Exciton-Plasmon Interactions and Fano Resonances in Nanostructures

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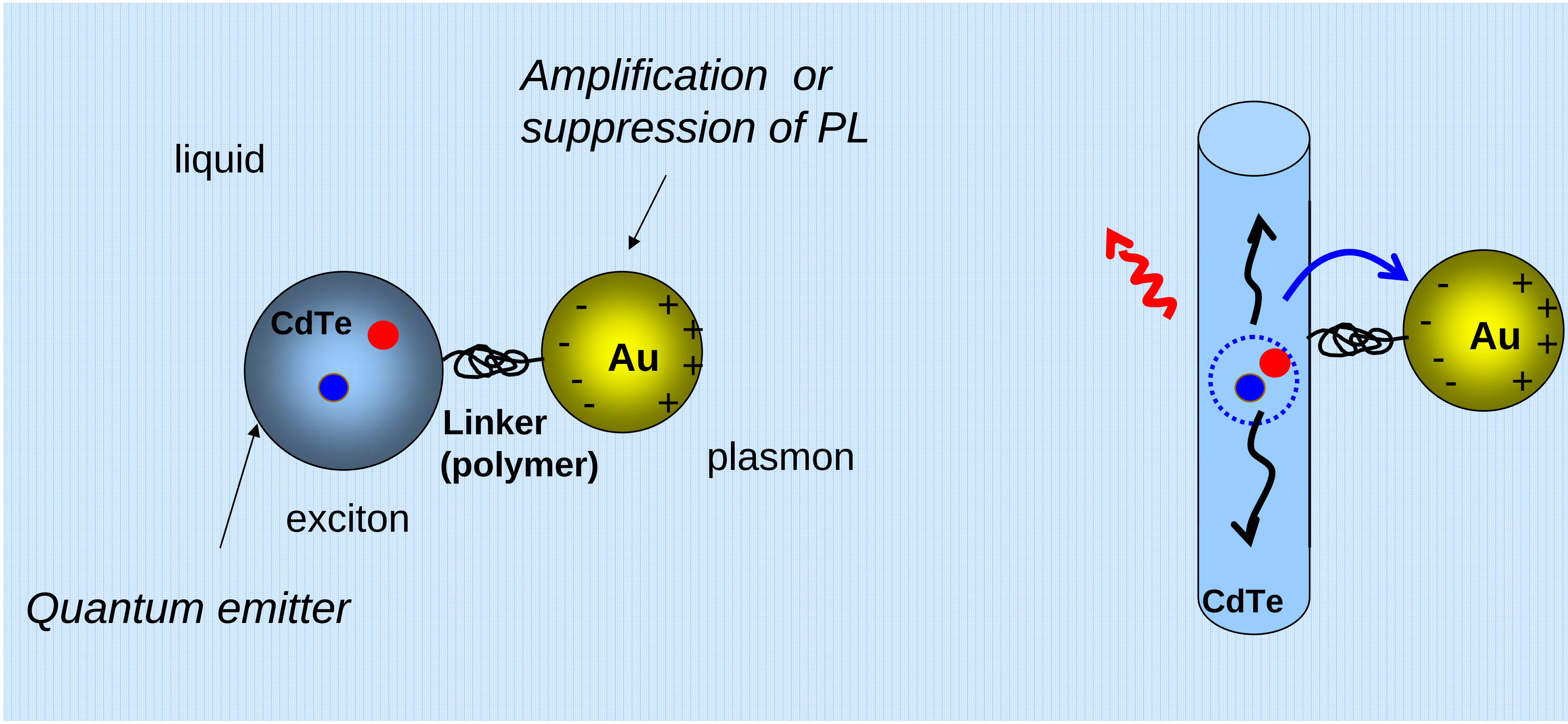
Fan Zhiyuan, Ohio U.
Wei Zhang, Ohio U. (now in China)

Nanoparticles as building blocks
Interaction between nanocrystals



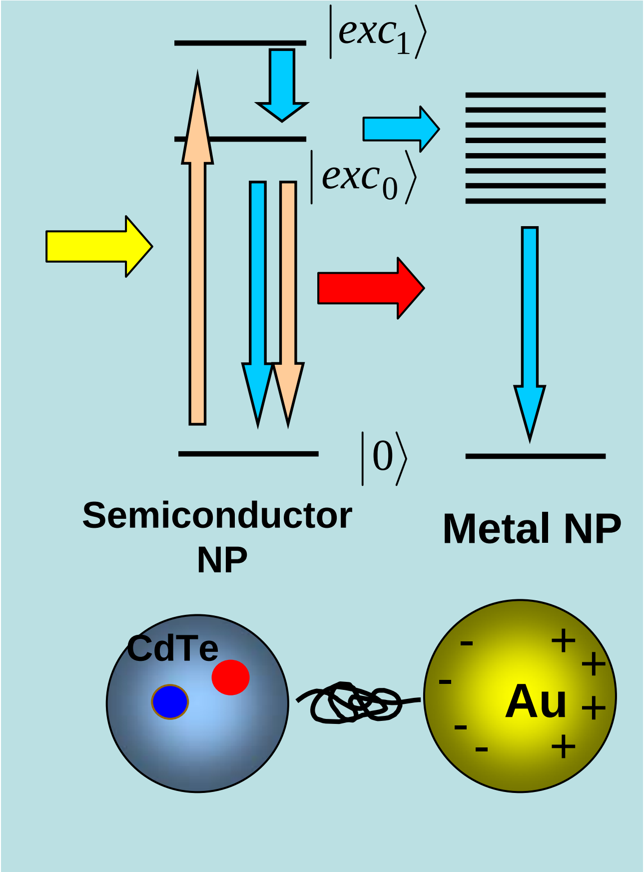
Exciton + plasmon + photons

$$\hbar\omega_p \approx E_{exc} = \hbar\omega_{emission}$$

$$\hbar\omega_{laser} \approx \hbar\omega_p$$

Incoherent exciton-plasmon interaction

$$\frac{dn_{exc0}}{dt} = -\left(\gamma_{rad} P(\omega_{exc}) + \gamma_{non-rad} + \gamma_{transfer}\right) n_{exc0} + P(\omega_l) I_0$$



Field enhancement factor:

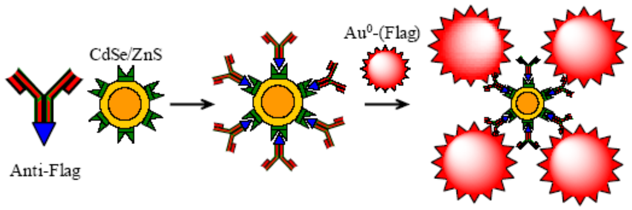
$$P(\omega) = \frac{\left\langle E_{actual}^{\;2} \right\rangle_t}{\left\langle E_{no\ metal}^{2} \right\rangle_t} \propto \left| E_{photon} \right|^2$$

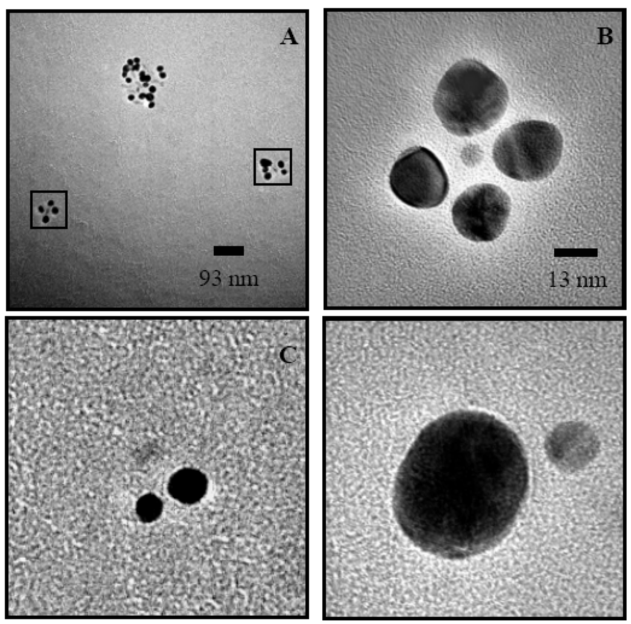
Energy transfer (FRET) rate:

$$\gamma_{non-rad,metal}(\omega_{exc}) = \frac{2\pi}{\hbar} \left\langle \sum_f \left| \langle 0; f \,|\, \hat{V}_{\text{int}} \,|\, exc; 0 \rangle \right|^2 \delta(\hbar\omega_{exc} - \hbar\omega_f) \right\rangle_T = -\frac{2}{\hbar} \text{Im}[\alpha(\omega_{exc})]$$

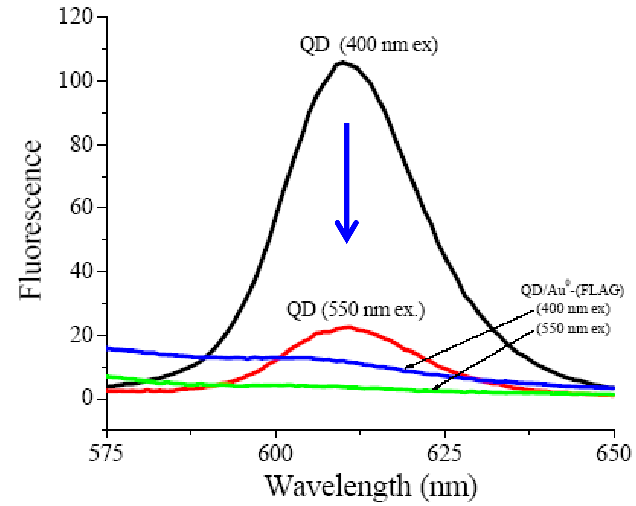
Book: Joseph R. Lakowicz
Principles of Fluorescence Spectroscopy

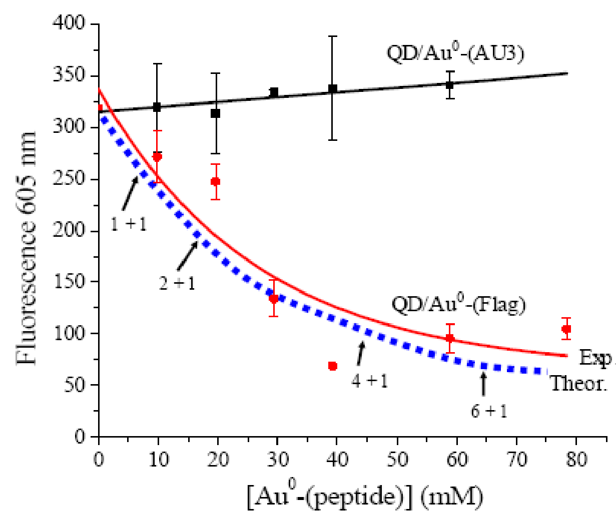
N Au-NP -- CdSe-NP



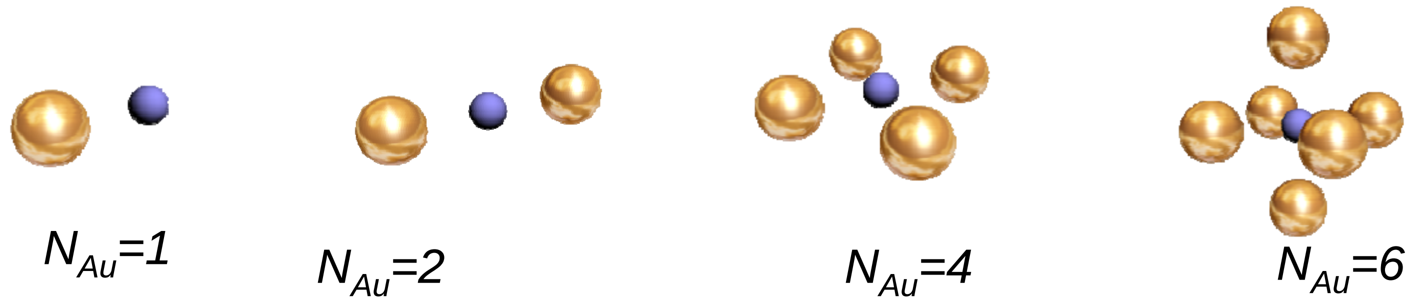


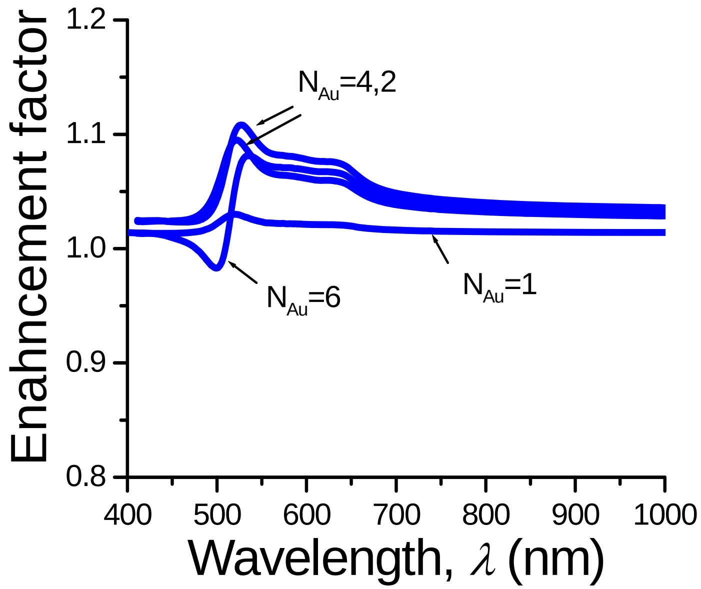
Slocik, J.M.; Govorov, A.O.; and Naik, R.R., *Supramolecular Chemistry, 2006.*

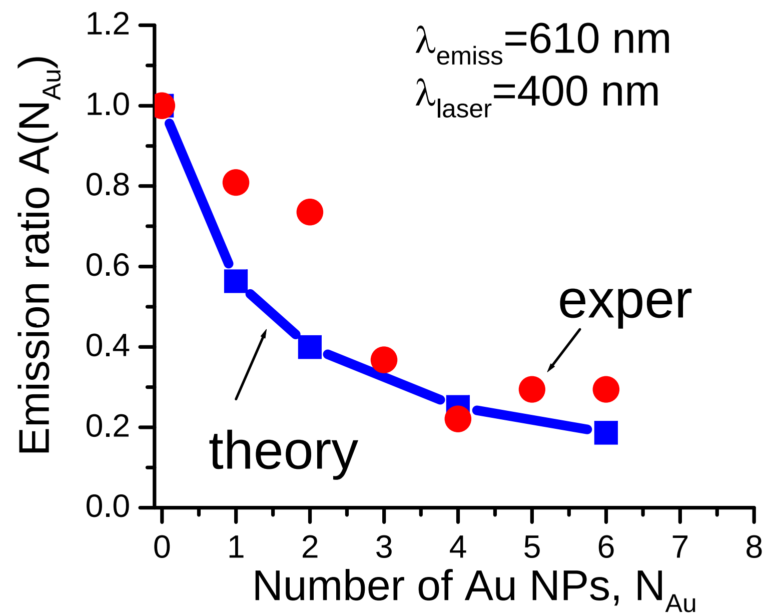




Number of Au NPs →





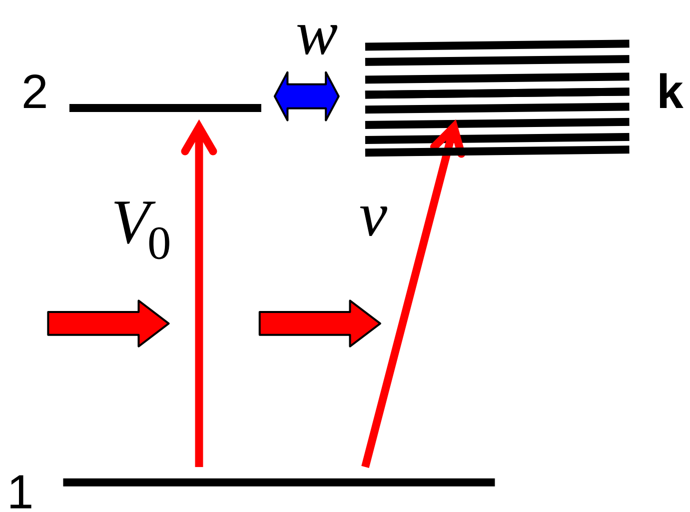


Emission ratio:

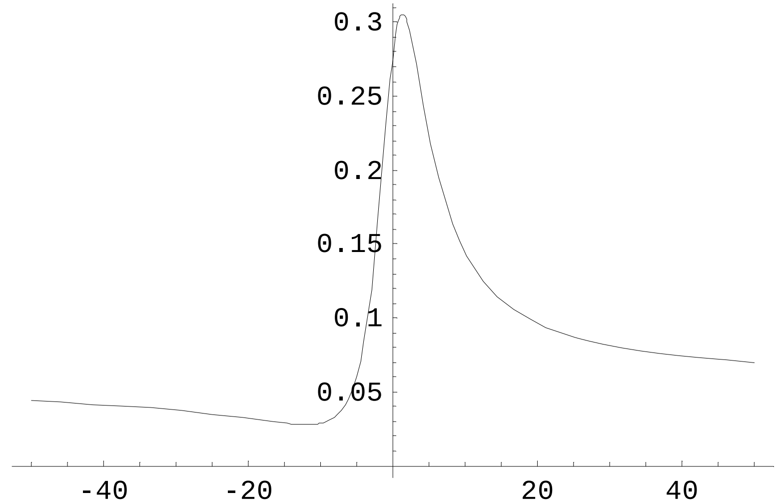
$$A = \frac{I_{emiss}(N_{Au-NPs})}{I_{emiss}(0)} \approx \frac{\gamma_0}{\gamma_0 + N \cdot \overline{\gamma}_{transfer}}$$

Govorov, et al., Nano Lett., 2006

Coherent interactions.
Fano effect

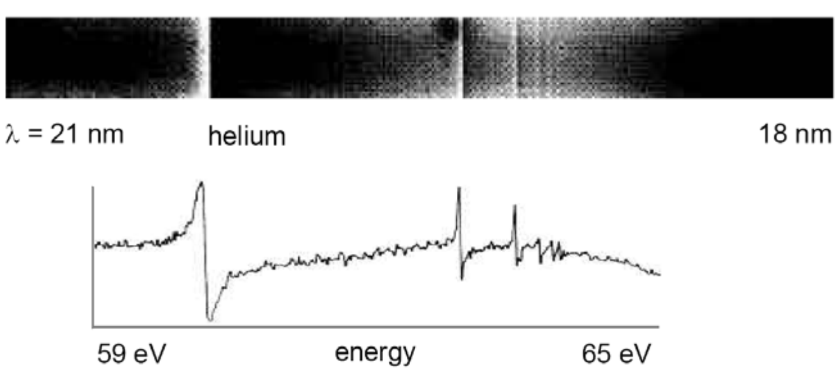


Absorption



Detuning, $\delta\omega = \omega - \omega_{12}$

X-ray absorption spectrum of He



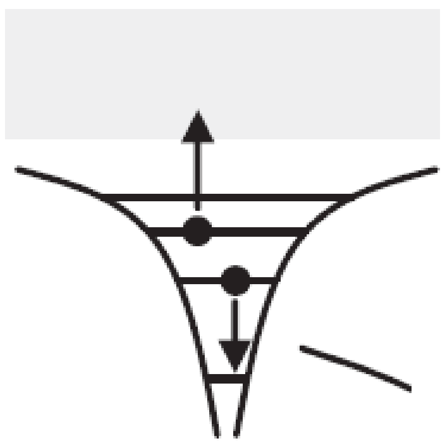
R.P.Madden and K. Codling, Phys. Rev. Lett. 10, 516 (1963)

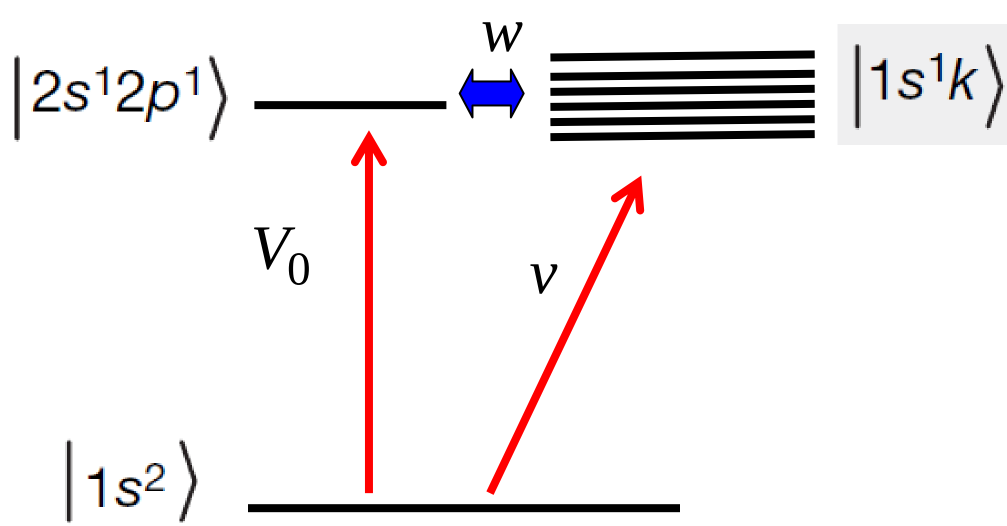
$$Abs = \frac{E_0^2}{2}\Gamma \frac{v^2}{w^2}\frac{(\delta\omega + q\cdot\Gamma)^2}{\delta\omega^2 + \Gamma^2}$$

$$\Gamma = \pi\rho w^2$$

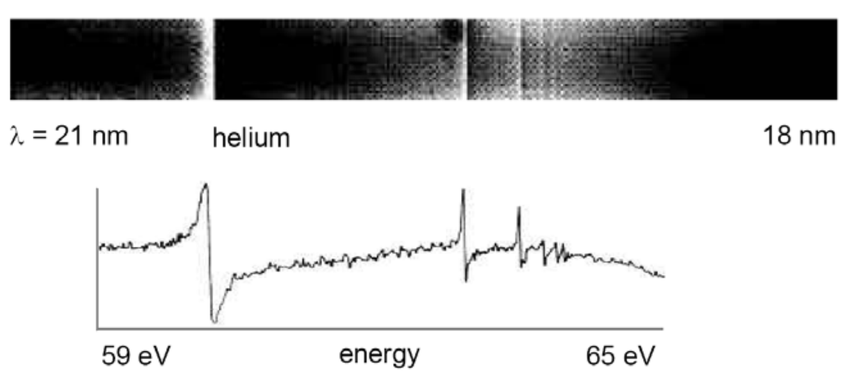
$$q = \frac{V_0 w}{v\Delta}$$

Fano effect in He





X-ray absorption spectrum of He



R.P. Madden and K. Codling, Phys. Rev. Lett. 10, 516 (1963)

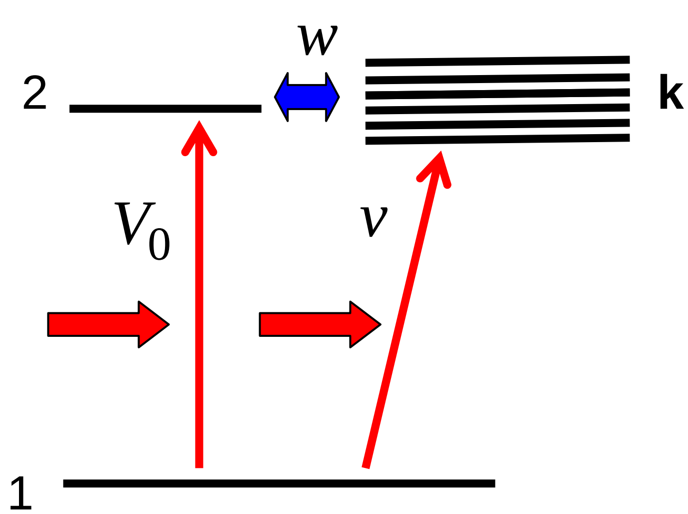
Fano lineshapes

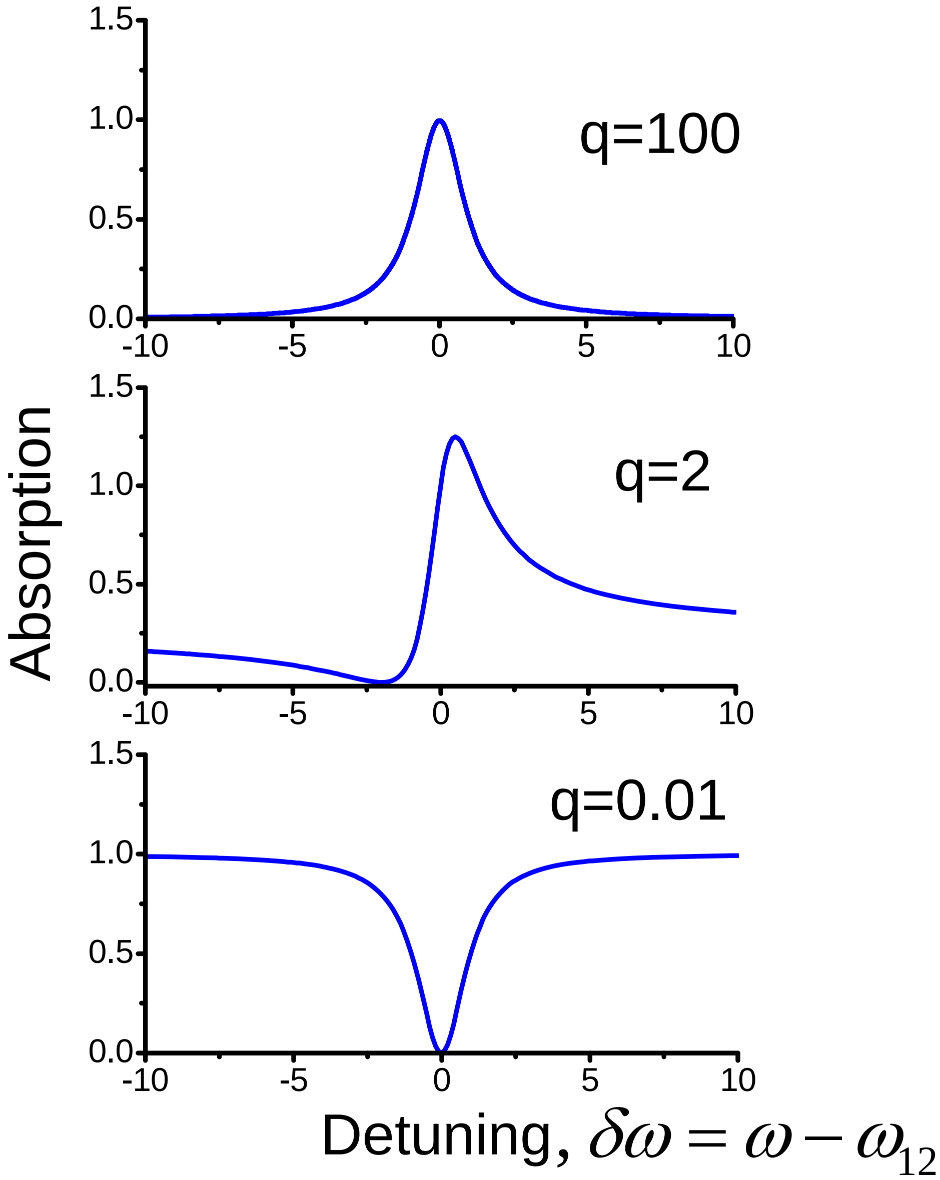
$$Abs \propto \frac{(\delta\omega + q \cdot \Gamma)^2}{\delta\omega^2 + \Gamma^2}$$

$$\delta\omega = \omega - \omega_{12}$$

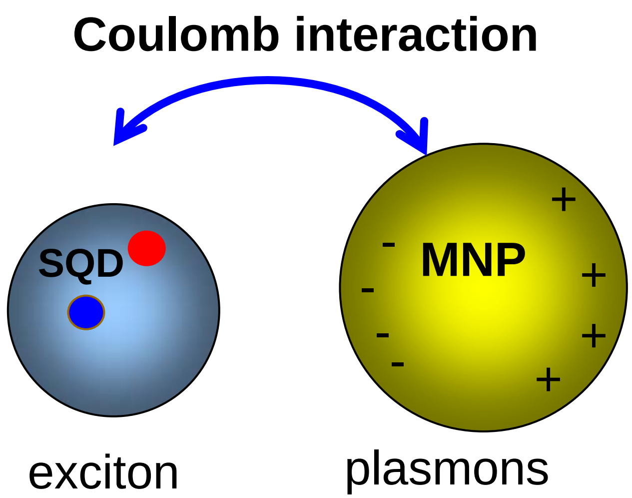
$$\Gamma = \pi \rho w^2$$

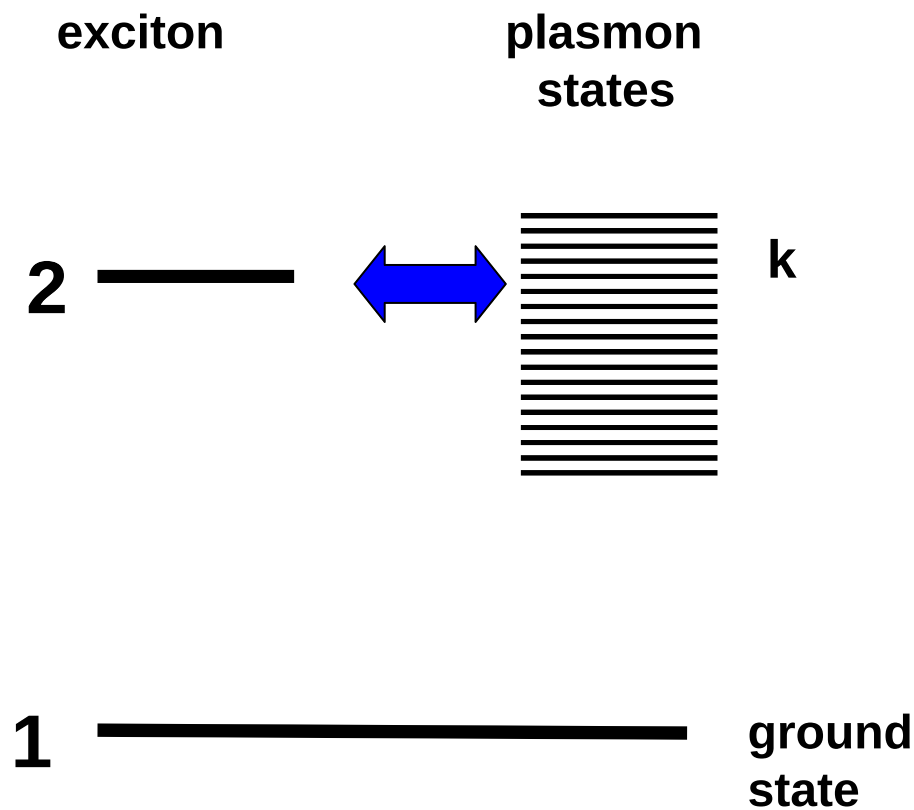
$$q = \frac{V_0 w}{v \Delta}$$





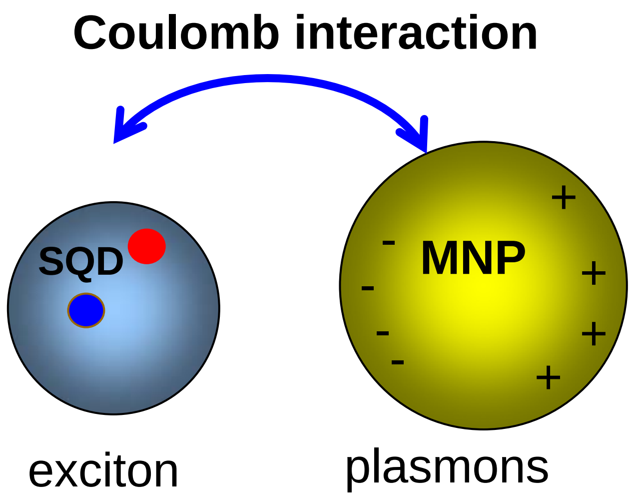
Colloidal nanocrystals

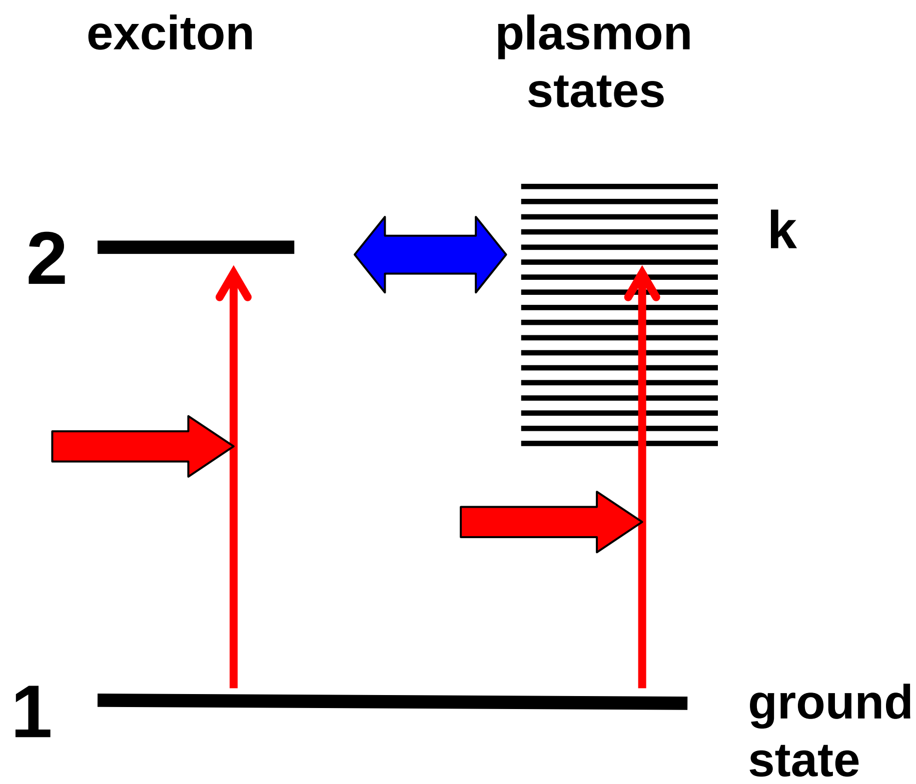




$$\hat{H}_0 = E_1\hat{c}_1^+\hat{c}_1 + E_2\hat{c}_2^+\hat{c}_2 + \sum_k \varepsilon_k \hat{a}_k^+\hat{a}_k + \sum_k U_{Coul}\hat{c}_2^+\hat{c}_1\hat{a}_k + U_{Coul}^*\hat{c}_1^+\hat{c}_2\hat{a}_k^+$$

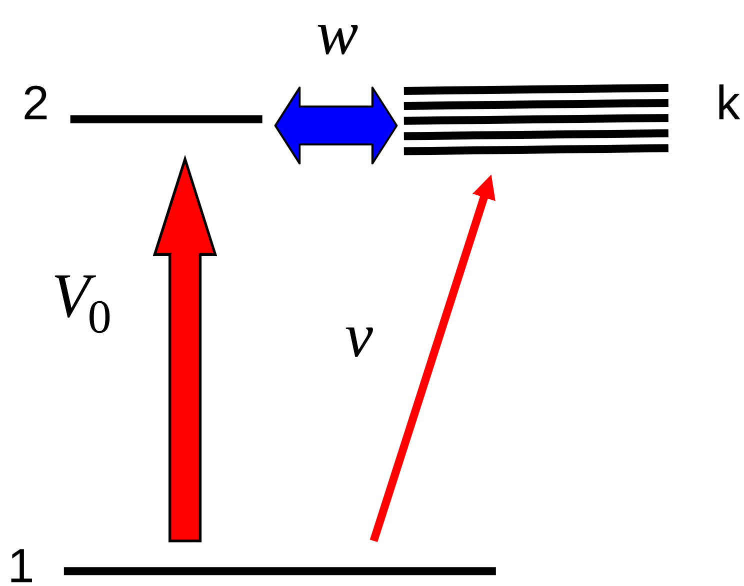
Optical absorption



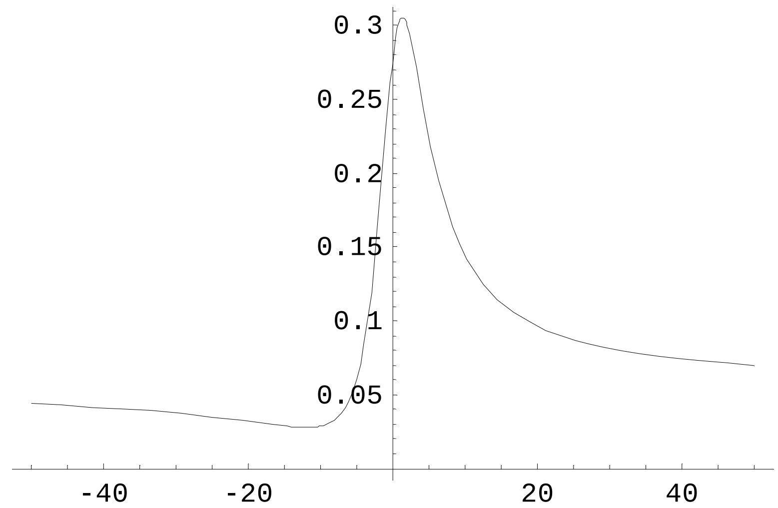


Two paths for excitation of plasmon →
interference effect (Fano effect)

Fano effect



absorption

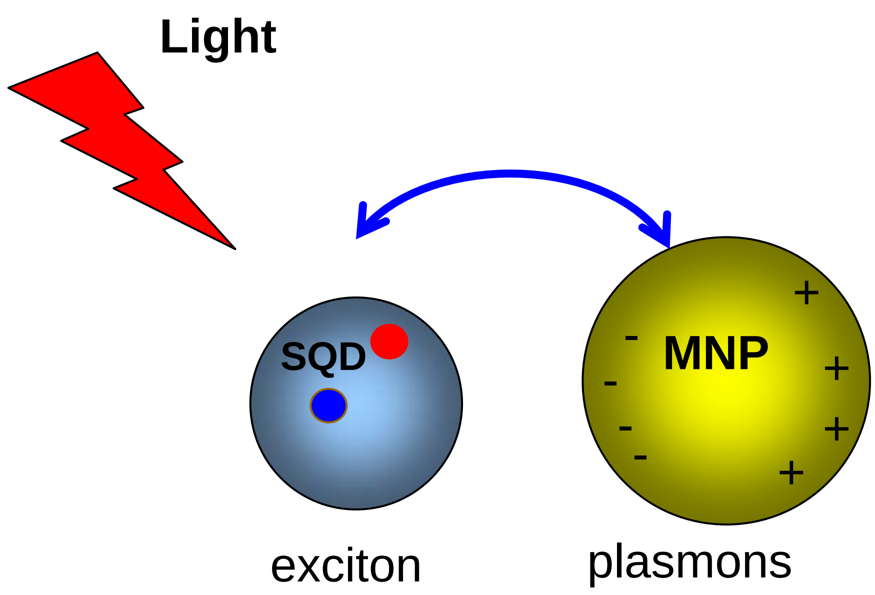


$$\delta\omega = \omega - \omega_{12}$$

$$Abs(\delta\omega) = \frac{E_0^2}{2}\Gamma\frac{v^2}{w^2}\frac{(\delta\omega + q\cdot\Gamma)^2}{\delta\omega^2 + \Gamma^2}$$

$$\Gamma = \pi\rho w^2$$

$$q = \frac{V_0 w}{v\Delta}$$



$$\hat{H}_0 = E_1 \hat{c}_1^+ \hat{c}_1 + E_2 \hat{c}_2^+ \hat{c}_2 + \sum_k \varepsilon_k \hat{a}_k^+ \hat{a}_k + \sum_k U_{Coul} \hat{c}_2^+ \hat{c}_1 \hat{a}_k + U_{Coul}^* \hat{c}_1^+ \hat{c}_2 \hat{a}_k^+$$

$$\frac{\partial \hat{\rho}}{\partial t} = \frac{i}{\hbar}(\hat{\rho} \cdot \hat{H} - \hat{H} \cdot \hat{\rho}) + \hat{\Gamma}\hat{\rho}$$

$$\hat{H} = \hat{H}_0 + \hat{V}_{opt}(t)$$

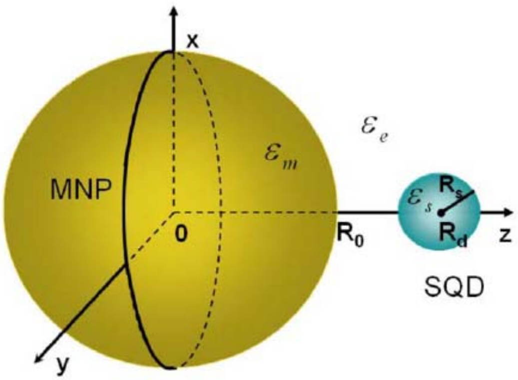
$$\hat{V}_{opt}(t) = -\mathbf{r} \cdot \mathbf{E}_0 \cos(\omega t)$$

Strong de-coherence in the metal NP
(fast relaxation of plasmon)

Electromagnetic enhancement
due to the plasmon

$$Q_{tot} = Q_{MNP} + Q_{SQD}$$

$$Q_{\rm tot} = Q^0_{\rm MNP} + \frac{A\bar{\Gamma}_{12}}{(\omega - \bar{\omega}_0)^2 + \bar{\Gamma}^2_{12}} + \frac{B(\omega - \bar{\omega}_0)}{(\omega - \bar{\omega}_0)^2 + \bar{\Gamma}^2_{12}}$$



Dipole limit:

$$A = \frac{\omega}{2\hbar}\left(\frac{\varepsilon_e \tilde{E}_0 \mu}{\varepsilon_{\rm eff1}}\right)^2 \left| 1 + \frac{s_\alpha \gamma_1 R_0^3}{R_d^3} \right| - \tilde{E}_0^2 \frac{\omega \mu^2 s_1 \varepsilon_e R_0^6 \,{\rm Im}[\gamma_1]}{3\hbar \varepsilon^2_{\rm eff1} R_d^6} \left| \frac{\varepsilon_e}{\varepsilon_{\rm eff2}} \right|^2 {\rm Im}[\varepsilon_m(\omega)],$$

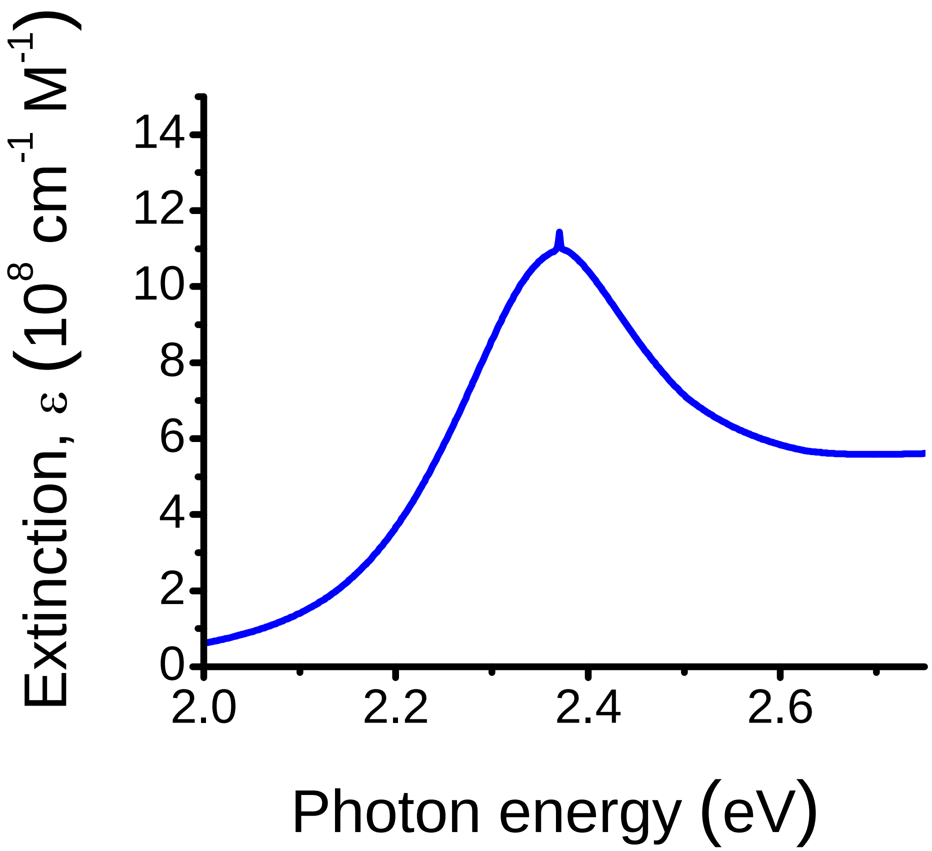
$$B = \frac{s_\alpha \mu^2 \varepsilon_e \tilde{E}_0^2 \omega R_0^3}{3\hbar \varepsilon^2_{\rm eff1} R_d^3} {\rm Im}[\varepsilon_m(\omega)] \left| \frac{\varepsilon_e}{\varepsilon_{\rm eff2}} \right|^2 \left(1 + \frac{s_\alpha R_0^3 \,{\rm Re}[\gamma_1]}{R_d^3} \right).$$

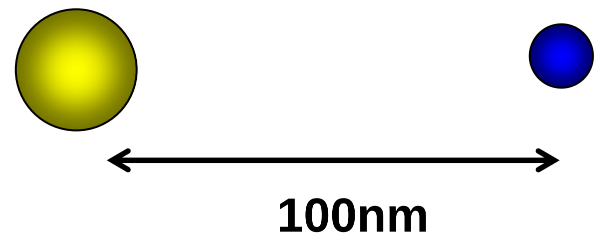
W. Zhang, A. Govorov, et al., PRB 2008.

$$\sigma_{metal\ NP} >> \sigma_{semiconductor\ NP}$$

$$R_{metal\ NP} = 10nm$$

$$\Gamma_{12} = 1meV$$

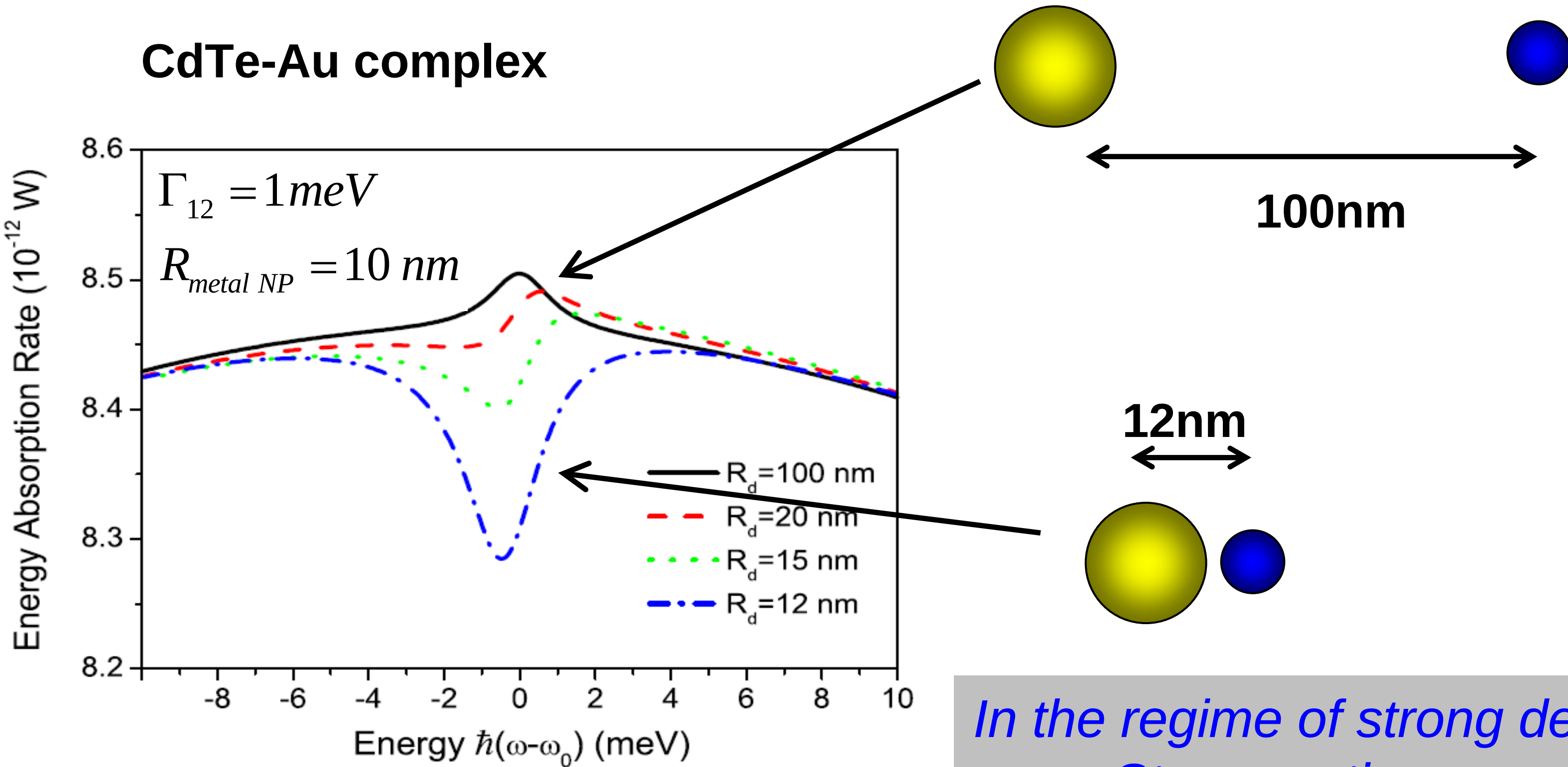




$$\sigma_{metal\ NP} >> \sigma_{semiconductor\ NP}$$

$$Q_{tot} = \boxed{Q_{MNP}} + Q_{SQD}$$

CdTe-Au complex



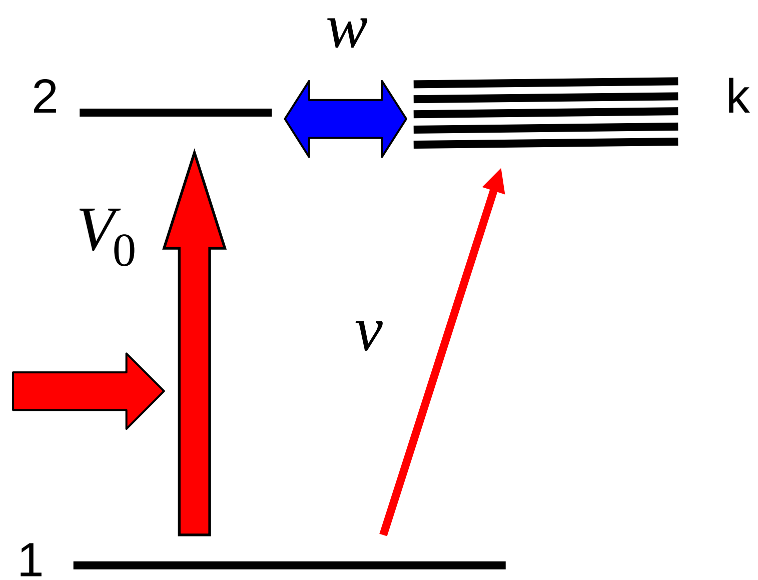
In the regime of strong de-coherence:
Strong anti-resonances in absorption and light scattering

<u>Weak lines become visible as anti-resonances</u>

Multipoles are important

W. Zhang, A. Govorov, et al., PRB 2008.

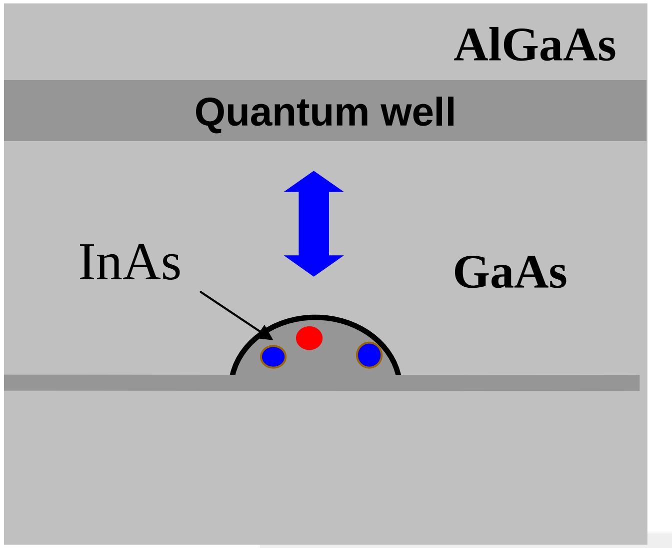
Nonlinear Fano effect



Strong light field
Transition 1→ 2 is partially saturated

$$Absorption_{1\to 2} \propto \left(\rho_{22} - \rho_{11}\right)$$

Self-assembled quantum dots at low temperatures

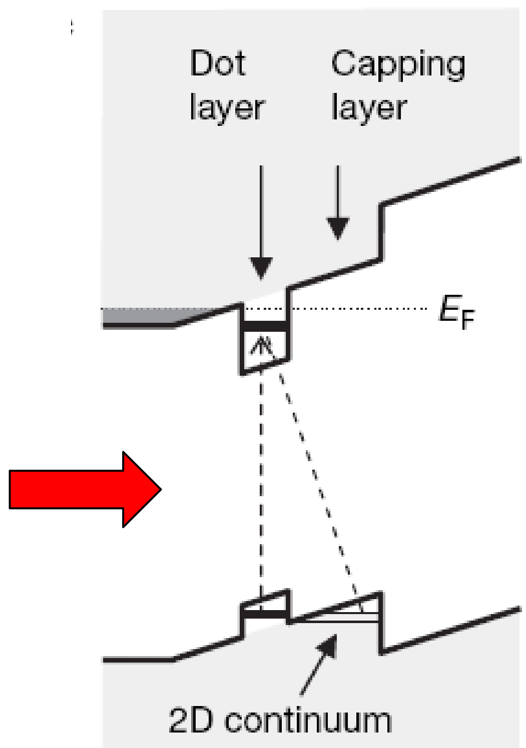


Experiments in Munich

A dot with weak tunnel coupling to a continuum

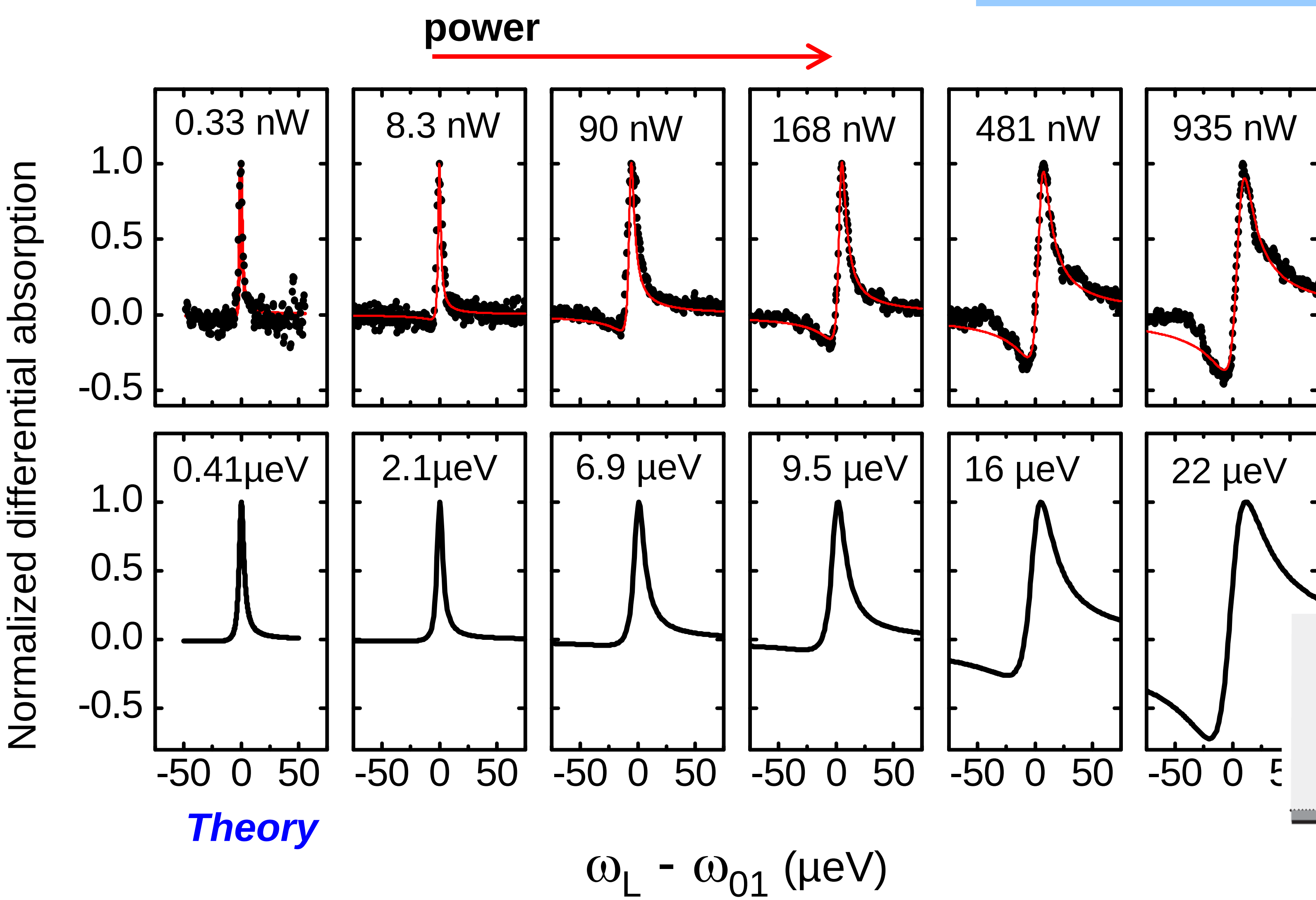
Fano factor $\left|q_{Fano}\right| >> 1$

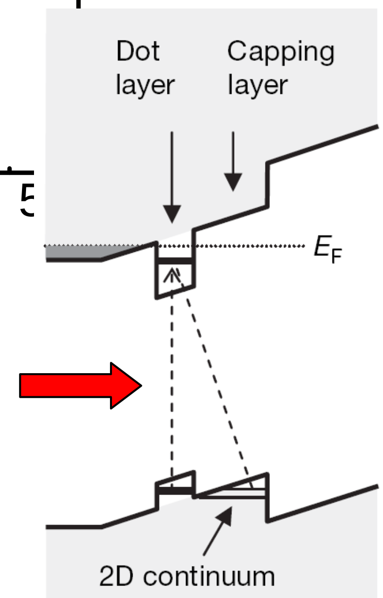
Narrow exciton resonances



Nonlinear Fano effect

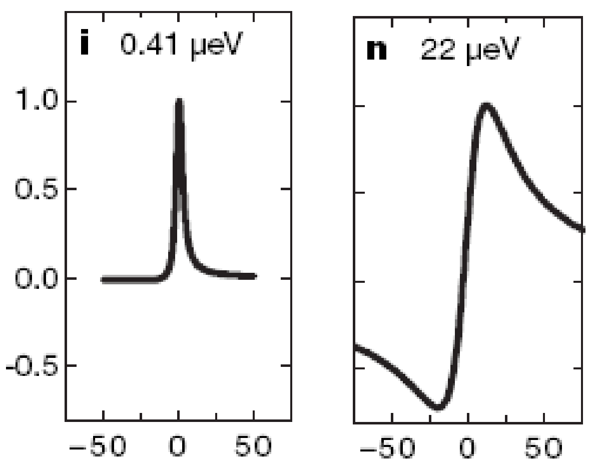
Martin Kroner, Khaled Karrai, at al., experiments



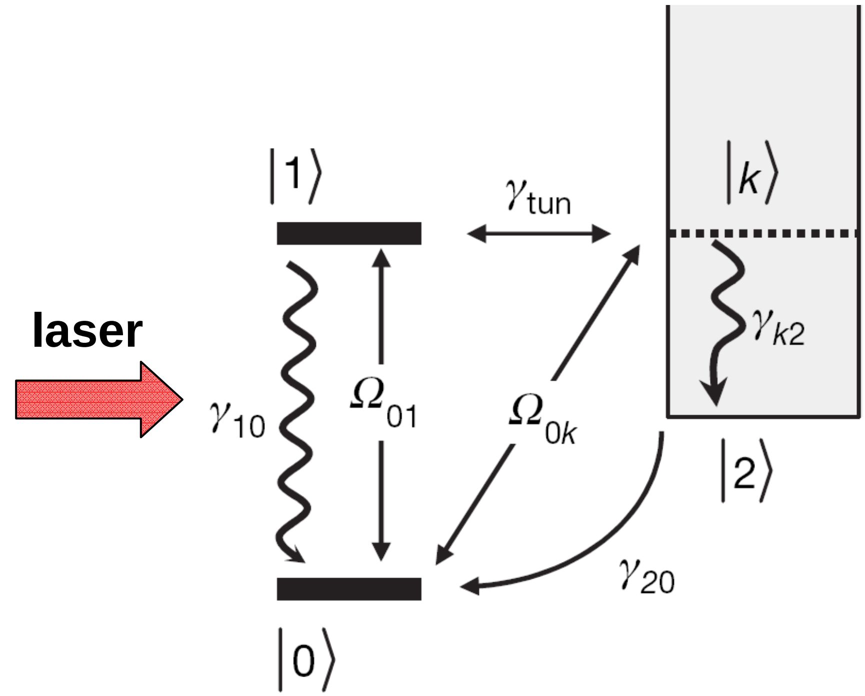


M. Kroner, A. O. Govorov, S. Remi, B. Biedermann, S. Seidl, A. Badolato, P. M. Petroff, W. Zhang, R. Barbour, B. D. Gerardot, R. J. Warburton & K. Karrai, *Nature*, 2008.

Low power High power



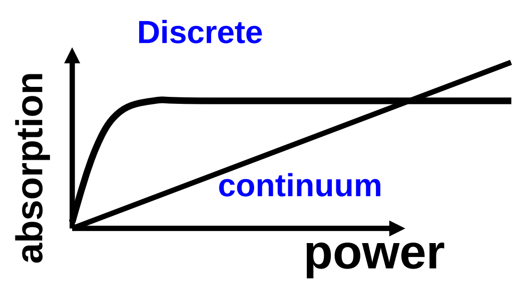
$$|q_{Fano}| >> 1$$

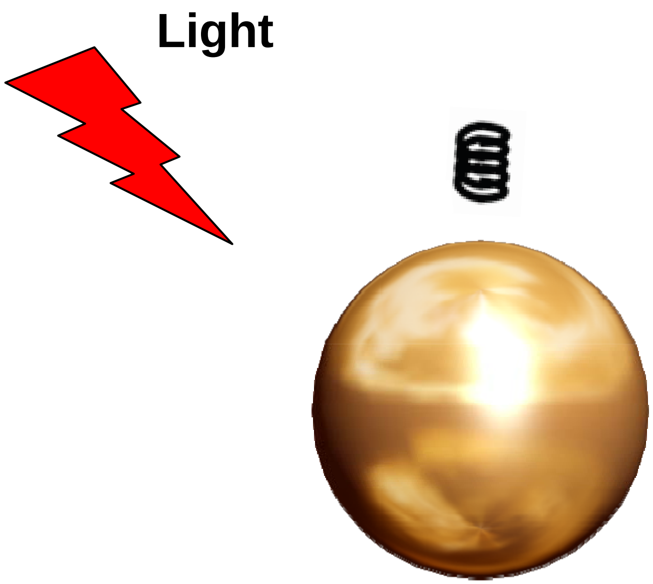


At low power, the natural broadening prohibits observation of weak processes

At high power, we can observe weak coherent processes

The discrete resonance is saturated
Transitions to the continuum become more important





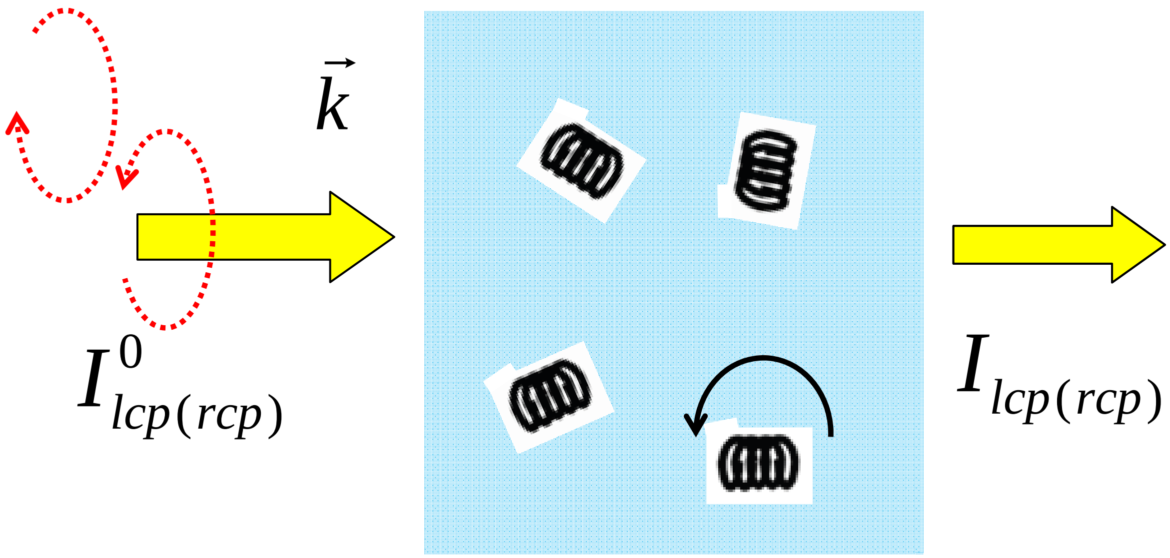
$$\sigma_{metal\ NP} >> \sigma_{molecule}$$

Optical chirality (circular dichroism)

$$CD_{metal\ NP} \approx 0$$

$$CD_{molecule} \neq 0$$

Circular dichroism spectroscopy

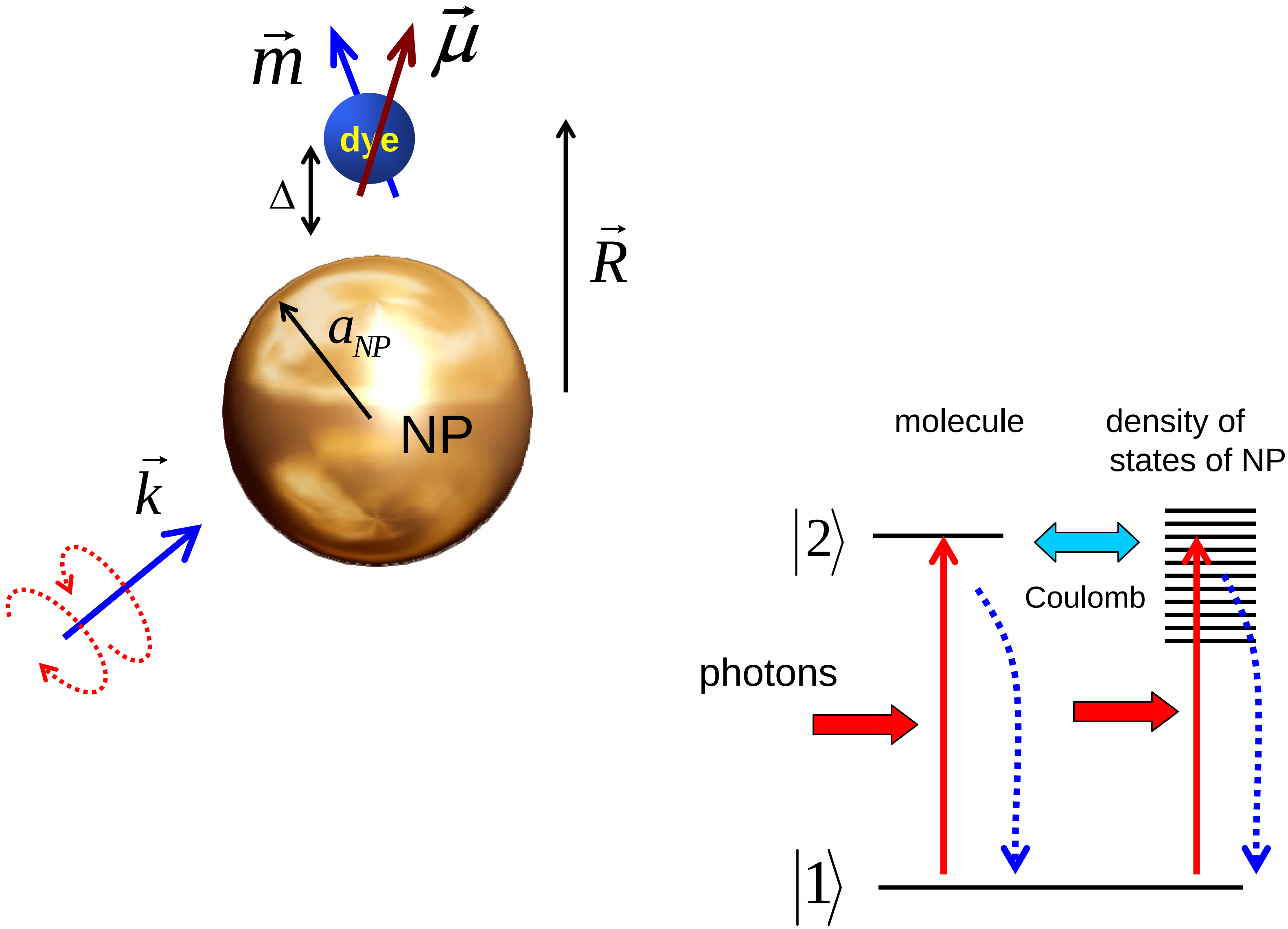


$$A_{lcp} = \log_{10} \frac{I^0_{lcp}}{I_{lcp}} = \varepsilon_{lcp} \cdot L \cdot c$$

$$\Delta A = A_{lcp} - A_{rcp}$$

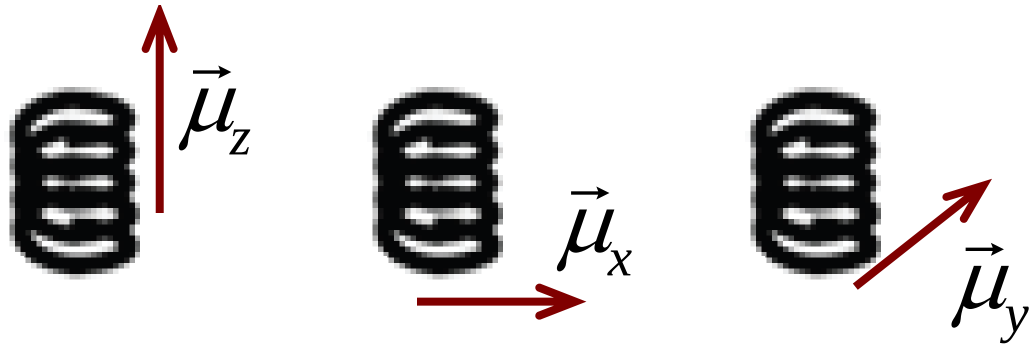
$$\Delta\varepsilon = \varepsilon_{CD} = \varepsilon_{lcp} - \varepsilon_{rcp}$$

Chiral objects:
No mirror symmetry planes
Example: Helix

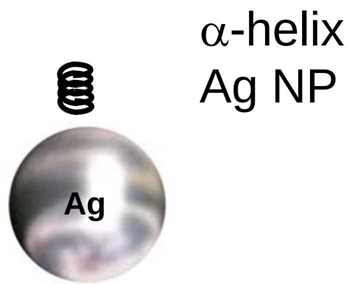


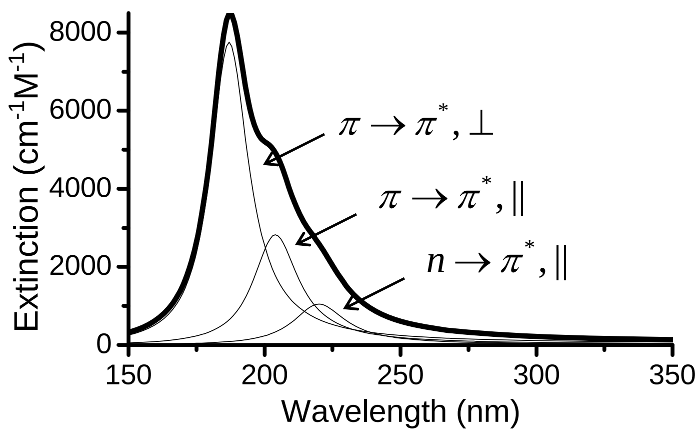
$\vec{m}$
$\vec{\mu}$
dye
Δ
$\vec{R}$
a_{NP}
NP
$\vec{k}$
molecule
density of
states of NP
$|2\rangle$
Coulomb
photons
$|1\rangle$

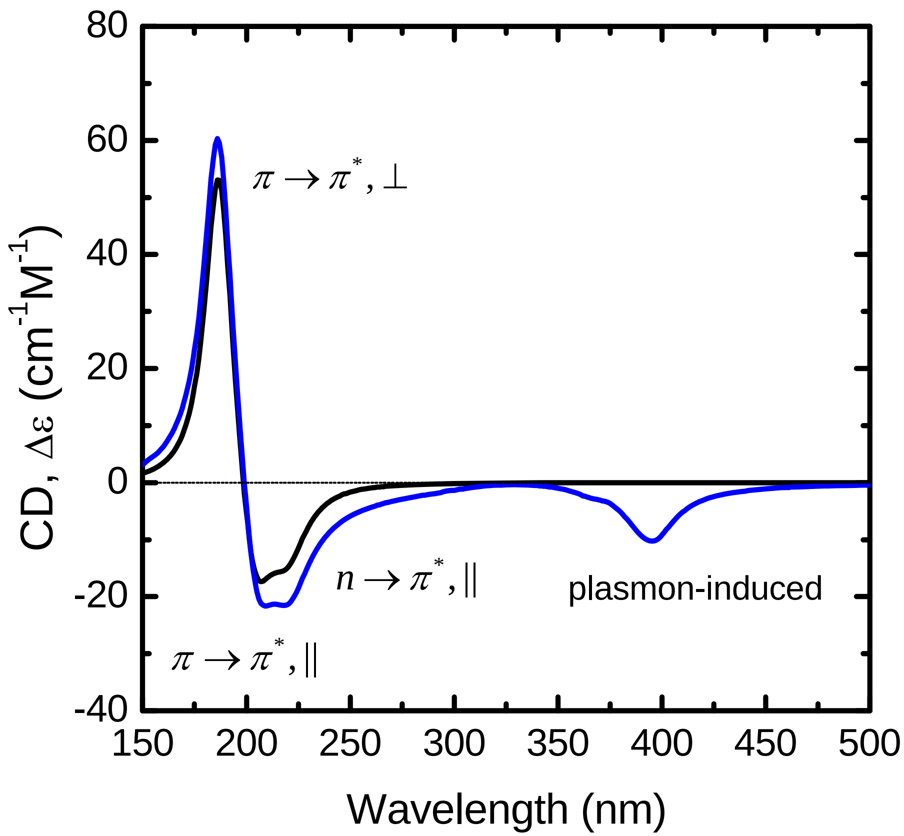
Chromophore excitons are delocalized in a helix structure



W. Moffitt, J. Phys. Chem. 25, 467 (1956).

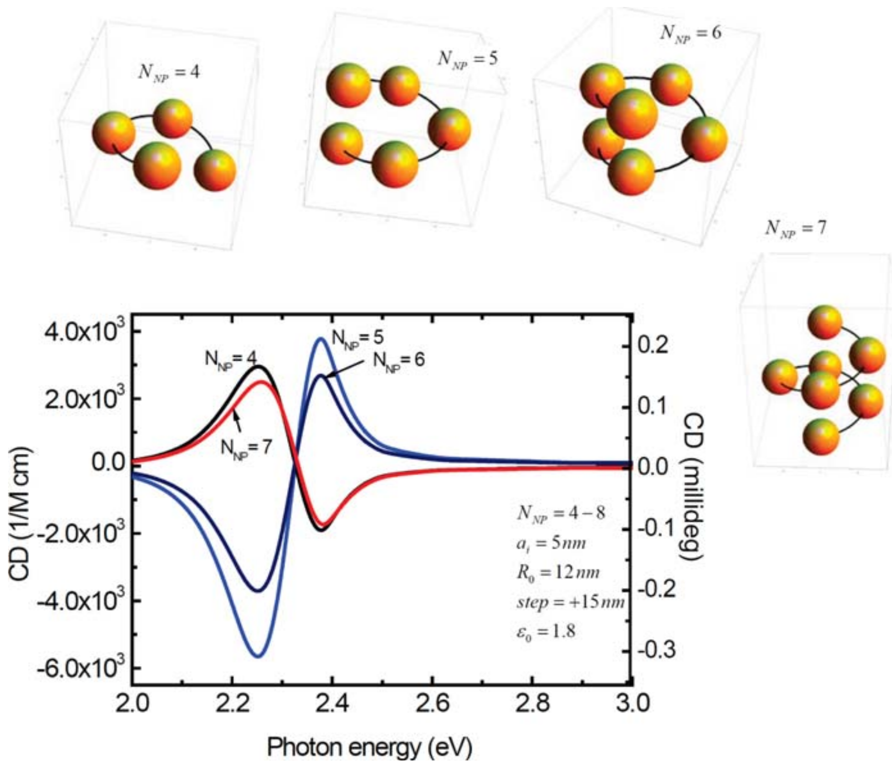


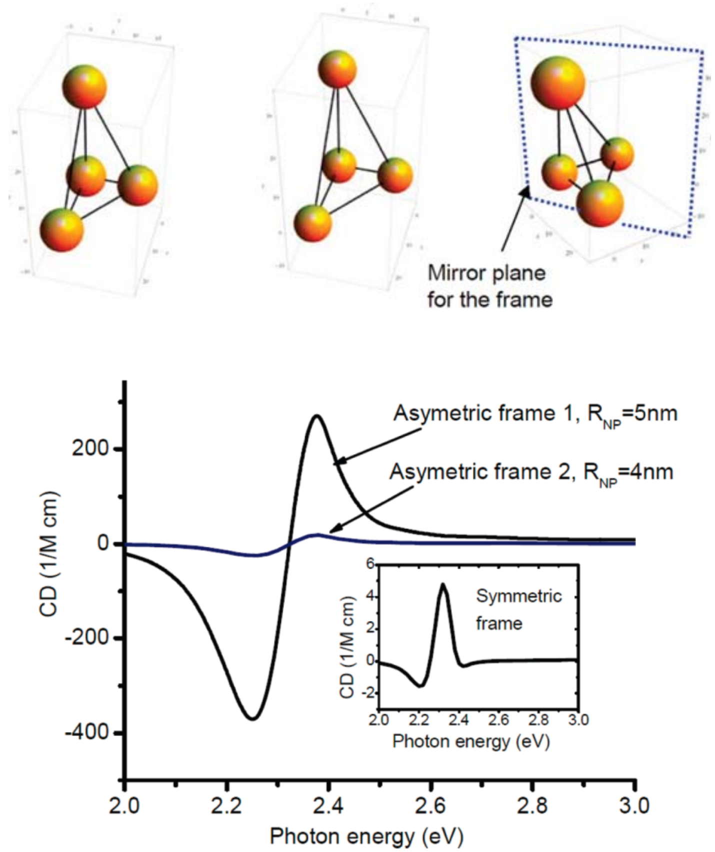




Govorov, A.O.; Fan, Z.; Hernandez, P.; Slocik, J.M; Naik, R.R., *Nano Letters*, 2010.

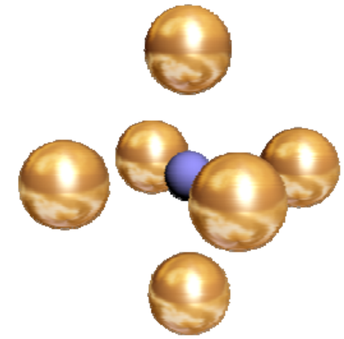
Purely plasmonic CD





Z. Fan, A. O. Govorov, Nano Letters 2010.

Conclusions



The exciton-plasmon interactions

Linear and nonlinear interference effects

Plasmon-induced CD