Spectroscopy and Microscopy of Single Molecules and Single Nanoparticles

N. Verhart, L. Hou, A. Carattino,
P. Navarro, M. Yorulmaz, M. Müller, S. Khatua, S. Faez
M. Orrit

Molecular Nano-Optics and Spins

Leiden University (Netherlands)

Han sur Lesse, 11 December 2013

Outline (Part I)

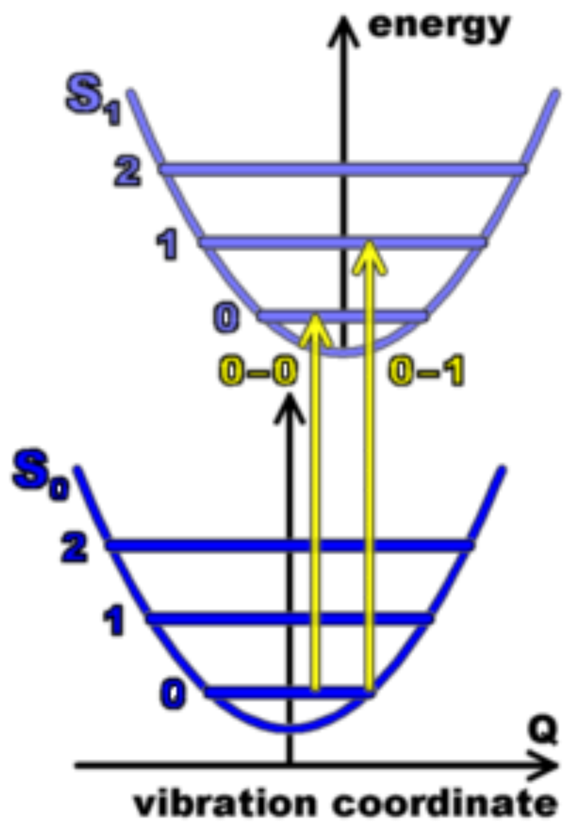
- Introduction on fluorescence microscopy
- Blinking
- Low-temperature spectroscopy

1. Introduction

- Optical detection of single molecules by fluorescence
- High signal/background ratio thanks to resonance
- Made possible by advances in sources, detectors, optics

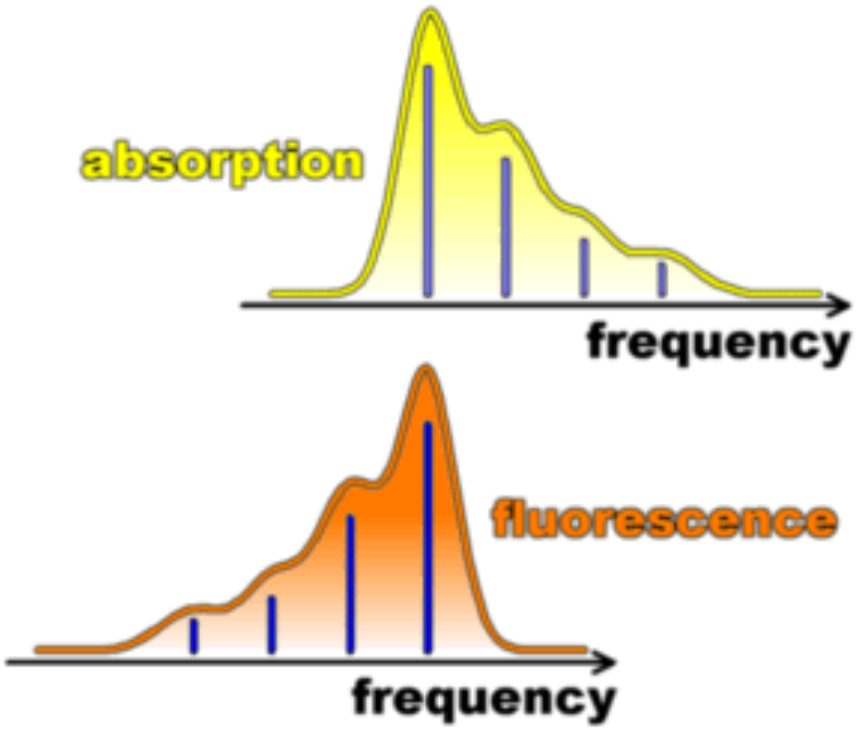
Molecular Photophysics

- Electronic levels are split in a series of harmonic oscillator levels
- Transitions between levels are related to overlaps between oscillator wavefunctions

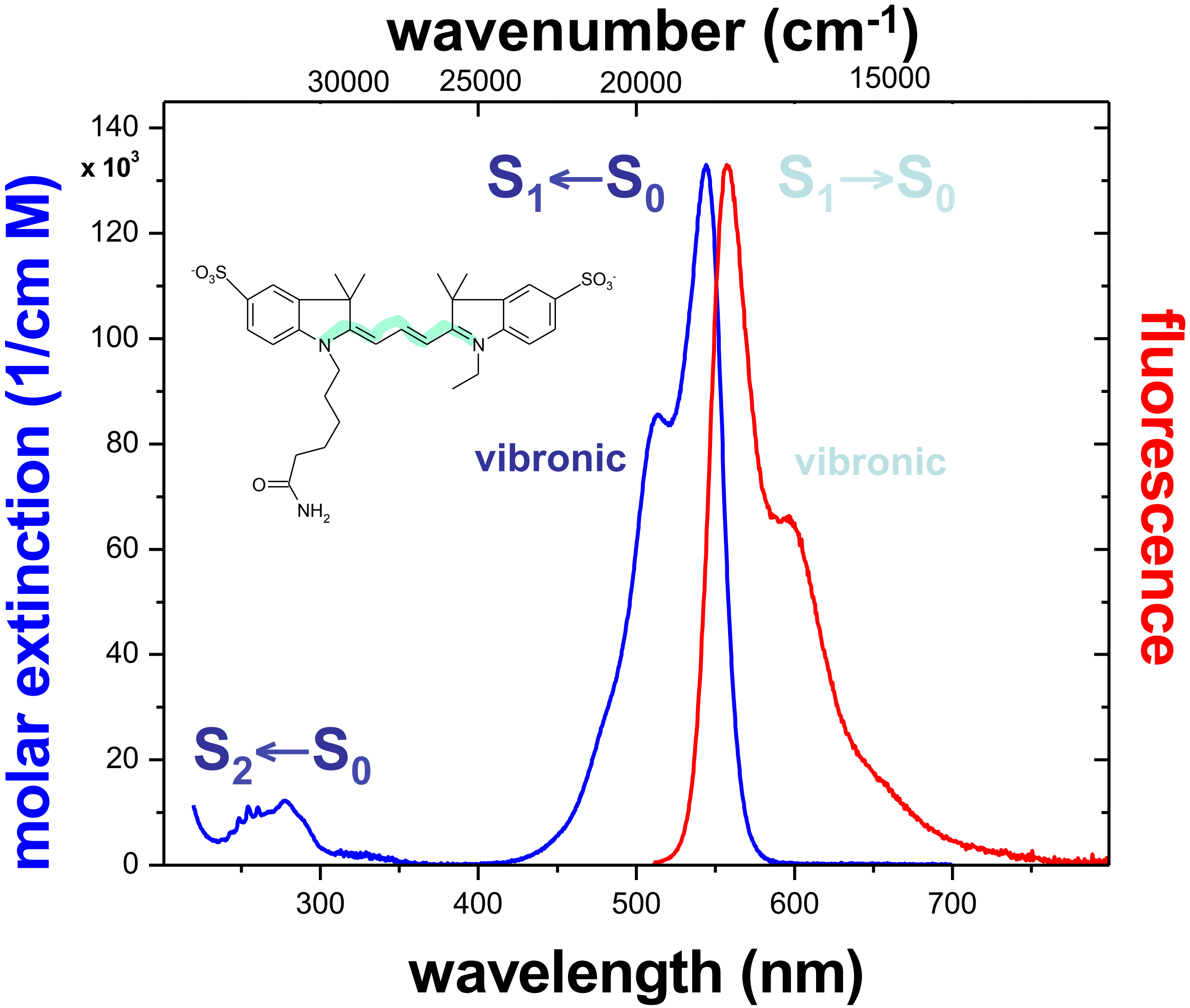


Mirror Image

Absorption and fluorescence spectra are related by a mirror symmetry around the 0-0 transition

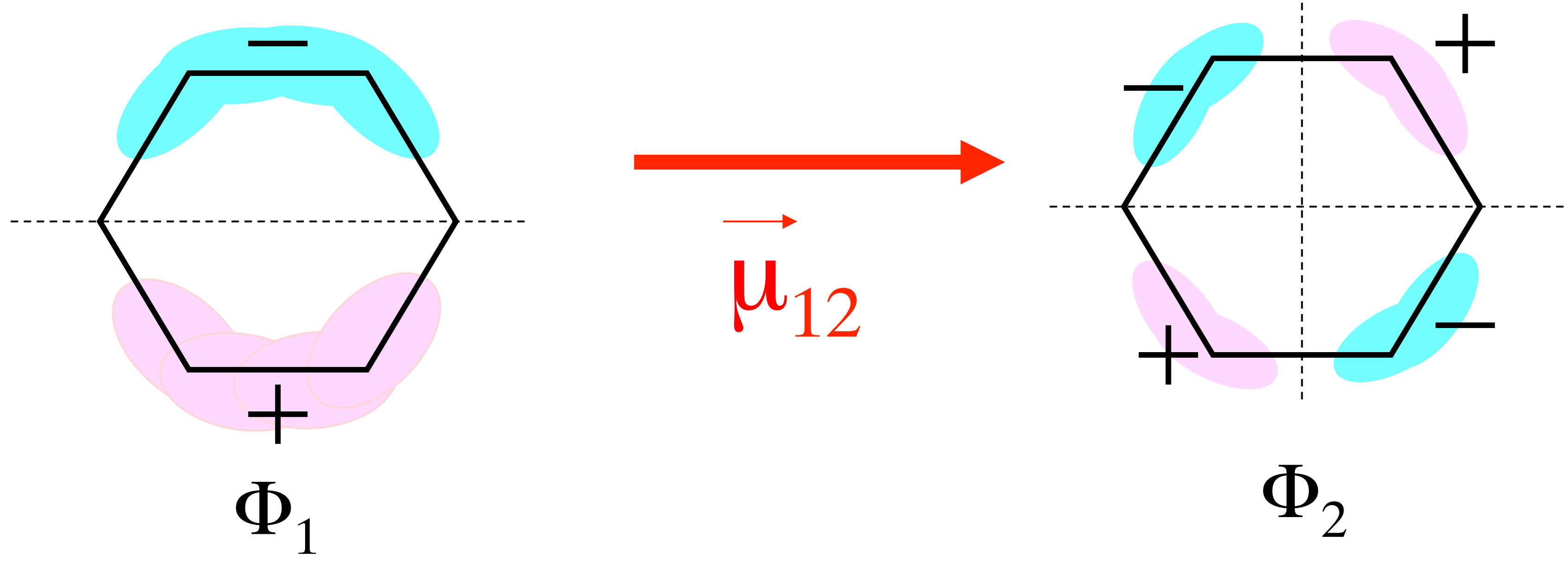


Absorption & Emission of Cy3



Transition dipole moment

$$\vec{\mu}_{12} = \langle \Phi_1 | -e\vec{r} | \Phi_2 \rangle$$



$|\vec{\mu}_{12}|^2$ characterizes the strength of the optical transition

Kasha's Rule

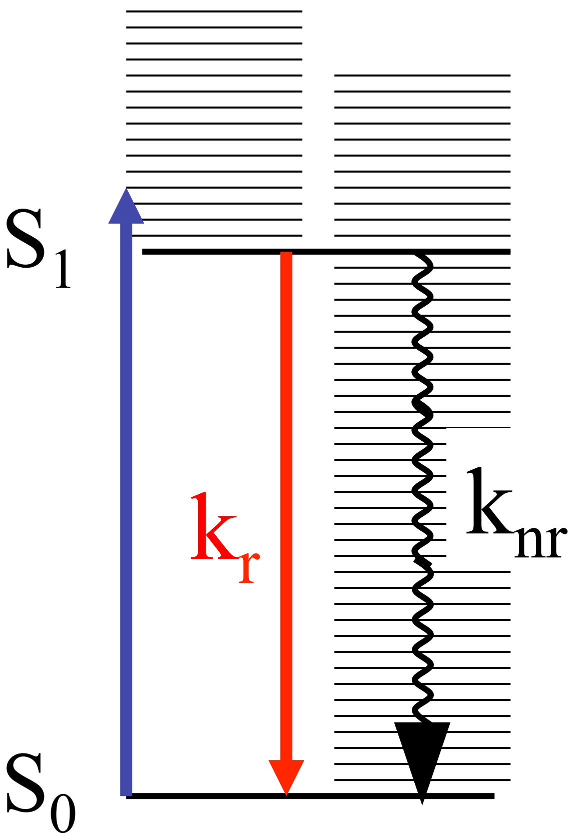
- Radiative and non-radiative relaxation between electronic levels

- Fluorescence can only arise from the lowest excited singlet state S_1;

- higher excited states relax to S_1 faster than they can emit;

- triplet states emit weak phosphorescence.

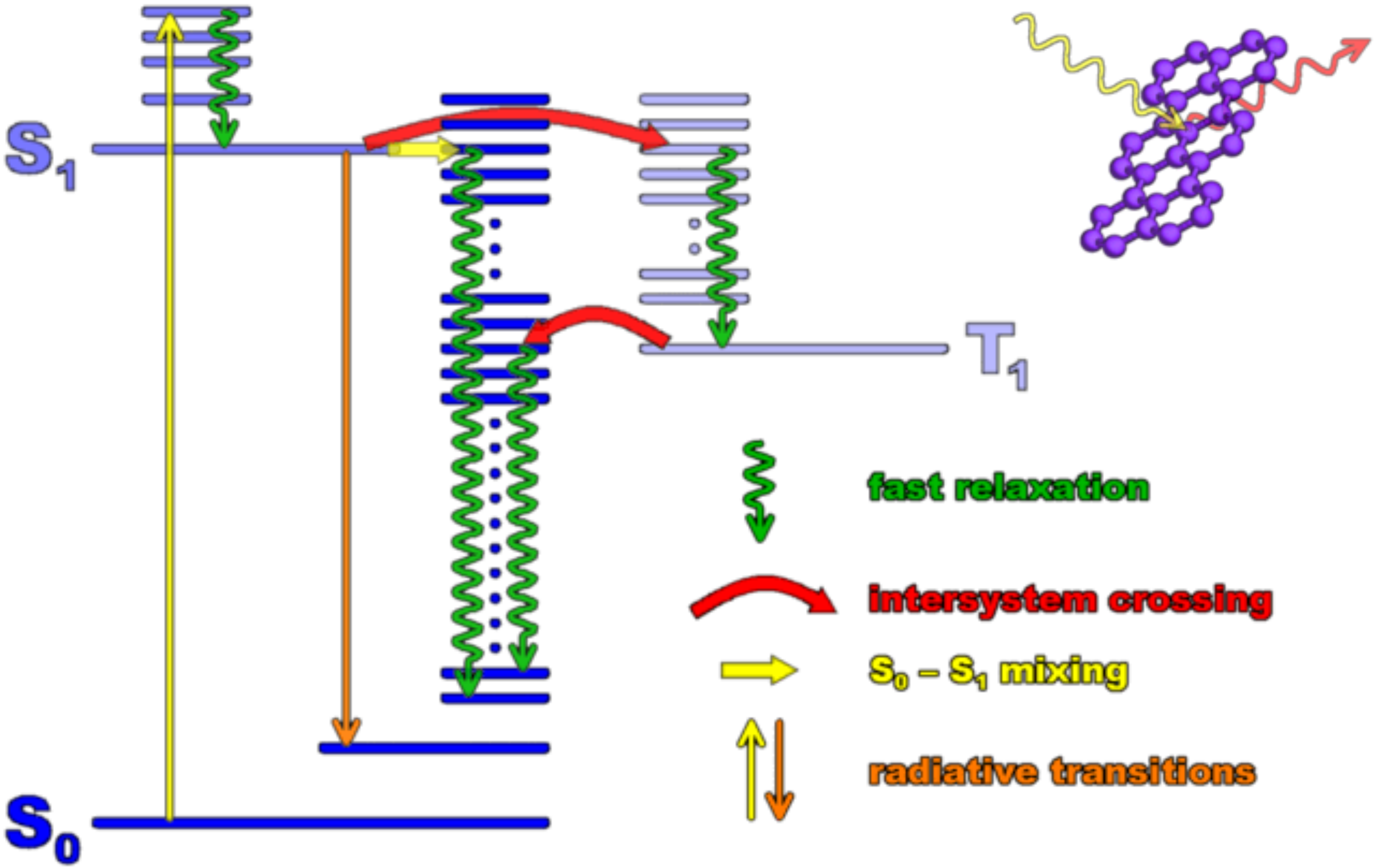
Fluorescence quantum yield



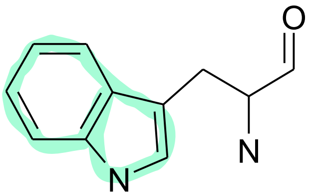
$$\tau_{fluo} = \frac{1}{k_r + k_{nr}}$$

$$\eta_{fluo} = \frac{k_r}{k_r + k_{nr}} \leq 1$$

Jablonski diagram: relaxation between electronic states

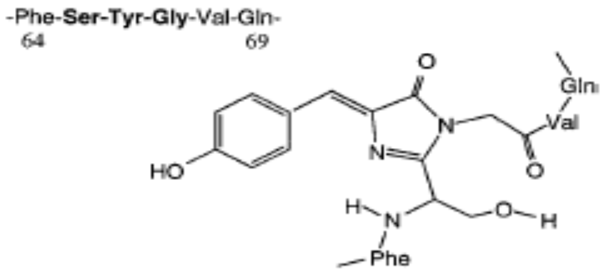


Typical fluorophores



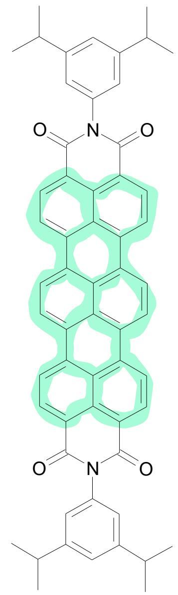
tryptophane

λ = 280 nm



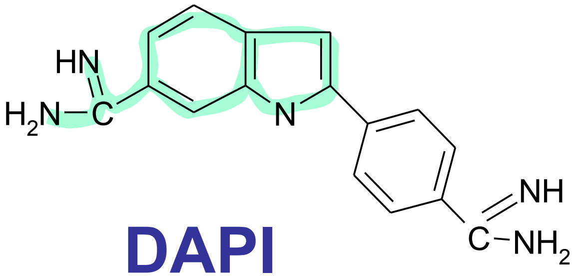
eGFP

λ = 490 nm



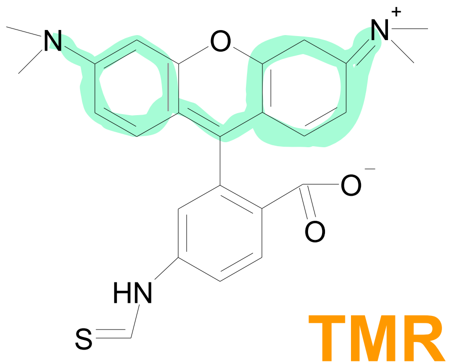
TDI

λ = 630 nm



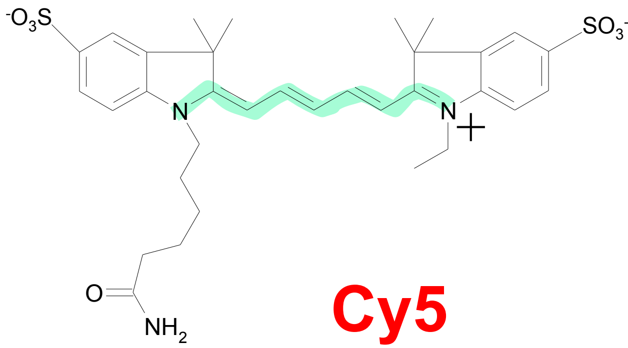
DAPI

λ = 355 nm



TMR

λ = 514 nm

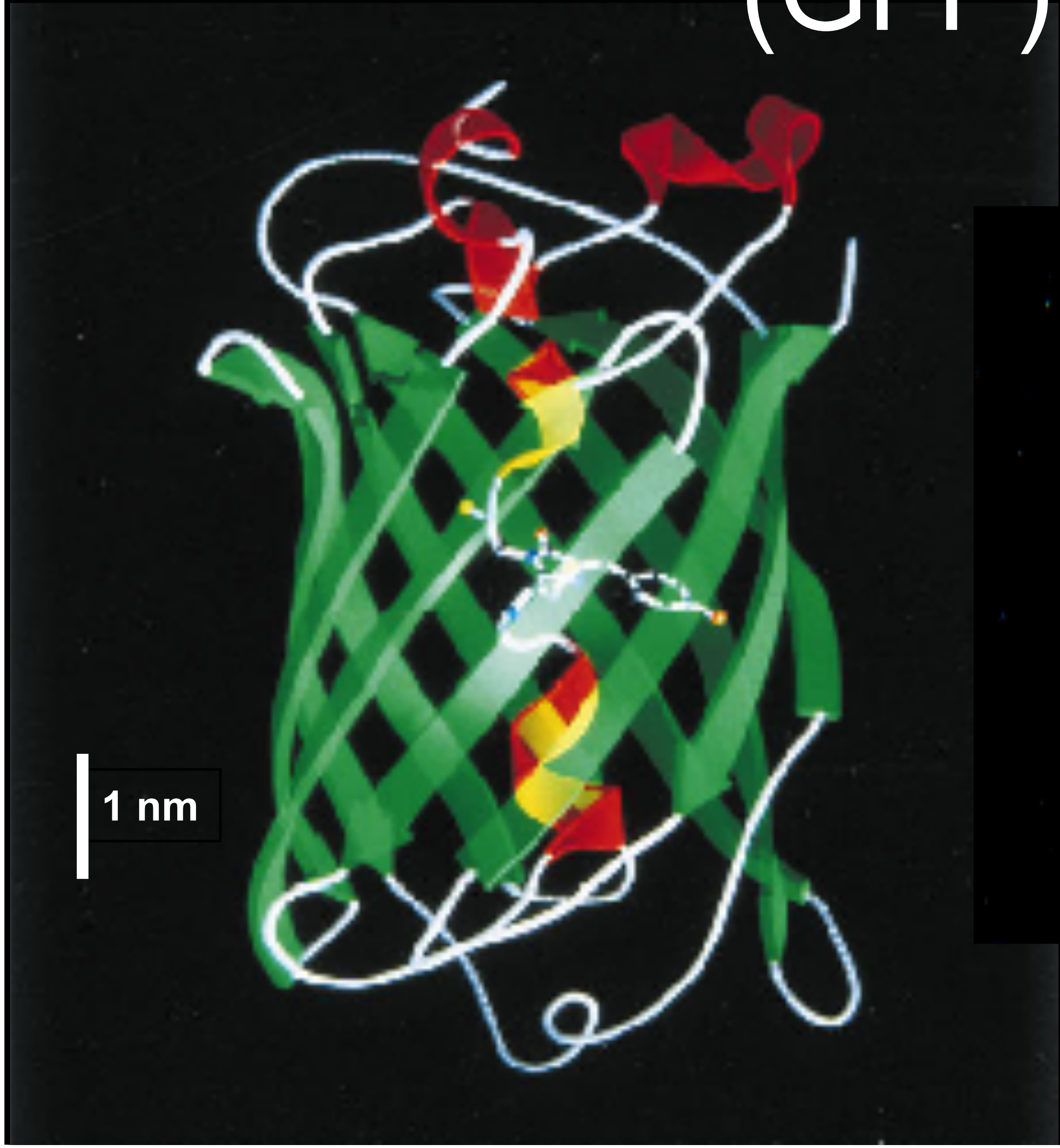


Cy5

λ = 630 nm

green-fluorescent protein (GFP)

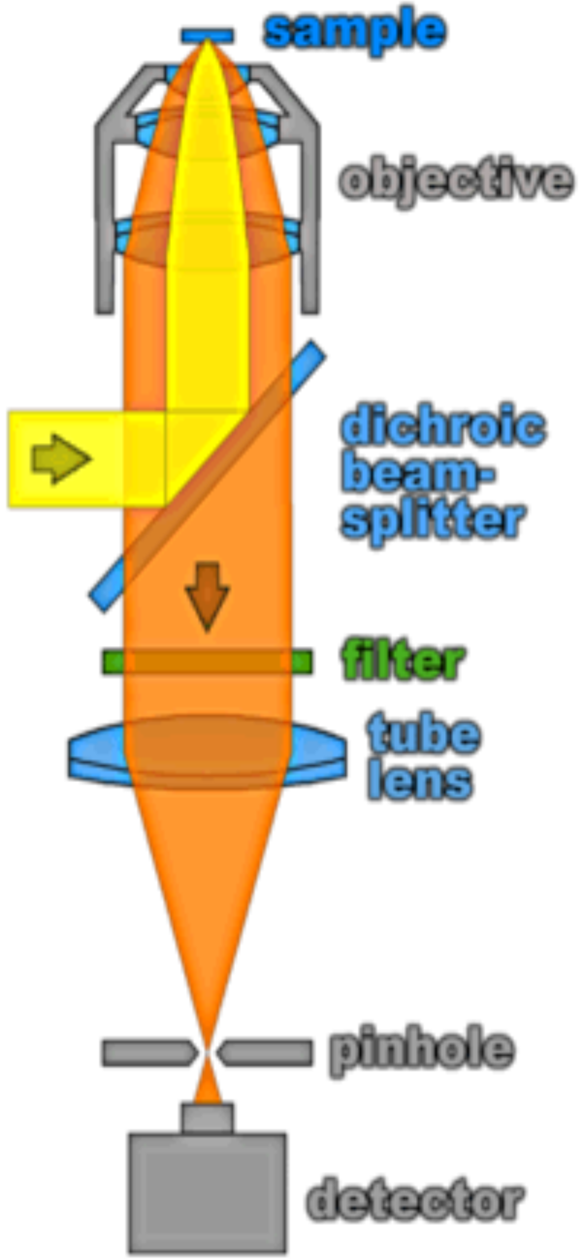
K. Brejc et.al., PNAS 94 (1997) 2306



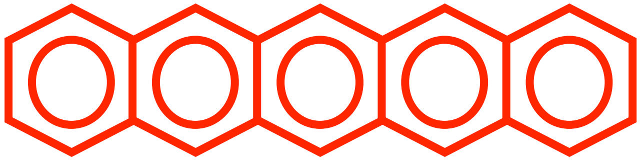
Optical microscope

$$V_{illum.} \approx 1 \mu m^3$$

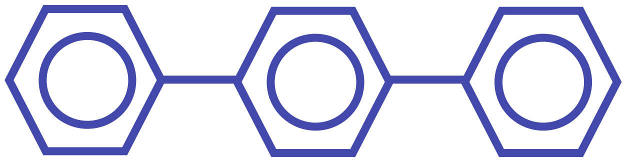
about 10^9 molecules in focal spot



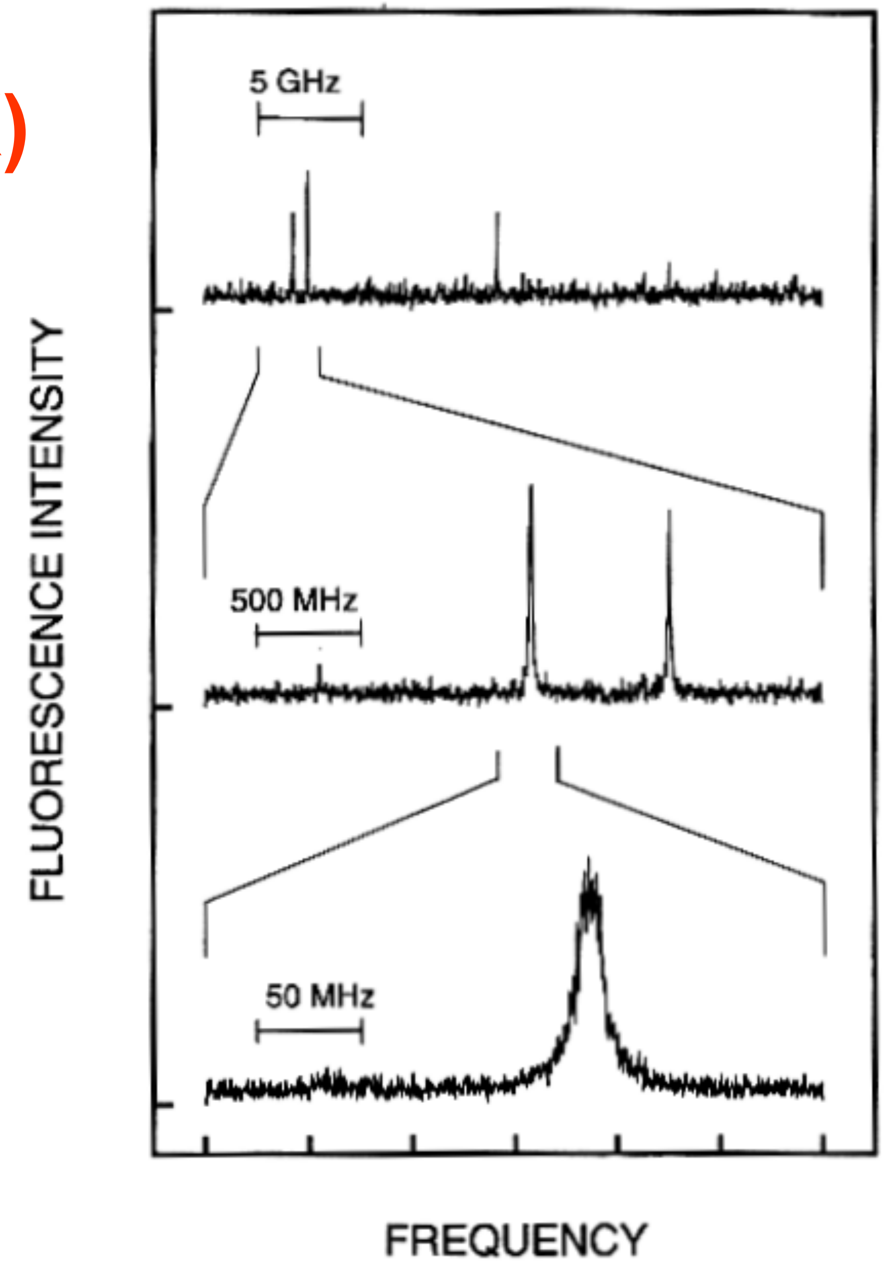
Fluorescence (T=2K)



pentacene



in p-terphenyl

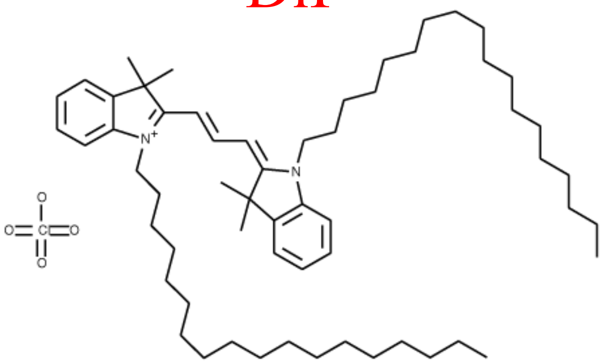


M. Orrit and J. Bernard, PRL 65 (1990) 2716

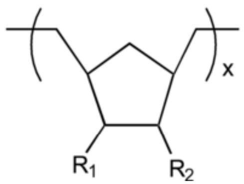
Room Temperature

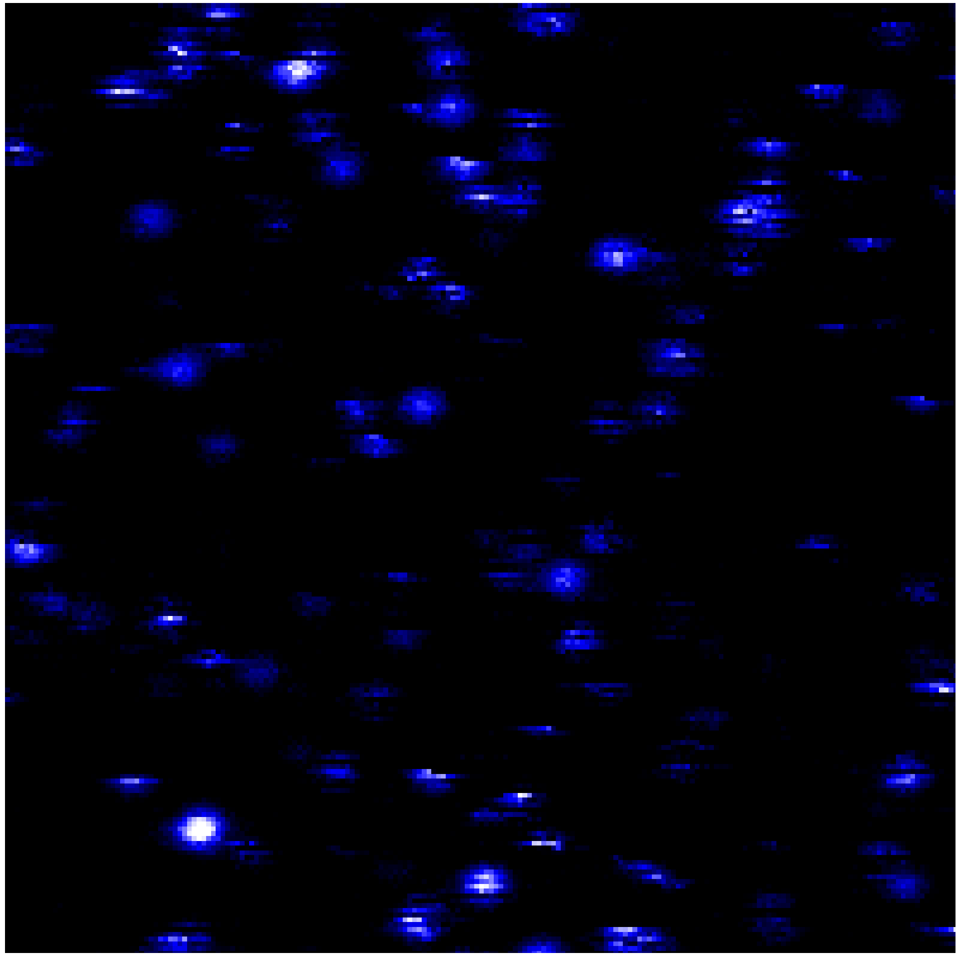
$$\frac{\sigma_{abs}(Room\,T.)}{\sigma_{abs}(Low\,T.)} \approx 10^{-6}$$

DiI



in Zeonex®





10 μm

Fluorescence and fluorescence excitation spectroscopy at cryogenic temperatures


Rogier Verberk

Fluorescence blinking

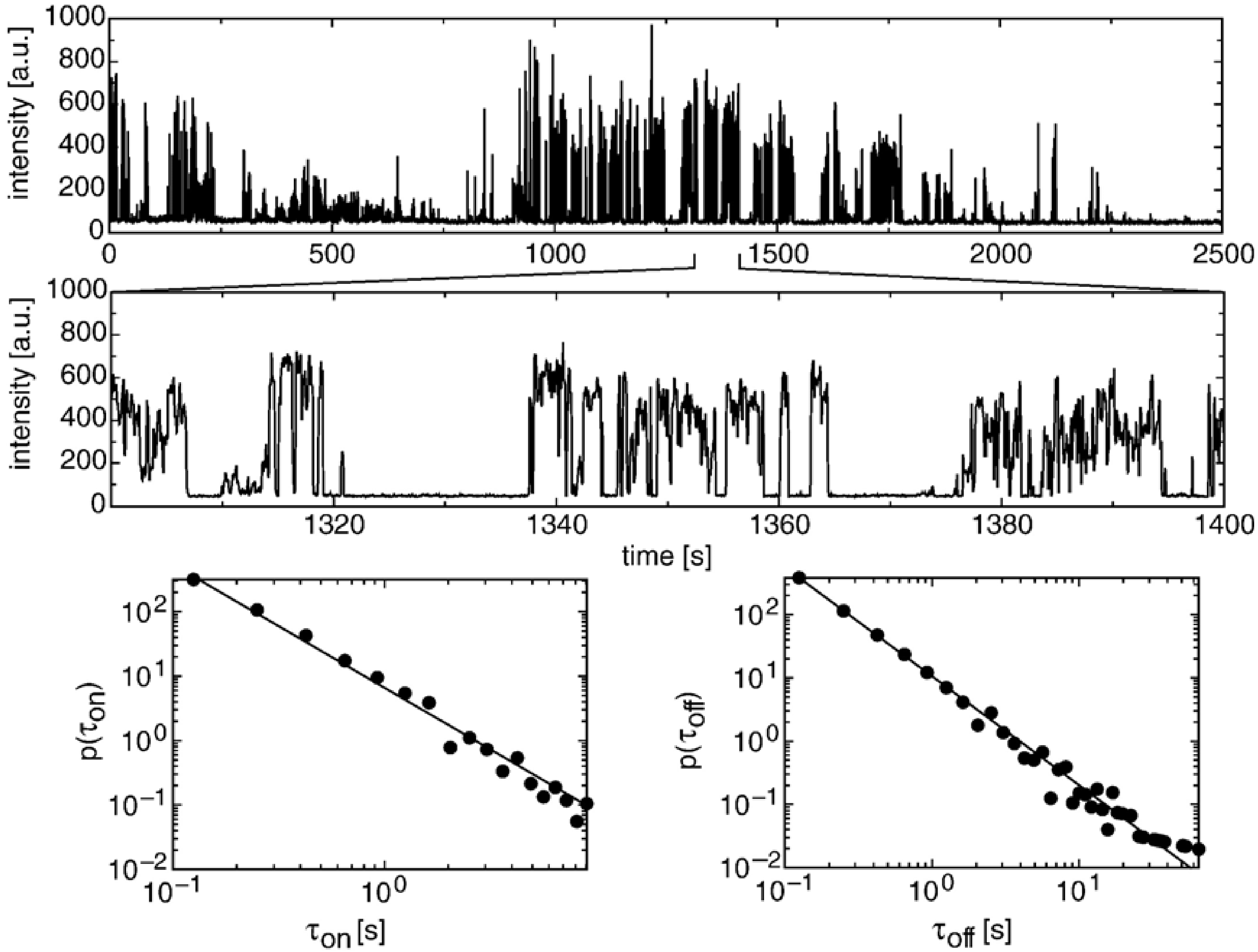
- power-laws for many different systems

- broad time dynamics (up to 9 decades)

- temperature dependence absent or weak

- effects of environment and disorder

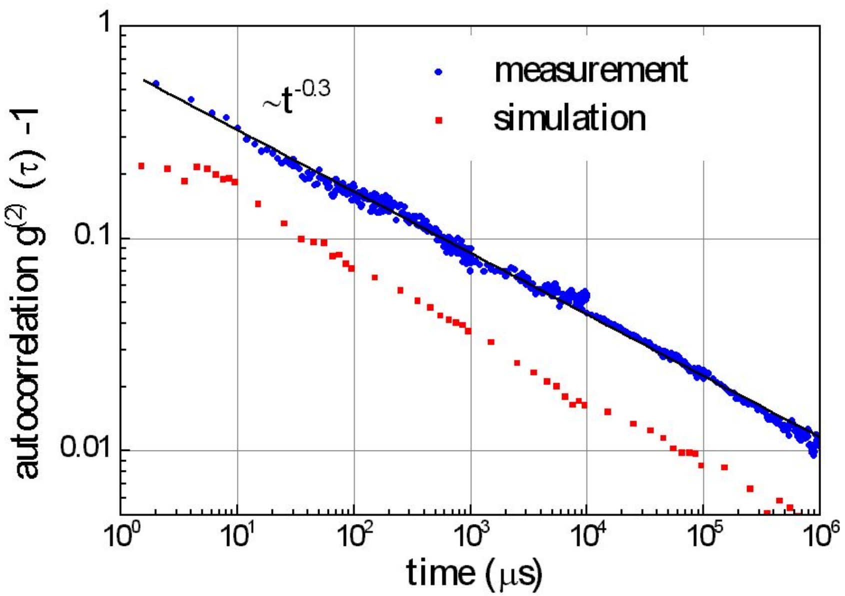
Blinking of CdSe nanocrystals



from: Issac et al., PRB **71** (2005) 161302

Wide distribution of blinking times

Sher et al., APL **92** (2008) 101111



Verberk et al., PRB **66** (2002) 233202

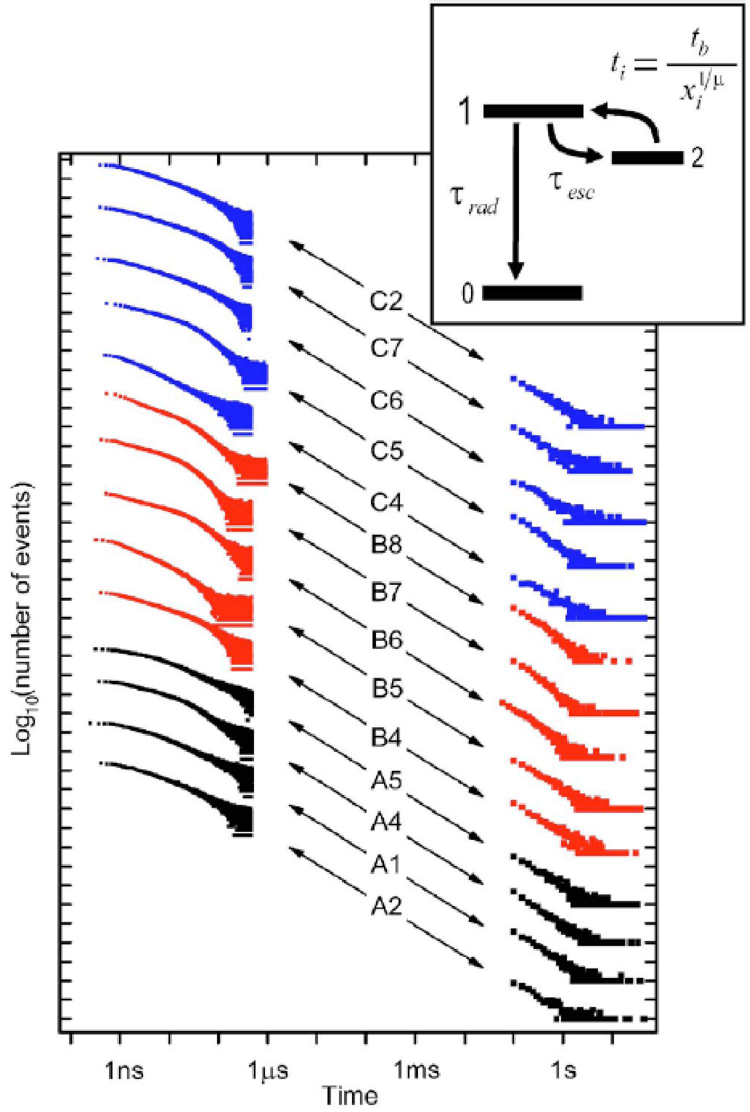
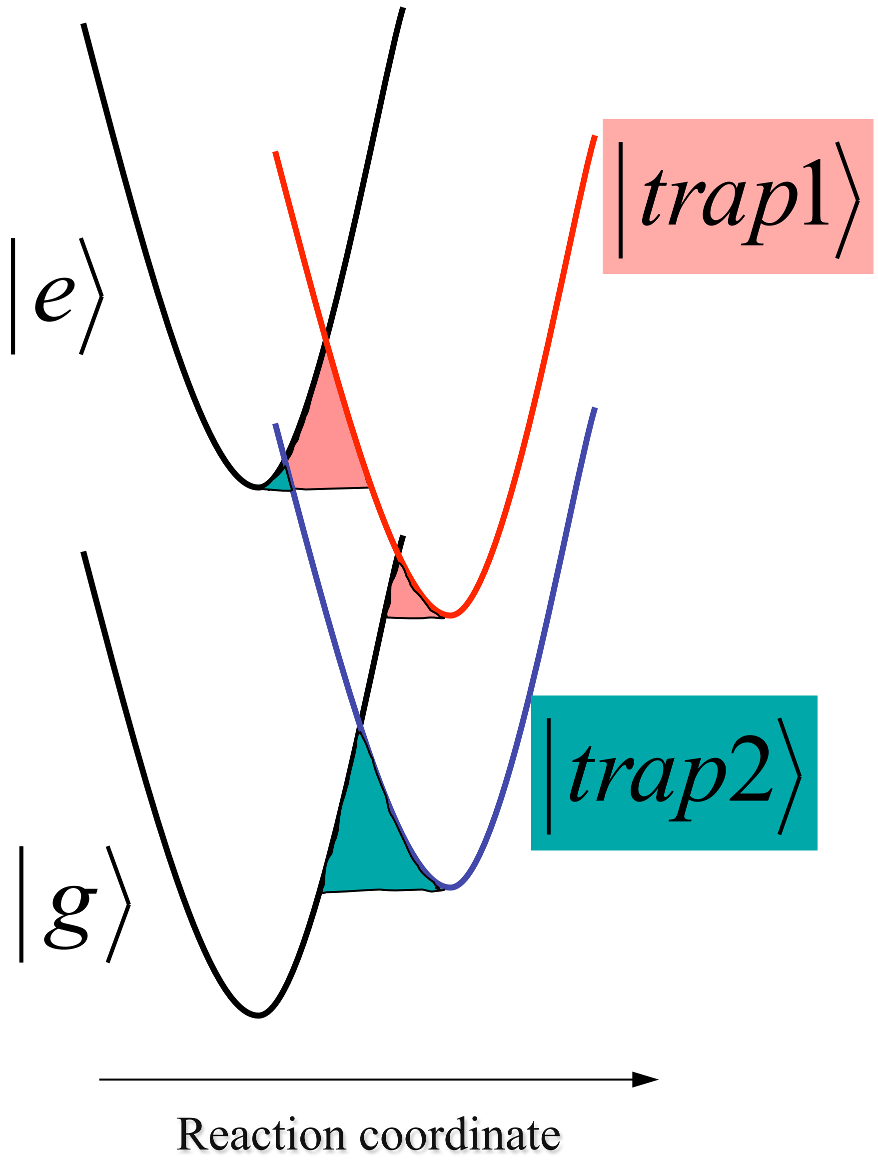


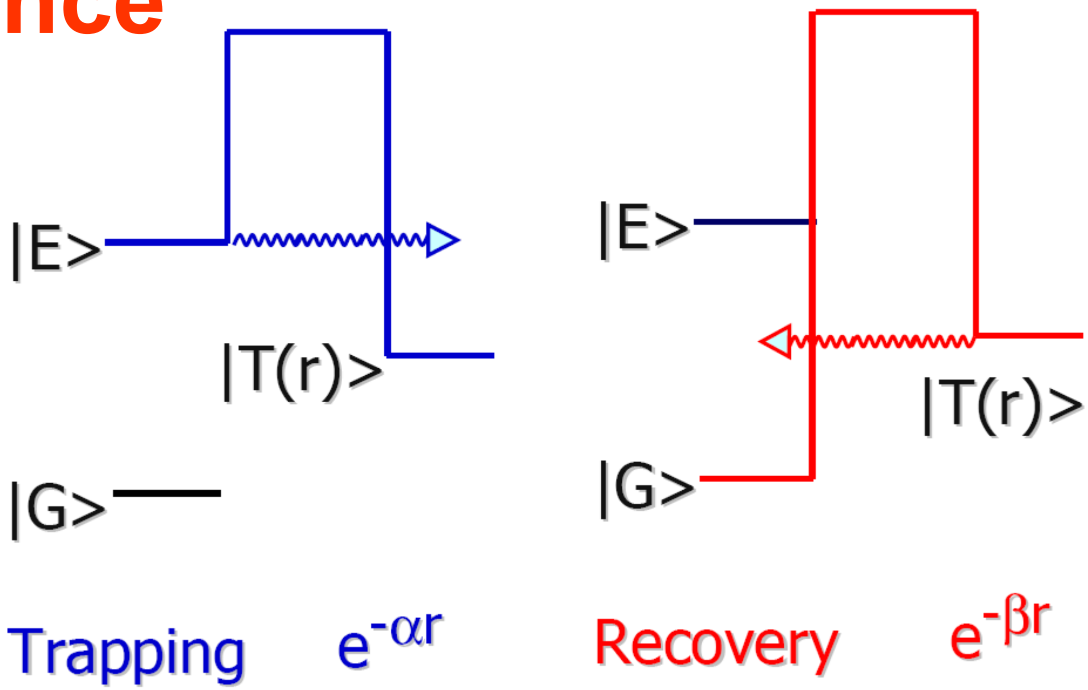
FIG. 2. (Color online) TCSPC and blinking data histograms on common logarithmic axes for 14 different single nanocrystals. The increments on both axes of the figure correspond to factors of 10. (Inset) Three level system used to simulate the tails of the TRPL data. Level 0 represents the nanocrystal ground state; level 1 the quantum confined exciton; and level 2 the charged fluorescence off state. τ_{rad} is the radiative lifetime that corresponds to the slower decay in the original biexponential fit. The two additional fitting parameters are the lifetimes for escape from the exciton state to the fluorescence off state, labeled as τ_{esc}, and the power law coefficient μ.

Reaction coordinate

Marcus theory



Tunneling Distance



- tunneling from excited emitter to trap
- self-trapping
- recovery to ground state of emitter
- continuous distribution of distances

Power Laws

- distribution of off-times follows

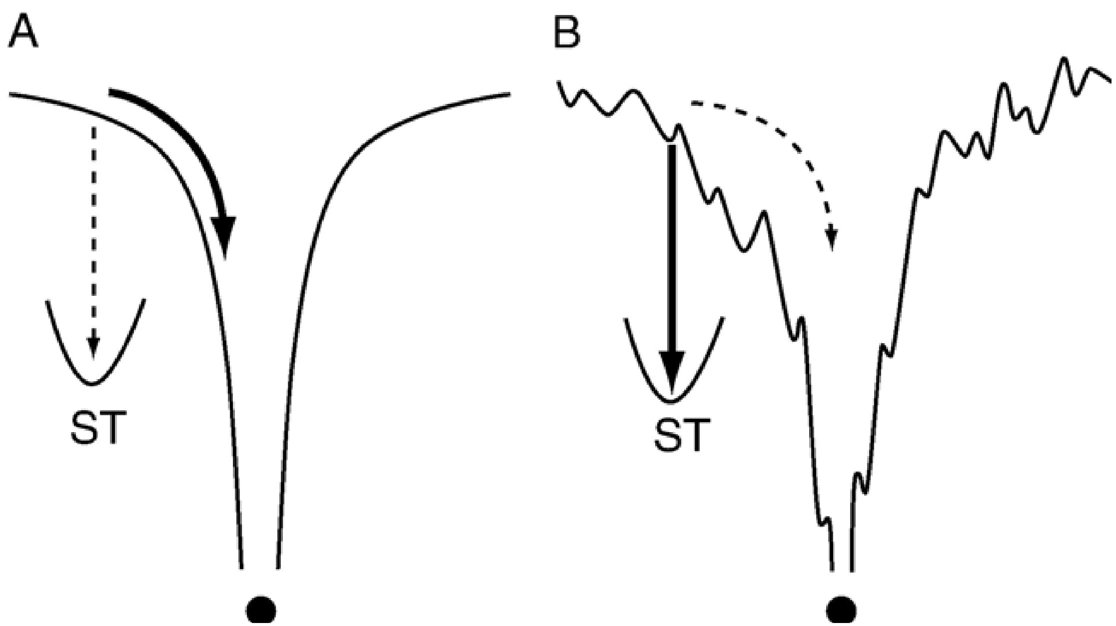
$$p(t) = A \times t^{-\mu}, \quad \mu = 1 + \frac{\alpha}{\beta}$$

- exponent μ verifies

$$1 < \mu < 2$$

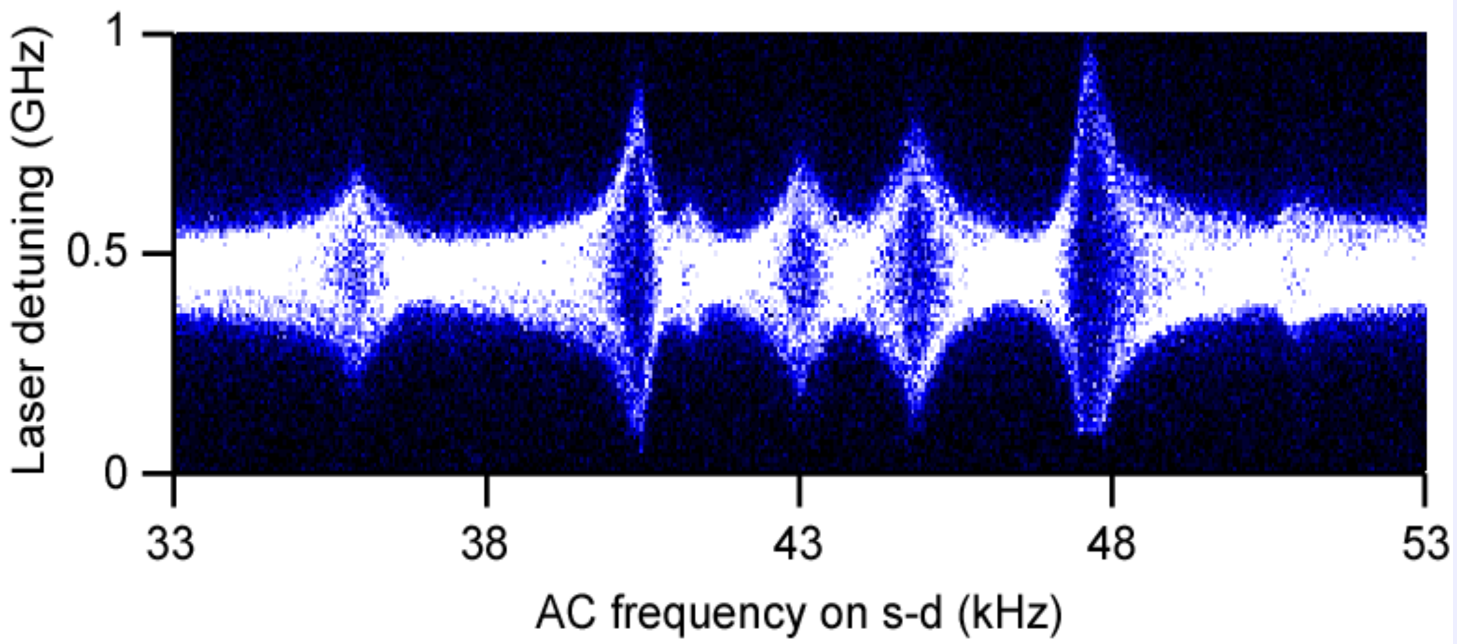
Open questions

- trap model explains exponents, robustness, broad dynamic range
- nature of long-lived charged state (self-trapped?)
- mechanism for long on-times, disorder



F. Cichos et al., Curr. Opin. Coll. Interf. Sci. **12** (2007) 272.

Low-temperature Fluorescence Excitation Spectroscopy



Dr. Aurélien Nicolet

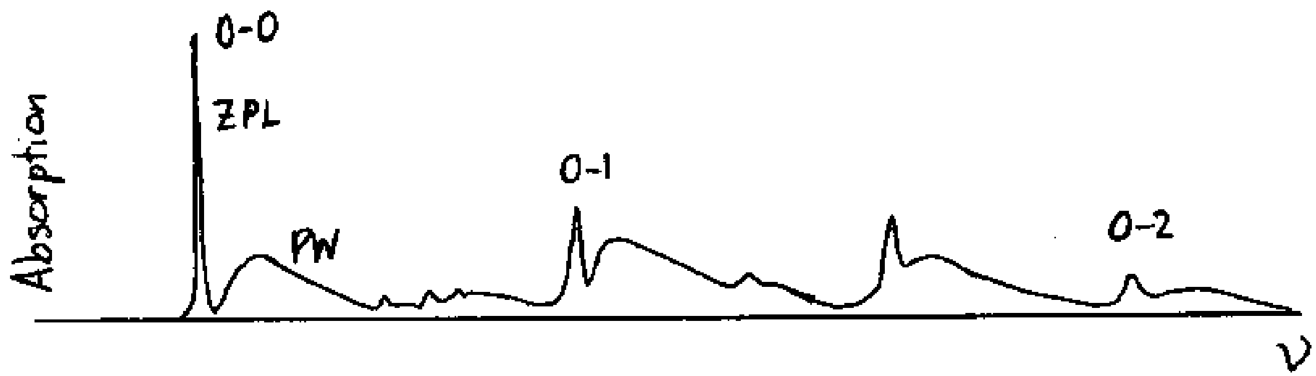
Dr. Mikhail Kol’chenko

Dr. Clemens Hofmann

Prof. B. Kozankiewicz

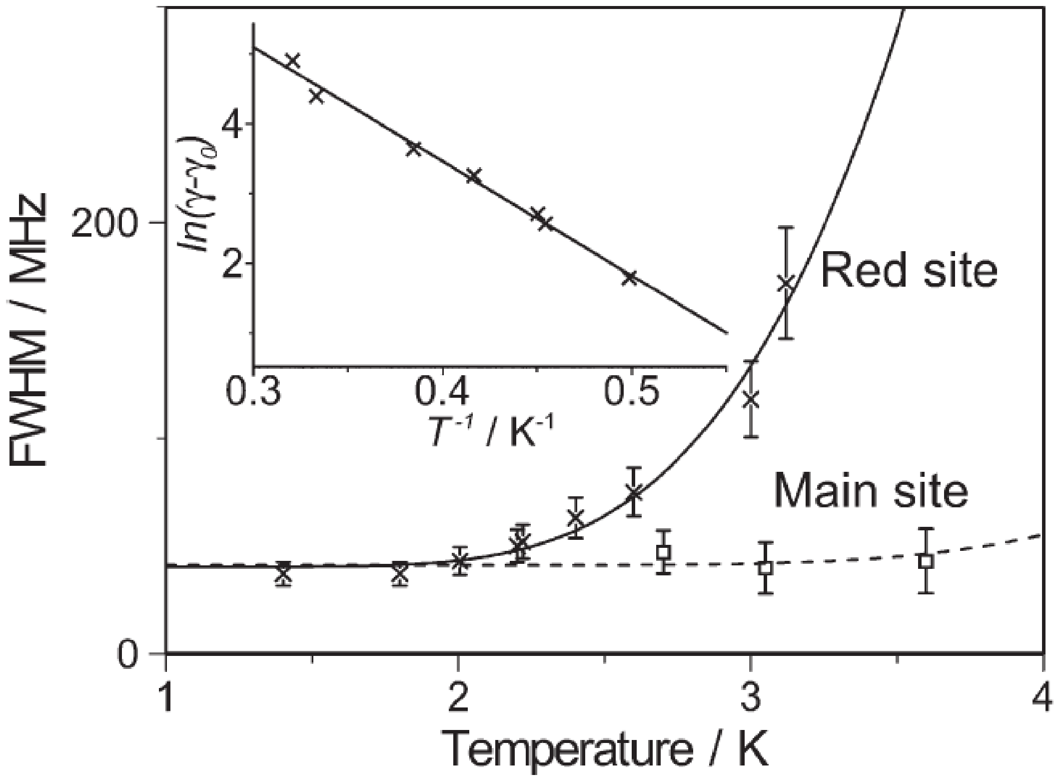
Optical Spectroscopy at Cryogenic Temperatures

- Zero-Phonon Line: transition without creation or destruction of phonons
- Phonon Wing: at T = 0 K, creation of one or more phonons



Intensity and Width of ZPL

- Intensity decreases steeply with T (DBT in Ac)

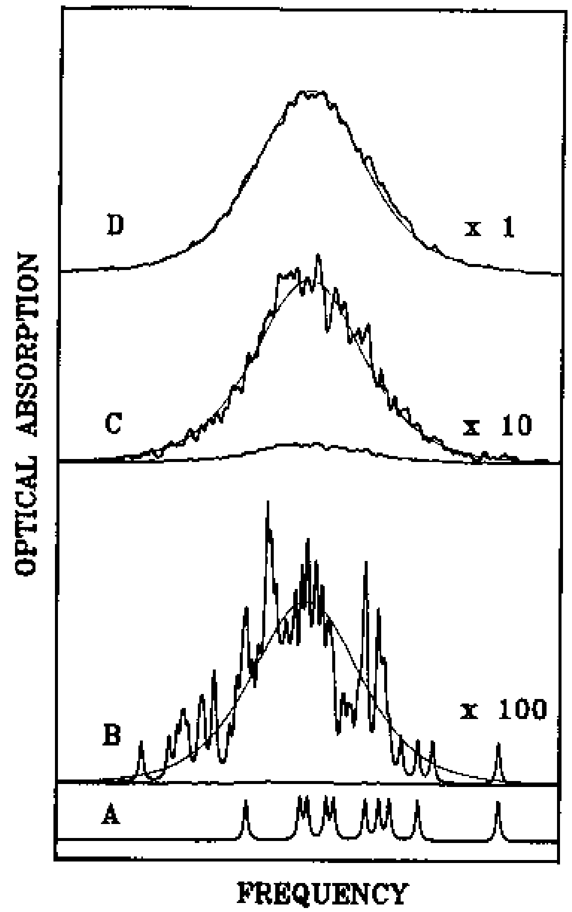


- Width limited by excited-state lifetime and dephasing

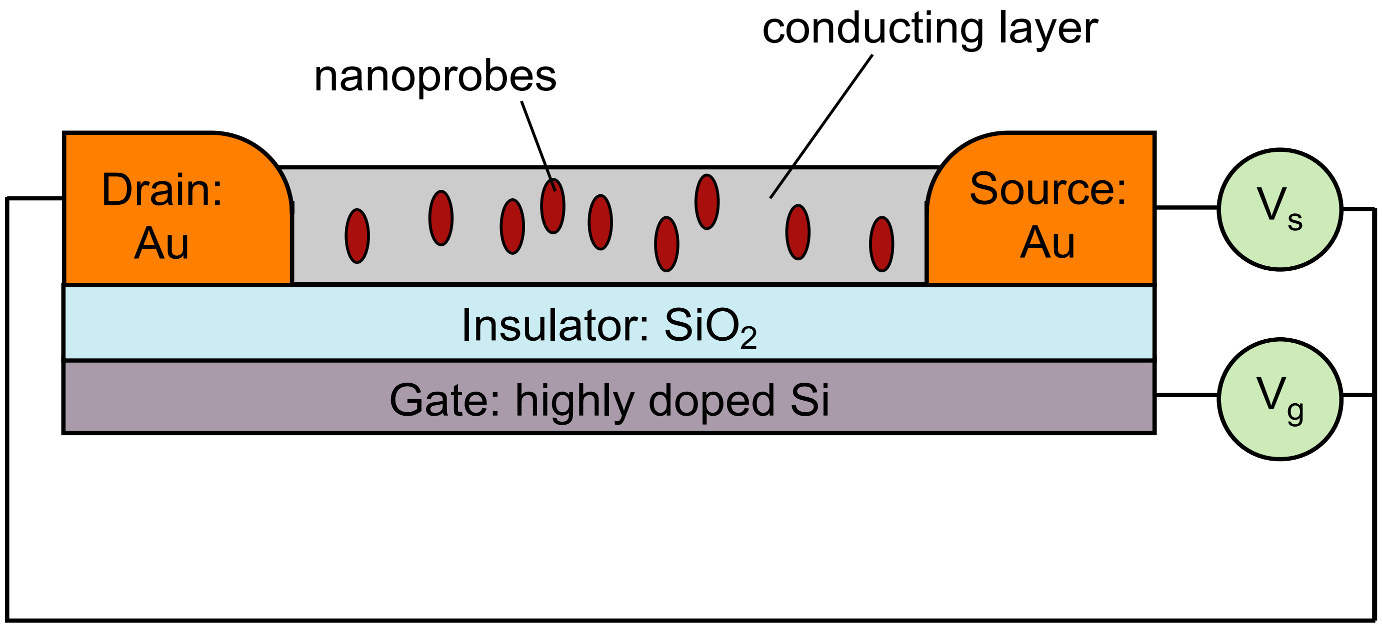
Spectral selection of single molecules

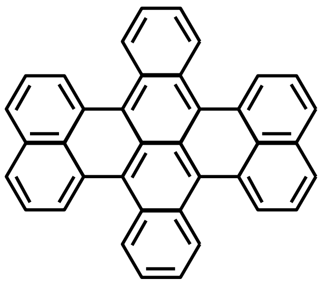
Decrease the number of molecules in the focal spot, until single molecules are resolved from each other.

Advantages: more molecules in the focal spot, possibility of spectral probing.

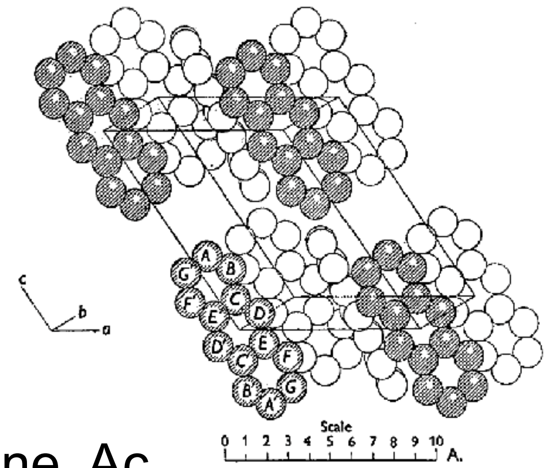


Field-Effect Transistor Geometry



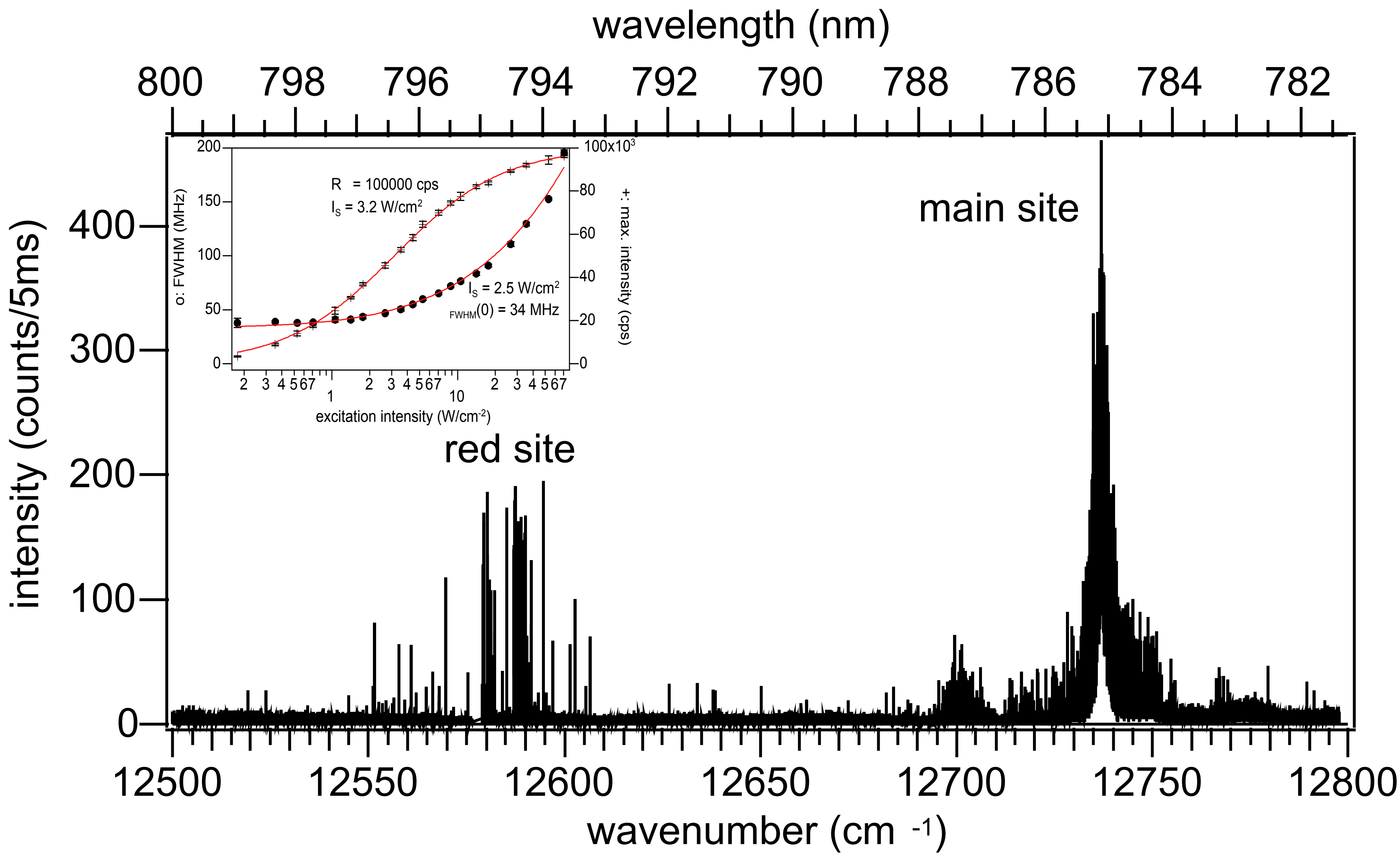


7.8,15.16-dibenzoterrylene, DBT



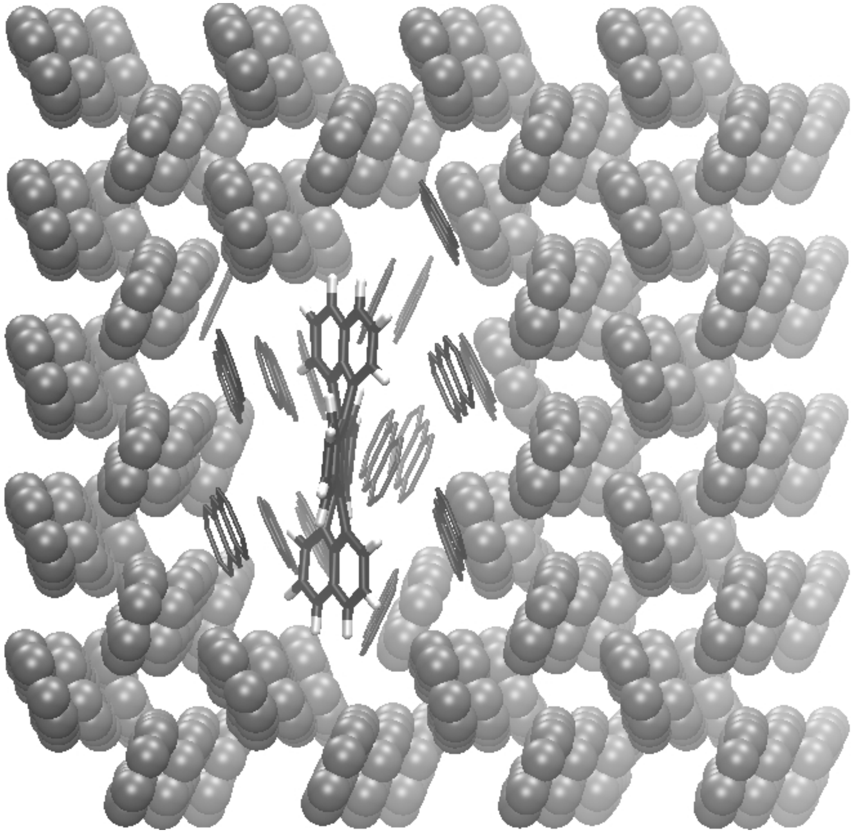
Anthracene, Ac

DBT in Anthracene : Photophysics

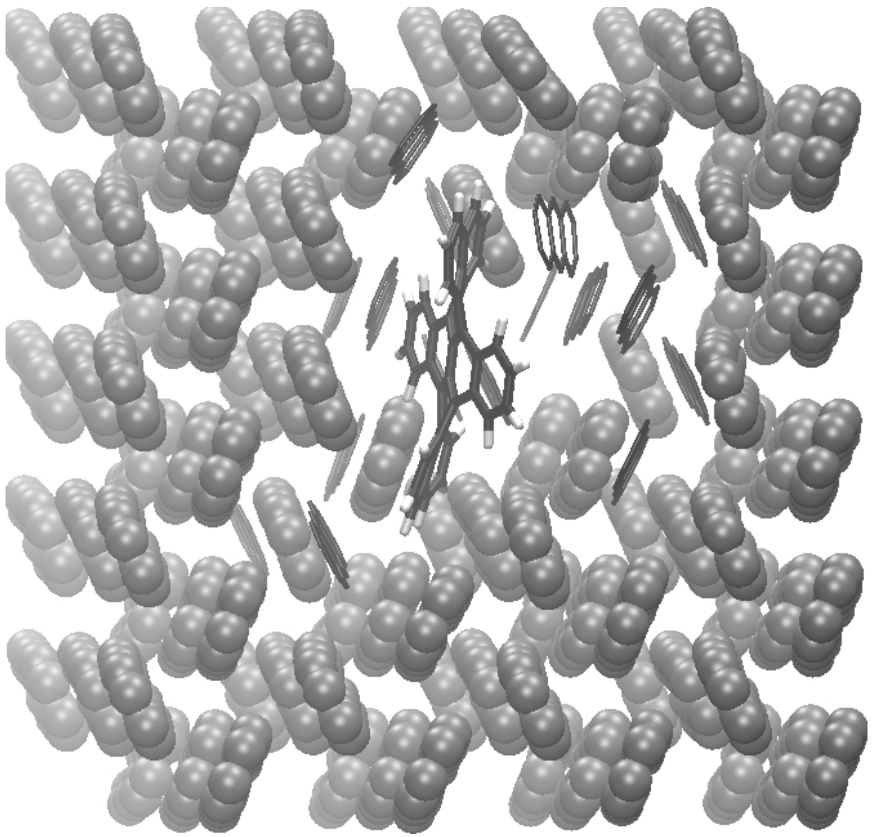


Molecular mechanics simulations

P. Bordat and R. Brown, Pau (France)

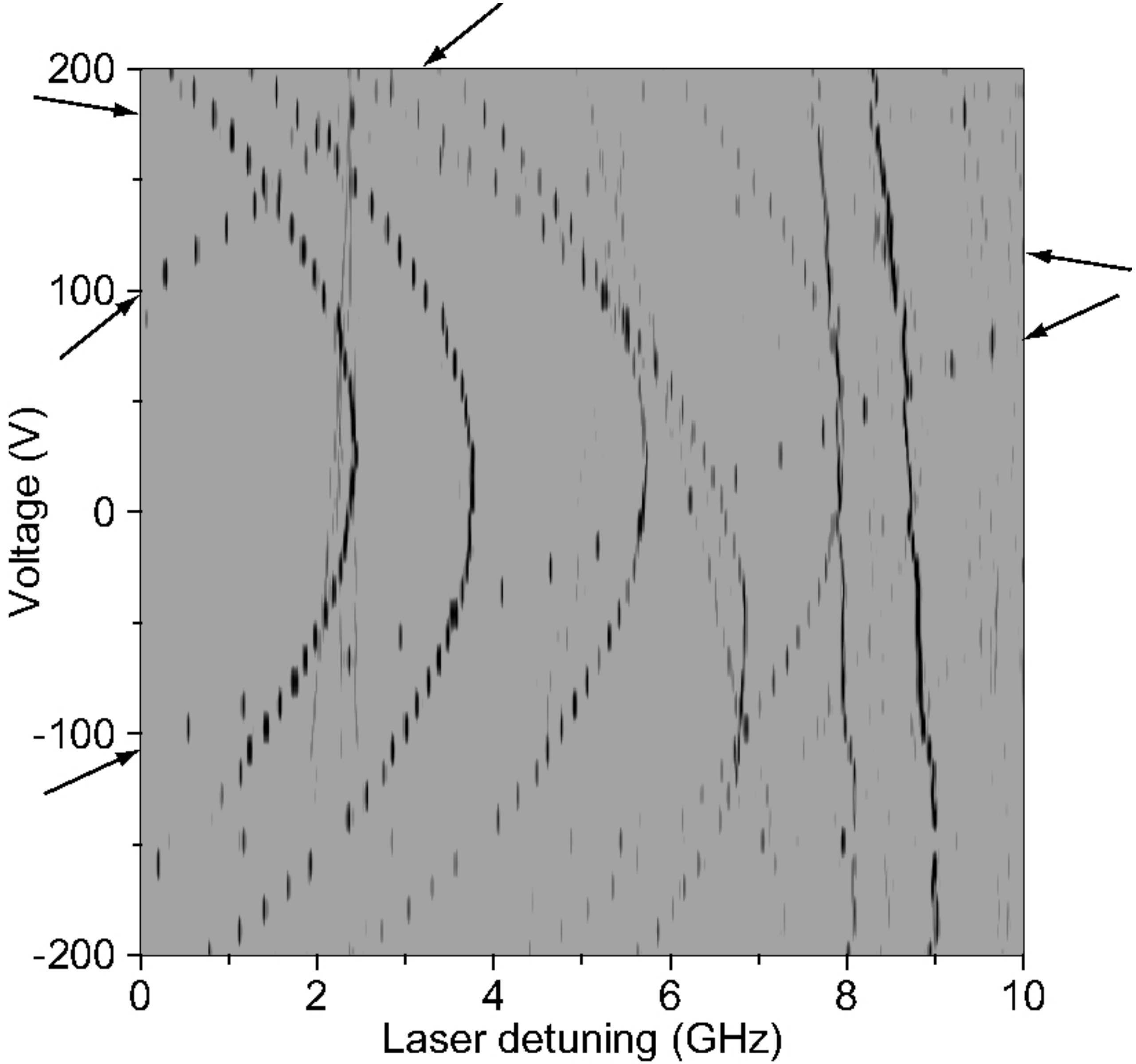


main site

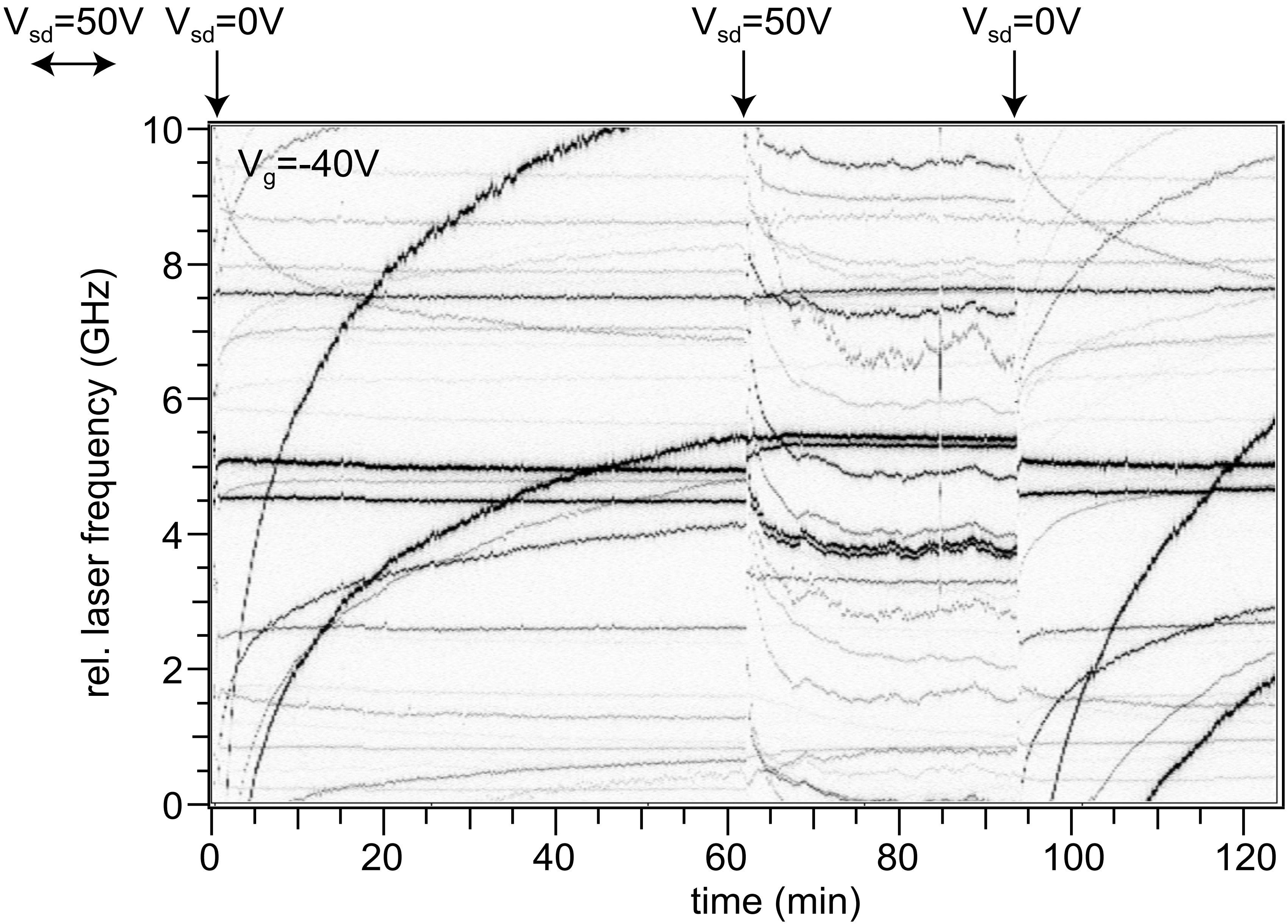


red site

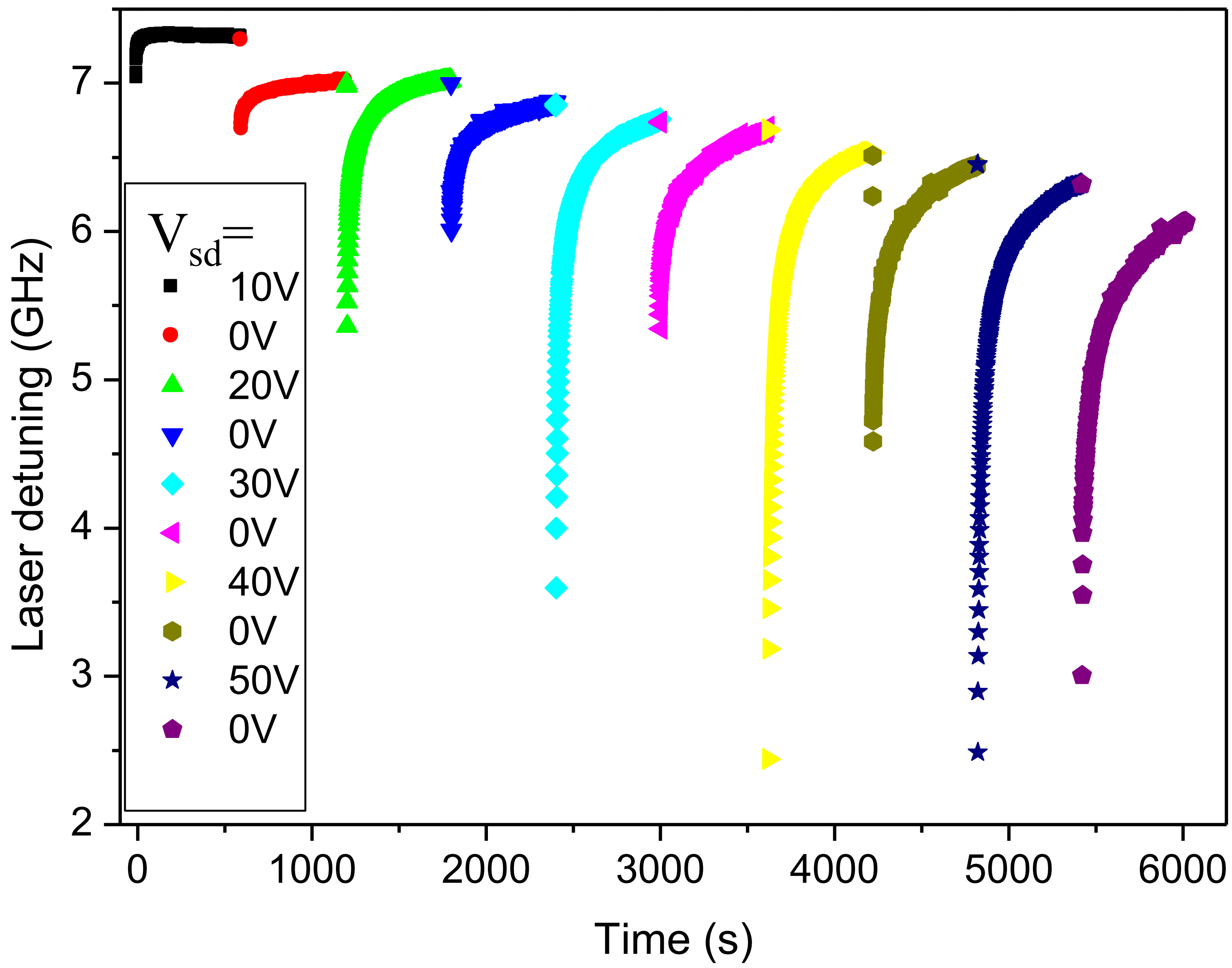
Stark effect with charge injection



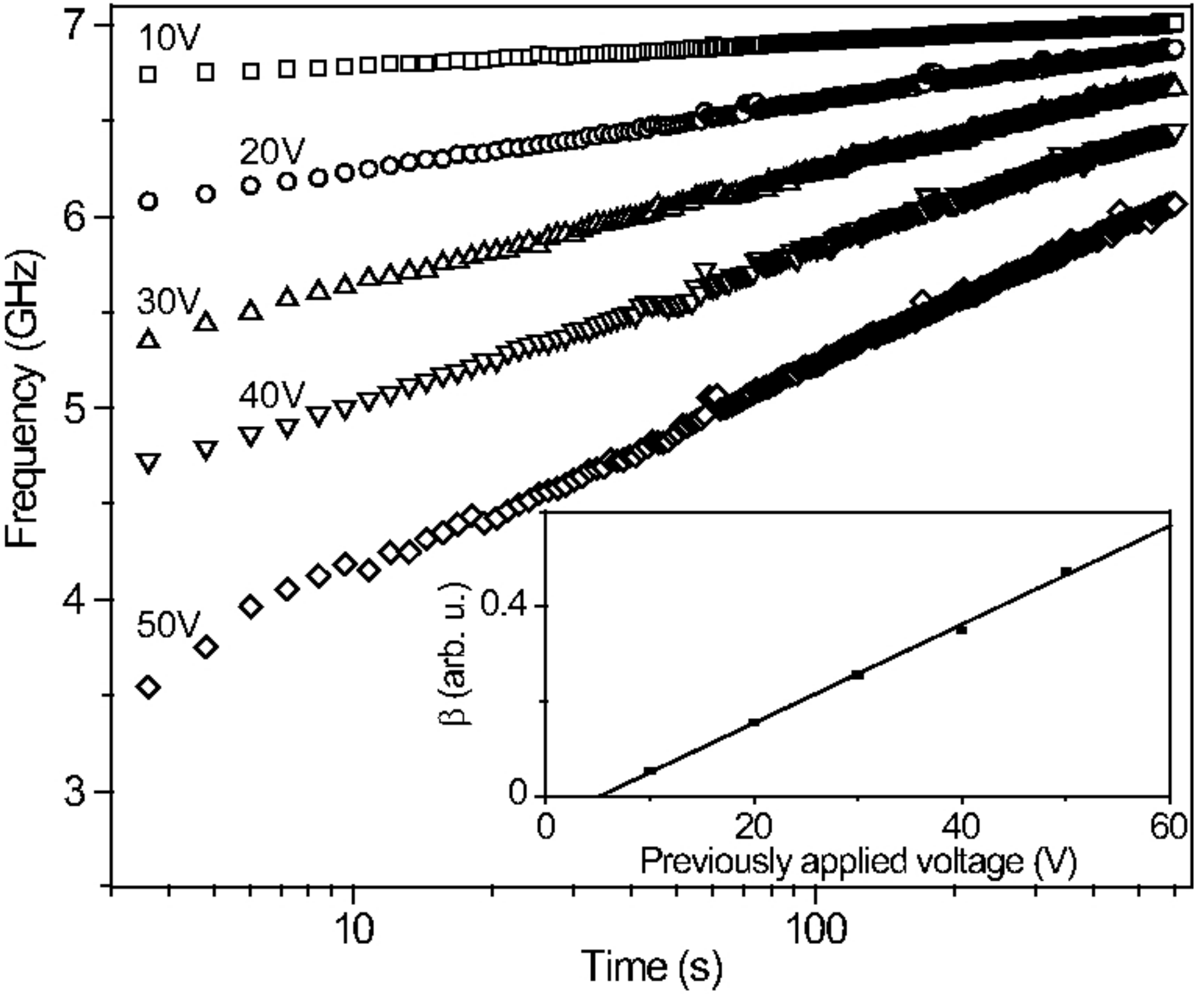
Slow relaxation after voltage changes



Strongly non-exponential relaxation



Relaxation from an applied bias voltage

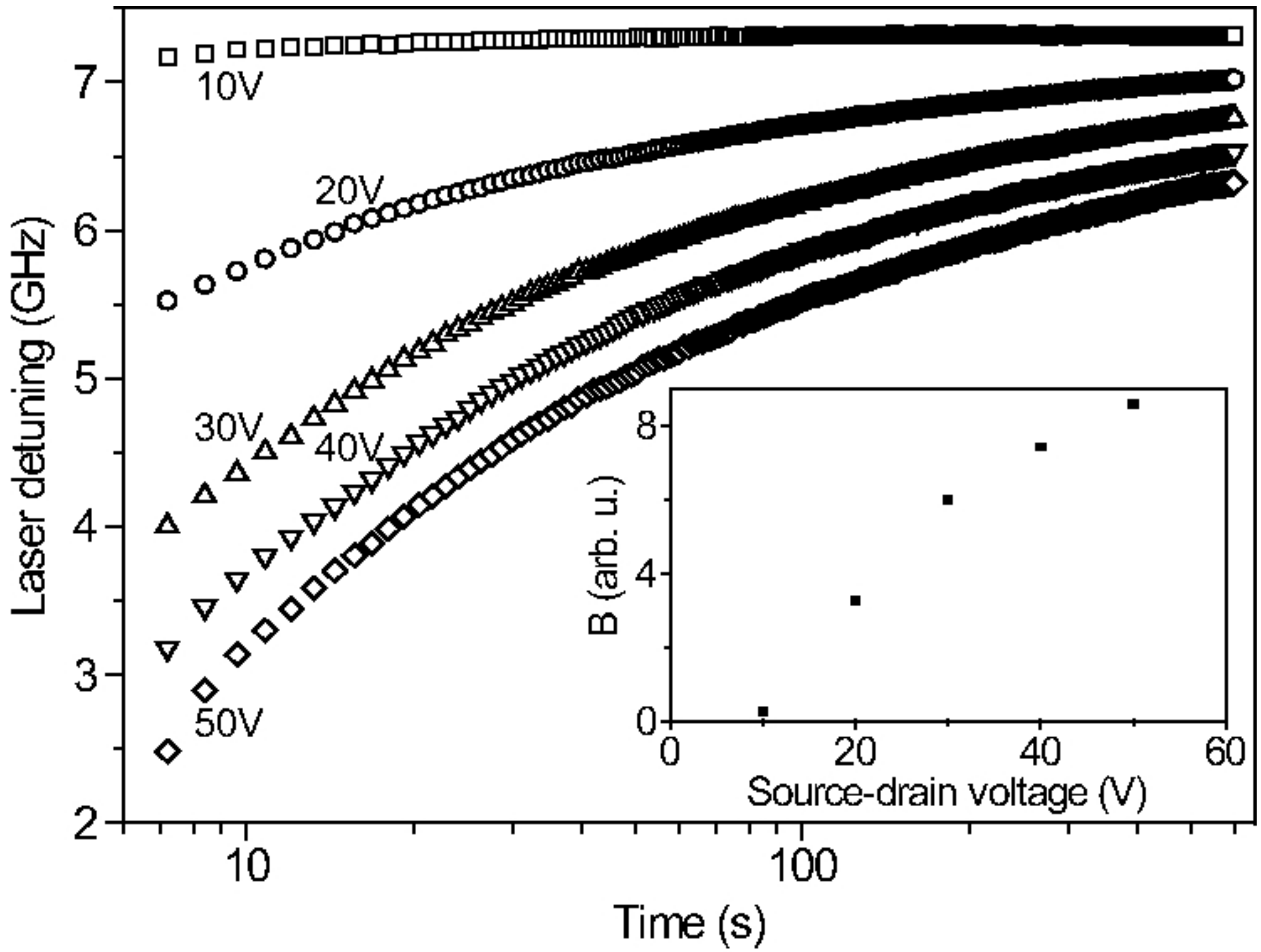


V_g= - 50 V

$$\nu(t) = \nu_0 + \beta \ln t$$

switching **off** V_{sd} from 10,… 50 to 0 V

Relaxation after applying a bias voltage



V_g = - 50 V

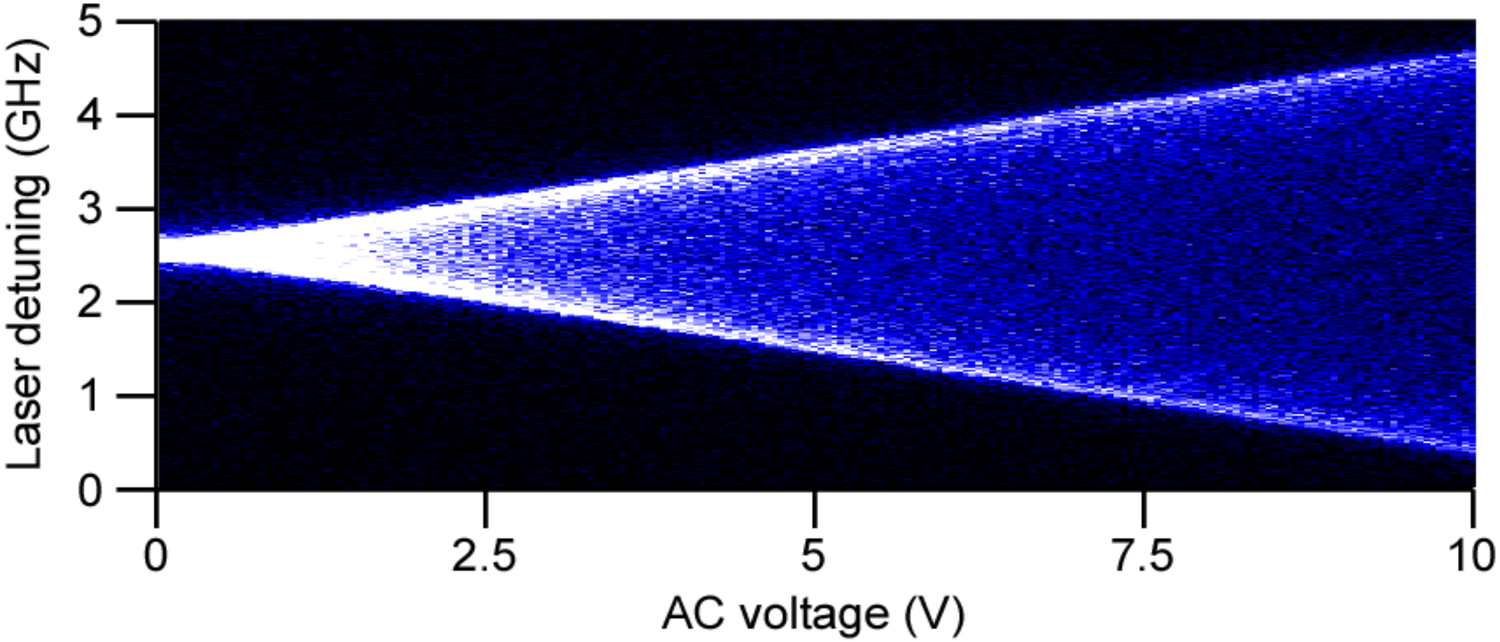
switching **on** V_{sd}

from 0 V to 10, 20, 50 V

$$\nu(t) = \nu_0 + B(t - t_0)^{-\alpha} \qquad \alpha \approx 0.4$$

AC-Stark Effect

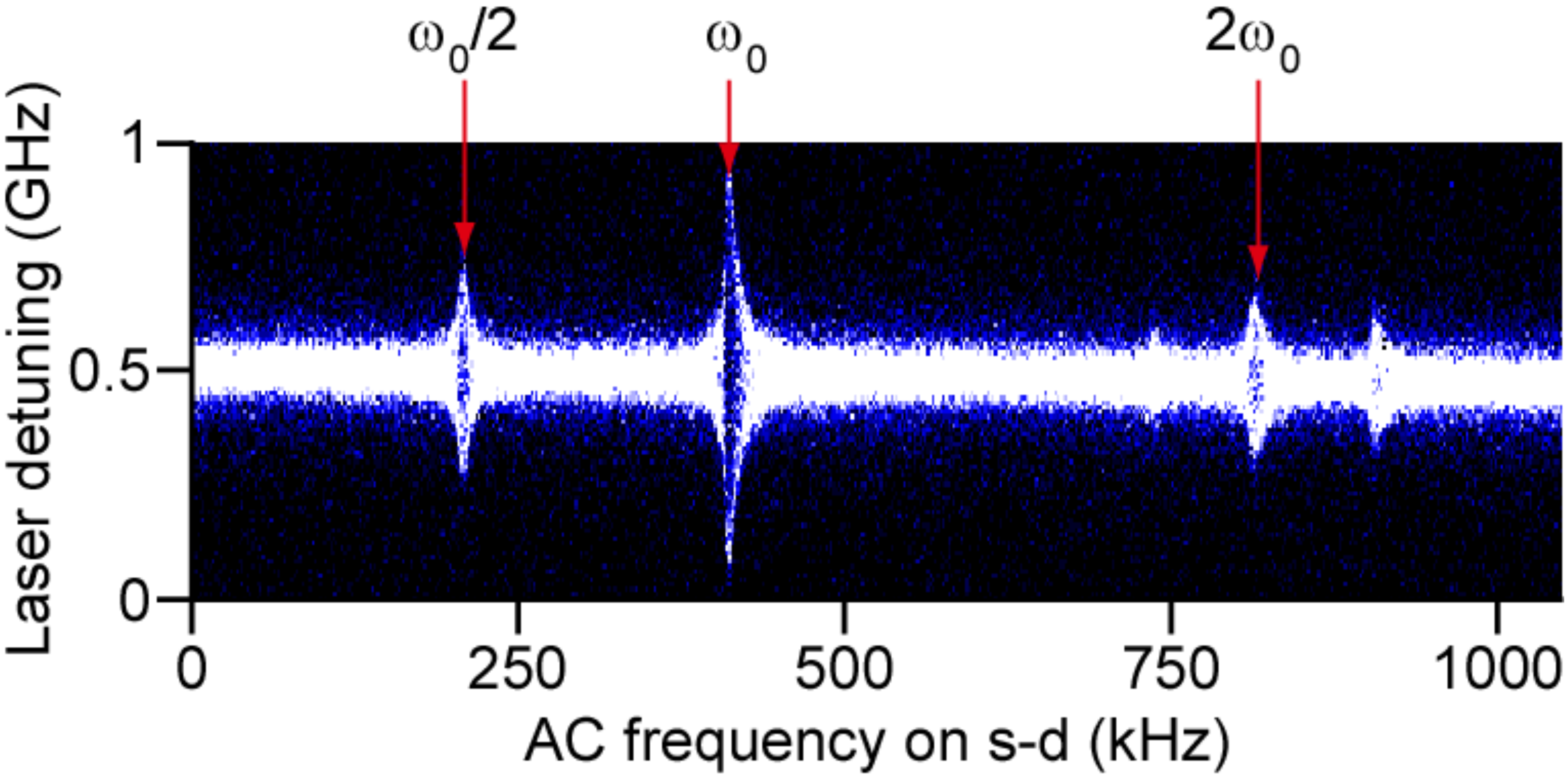
Linear shift of molecular line



Variable voltage amplitude

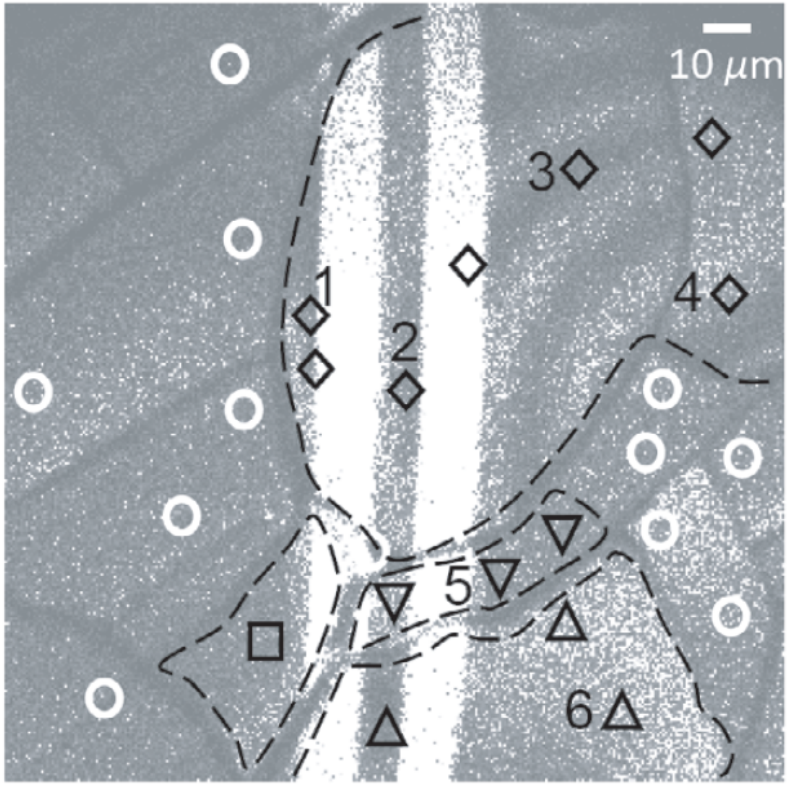
M. A. Kol'chenko et al., New J. Phys. 2009

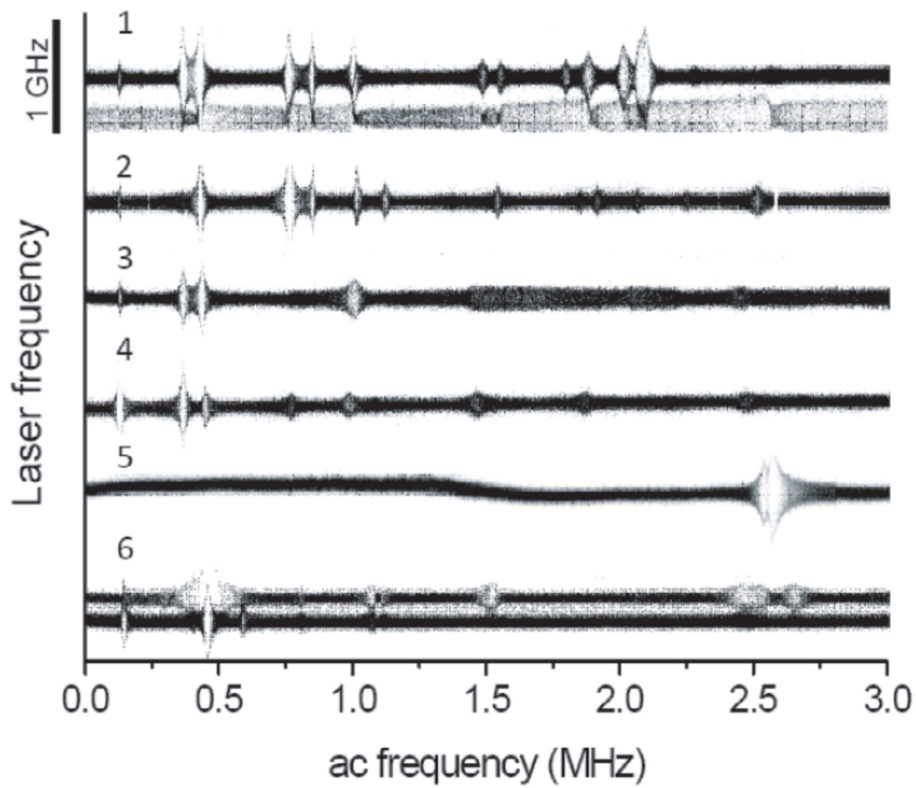
Stark shift resonances under ac-V_{sd}



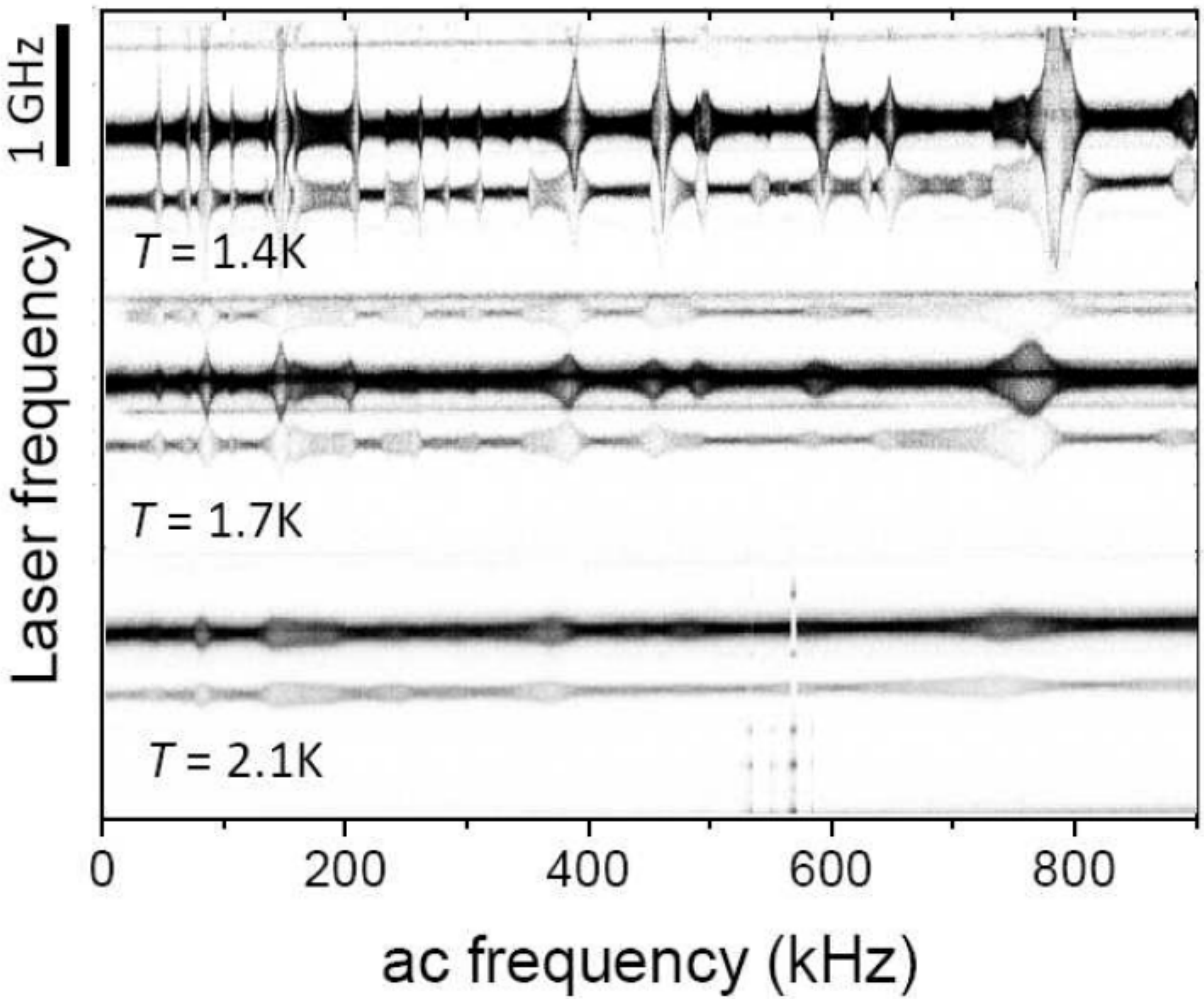
Variable voltage frequency

Spatial correlation of resonance frequencies





Strong temperature dependence



Nature of oscillators?

- Low frequency: kHz-MHz
- Found in hexadecane and anthracene
- Spatial distribution (microcrystals)
- Frequency indep. of voltages (intensity dep.)
- Temperature dependence
- Anharmonicity and overtones
- Effect of deformation

Conclusion:

Acoustic modes localized around soft links in crystal (tuning fork)

Coupling between oscillators (fine structure)

Relation with boson peak and QLM's