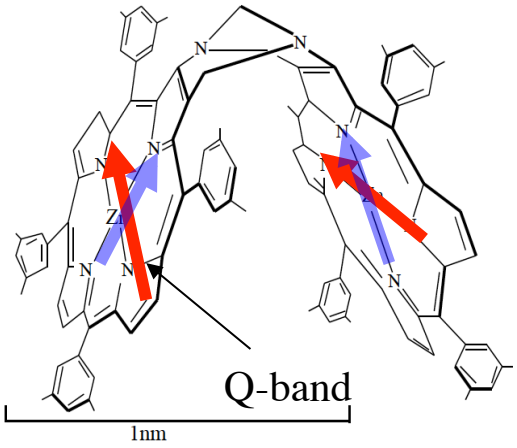
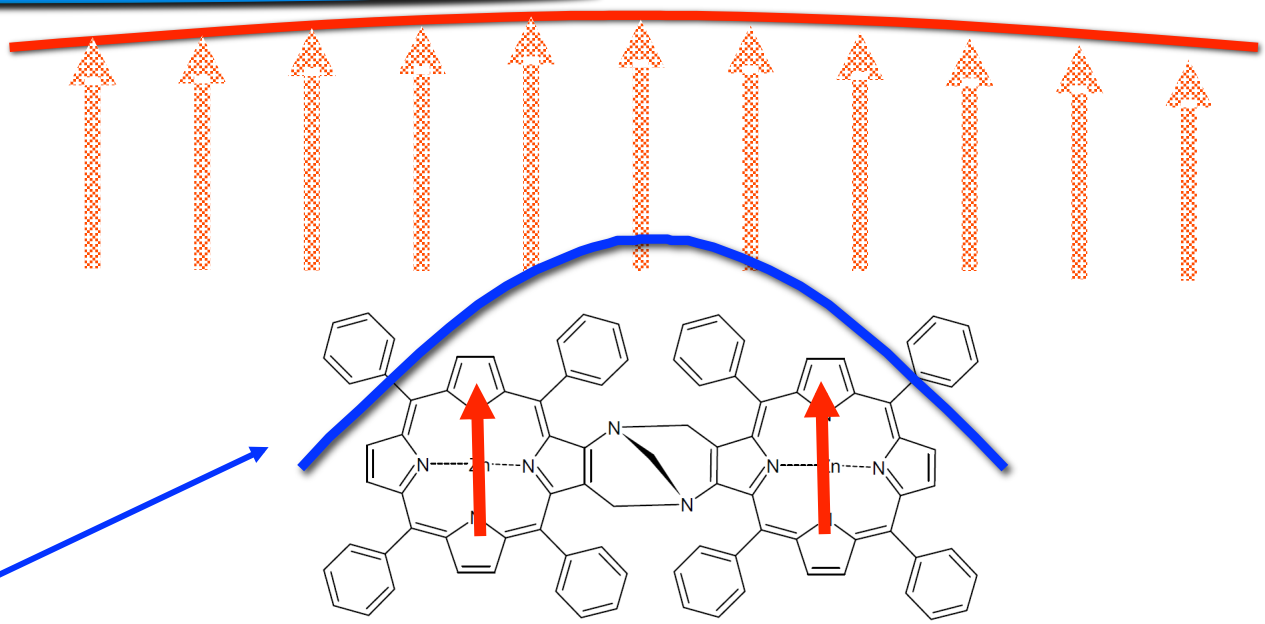
光で操るナノ物質のミクロな状態

- 局在電場による遷移選択則の破綻

分子系の長波長近似

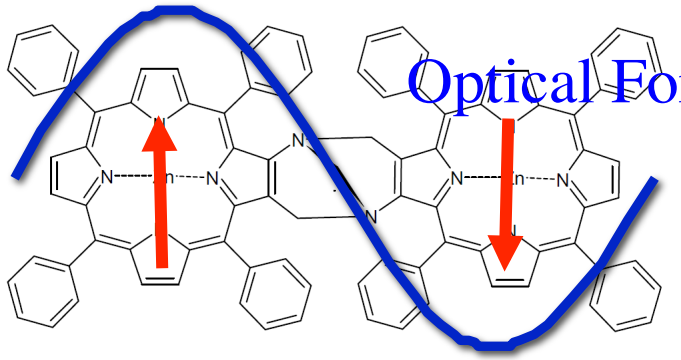


Tröger’s base porphyrin dimer



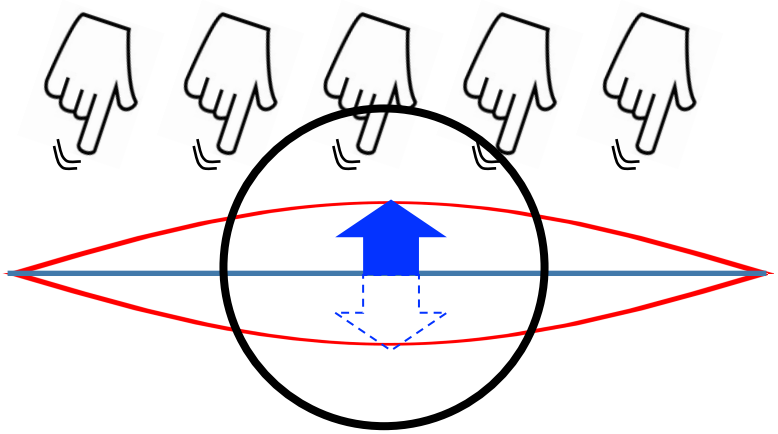
Optical Allowed

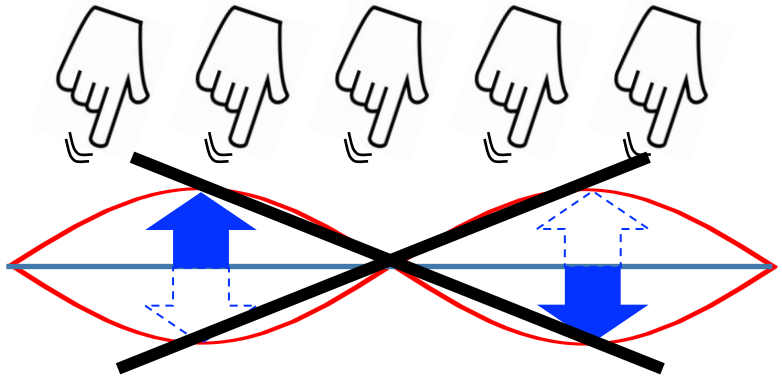
Split by interaction between molecules

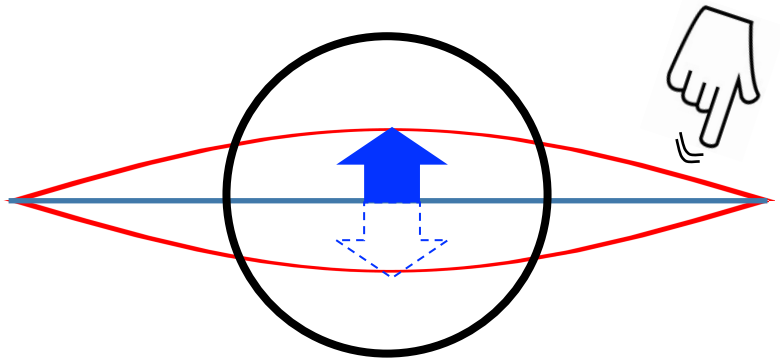


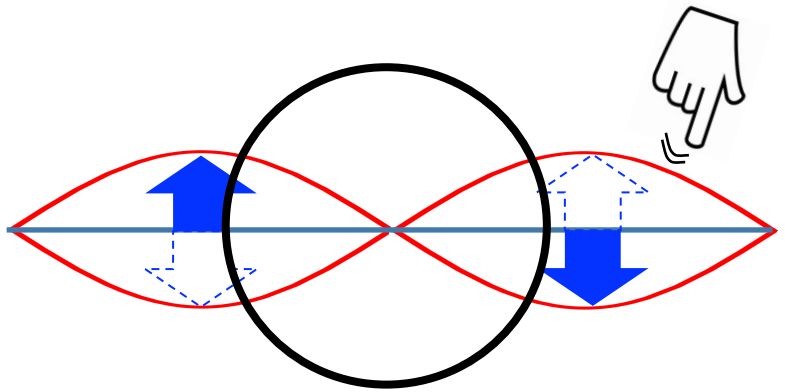
Optical Forbidden

楽器と閉じ込め電子系

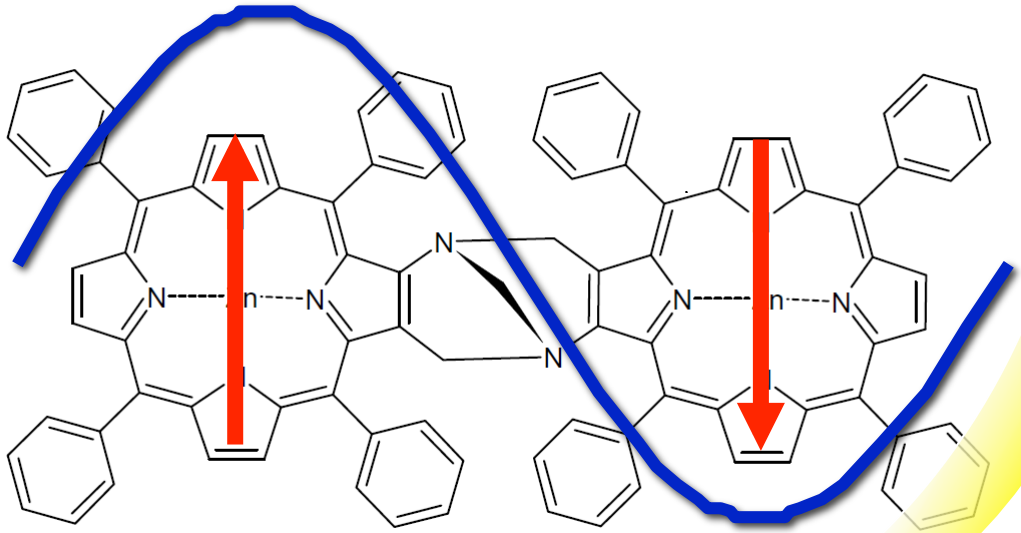








局在光源？



Optical Forbidden

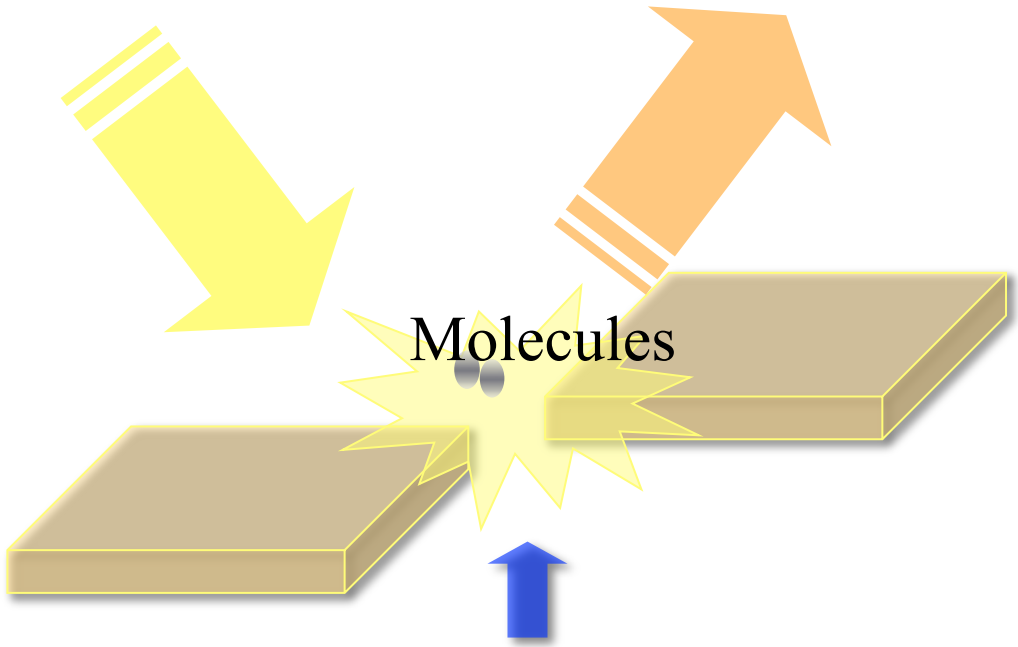
Optical Allowed ?

金属アンテナ構造による分子励起過程の制御

Molecules (Nano objects) Light wavelength

10^{-9} m << 10^{-6} m

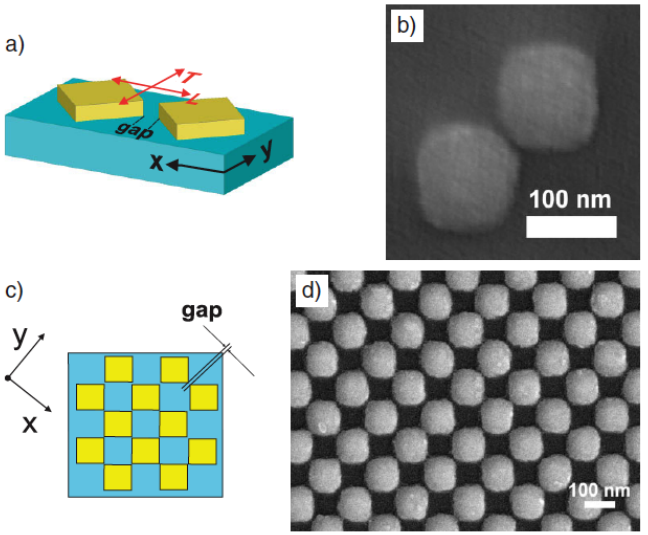
Difficulty in exciting molecules with a few photons



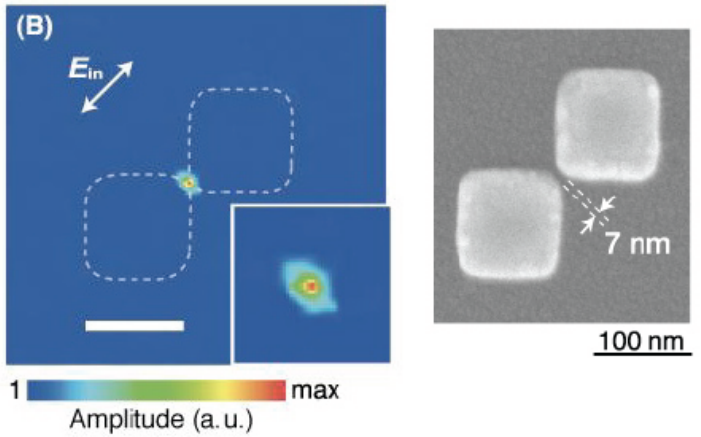
Localized plasmons at the metallic nanogap

Photon-harvesting by metallic antenna

Metal sub-microstructure nanogaps



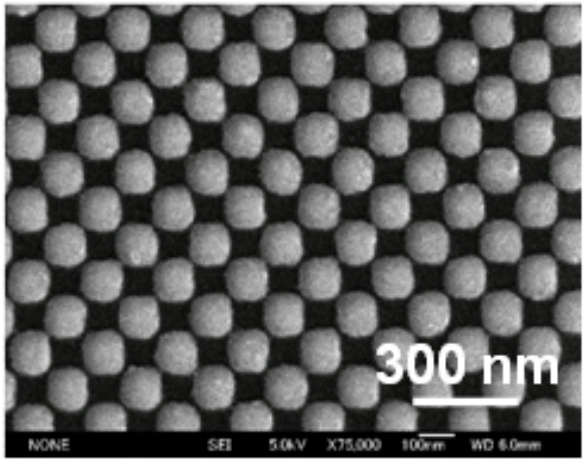
K. Ueno et al..Ad. Mater. **20** (2008) 26



Y. Tanaka, et al, Opt. Express **19** (2011) 7726.

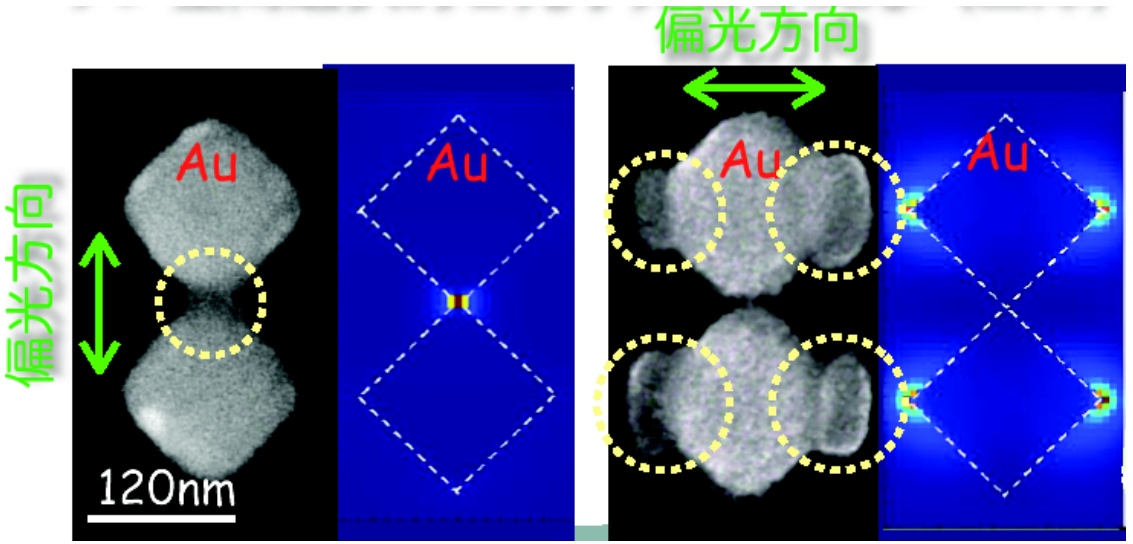
局在光電場による局所化学反応誘起

電場増強を誘起する金属ナノ構造



Misawa et al.,
J. Am. Chem. Soc. 2006

ナノギャップによる位置選択制

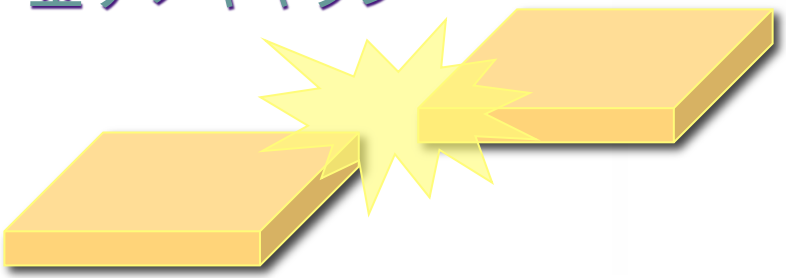


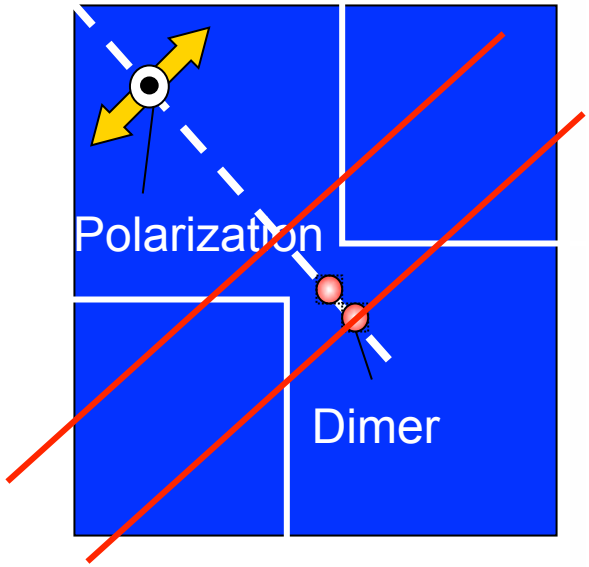
High efficient two photon polymerization is caused even by incoherent light source.

K. Ueno et al. Adv. Mater. **20**, 26 (2008)
K. Ueno, et al. J. Am. Chem. Soc., **130**, 6928 (2008)

金ナノギャップ近傍での光誘起電場強度

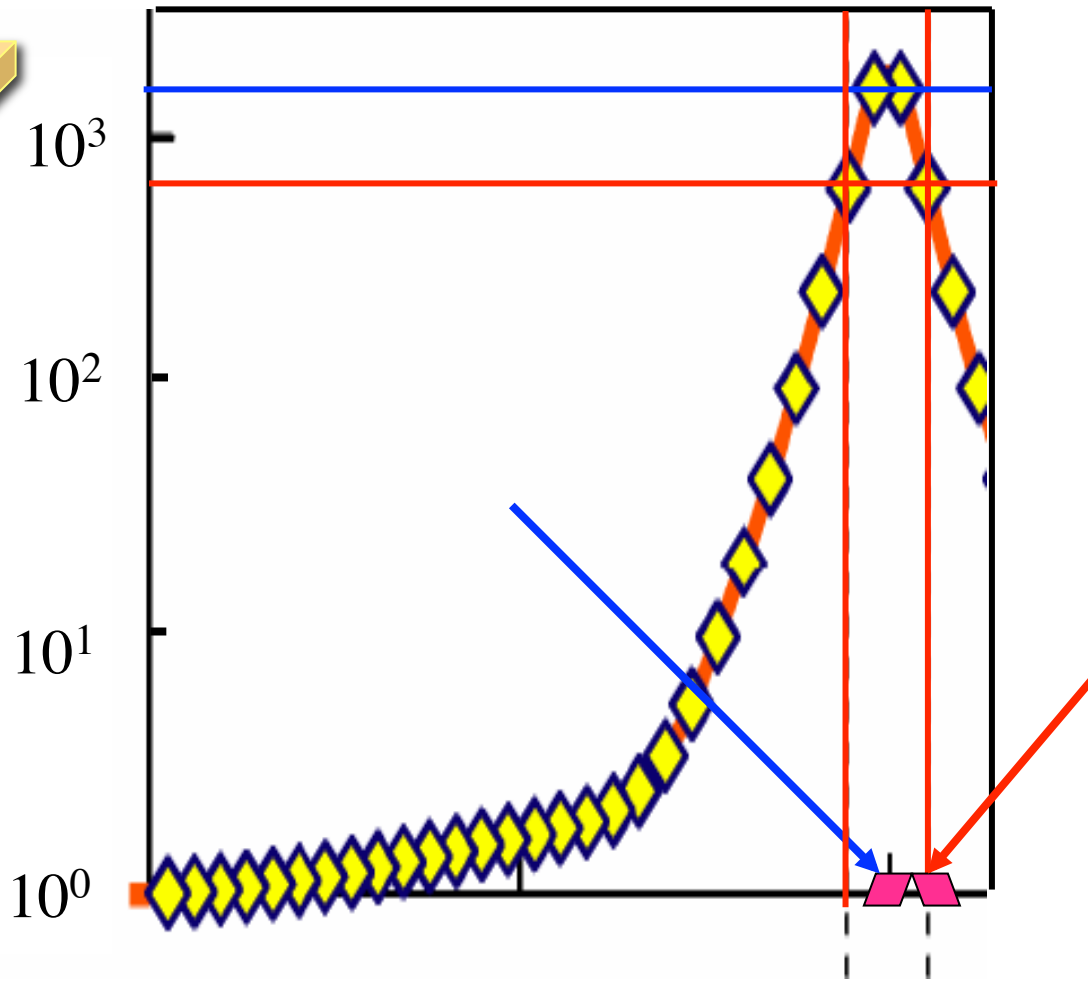
金ナノギャップ





L=T=24 nm, H=10 nm
Gap width=2.8 nm

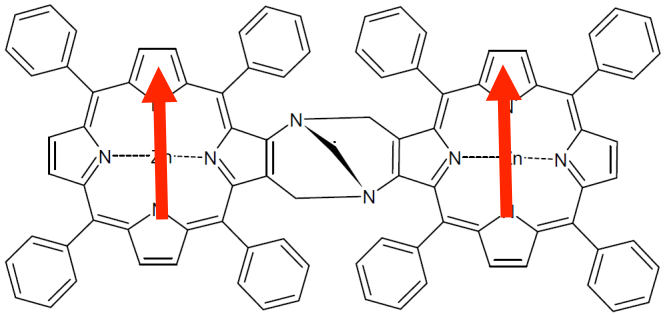
金ナノギャップ近傍での応答電場強度

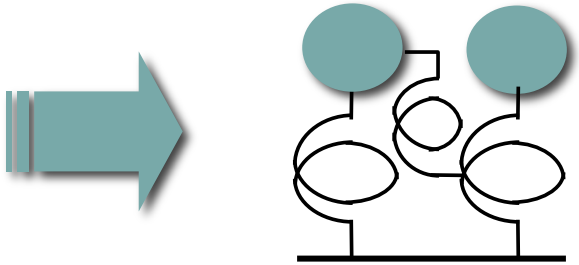


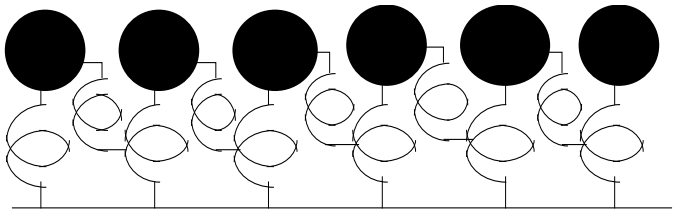
Forbidden state: 1.998eV

Nonlocal Response

Nonlocal response due to the polarization wave

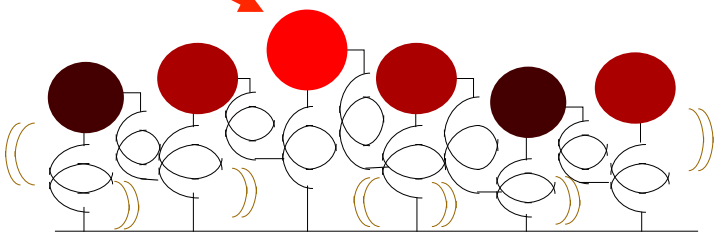






$$\mathbf{P}(\mathbf{r},\omega) = \chi(\mathbf{r},\omega)\mathbf{E}(\mathbf{r},\omega)$$

Photon



$$\mathbf{P}(\mathbf{r},\omega) = \int \chi(\mathbf{r},\mathbf{r}',\omega)\mathbf{E}(\mathbf{r}',\omega)\,d\mathbf{r}'$$

Nonlocal response

ナノギャップ近傍にある分子の光学応答計算手法

離散双極子近似方

Discrete-Dipole Approximation (DDA)

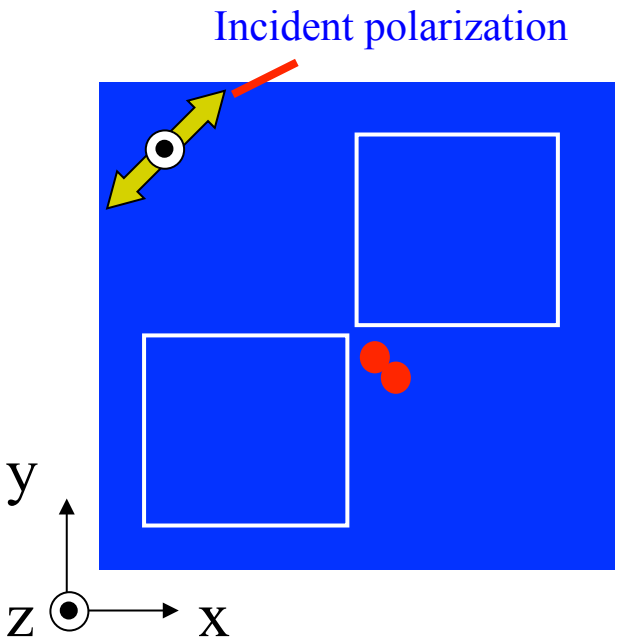
Refs. E.M. Purcell, C.R. Pennypacker, Astrophys. J. 186, 705-714 (1973)
J.J. Goodman et al. Optics Lett.**16**, 1198 (1991)

Discretized Maxwell equation

$$\mathbf{E}_i = \mathbf{E}_i^0 + \{ \sum_{j=1}^{Np} \mathbf{G}_{i,j}^{med} \mathbf{P}_j V_j \}$$

i: observation position,
j: source position

$$\mathbf{E}_i = \chi_i^{-1} \mathbf{P}_i \quad \Rightarrow \quad \sum_{j=1}^{Np} \mathbf{A}(i,j) \cdot \mathbf{P}_j = \mathbf{E}_i^0$$



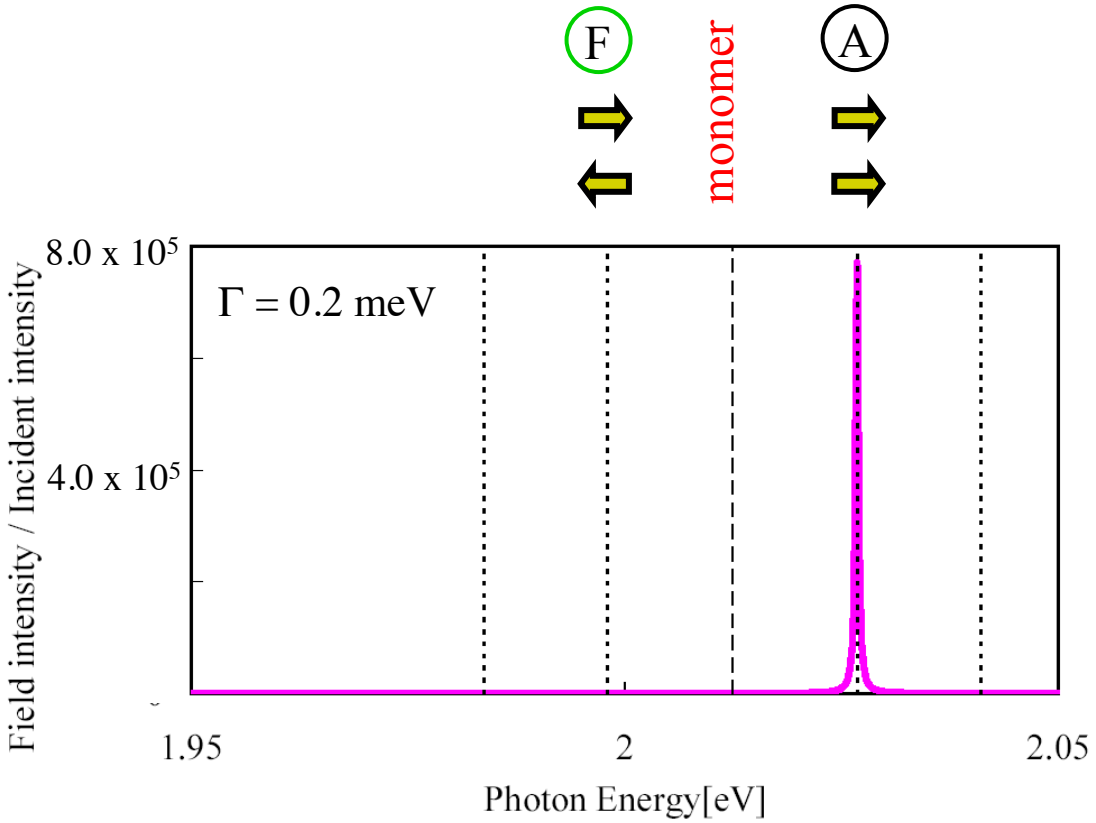
Each gold block :
L24nm x H24nm x H10 nm
Gap distance 2.8nm

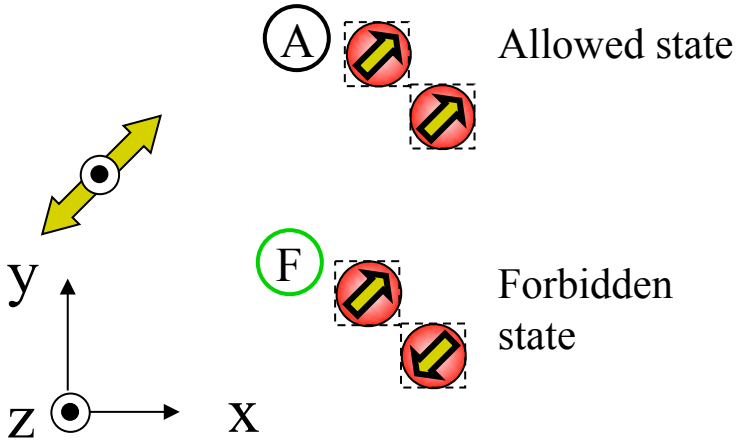
$\mathbf{P}_i$: both resonance structures (molecules)
and environmental structures (metal nanostructures, substrate, and so on)

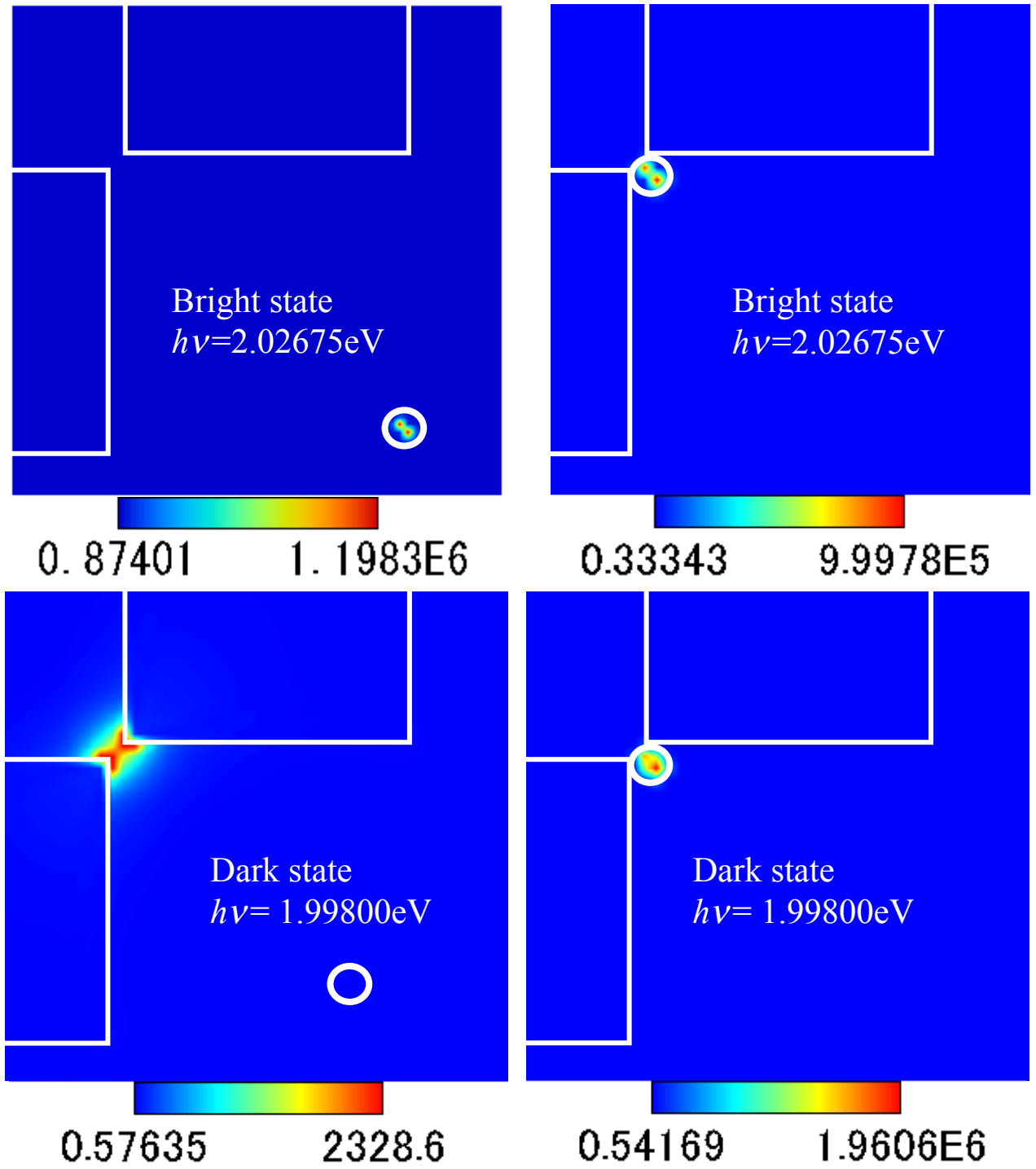
自由空間中における分子二量体の応答場スペクトル

Dimer: Effective size of each molecule is 1nm

Dipole moment: 8.0 debye
Nonradiative damping: 0.2 meV







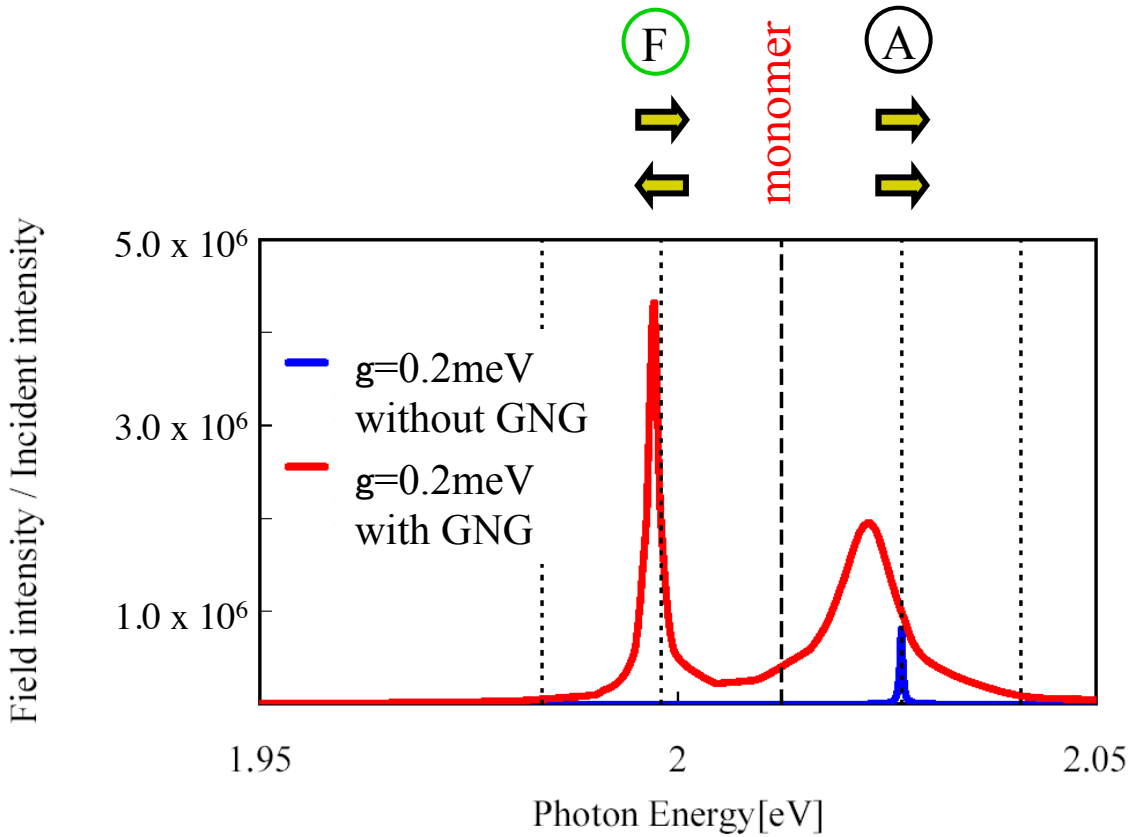
ナノギャップ近傍における分子二量体の応答場

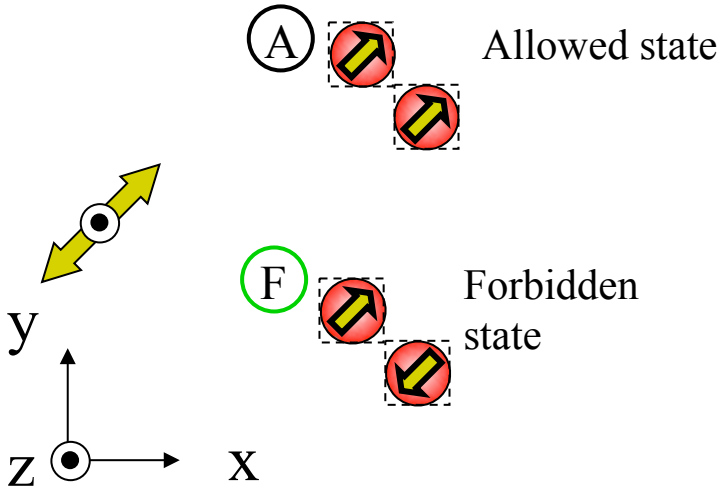
Allowed state

Forbidden state

禁制準位の励起

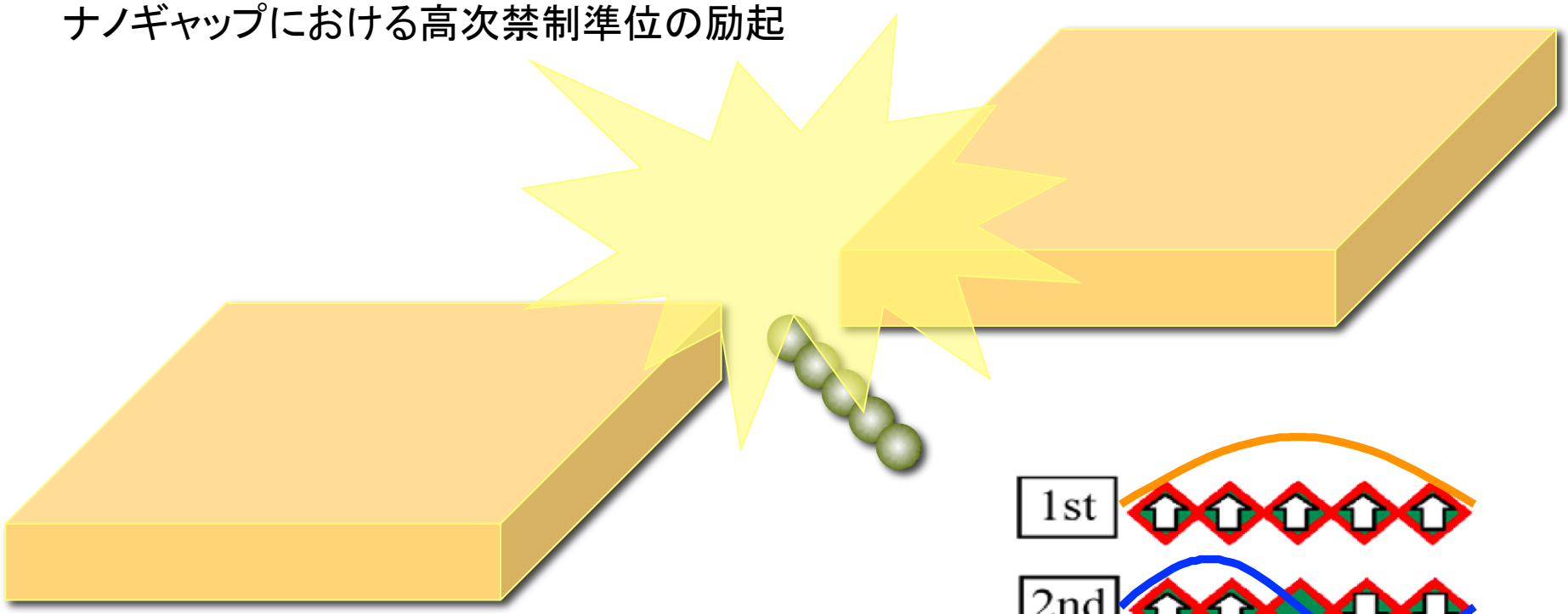
T. Iida and H. Ishihara
phys. stat. solid. (a) **206**, 980 (2009)



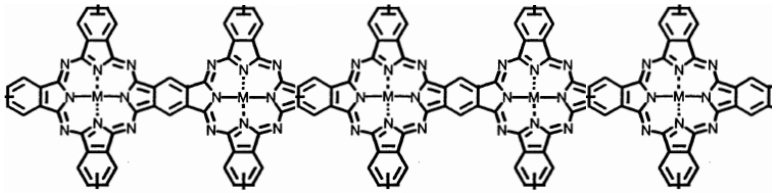


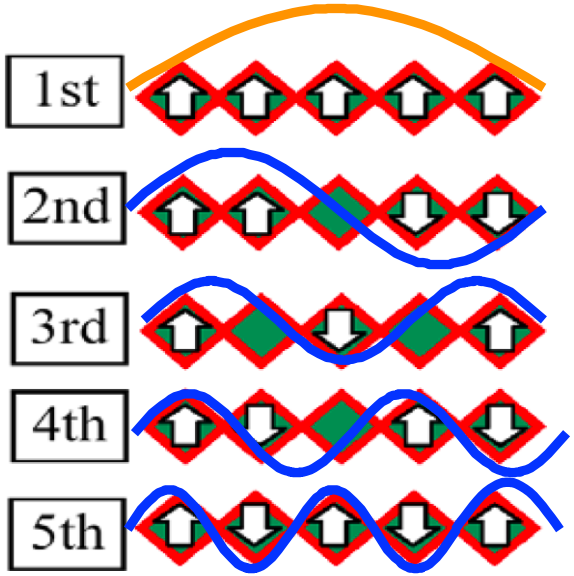
局在光電場によるサイト選択励起

ナノギャップにおける高次禁制準位の励起

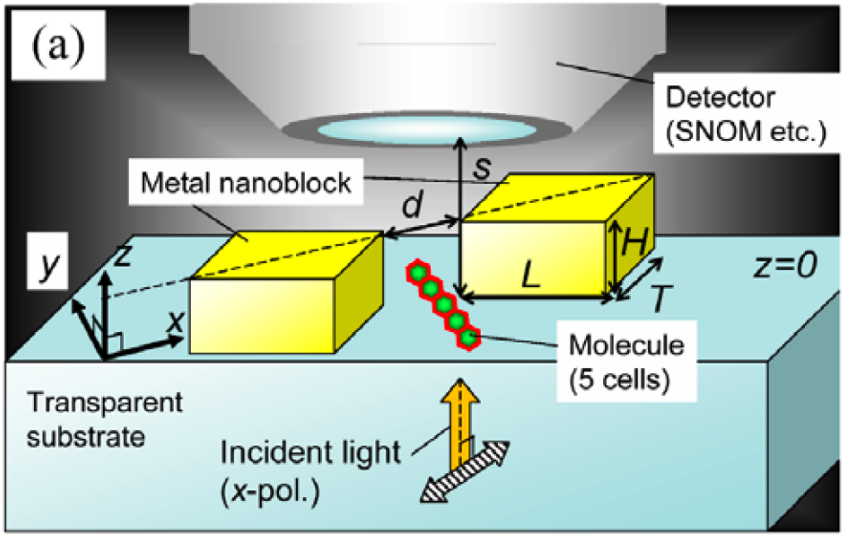


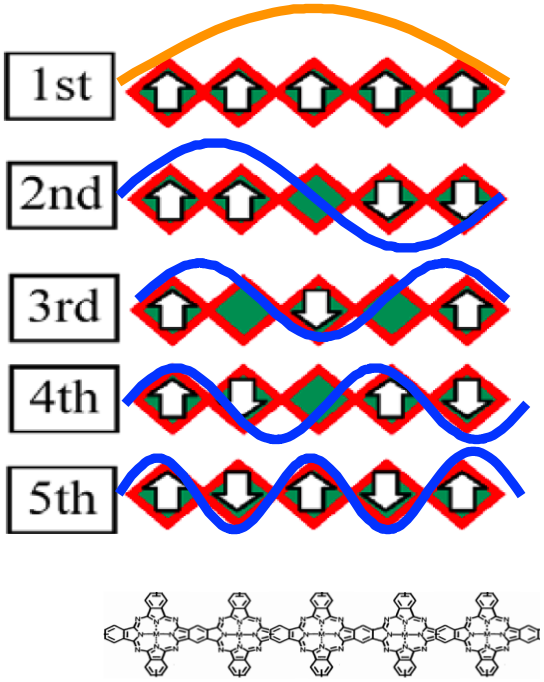
フタロシアニン（Qバンド）ペンタマーを想定





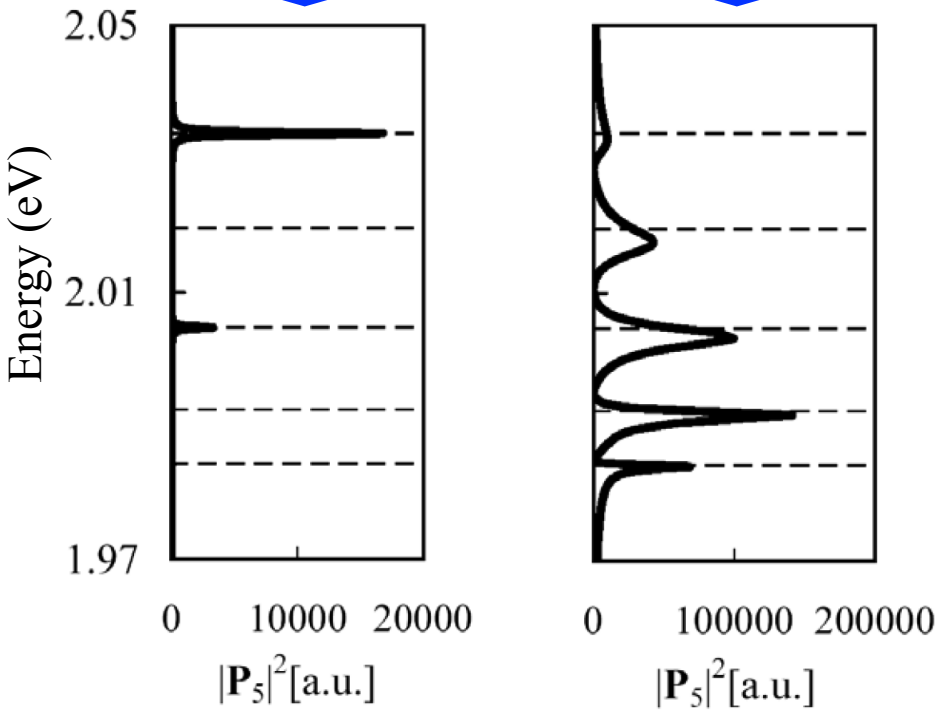
T. Iida, Y. Aiba and H. Ishihara:
Appl. Phys. Lett. **98**, 053108 (2011)



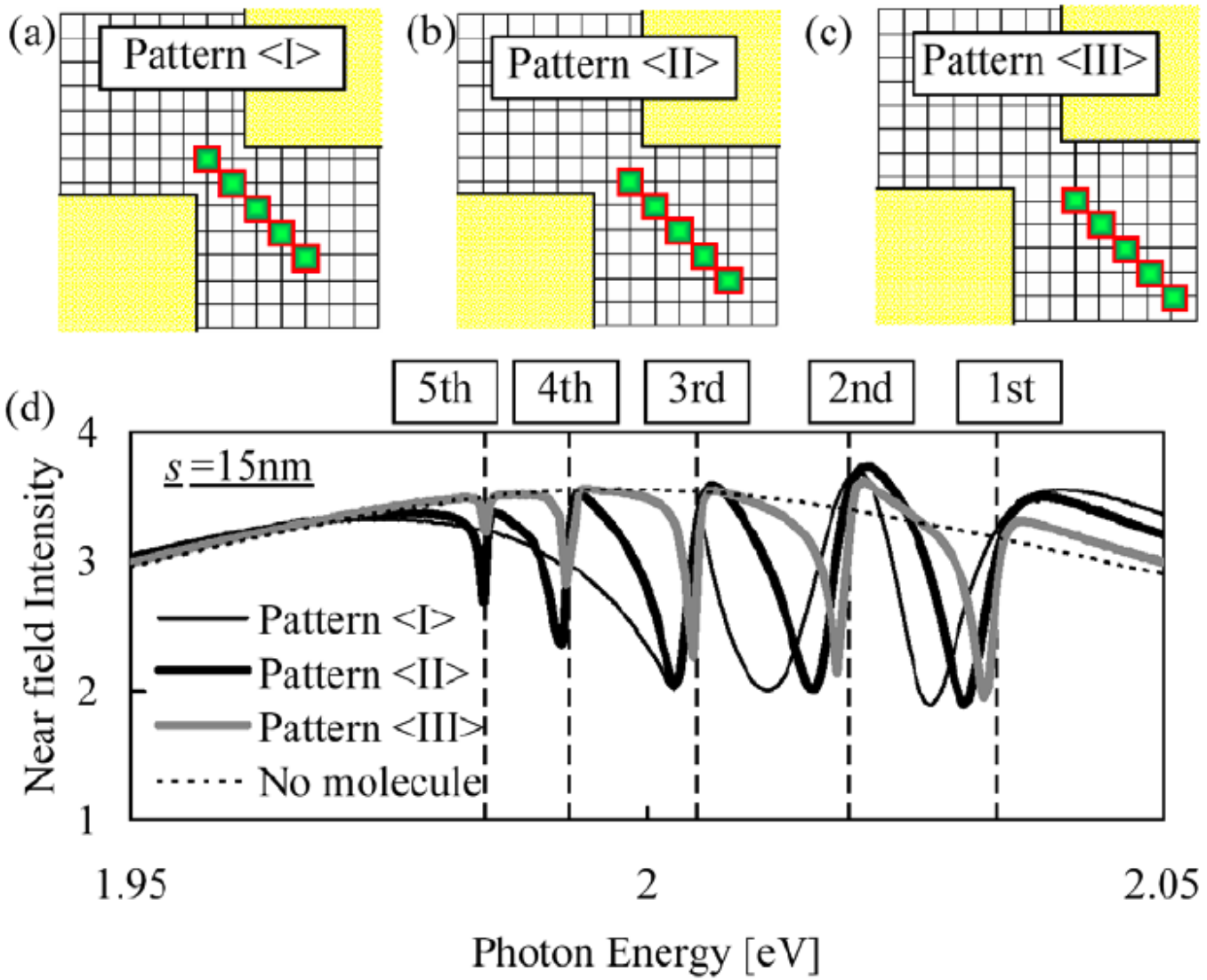


without nanoblocks

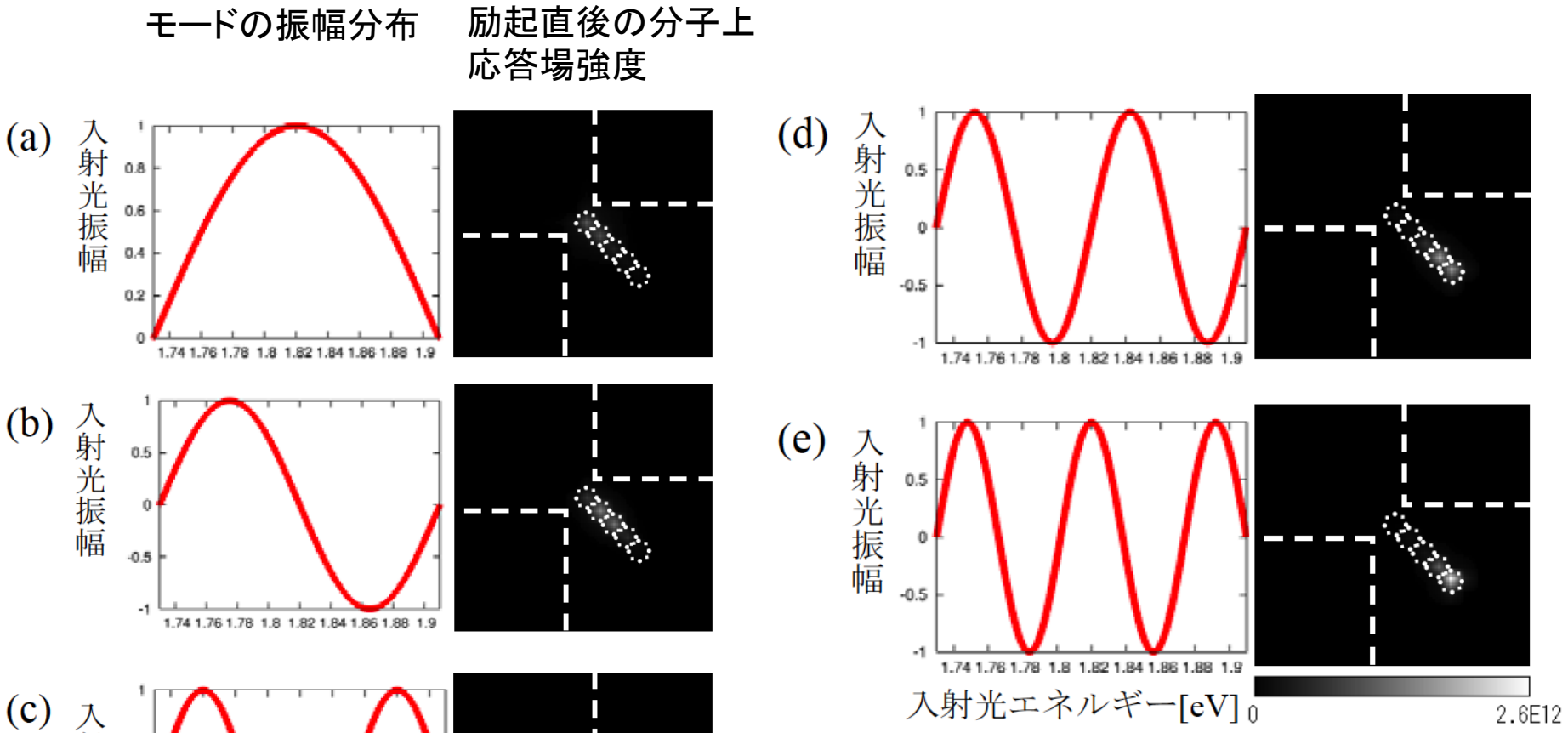
with nanoblocks



非双極子的励起状態の観測可能性



ナノギャップ近傍におけるサイト選択的局所励起

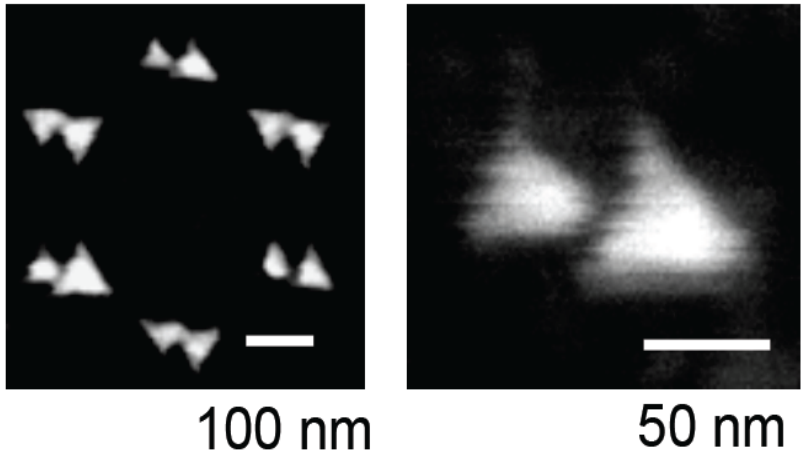


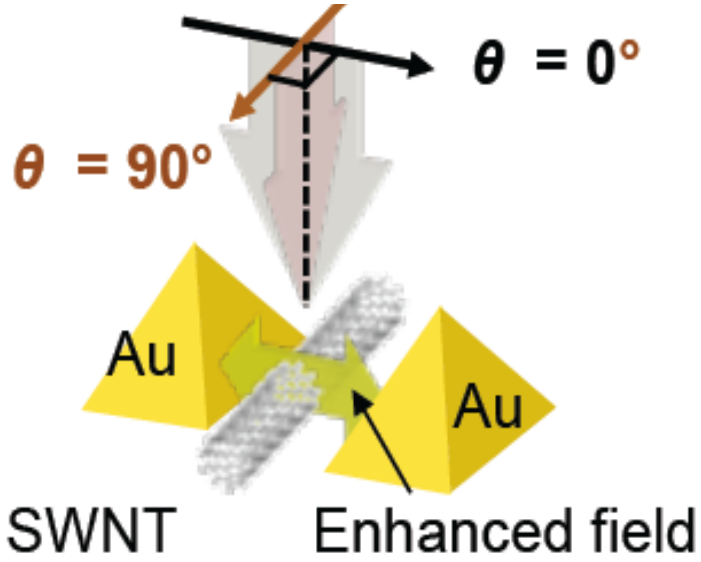
Breakdown of selection rule for a single CNT at metallic nanogap

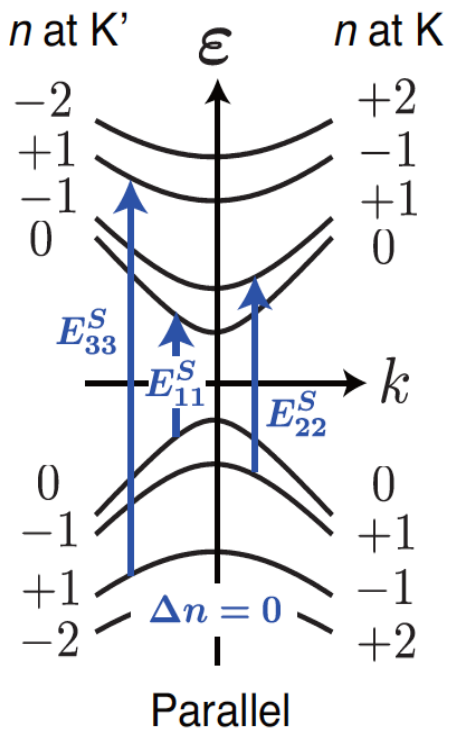
北海道大学　村越敬教授グループ
大阪大学　　安食博志教授

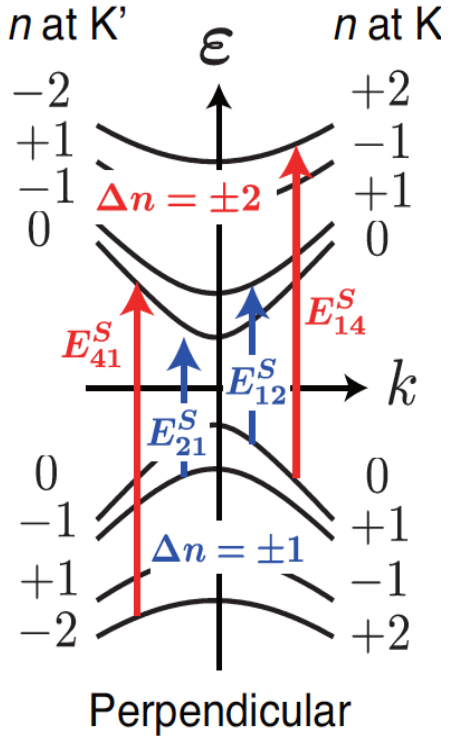
M. Takase, et al., ***Nature Photonics***, **7**, 550–554 (2013)

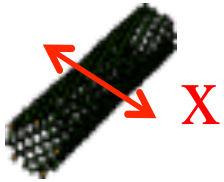
軸断面内での非局所応答



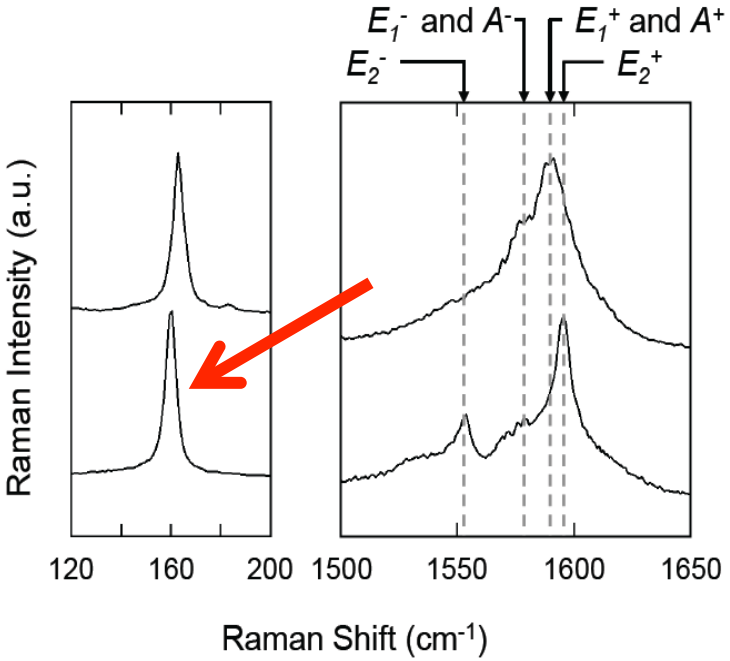


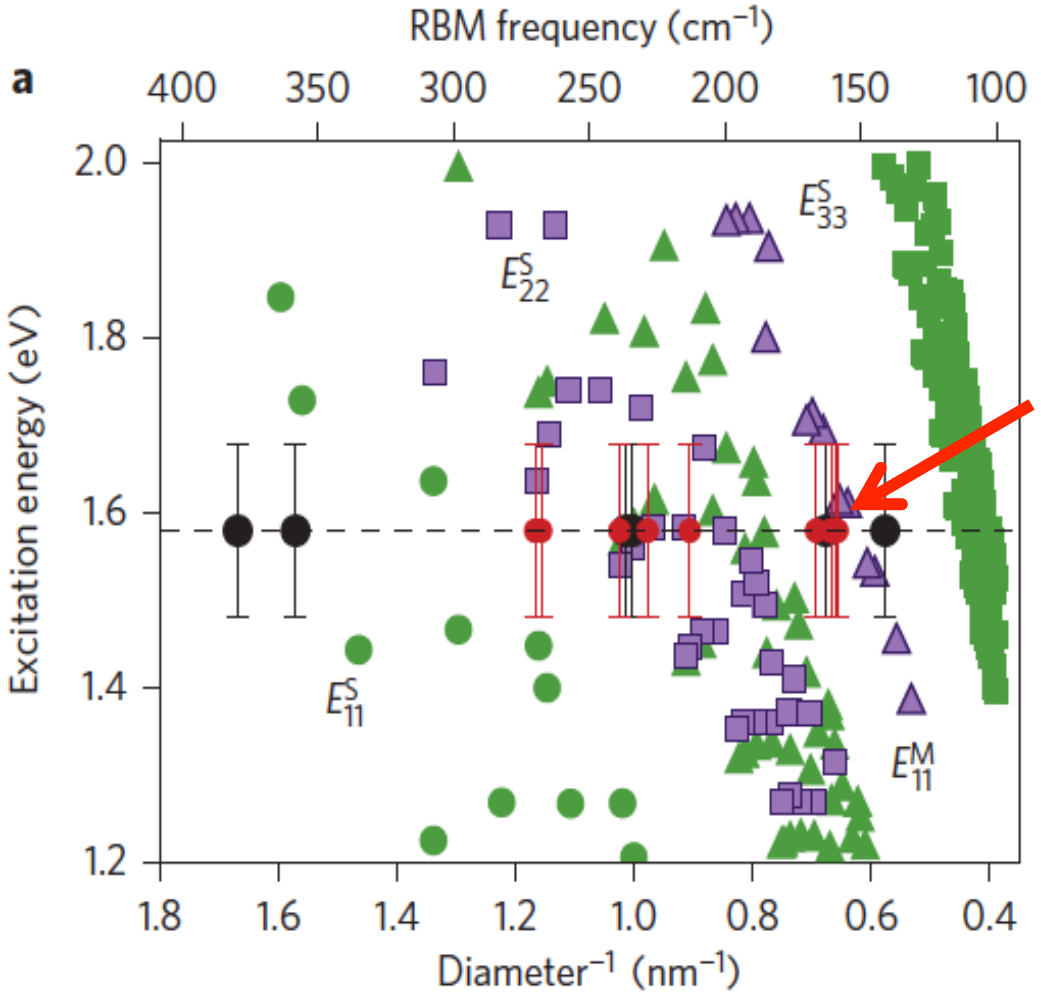






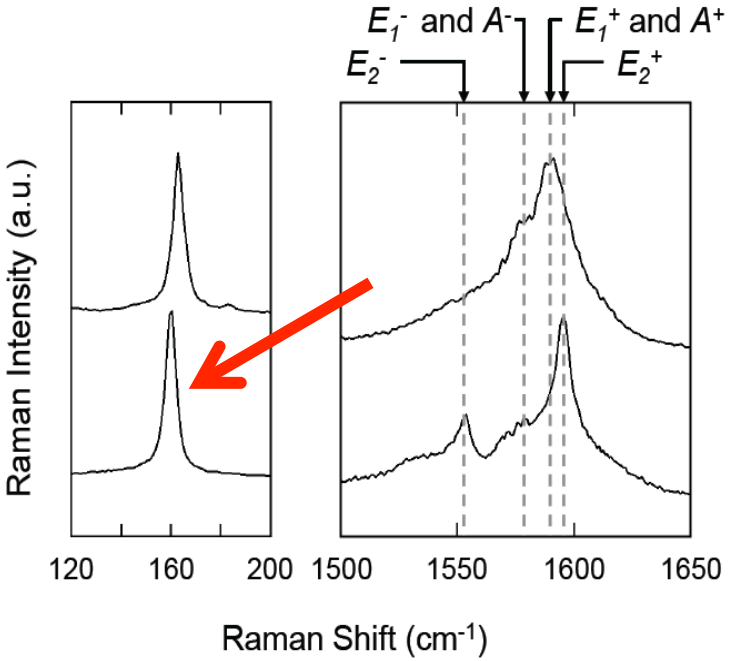
観測されたラマン信号とその帰属 I

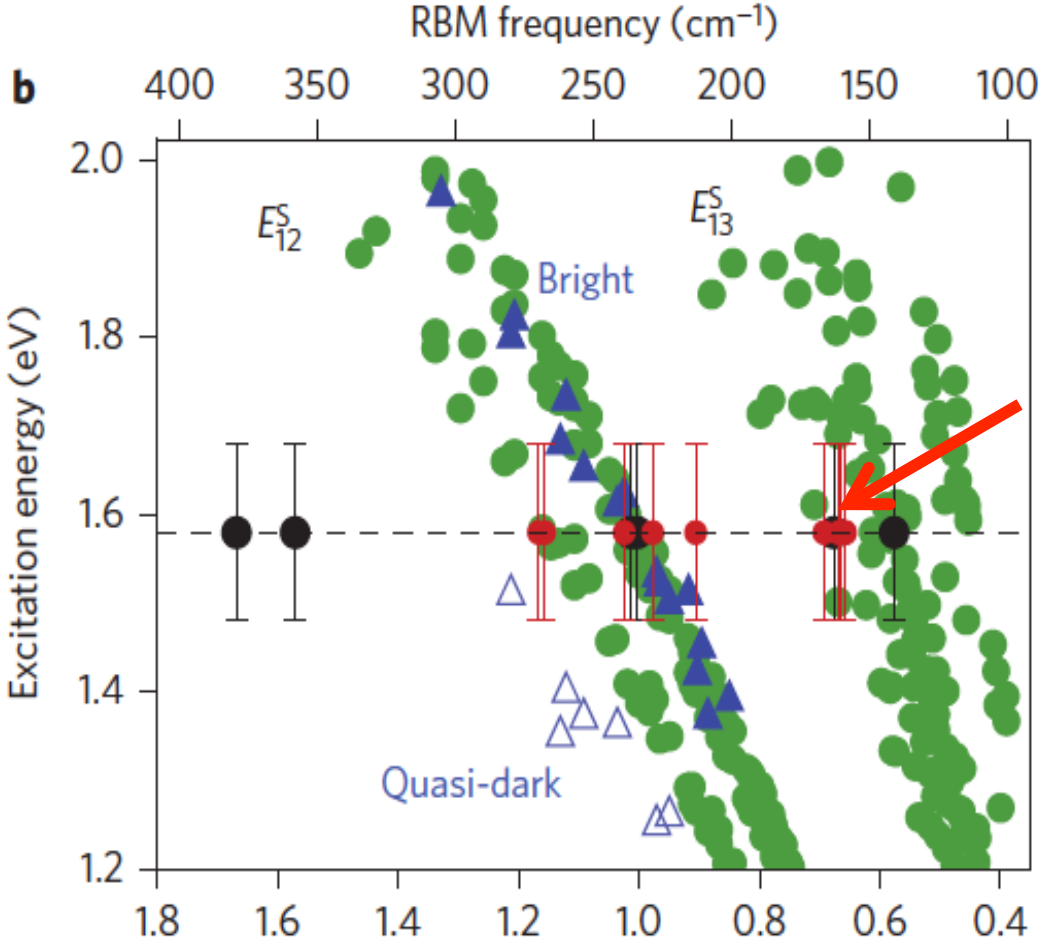




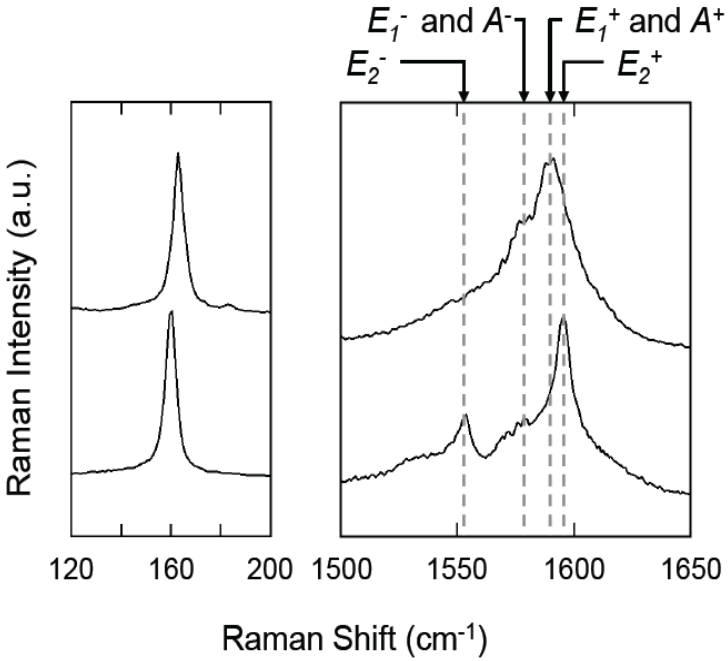
赤丸はチューブに垂直電場で励起

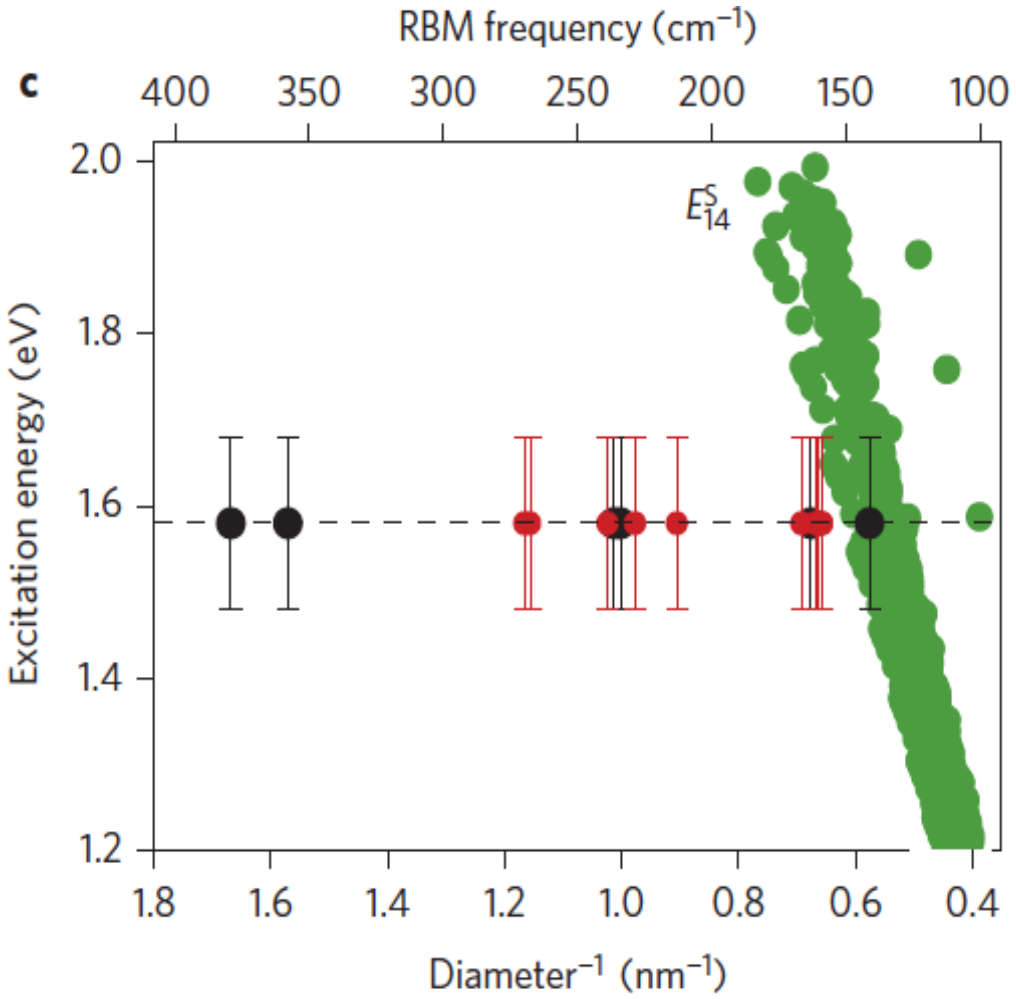
観測されたラマン信号とその帰属 II

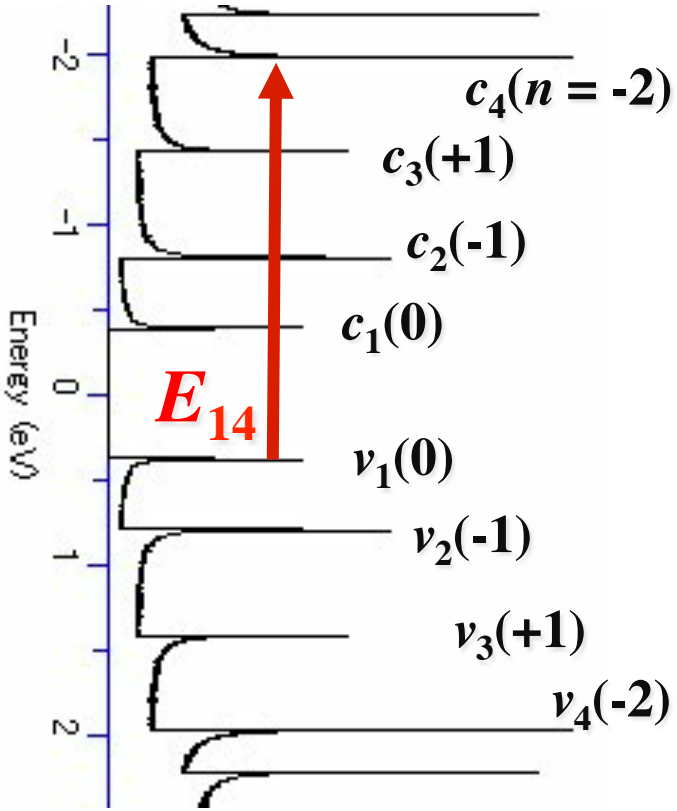




観測されたラマン信号とその帰属 III

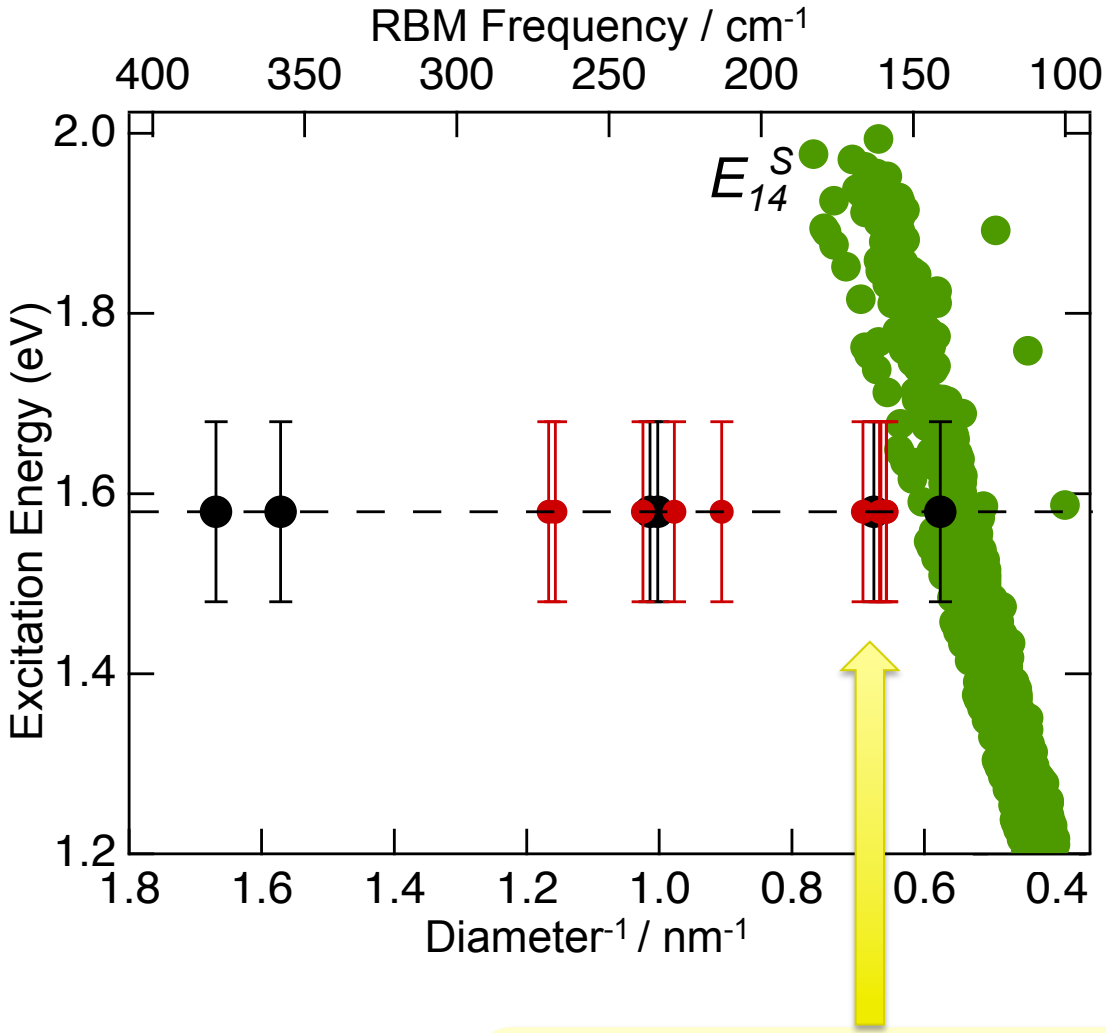






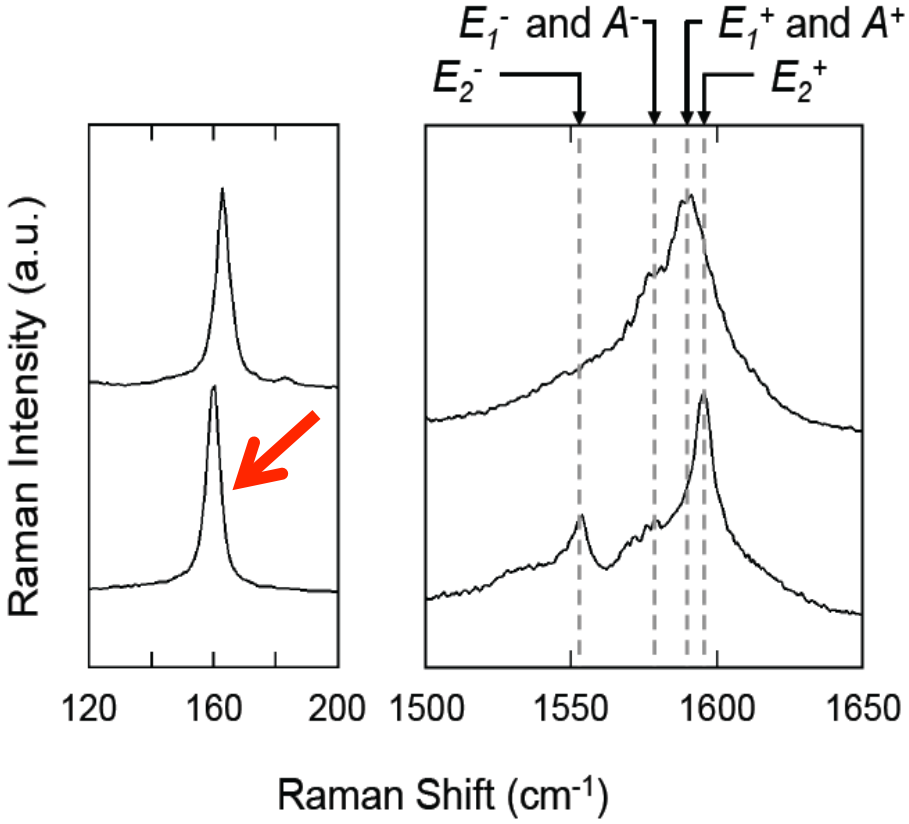
$$\Delta n = \pm 2$$

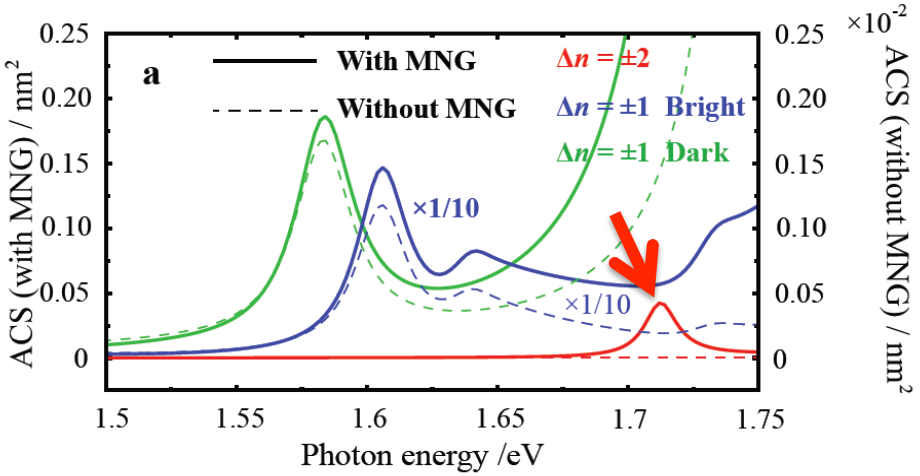
forbidden

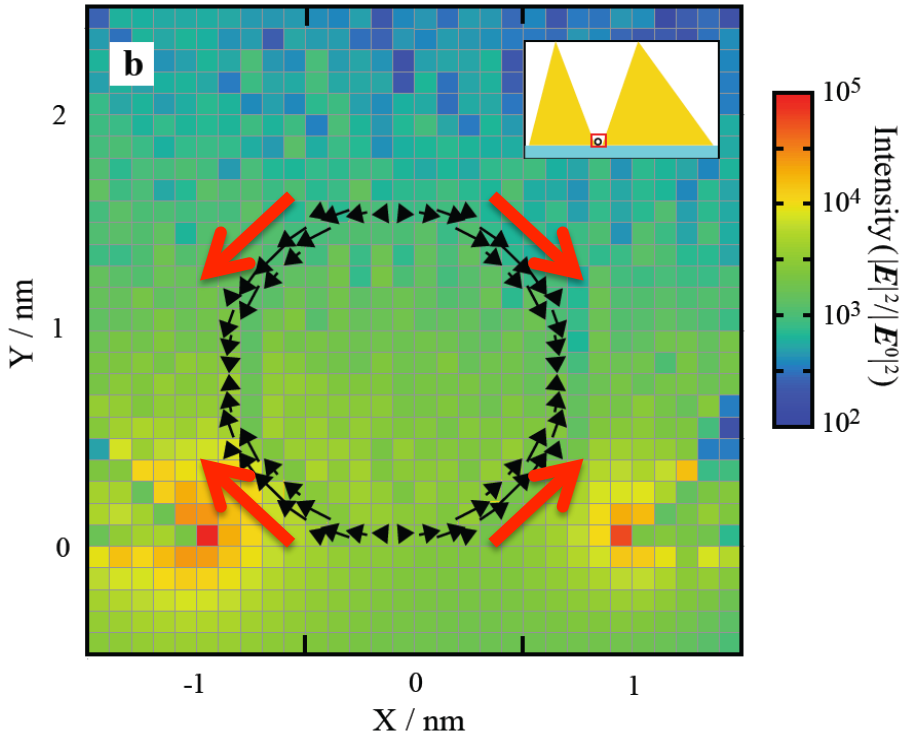


Semiconductor SWNT observed by SERS

Breakdown of selection rule for a single CNT at metallic nanogap



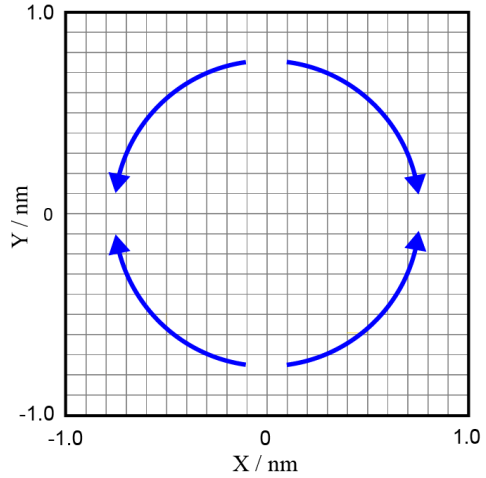




遷移双極子密度

$$\rho_m(r\theta, z) = \rho_m e^{-i2m\theta}$$

$m = 2$: 禁制遷移

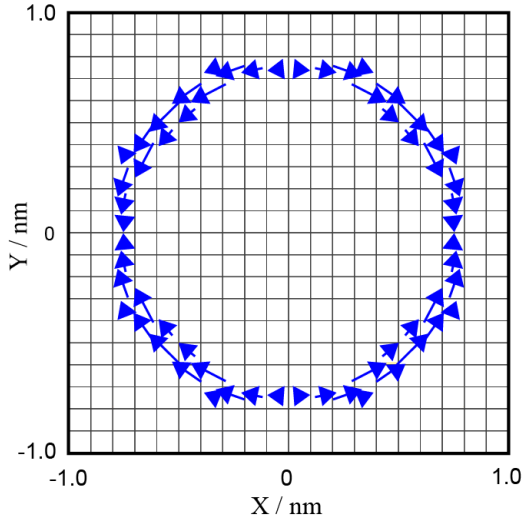


空間分割

双極子密度を
セル内で平均化

遷移双極子密度(セル毎)

総和=0：禁制

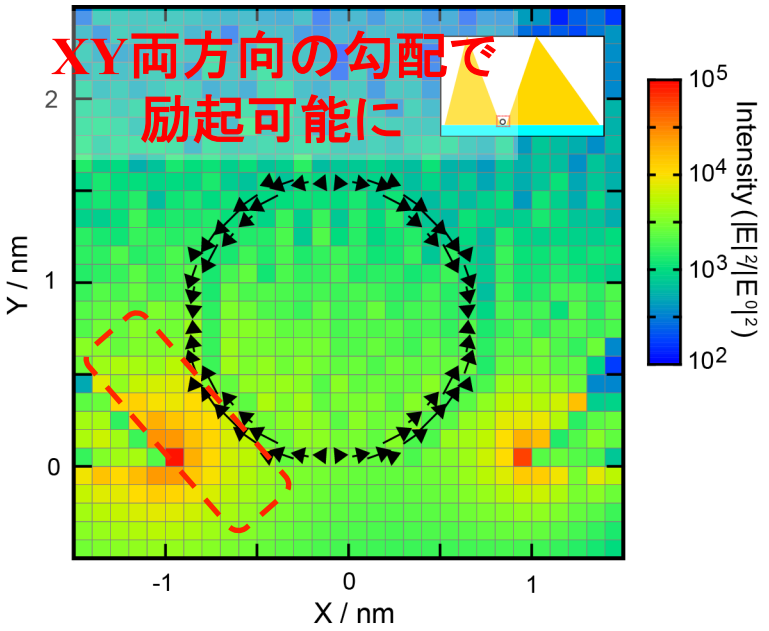


LWA

$$\boldsymbol{P}_{\mathrm{CNT}}(\boldsymbol{r}_i) = \frac{\bar{\boldsymbol{E}}\boldsymbol{d}_i^*}{V_i(E_{\mathrm{ex}} - \hbar\omega - i\Gamma)} \boxed{\sum_j \boldsymbol{d}_j} = 0$$

Molecular internal structure
＋spatial structure of EM field

$$\boldsymbol{P}_{\mathrm{CNT}}(\boldsymbol{r}_i) = \frac{\boldsymbol{d}_i^*}{V_i(E_{\mathrm{ex}} - \hbar\omega - i\Gamma)} \boxed{\sum_j \boldsymbol{d}_j \cdot \boldsymbol{E}(\boldsymbol{r}_j)}$$



Nature Photonics "News & View"

RAMAN SPECTROSCOPY

The effect of field gradient on SERS

Surface-enhanced Raman spectroscopy is normally associated with the enhanced electric fields that arise near metal nanoparticle surfaces. The contribution of field gradients has been unclear, but new research provides insights into their effect.

Christine M. Aikens, Lindsey R. Madison and George C. Schatz

Surface-enhanced Raman spectroscopy (SERS) is an important analytical tool because it has low detection limits and can provide molecular fingerprints of adsorbates. It typically gives Raman signal enhancements of the order of 10^4–10^9, although enhancements as high as 10^{14}–10^{15} have been reported for single-molecule SERS. Many enhancement mechanisms have been proposed, but it is generally accepted that the largest enhancements arise from electromagnetic factors because the local Raman signal scales as the fourth power of the local electromagnetic field amplitude. An accurate description of electromagnetic fields near metal surfaces is therefore critical for understanding SERS. Although it is well accepted that the local electric field is greatly enhanced