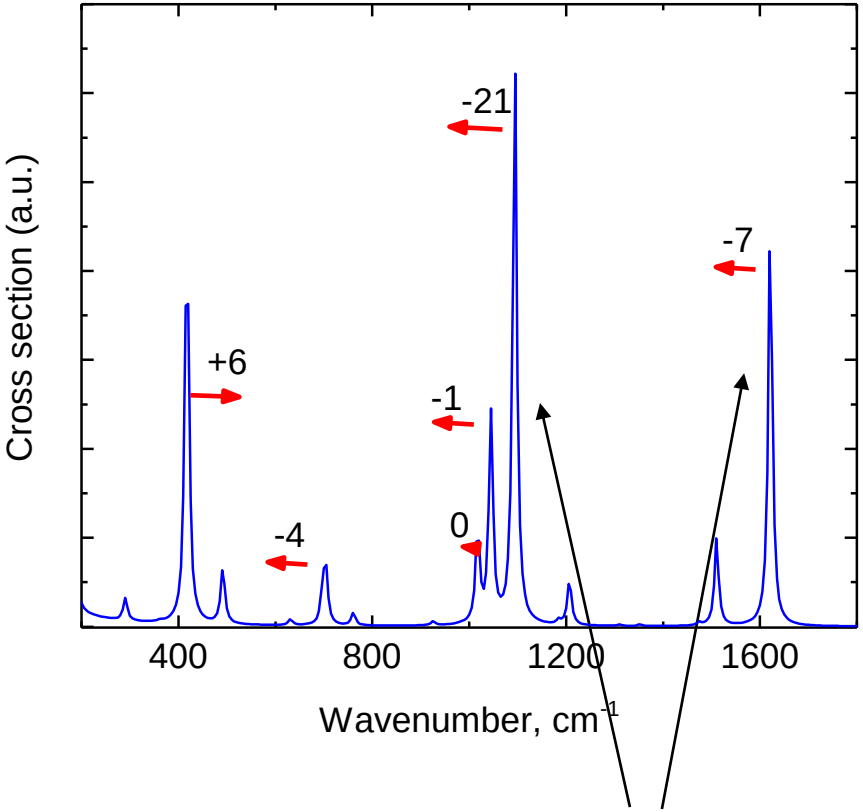
Chemical adsorption effects

Computed results

Isolated molecule



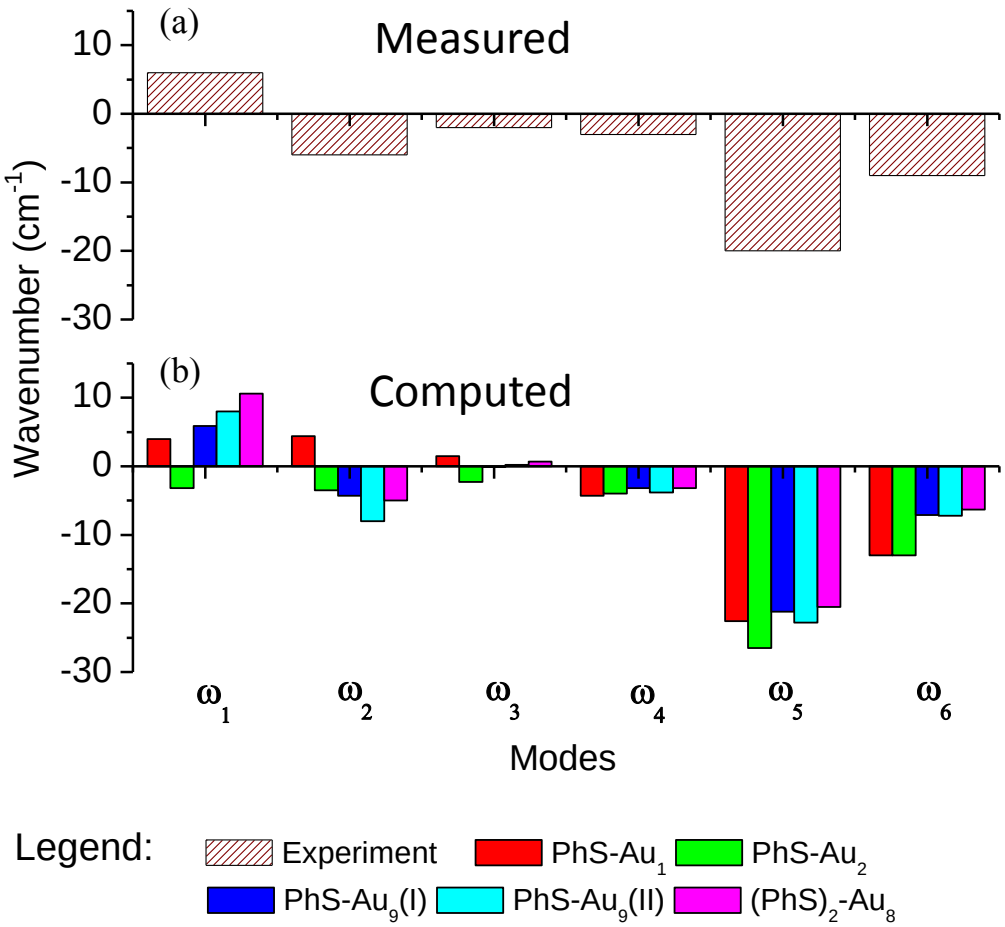
PhS-Au_9



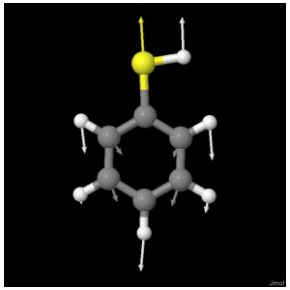
Strongest enhancement

- Computed spectral modifications are consistent with the measured results

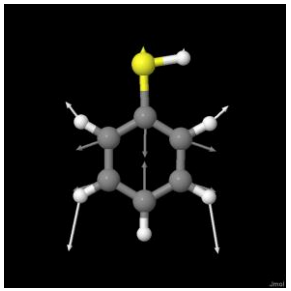
Mode shifts theory vs. experiments



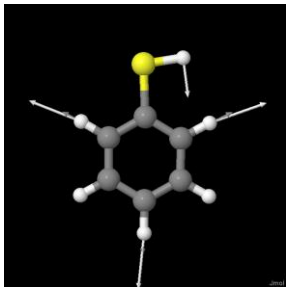
Modes



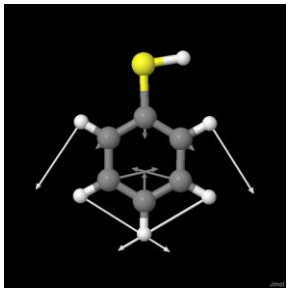
ω_1 = 415 cm^{-1}



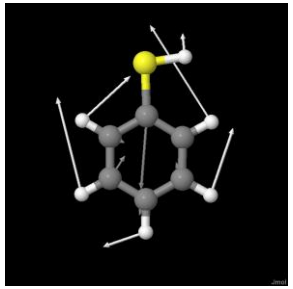
ω_2 = 700 cm^{-1}



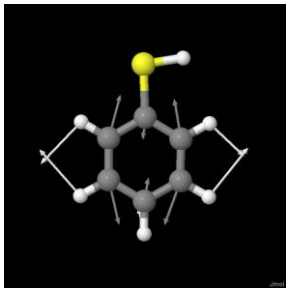
ω_3 = 1002 cm^{-1}



ω_4 = 1026 cm^{-1}



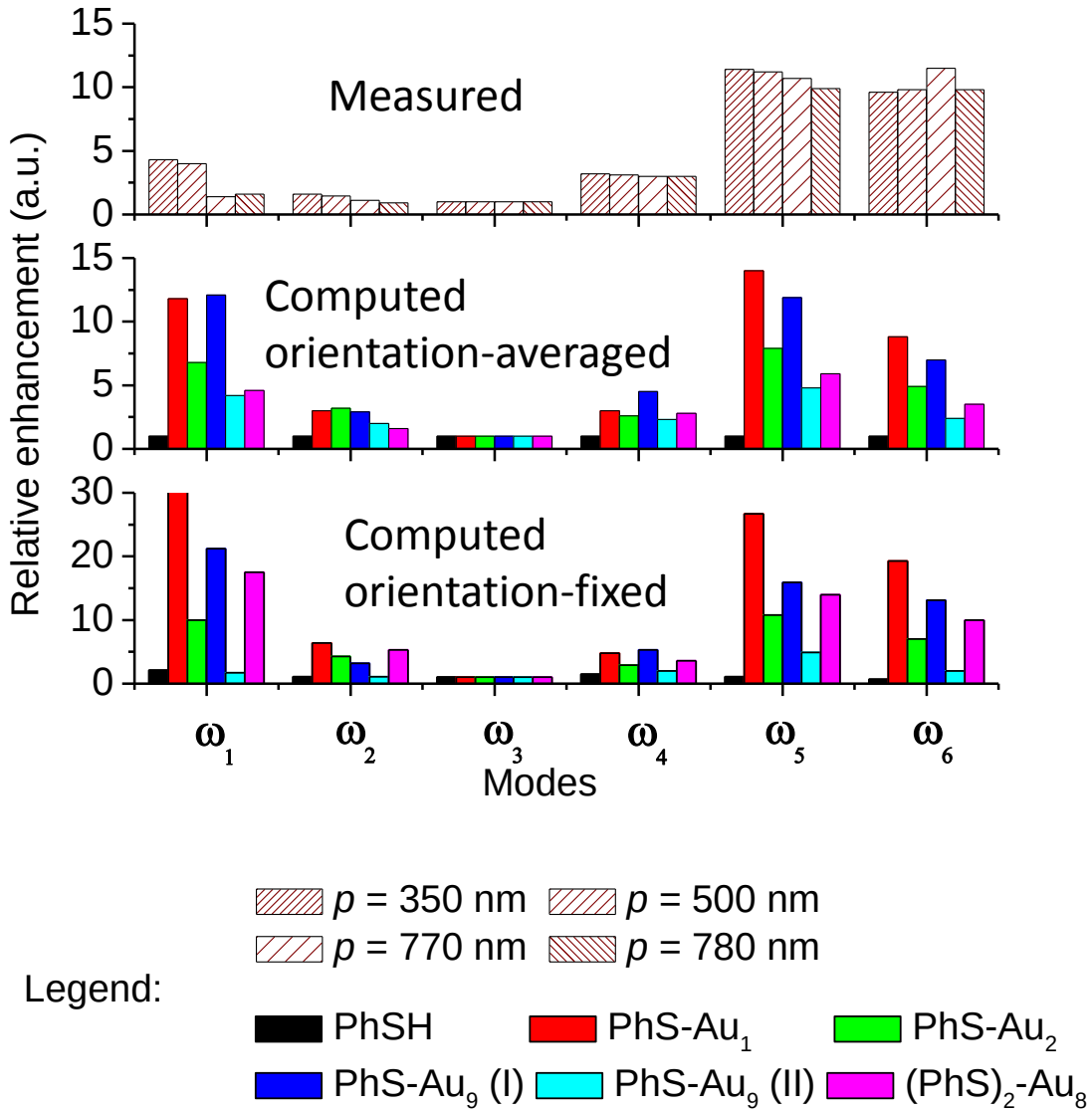
ω_5 = 1094 cm^{-1}



ω_6 = 1584 cm^{-1}

- Molecule-cluster model describes mode shifts quantitatively

Mode intensities theory vs. experiments



- Molecule-cluster model describes relative mode enhancement qualitatively