Università di Pisa
LM Materials and Nanotechnology - a.a. 2016/17

Spectroscopy of Nanomaterials II sem – part 5

Version 0, Apr 2017
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Beyond the diffraction limit through quantum mechanics: STED microscopy (and PALM/STORM)

OUTLOOK

Let's go back to our main topic: realizing a method able to offer truly nanosized spatial resolution in optical spectroscopy of nanomaterials

Many approaches have been proposed, introduced and developed in the last decades to attain a resolving power exceeding the diffraction limit

A recent method, Nobel Prize awarded, foresees using the peculiarities of light/matter interaction in the quantum regime and advanced optical methods to reach a virtually unlimited resolving power

Motivations for our interest (here and now):
- to revisit already known concepts, with a larger breath than microscopy
- to see how their brilliant combination leads to a new, extremely powerful, nanospectroscopy

Today's menu:
- Starters of dyes, with a few words on their nature
- First dish recalling stimulated emission and optical donuts (how to obtain them)
- Main course of STED, prepared according to Stefan Hell's recipes
- Some words on PALM and STORM as the dessert

THE NOBEL PRIZE IN CHEMISTRY, 2014

The Nobel Prize in Chemistry 2014

Photo: A. Mahmoud
Eric Betzig
Prize share: 1/3

Photo: A. Mahmoud
Stefan W. Hell
Prize share: 1/3

Photo: A. Mahmoud
William E. Moerner
Prize share: 1/3

The Nobel Prize in Chemistry 2014 was awarded jointly to Eric Betzig, Stefan W. Hell and William E. Moerner *"for the development of super-resolved fluorescence microscopy"*.

The point of the Nobel Prize is the achievement of **super-resolution** in optical microscopy

We will mostly be concerned with STED, invented by Stefan Hell in mid 90's.

STED exploits a specific spectroscopy based on **stimulated emission**

STED (STimulated Emission Depletion) is a kind of spectroscopy originally developed for being used with molecular chromophores and ultrashort laser pulses

Further deployment oriented towards exploitation with other nanoparticles (e.g., quantum dots and also plasmon nanoparticles) and conitnuos wave laser has been reported

We will start with a short description of molecular chromophores

MOLECULAR CHROMOPHORES I

Molecular chromophores (or dyes, or fluorophores) are protagonist of microscopy since their spectroscopy enables straightforward implementation of high-contrast, large signal-to-noise ratio mechanism: in principle, it is enough to use bandpass filters in order to discriminate bewteen excitation and emission, leading to enhanced contrast (in very general terms!)

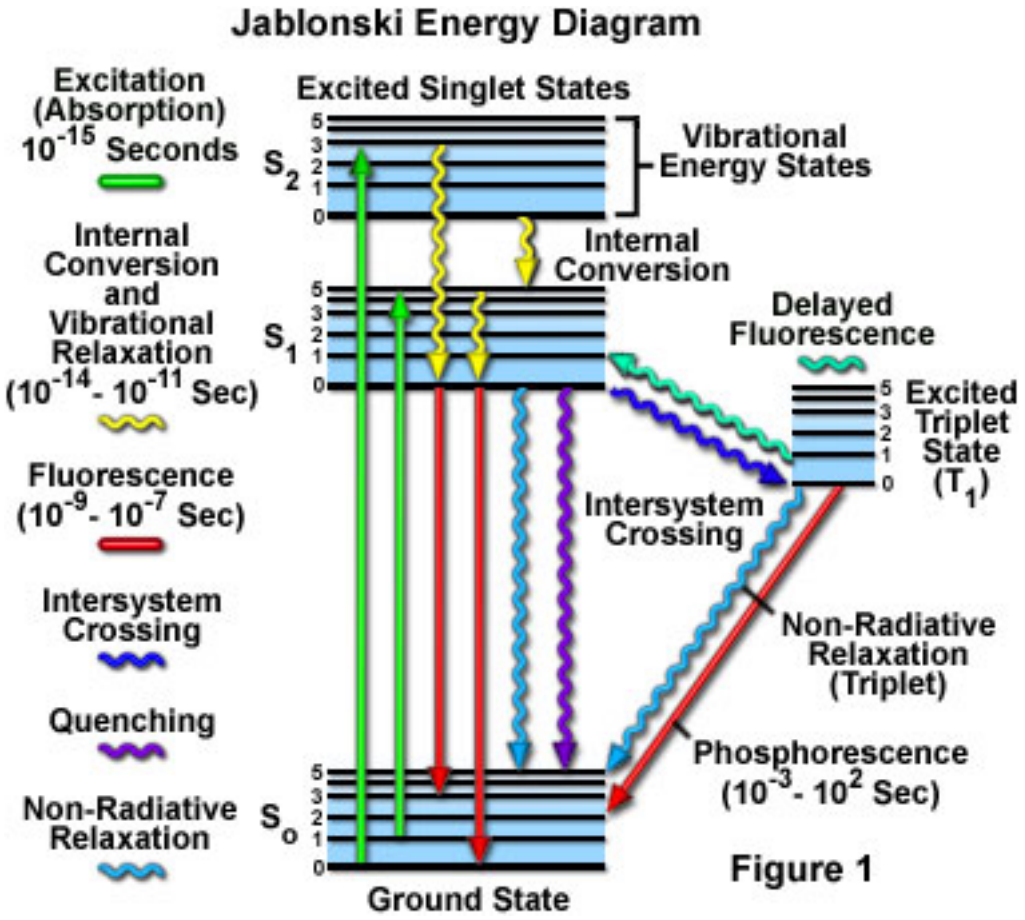


Figure 1

Molecular systems are excellent systems to show the variety of light/matter interaction effects

Relevant for a molecular dye:

- Electronic transitions with energy in the visible range
- Large transition probability (unless phosphorence is purposely involved) with typical lifetime in the ns range
- Many vibrational (eventually rotational) sublevels with fast vibrationall relaxation with typical times in the ps-fs range

Molecular dyes feature an almost continuum absorption spectrum (emission as well, typically slightly shifted to the red side)

MOLECULAR CHROMOPHORES II

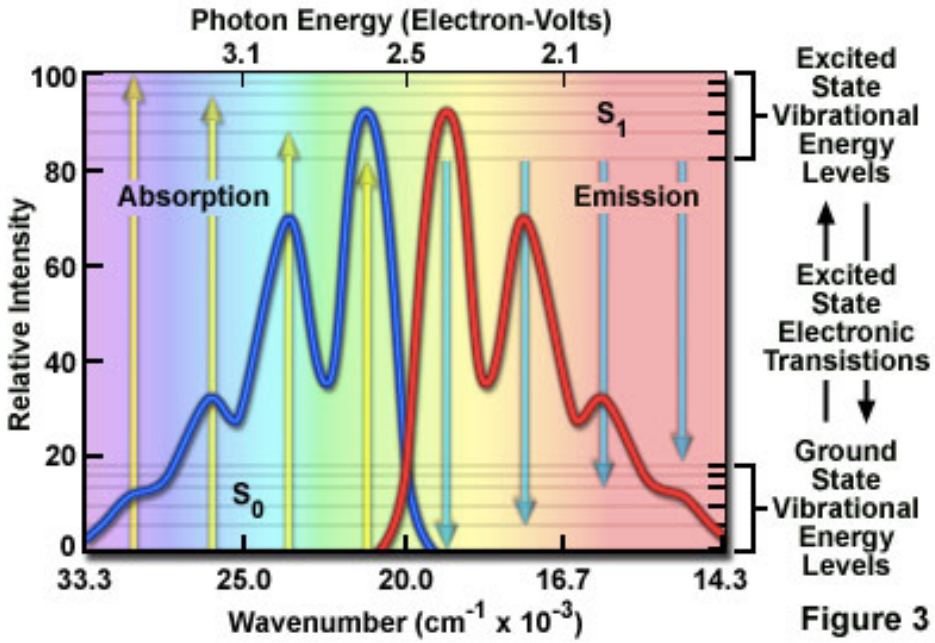
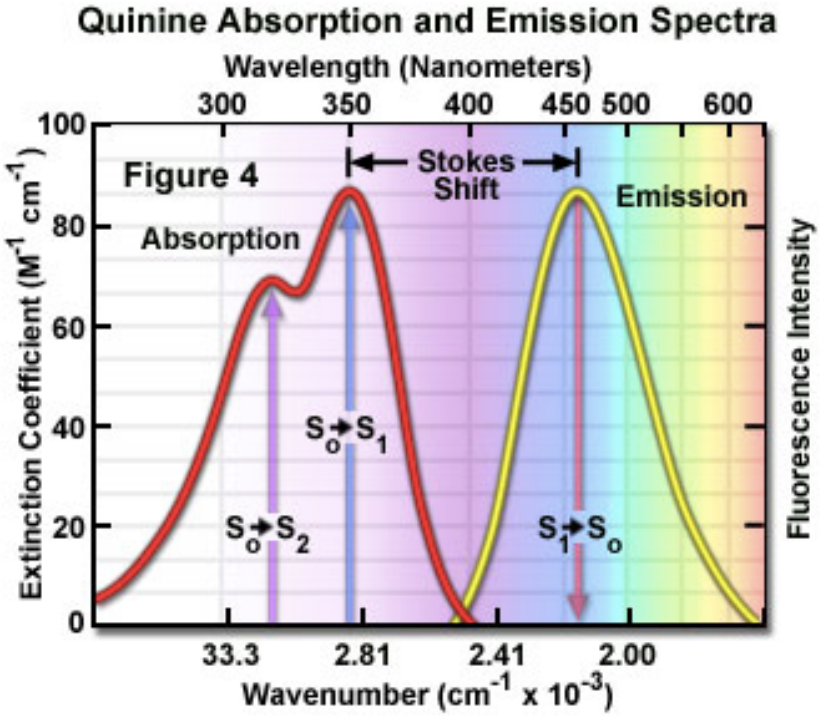


Figure 3



Molecular dyes are excellent systems able to efficiently convert photon absorption in photon emission; typical quantum yield can be very large (similar to the one for Q-dots) and a broad range of wavelengths is available (mostly in the visible-NIR)

Main issue is **photobleaching**: molecules can be damaged by prolonged exposition to light and/or thermal degradation → a maximum number of absoprtion/emission cycles (typ 10^4-10^6) is possible before the emission efficiency drops down

Timescale Range for Fluorescence Processes

Transition	Process	Rate Constant	Timescale (Seconds)
S(0) => S(1) or S(n)	Absorption (Excitation)	Instantaneous	10^{-15}
S(n) => S(1)	Internal Conversion	k(ic)	10^{-14} to 10^{-10}
S(1) => S(1)	Vibrational Relaxation	k(vr)	10^{-12} to 10^{-10}
S(1) => S(0)	Fluorescence	k(f) or Γ	10^{-9} to 10^{-7}
S(1) => T(1)	Intersystem Crossing	k(pT)	10^{-10} to 10^{-8}
S(1) => S(0)	Non-Radiative Relaxation Quenching	k(nr), k(q)	10^{-7} to 10^{-5}
T(1) => S(0)	Phosphorescence	k(p)	10^{-3} to 100
T(1) => S(0)	Non-Radiative Relaxation Quenching	k(nr), k(qT)	10^{-3} to 100

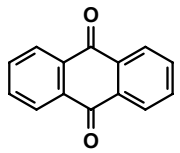
CHEMISTRY/STRUCTURE

Most dyes involve highly conjugated polycyclic aromatic molecules

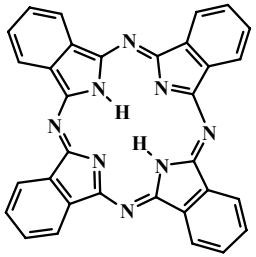
Non-protein organic fluorophores belong to following major chemical families:

- Xanthene derivatives: fluorescein, rhodamine, Oregon green, eosin, and Texas red
- Cyanine derivatives: cyanine, indocarbocyanine, oxacarbocyanine, thiacarbocyanine, and merocyanine
- Squaraine derivatives and ring-substituted squaraines, including Seta, SeTau, and Square dyes
- Naphthalene derivatives (dansyl and prodan derivatives)
- Coumarin derivatives
- oxadiazole derivatives: pyridyloxazole, nitrobenzoxadiazole and benzoxadiazole
- Anthracene derivatives: anthraquinones, including DRAQ5, DRAQ7 and CyTRAK Orange
- Pyrene derivatives: cascade blue, etc.
- Oxazine derivatives: Nile red, Nile blue, cresyl violet, oxazine 170, etc.
- Acridine derivatives: proflavin, acridine orange, acridine yellow, etc.
- Arylmethine derivatives: auramine, crystal violet, malachite green
- Tetrapyrrole derivatives: porphin, phthalocyanine, bilirubin

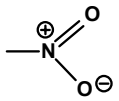
Fluorescence of different substances under UV light. Green is a fluorescein, red is Rhodamine B, yellow is Rhodamine 6G, blue is quinine, purple is a mixture of quinine and rhodamine 6g. Solutions are about 0.001% concentration in water.



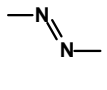
Anthraquinone



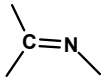
Phthalocyanine



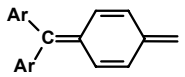
Nitro



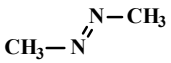
Azo



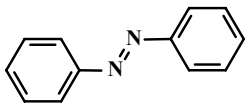
Methine



Triarylmethane



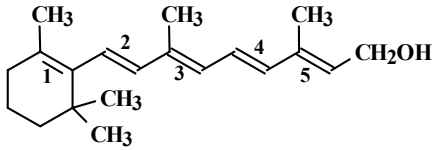
Colourless

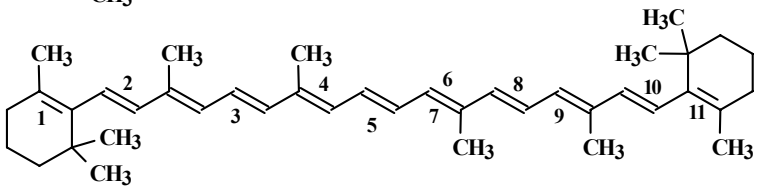


Orange

Thanks to conjugation, orbitals involved in the transitions are typically delocalized pi-bonds

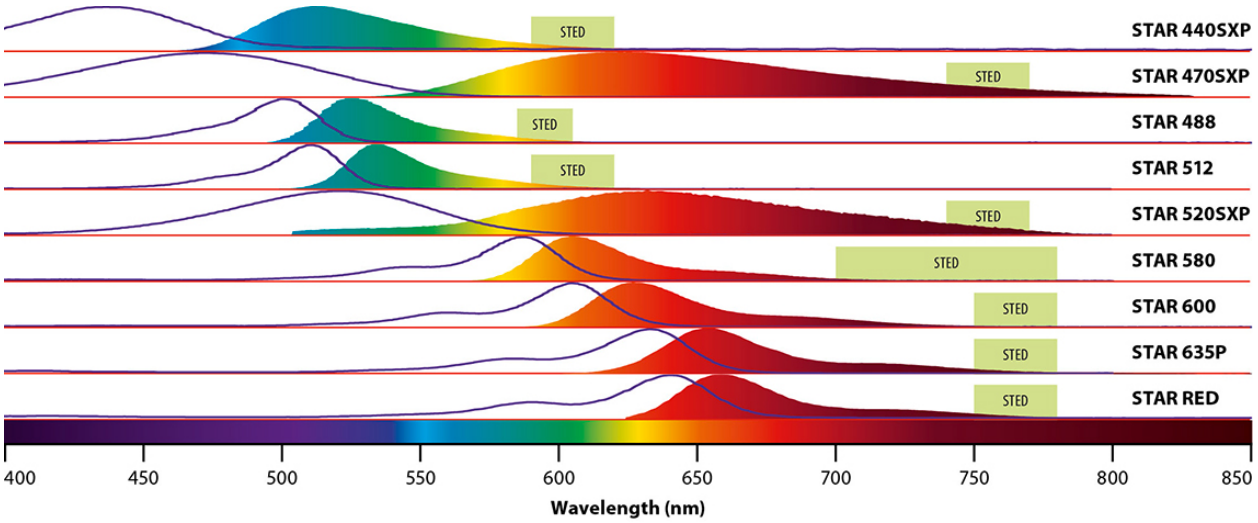
Conjugated systems in Vitamin A (top) and β-carotene (bottom)



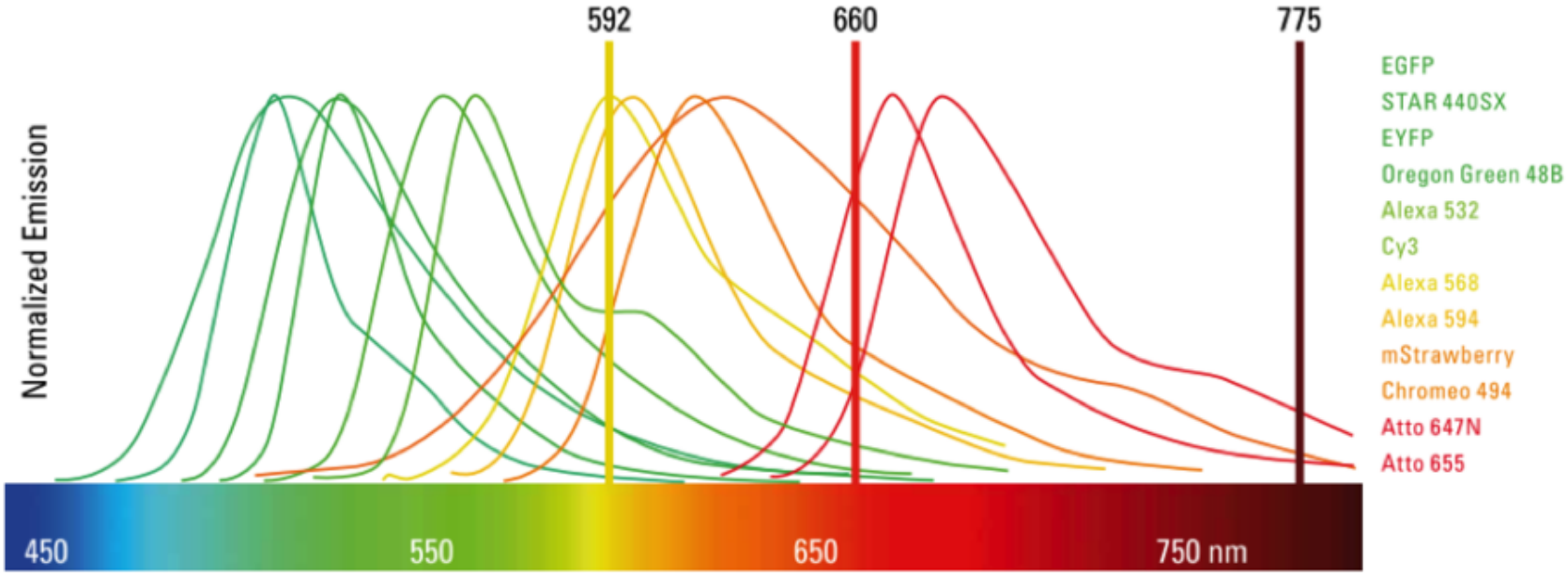


https://monographs.iarc.fr/ENG/Monographs/vol99/mono99-7.pdf

COMMERCIAL DYES



A huge variety of dye molecules is commercially available for a broad range of applications



FLUORESCENT PROTEINS (a few words)

From Wikipedia: The green fluorescent protein (GFP) is a protein composed of 238 amino acid residues (26.9 kDa) that exhibits bright green fluorescence when exposed to light in the blue to ultraviolet range.[2][3] Although many other marine organisms have similar green fluorescent proteins, GFP traditionally refers to the protein first isolated from the jellyfish Aequorea victoria. The GFP from A. victoria has a major excitation peak at a wavelength of 395 nm and a minor one at 475 nm. Its emission peak is at 509 nm, which is in the lower green portion of the visible spectrum. The fluorescence quantum yield (QY) of GFP is 0.79. The GFP from the sea pansy (Renilla reniformis) has a single major excitation peak at 498 nm. GFP makes for an excellent tool in many forms of biology due to its ability to form internal chromophore without requiring any accessory cofactors, gene products, or enzymes / substrates other than molecular oxygen.[4]

In cell and molecular biology, the GFP gene is frequently used as a reporter of expression.[5] It has been used in modified forms to make biosensors, and many animals have been created that express GFP, which demonstrates a proof of concept that a gene can be expressed throughout a given organism, in selected organs, or in cells of interest. GFP can be introduced into animals or other species through transgenic techniques, and maintained in their genome and that of their offspring. To date, GFP has been expressed in many species, including bacteria, yeasts, fungi, fish and mammals, including in human cells. Scientists Roger Y. Tsien, Osamu Shimomura, and Martin Chalfie were awarded the 2008 Nobel Prize in Chemistry on 10 October 2008 for their discovery and development of the green fluorescent protein.

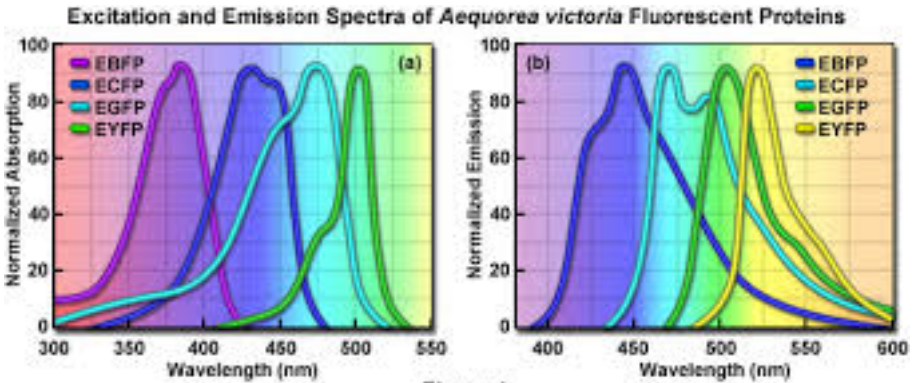
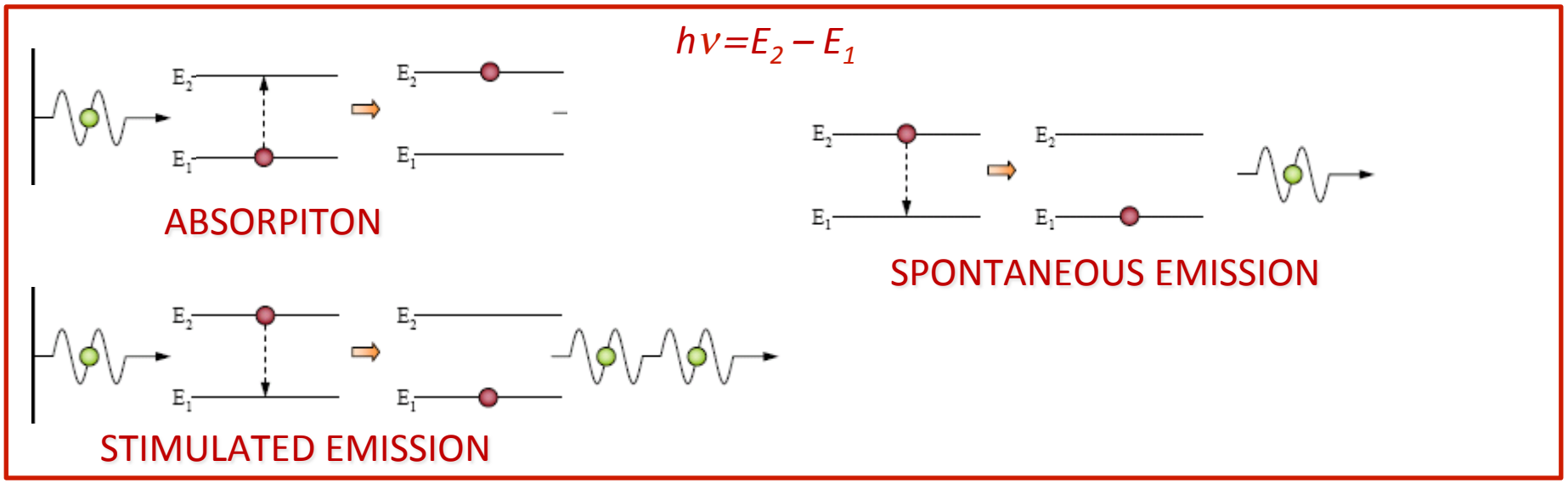


Figure 4

REMINDERS OF LIGHT-MATTER INTERACTION

In a two-level system (ideal), according to Einstien the following processes are possible



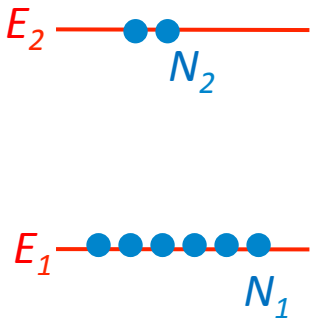
Stimulated emission is the process involved in laser action ("SE" stands for that!)

Photon emitted in stimulated emission are **indistinguishable** from those of the excitation

Stimulated emission requires the atom to be "pumped" (**inverted population**)

The semiclassical light-matter interaction treatment leads to two distinct emission processes: spontaneous (fluorescence) and stimulated

RATE EQUATIONS



N_1, N_2 level population (in a macroscopic sample)

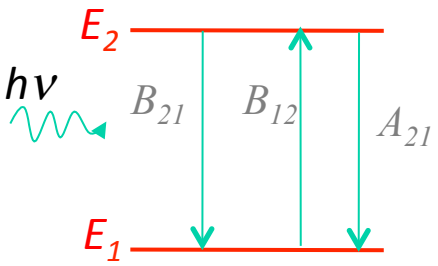
At thermal equilibrium (Boltzmann):

$$\frac{N_2}{N_1} = \exp\left(\frac{E_1 - E_2}{kT}\right)$$

Note: kT ~ 1/40 eV @ room temp, while ΔE ~ eV

→ $N_2 << N_1$ in ordinary conditions

- We assume radiation with $h\nu = E_2 - E_1$ (with energy density u_ν)
- Account for:
  - Absorption 1→ 2 with rate R_{12}
  - Stimulated emission 2 → 1 with rate R_{21}
  - Spontaneous emission 2 → 1 with rate A_{21}



Absorption and stimulated emission rate R_{21} depends linearly on the energy density u_ν of the radiation: $R_{21} = B_{21} u_\nu$

We assume $B_{12} = B_{21}$

Note: $B_{12}/B_{21} = g_1/g_2$ con g_j degeneration of level j
(in practice, the density-of-states)

COMPARISON OF RATES

$$\frac{dN_2}{dt} = -B_{21}u_\upsilon N_2 + B_{12}u_\upsilon N_1 - A_{21}N_2$$

$$\frac{dN_1}{dt} = B_{21}u_\upsilon N_2 - B_{12}u_\upsilon N_1 + A_{21}N_2$$

With B_{12}=B_{21} , the steady state solution is: $N_2^0 = N_1^0 \dfrac{B_{21}u_\nu}{B_{21}u_\nu + A_{21}}$

Boltzmann requires:

$$\frac{B_{21}u_\nu}{B_{21}u_\nu + A_{21}} = \exp\left(\frac{-h\nu}{kT}\right)$$

Assuming blackbody radiation (e.g., a filament lamp): $u_\nu = \dfrac{8\pi h\nu^2}{c^3}\dfrac{1}{\exp(h\nu/kT)-1}$

Therefore:

$$A_{21} = B_{21}\frac{8\pi h\nu^3}{c^3}$$

In terms of rates, spontaneous emission prevails unless "unconventional" (e.g., laser) radiation is used

CONCEPT OF SATURATION

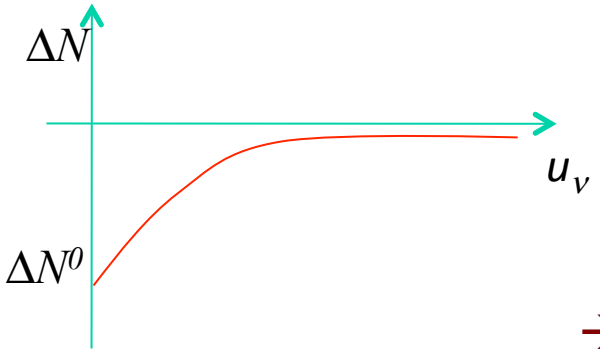
$$\frac{dN_2}{dt} = -B_{21}u_\nu N_2 + B_{12}u_\nu N_1 - \gamma(N_2 - N_2^0)$$

$$\frac{dN_1}{dt} = B_{21}u_\nu N_2 - B_{12}u_\nu N_1 - \gamma(N_1 - N_1^0)$$

Rate equations including **relaxation** to the ground state (with rate γ) and explicit mention of the **population difference** ΔN

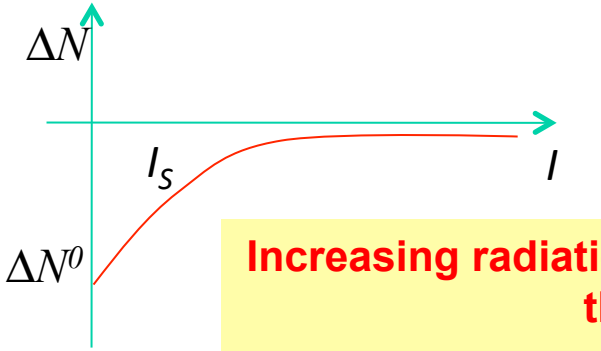
$$\frac{d(\Delta N)}{dt} = \frac{dN_2}{dt} - \frac{dN_1}{dt} = -2B_{21}u_\nu \Delta N - \gamma(\Delta N - \Delta N^0) = 0$$

$$\Delta N = \frac{\gamma \Delta N^0}{2B_{21}u_\nu + \gamma}$$



Alternative formulation:

$$\Delta N = \frac{\Delta N^0}{\frac{2B_{21}u_\nu}{\gamma} + 1} = \frac{\Delta N^0}{\frac{I}{I_S} + 1}$$



In a two-level system
→ $N_2 = N_1$ for $I >> I_S$, $\Delta N \leq 0$

with I_S **saturation intensity:**

$$I_S = \frac{2B_{21}u_\nu}{\gamma}$$

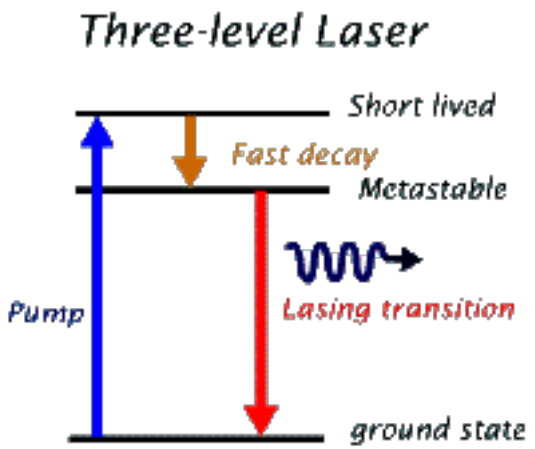
or

$$I_S = \frac{2B_{21}u_\nu g(\nu - \nu_0)}{\gamma}$$

Increasing radiation intensity leads to saturate the transition

Exploitation of stimulated emission, as in laser, requires pumping

BASIC MECHANISM OF STED

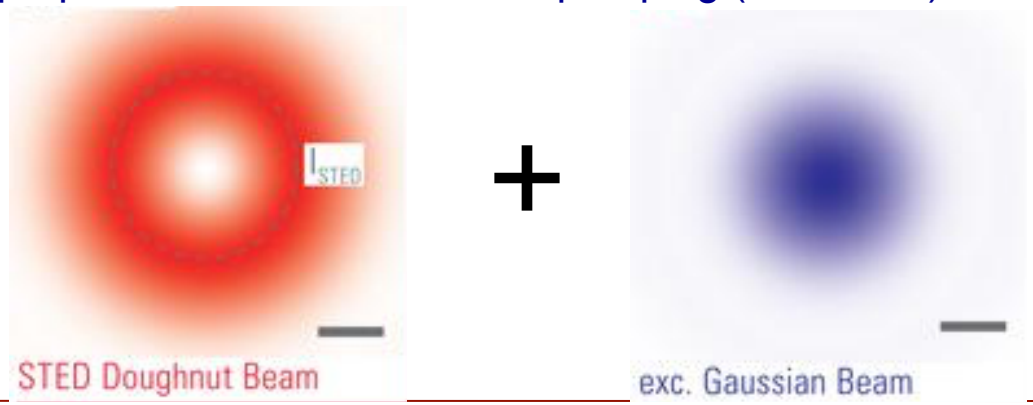


Similar to three-level (or more-level) laser, in STED:
- Pumping radiation populates an upper state
- Non-radiative (**fast**) transitions bring population to a lower state
- Emission is stimulated by an additional radiation beam

However, differently to three-level laser, in STED stimulated emission acts only as a **controlled depletion agent** for excited state population

Stimulated emission is the main ingredient of STED, but an additional ingredient is needed to spatially manipulate the shape and intensity distribution of the STED laser

We will mention here only the “traditional” technique involving production of **donut mode STED** laser beam, to be superposed on Gaussian mode pumping (excitation) laser beam

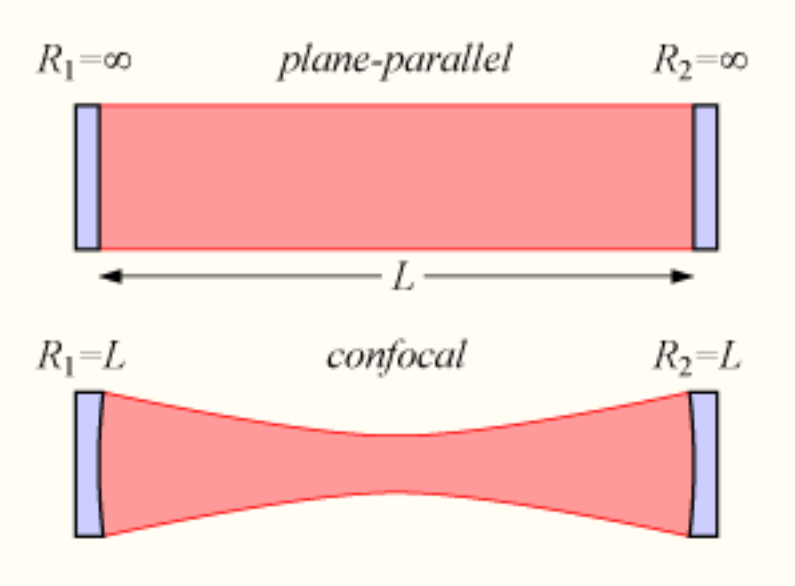


GAUSSIAN SHAPE OF LASER BEAMS I

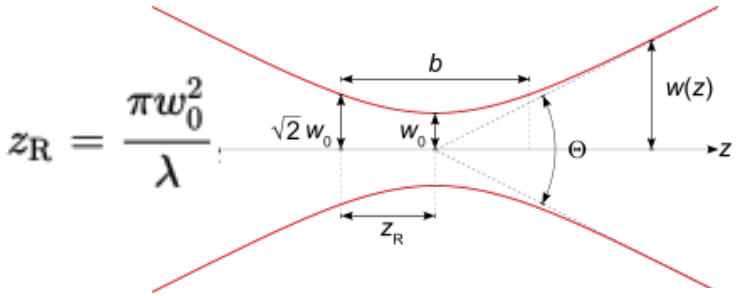
Remember that, in a laser, an **optical cavity** is needed to convert amplification by stimulated emission into **oscillation** (that occurs when gain overcomes losses)

Plane-parallel optical cavity are not a feasible option: **diffraction** from plane mirrors leads to radiation loss (*unstable resonators*)

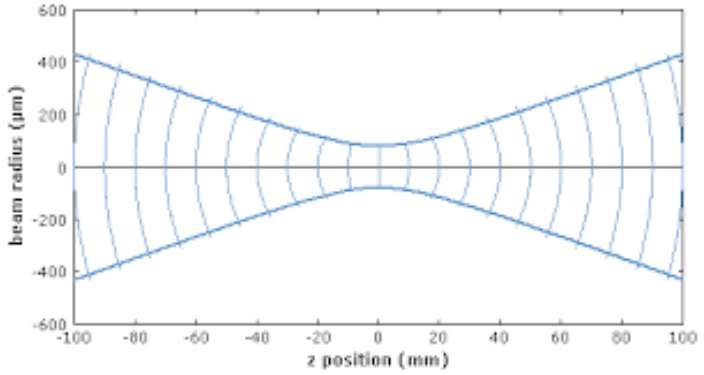
Confocal cavities are by far preferred, since they limit diffraction losses



As a consequence, a specific spatial distribution following a **Gaussian** behavior is typically found in a laser beam



$$w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2}$$

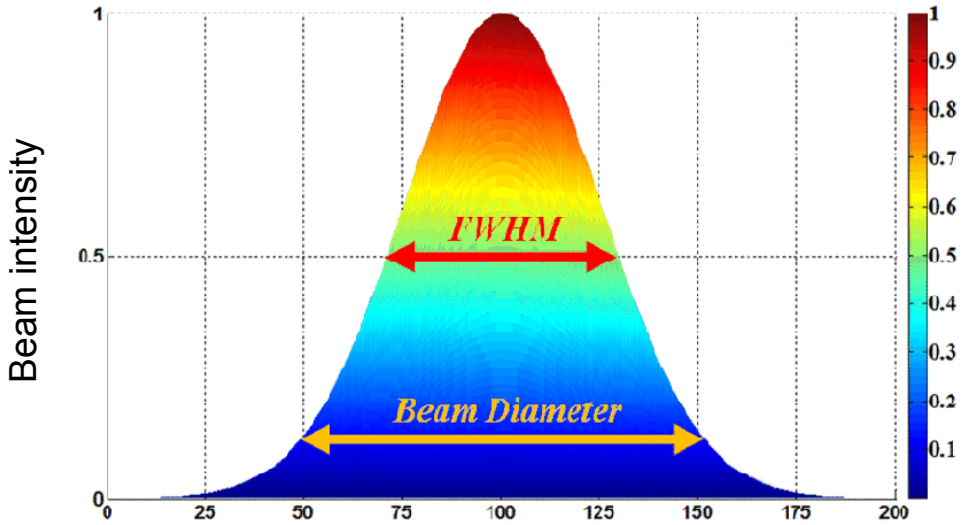


GAUSSIAN SHAPE OF LASER BEAMS II

A (ideal) laser beam, focused to a waist w_0 at the position $z_0 = 0$ (z being the propagation direction) shows an intensity distributon:

$$I(r,z) = \frac{|\Re(\mathbf{E}\times\mathbf{H}^*)|}{2} = \frac{|E(r,z)|^2}{2\eta} = I_0\left(\frac{w_0}{w(z)}\right)^2 \exp\left(\frac{-2r^2}{w(z)^2}\right)$$

Non-ideality of the beam is charactierized by the M^2 parameter:
$M^2 = 1$ for ideal, $M^2 > 1$ for non-ideal beams



Radial direction at a fixed z position

Note that reality is much different with respect to the textbook picture of plane waves!

If e.m. waves were only of the plane wave type, no diffraction would exist (and no possibility to have localization, as well)!

SHORT REMINDER OF POLARIZATION

Polarization of a e.m. wave indicates the direction of oscillation of the electric field

A propagating e.m. wave has a **transversal** character as a consequence of Maxwell's and wave equations → the electric field vector belong to a plane orthogonal to the propagation direction

Plane waves!!

Linearly polarized wave

$$\vec{E} = A\cos(kz - \omega t)\hat{x} + B\cos(kz - \omega t)\hat{y}$$

Elliptical polarized wave (circular in case *A* = *B* and dephasing is π/2)

$$\vec{E} = A\cos(kz - \omega t)\hat{x} + B\cos(kz - \omega t \pm \pi/2)\hat{y} =$$
$$= A\cos(kz - \omega t)\hat{x} + B\sin(kz - \omega t)\hat{y}$$

Manipulation of polarization (i.e., its modification, control, analysis) can be accomplished according to various methods, inlcuding Brewster's angle (see Fresnel equations), **dichroism** and **birefringence**

Dichroism: differential absorption of radiation polarized along certain directions (e.g., polaroid materials, i.e., arrays of mutually aligned dipolar absorbers)

Birefringence: differential propagation velocity (phase velocity) of radiation polarized along certain directions (e.g., anisotropic crystals like mica, calcite, quartz, or stressed transparent polymer sheets) → **modulation of the refractive index**

SPIRAL PHASE PLATES

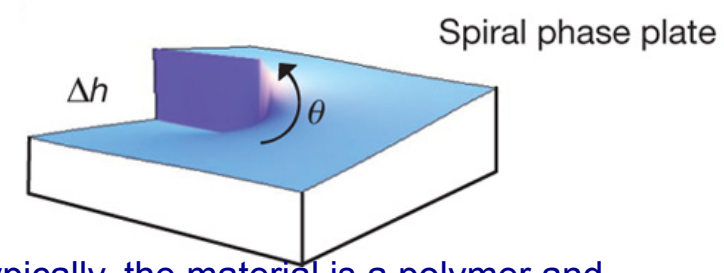
When a (plane) wave crosses a trasnparent material with refractive index *n* , the wavenumber is multiplied by *n* , the phase velocity is reduced, and the wave oscillation is **retarded**

$$\vec{E} = E_0 \cos(knz - \omega t)\hat{e}$$

with Δz thickness of the material

$$\Delta\varphi = \frac{2\pi}{\lambda} n\Delta z$$

with $\Delta\varphi$ retardation in units of radiants

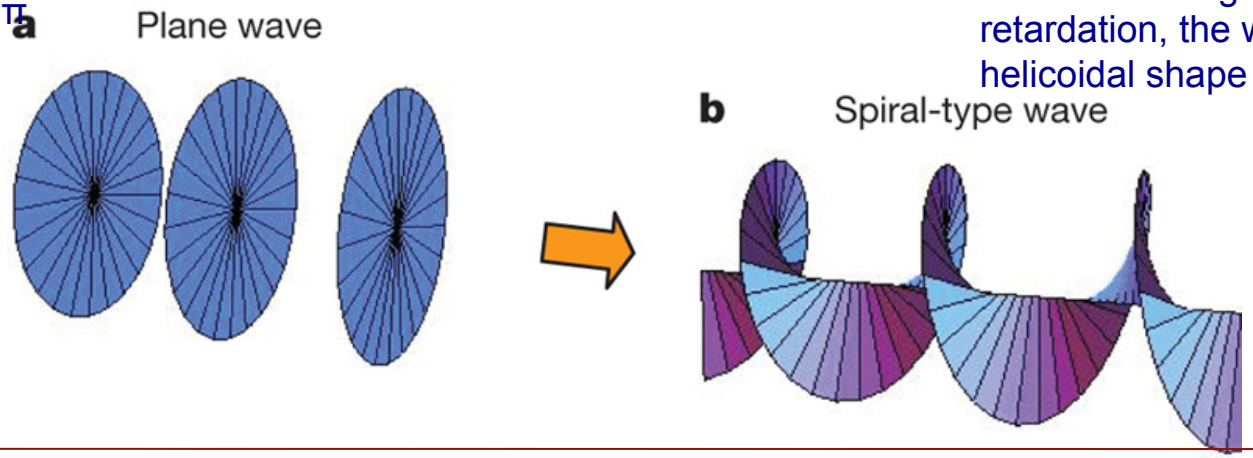


Typically, the material is a polymer and the maximum height is chosen so that $\Delta h\ n\ 2\pi/\lambda = \pi$, or 2π

A spiral phase plate consists of a retarding plate made of a transparent material with refractive index *n* whose thickness linearly depends on the angular coordinate

→ **retardation of the beam is a function of the angular position** (assuming paraxial alignment)

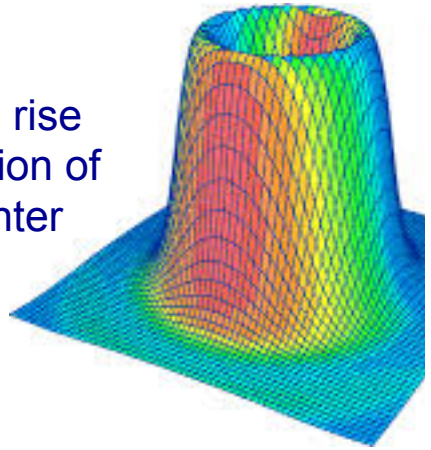
Because of angle-depending retardation, the wavefront gets an helicoidal shape

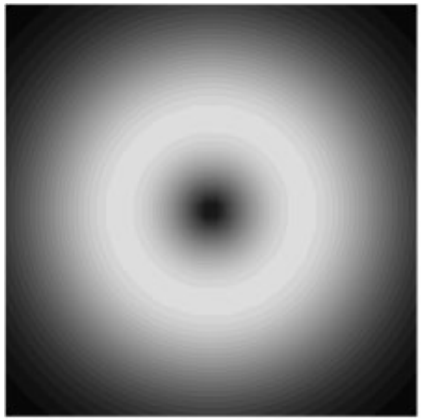


DONUT MODE

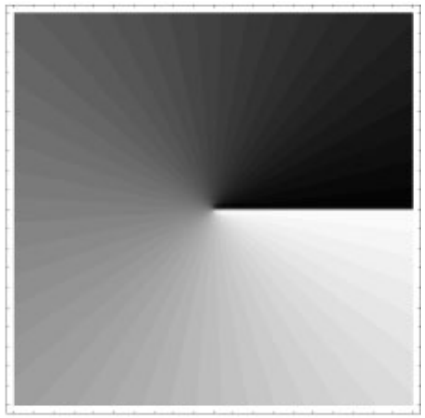
After crossing a (properly aligned) spiral phase plate, the incoming wave, supposed plane and Gaussian-shaped, is converted into a spiral (helicoidal) wave, also called **optical vortex**

Projected onto a plane, the optical vortex gives rise to a **doughnut mode**, with an annular distribution of intensity and an almost zero intensity in the center





intensity



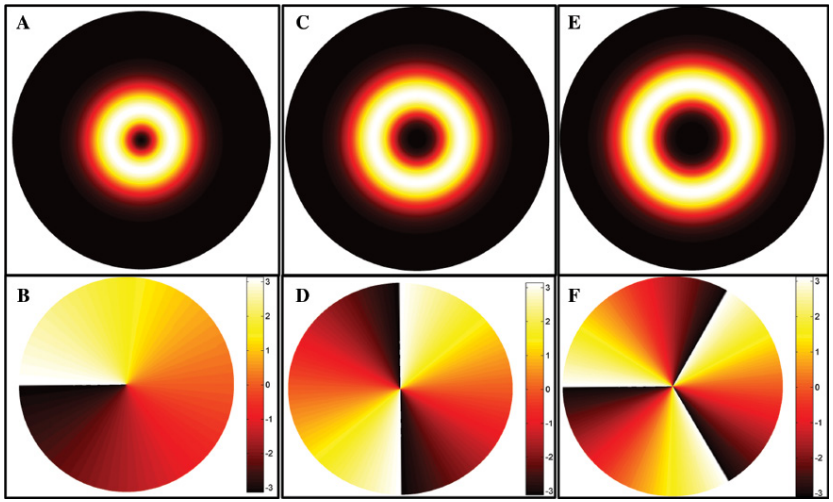
phase

Another possible interpretation is that, close to the axis, destructive interference between almost plane waves with mutually opposite polarization directions takes place, leading to an almost zero intensity

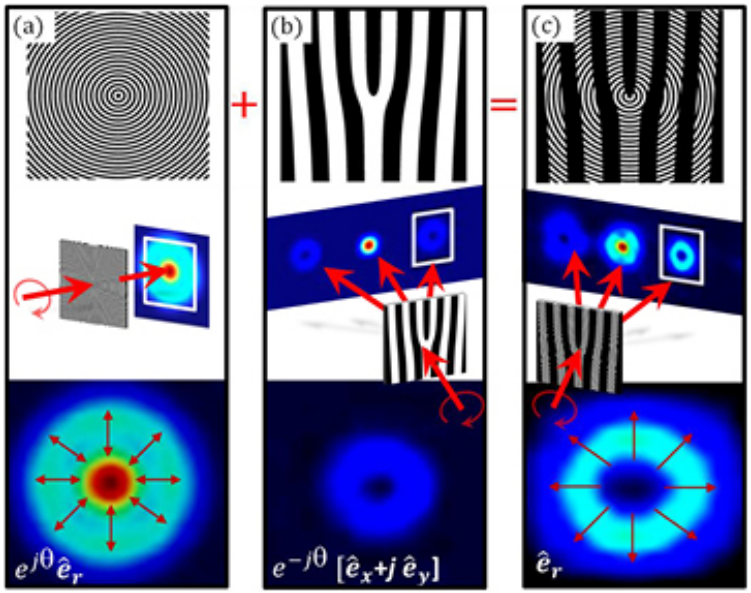
Spiral phase plates are among the simplest methods to effectively produce a donut mode with cylindrical symmetry
Note: the “diameter” of the central “hole” is still diffraction limited!

http://skullsinthestars.scientopia.org/2010/05/04/singular-optics-light-chasing-its-own-tail/

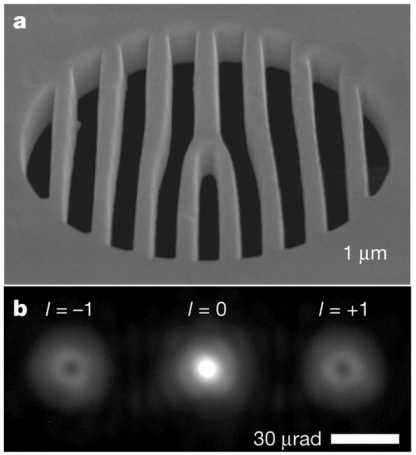
A FEW WORDS ON OTHER TECHNIQUES



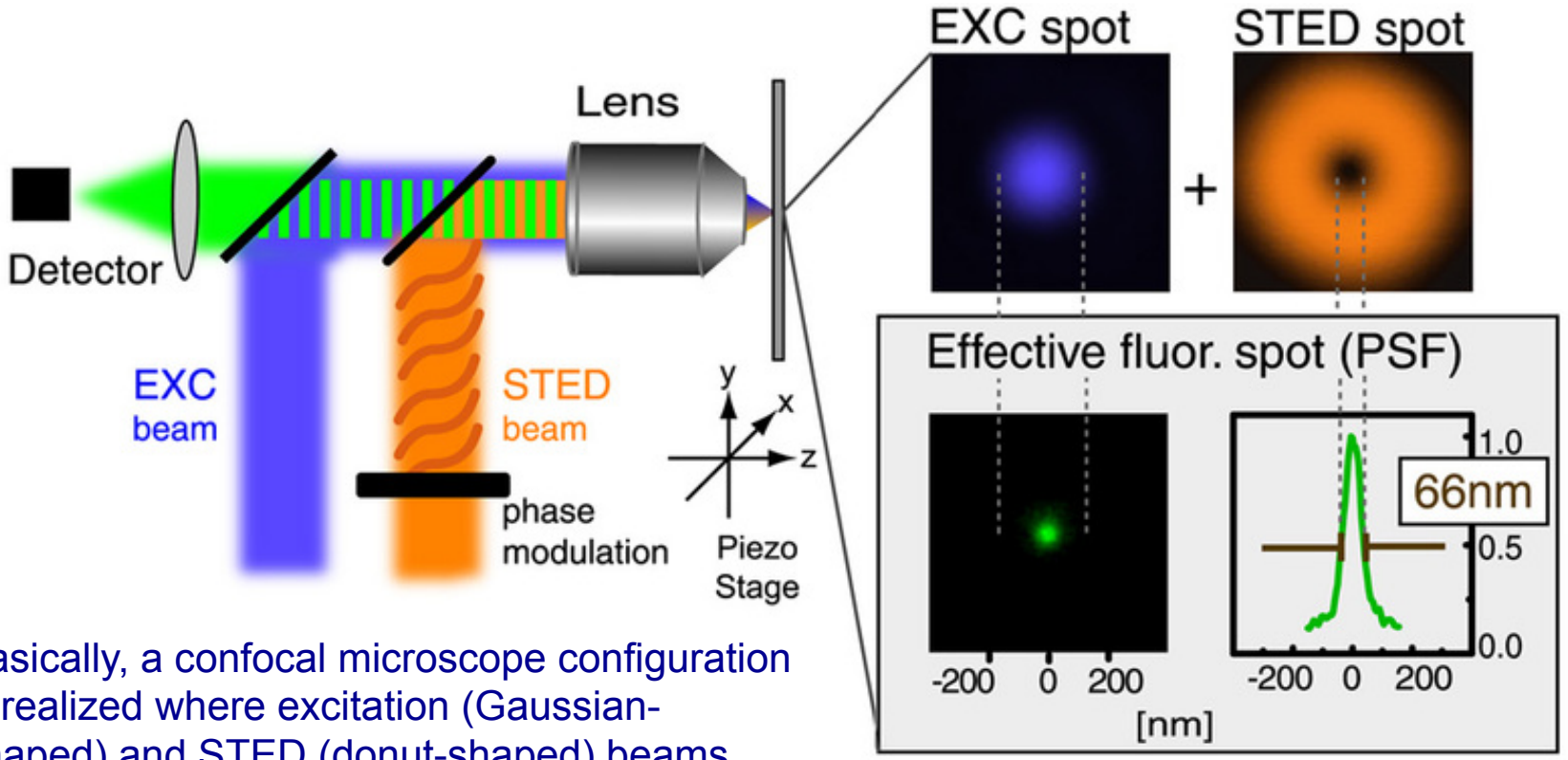
Spiral phase plate with other thickness modulation (i.e., other retardation modulation) lead to various donut-like modes



Diffraction from specifically shaped, non regular, gratings (e.g., “forked”) can lead to donut modes with radial polarization



STED OPTICAL CONFIGURATION

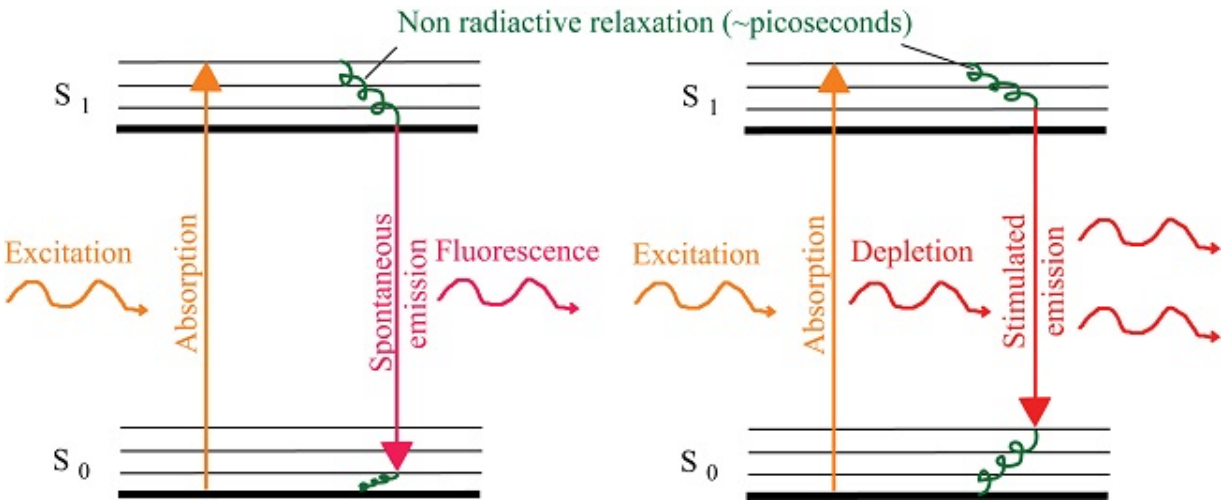


Basically, a confocal microscope configuration is realized where excitation (Gaussian-shaped) and STED (donut-shaped) beams are carefully superposed

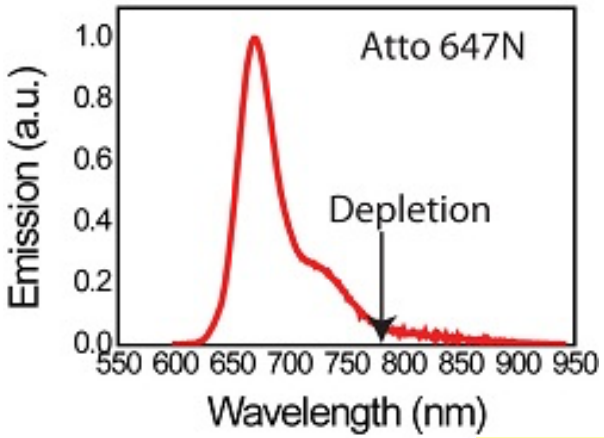
Note that each beam, when focused onto the sample, keeps a diffraction-limited size

The "subtractive" combination of them shows, instead, a lateral size below the diffraction limit, hence a PSF below the Abbe limit

STED OPERATING PRINCIPLE



1. The excitation beam (Gaussian-shaped) promotes an electronic transition in the molecule to some excited vibrational state: this occurs in a sub-ps timescale
2. Fast non-radiative relaxation brings population to a lower-energy vibrational level of the excited state
3. In the absence of STED radiation, spontaneous emssion occurs, with a typical timescale in the ns-range, and fluorescence is produced and collected
4. Wherever the STED beam (donut-shaped) is present, stimulated emission to some vibrational level of the gorund state is realized



- ✓ STED acts to locally deplete (in the annular region) fluorescence
- ✓ STED and fluorescence wavelengths are different and can be spectrally resolved (by bandpass filters)

Fluorescence emission survives only in the very center of the superposed beams!

PULSED vs CW LASERS

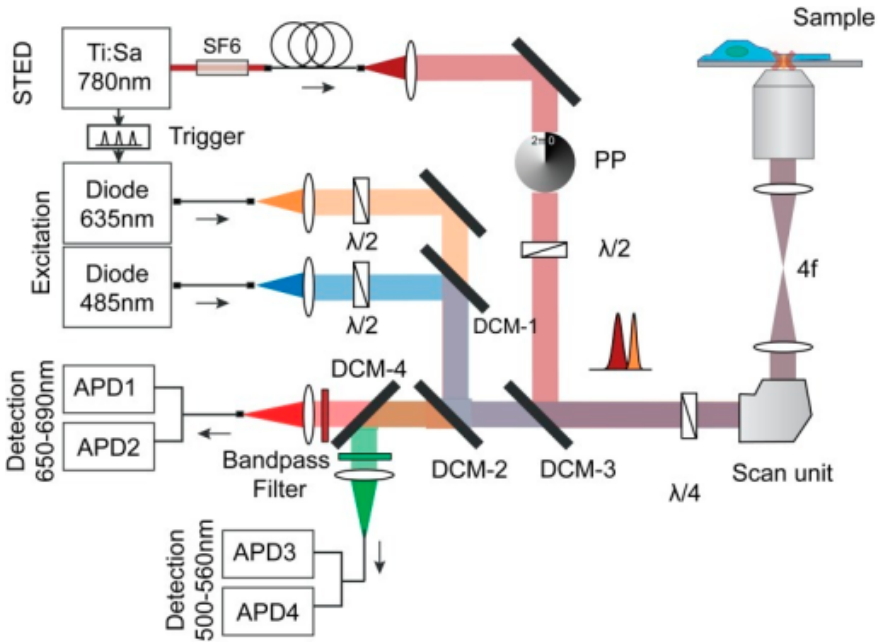
In the original implementation, STED uses ultrashort (sub-ps) laser pulses:

- A relatively weak pulse, tuned within the absorption curve of the molecule, is used for excitation
- A strong pulse, tuned on the tail of the absorption curve (i.e., red-shifted with respect to excitation) is used for the STED
- The STED pulse is electronically delayed (typ in the ps range) with respect to excitation
- Band pass filters are placed in front of the detector in order to remove STED light and be concerned solely by the fluorescence stemming from the very center of the superposed beams

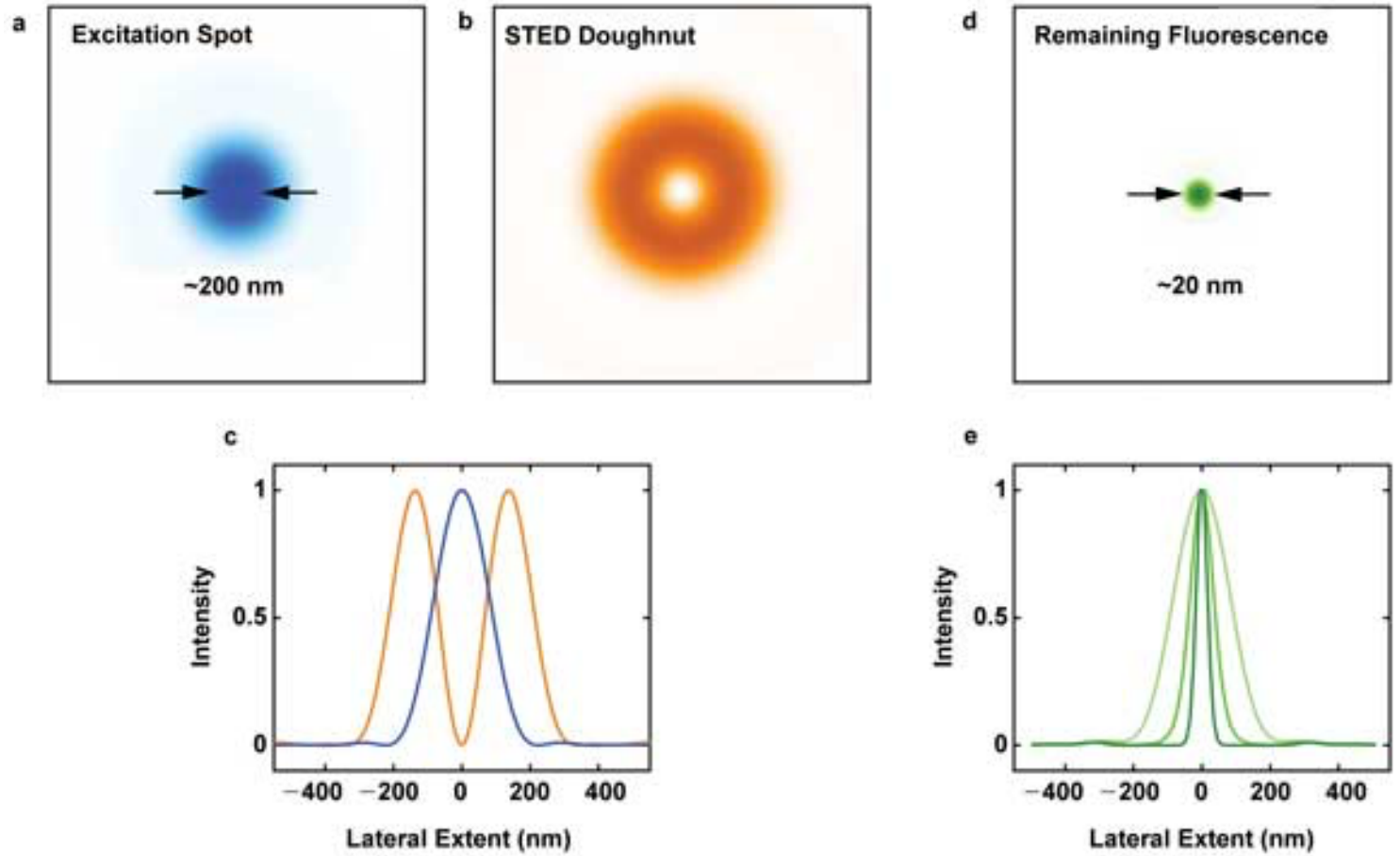
Presently, a great deal of efforts is devoted to use much less expensive cw (continuous) laser sources

Main issue to be faced: photobleaching of the molecules due to large average power

Note: intensity is, practically, average power divided by pulse duration, and can be huge for short laser pulses!



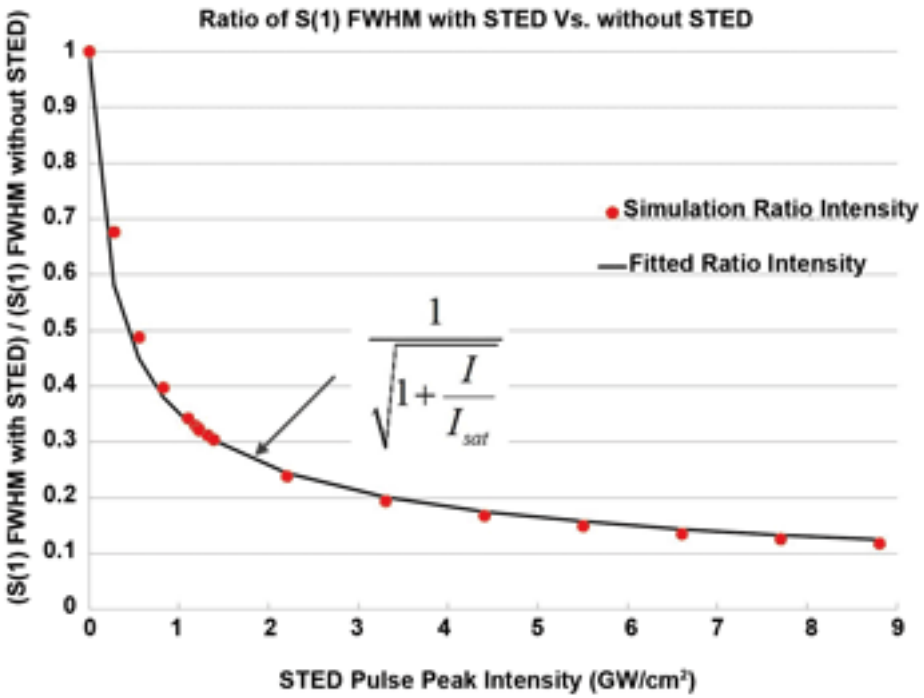
RESOLVING POWER IN STED



Depletion occurs in a region whose size is determined by the stimulated emission rate, that is, ultimately, by the STED intensity

The “difference” (not-depleted region, originating fluorescence) shows a lateral size depending on the STED intensity!

"UNLIMITED" SPATIAL RESOLUTION



No fundamental limitation exists for the resolving power

Virtually, by increasing STED intensity resolving power can be increased at wish

It can be shown that:

$$d_{STED} \simeq \frac{0.61\lambda}{NA\sqrt{1+\frac{I_{STED}}{I_{SAT}}}}$$

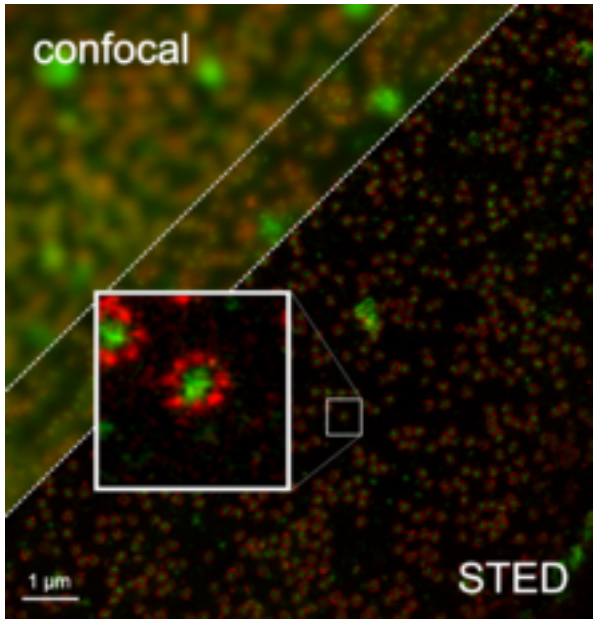
with I_{STED} STED laser intensity and I_{SAT} saturation intensity for the chosen transition (depends on the molecule)

Obviously, even assuming ideal optical conditions (alignment, absence of any aberration, etc.), technical limitations exist, for instance related to photobleaching and maximum allowed STED intensity preventing molecule damage

However, spatial resolution in the order of a few nm has been reported!

EXAMPLES I

Proteins in the cellular nucleus labeled with red and green fluorscent molecules



Astonishing increase of resolution clearly seen

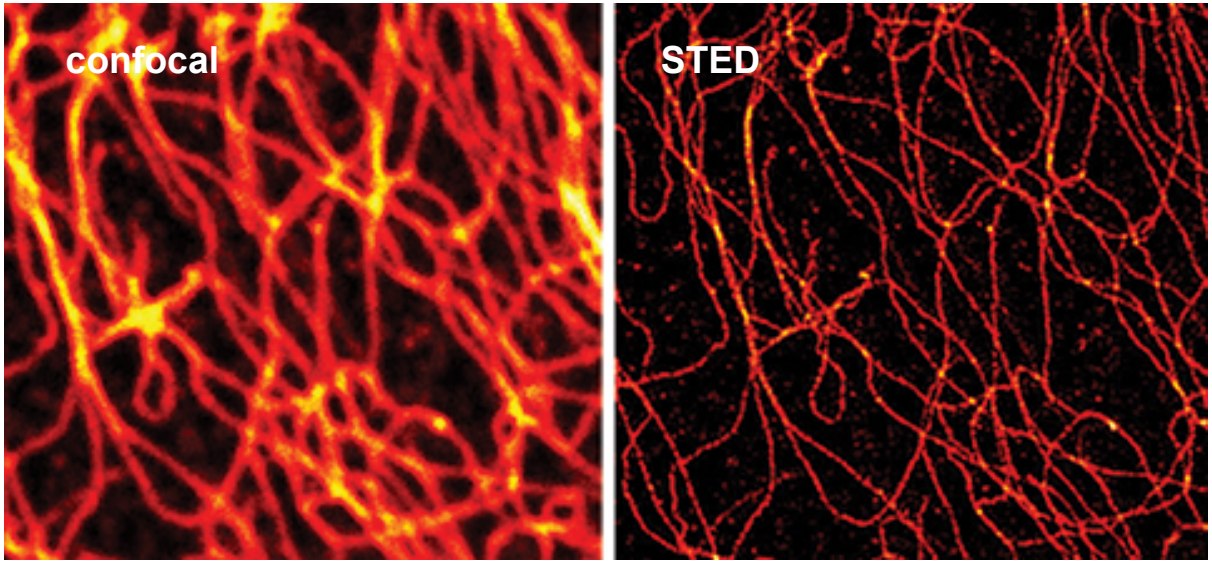
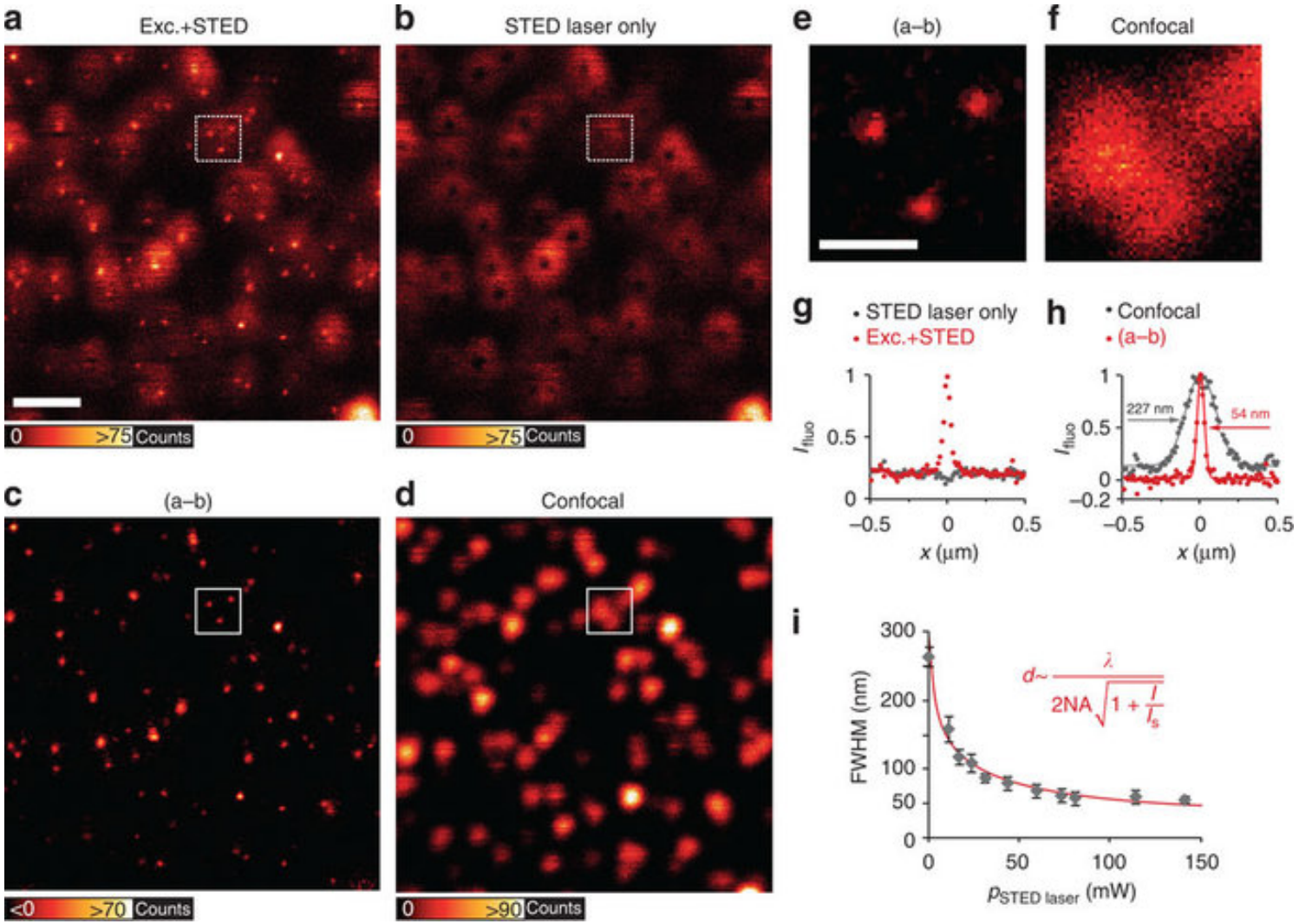


Figure 5. STED microscopy of intermediate filaments visualized with Oregon Green® 488 staining. PtK2 cells were methanol-fixed, and vimentin was labeled with Oregon Green® 488 dye by indirect immunofluorescence. Confocal **(A)** and STED **(B)** images were acquired with a Leica TCS STED CW microscope. Images provided by Leica Microsystems.

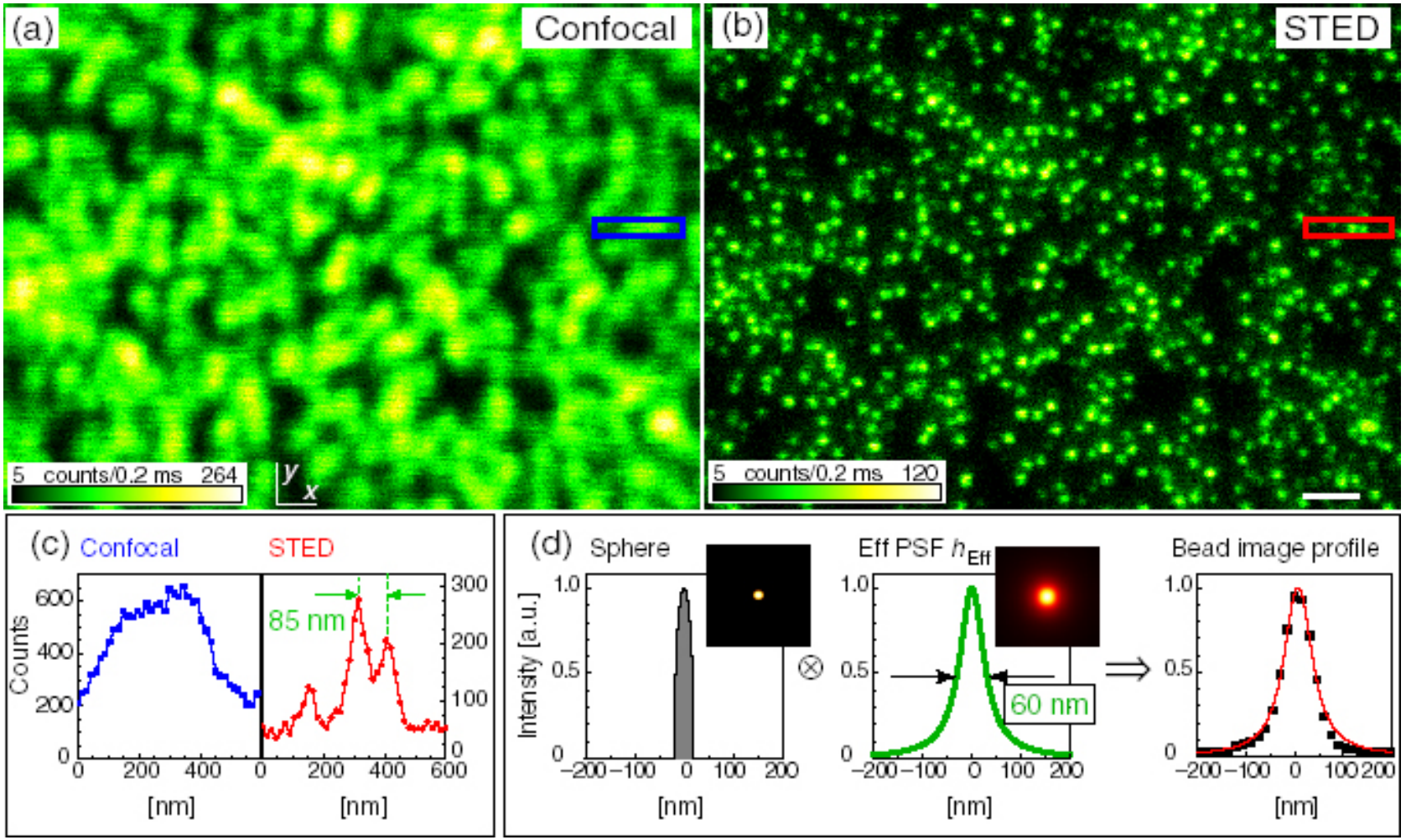
EXAMPLES II



STED has been demonstrated also with emitting Q-dots (involving interband transitions)

Nature Communications **6**, Article number: 7127 (2015)
doi:10.1038/ncomms8127

EXAMPLES III



New Journal of Physics, Volume 8, June 2006
doi:10.1088/1367-2630/8/6/106

STED can discriminate even plasmon (noble metal) nanoparticles

OTHER SUPER-RESOLUTION MICROSCOPIES

In parallel and besides STED, many other methods have been developed to push the resolving power of optical spectroscopy of nanomaterials beyond the diffraction limit

We will see one of such techniques (SNOM), showing again a virtually unlimited resolution at the expenses of many tehcnical issues, in the future

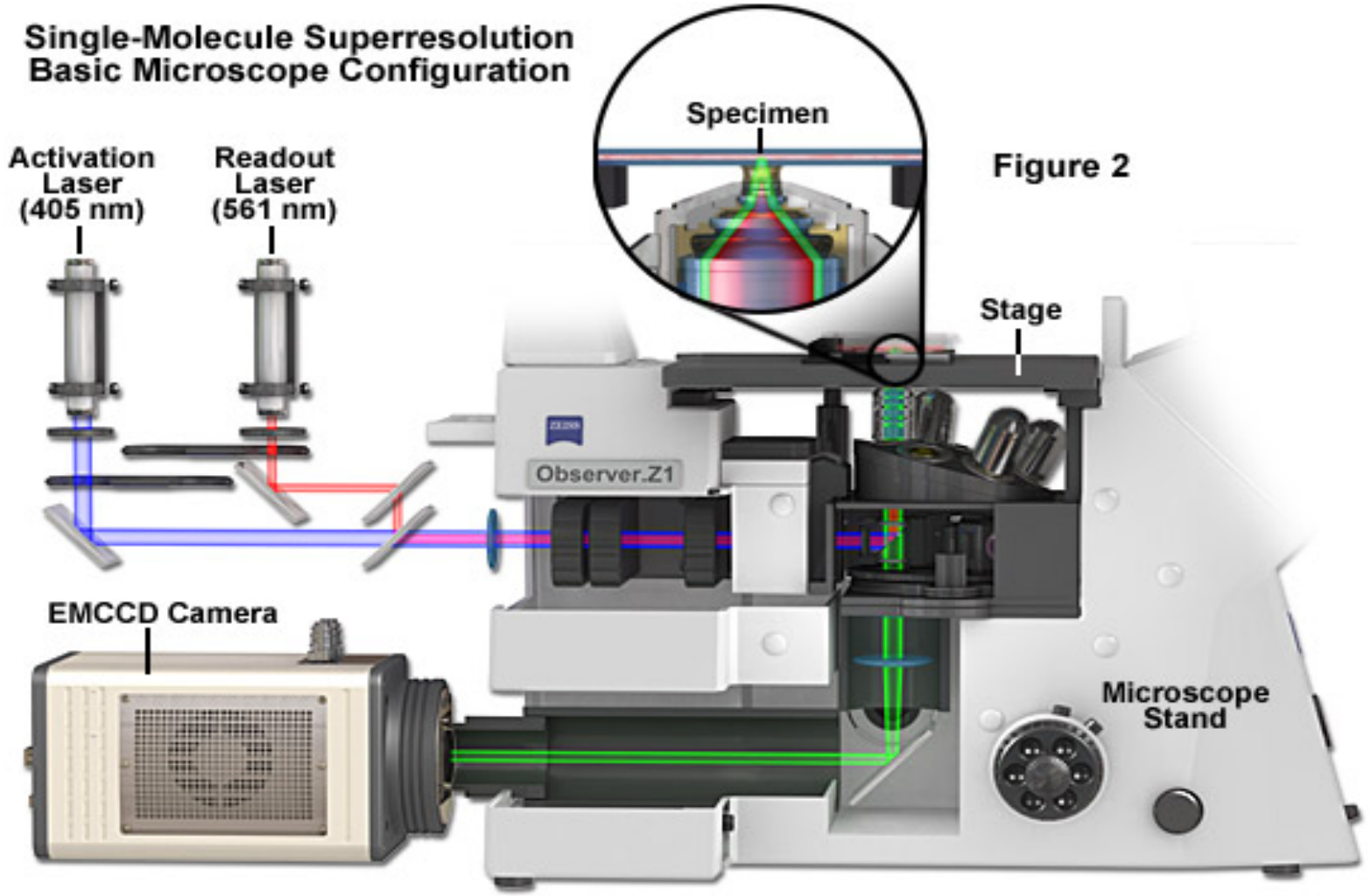
Here we very briefly recall some “statistical-based” techniques leading to nanometer resolving power: PALM and STORM (and their variants, with a number of acronyms…)

PhotoActivated Localization Microscopy (PALM) and STochastic Optical Reconstruction Microscopy (STORM), both awarded with the 2014 Nobel Prize in Chemistry, exploits, basically, an otherwise troublesome feature of chromophores, that is their **ability to photobleach** or to be photoactivated-photodeactivated

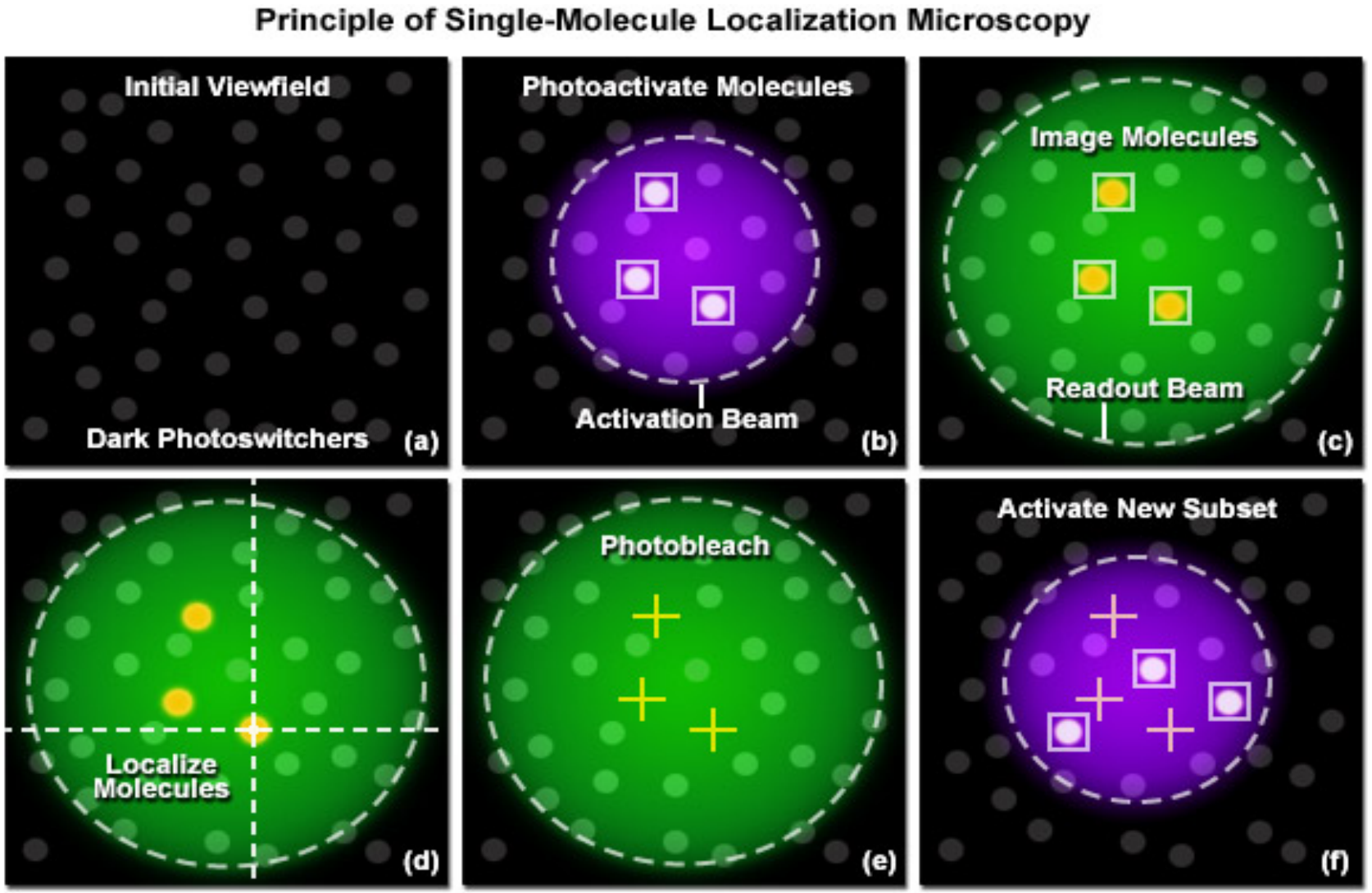
Numerical reconstruction of the center of mass of the intensity distribution, i.e., localization of single molecular emitters, is accomplished based on the sequential acquisition of stacks of images and subsequent numerical treatment through best-fit procedures

PALM, STORM (and similar techniques) have not a scanning nature, but rather use multiple sequential images captured with a CCD

SETUP FOR SUPER-RESOLUTION



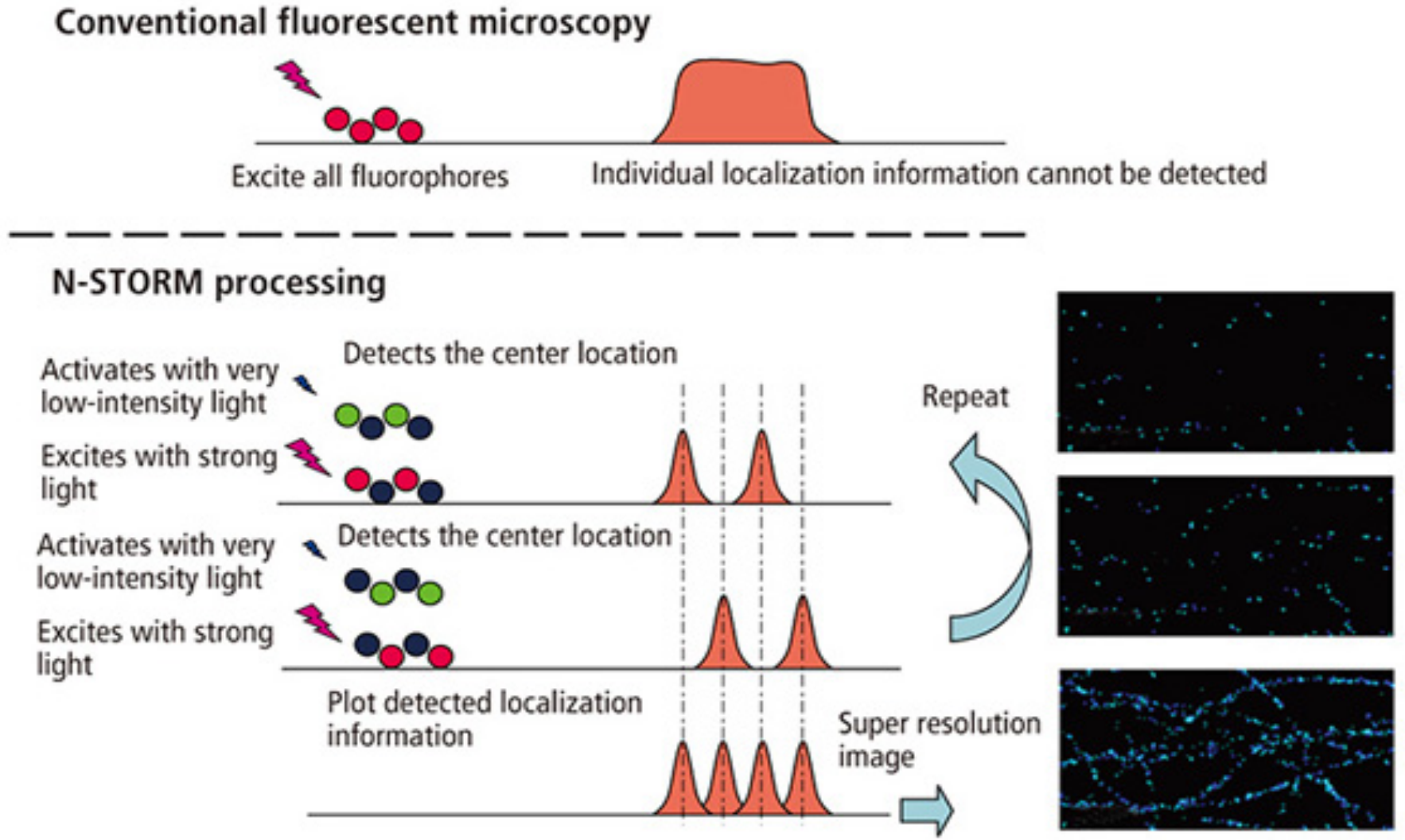
BASICS OF PALM



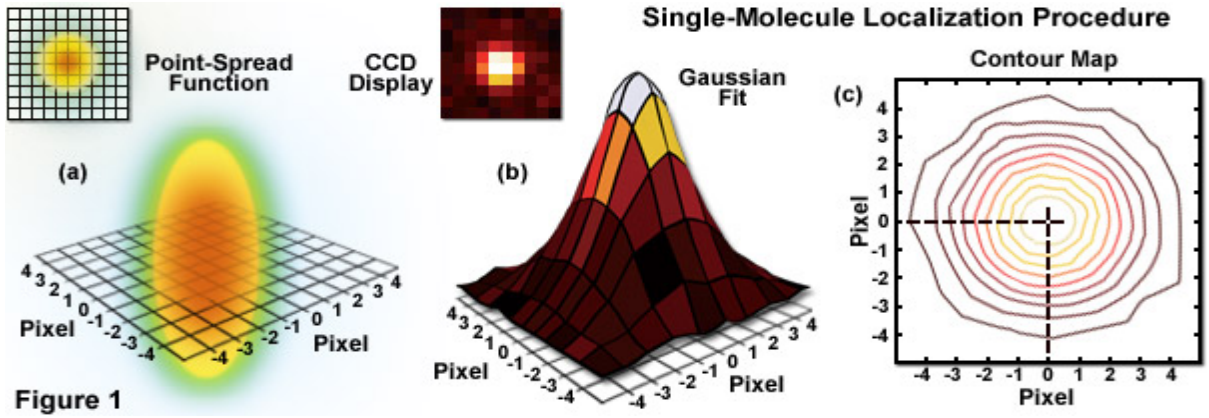
Different subsets of dye molecules are photoactivated and imaged until bleaching occurs

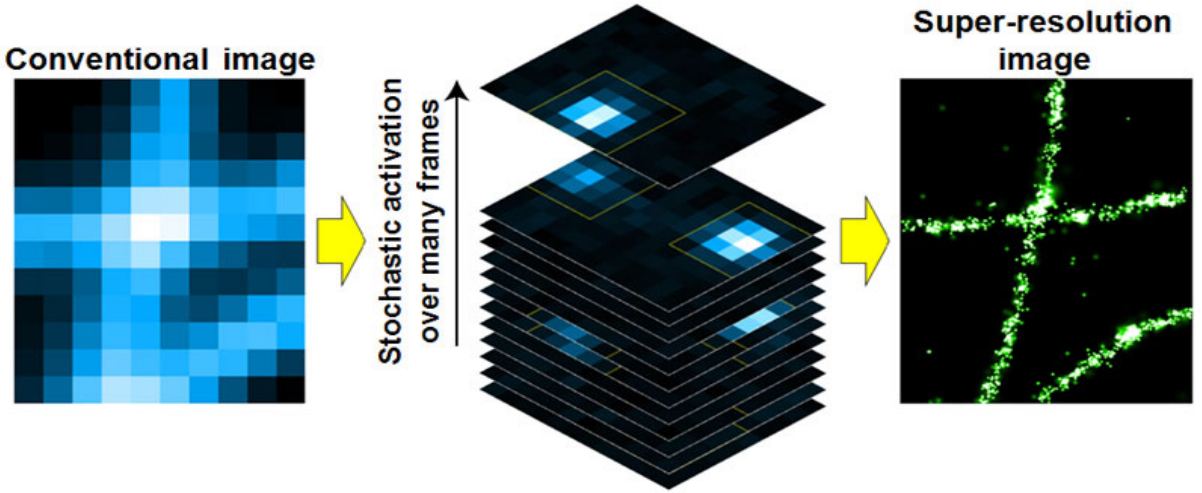
https://www.microscopyu.com

BASICS OF STORM

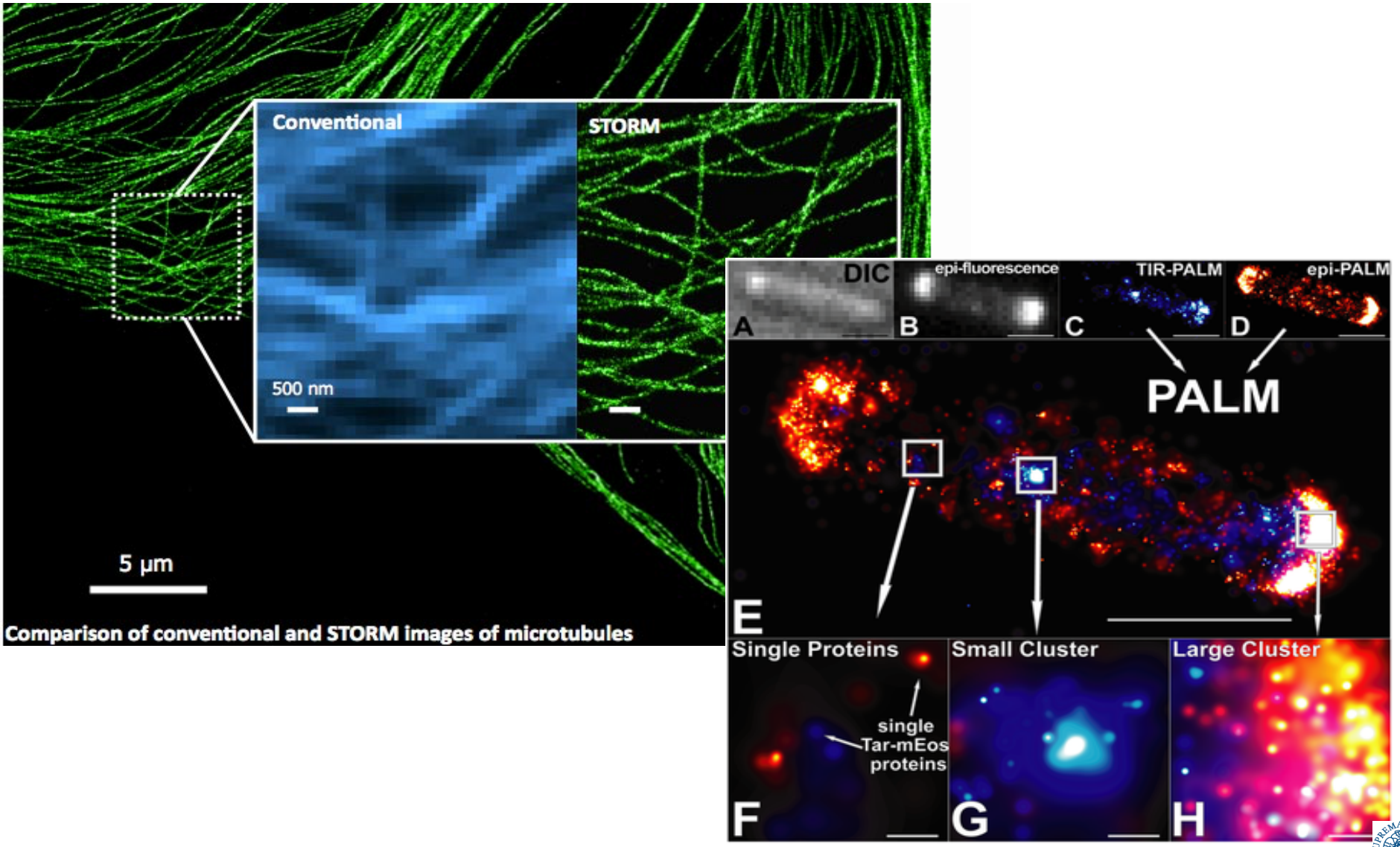


NUMERICAL TREATMENT (UNCOMMENTED)





EXAMPLES (UNCOMMENTED)



CONCLUSIONS

- ✓ Large efforts have been devoted in the last decades to attain super-resolved methods for optical spectroscopy of nanomaterials

- ✓ One of them sounds particularly interesting and tricky, the STED, being based on:
  (i) stimulated emission in molecular systems
  (ii) production of donut laser spots and superposition with a Gaussian spot
  (iii) achievement of virtually unlimited spatial resolution through stimulated emission depletion of the emitted fluorescence

- ✓ The diffraction limit is thus overcome and extremely high resolving power is reported

- ✓ Efforts are now oriented towards broadening the application spectrum of STED, for instance by implementing less expensive cw laser sources and by applying it to other nanostructures of interest in nanophotonics such as, quantum dots, metal nanoparticles featuring ocalized plasmon resonances, photonic nanostructures, etc.

In the next lecture we will describe such plasmonic systems and locate them within the frame of optical nanoscopy

FURTHER READING

For a reference on semiclassical light-matter interaction and laser operating principles:

W. Demtroeder, Laser Spectroscopy, Springer-Verlag, Berlin (2002).

For a comprehensive introduction to super-resolution microscopy:

P. Xi, Optical Nanoscopy and Novel Microscopy Techniques, CRC Press, Boca Raton (2015). [In particular Chapter 1 and Chapter 3]
A. Diaspro, Nanoscopy and Multidimensional Fluorescence Microscopy, CRC Press, Boca Raton (2010). [many specific topics of potential interest are collected in the book]

For a positioning of the super-resolution:

Nobel Prize in Chemistry 2014, Advanced Information
https://www.nobelprize.org/nobel_prizes/chemistry/laureates/2014/advanced-chemistryprize2014.pdf

Seminal Hell's papers:

Hell SW and Wichman J (1994) Breaking the diffraction resolution limit by stimulated emission: stimulated-emission-depletion-microscopy. Opt. Lett. 19:780-782.
Hell SW and Kroug M (1995) Ground-state depletion fluorescence microscopy, a concept for breaking the diffraction resolution limit. Appl. Phys. B. 60:495-497.

For a very simple and straightforward review on practical STED:

Stimulated Emission Depletion (STED) Microscopy: from Theory to Practice
http://www.formatex.info/microscopy4/1539-1547.pdf [open access]