Light-Matter Interaction at the Nano Scale

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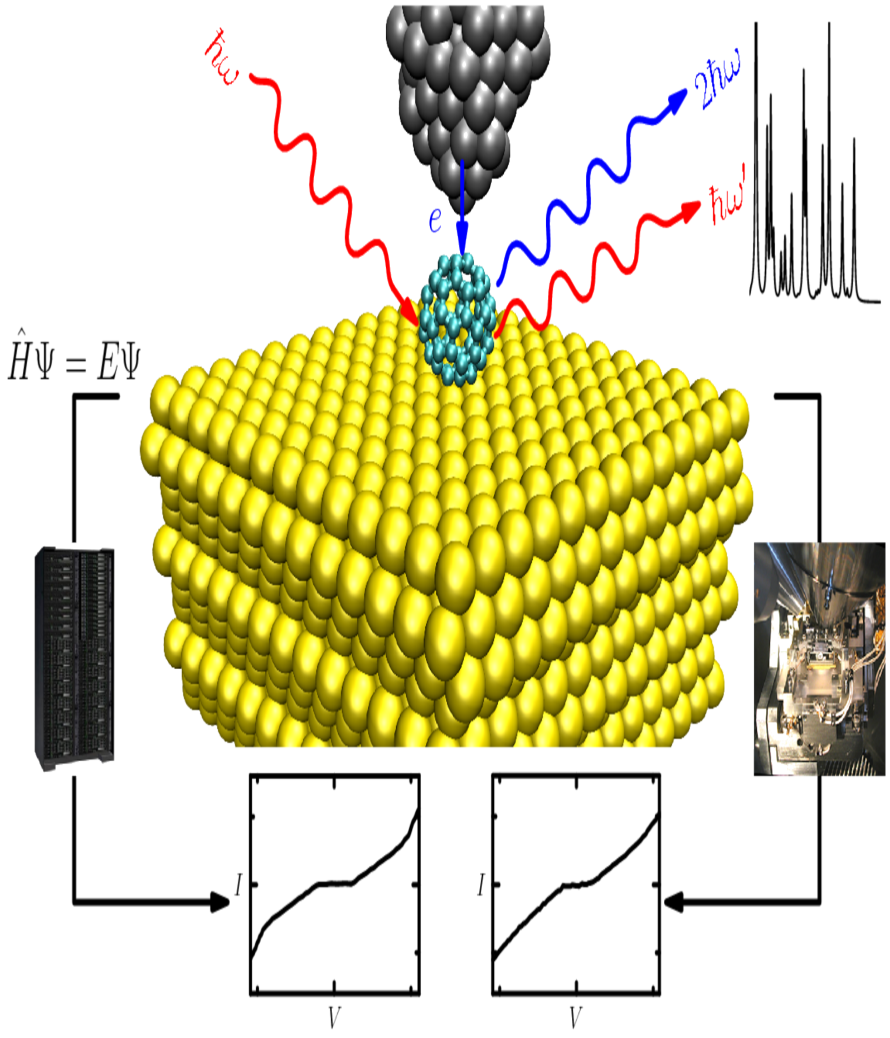
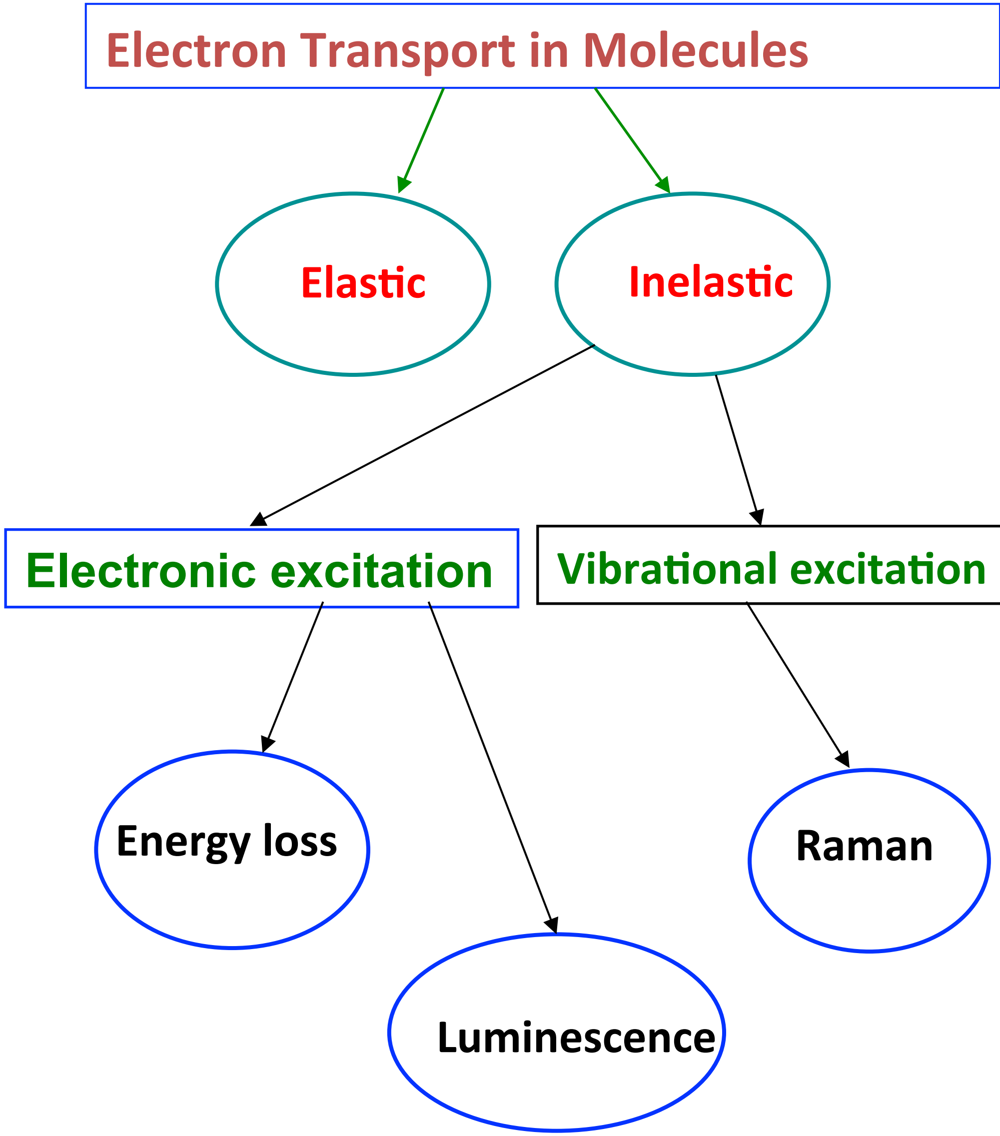
Stockholm, 2016-10-07

Elastic and Inelastic Electron/Photon Scattering





Electron Transport in Molecules

Elastic

Inelastic

Electronic excitation

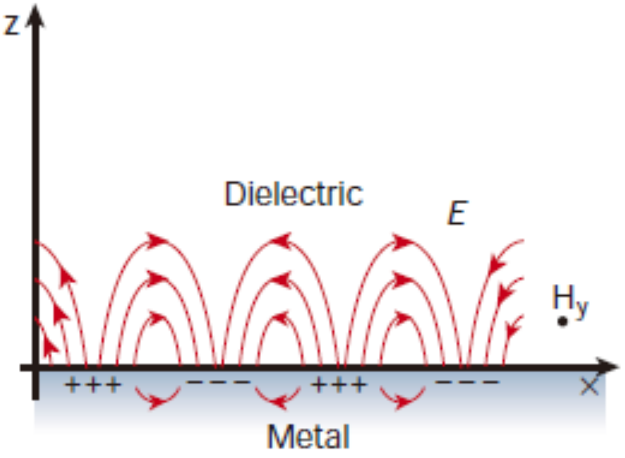
Vibrational excitation

Energy loss

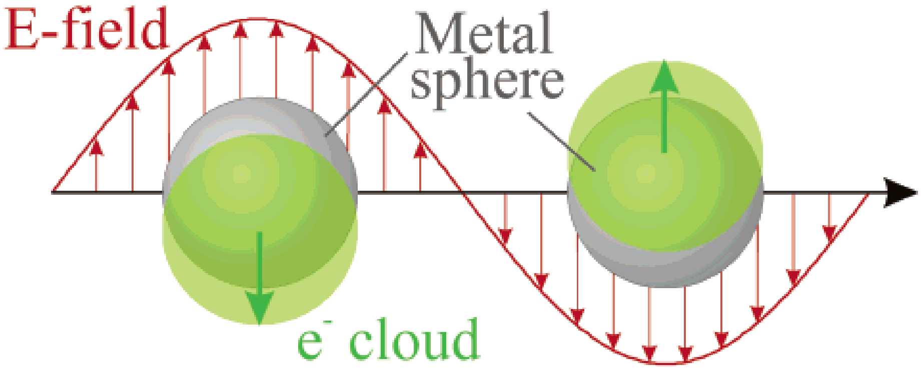
Luminescence

Raman

Surface plasmon



Barnes, et al., *Nature* 424 (2003), 824.



Kelly, et al., *J. Phys. Chem. B* 107 (2002), 668.

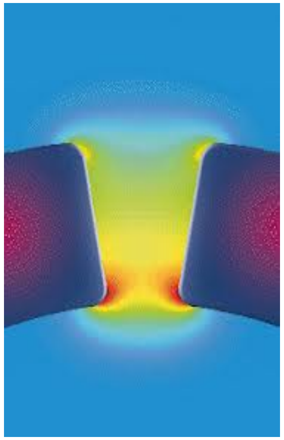
Electromagnetic field:

$$\mathbf{E}\left(\mathbf{r},t\right) = E_0(\mathbf{r},t)W_{\mathbf{k}}(\mathbf{r})e^{-\iota\omega t}$$

Field Strength

Time Structure

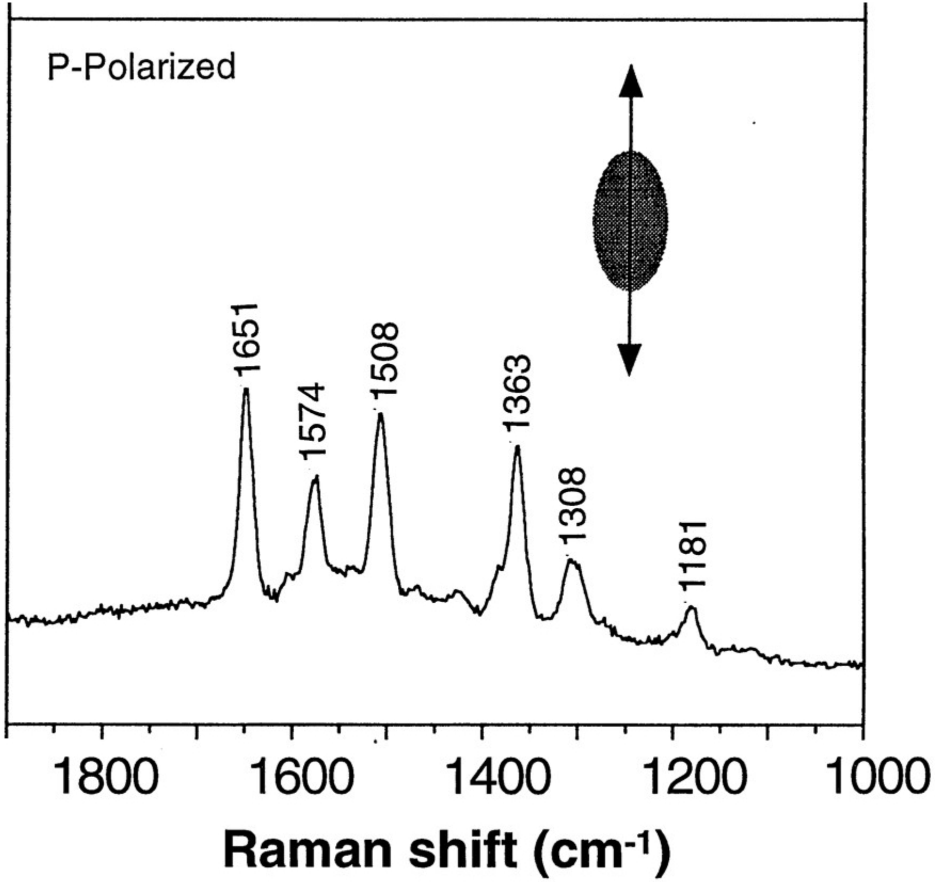
Spatial Distribution



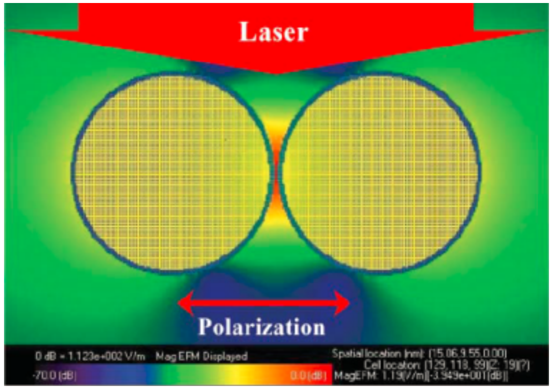
W_{k}: node function

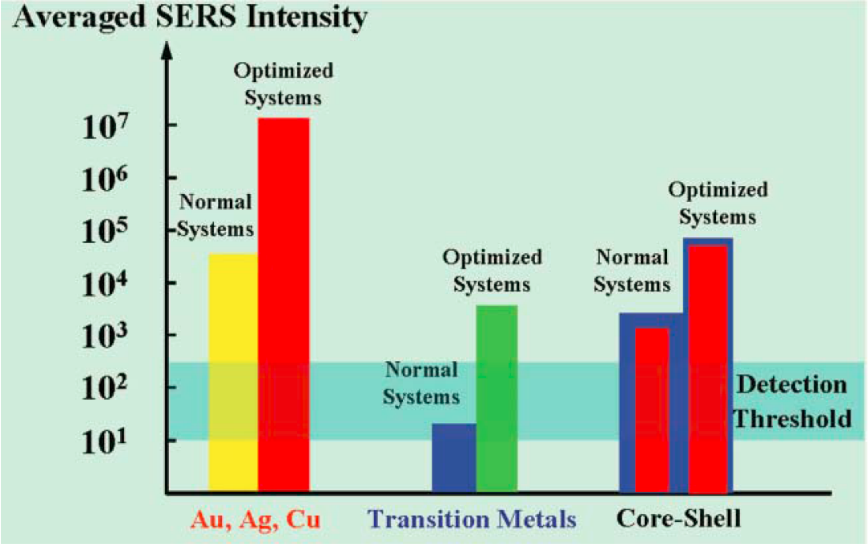
Gaint Field Strength: Surface enhance Raman scattering

Single Molecular SERS: R6G



Nie S. and Emory S. R. *Science*, 275 (1997) 1102

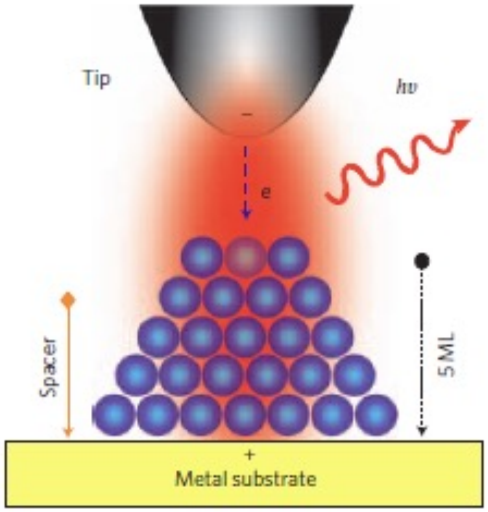


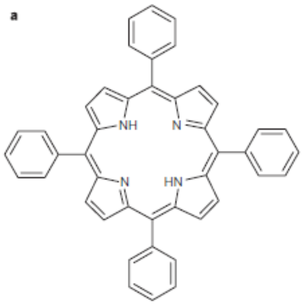


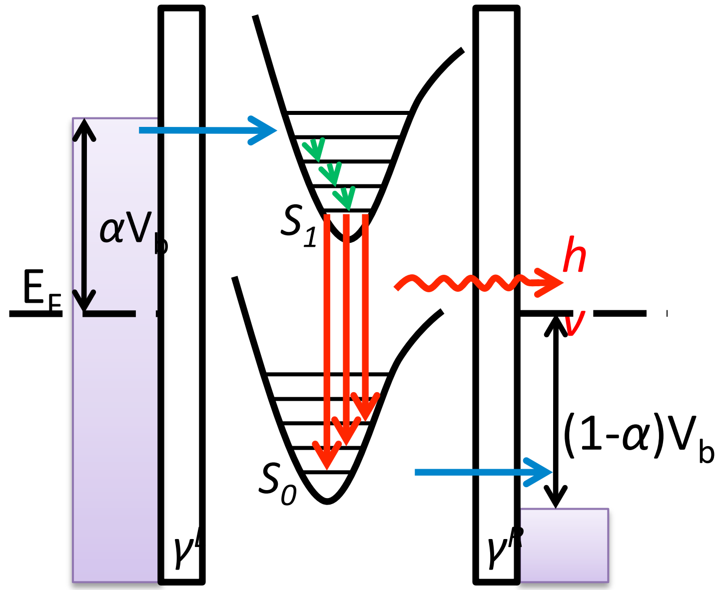
Tian, et al., *Chem. Commun.*, 2007, 3514.

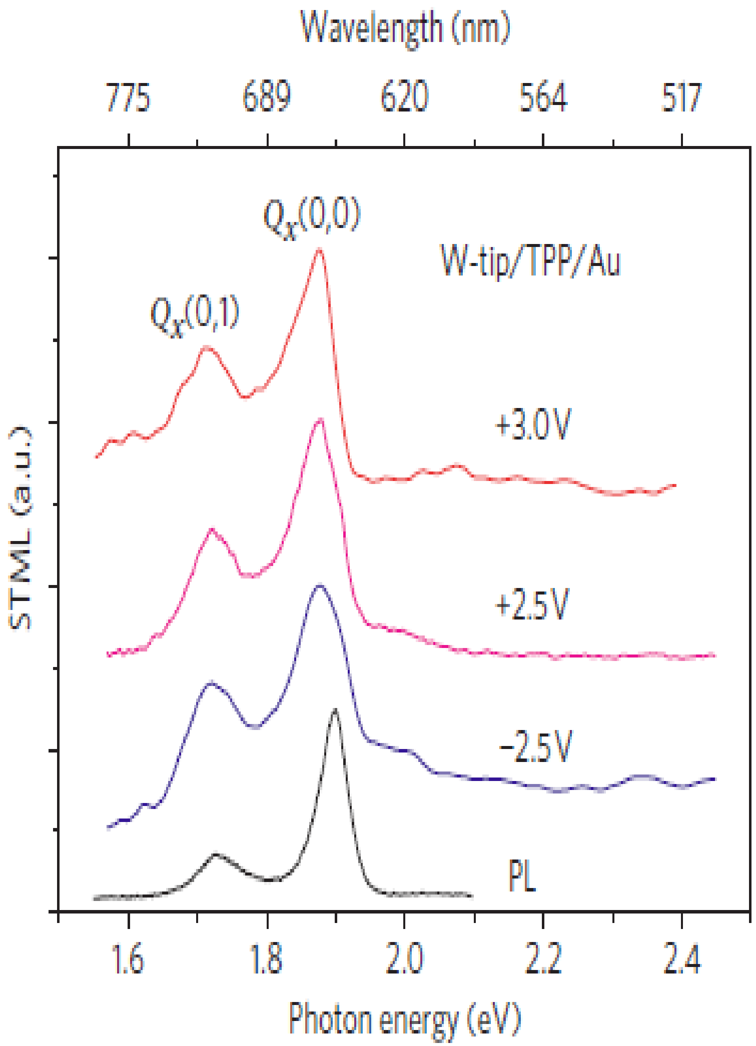
High intensity of the plasmon enables to achieve effective detection of a very small numbers of molecules.

Electro-luminescence of molecules in a nano-cavity (time-structure)







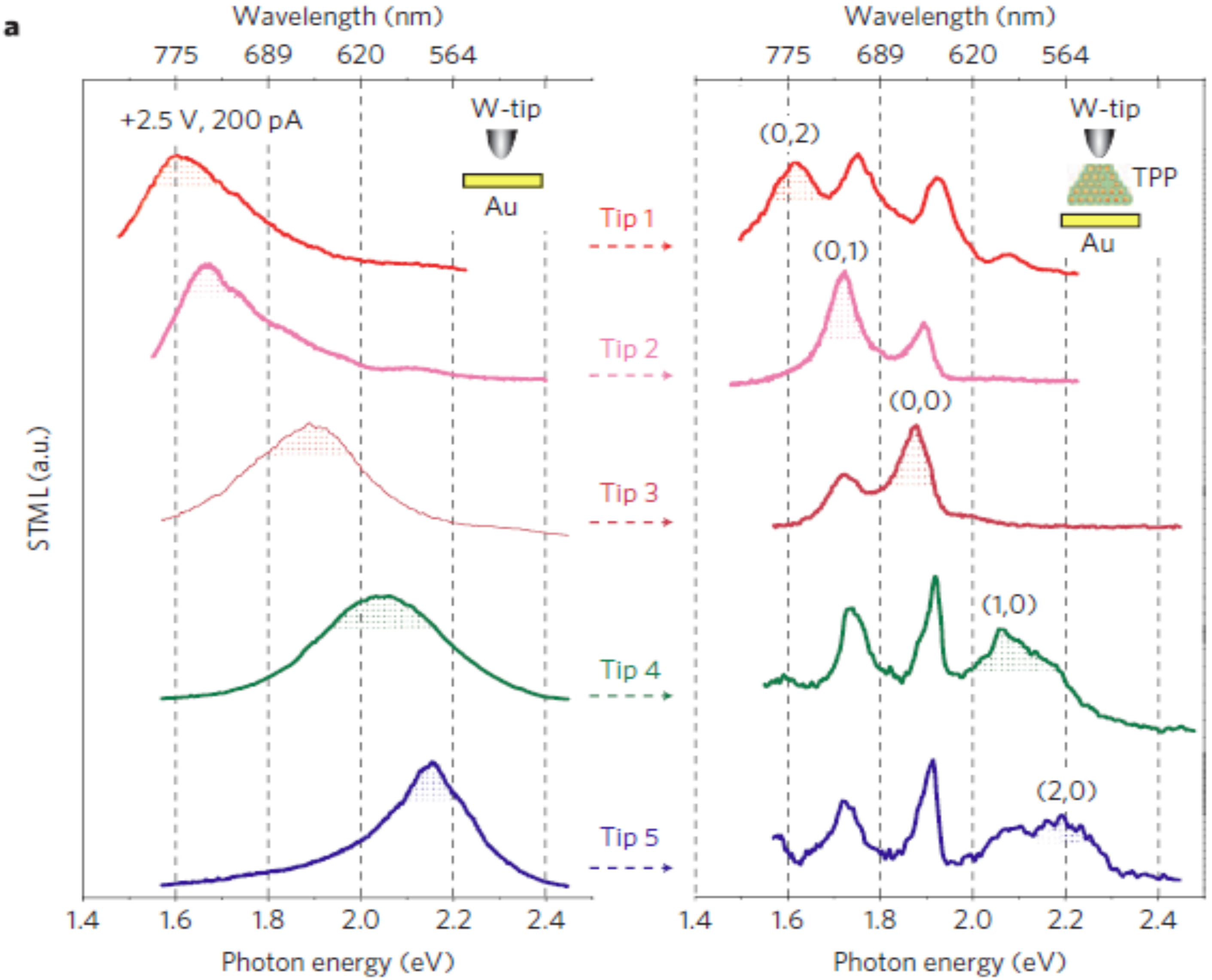


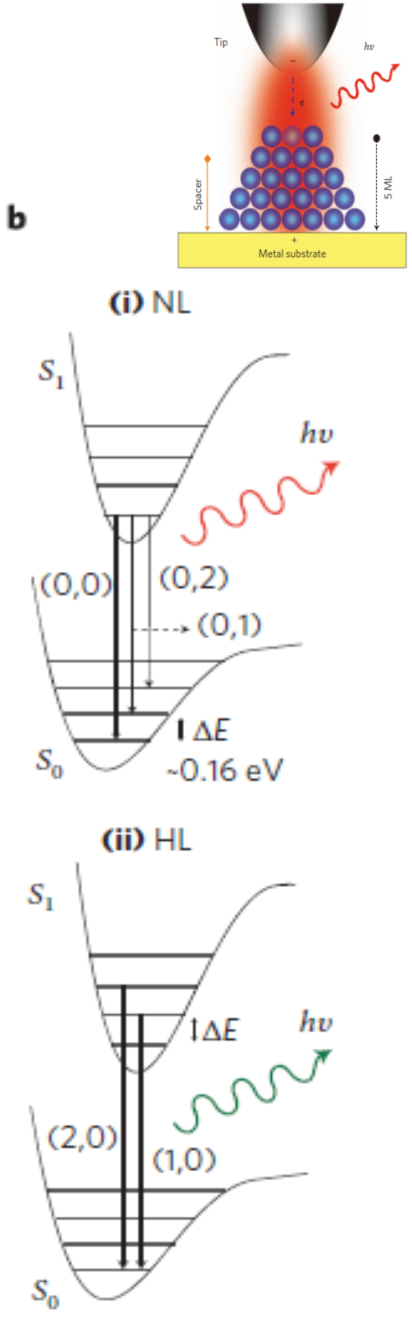
Franck-Condon Profile

Dong, et al., *Nature Photonics*, 2010, *4*, 50-54.

Plasmon assisted electro-luminescence of molecules

Beyond the Kasha's rule





Dong, et al., *Nature Photonics*, 2010, *4*, 50-54.

Simulation of vibronic coupling in polyatomic molecules

Transition dipole moment $\mu = \langle g, v | \hat{\mu} | e, \mu \rangle$

Apply *BO approximation* and including the *non-Condon effect*

$$\mu = \mu^e(q_0)\langle v | \mu \rangle + \sum_a \frac{\partial u^e}{\partial q_a} \langle v | q_a | \mu \rangle$$

$\Downarrow$ ***Franck-Condon term***

$\Downarrow$ ***Herzberg-Teller term***

$\mu^e(q_0)$ is the electronic transition dipole moment at q_0

$$\langle v | q_a | \mu \rangle = \sqrt{\frac{h}{2\omega_a}} \left[\sqrt{\mu_a} \langle v | \mu - 1_a \rangle + \sqrt{\mu_a + 1} \langle v | \mu + 1_a \rangle \right]$$

Remaining problem is to calculate the Franck-Condon integral

Simulation of vibronic coupling in polyatomic molecules

Duschinsky Transformation[1]:

$$Q' = JQ + K$$

$$J = (L')^T L \qquad K = (L')^T M^{1/2}\left(X - X'\right)$$

<0|0> can be calculated analytically as[2]:

$$\langle 0|0\rangle = \left(\frac{2^N \det(\Gamma'\Gamma)1/2}{\det(J(J^T\Gamma' J + \Gamma))}\right)^{1/2} \times \exp\left(\frac{1}{2}K^T[\Gamma' J(J^T\Gamma' J + \Gamma)^{-1}J^T - 1]\Gamma' K\right)$$

All other terms can be computed recursively[3], for example, at 0K we have:

$$\langle 0|\mu\rangle = \frac{1}{\left(2\mu_a\right)^{1/2}}\Big[d_a\langle 0|\mu - 1_a\rangle + \sqrt{2\left(\mu_a - 1\right)}C_{aa}\langle 0|\mu - 2_a\rangle$$

$$+ \sum_{b=a+1}^{N}\left(C_{ab} + C_{ba}\right)\langle 0|\mu - 1_a - 1_b\rangle\Big]$$

[1] F. Duschinsky, *Acta Physicochimica URSS* 7, 551 (1937)

[2] T. E. Sharp and H. M. Rosenstock , *J. Chem. Phys.* 41, 3453 (1964).

[3] P. T. Ruhoff and M. A. Ratner, *Int. J. Quantum Chem.*, 77,383 (2000).

Simulation of vibronic coupling in polyatomic molecules

Convergence of the calculation can be checked by the intensity sum rule:

$$I^{tot} = \left|\mu^{e}\left(q_{0}\right)\right|^{2} + \sum_{a}\sum_{v} p_{v}\left(\frac{\partial u^{e}}{\partial q_{a}}\right)^{2}\frac{h}{2\omega_{a}}\left(2\nu_{a}+1\right)$$

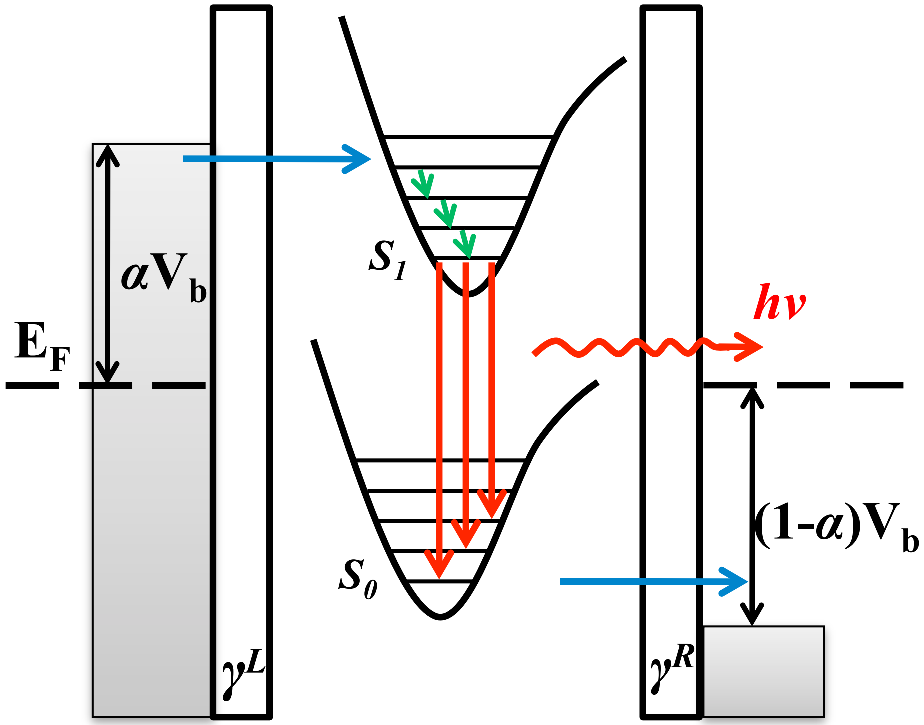
p_v is the population of initial states.

Implemented in *DynaVib* software package with applications in the following areas:

(1) STM induced electroluminescence from single molecules
(2) Vibrationally-resolved optical and X-ray spectroscopy
(3) Electron transport properties of single molecules with the inclusion of electron-vibration coupling

DynaVib, Version 1.0, Tian, Duan, Hua, and Luo, 2012.

Theoretical model: electron tunneling induced photon emission

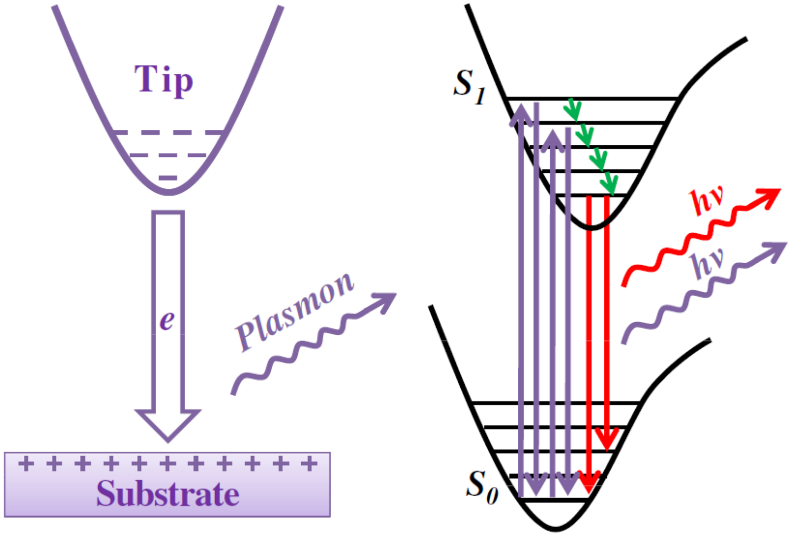


Schematic picture of the electron tunneling induced photon emission process.

Both HOMO and LUMO in the bias window, electron tunneling leaves a molecular excited state for photon emission.

Photon emission from the ground vibrational level due to the fast internal decay rate.

Theoretical model: Plasmon-assist emission



Plasmons behave like strong electromagnetic sources and can excite the molecule resonantly into higher vibrational levels in the first excited state following a resonant emission.

Schematic picture of the generation of the localized surface plasmon and the plasmon-assist photon emission process.

Remaining question, how to describe all the processes ?

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}, \rho\right] + \Gamma_{tr}\rho + \Gamma_{ph}\rho + R\rho$$

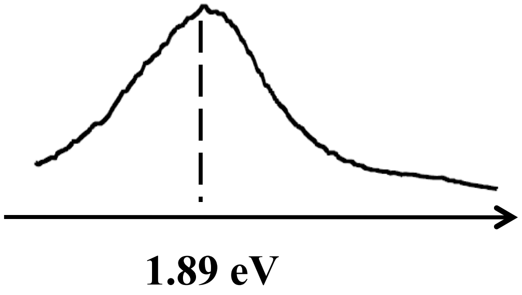
DynaVib, Version 1.0, G. Tian, S. Duan, W. Hua, Y. Luo, 2012.

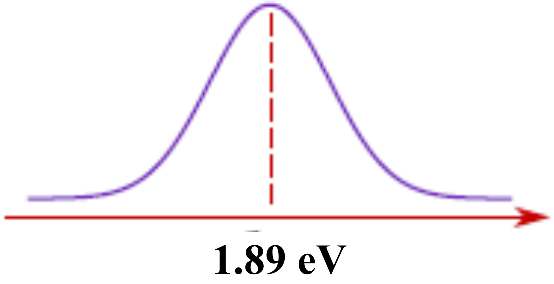
Description of the plasmon

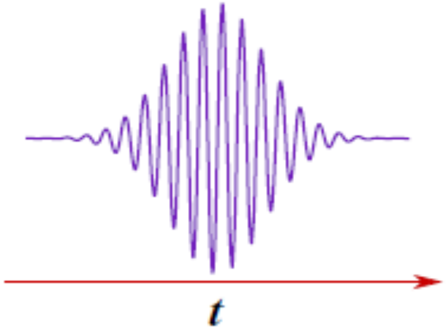
Plasmon-molecule interaction

$$\hat{H} = \hat{H}_{mol} + \hat{V}(r,t)$$

$$\hat{V}(r,t) = -\mu \cdot \varepsilon(t) \quad \varepsilon(t) = eE(t)\cos(\omega t)$$

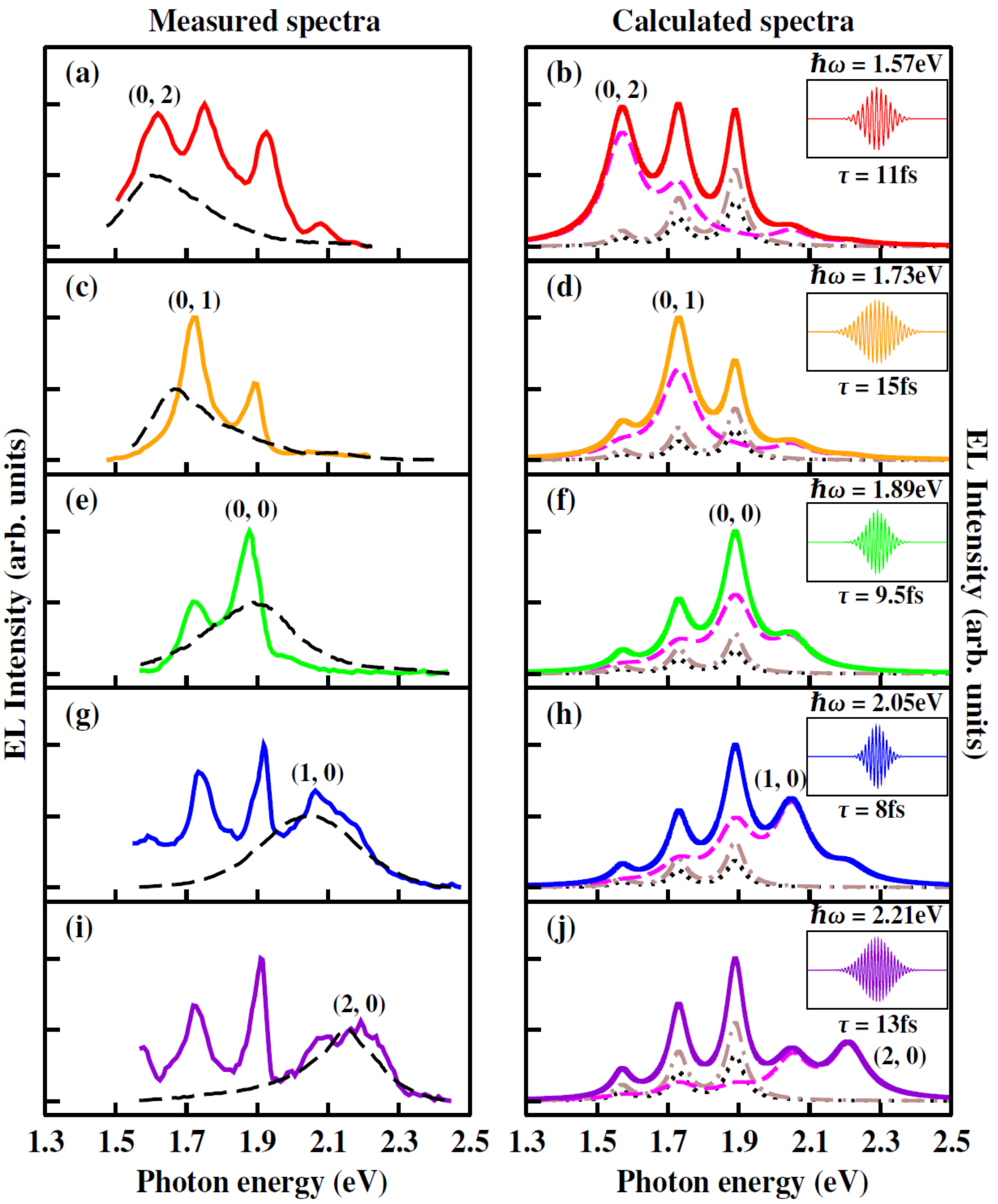






$$E(t) = E_0 \exp\left[-2\ln 2\left(\frac{t-t_0}{\tau}\right)^2\right]$$

EL spectra for TPP molecules



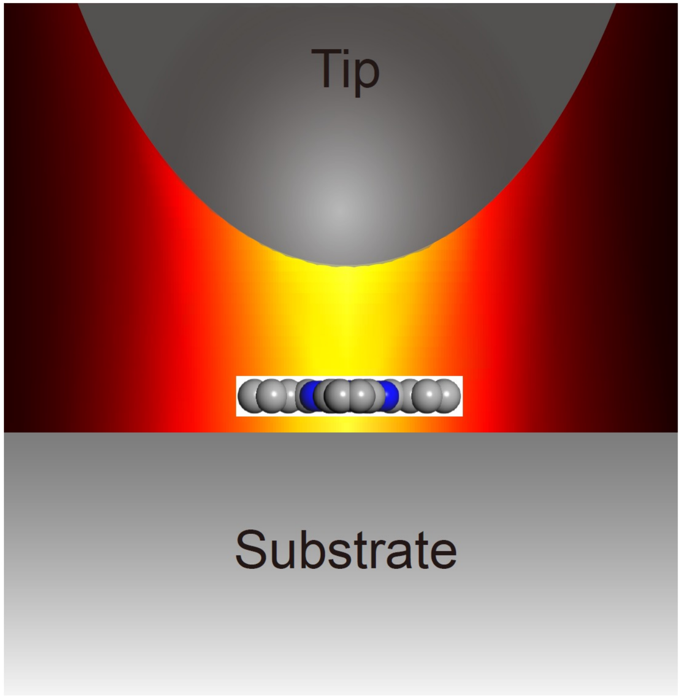
EL spectra modified by the resonant plasmonic excitation. (Left) Measured EL spectra of TPP molecules together with the corresponding NCP modes (black dashed line).[1] (Right) Calculated EL spectra together with the contributions from the three processes.

γ^L=4.1 μeV, γ^R=1.2 μeV, α=0.5, T=80 K

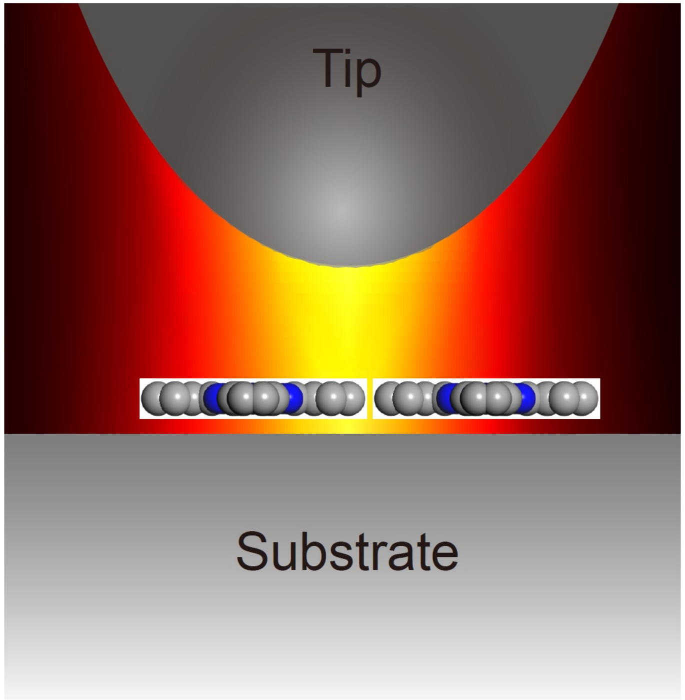
$$E(t) = E_0 \exp\left[-2\ln 2\left(\frac{t-t_0}{\tau}\right)^2\right]$$

Tian et al. , *Phys. Rev. Lett.,* 106, 177401 (2011)

Photo-images：
Inter- Molecular Energy Transfer

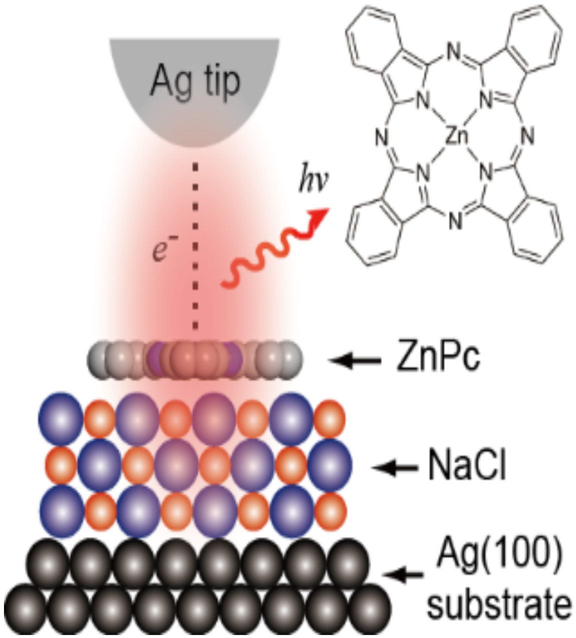


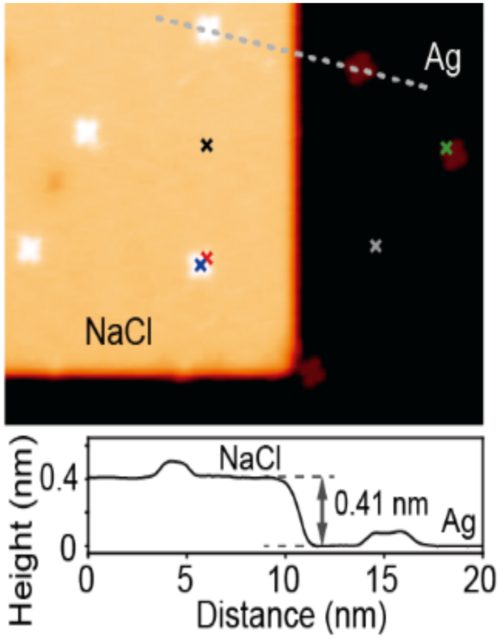
Single Molecule



Molecular dimer

Electroluminescence of a single Zn-Porphyrin molecule





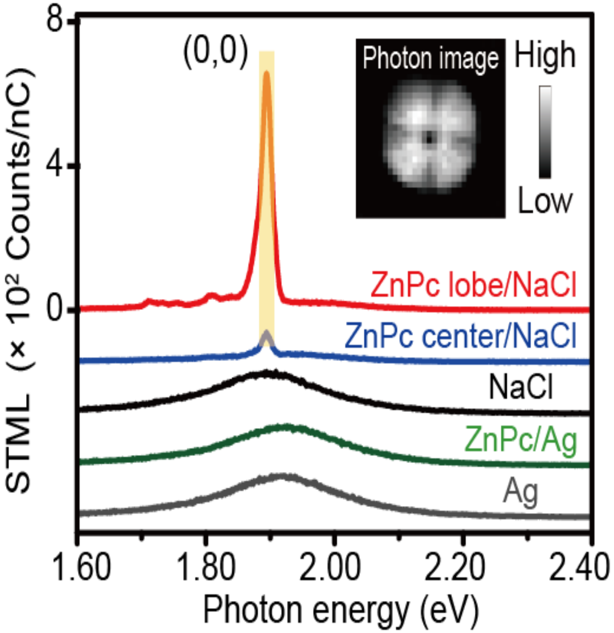
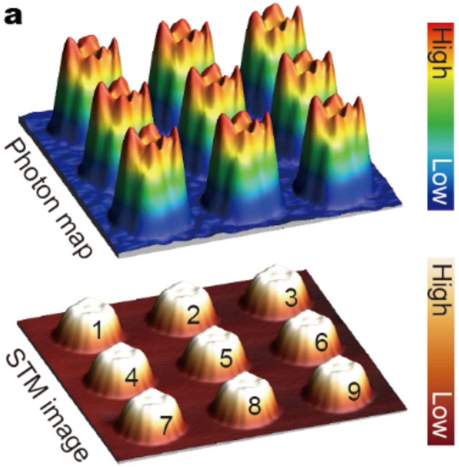
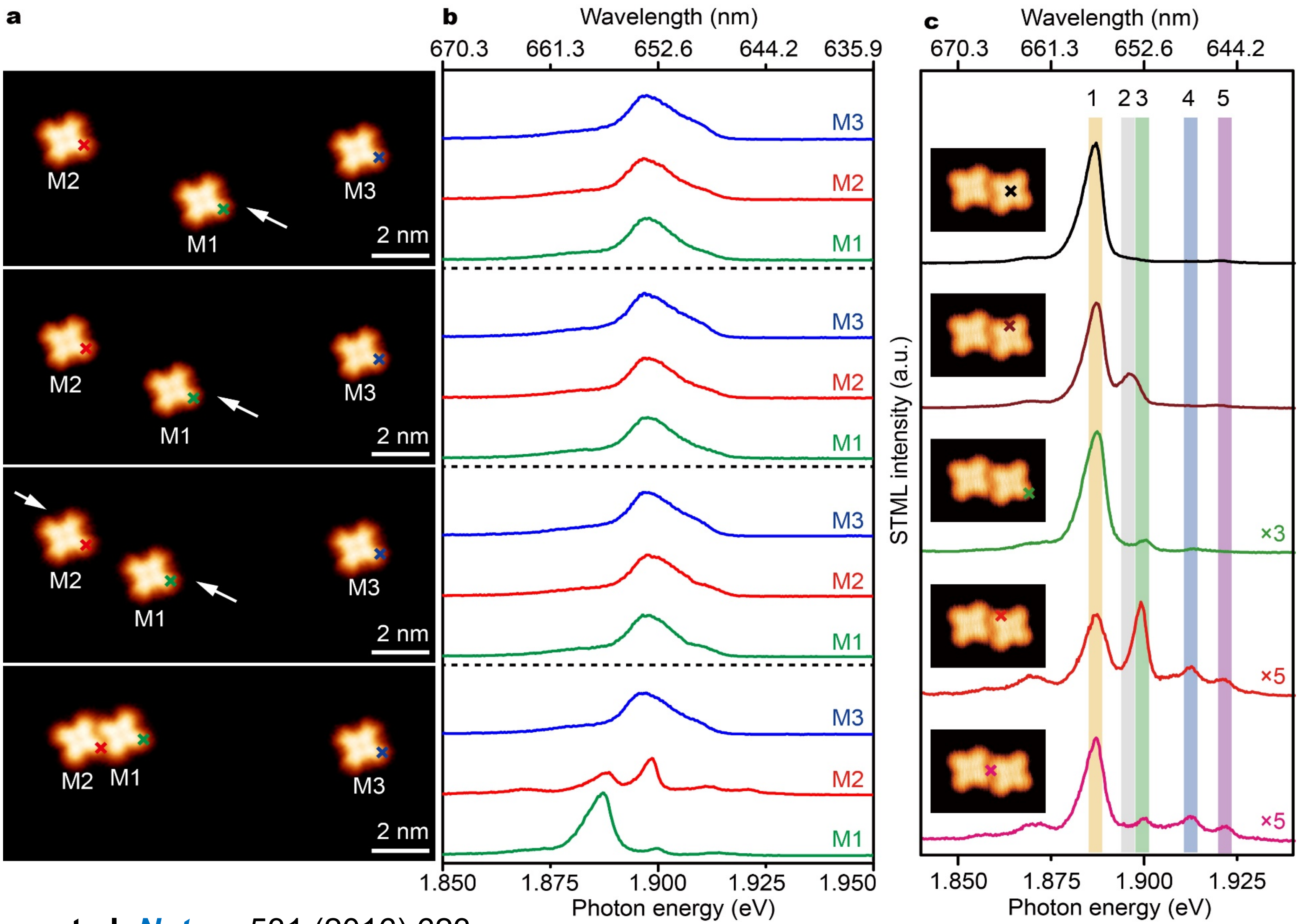


Photo-images

STM images

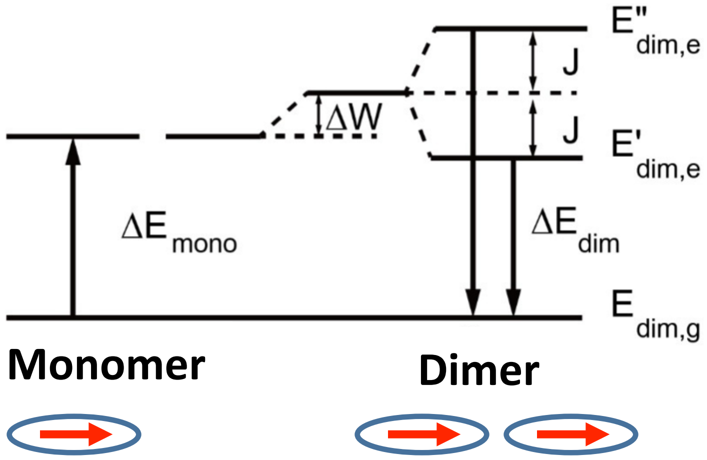


Evolution of Intermolecular interaction



Zhang et al. *Nature* 531 (2016) 623

Dipolar Interaction

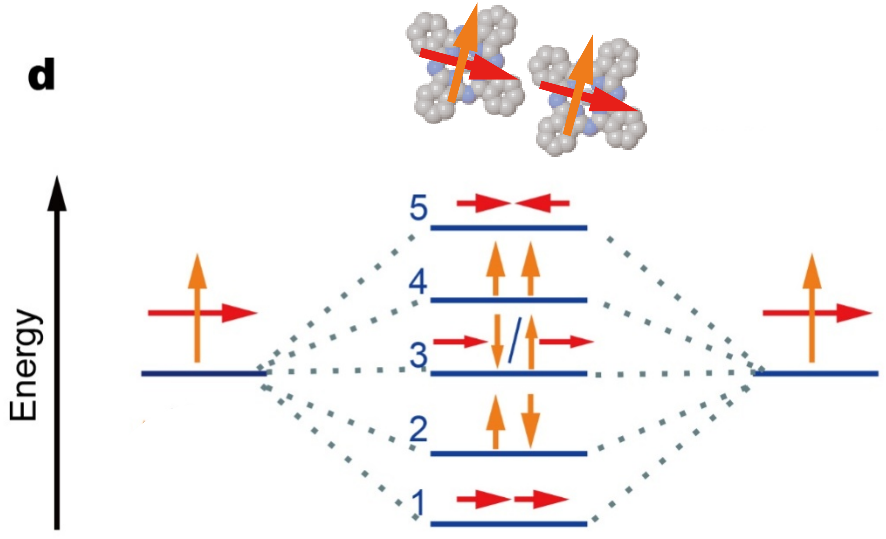


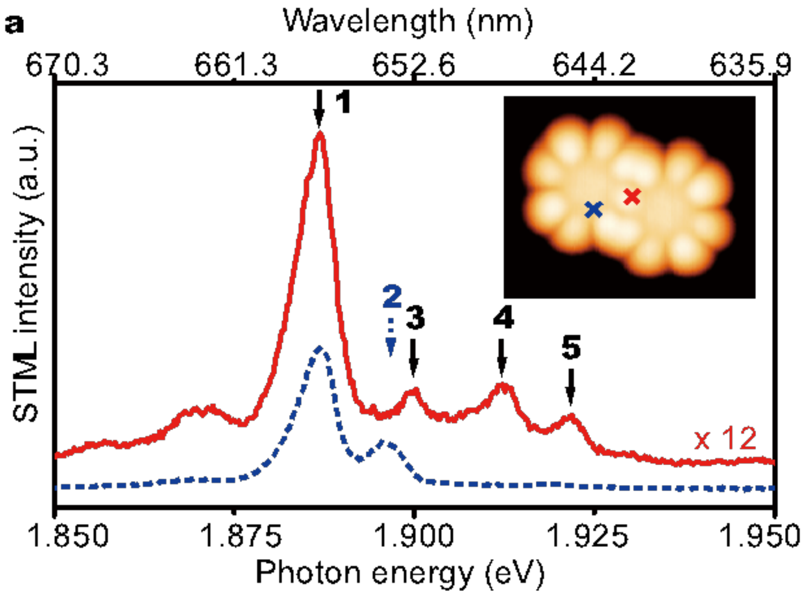
Excited Wavefunction：

$$\Psi_{\mathrm{dim},e} = (\psi_{1,e}\psi_{2,g} \pm \psi_{1,g}\psi_{2,e})/\sqrt{2}$$

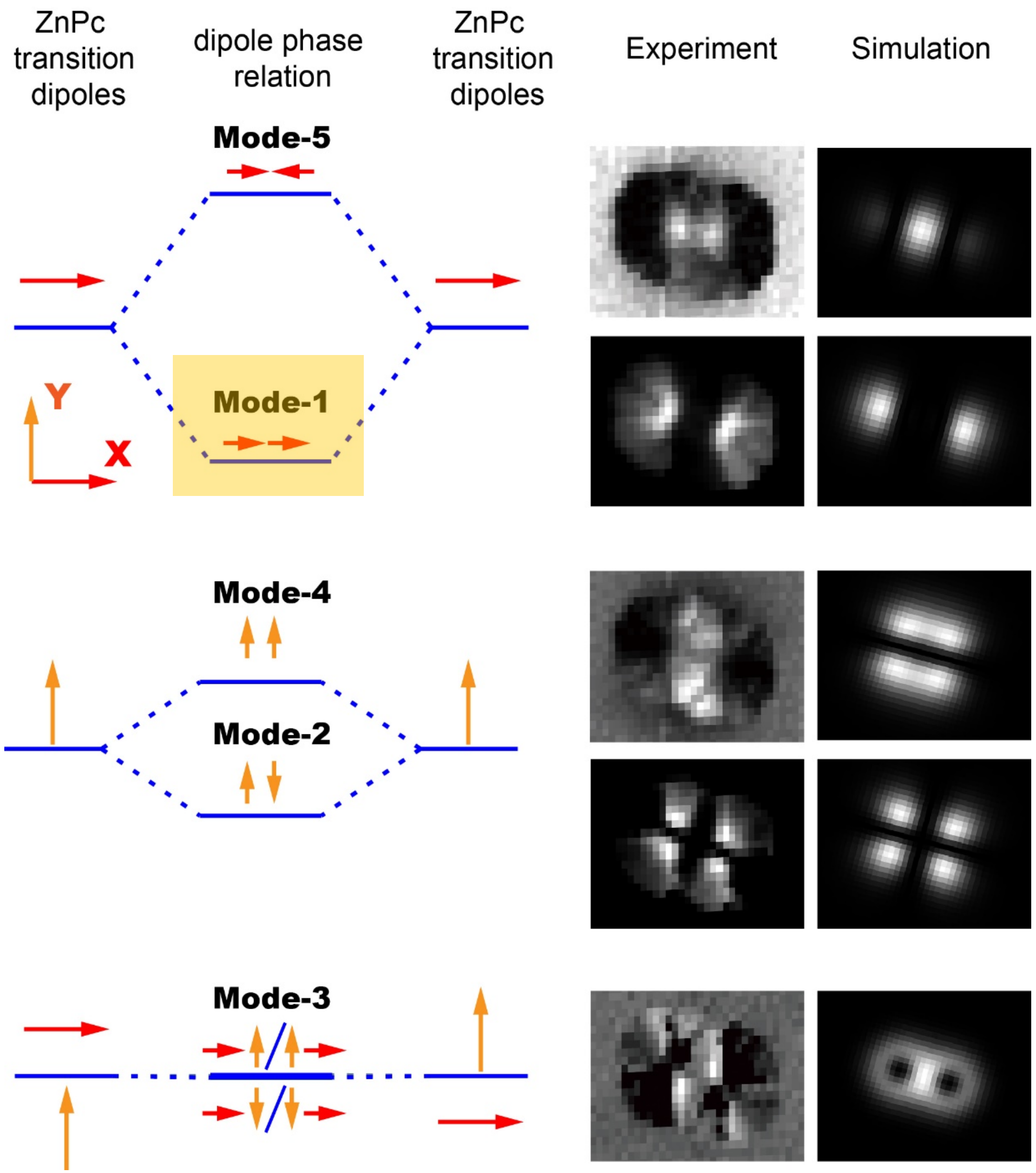
Interactive energy of two dipoles

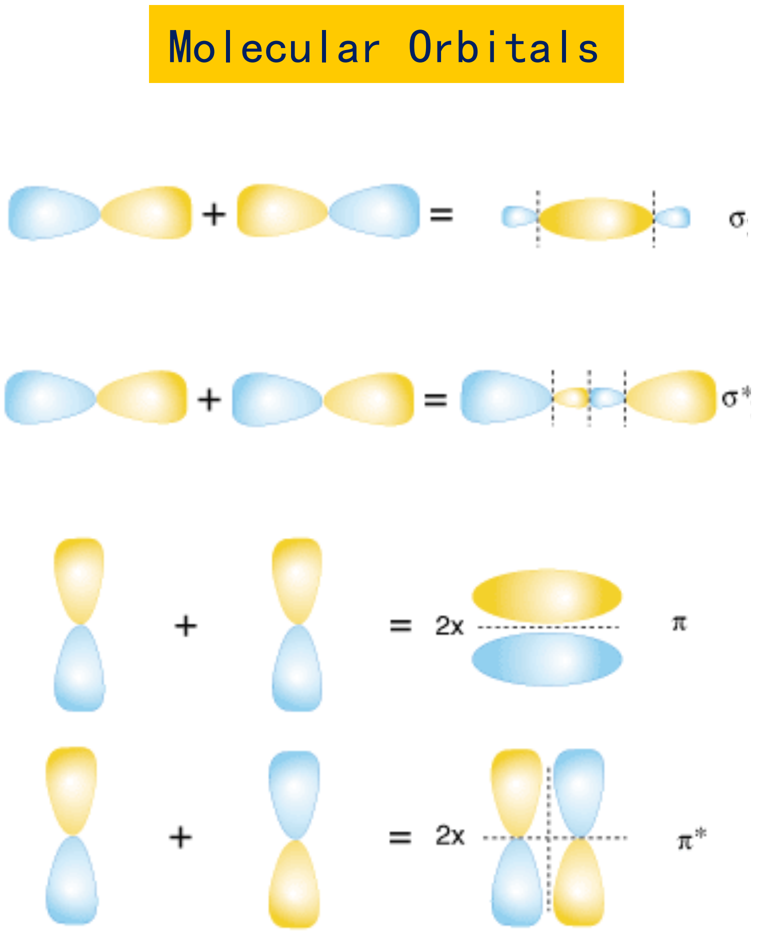
$$J = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{4\pi\varepsilon_0 r^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{4\pi\varepsilon_0 r^5}$$



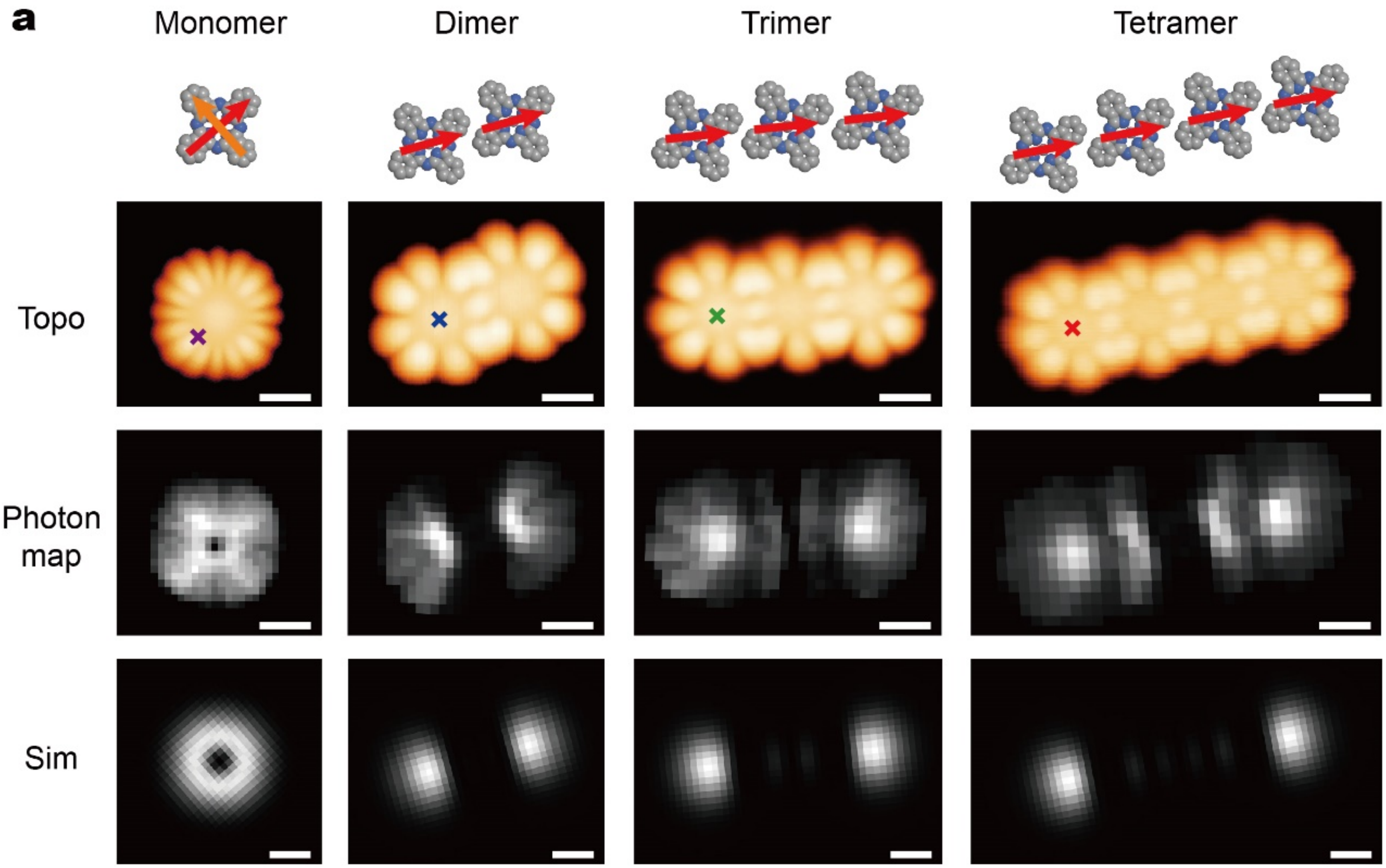


Orbital-like Dipolar Interaction





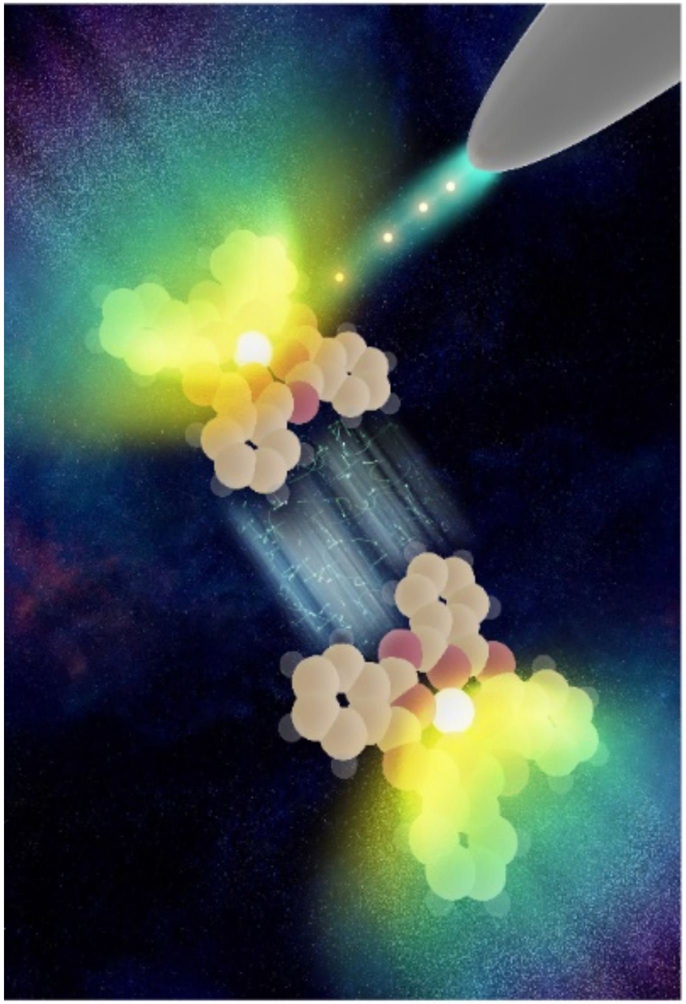
Extension to multi-molecule entangled systems — Superradiant mode-1

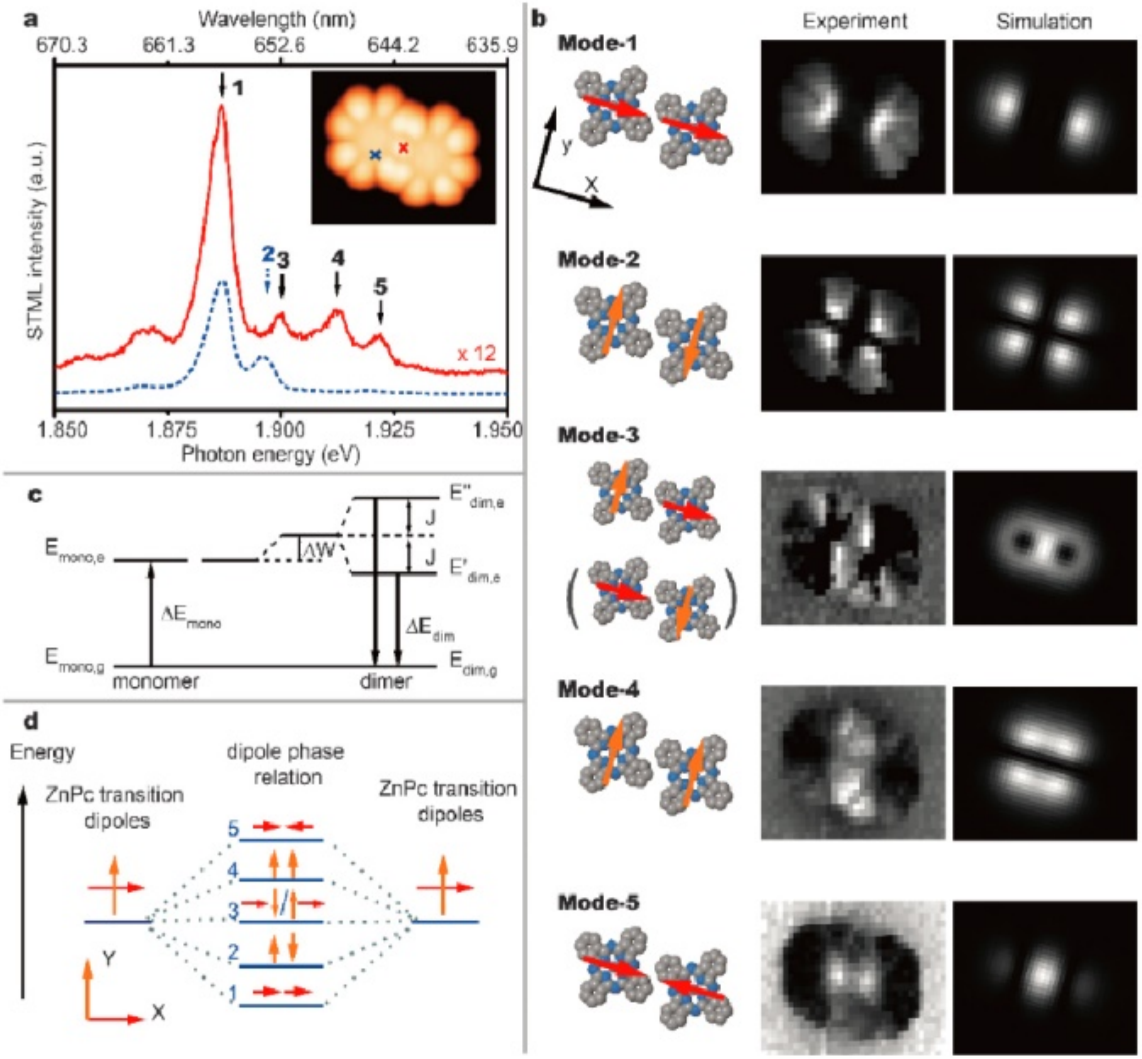


Superradiant mode-1: In-line in-phase coupling!

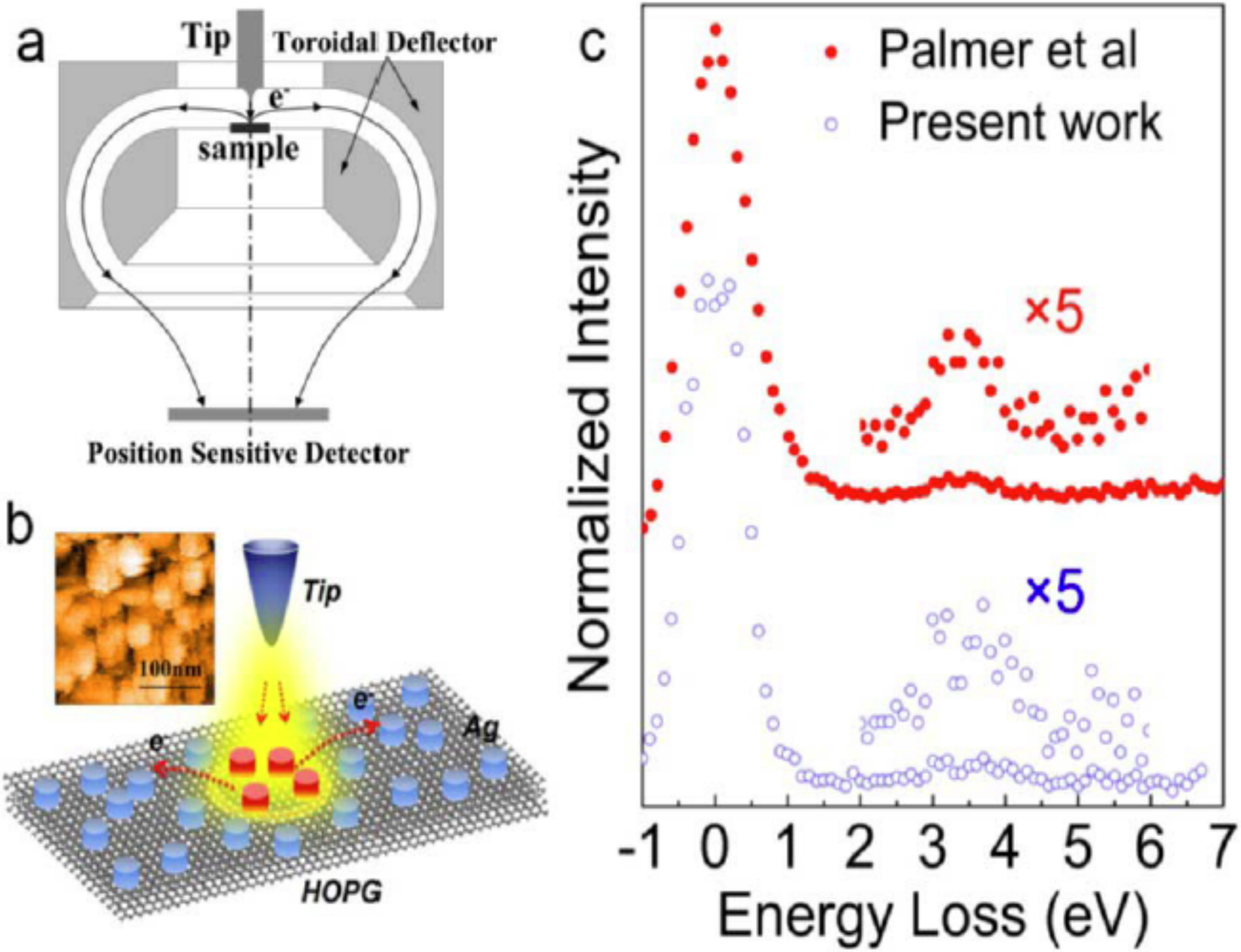
Visualizing coherent intermolecular dipole–dipole coupling in real space

Zhang et al. ***Nature*** 531 (2016) 623



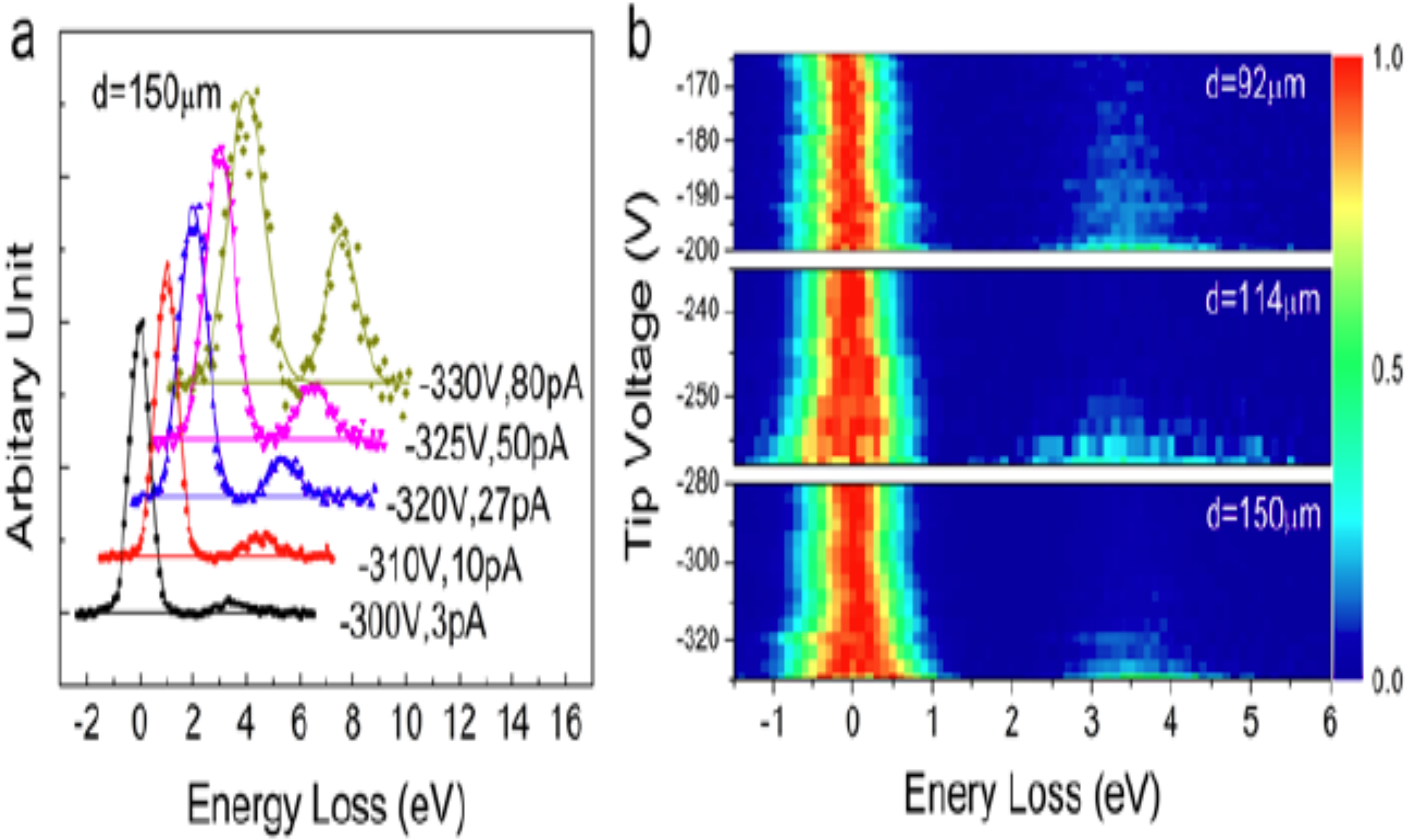


Electron energy loss spectroscopy

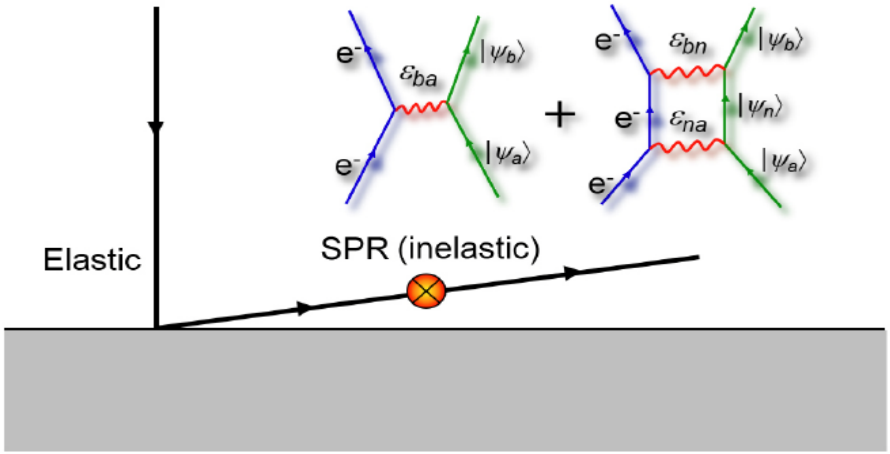


First observation of nonlinear electron scattering

Nonlinear Electron Scattering Spectroscopy (NESS)



Xu et al. , *Nature Physics*, 10 (2014) 753



$$W_{\mathrm{ba}} = W_{\mathrm{ba}}^{(1)} + W_{\mathrm{ba}}^{(2)} \propto |\langle b|\mathbf{E}_1 \cdot \mathbf{D}_{\mathrm{ba}}|a\rangle|^2 + \left| \sum_n \frac{\langle b|\mathbf{E}_2 \cdot \mathbf{D}_{\mathrm{bn}}|n\rangle \langle n|\mathbf{E}_1 \cdot \mathbf{D}_{\mathrm{na}}|b\rangle}{\Gamma_n/2} \right|^2$$

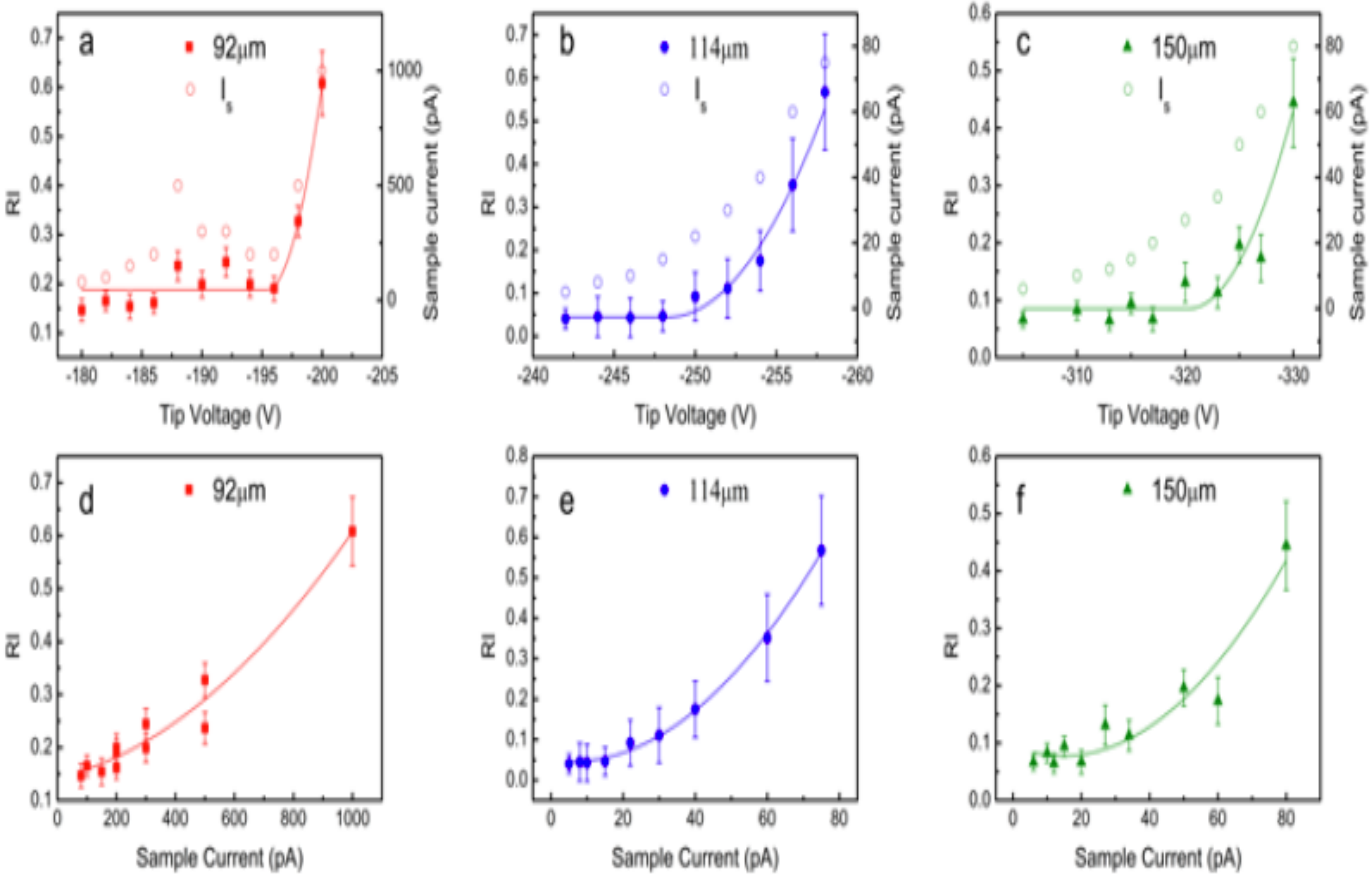
$$W_{\mathrm{ba}} \approx W_{\mathrm{ba}}^{(1)} \propto |\langle b|\mathbf{E}_1 \cdot \mathbf{D}_{\mathrm{ba}}|a\rangle|^2 \propto (\mu_{\mathrm{ba}} E_1)^2$$

$$W_{\mathrm{ba}}^{(2)} \propto \left| \frac{\langle b|\mathbf{E}_2 \cdot \mathbf{D}_b|b\rangle \langle b|\mathbf{E}_1 \cdot \mathbf{D}_{\mathrm{ba}}|a\rangle}{\Gamma_b/2} \right|^2 \propto \left(\frac{2\mu_b E_2}{\Gamma_b} \right)^2 W_{\mathrm{ba}}^{(1)}$$

$$W_{ba} = (1+\beta) W_{ba}^{(1)} \qquad \beta \propto \left(\frac{2\mu_b E_2}{\Gamma_b} \right)^2$$

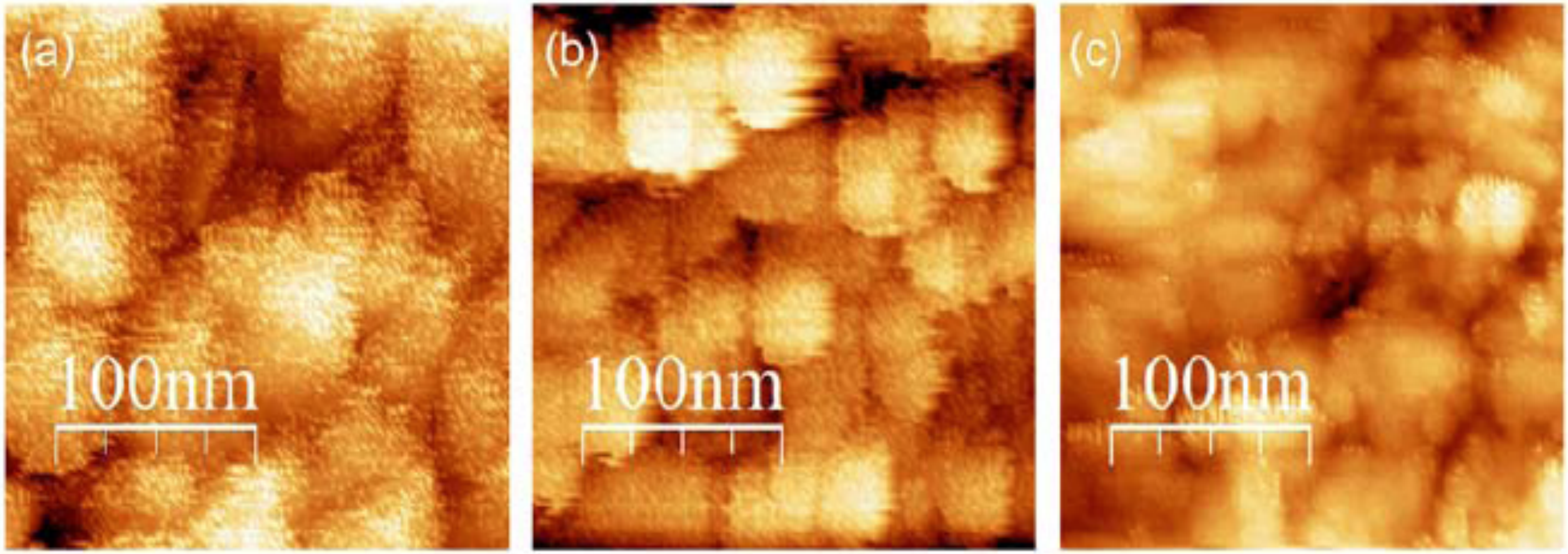
Xu et al. , *Nature Physics*, 10 (2014) 753

Electric field effects



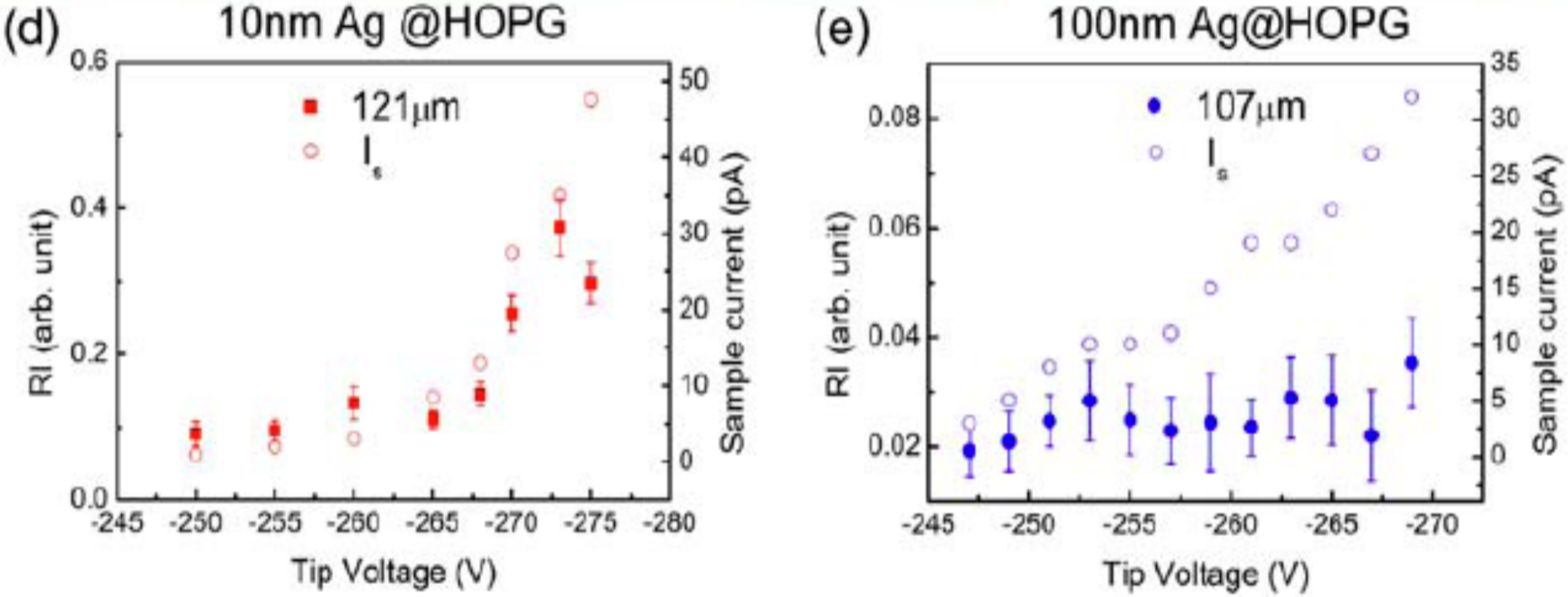
$$\frac{n_{\mathrm{SPR}}}{n_{\mathrm{els}}} = \mathrm{RI}$$

Hot spots

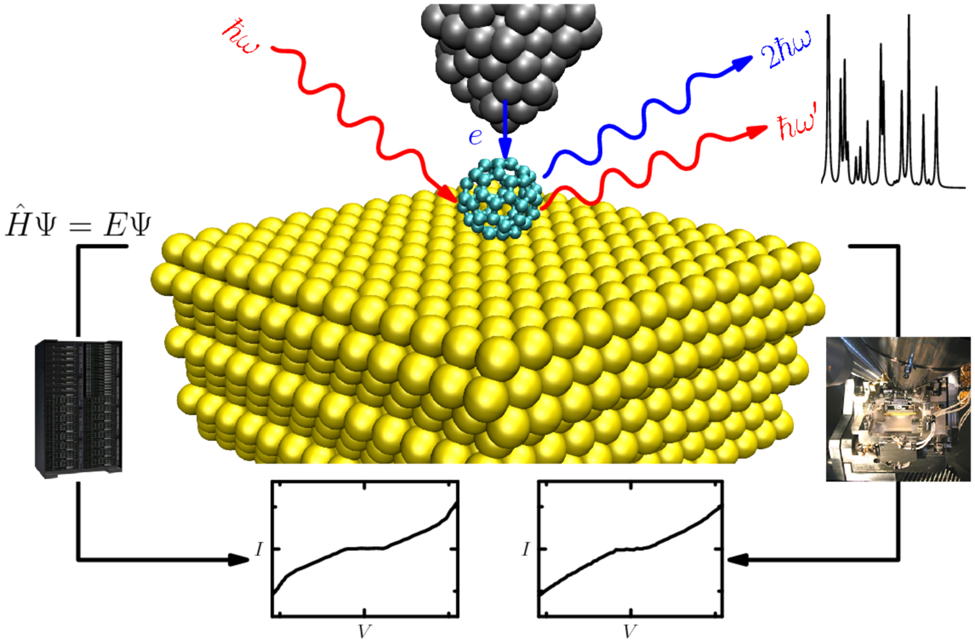

10nm

30nm

100nm

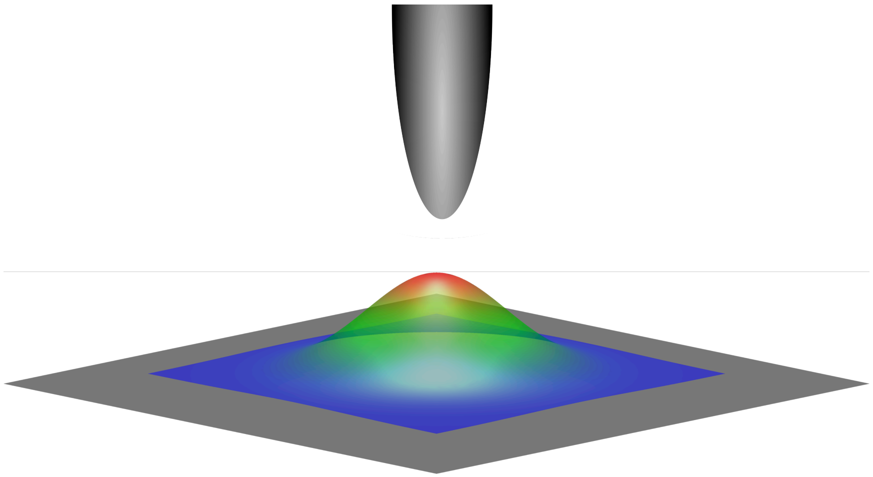


How about the spatial distribution?



Nonlinear effects?

Super-high spatial resolution?



Advantages of near field images: Beyond the diffraction limit

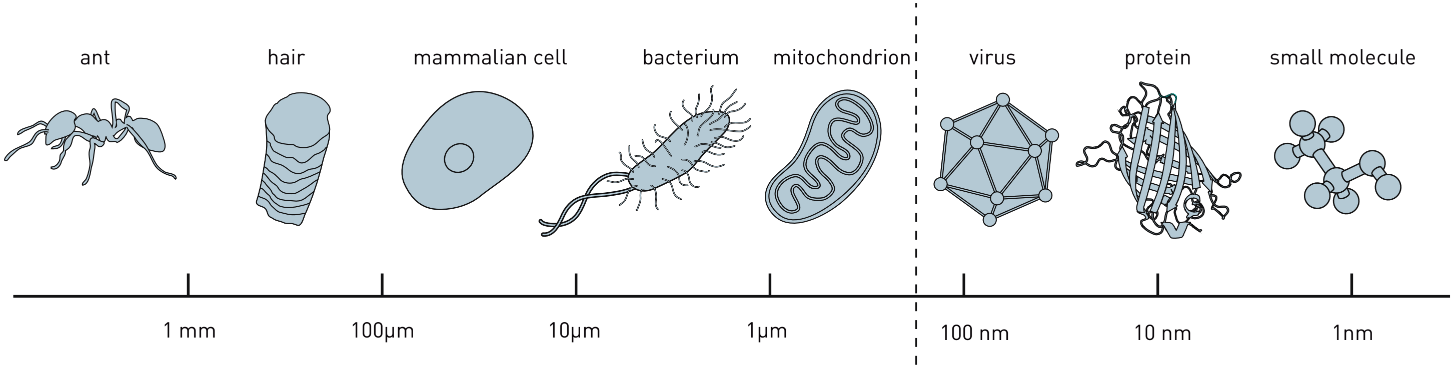
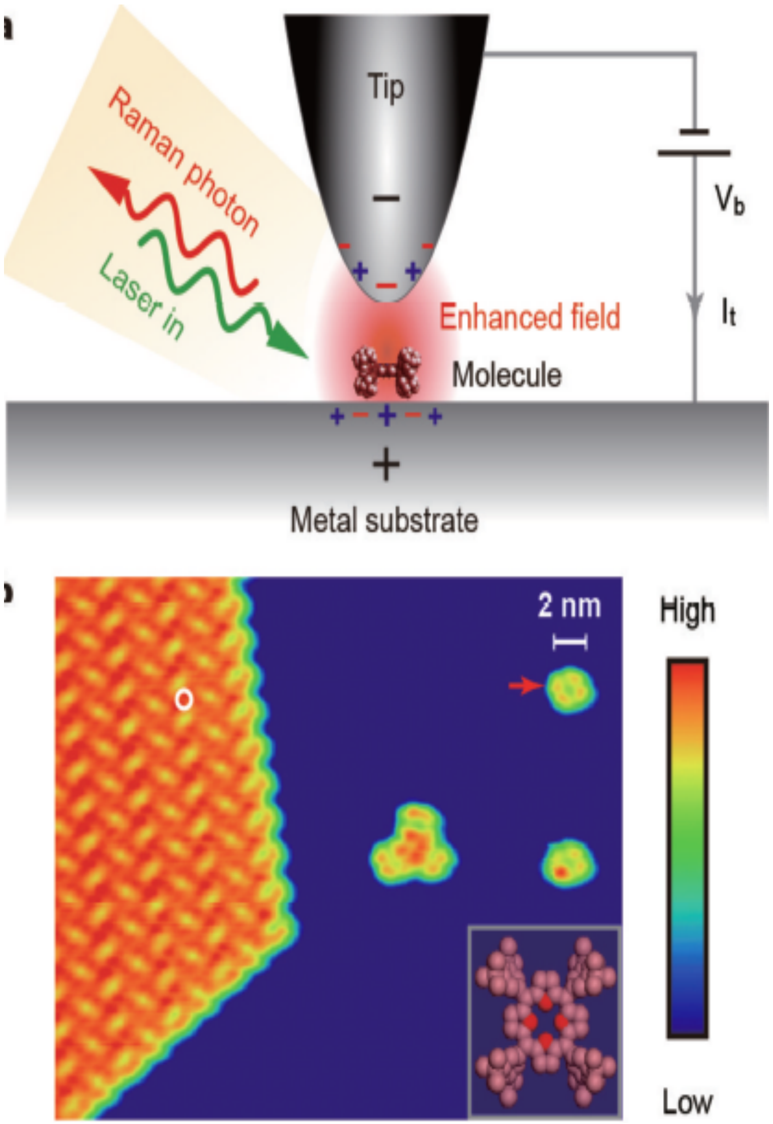
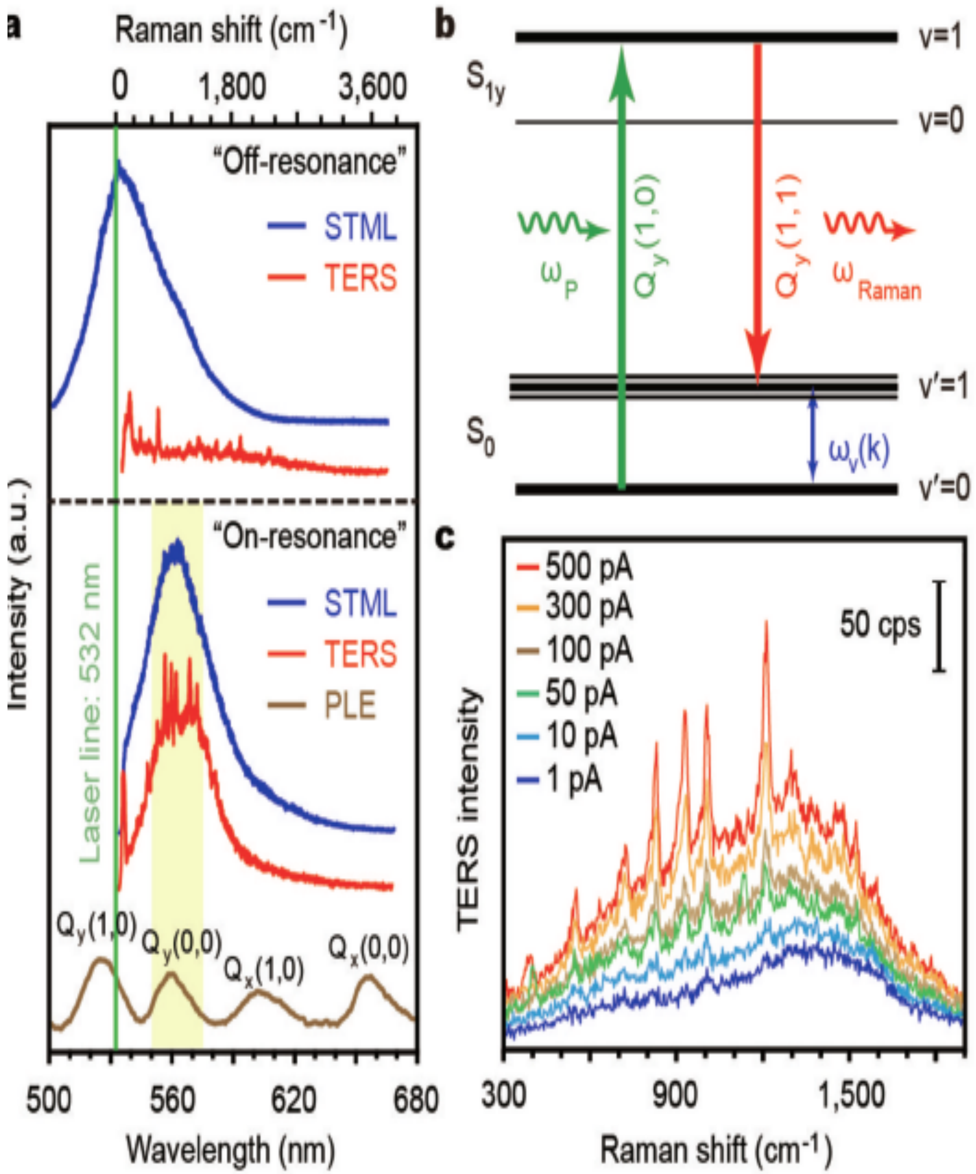


Illustration: © Johan Jarnestad/The Royal Swedish Academy of Sciences

Tip Enhanced Raman Scattering (TERS)

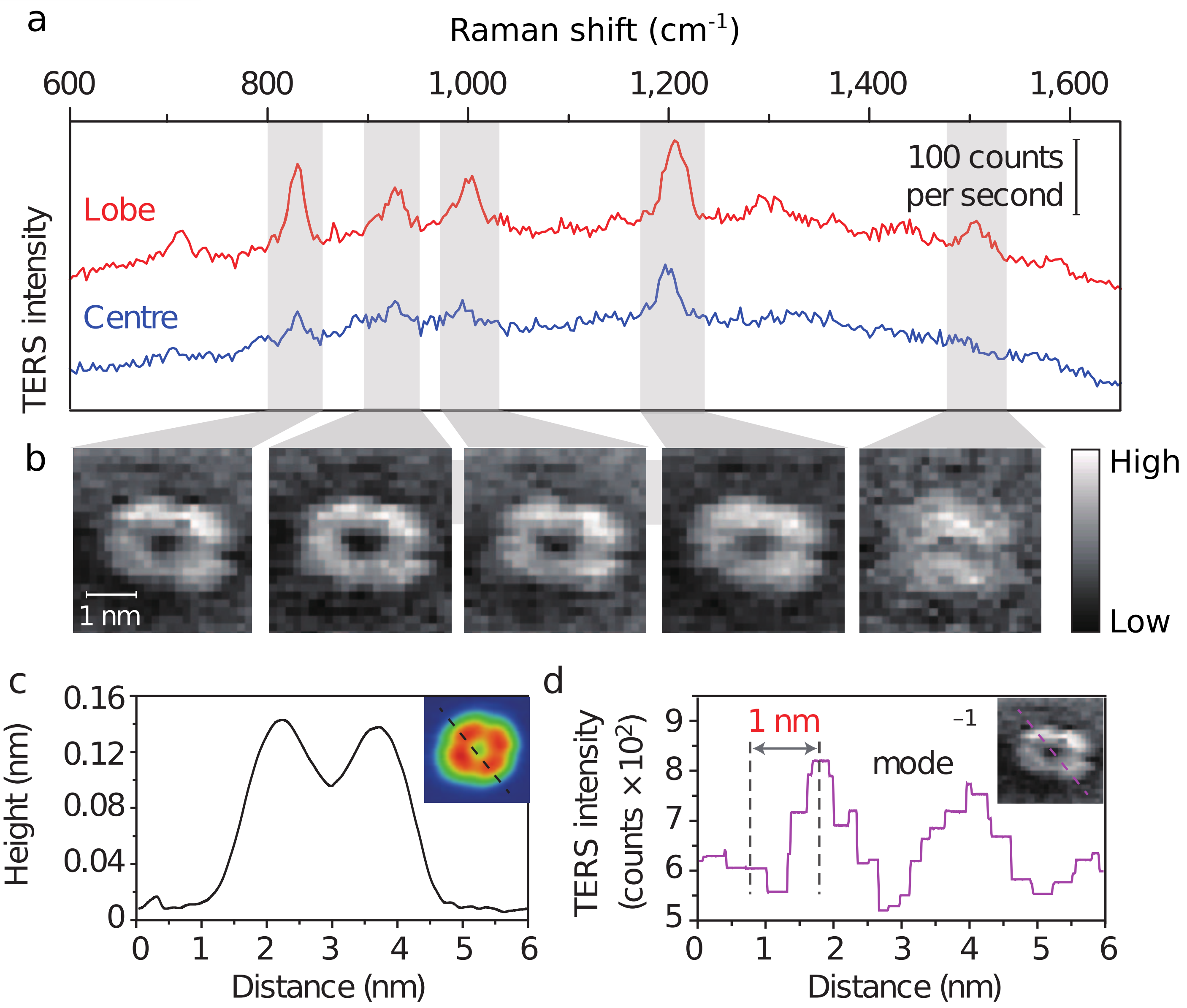




Zhang, et al., *Nature*, **298 (2013) 82.**

H2TBPP on Ag(111)

Sub-nm resolution of optical Raman mapping of a single molecule: structure details



Zhang, et al., *Nature*, 298 (2013) 82.

Light-matter interaction

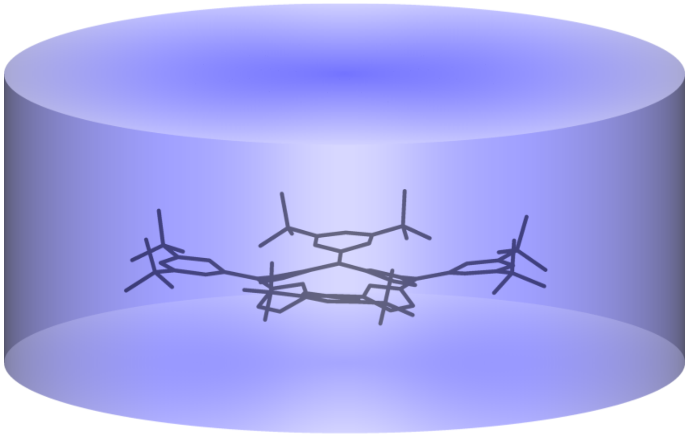
$$\hat{V}(r,t) = -\mu \cdot E(r,t)$$

µ is a position (r) operator, the electric field is position independent.

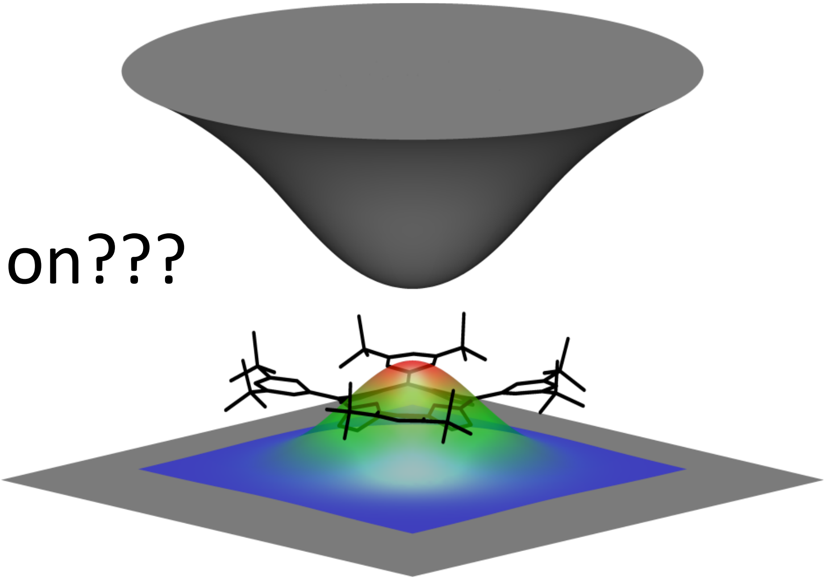
Fine with light: 530nm light, the focusing spot size less than 265nm, much larger than the size of the molecule

$$\Delta x \cdot \Delta p \geq \hbar / 2$$

Plane Wave (Uniform)



Plasmon???



Calling for new theory!!!

Theory: Uniform EM

$$E_p = E_p^0 e^{-\imath\omega_p t}$$

The Albrecht's theory for Raman Intensity

A term:

$$P_0^L(A) = \frac{E_p^0}{\hbar}\langle\psi_g|\mu|\psi_r\rangle\langle\psi_r|\mu|\psi_g\rangle\sum_{v^r=0}^{\infty}\frac{\langle v^f|v^r\rangle\langle v^r|v^i\rangle}{\omega_{e^r v^r:e^g v^i}-\omega_p-\imath\Gamma}+\mathrm{NRT}$$

B term:

$$P_0^L(B) = \frac{E_p^0}{\hbar}\left[\frac{\partial\langle\psi_g|\mu|\psi_r\rangle}{\partial Q_k}\langle\psi_r|\mu|\psi_g\rangle\sum_{v^r=0}^{\infty}\frac{\langle v^f|Q_k|v^r\rangle\langle v^r|v^i\rangle}{\omega_{e^r v^r:e^g v^i}-\omega_p-\imath\Gamma}\right.$$

$$\left.+\langle\psi_g|\mu|\psi_r\rangle\frac{\partial\langle\psi_r|\mu|\psi_g\rangle}{\partial Q_k}\sum_{v^r=0}^{\infty}\frac{\langle v^f|v^r\rangle\langle v^r|Q_k|v^i\rangle}{\omega_{e^r v^r:e^g v^i}-\omega_p-\imath\Gamma}\right]+\mathrm{NRT}$$

Theory: Confined localized electromagnetic field

$$E_p = M_i E_p^0 g(\mathbf{r}) e^{-\imath\omega_p t}$$

Raman Intensity:

A term:

$$P_0^L(A) = \frac{\sqrt{F_P}\, M_i E_p^0}{\hbar}\left[\langle\psi_g|\mu|\psi_r\rangle\langle\psi_r|\mu g(\mathbf{r})|\psi_g\rangle\sum_{v^r=0}^{\infty}\frac{\langle v^f|v^r\rangle\langle v^r|v^i\rangle}{\omega_{e^r v^r:e^g v^i}-\omega_p-\imath\Gamma}\right]+\mathrm{NRT}$$

B term:

$$\begin{aligned}P_0^L(B) = \frac{\sqrt{F_P}\, M_i E_p^0}{\hbar}\Bigg[&\frac{\partial\langle\psi_g|\mu|\psi_r\rangle}{\partial Q_k}\langle\psi_r|\mu g(\mathbf{r})|\psi_g\rangle\sum_{v^r=0}^{\infty}\frac{\langle v^f|Q_k|v^r\rangle\langle v^r|v^i\rangle}{\omega_{e^r v^r:e^g v^i}-\omega_p-\imath\Gamma}\\ &+\langle\psi_g|\mu|\psi_r\rangle\frac{\partial\langle\psi_r|\mu g(\mathbf{r})|\psi_g\rangle}{\partial Q_k}\sum_{v^r=0}^{\infty}\frac{\langle v^f|v^r\rangle\langle v^r|Q_k|v^i\rangle}{\omega_{e^r v^r:e^g v^i}-\omega_p-\imath\Gamma}\Bigg]+\mathrm{NRT}\end{aligned}$$

Uniform Confined

$$\langle\psi_r|\mu|\psi_g\rangle \rightarrow \langle\psi_r|\mu g(\mathbf{r})|\psi_g\rangle$$

Duan et al. J. Am. Chem. Soc. **137 (2015) 9515**

Theory: Confined localized field induced nonlinear effects

$$E_p = M_i E_p^0 g(\mathbf{r}) e^{-\imath\omega_p t} \qquad E_s = M_s E_p^0 g(\mathbf{r}) e^{-t^2/2\tau_s^2} e^{-\imath\omega_s t}$$

Induced nonlinear polarization:

A term:

$$P_0^{NL}(A) = \frac{M_i^2 M_s |E_p^0|^2 E_s^0 \sqrt{2\pi}\tau_s}{\hbar^3} \langle\psi_r|\mu|\psi_g\rangle \langle\psi_r|\mu g(\mathbf{r})|\psi_g\rangle^3$$

$$\times \sum_{v^r,v^{r'}} \langle v^f|v^r\rangle\langle v^r|v^i\rangle\langle v^i|v^{r'}\rangle\langle v^{r'}|v^f\rangle \lambda^{(3)} + \text{NRT}$$

B term:

$$P_0^{NL}(B) = \frac{M_i^2 M_s |E_p^0|^2 E_s^0 \sqrt{2\pi}\tau_s}{\hbar^3} \left[\frac{\partial\langle\psi_r|\mu|\psi_g\rangle}{\partial Q_k} \langle\psi_r|\mu g(\mathbf{r})|\psi_g\rangle^3 \right.$$

$$\times \sum_{v^r,v^{r'}} \langle v^f|v^r\rangle\langle v^r|v^i\rangle\langle v^i|v^{r'}\rangle\langle v^{r'}|v^f\rangle \lambda^{(3)}$$

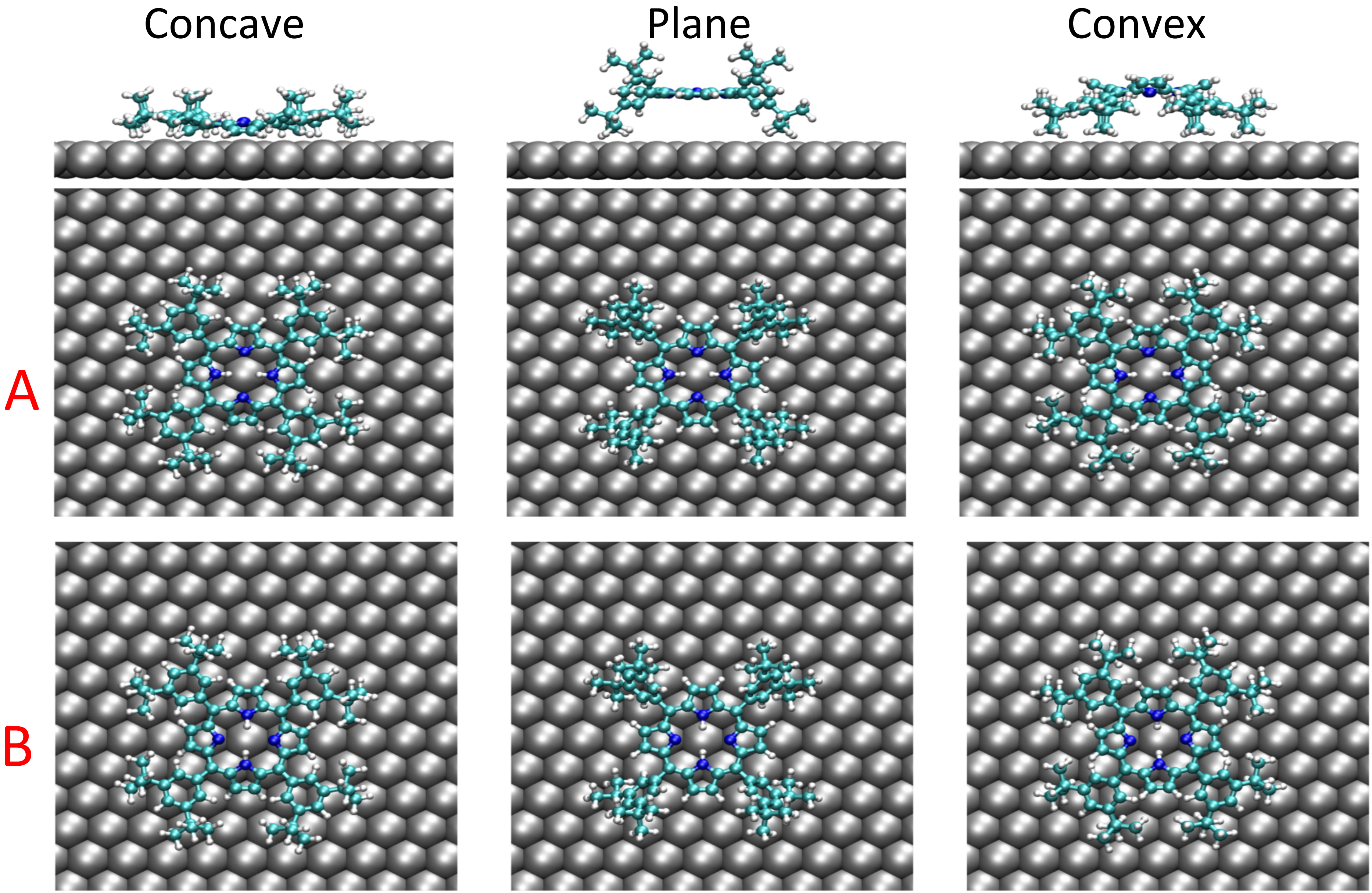
$$+ \langle\psi_r|\mu|\psi_g\rangle \frac{\partial\langle\psi_r|\mu g(\mathbf{r})|\psi_g\rangle}{\partial Q_k} \langle\psi_r|\mu g(\mathbf{r})|\psi_g\rangle^2$$

$$\times \sum_{v^r,v^{r'}} \Big(\langle v^f|v^r\rangle\langle v^r|Q_k|v^i\rangle\langle v^i|v^{r'}\rangle\langle v^{r'}|v^f\rangle$$

$$+ \langle v^f|v^r\rangle\langle v^r|v^i\rangle\langle v^i|Q_k|v^{r'}\rangle\langle v^{r'}|v^f\rangle$$

$$\left. + \langle v^f|v^r\rangle\langle v^r|v^i\rangle\langle v^i|v^{r'}\rangle\langle v^{r'}|Q_k|v^f\rangle \Big) \lambda^{(3)} \right] + \text{NRT}$$

Possible structures of H2TBPP on Ag(111)



Concave

Plane

Convex

A

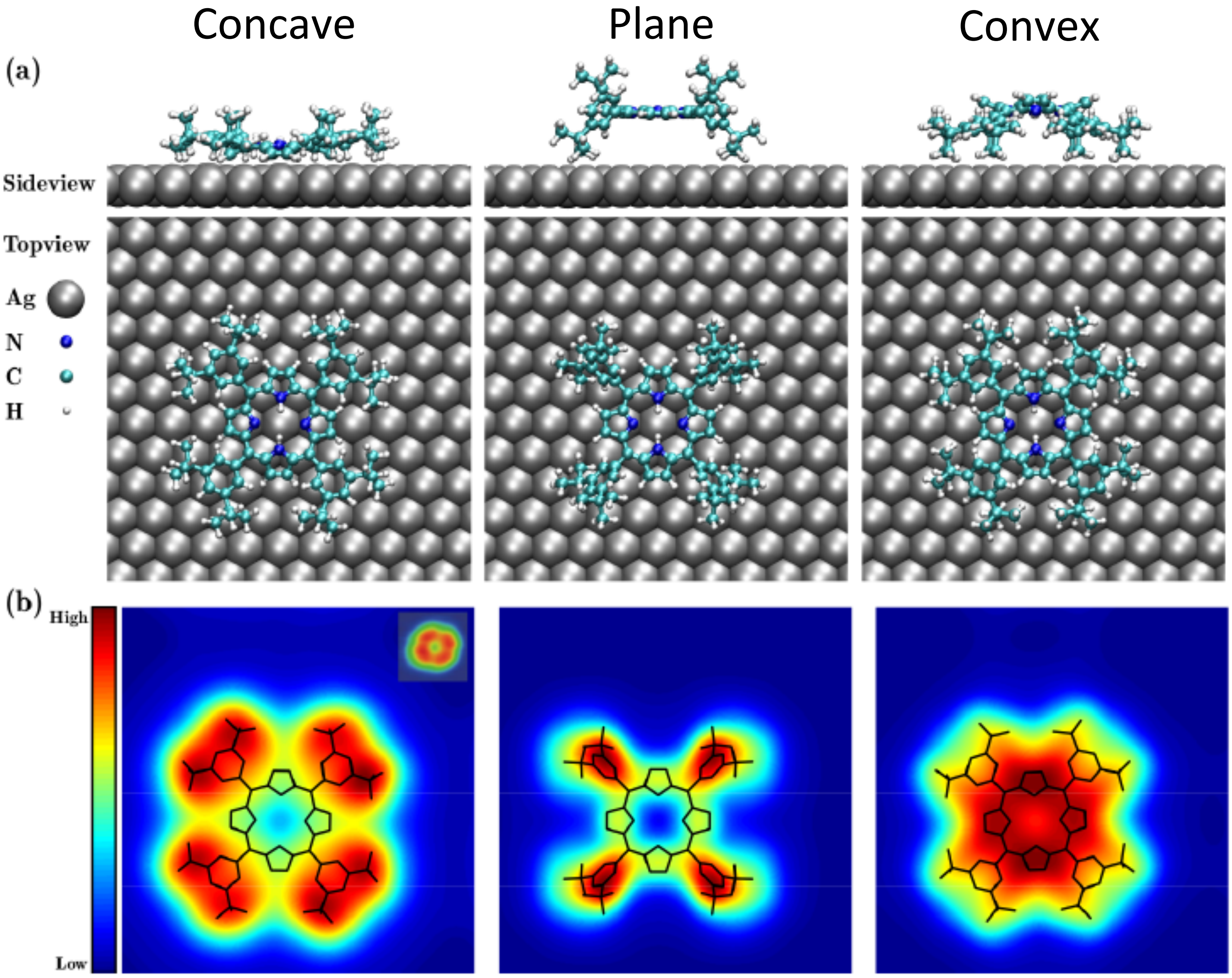
B

Energies (in eV)

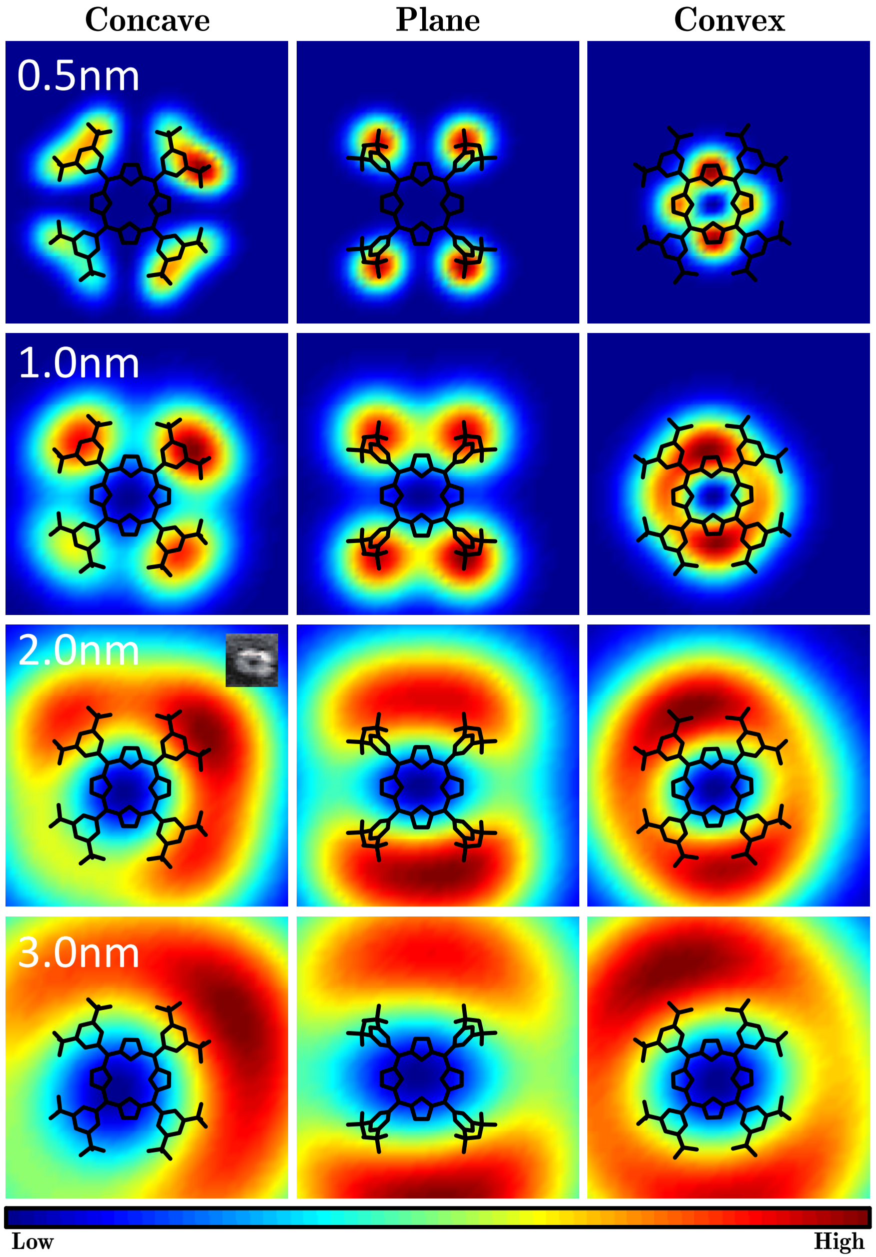
	Concave		Plane		Convex	
Conf.	**A**	**B**	**A**	**B**	**A**	**B**
E_{ads}	4.17	4.19	2.69	2.68	1.26	1.22
E_{s1}	1.66	1.67	2.11	2.11	1.59	1.60
E_{s2}	1.78	1.78	2.25	2.25	1.70	1.67
E_{s3}	2.47	2.48	3.11	3.10	2.36	2.37
E_{s4}	2.57	2.56	3.20	3.20	2.43	2.42

- Experimental excitation energy is 2.33 eV

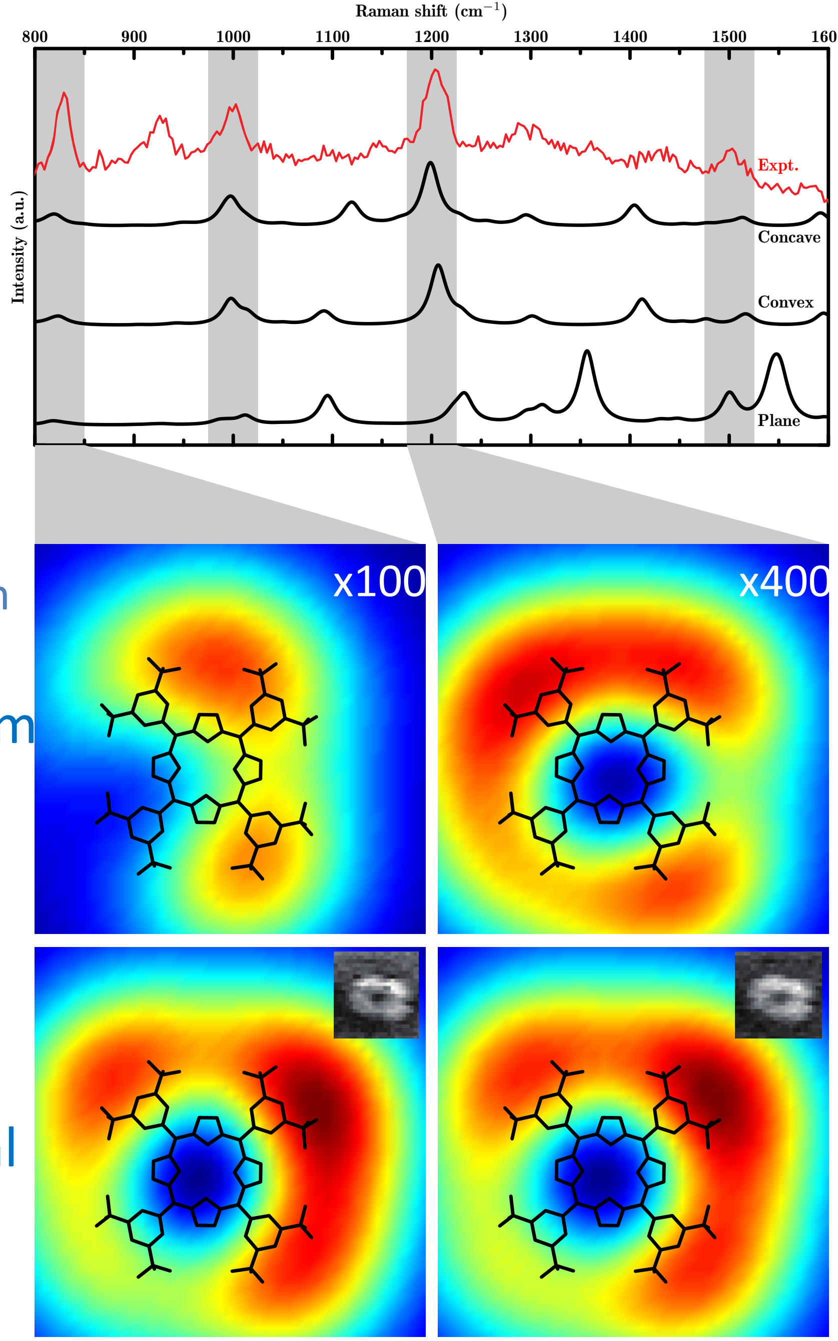
Calculated STM images



Calculated Raman images



A term

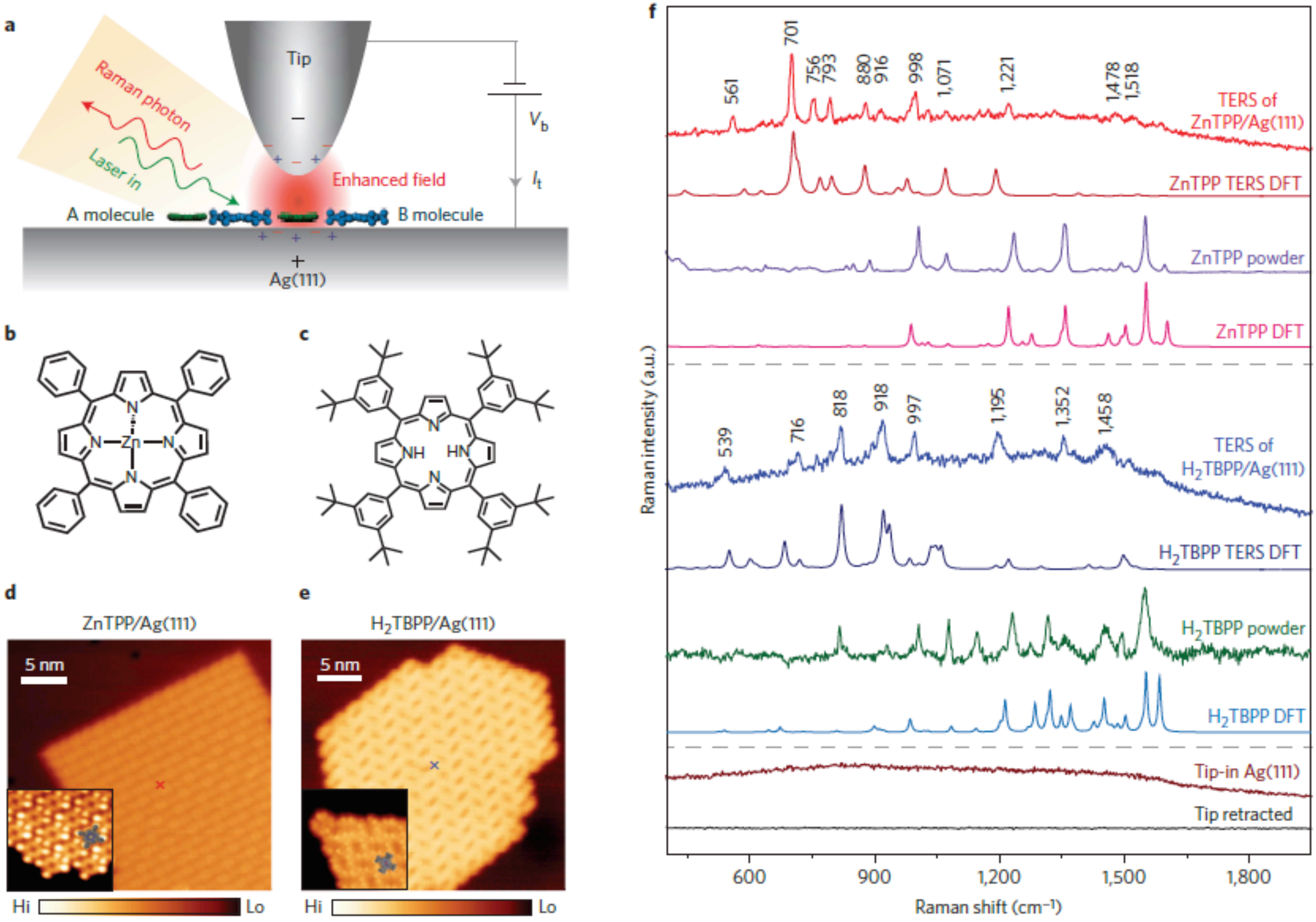


2.0nm

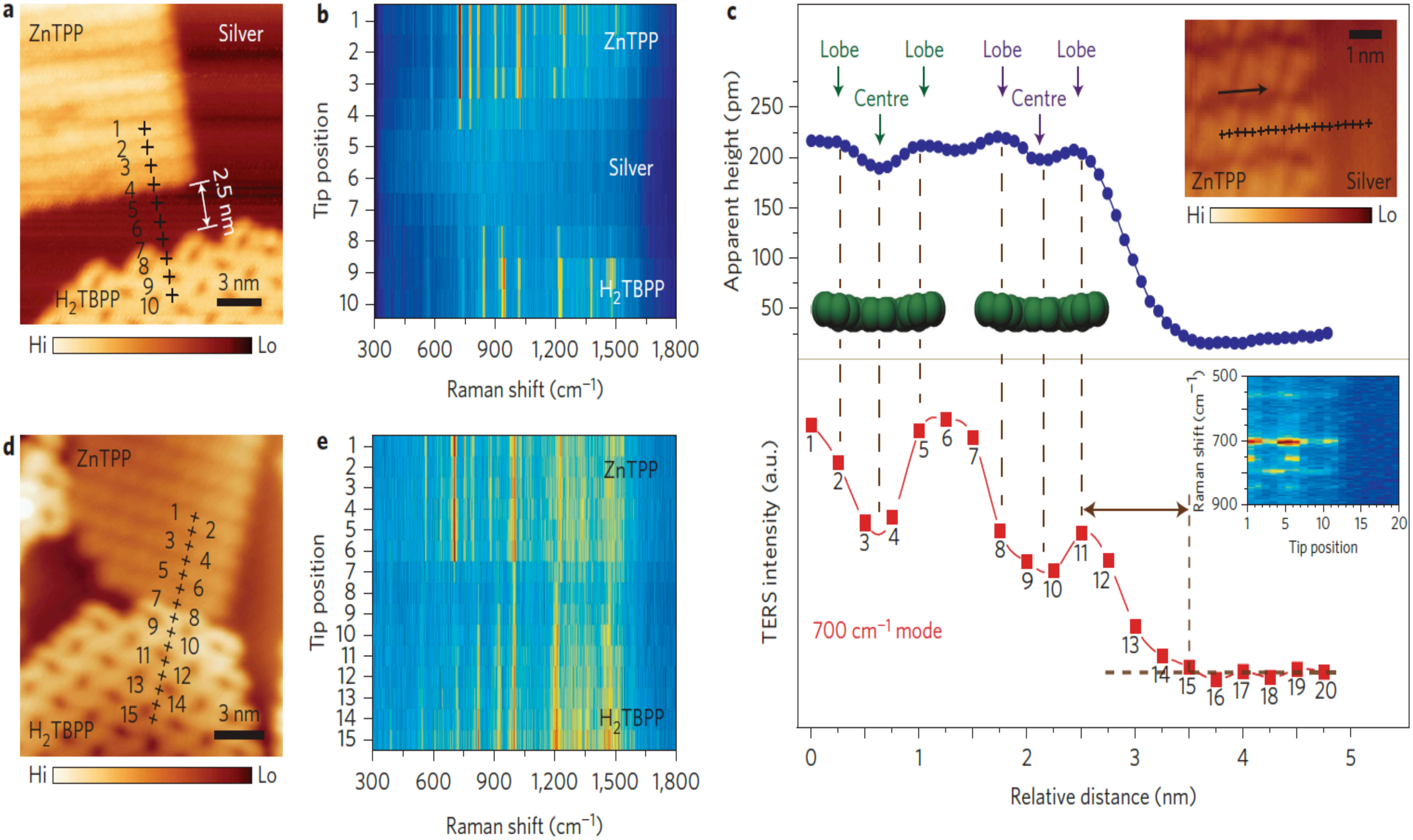
B term

Total

Distinguishing adjacent molecules on a surface



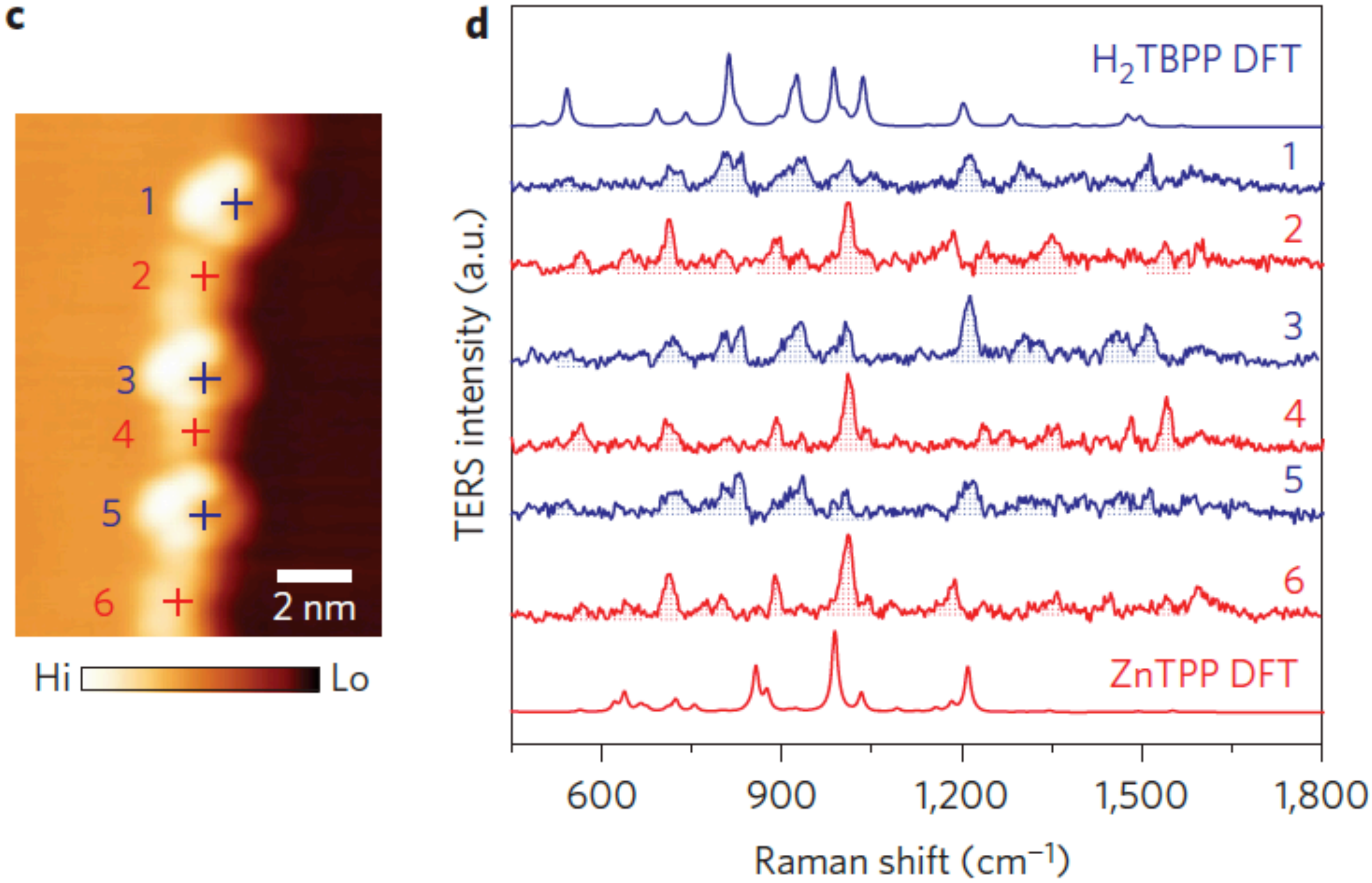
Jiang et al. ***Nature Nanotechnology*** **10**, (2015) 865



Distinguishing between ZnTPP and H2TBPP domains. a, STM topograph of two separated molecular islands (1 V, 100 pA). b, Corresponding spectral evolution for ten sequential TERS measurements along the line trace marked in a (0.1 V, 1 nA, 30 s) with a step size of 1 nm. c, Fine details of spectral evolution across the molecular island edge for ZnTPP molecules with a step size of 0.25 nm. Top: height profile for the line trace marked in the right inset (0.75 V, 10 pA). Bottom: corresponding TERS intensity profile for the 700 cm−1 mode (integrated over 670−730 cm−1) shown in the right inset (0.1 V, 1 nA, 10 s). d, STM topograph of two adjacent molecular islands (0.6 V, 10 pA). e, Corresponding spectral evolution for 15 sequential TERS measurements along the line trace marked in d (0.1 V, 1 nA, 10 s) with a step size of 0.75 nm.

Distinguishing adjacent molecules on a surface

The spatial distribution of the plasmonic field should be localized within 2nm



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Nonresonant Raman: Theory

- Sum over all possible states
- Take care of prior summation of the vibrational states

Linear:

$$P_0^L = 2\sqrt{F_P}\, M_i E_i^0 \frac{\partial \alpha_{\mathrm{eff}}}{\partial Q_k} \langle v^f \,|\, Q_k \,|\, v^i \rangle$$

Noninear:

$$P_0^{NL} = \lambda \frac{\partial \alpha_{\mathrm{eff}}}{\partial Q_k} \frac{\partial \alpha'_{\mathrm{eff}}}{\partial Q_k} \langle v^f \,|\, Q_k \,|\, v^i \rangle^2$$

where

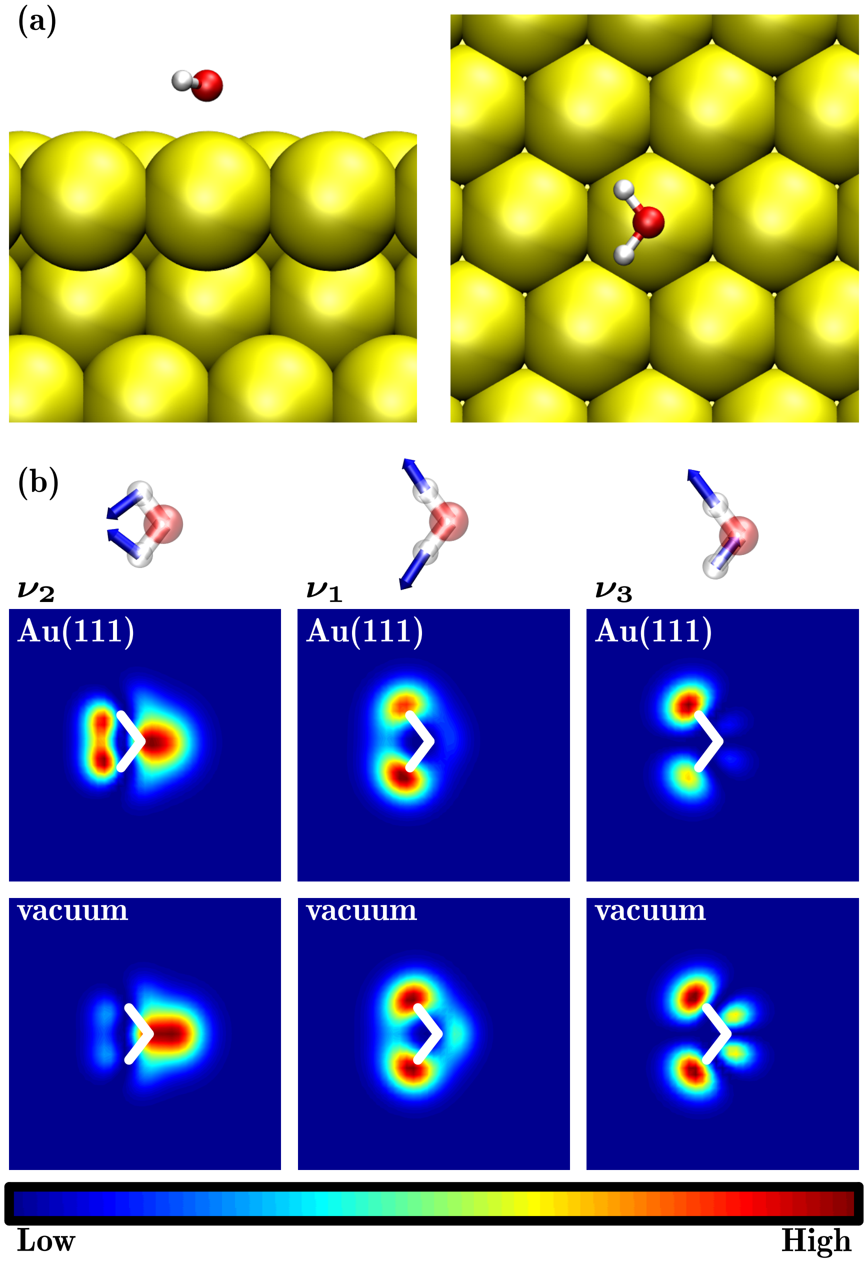
$$\alpha_{\mathrm{eff}} = \sum_r \frac{\langle \psi_g \,|\, \mu \,|\, \psi_r \rangle \langle \psi_r \,|\, \mu g \,|\, \psi_g \rangle}{E_{e^r:e^g}}$$

$$\alpha'_{\mathrm{eff}} = \sum_r \frac{\langle \psi_g \,|\, \mu g \,|\, \psi_r \rangle \langle \psi_r \,|\, \mu g \,|\, \psi_g \rangle}{E_{e^r:e^g}}$$

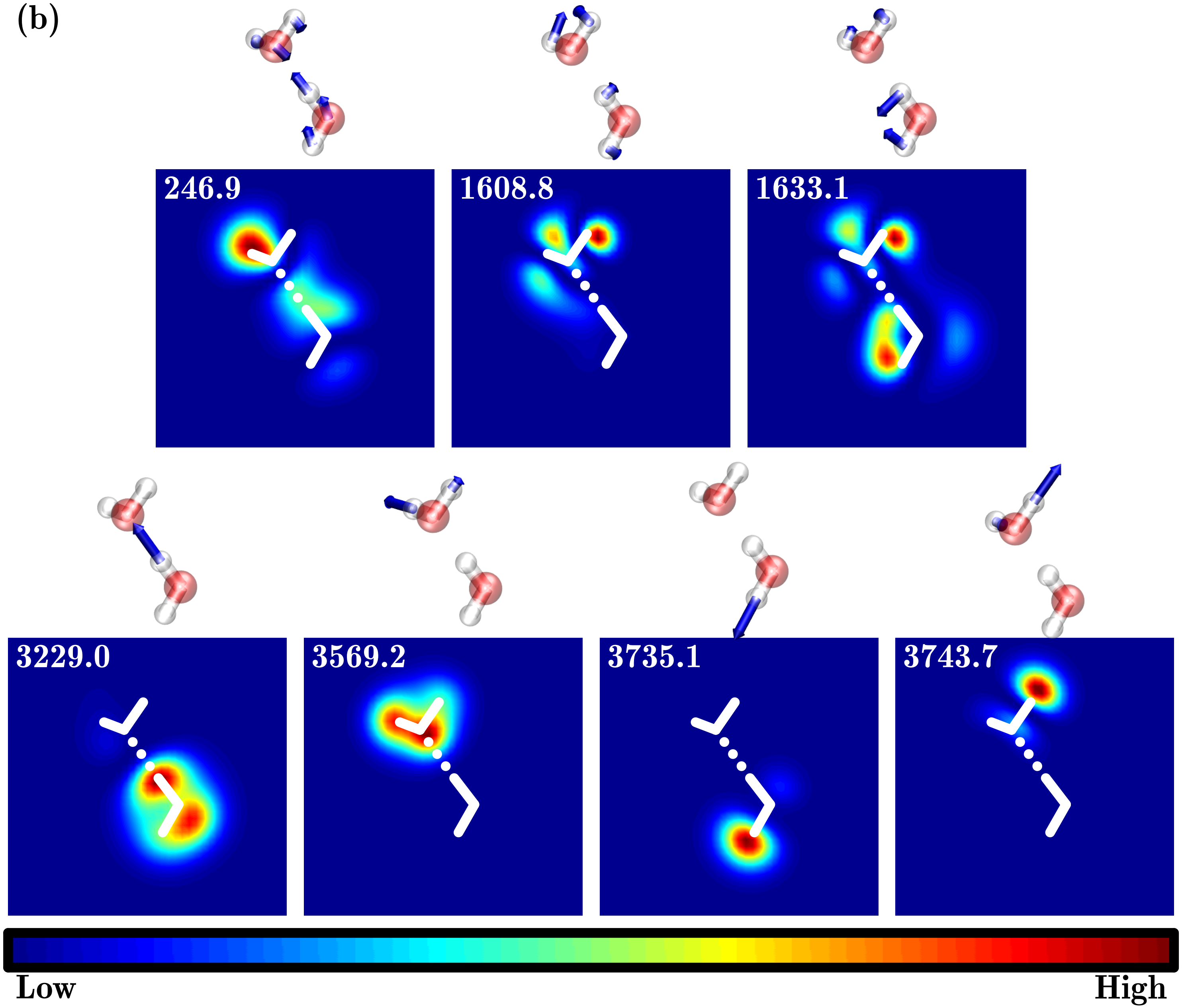
Duan et al., Angew. Chem. Int. Ed., 128 (2016) 1053 –1057

Nonresonant Raman: Water monomer

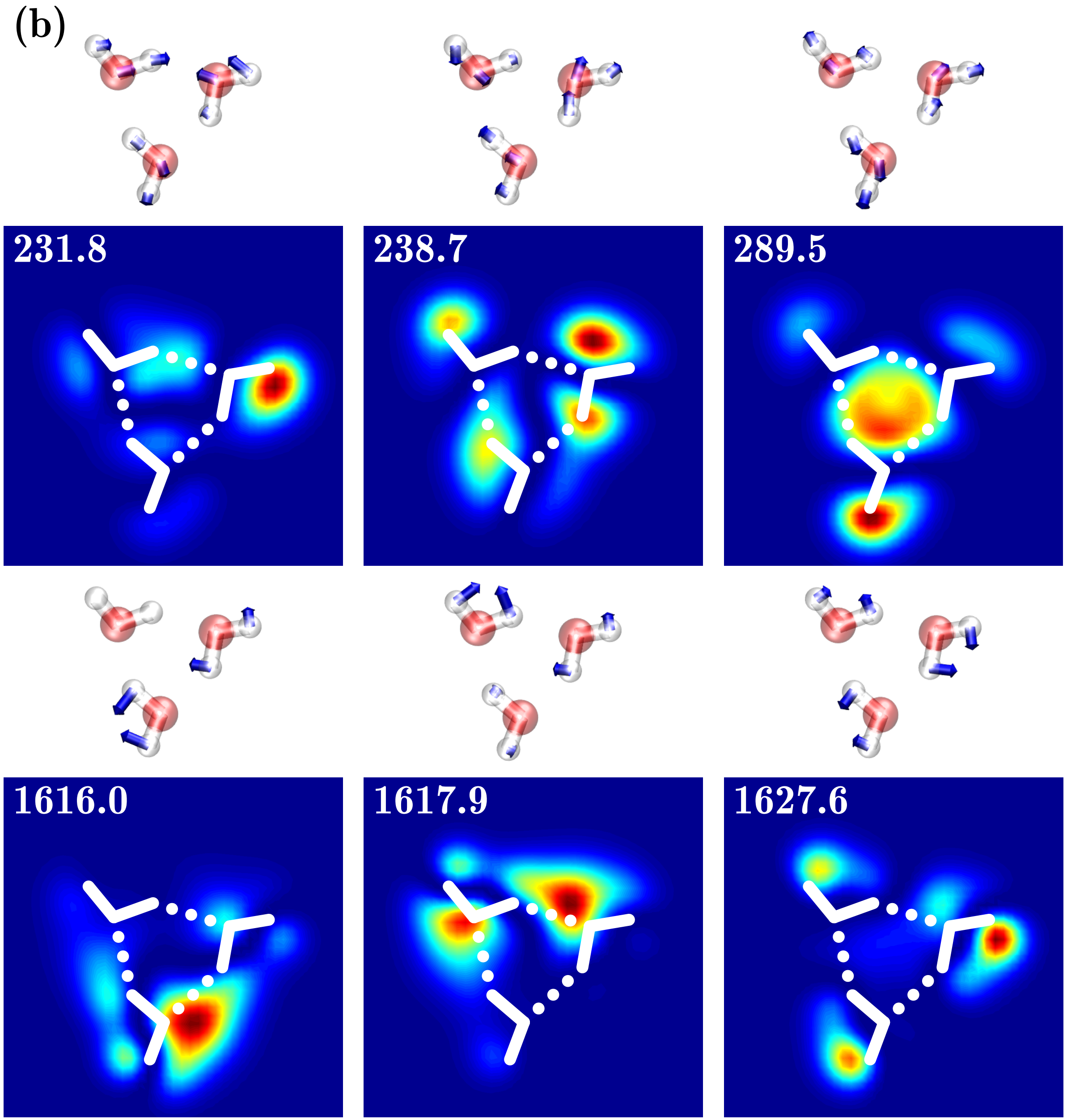
1 Å



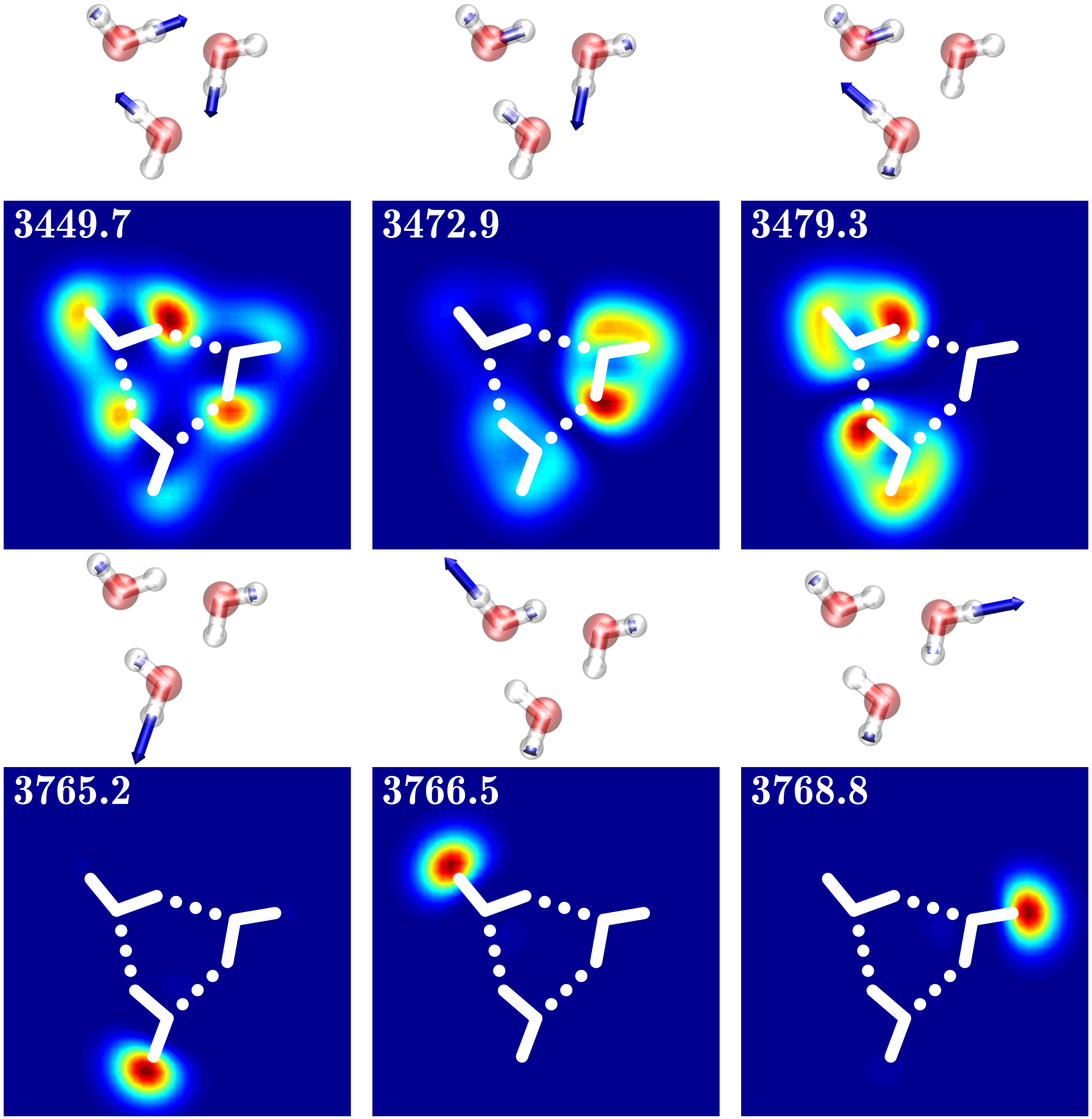
Nonresonant Raman: Water dimer



Nonresonant Raman: Water trimer



Nonresonant Raman: Water trimer



Acknowledgement

Dr. Sai Duan
KTH, Sweden

Dr. Guangjun Tian
KTH, Sweden

Dr. Yongfei Ji
KTH, Sweden

USTC

Experiments

Prof. ZhenChao Dong
Prof. Jianguo Hou
Prof. Xiangjun Chen

Swedish Research Council (VR)
Göran Gustafsson Foundation
Natural Science Foundation of China
Chinese Academy of Science
Ministry of Science and Technology of China