Enhancing quantum coherence of organic molecules with nanophotonic structures

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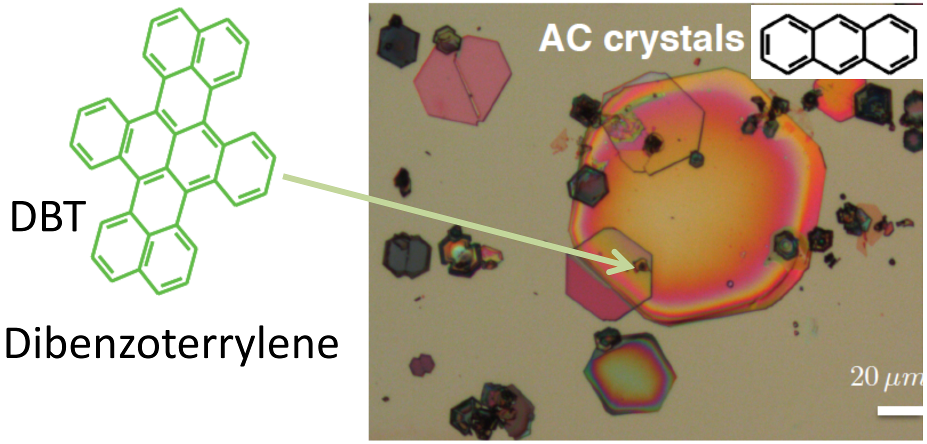
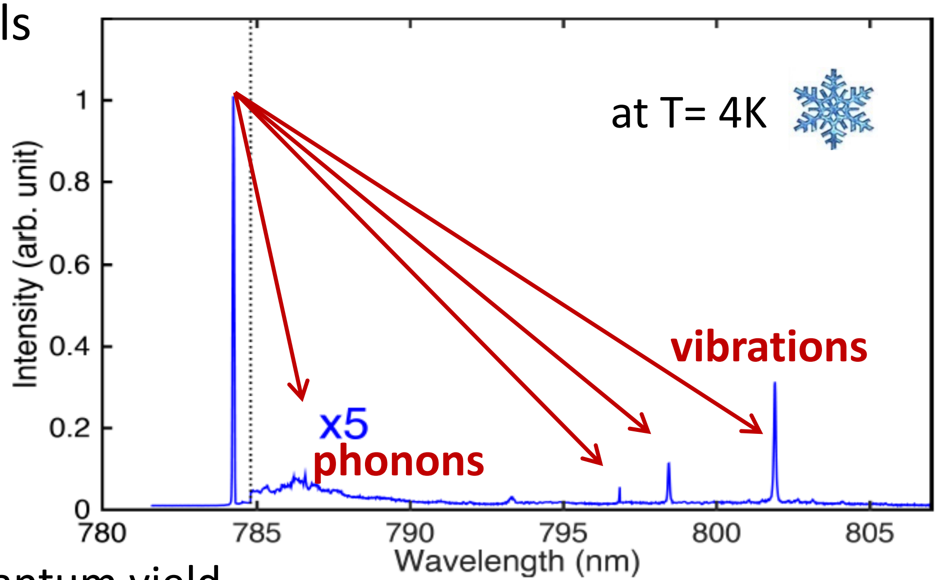
Polycyclic aromatic hydrocarbons coherence properties

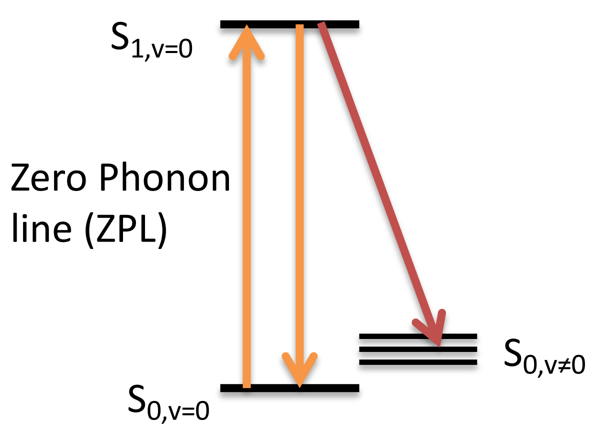
Organic molecules in certain organic crystals





Not ordinary molecules: No quenching, 100% quantum yield

Electronic levels



Small electron-vibrational couplings (Holstein model) and fast vibrational decays $\gamma_v \sim 10^3\,\gamma$

→Effective two-level emitter: Radiative limited

Decay rate:

$$\gamma = \gamma_{ZPL} + \gamma_{01} + \gamma_{02} + \ldots.$$

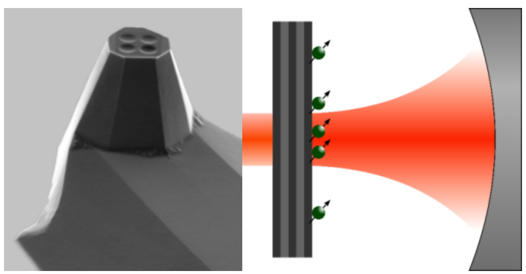
Limited resonant coherence

Control molecule interactions→Nanostructures

Key: Sub-λ confinement→ Enhance & control resonance fluorescence

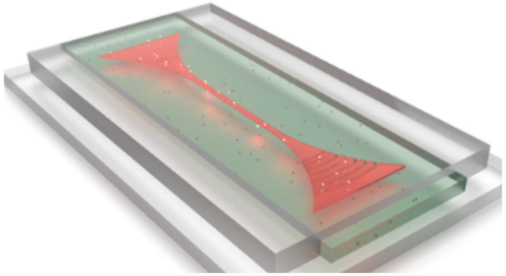
Mode volume $$V = \frac{\int[\tilde{\mathbf{E}} \cdot \frac{\partial(\omega\epsilon)}{\partial\omega}\tilde{\mathbf{E}} - \tilde{\mathbf{H}} \cdot \frac{\partial(\omega\mu)}{\partial\omega}\tilde{\mathbf{H}}]d^3\mathbf{r}}{2\epsilon_0 n^2[\tilde{\mathbf{E}}(\mathbf{r}_0) \cdot \mathbf{u}]^2},$$

Sub-λ cavities



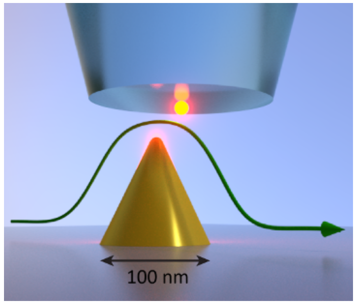
H. Kelkar *et al.*, PRApp. **4**, 54010 (2015)

Nanowaveguides



P. Turschmann *et al.*, Nano Lett. **17**, 4941 (2017)

Nanoantennas



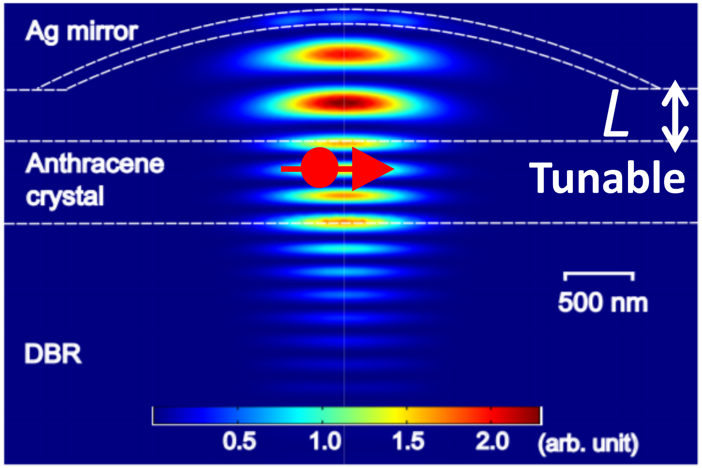
Matsukaki *et al.*, Sci. Rep. 7, 42307, (2017)

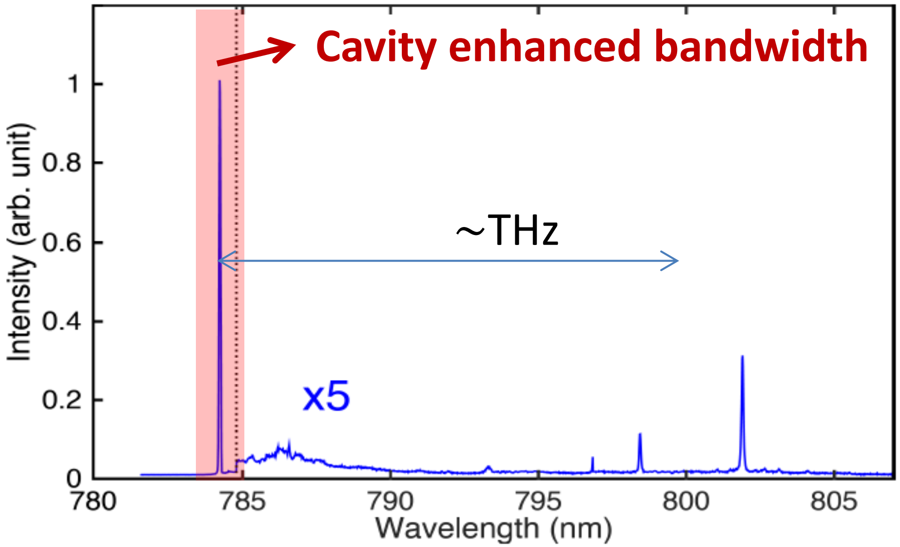
Goals and problems:

- Enhance collection efficiency & classical coherence
- Non-classical coherent effects
- Collective-molecule coherent interactions
- Decoherence, quenching (phonons,..)

Enhance resonant coherence with limited cavity bandwidths

D. Wang, H. Kelkar, D. Martin-Cano, T. Utikal, S. Götzinger, V. Sandoghdar, PRX. **7**, 021014, (2017)





$Q\sim 100-10000$, $V\sim 0.5\lambda^3$, $F\sim 10-1000$

Modified Jaynes-Cumming model→ Single quasi-mode & single emitter

$$H = \hbar\omega\sigma^\dagger\sigma + \hbar\omega_p a^\dagger a + \hbar g(a^\dagger\sigma + \sigma^\dagger a),$$

Open system → dissipation

Cavity FWHM $\gamma, \kappa = \omega_r / Q$

Purcell

Change of branching ratio $\Gamma_{tot} = F\,\gamma_{zpl} + \gamma$

Coherence limited by Cooperativity: $C = 4g^2/\kappa\gamma = F\gamma_{zpl}/\gamma = F\alpha$

Branching ratio $\alpha_{DBT}\sim 1/3$

Enhance resonant coherence with limited cavity bandwidths

Beta factor:

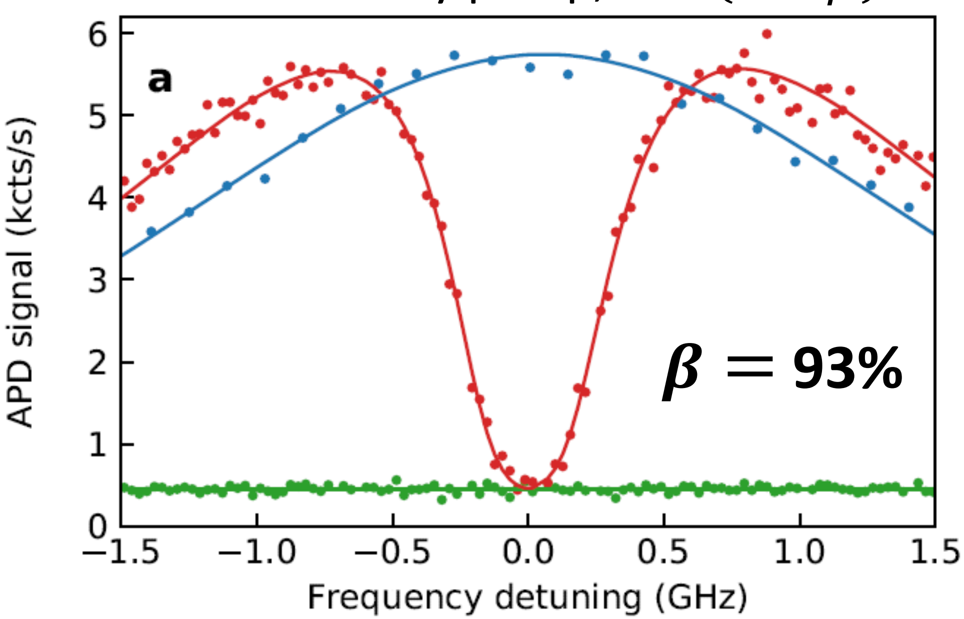
$$\beta = \frac{F\,\gamma_{00}}{\Gamma_{tot}} = C/(C+1) = \frac{(F+1)\gamma_{zpl}}{F\,\gamma_{zpl}+\gamma}\,\frac{(F)\gamma_{zpl}}{(F+1)\gamma_{zpl}} = \alpha_{cav}\,\beta_{\text{zpl}}$$

Cavity branch ratio

x Resonant beta

Classical coherent effect→ Transmission Extinction $\mathbf{T} = \langle a^{\dagger} a \rangle$

At weak cavity pump, T ≈ $(1-\beta)^2$



Close to 100% extinction with a single molecule

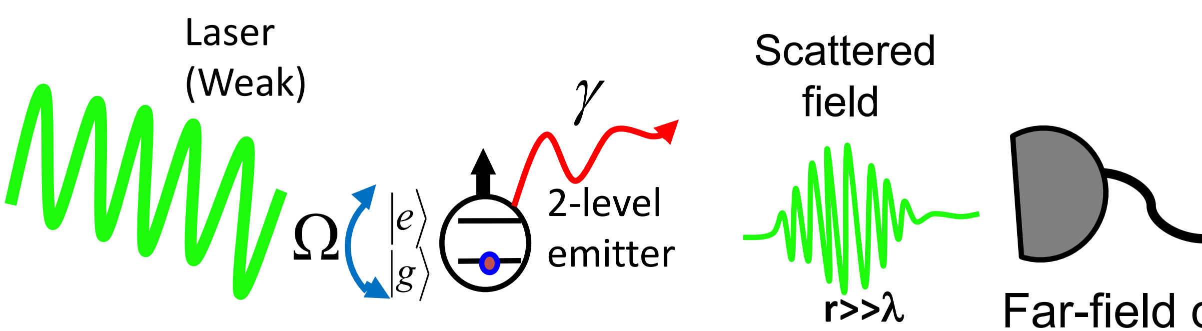
D. Wang, H. Kelkar, D. Martin-Cano, T. Utikal, S. Götzinger, V. Sandoghdar, Nature Physics, **15**, 483–489 (2019)

$g \sim \kappa$ **intermediate coupling regime, how to increase it? Nonclassical coherent effects?**

Nonclassical coherent effect→Quadrature Squeezing

Resonance fluorescence in free space

D. Walls & P. Zoller, *Physical Review Letters*, **47**, 709 (1981)



$$\langle : \Delta\hat{E}^2(\bar{r},t) : \rangle < 0$$

Challenging measurement at the single-emitter level:
small signal intensity & collection efficiency, phase-dependent

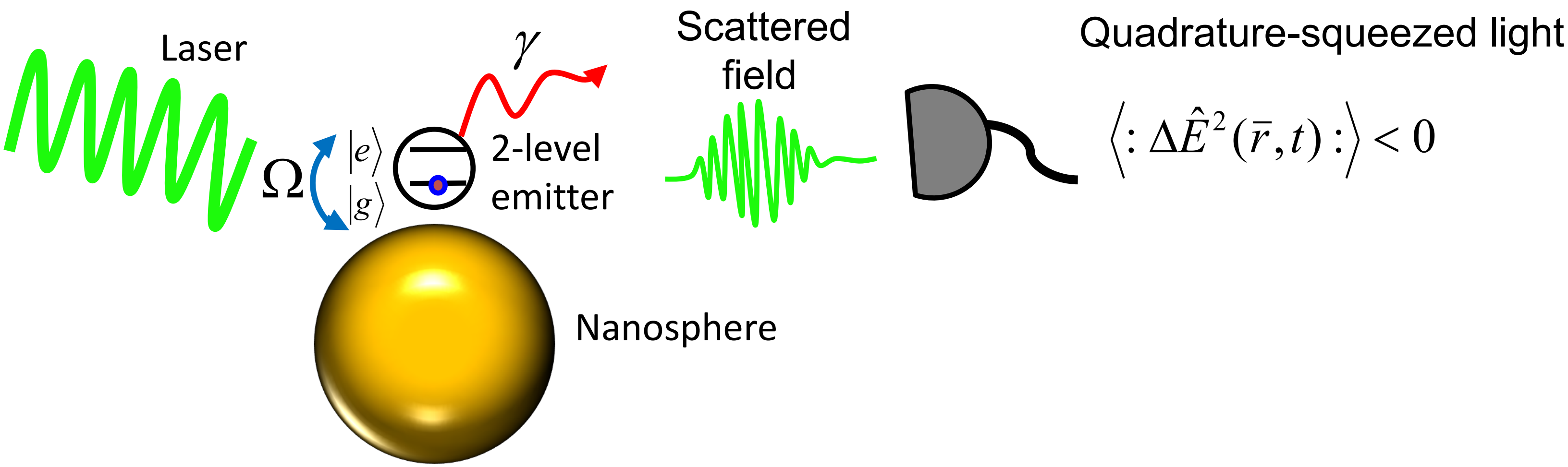
Quote from Welsch and Vogel's quantum optics book:

"In single atom light scattering the sub-Poissonian effect is expected to be extremely small due to a very small overall quantum efficiency, so that it seems hopeless to measure it"

Tailoring quadrature squeezing by optical nanostructures

Motivation: Fundamental proof and assist difficult detection

D. Martín-Cano, H. R. Haakh, K. Murr & M. Agio, *Physical Review Letters* **113**, 263605 (2014)



Heisenberg equations of motion (Markovian and rotating wave approx)

Scattered field from hybrid system

$$\hat{E}_s^+(\bar{r},t) = |g_i(\mathbf{r})| e^{\imath\phi_i(\mathbf{r})} \hat{\sigma}(t),$$

coherence

$$\propto \hat{\sigma} = |g\rangle\langle e|$$

Quantum emitter + nanostructure squeezing

Normally ordered E_i field variance for $\hat{E}_i(\bar{r},t) = \hat{E}_i^{+}(\bar{r},t) + \hat{E}_i^{-}(\bar{r},t)$

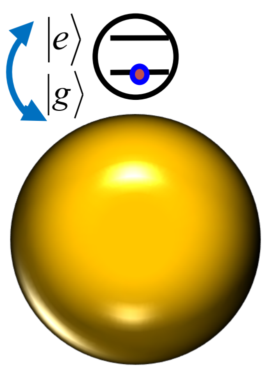
$$\langle : [\Delta \hat{E}_i(\mathbf{r},t)]^2 : \rangle = |g_i(\mathbf{r})|^2 \langle : [\Delta \hat{\sigma}_{\phi_i}]^2(t) : \rangle$$

$$= 2|g_i(\mathbf{r})|^2 \left[\underbrace{\langle \hat{\sigma}^\dagger(t)\hat{\sigma}(t)\rangle - |\langle \hat{\sigma}(t)\rangle|^2}_{\text{Positive term}} - \underbrace{\mathrm{Re}\left(e^{i2\phi_i(\mathbf{r})}\langle \hat{\sigma}(t)\rangle^2\right)}_{\text{Coherence fluctuations (Phase-dependent)}} \right]$$

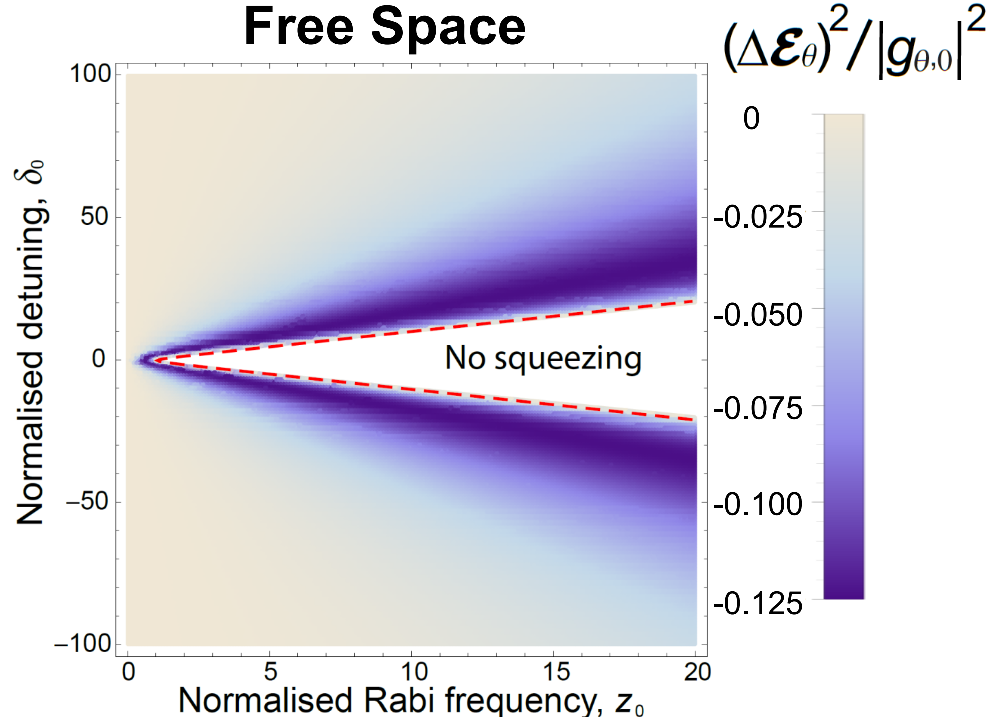
- If $\langle : [\Delta \hat{\sigma}_{\phi_i}]^2(t) : \rangle < 0$ → Squeezed light

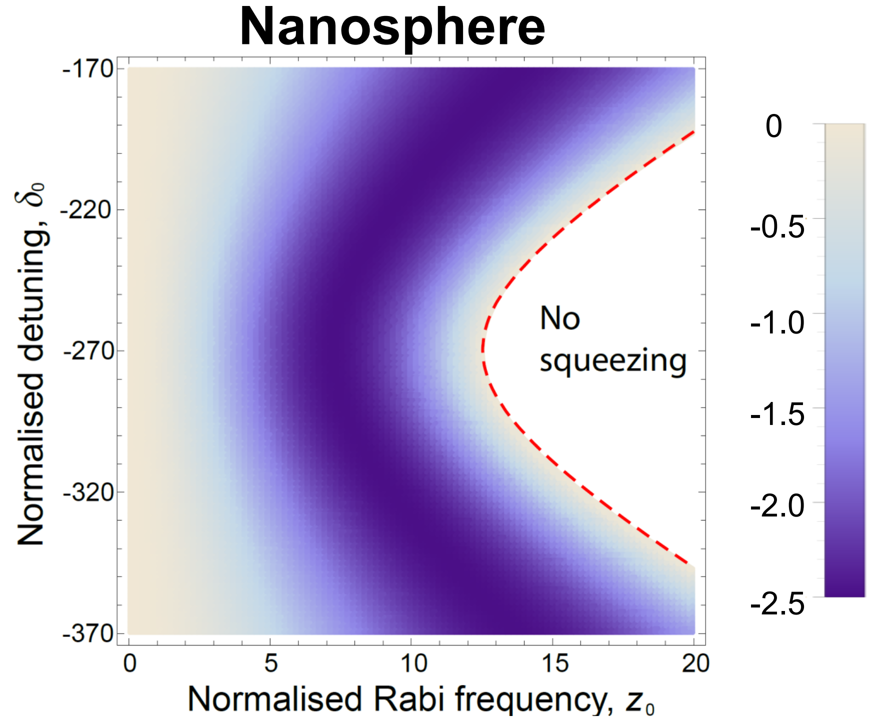
~~$|1\rangle$~~ $(|0\rangle + |1\rangle)/\sqrt{2}$ Maximum squeezing, quantum coherence

Effect of nanosphere

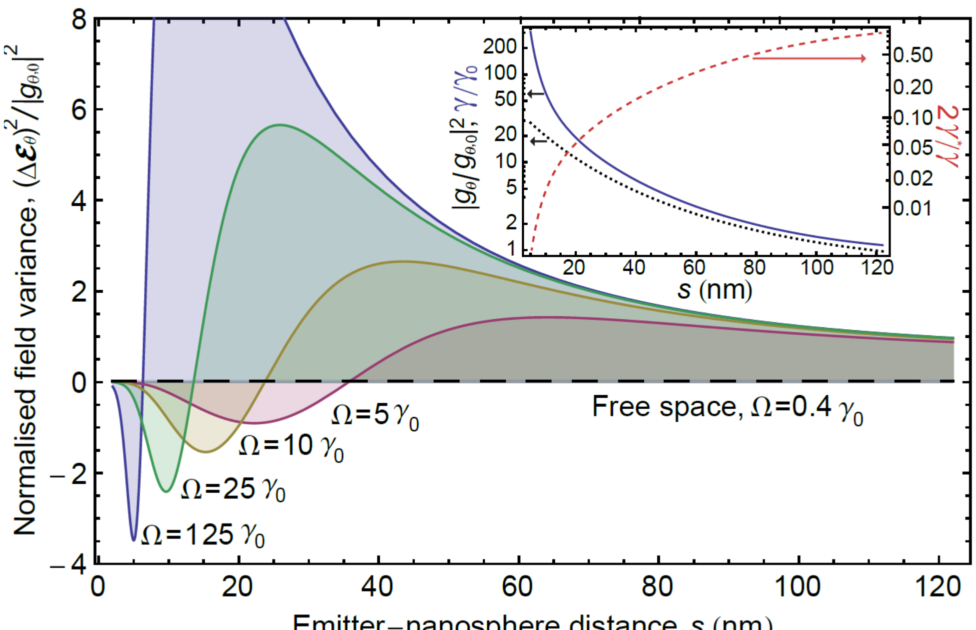


$$\langle \hat{\tilde{\sigma}}(\infty)\rangle = \frac{-\Omega[2\delta_L - i(\gamma + 2\gamma^*)]}{4\delta_L^2 + 2|\Omega|^2(1 + \frac{2\gamma^*}{\gamma}) + (\gamma + 2\gamma^*)^2}$$





More counts, larger bandwidth



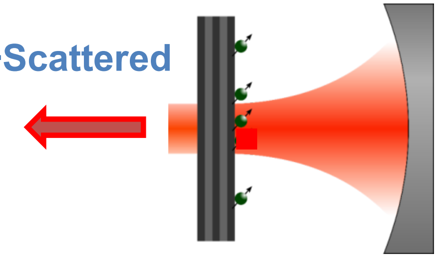
$2\gamma^* = \gamma$

No squeezing in free space

Nanoparticle recovers it

Evidence of squeezing via g²(0): single molecule in cavity

$$g^2(0) = \langle a^\dagger a^\dagger a a\rangle / \langle a^\dagger a\rangle^2$$

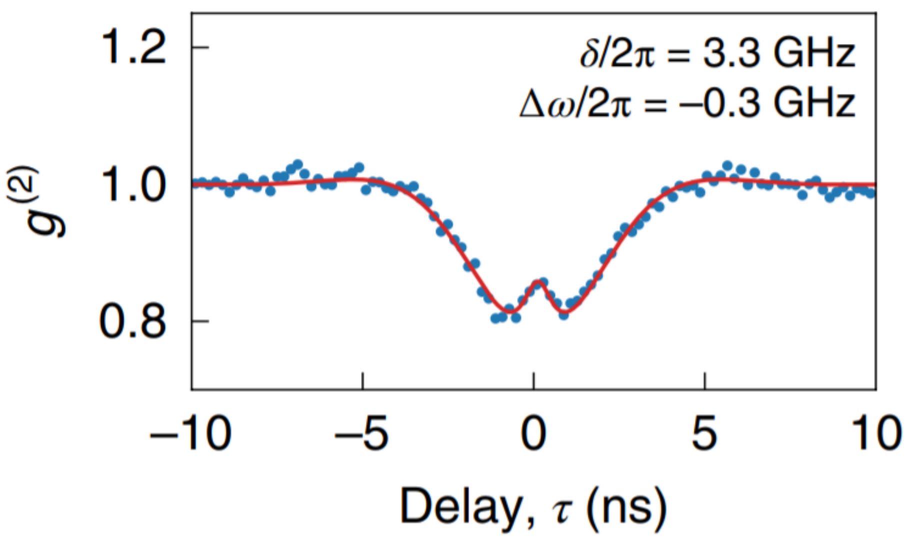


Weak driving (analytical)

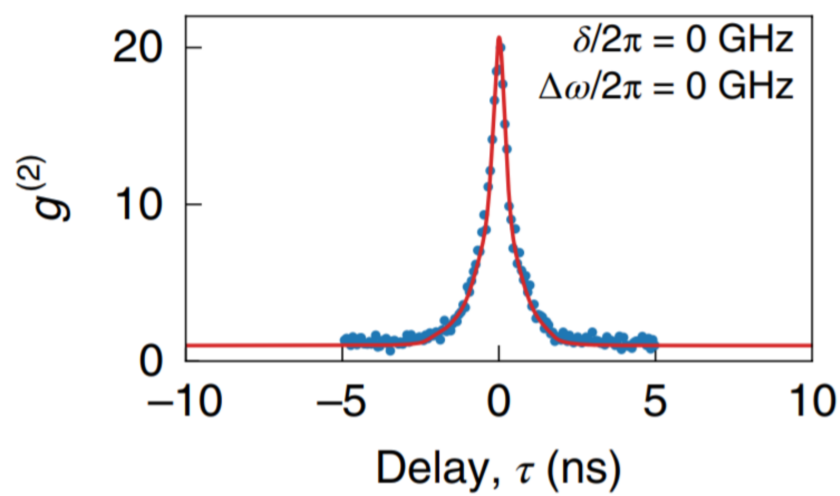
negative positive

$$g^2(0) \approx 1 + \frac{|\langle a\rangle|^2 \langle : \Delta(a e^{-i\phi} + a^\dagger e^{i\phi})^2 : \rangle + \langle \Delta a^\dagger \Delta a^\dagger \Delta a \Delta a\rangle}{|\langle a\rangle|^4}$$

Detuned

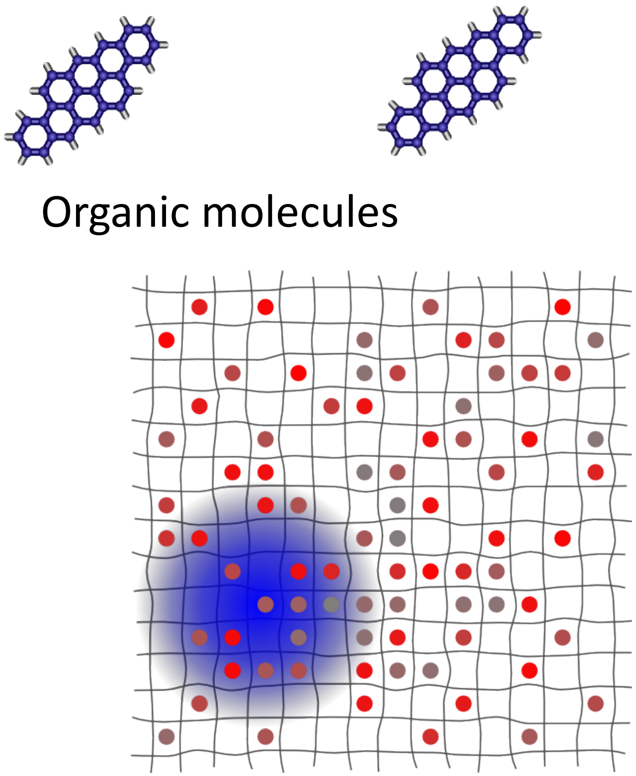


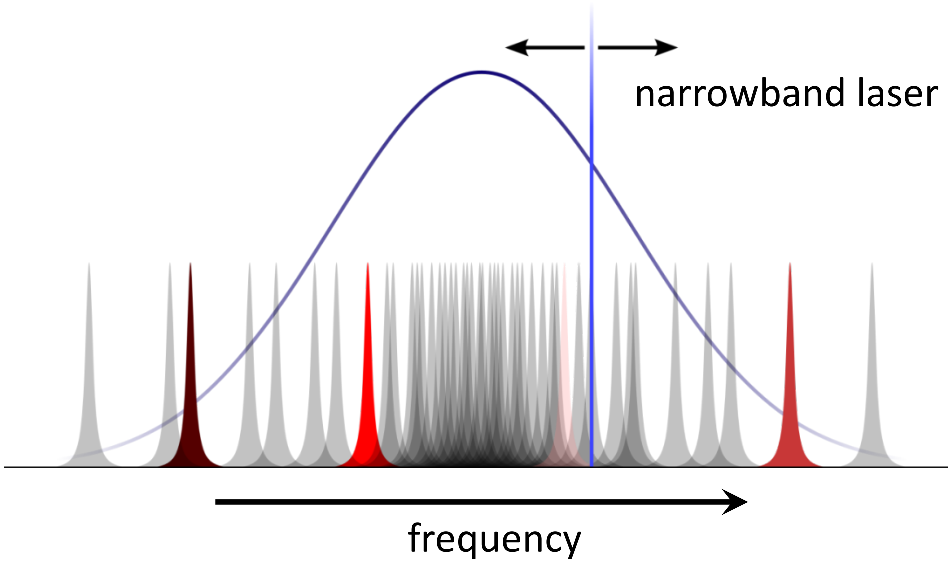
Resonant



D. Wang, H. Kelkar, D. Martin-Cano, T. Utikal, S. Götzinger, V. Sandoghdar, Nature Physics, **15**, 483–489 (2019)

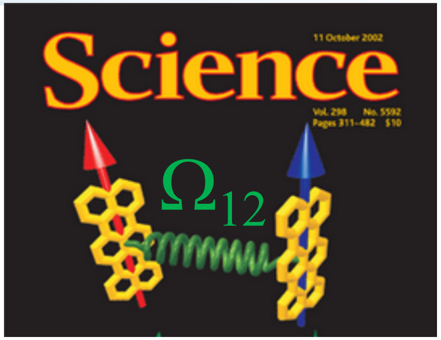
Two emitters interactions→Problem: Inhomogeneous distribution of emitters frequencies



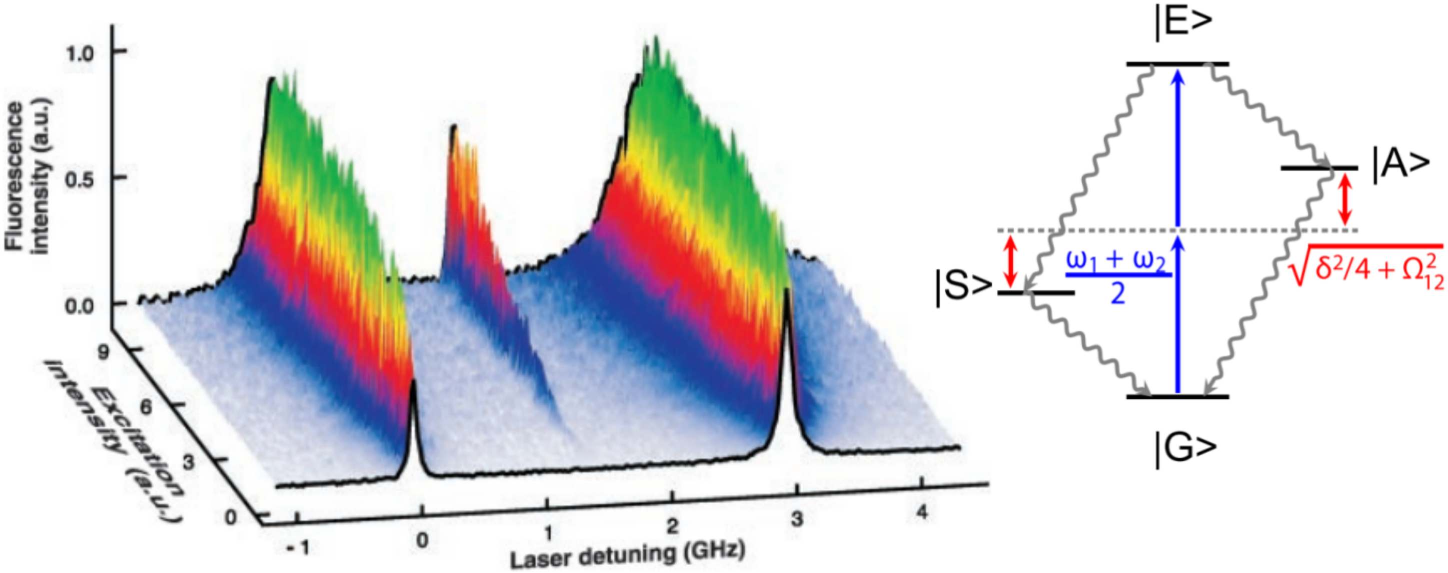


Local differences disperse the two-level emitters to several linewidths →decrease linear interactions

One solution: Two-photon nonlinearity between two detuned emitters



Hettich, C., Schmitt, C., Zitzmann, J., Kühn, S., Gerhardt, I., & Sandoghdar, V. *Science* **298**, 385 (2002)



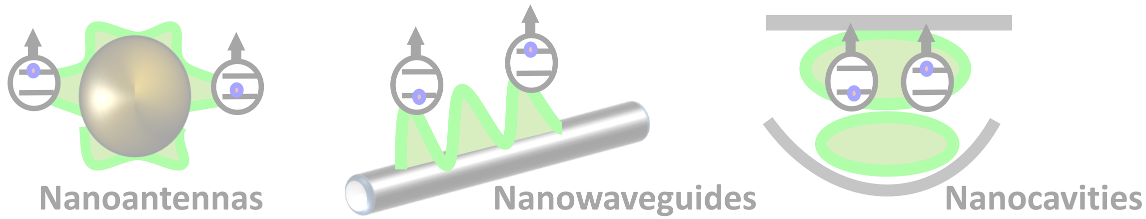
Dipole-dipole coupling Ω_{12} allows the two-photon incoherent transition

At low driving $\Omega^2 < \delta^2 / \Omega_{12}$ → exploit two-photon coherence

Dipole-dipole induced by an optical nanostructure

Proposal for collective squeezing→Broadband nanostructures:

Harald R. Haakh and D. Martín-Cano, *ACS Photonics*, **2** 1686 (2015)



Enhanced dipole-dipole coupling Ω_{12},

Far-detuned emitters

Larger distances (>100 nm)

Master equation: Relevant parameters →determined by the nanostructure Green's tensor

Dissipative (medium modified lifetimes)

$$\dot{\rho} = -\frac{i}{\hbar}[H, \rho] - \sum_{i,j=1,2} \frac{\gamma_{ij}}{2}\left(\sigma_i^\dagger \sigma_j \rho + \rho \sigma_i^\dagger \sigma_j - 2\sigma_i \rho \sigma_j^\dagger\right)$$

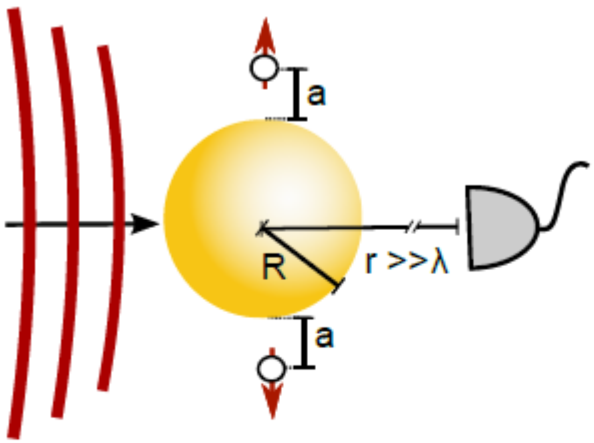
Coherent terms (medium modified energy shifts)

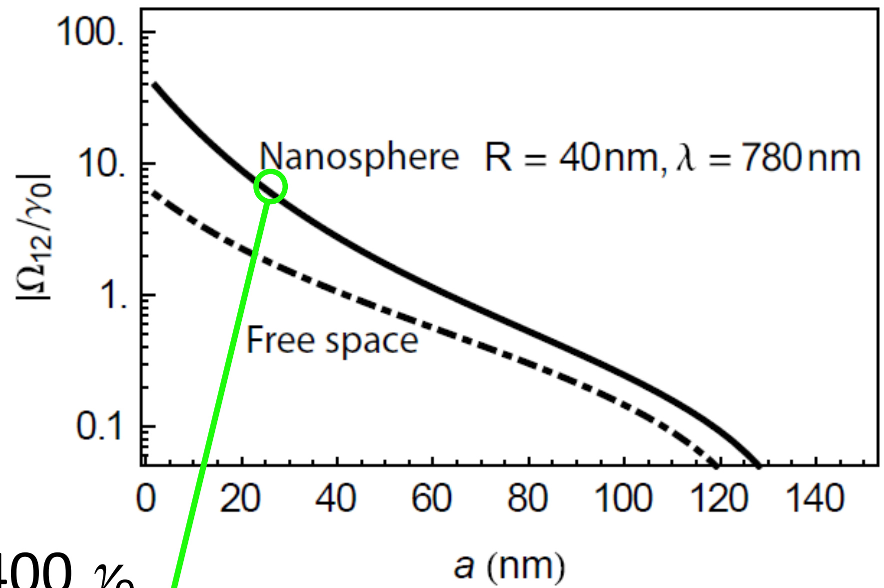
$$H = \sum_{i=1,2} \hbar(\omega_i - \omega_L)\sigma_i^\dagger \sigma_i - \Omega_{12}\sigma_1^\dagger \sigma_2 - \Omega_{12}\sigma_2^\dagger \sigma_1 - \sum_{i=1,2}\left(\frac{\hbar\Omega_i}{2}\sigma_i^+ + \text{H.c.}\right)$$

Averaging with appropriate wavefunction basis→ field & emitter correlations

Nanosphere-mediated two-photon nonlinearity

Proof-of-principle→Nanosphere





Detuning between emitters, $\delta = 400\ \gamma_0$

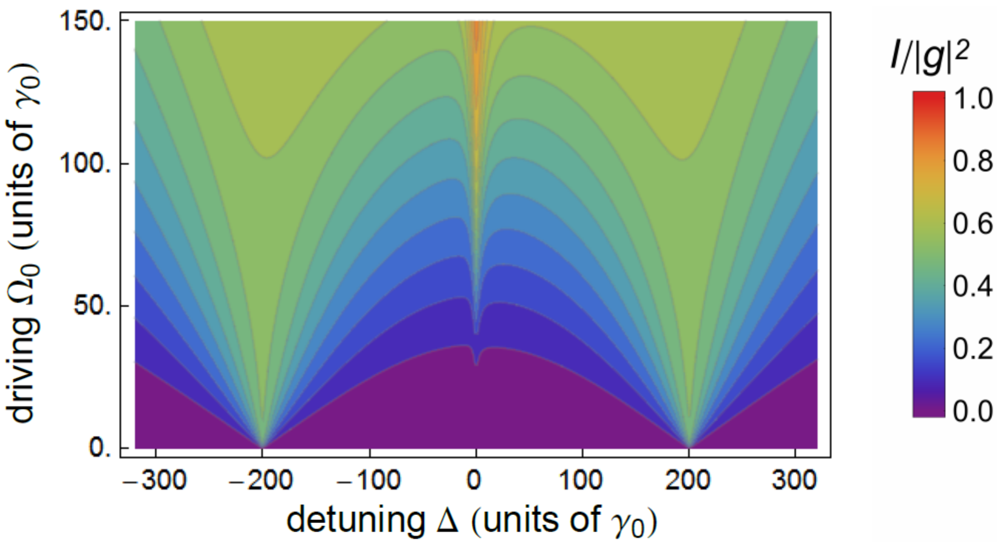
$\mathbf{\Omega_{12} = -6.4\ \gamma_0}$

a = 25 nm

$\gamma = 2.9\ \gamma_0$

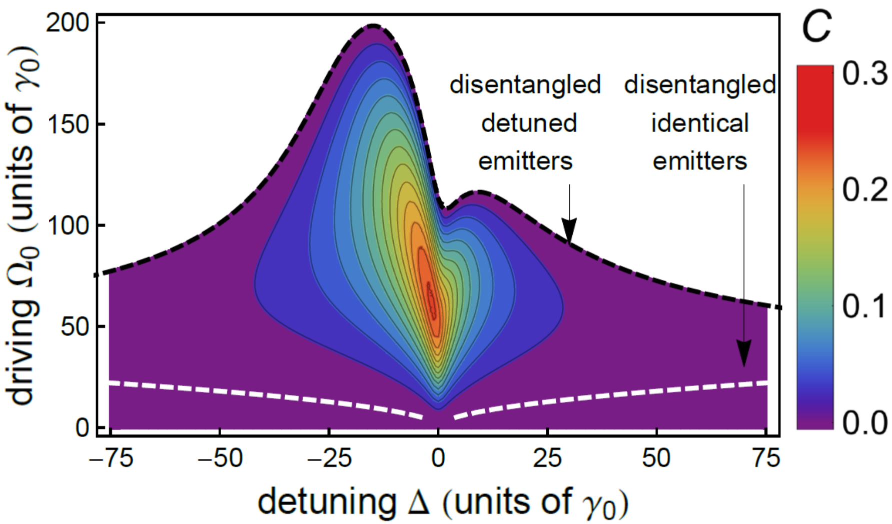
$\gamma_{12} = -2.6\ \gamma_0$

$\Omega = 2\Omega_0$

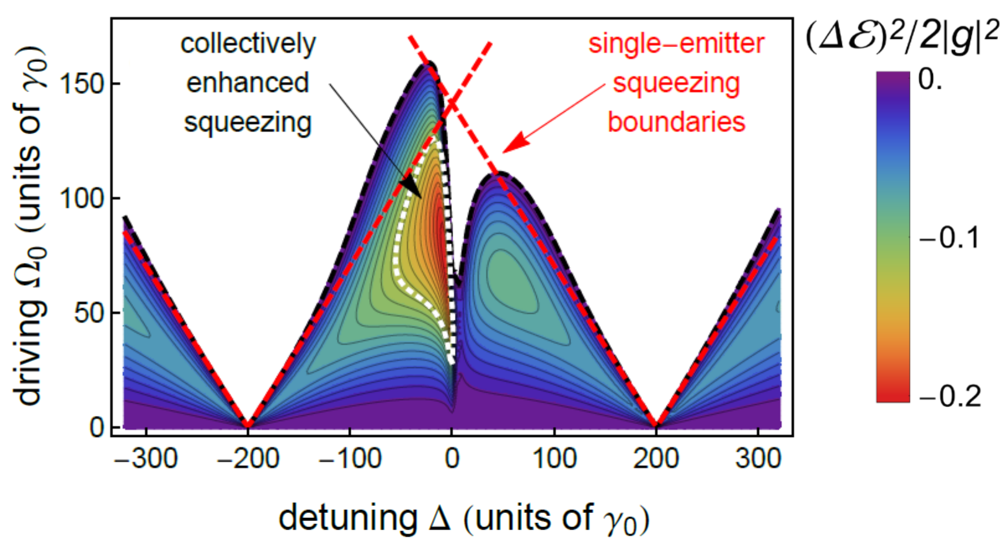


Exploit the two-photon coherence →quadrature squeezing from entanglement

Entanglement, Concurrence (C≠0)



Squeezing, E-field fluctuations ($\Delta E^2<0$)



E-field quadrature fluctuations (with respect to shot-noise)

$$\left\langle :\Delta\hat{E}^2(\bar{r},t):\right\rangle = (\Delta\mathcal{E})^2 = \underbrace{(\Delta\mathcal{E}_1)^2 + (\Delta\mathcal{E}_2)^2}_{\text{Single-emitter terms}} + \underbrace{(\Delta\mathcal{E}_{12})^2}_{\text{Crossed-correlation term}}$$

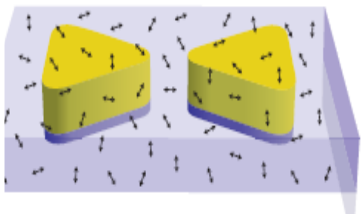
Crossed-correlation term

$$\frac{(\Delta\mathcal{E}_{12})^2}{2|g_1 g_2|} = 2\mathrm{Re}\left[e^{i(\phi_1-\phi_2)}\left(\langle\hat{\sigma}_2^\dagger\hat{\sigma}_1\rangle - \langle\hat{\sigma}_2^\dagger\rangle\langle\hat{\sigma}_1\rangle\right) + e^{i(2\theta+\phi_1+\phi_2)}\left(\langle\hat{\sigma}_2\hat{\sigma}_1\rangle - \langle\hat{\sigma}_2\rangle\langle\hat{\sigma}_1\rangle\right)\right]$$

Crossed-term can only provide squeezing if there is entanglement

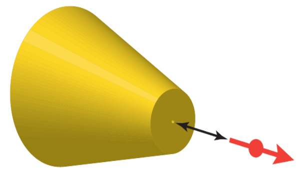
Increase cavity interaction→Nanoantennas, absorption?

Bowtie



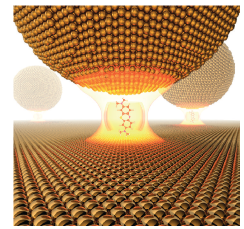
W.E. Moerner group, PRL (2005)

Nanocones



Sandoghdar group PRL (2012)

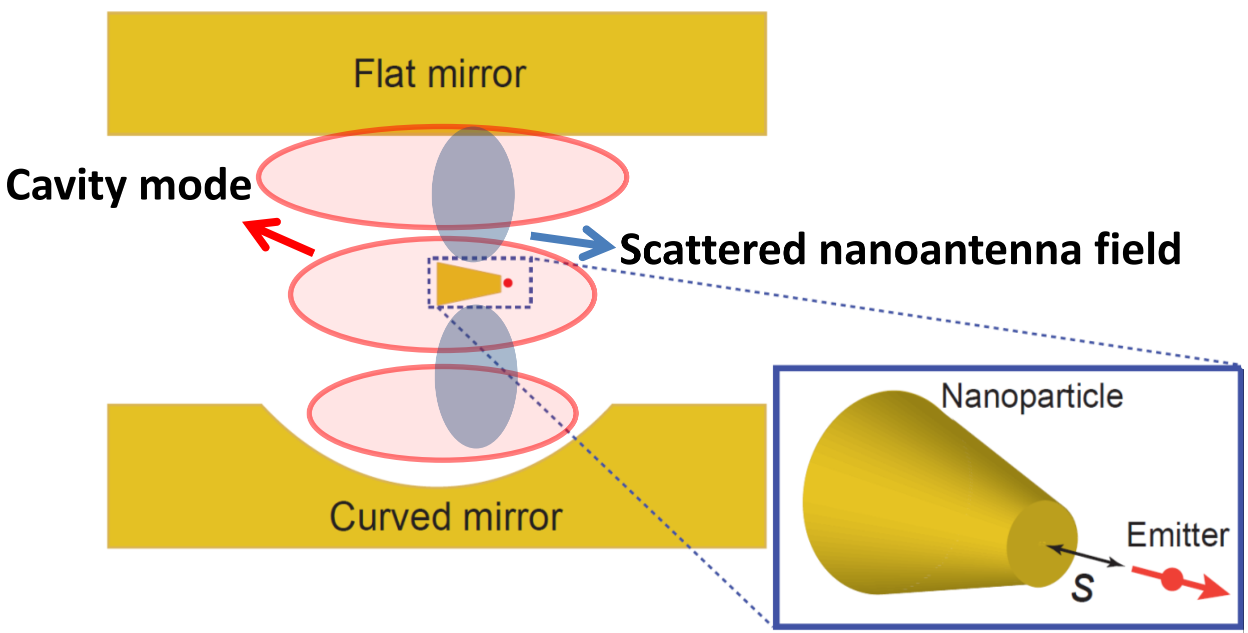
Nanocavities



J. Baumberg group, Nature (2016)

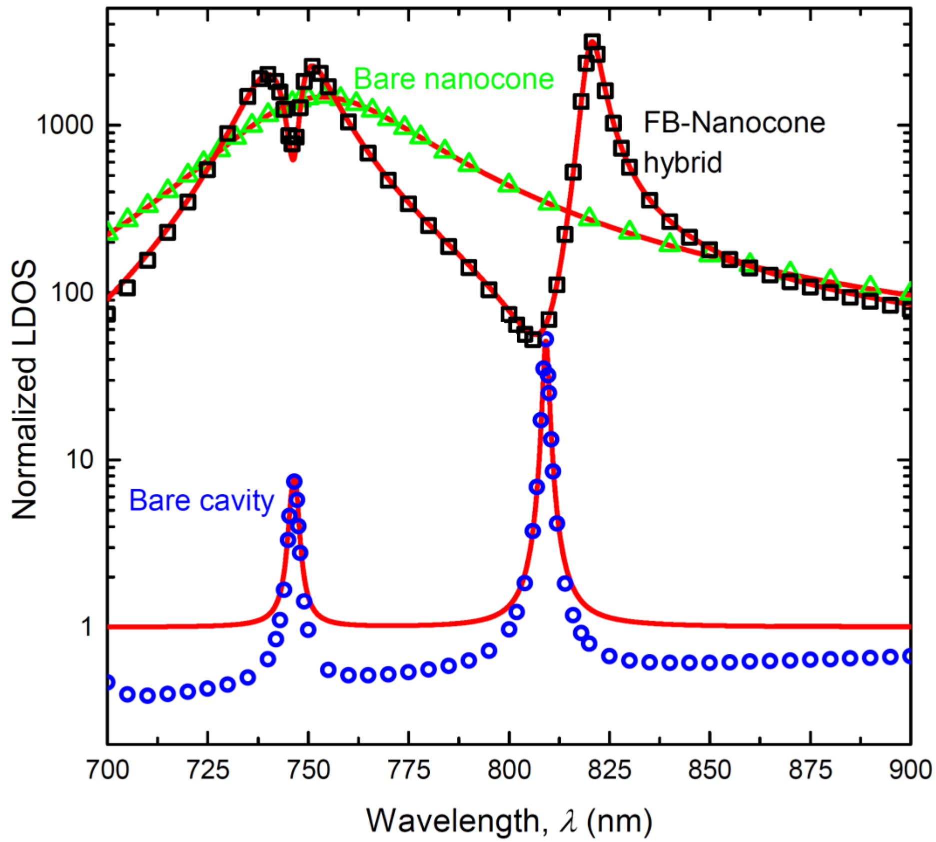
Purcell factors $10^3 - 10^6$ →quenching close to particle

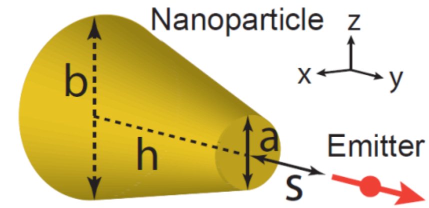
→Hybrid cavity: nanoparticle + Fabry Perot cavity



Fabry-Pérot+nanoparticle hybrid LDOS

Centered gold nanocone b=60 nm,a=20 nm,h=150 nm, s=10 nm



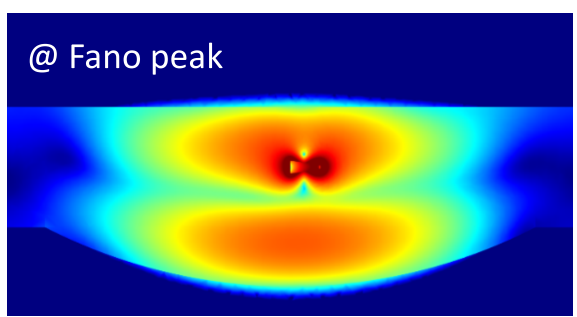


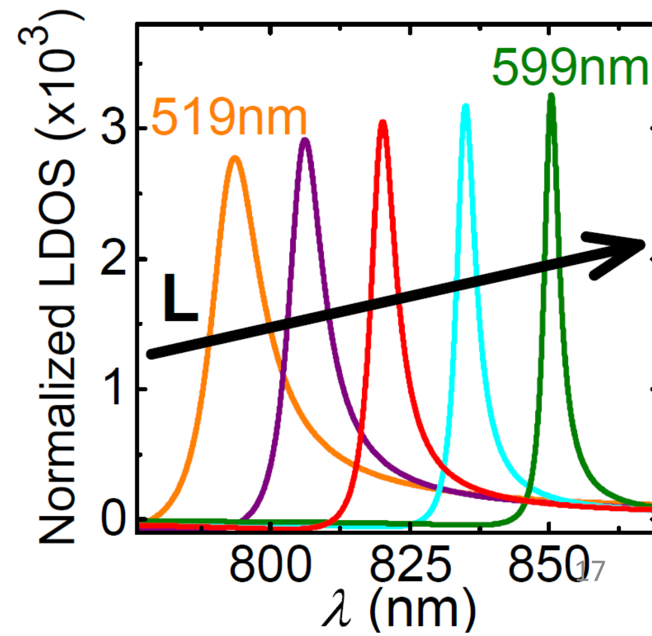
-Higher F +narrower linewidth
→good for strong coupling

-General for any nanoantenna

-Tunable with L and broadband

81% overlap
with TEM00

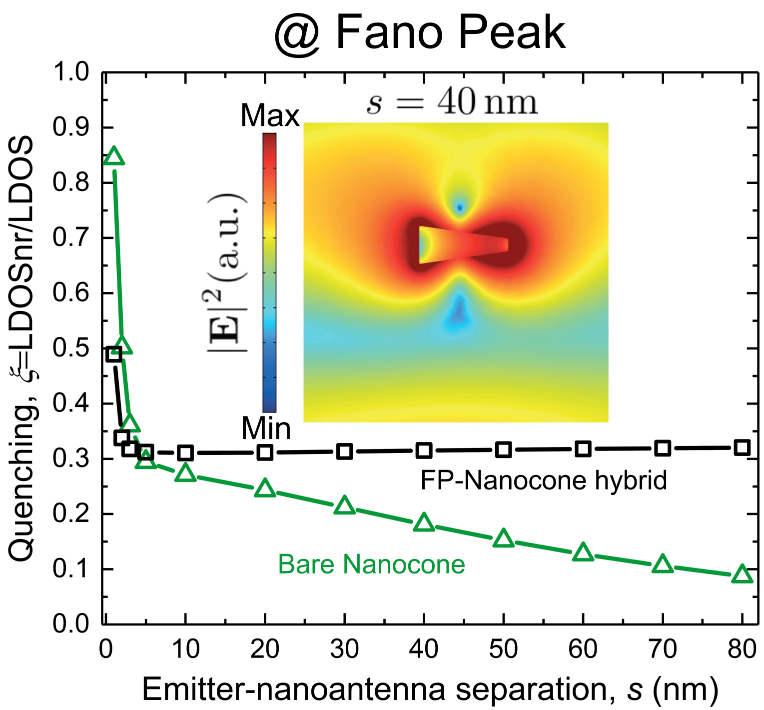


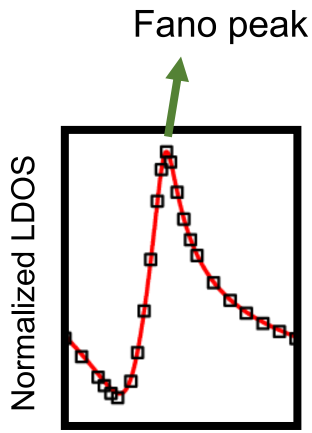


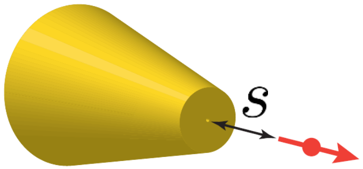
Emission efficiency: non-radiative emission

$$\text{Non-radiative LDOS} \propto \int_{V_{particle}} \mathrm{Im}\,\varepsilon |E|^2 \, dV$$

Quenching: $\xi = \dfrac{\gamma_{nr}}{\gamma_r + \gamma_{nr}}$







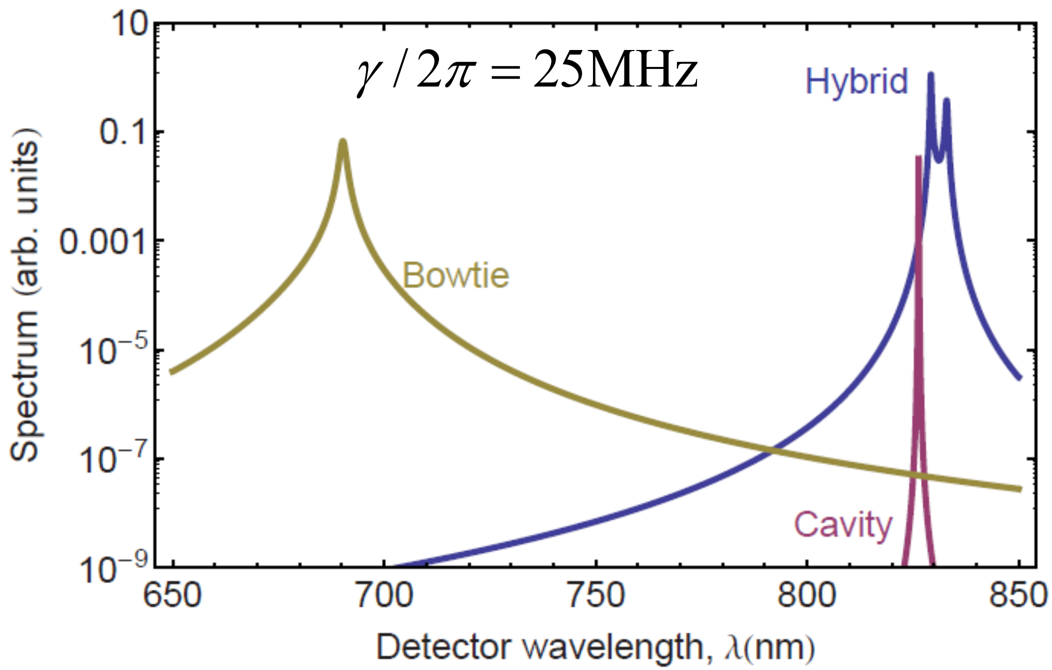
Quenching can be modified externally

Suppressed at maximum LDOS enhancement

Strong coupling: Emission spectrum

Emission spectrum A. Delga et al. PRL **112** 253601 (2014)

$$S(\bar{r},\omega)=\left|\frac{\overleftrightarrow{G}_{\mathrm{QNM}}(r,r_D)\cdot\bar{d}\,\dfrac{\omega^2}{\varepsilon_0 c^2}}{\omega^2-2i\omega\gamma-\omega_D{}^2+2\omega_D\bar{p}\cdot\overleftrightarrow{G}_{\mathrm{QNM}}(r,r_D)\cdot\bar{d}\,\dfrac{\omega^2}{\hbar\varepsilon_0 c^2}}\right|^2 2(\omega^2+\omega_D{}^2)$$



FP-Hybrid $F_P = 2.7\times10^5$

$4g/\kappa = 8.6$, Q=986

FP (no particle) $F_P = 587$

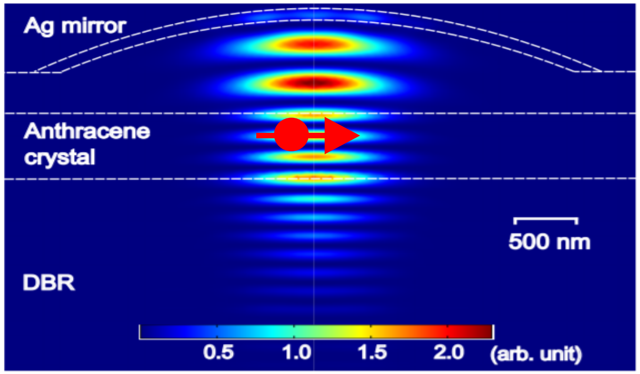
$4g/\kappa = 0.7$, Q=3400

Bare nanoparticle $F_P = 3.9\times10^4$

$4g/\kappa = 0.4$, Q=20

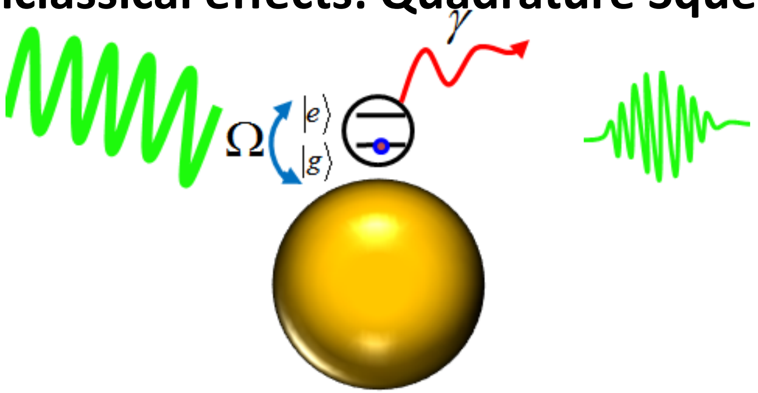
Conclusions

Organic molecules in microcavities



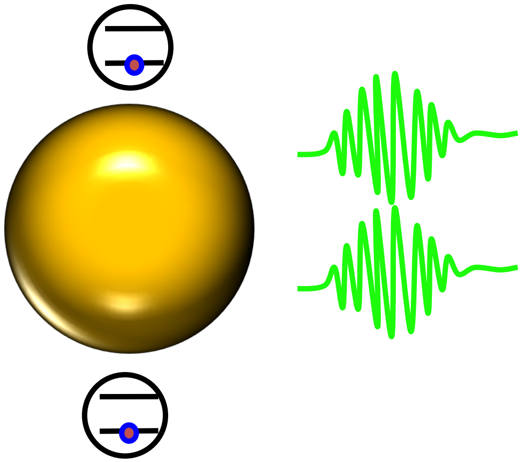
- Enhance resonant coherence
- Close to unity efficiency

Nonclassical effects: Quadrature Squeezing



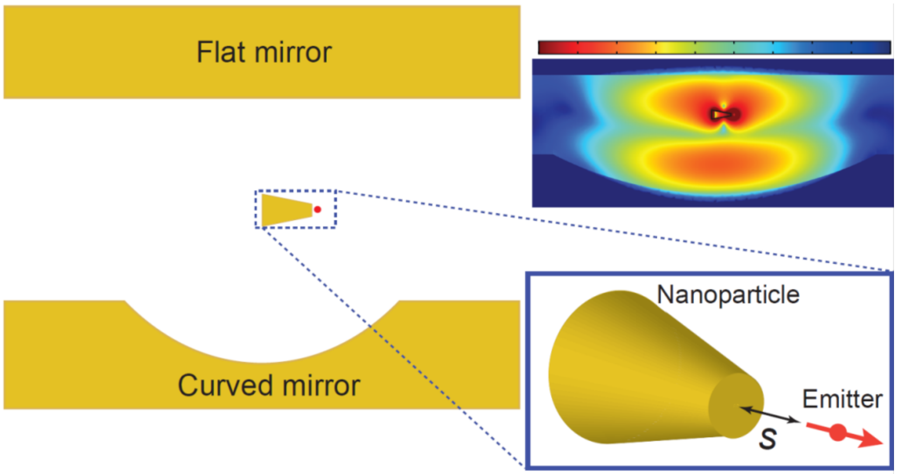
- Assist detection (boundaries, larger signals)
- Improve bad emitters

Large-detuned 2-photon interactions



- Entanglement similar to resonant cases
- Witnessed by squeezing

Detuned nanoparticle-microcavity hybrid



- Assist strong coupling
- Manipulate quenching externally

Collaborators involved

Dr. Harald Haakh

Burak Gurlek
(MPL)

Dr. Karim Murr

Prof. Mario Agio
(Siegen University)

Drs. Daqing Wang, Hrishi Kelkar, T. Utikal
Profs. S. Götzinger & Vahid Sandoghdar
(MPL)

Publications:

D. Martín-Cano, H. R. Haakh, K. Murr & M. Agio, *Physical Review Letters* **113**, 263605 (2014)

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Thank you for your attention!