Single Emitter Detection with Fluorescence and Extinction Spectroscopy

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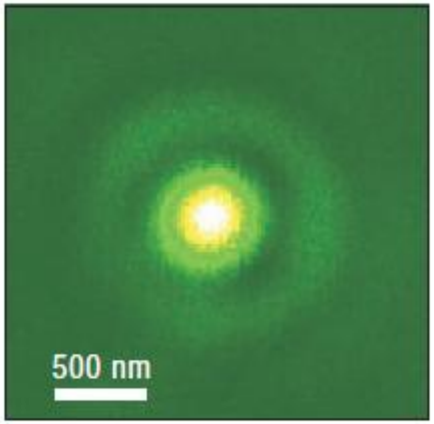
Elements of Nanophotonics
Associated Seminar „Recent Progress in Nanooptics & Photonics“

May 07, 2009

Outline

- Single molecule fluorescence detection
- Single molecule extinction measurements
- Theoretical limits
- Comparison in terms of SNR
- Single quantum dot spectroscopy
- Outlook

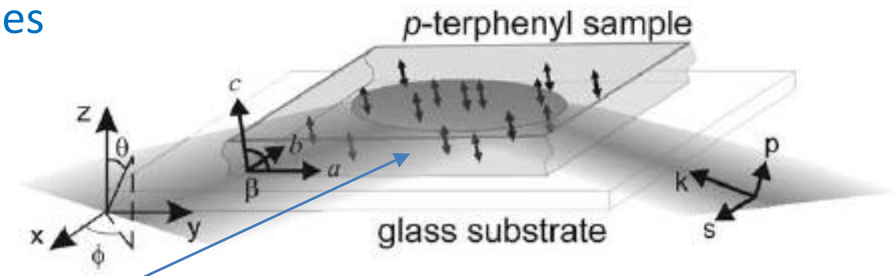


Laser scan image of a single molecule (FWHM focus spot ≈ 370 nm).

Single molecule fluorescence detection

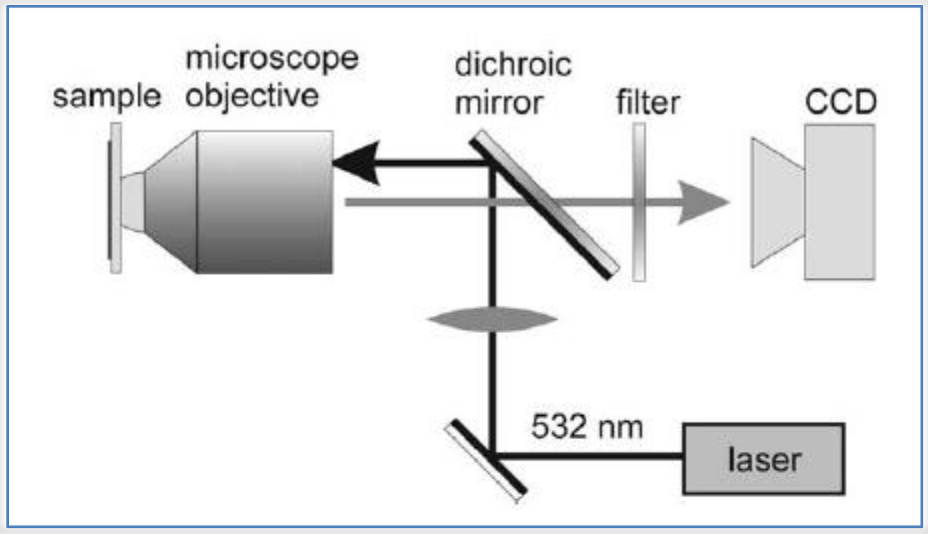
R.J. Pfab et al., Chem. Phys. Lett. 387, 490 (2004)

- Single molecule fluorescence studies



transition dipole moments of terrylene molecules are oriented approximately perpendicular to substrate

p-terphenyl film on a glass substrate with dopant terrylene molecules.

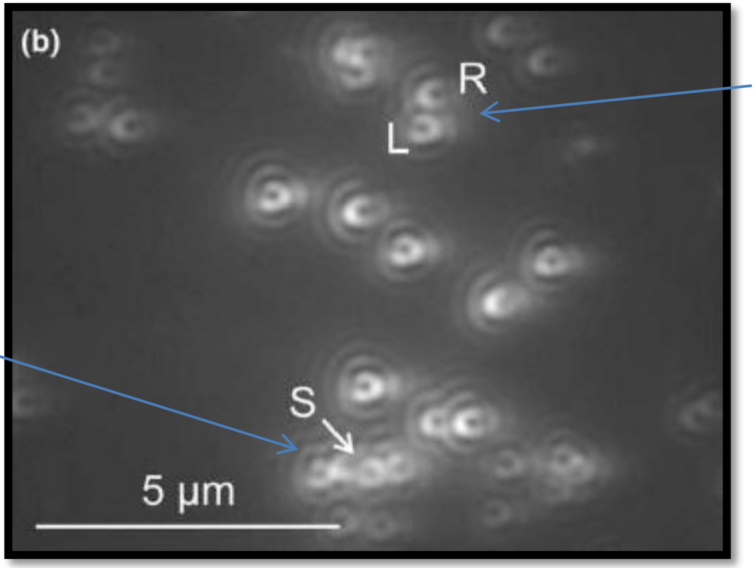


Experimental fluorescence microscopy setup.

Single molecule fluorescence detection

R.J. Pfab et al., Chem. Phys. Lett. 387, 490 (2004)

- Single molecule fluorescence studies



asymmetries attributed to a slight tilt of the emission dipole with respect to optical axis

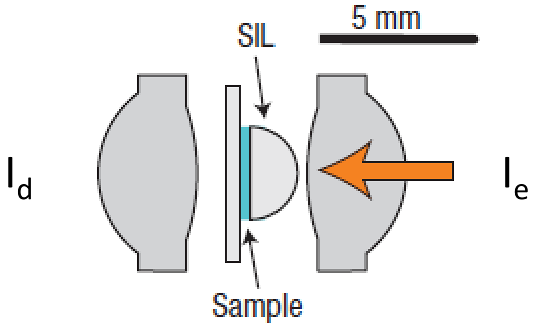
nearly ring-like emission pattern = characteristic of vertically oriented dipoles

Fluorescence image.

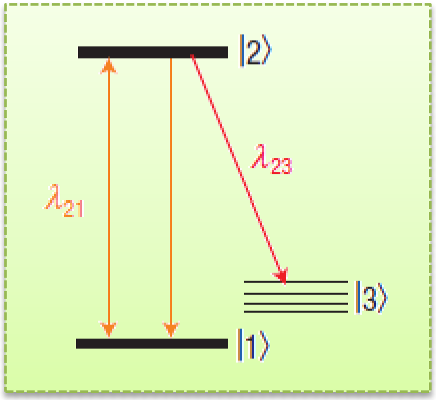
Single molecule extinction measurements

G. Wrigge et al., Nature Phys. 4, 60 (2008)

- Detection of a single emitter in transmission



Arrangement of the lenses in the illumination and collection paths.



Energy-level scheme of a molecule.

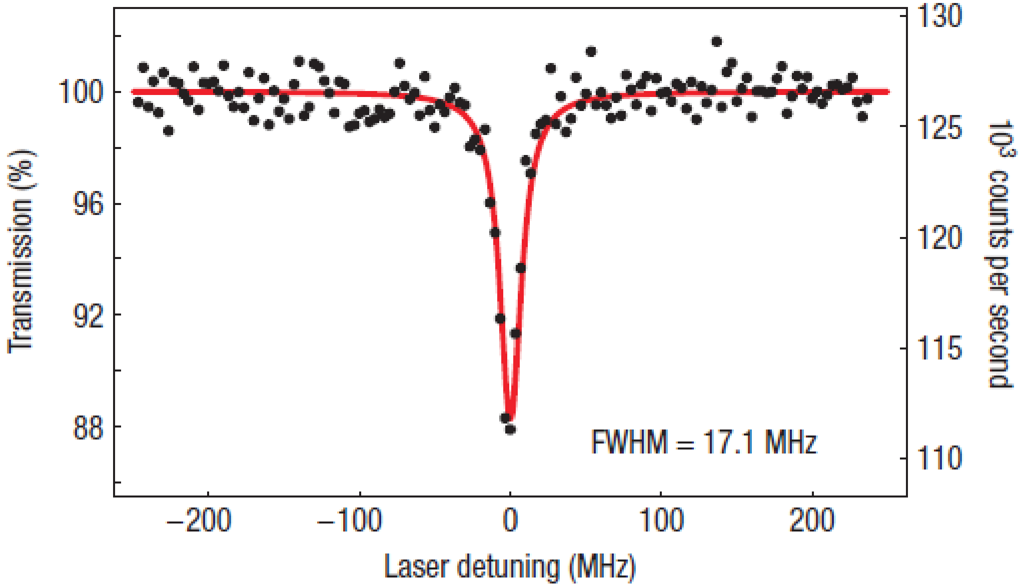
$$I_{\mathrm{d}} = (1 - \sigma/F) I_{\mathrm{e}}$$

$$I_{\mathrm{d}} = \langle \widehat{\mathbf{E}}_{\mathrm{e}}^{-} \cdot \widehat{\mathbf{E}}_{\mathrm{e}}^{+} \rangle + \langle \widehat{\mathbf{E}}_{\mathrm{m}}^{-} \cdot \widehat{\mathbf{E}}_{\mathrm{m}}^{+} \rangle + 2\mathrm{Re}\{ \langle \widehat{\mathbf{E}}_{\mathrm{e}}^{-} \cdot \widehat{\mathbf{E}}_{\mathrm{m}}^{+} \rangle \}$$

Single molecule extinction measurements

G. Wrigge et al., Nature Phys. 4, 60 (2008)

- Detection of a single emitter in transmission

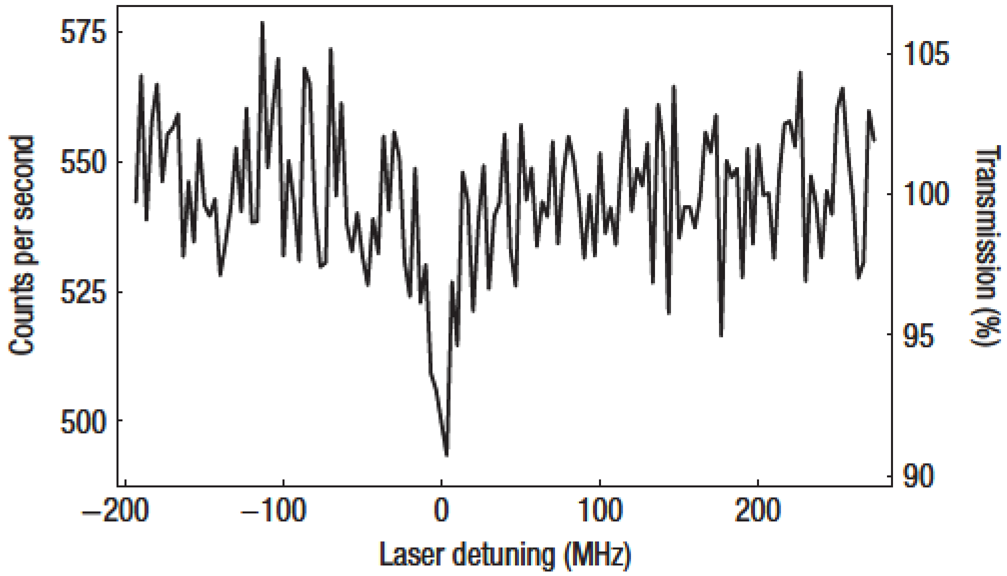


Example of a transmission spectrum (11.5% dip).

Single molecule extinction measurements

G. Wrigge et al., Nature Phys. 4, 60 (2008)

- Single-molecule detection with ultrafaint light sources



Extinction spectrum recorded from a single molecule under an ultrafaint detected power of ***550 photons per second****.*

Theoretical limits

G. Zumofen et al., PRL 101, 180404 (2008)

- Scattering by a classical oscillator

→ Abraham-Lorentz equation:

$$\boxed{\ddot{\mathbf{q}} + \Gamma'\dot{\mathbf{q}} - \tau\,\dddot{\mathbf{q}} + \omega_0^2\mathbf{q} = \frac{e}{m}E_0\epsilon\,e^{-i\omega_\mathrm{L}t}}$$

(see Jackson: Classical Electrodynamics)

q .. displacement of electron

Γ' .. damping by non-radiative channels (≈ 0)

E_0 .. electric field amplitude at place of oscillator

ε .. unit vector along direction of driving field E

τ .. characteristic time of damping by radiation reaction

gives stationary state solution of q:

$$\mathbf{q} = -\frac{e}{m\omega_0}\frac{E_0e^{-i\omega_\mathrm{L}t}}{2\Delta + i\Gamma}\epsilon$$

$$\Delta = \omega_\mathrm{L} - \omega_0$$

$$\Gamma = \tau\,\omega_0^2 = \frac{2e^2\omega_0^2}{3mc^3}$$

Δ .. laser frequency detuning

Γ .. damping rate

which allows to calculate stationary state scattered far-field:

$$\mathbf{E}_\mathrm{sca}(\mathbf{r}) = \frac{e}{c^2}\frac{1}{r}\left[\hat{\mathbf{r}}\times(\hat{\mathbf{r}}\times\ddot{\mathbf{q}})\right]e^{ikr}$$

(Gaussian units)

Theoretical limits

G. Zumofen et al., PRL 101, 180404 (2008)

- Scattering by a classical oscillator

→ total scattered power: $P_{\mathrm{sca}} = \frac{1}{2} c\epsilon_0 \int_{4\pi} r^2 |\mathbf{E}_{\mathrm{sca}}(\mathbf{r})|^2 d\Omega = 2cW_{\mathrm{inc}}^{\mathrm{el}}(O)\sigma$

where $W_{\mathrm{inc}}^{\mathrm{el}}(O) = \epsilon_0 |\mathbf{E}_{\mathrm{inc}}(O)|^2/4$ is the time-averaged electric energy density at O

and $\sigma = \sigma_0 \frac{\Gamma^2}{4\Delta^2 + \Gamma^2}$ the total scattering cross section of the oscillator

$\sigma_0 = 3\lambda^2/(2\pi)$ .. cross section at resonance: **depends only on wavelength!**

Theoretical limits

G. Zumofen et al., PRL 101, 180404 (2008)

❖ Scattering by a two-level system (semi-classical description)

➞ stationary state population of the upper state:

$$\boxed{\rho_{22}^{\mathrm{ss}} = \frac{\Gamma_2 \mathcal{V}^2}{2\Gamma_1 \left(\Delta^2 + \Gamma_2^2 + \mathcal{V}^2 \Gamma_2/\Gamma_1\right)}}$$

(see *Cohen-Tannoudji* et al.: Atom-Photon interactions)

Γ_1 .. radiative decay rate

Γ_2 .. damping rate of polarization

Γ_2^* .. dephasing rate for nonradiating processes

V .. Rabi frequency

d_{12}.. transition dipole moment

$$\Gamma_2 = \Gamma_1/2 + \Gamma_2^*$$

$$\mathcal{V} = -\mathbf{d}_{12} \cdot \mathbf{E}_{\mathrm{inc}}(\mathrm{O})/\hbar$$

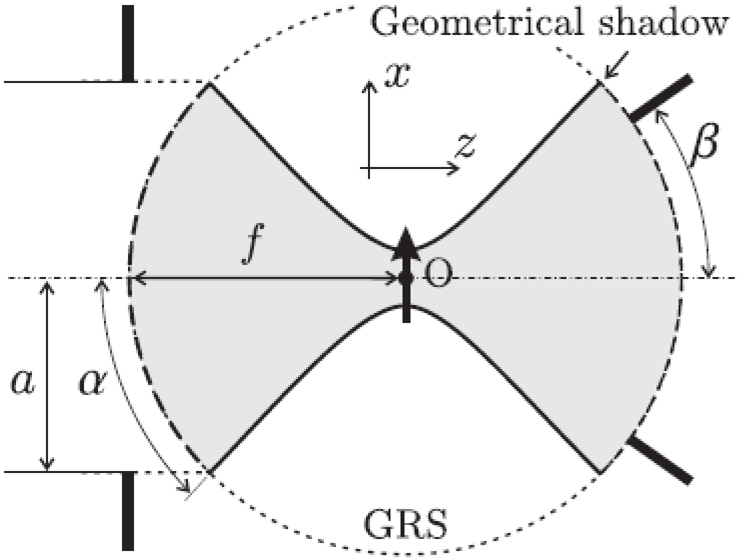
gives power scattered into solid angle of 4π:

$$P_{\mathrm{sca}} = \hbar\omega\Gamma_1\rho_{22}^{\mathrm{ss}} = \sigma_0 \frac{\Gamma_1\Gamma_2}{2\left(\Delta^2 + \Gamma_2^2 + \mathcal{V}^2\Gamma_2/\Gamma_1\right)} \left(2c\,W^{\mathrm{el}}\right)$$

Theoretical limits

G. Zumofen et al., PRL 101, 180404 (2008)

- Light scattering by an oscillating dipole in a focused beam



a .. entrance-aperture radius
α .. entrance half angle
β .. collection half angle
f .. focal length

ratio of scattered to incident power:

$$\boxed{\mathcal{K} = \frac{P_{\text{sca}}}{P_{\text{inc}}} = \frac{2cW^{\text{el}}_{\text{inc}}(O)\,\sigma}{\int \mathbf{S}(\mathbf{r})\cdot\mathbf{n}\,d^2r} = \frac{\sigma}{\mathcal{A}}}$$

effective cross section:

$$\sigma = \begin{cases} \sigma_0 \dfrac{\Gamma^2}{4\Delta^2 + \Gamma^2} & \textit{classical oscillator} \\ \sigma_0 \dfrac{\Gamma_1^2}{4\Delta^2 + \Gamma_1^2 + 2\Omega^2} & \textit{two-level system} \end{cases}$$

effective focal area in the case of a focused plane wave:

$$\mathcal{A} = \frac{\int_{\text{FP}} S_z d^2r}{S_z(O)}$$

power transmitted through focal plane

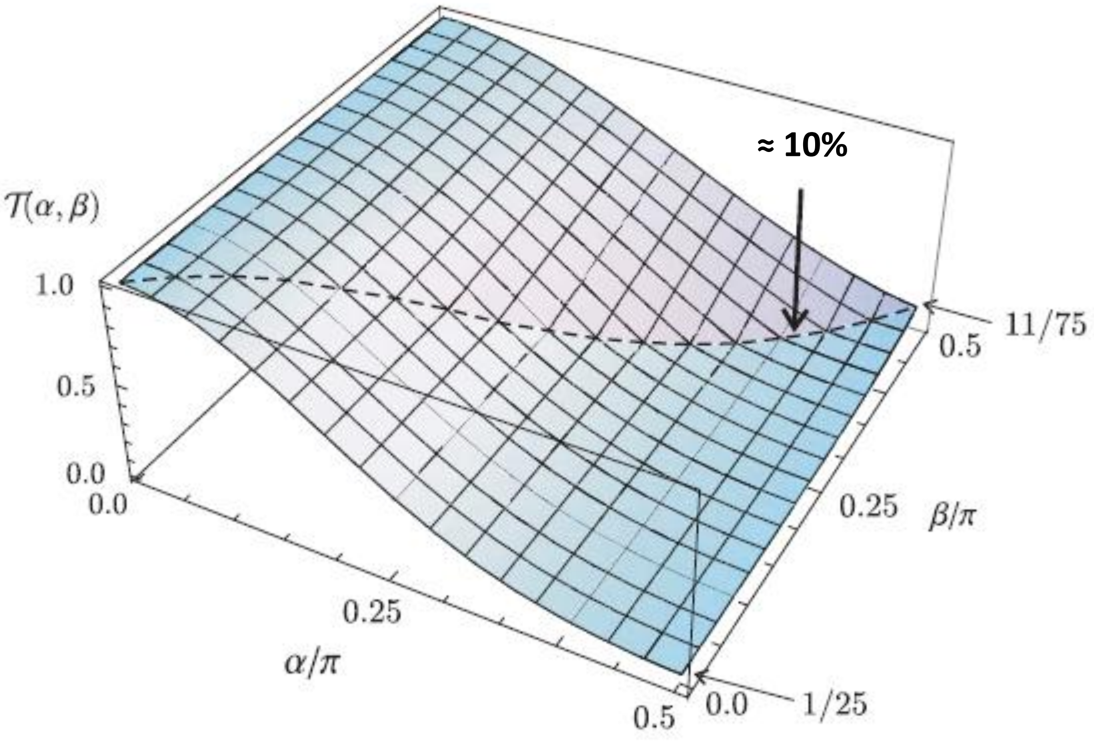
electric energy density at focal spot

scattered power depends only on field strength at position of oscillator!

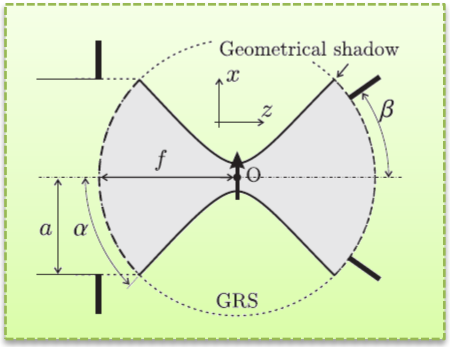
Theoretical limits

G. Zumofen et al., PRL 101, 180404 (2008)

- Light scattering by an oscillating dipole in a focused beam



Transmittance of a focused plane wave as a function of the angles α and β.



a .. entrance-aperture radius

α .. entrance half angle

β .. collection half angle

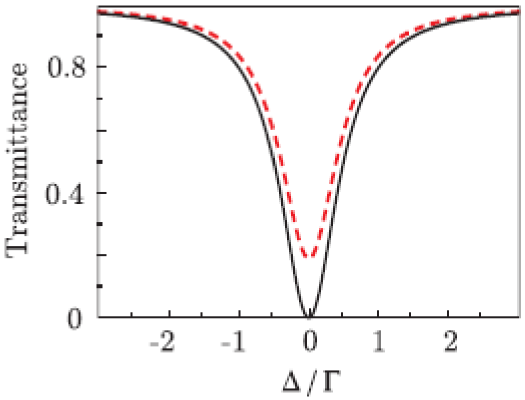
f .. focal length

⟶ **focused plane wave can be attenuated up to 90%!**

Theoretical limits

G. Zumofen et al., PRL 101, 180404 (2008)

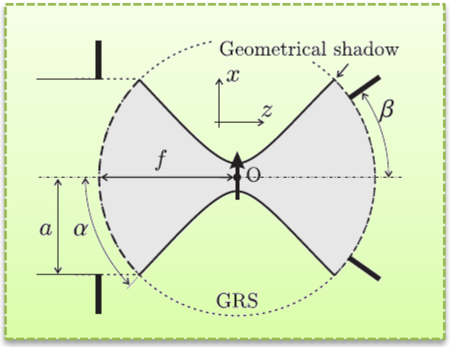
- Light scattering by an oscillating dipole in a focused beam



- - - - focused plane wave (α=β=π/3)

— directional dipolar wave (α=β=π/2)

Transmittance as a function of the detuning.



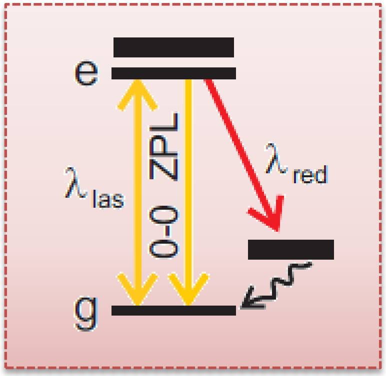
a .. entrance-aperture radius
α .. entrance half angle
β .. collection half angle
f .. focal length

⟶ **directional dipolar wave can be completely attenuated!**

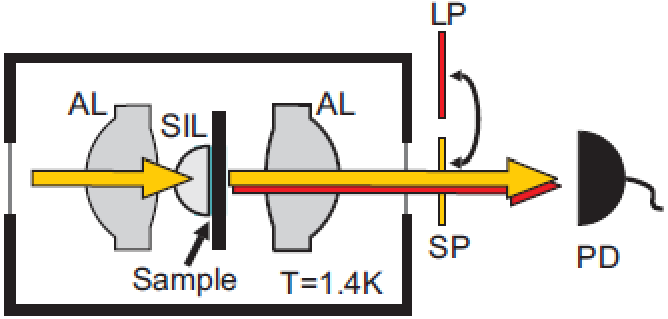
Comparison in terms of SNR

G. Wrigge et al., Opt. Express 16, 17360 (2008)

- Limits of single emitter detection in fluorescence and extinction



Level scheme of a dye molecule.
($\lambda_{las} \approx 590$ nm, $\lambda_{red} > 600$ nm)



Schematics of the experimental setup.
(Sample: DBATT molecules embedded in a n-tetradecane matrix)

AL .. aspheric lens
SIL .. solid immersion lens
LP /SP.. long/short pass
PD .. photodetector

Power on PD:
(without filter)

$$
\begin{aligned}
P &= \frac{\varepsilon_0 c r^2}{2\hbar\omega}\int_\Omega \left(\left\langle \hat{\mathbf{E}}^-_{\mathrm{las}} \cdot \hat{\mathbf{E}}^+_{\mathrm{las}} \right\rangle + \left\langle \hat{\mathbf{E}}^-_{\mathrm{m}} \cdot \hat{\mathbf{E}}^+_{\mathrm{m}} \right\rangle + 2\mathrm{Re}\left\langle \hat{\mathbf{E}}^-_{\mathrm{las}} \cdot \hat{\mathbf{E}}^+_{\mathrm{m}} \right\rangle \right) d\Omega \\
&= P_{\mathrm{las}} + P^{\Omega}_{\mathrm{m}} - P_{\mathrm{ext}} \,,
\end{aligned}
$$

laser

molecular
emission

interference

Comparison in terms of SNR

G. Wrigge et al., Opt. Express 16, 17360 (2008)

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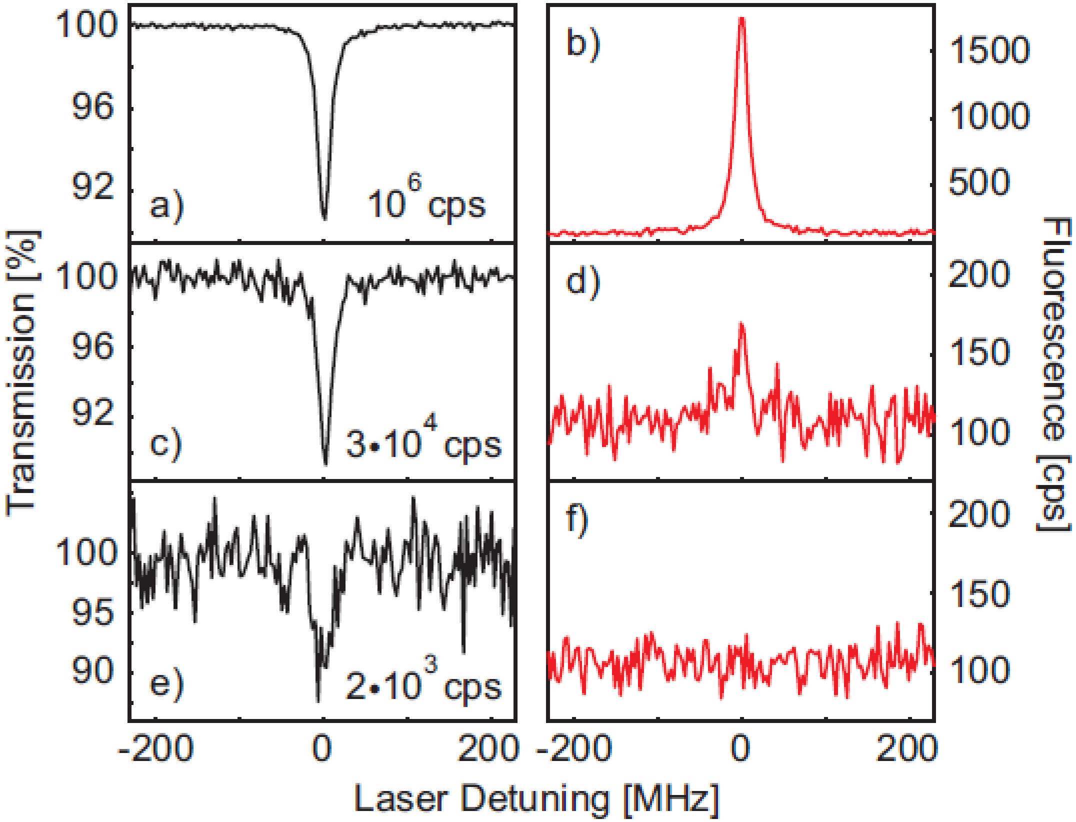


Extinction and fluorescence excitation spectra recorded from a single molecule in transmission at three different detected laser powers.

Comparison in terms of SNR

G. Wrigge et al., Opt. Express 16, 17360 (2008)

❖ Limits of single emitter detection in fluorescence and extinction

Power on PD:
(without filter)

$$P = \frac{\varepsilon_0 c r^2}{2\hbar\omega}\int_\Omega \left(\left\langle \hat{\mathbf{E}}^-_{\mathrm{las}}\cdot\hat{\mathbf{E}}^+_{\mathrm{las}}\right\rangle + \left\langle \hat{\mathbf{E}}^-_{\mathrm{m}}\cdot\hat{\mathbf{E}}^+_{\mathrm{m}}\right\rangle + 2\mathrm{Re}\left\langle \hat{\mathbf{E}}^-_{\mathrm{las}}\cdot\hat{\mathbf{E}}^+_{\mathrm{m}}\right\rangle\right) d\Omega$$
$$= P_{\mathrm{las}} + P^\Omega_{\mathrm{m}} - P_{\mathrm{ext}}\,,$$

$$P^{4\pi}_{\mathrm{m}} = \Gamma_1\rho_{22} = \frac{\Gamma_1}{2}\frac{S}{1+S} \qquad P^\Omega_{\mathrm{m}} = \zeta P^{4\pi}_{\mathrm{m}}$$

resonant: $P^{\mathrm{res}}_{\mathrm{m}} = \alpha P^\Omega_{\mathrm{m}}$

red-shifted: $P^{\mathrm{red}}_{\mathrm{m}} = (1-\alpha)P^\Omega_{\mathrm{m}}$

Saturation parameter: $S = \frac{\alpha}{\Gamma_2}\mathscr{K} P_{\mathrm{las}}$

α .. power emitted on 0-0 ZPL to total excited state emission

Γ_1.. total spontaneous emission rate

Γ_2.. transverse decay rate

ζ .. collected fraction of total emitted molecular power

μ .. account for losses and detector efficiency

K .. ratio of scattered to incident power

Comparison in terms of SNR

G. Wrigge et al., Opt. Express 16, 17360 (2008)

❖ SNR for a fluorescence excitation measurement

$$\mathrm{SNR_{red}} = \frac{\mu P_{\mathrm{m}}^{\mathrm{red}}}{N_{\mathrm{red}}} = \begin{cases} \dfrac{\mu\zeta(1-\alpha)\Gamma_1}{2\sqrt{P_{\mathrm{drk}}}}\,\dfrac{S}{1+S}, & \mu P_{\mathrm{red}} \ll P_{\mathrm{drk}} \\ \sqrt{\dfrac{\mu\zeta(1-\alpha)\Gamma_1}{2}\,\dfrac{S}{1+S}}, & \mu P_{\mathrm{red}} \gg P_{\mathrm{drk}} \end{cases}$$

noise sources:

- shot noise of the fluorescence
- fluctuations in the detectors dark counts

❖ SNR for an extinction measurement

$$\mathrm{SNR_{res}} = \frac{\mu P_{\mathrm{dip}}^{\mathrm{res}}}{N_{\mathrm{res}}} \simeq (1-\zeta\alpha)\frac{\Gamma_1}{2}\sqrt{\frac{\mu\alpha\mathscr{K}}{\Gamma_2}\,\frac{\sqrt{S}}{1+S}}$$

$$P_{\mathrm{dip}}^{\mathrm{res}} = P_{\mathrm{ext}} - P_{\mathrm{m}}^{\mathrm{res}}$$

noise sources:

- shot noise of the detected signal
- fluctuations on the laser intensity
- fluctuations on the detector dark counts

total noise ≈ shot noise of laser

Comparison in terms of SNR

G. Wrigge et al., Opt. Express 16, 17360 (2008)

- SNR for fluorescence excitation vs. extinction measurements

$\mu = 0.2$

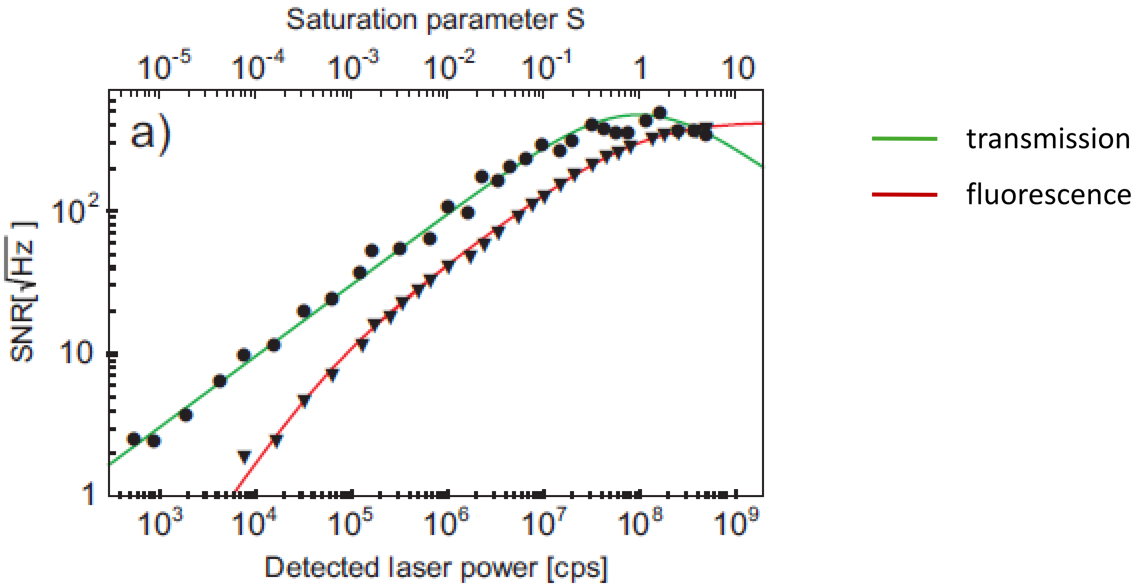
$K = 0.5$ (**strong focusing!**)

$\alpha = 0.2$

$\zeta = 0.02$

$\Gamma_2 = \Gamma_1/2$

$\Gamma_1/2\pi = 17$ MHz



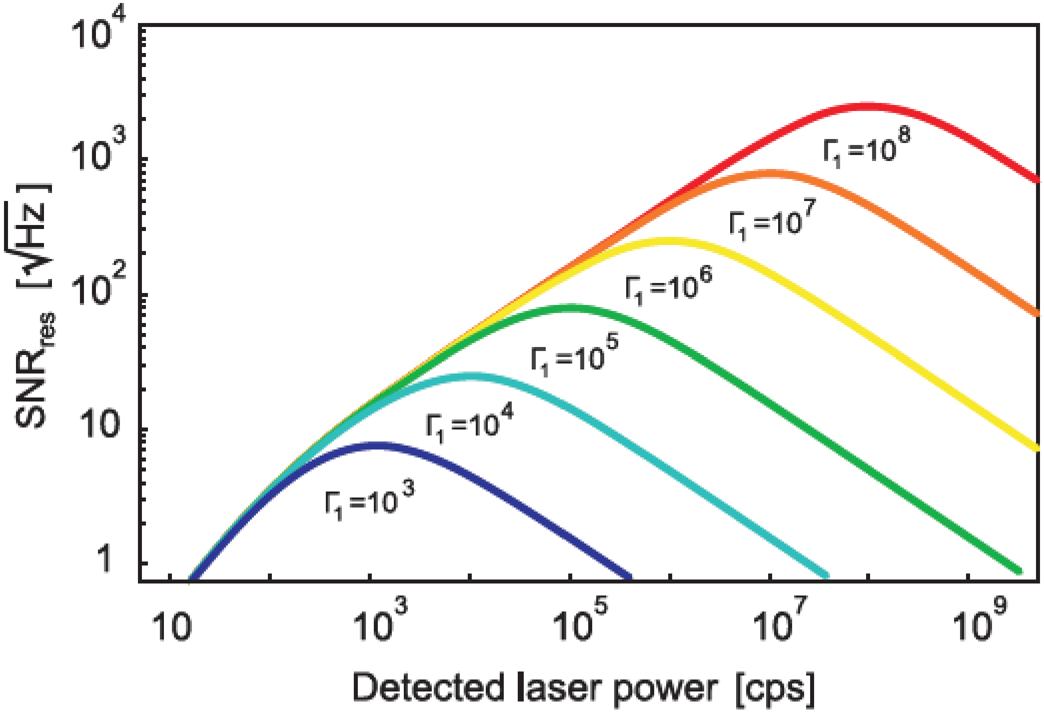
Signal-to-noise ratios of the resonant transmission and fluorescence signals as a function of the excitation power and saturation parameter.

→ **SNR of extinction measurements wins in the case of stronger excitations up to saturation!**

Comparison in terms of SNR

G. Wrigge et al., Opt. Express 16, 17360 (2008)

- Limit of extinction measurements



$\mu = 1$

K = 0.5 (**strong focusing!**)

$\alpha = 1$

$\Gamma_2 = \Gamma_1/2$

The SNR for a resonant transmission detection of emitters with different radiative decay rates.

→ **single emitters with spontaneous emission times as long as a millisecond detectable using extinction spectroscopy!**

Single quantum dot spectroscopy

A.N. Vamivakas et al., Nano Lett. 7, 2892 (2007)

- Strong extinction of a far-field laser beam by a single quantum dot

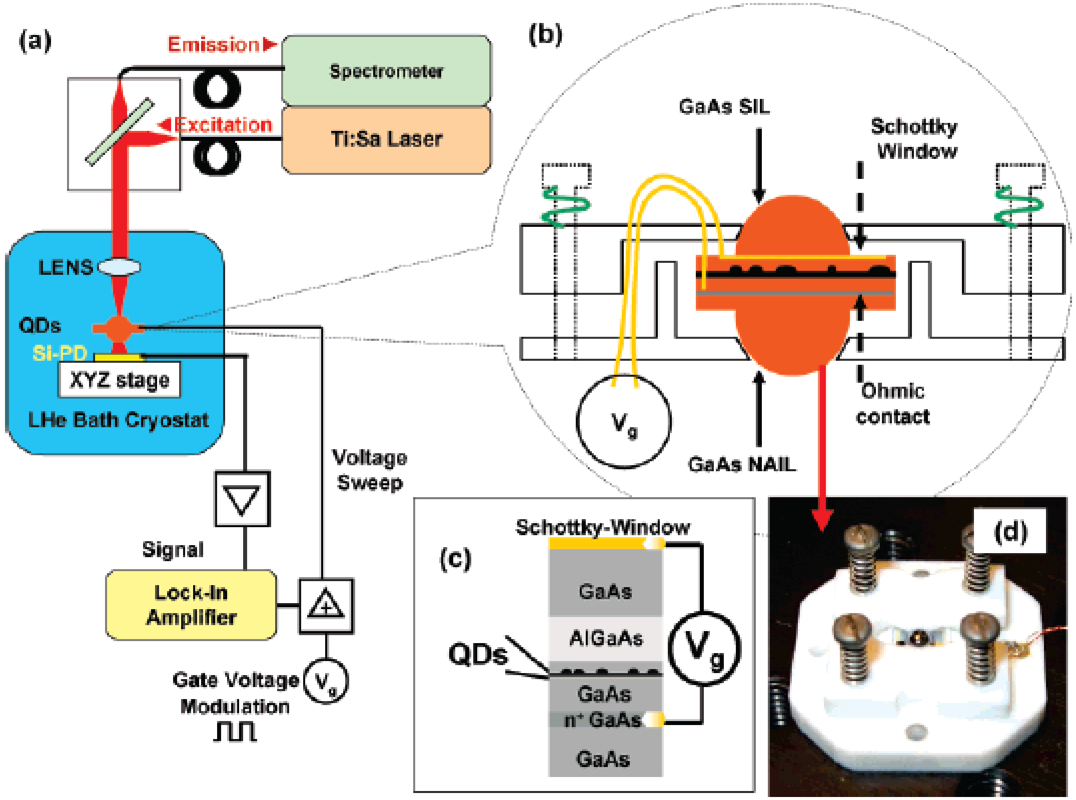


Illustration of the experimental apparatus used for both microphotoluminescence and resonant scattering measurements.

Single quantum dot spectroscopy

A.N. Vamivakas et al., Nano Lett. 7, 2892 (2007)

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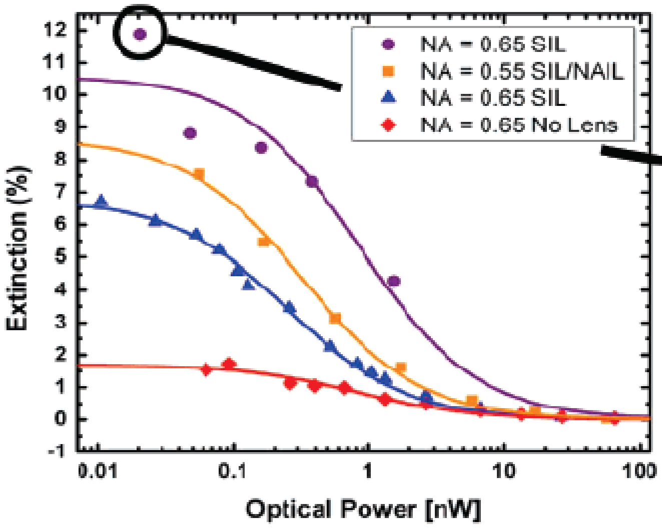
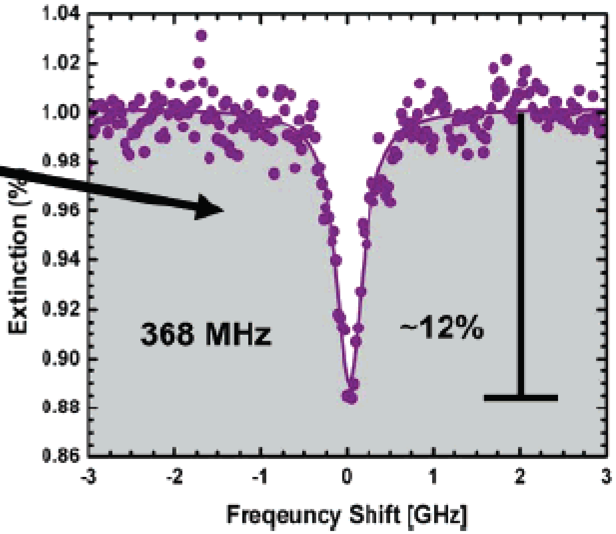


Strength of the scattered light signal as a function of incident laser power.



Best line scan recorded for the lowest power point.

⟶ **The measured contrast is 12% and the line width is 368 MHz (1.47 μ*eV).***

Single quantum dot spectroscopy

A.N. Vamivakas et al., Nano Lett. 7, 2892 (2007)

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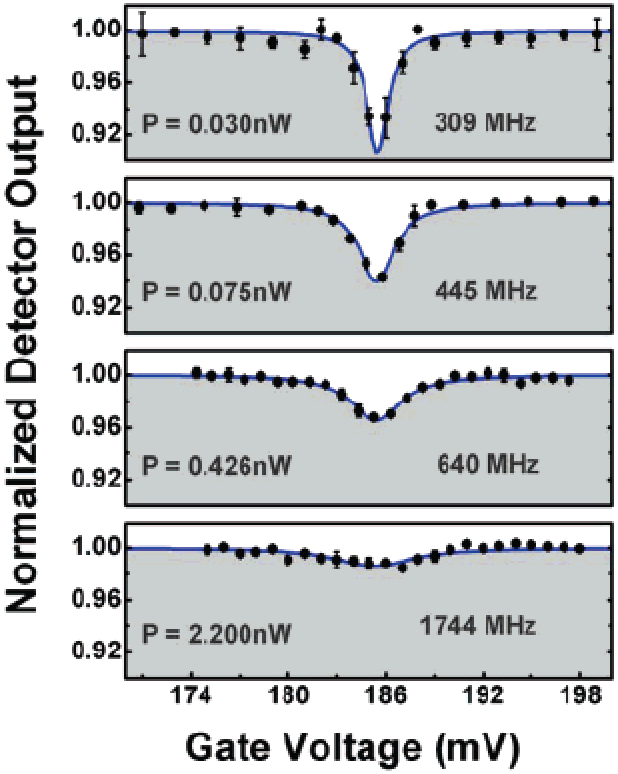
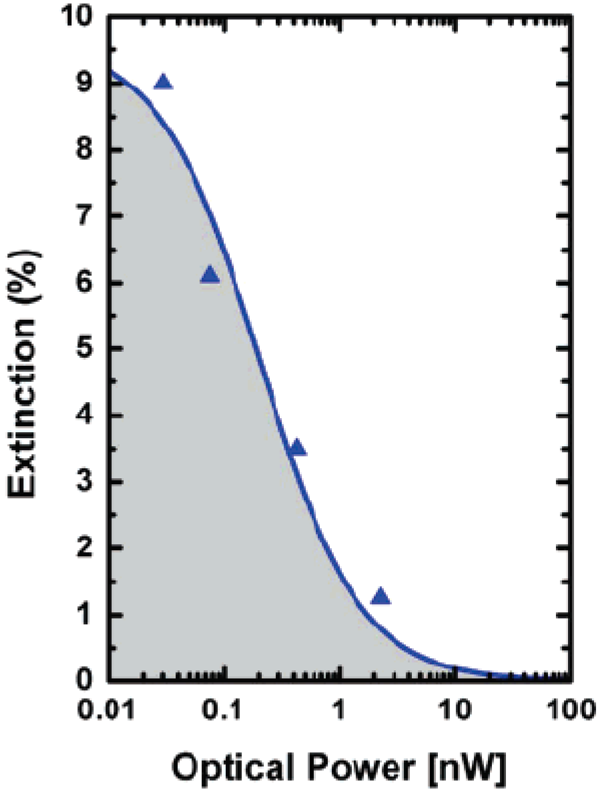


Line scans as a function of incident laser power to demonstrate power broadening of the QD X^0 transition.



Saturation curve.

Conclusions & Outlook

- single emitters with spontaneous emission times as long as milliseconds detectable
- direct access to coherent interaction of incident light and emitter
- detection of single solid-state quantum emitters at room temperature
- imaging of small metallic and dielectric nanoparticles
- possibility for a strong coupling of few photons with a single quantum emitter

Thanks for your attention!

References:

R.J. Pfab et al., Chem. Phys. Lett. 387, 490 (2004)
G. Wrigge et al., Nature Phys. 4, 60 (2008)
G. Zumofen et al., PRL 101, 180404 (2008)
G. Wrigge et al., Opt. Express 16, 17360 (2008)
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