Qualitative and Quantitative Analysis of Bulk SWNT Samples using Near-IR Fluorimetry

R. Bruce Weisman
Rice University
Houston, Texas USA

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SWNT Fluorescence Characteristics

Near-IR emission following visible excitation

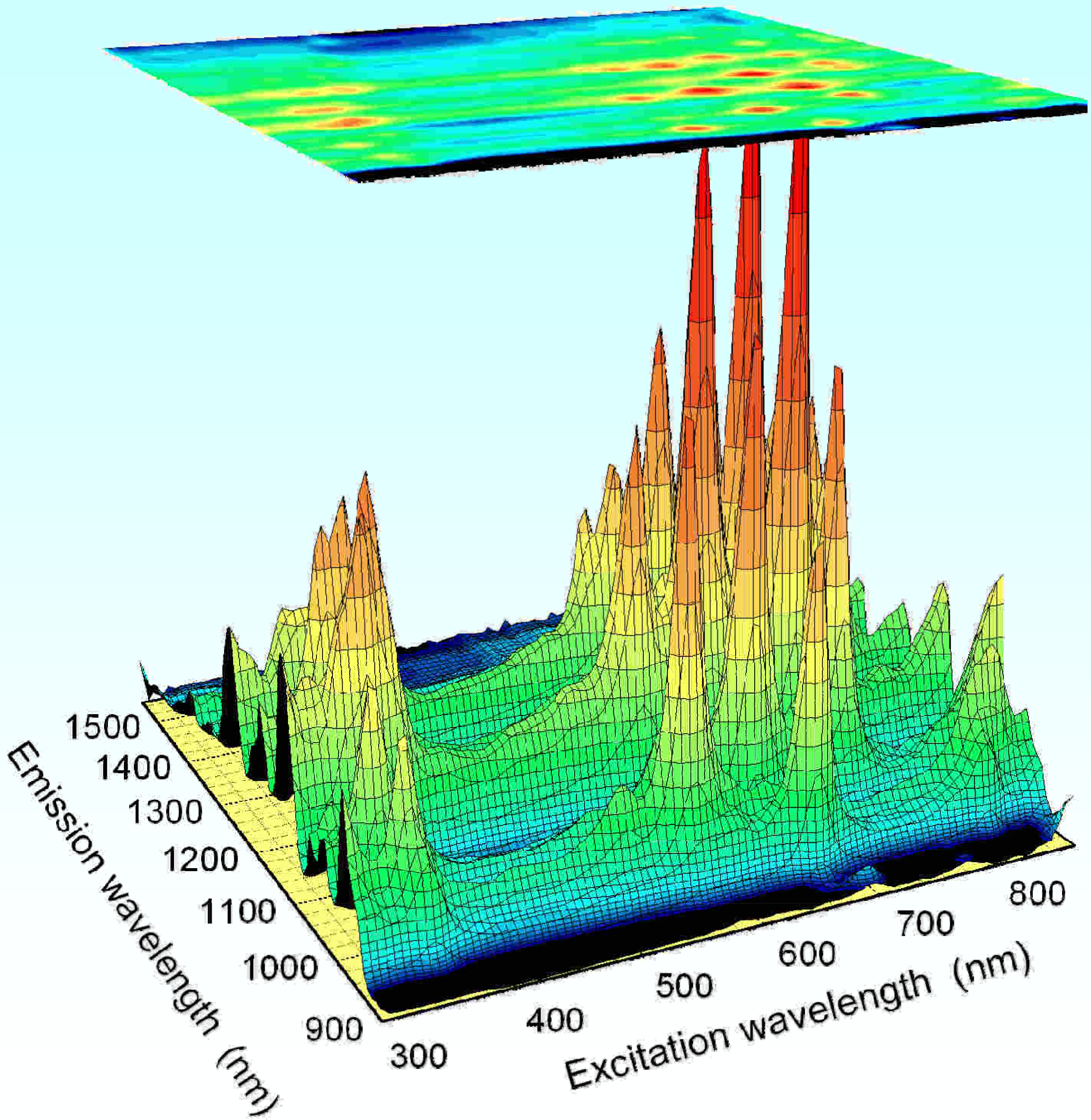
Low average quantum yield (but maybe >1%)

Lifetime ~10^{-10} s

Highly photostable, blink-free

Strongly polarized parallel to tube axis

Quenched by bundling, chemical damage, close contact with SiO_2



1500
1400
1300
1200
1100
1000
900
Emission wavelength (nm)
300
400
500
600
700
800
Excitation wavelength (nm)

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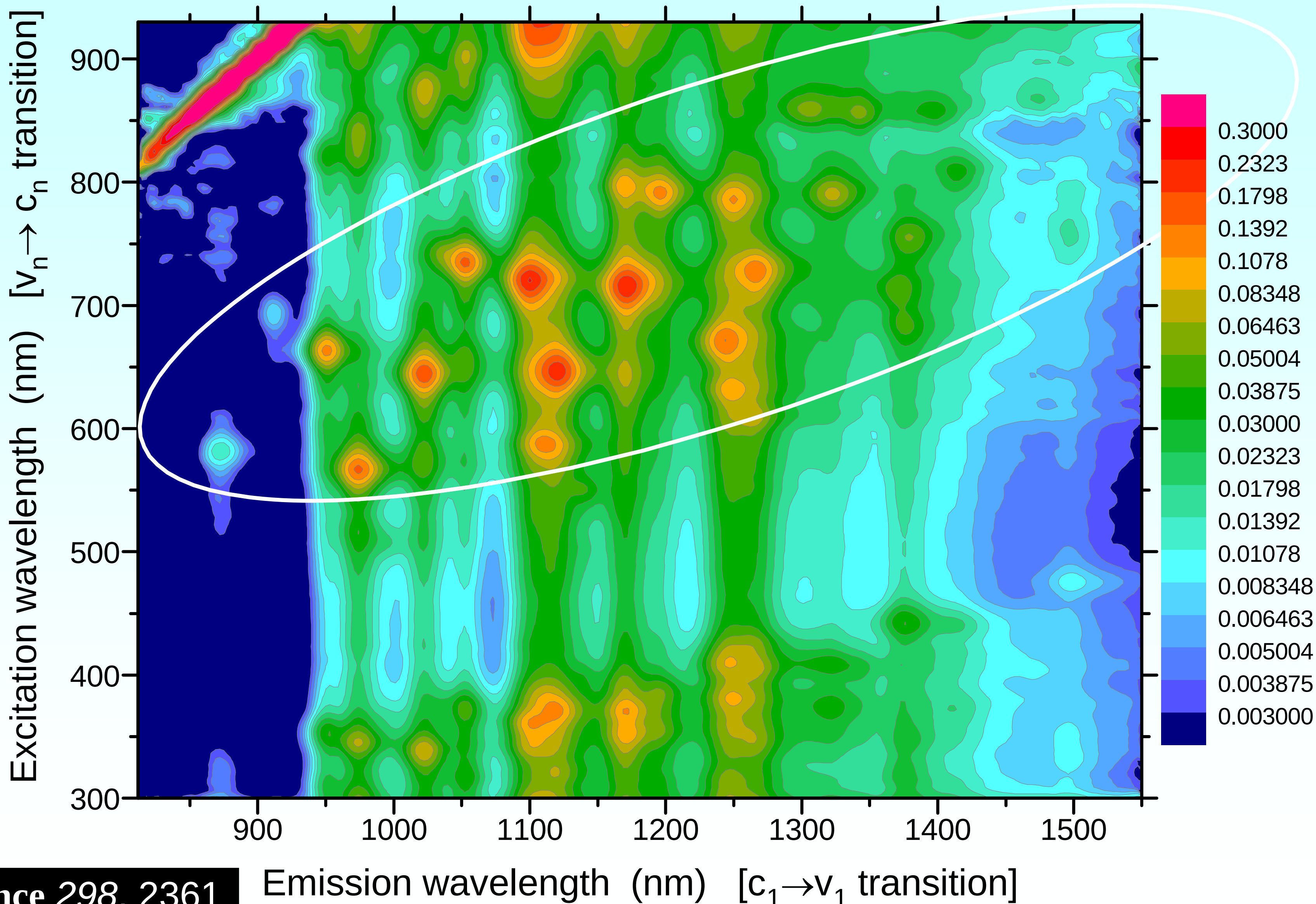
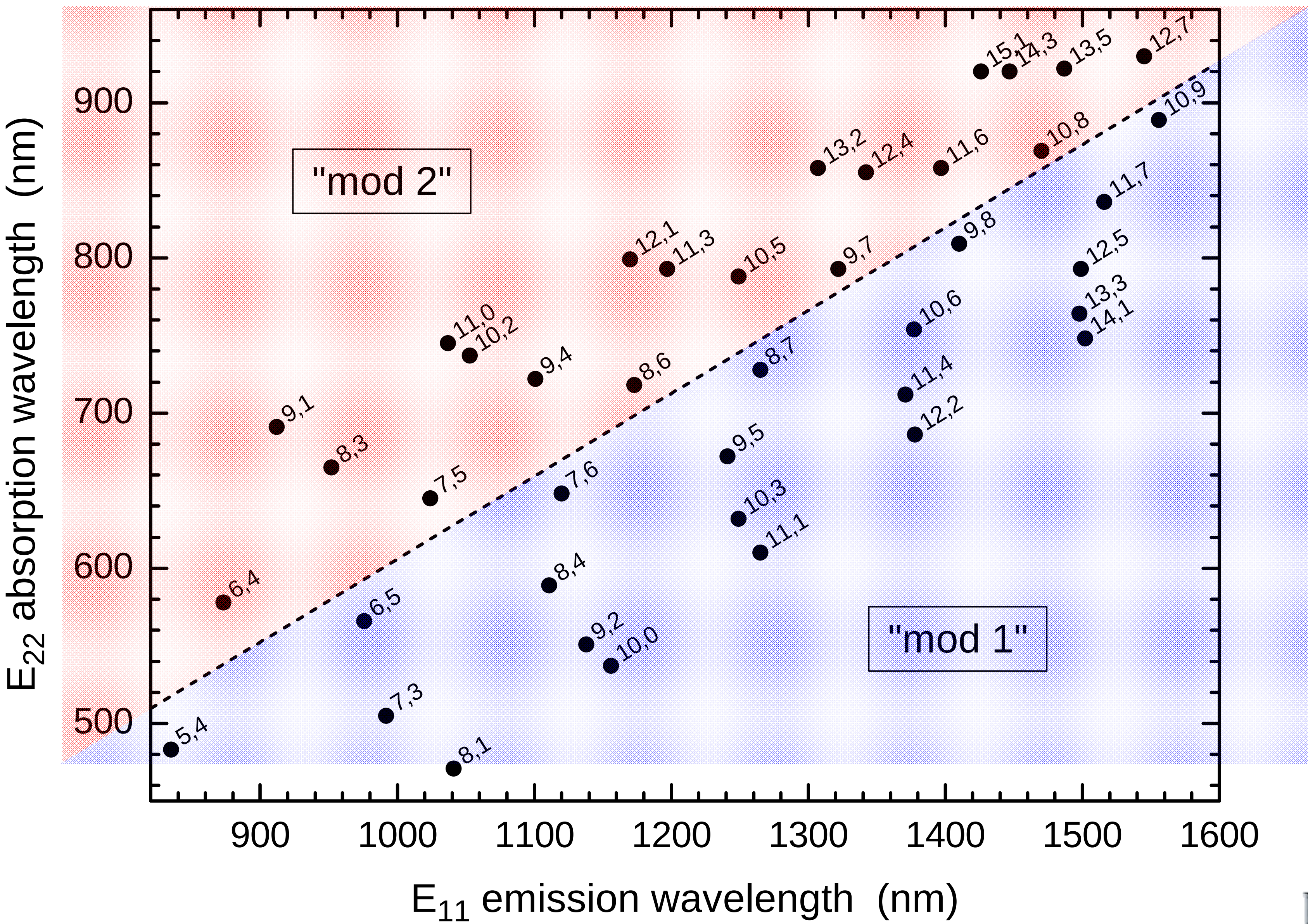
Contour Plot of Emission Intensity



Science *298*, 2361 (2002)

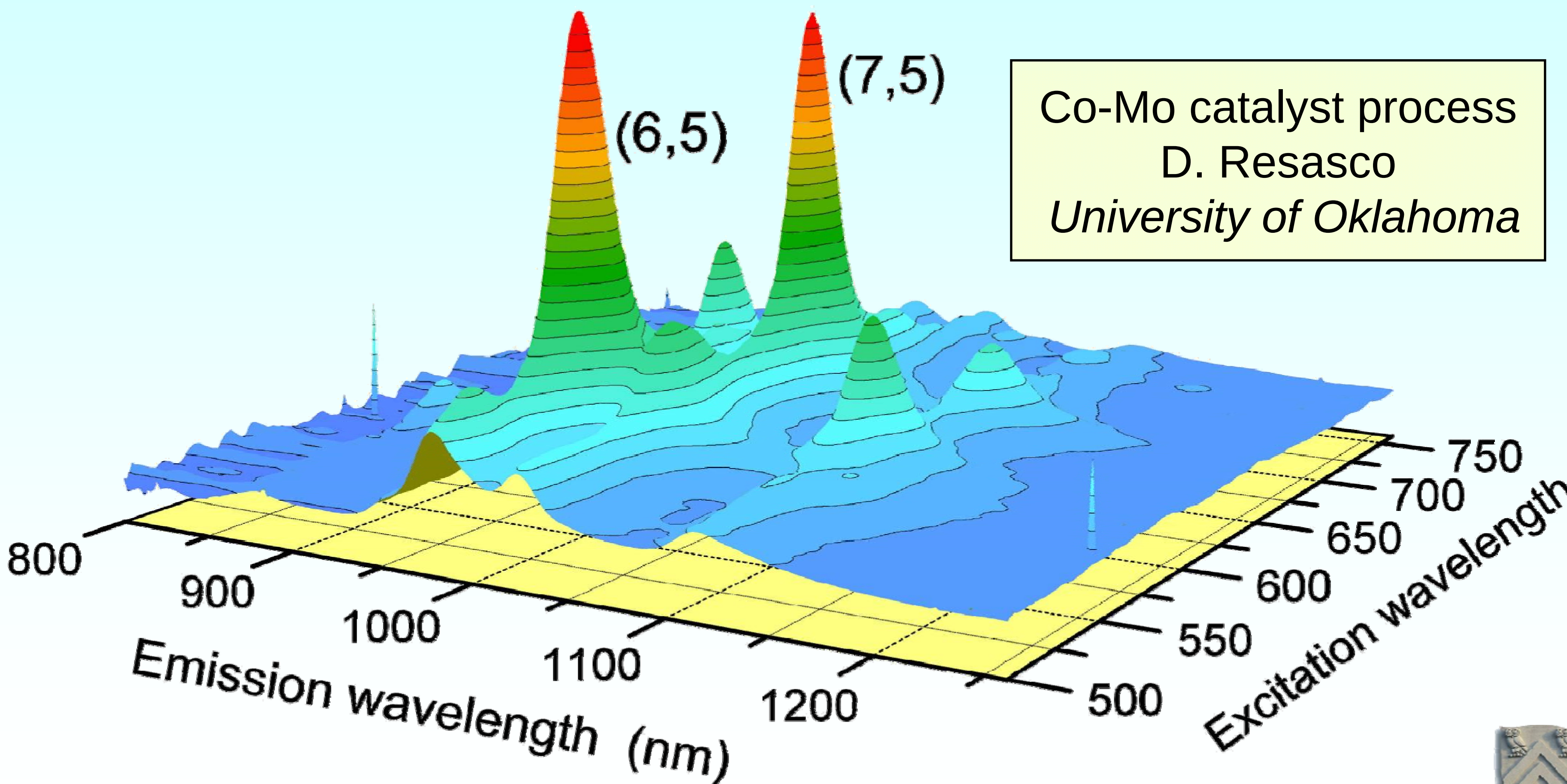
Structure-assigned Spectral Transitions



Benefits of Fluorimetric Analysis

- High sensitivity
- Simple sample preparation
- Excellent (*n,m*) identification
- High selectivity against impurities, bundles, imperfect tubes
- No background subtraction needed in analysis (unlike absorption methods)
- Relatively simple instrumentation

Narrow (*n*,*m*) Distribution from Supported Catalyst Synthesis



Co-Mo catalyst process
D. Resasco
University of Oklahoma

JACS 125, *11186 (2003)*

Why not use 2D Spectrofluorimetry for routine analyses?

- Slow data acquisition
- Limited sensitivity
- Tedious manual data reduction and interpretation

Is there a more efficient approach?

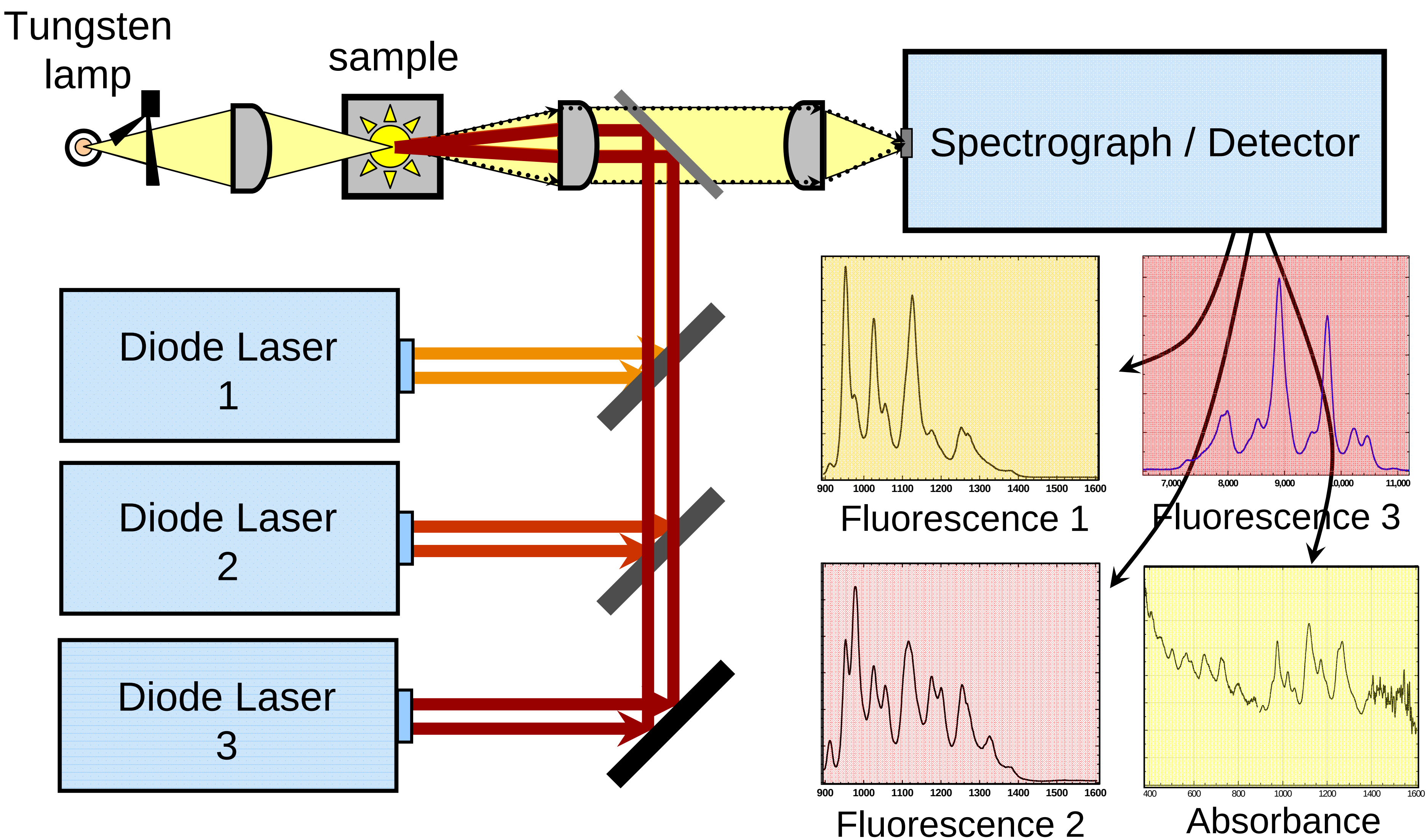
Efficient Analysis using Discrete Excitation Wavelengths

+ E_{22} spectral structure allows many species to be excited at once

+ Experimentally simple and fast

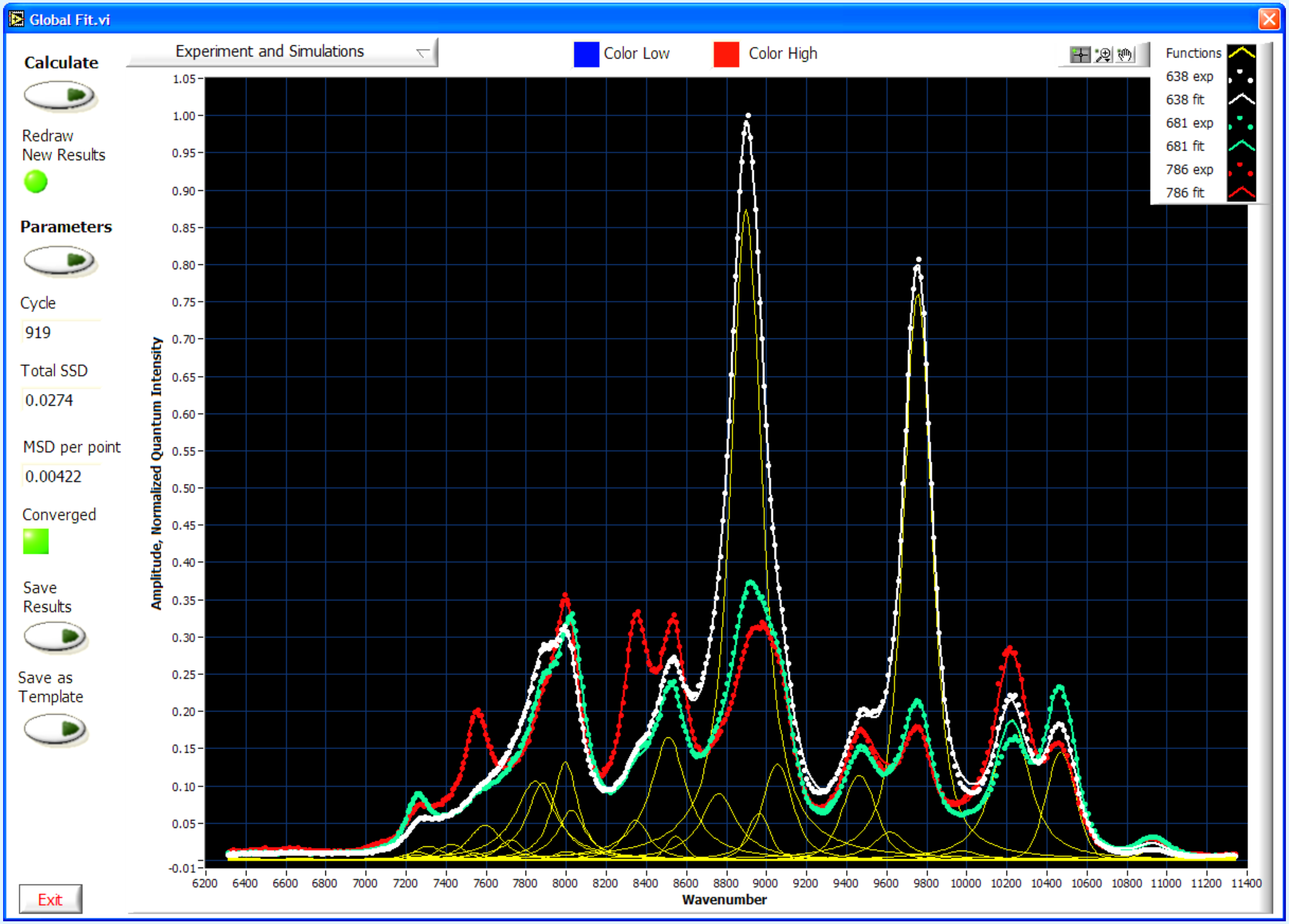
- But reduced (*n*,*m*) discrimination for larger diameter species

NanoSpectralyzer® Operation

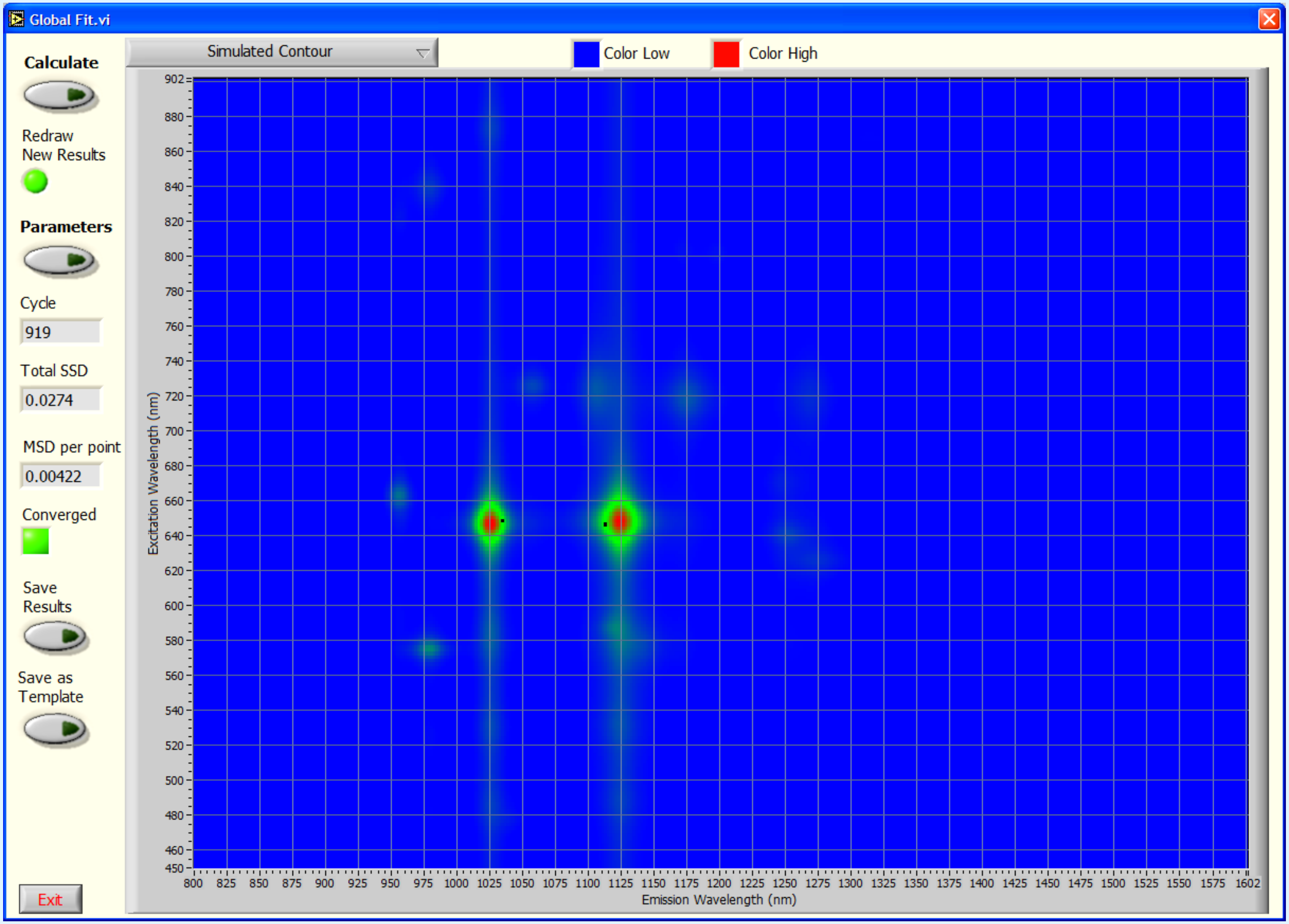


Model NS1 NanoSpectralyzer

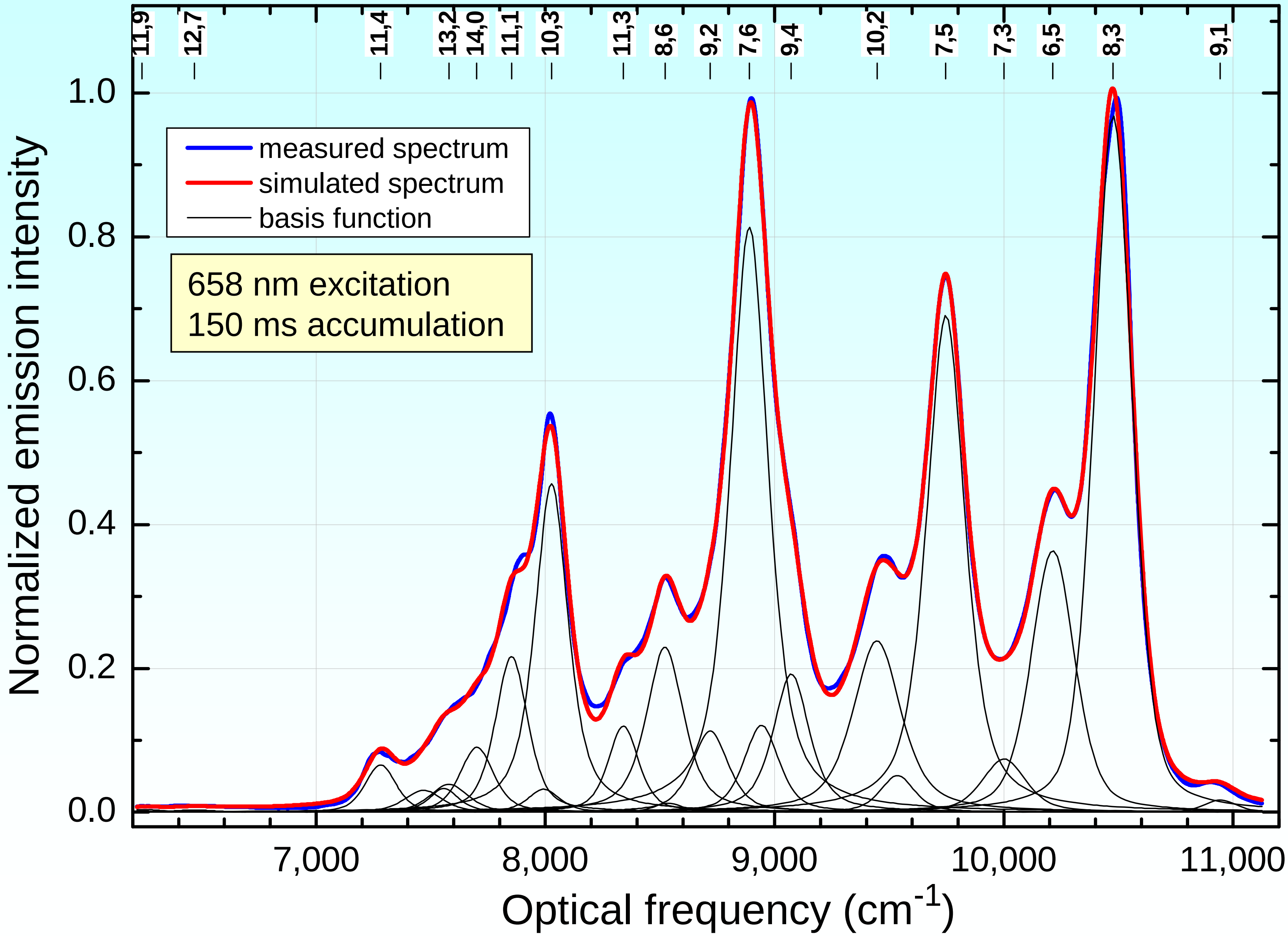
Rapid global fitting with 3 excitation wavelengths



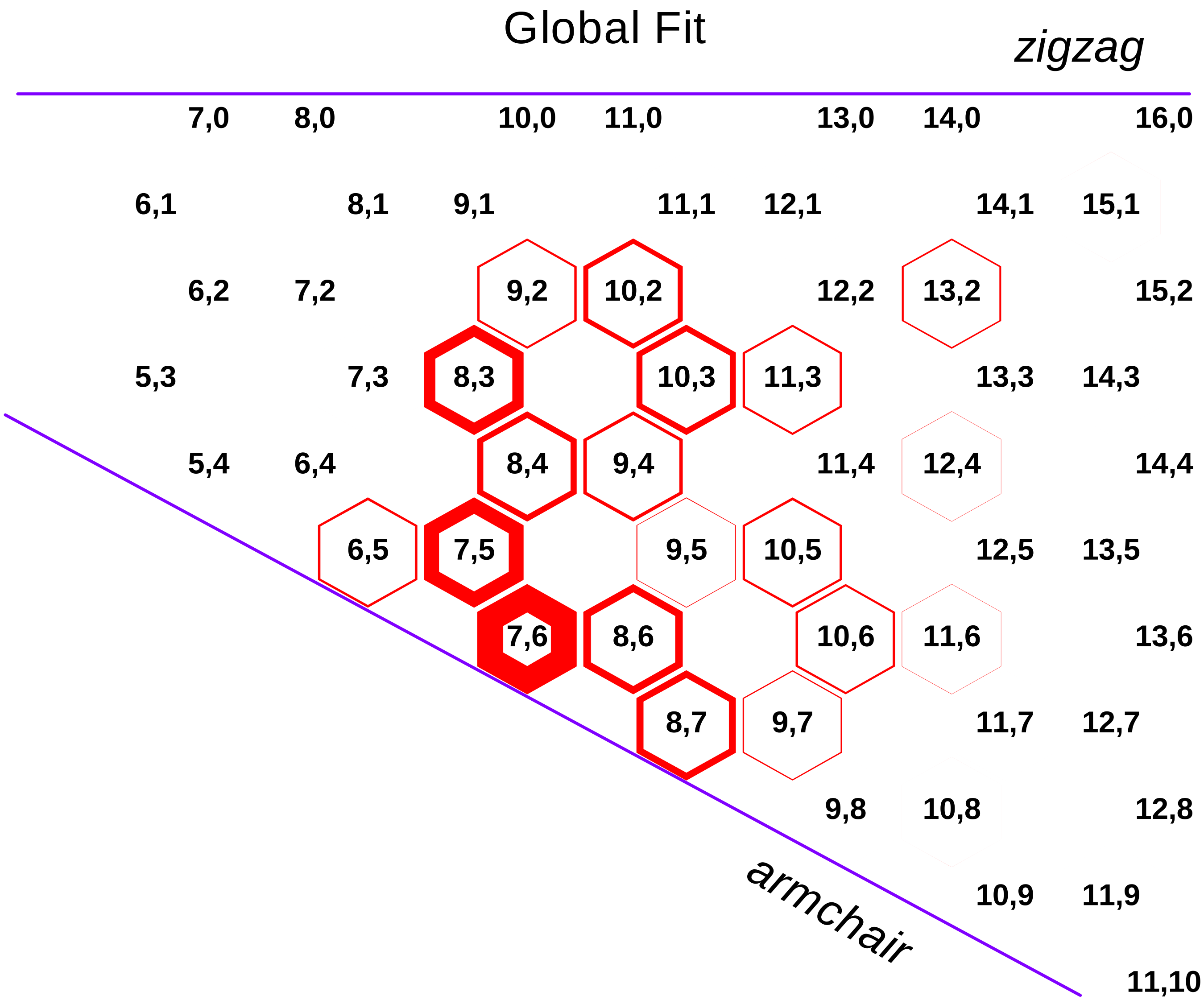
Synthesized Contour Plot



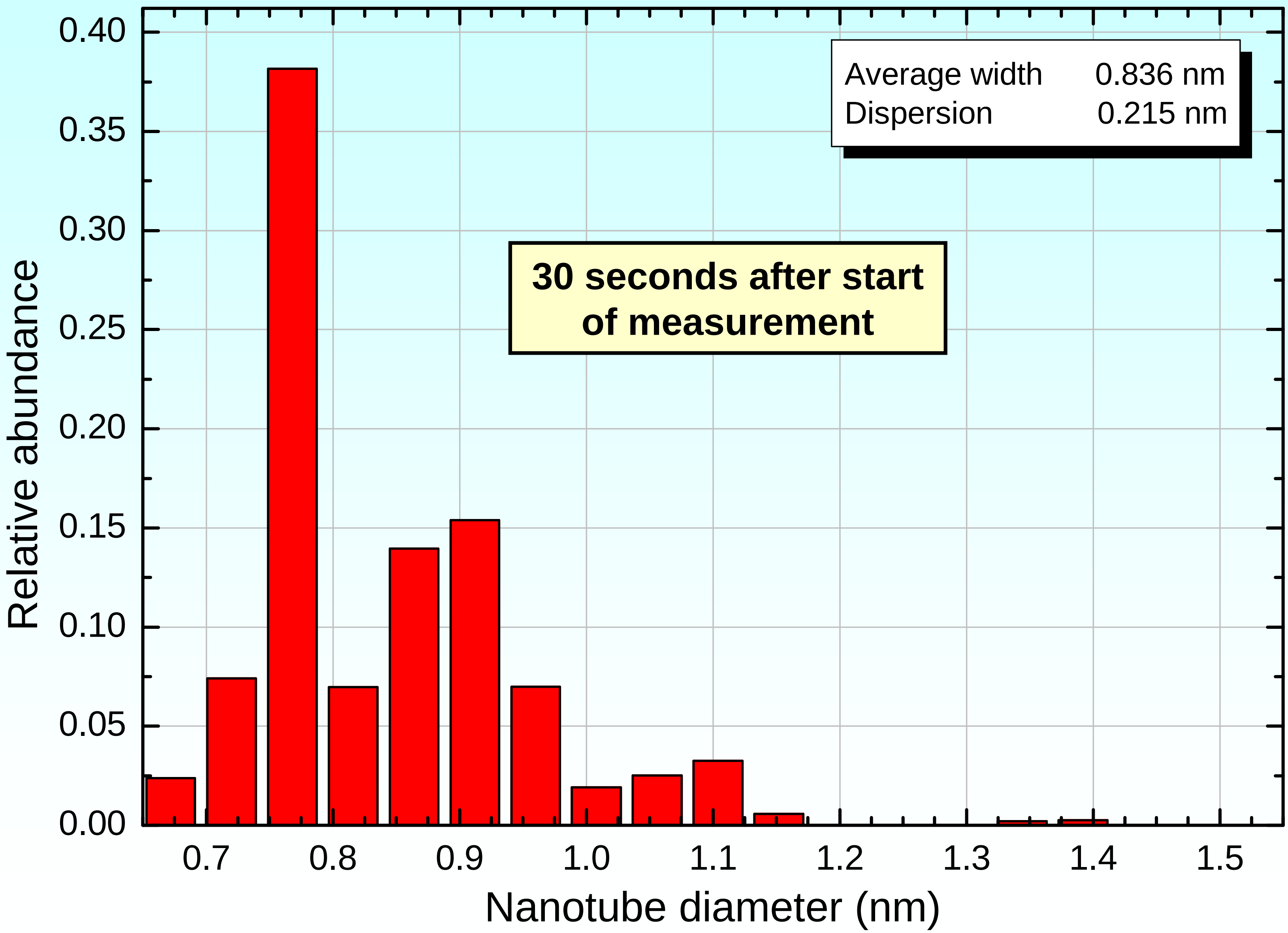
Fluorescence Spectrum with Global Fit Simulation



Automatically Deduced (*n*,*m*) Distribution



Automatically Deduced Diameter Distribution



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Fluorimetric (*n*,*m*) analysis of bulk SWNT samples

<u>Advantages</u>

See many species with few excitation wavelengths

Detect 10 pg SWNT in 50 μL (~10^{-10} by mass)

Suitable for many environments

Sensitive to aggregation state

<u>Limitations</u>

Detects only semiconducting species

Sensitive to aggregation state

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Fluorimetric (*n*,*m*) analysis of bulk SWNT samples

Qualitative analysis

OK

Quantitative analysis

Not OK: need to know factors controlling fluorescence intensities

Factors controlling fluorescence intensities

Intrinsic: diameter
chirality
mod 1 or 2 identity

Extrinsic: structural defects
bundling
surfactant environment
end quenching (length)
chemical processing

Sample inhomogeneity makes SWNT photophysics confusing

- Many (*n*,*m*) structures
- Many lengths
- Many imperfect nanotubes
- Some small emissive bundles
- Differences in environment (?)
- Differences in sidewall species (?)

Useful approach:
measure single SWNTs instead of ensembles

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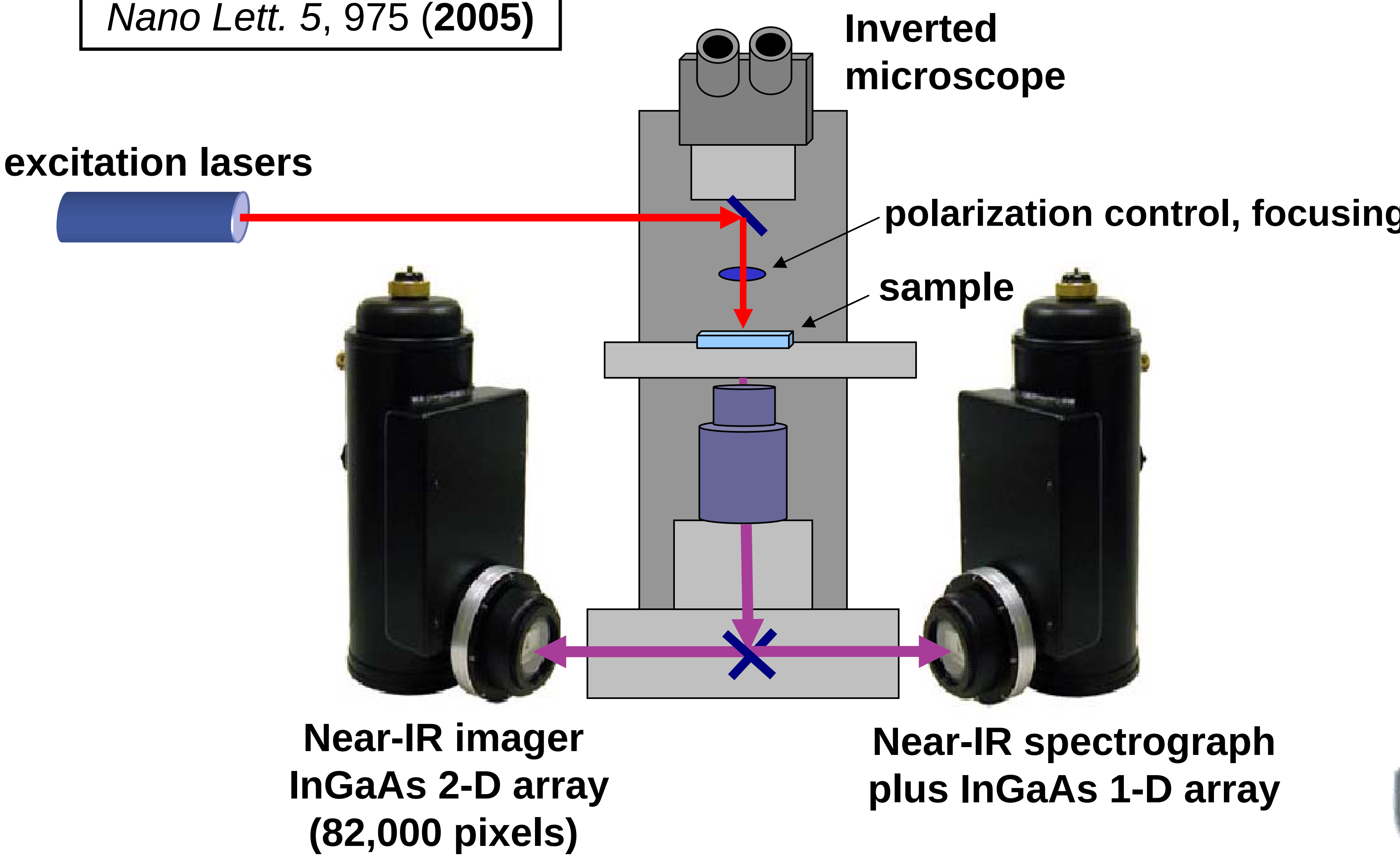
<u>Intrinsic</u> factors: Experimental plan

1. Prepare aqueous SDBS sample with minimal processing
2. Find a bright, long SWNT under the microscope
3. Identify its (*n*,*m*) from emission spectrum
4. Excite near its E_{22} resonance peak in linear intensity regime
5. Measure emission intensity per unit SWNT length with calibrated excitation and detection

Apparatus for Near-IR Fluorescence Microscopy

Tsyboulski, et al.
Nano Lett. 5, 975 (**2005**)



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Measured emission flux =

excitation intensity x

λ_{22} / hc x

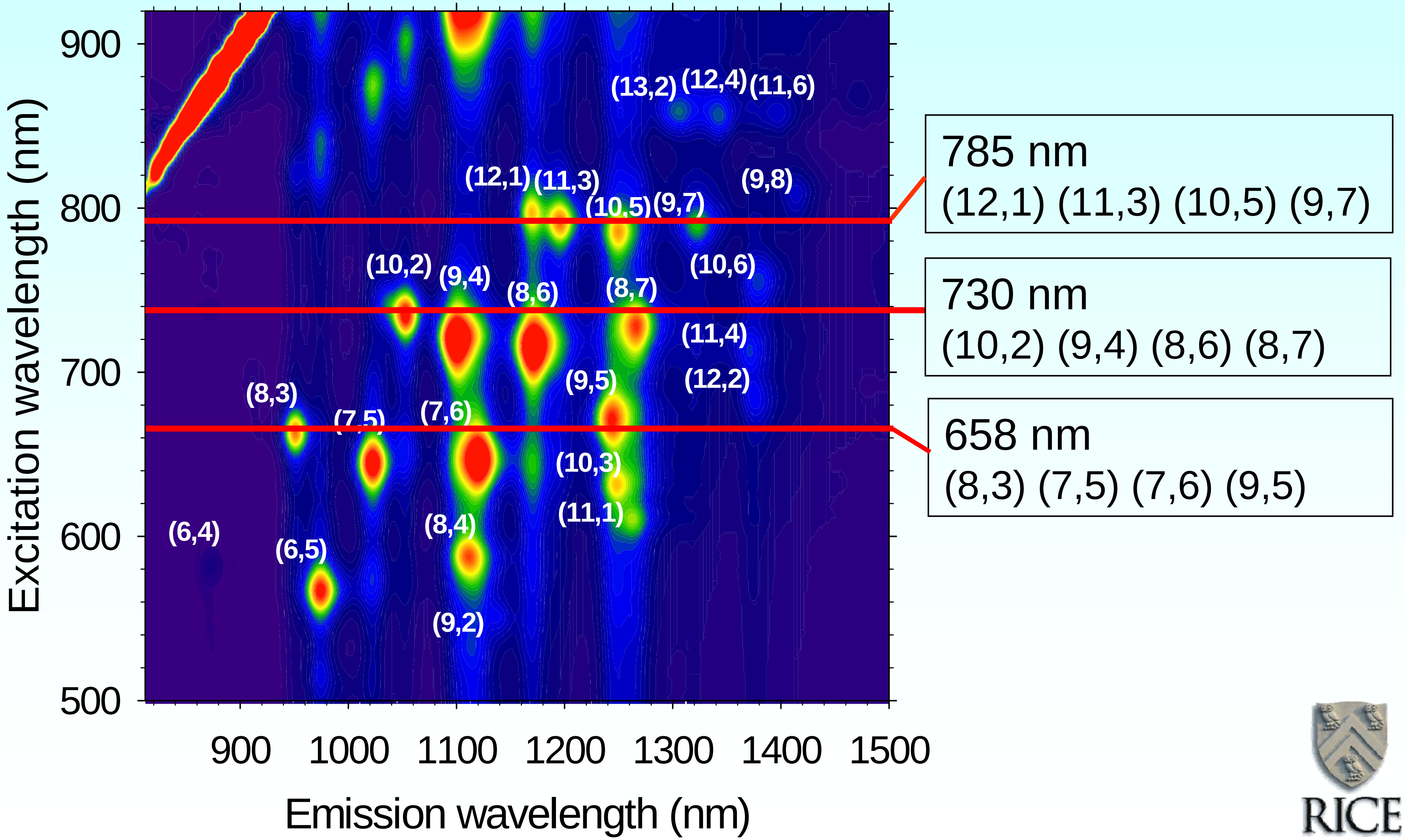
$\sigma(\lambda_{22})$ x

Φ_{Fl} x

instrumental detection efficiency

Obtain absolute values of $\sigma_{22}\ \Phi_{Fl}$

Use three laser wavelengths to excite near E_{22} resonances



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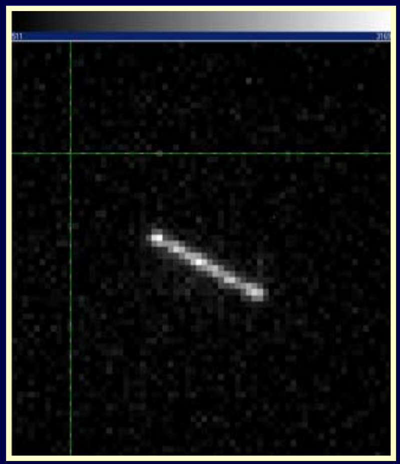
Criteria for selecting SWNTs

- Length greater than 3 μm
- Emission peak within 20 cm^{-1} of standard value (not bundled)
- Few or no dark regions along entire tube length
- Isolated and moving freely (not stuck)

SWNT selection

Good tubes



7.4 μm long (9,7)

6.3 μm long (10,2)

10.6 μm long (8,7)

Bad tube

Use the brightest segment

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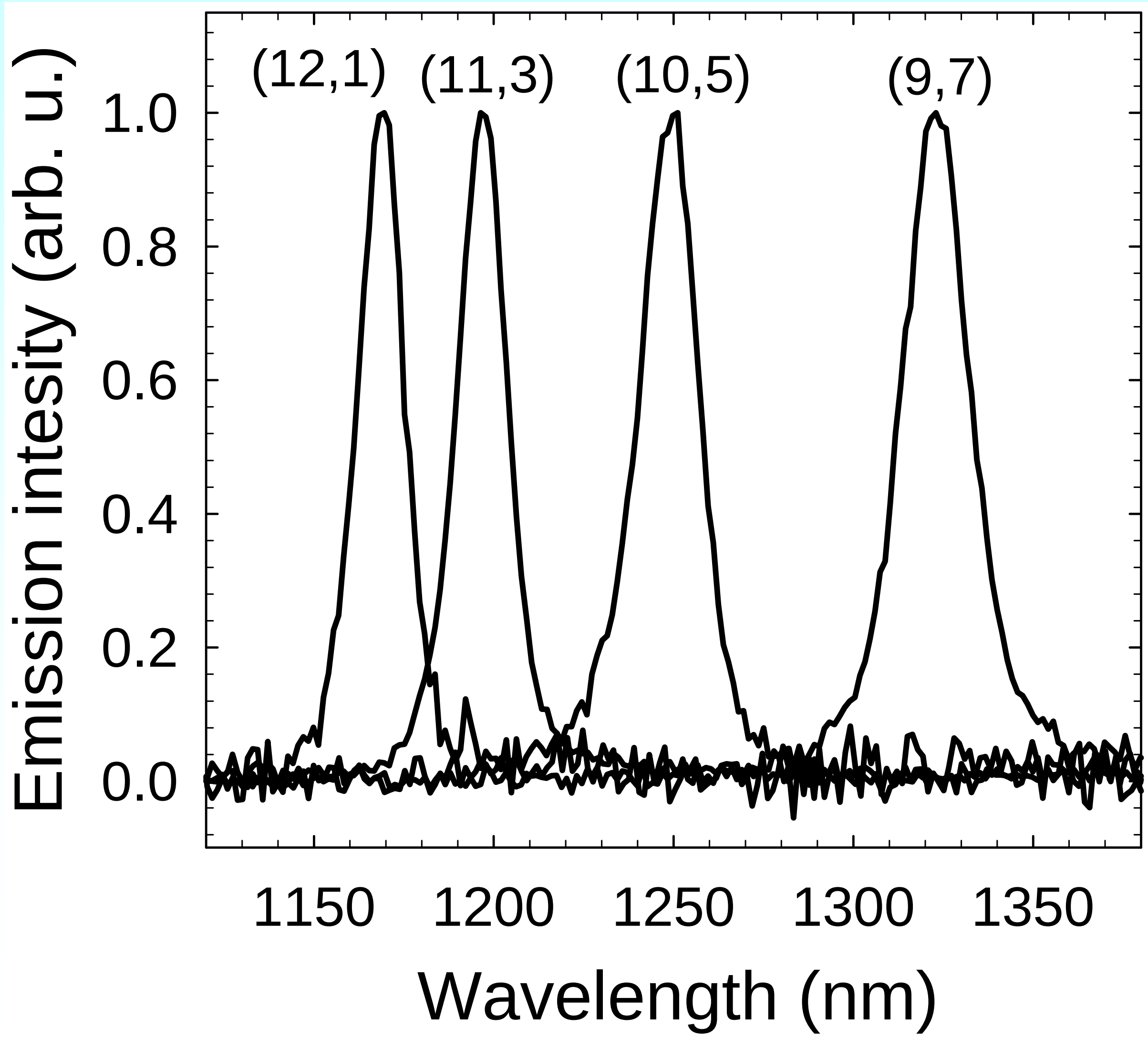
Emission spectra allow (*n*,*m*) identification of single SWNTs in aqueous suspension



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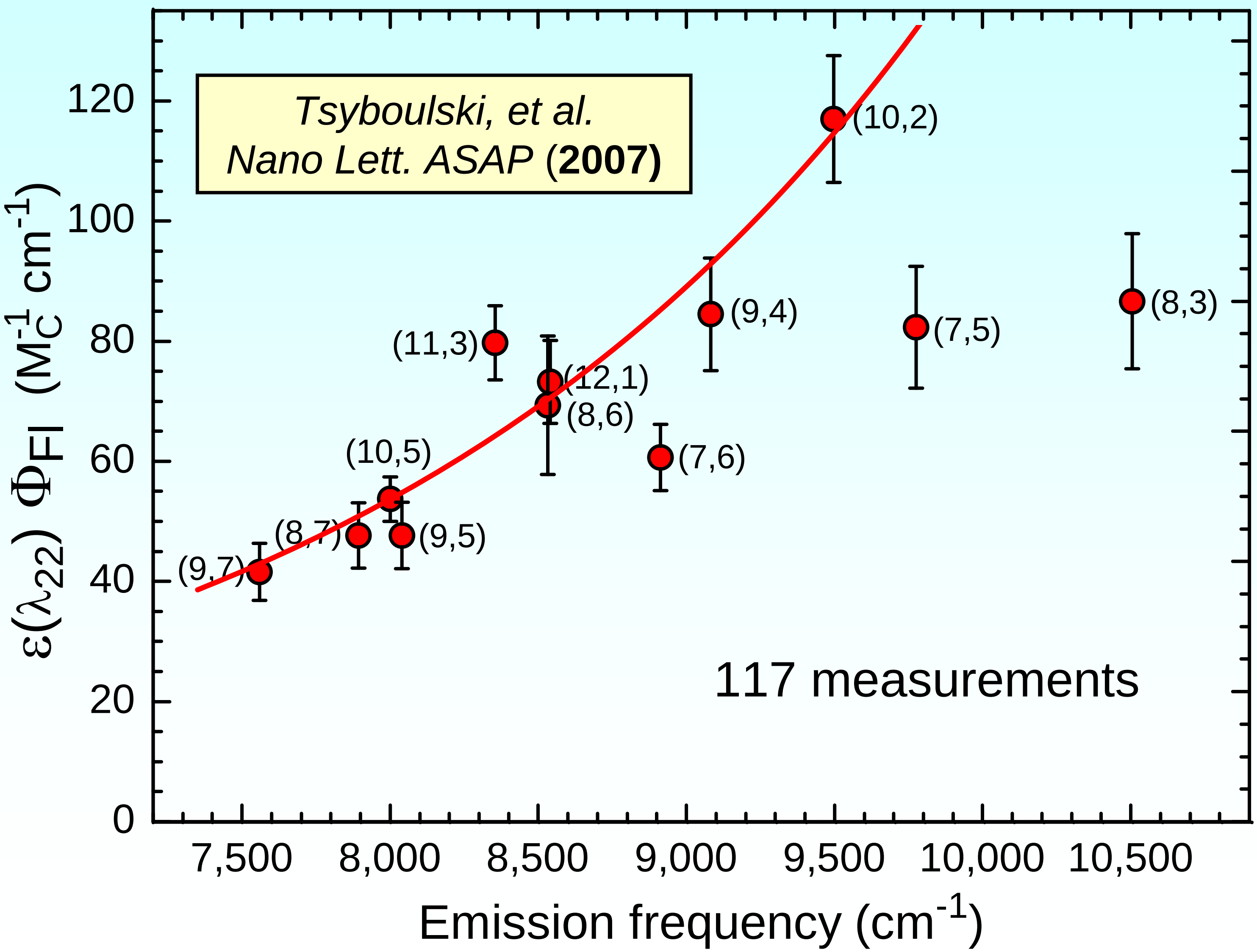
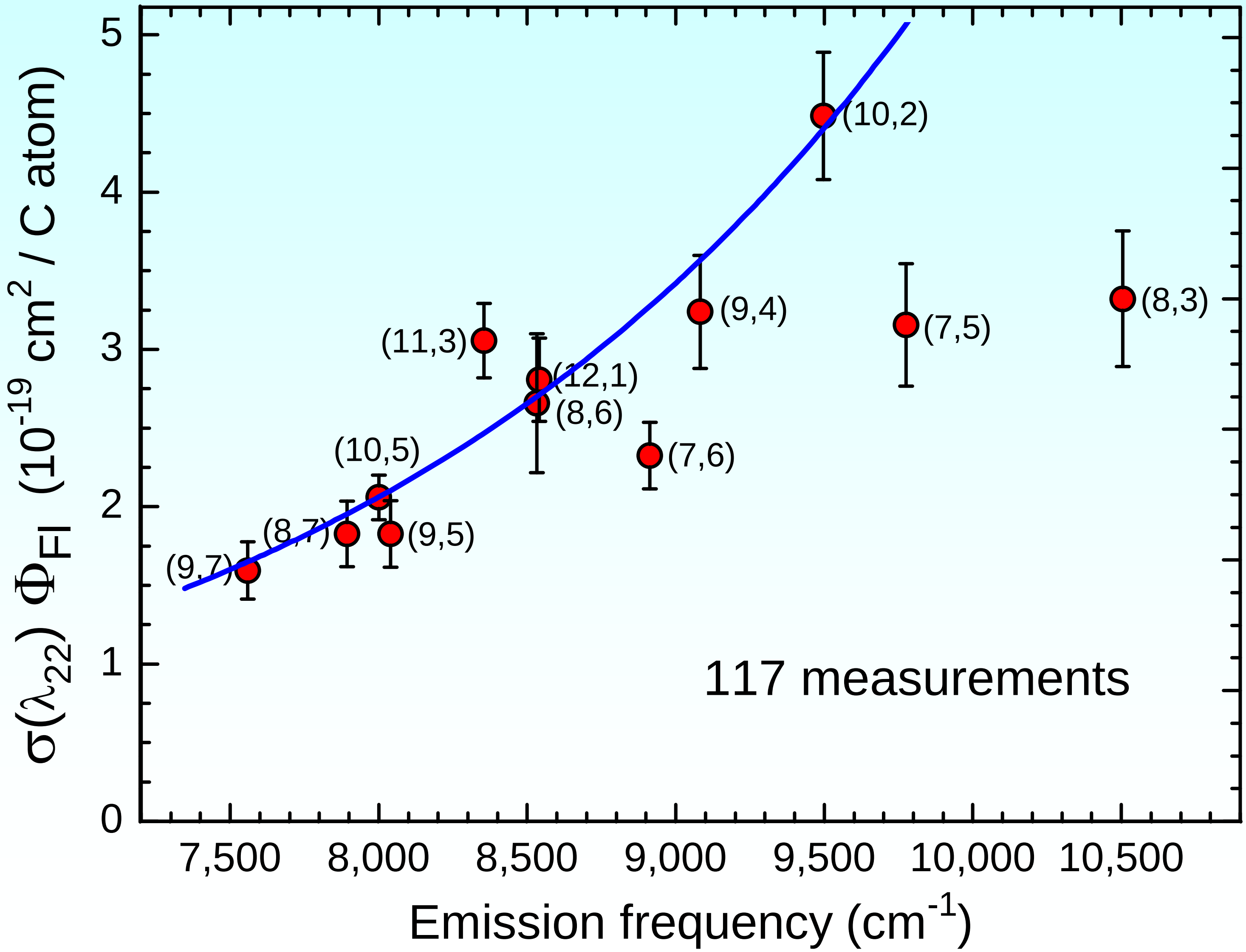
Results: Absolute fluorimetric efficiencies measured on selected SWNTs



Results: Absolute fluorimetric efficiencies measured on selected SWNTs

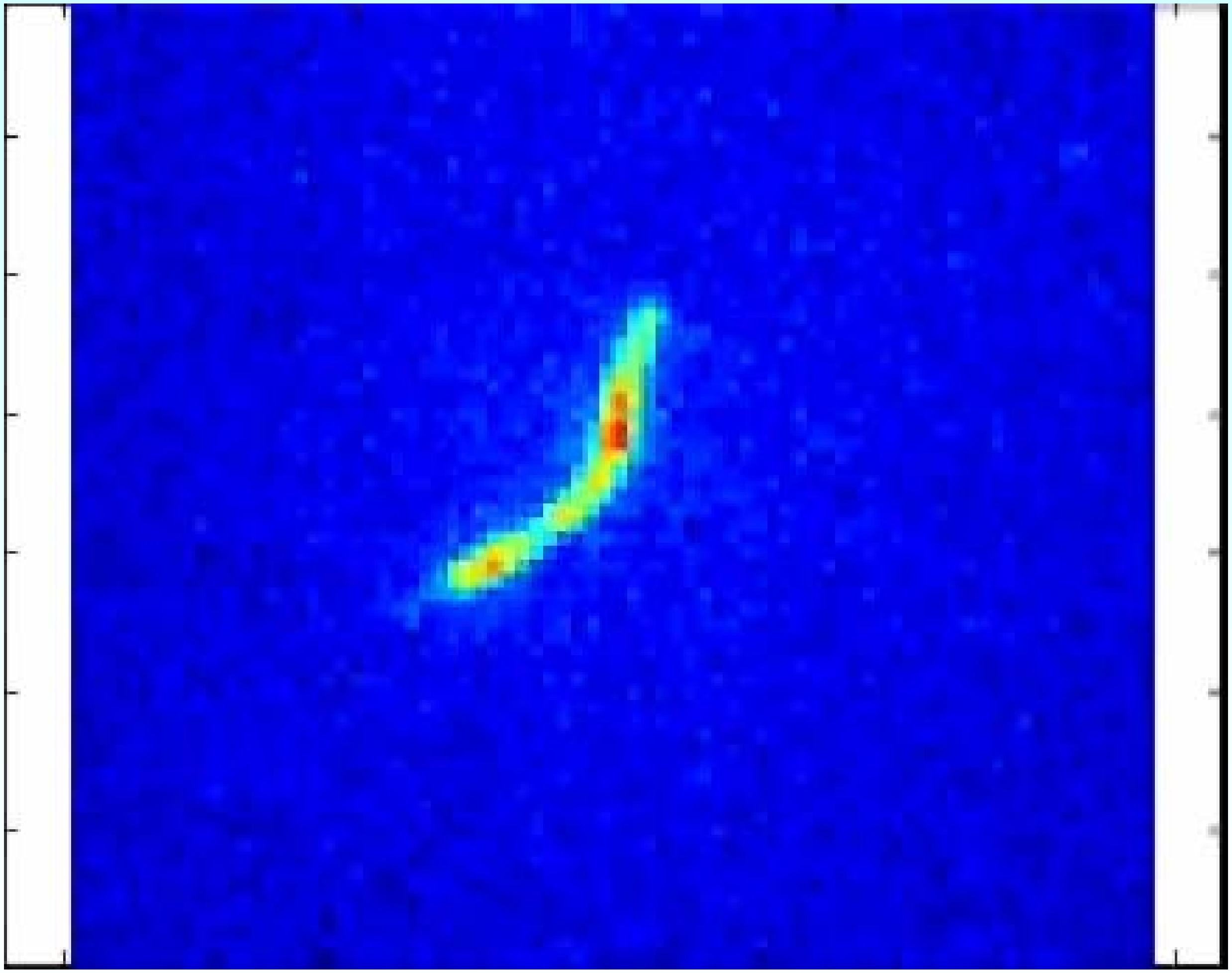


Findings

- Fluorimetric efficiencies vary rather systematically, tend to increase with optical emission frequency
- The variation spans a factor of ~3 in HiPco samples
- Brightest SWNT found so far is (10,2)
- Variation probably dominated by E_{11}-dependent nonradiative decay rates from lowest excited state
- Quantum yields of good tubes may be ~10%

Studying extrinsic effects at the single nanotube level

Fluorescence image of a free SWNT in water suspension



Real time
Nanotube length = 10 μm

Length dependence: Experimental plan

1. Prepare dilute aqueous SDBS sample for the microscope
2. Spectrally filter the near-IR camera to show only (10,2) SWNTs
3. Capture near-IR micrograph video sequences
4. Analyze each SWNT trajectory to find its translational diffusion coefficient
5. Deduce lengths from diffusion coefficients
6. Plot emission intensity vs. length for all tubes

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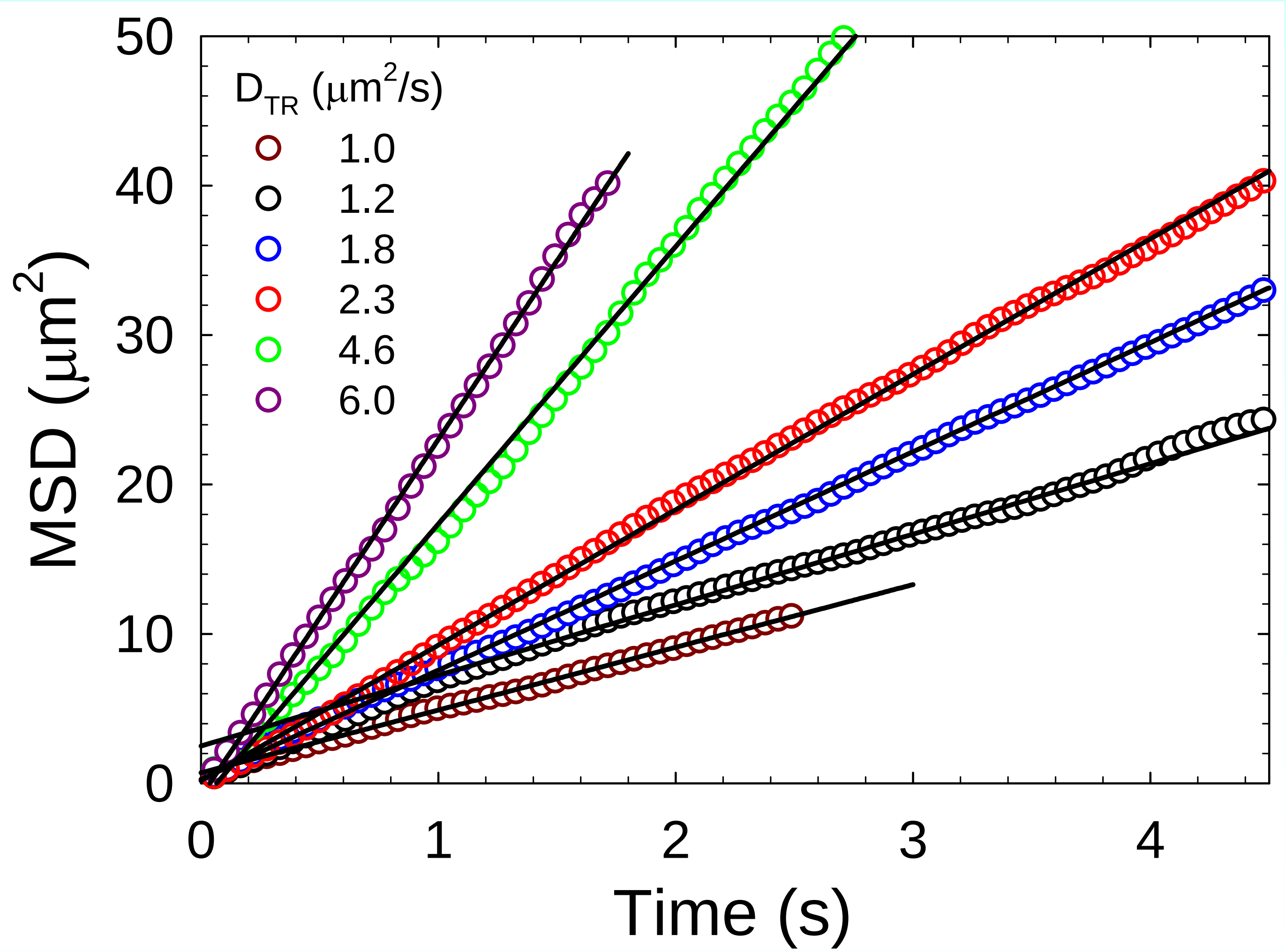
Translational Diffusion of Single SWNTs



D_{TR} values between 1 and 6 μm^2/s → Deduced lengths of 200 to 1400 nm (adjusted for wall-drag effects)

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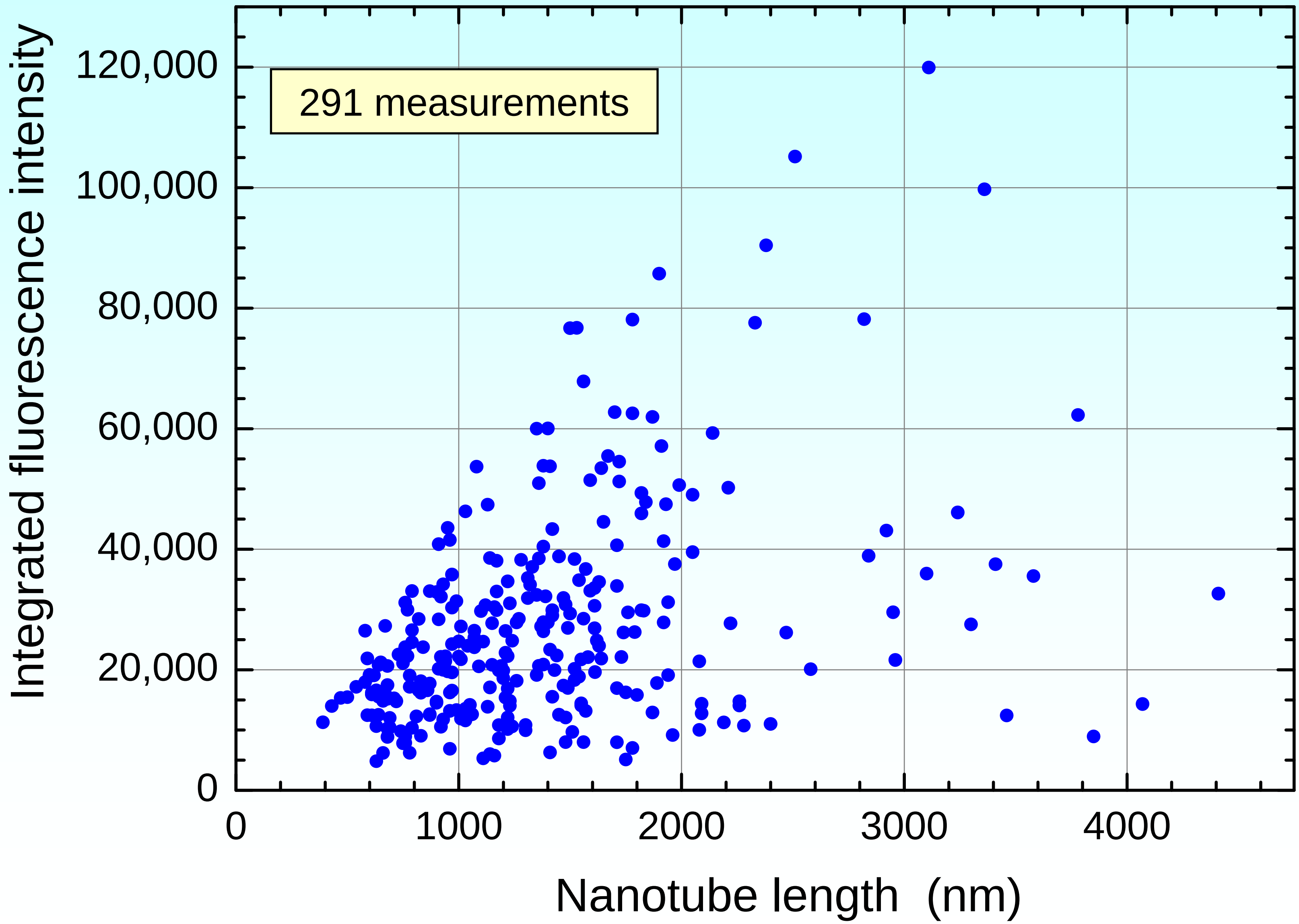
Fluorescence intensity vs. Length for (10,2) SWNTs



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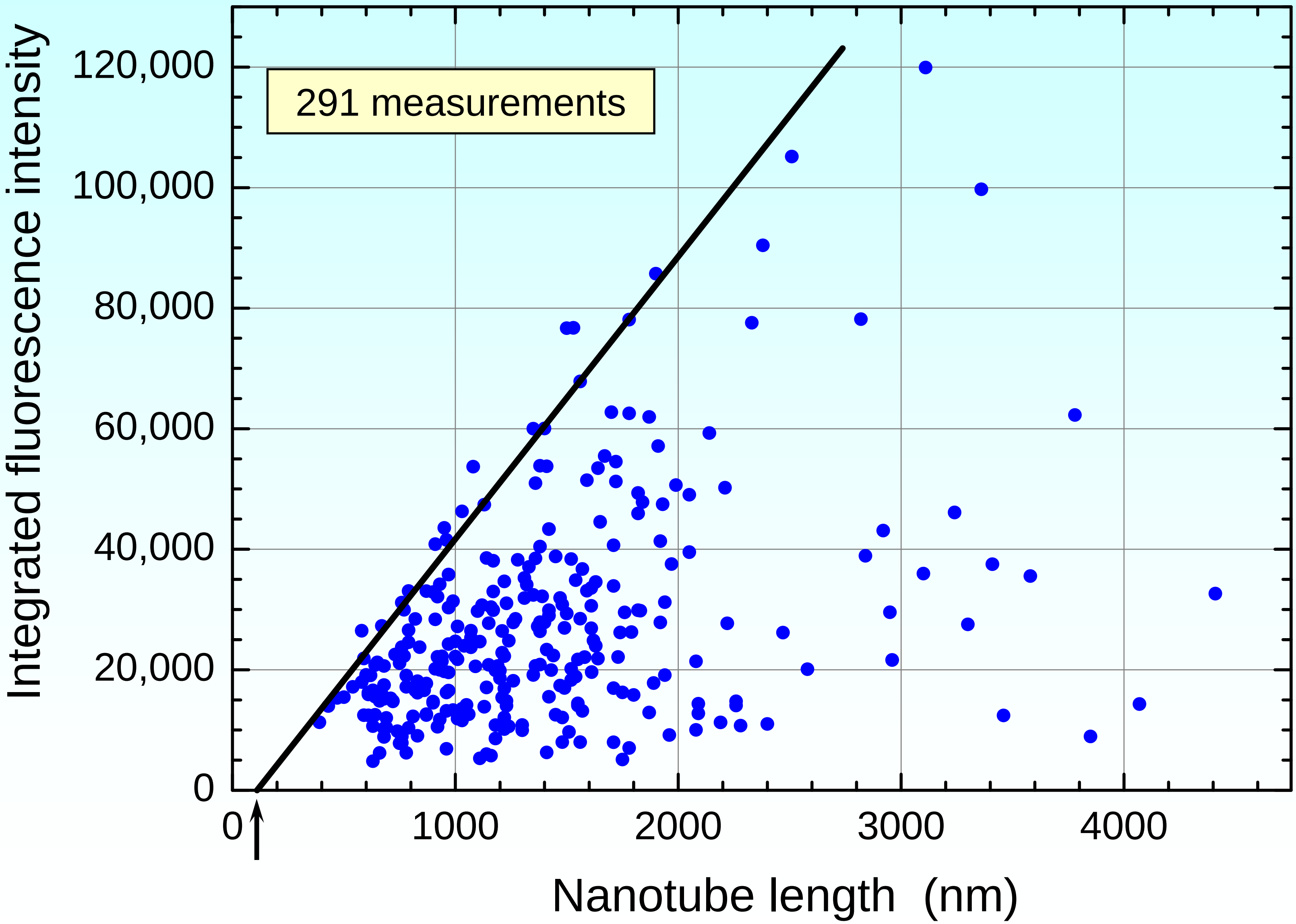
Fluorescence intensity vs. Length for (10,2) SWNTs



Findings

- Fluorescence quantum yield varies widely for all lengths
  (distribution of extrinsic quenching)

- Maximum emission intensity is linear with length

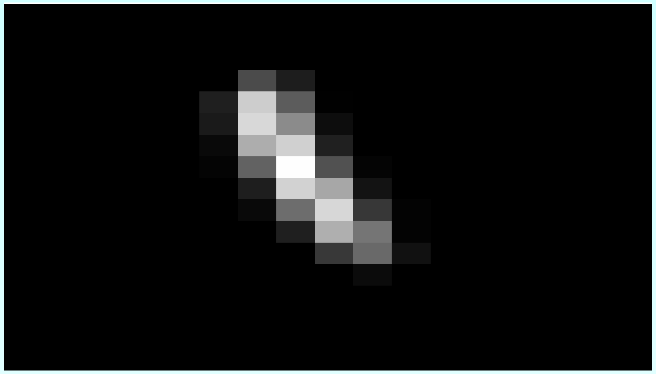
- SWNTs shorter than ~100 nm have unusually low emission yields
  (strong exciton quenching by ends)

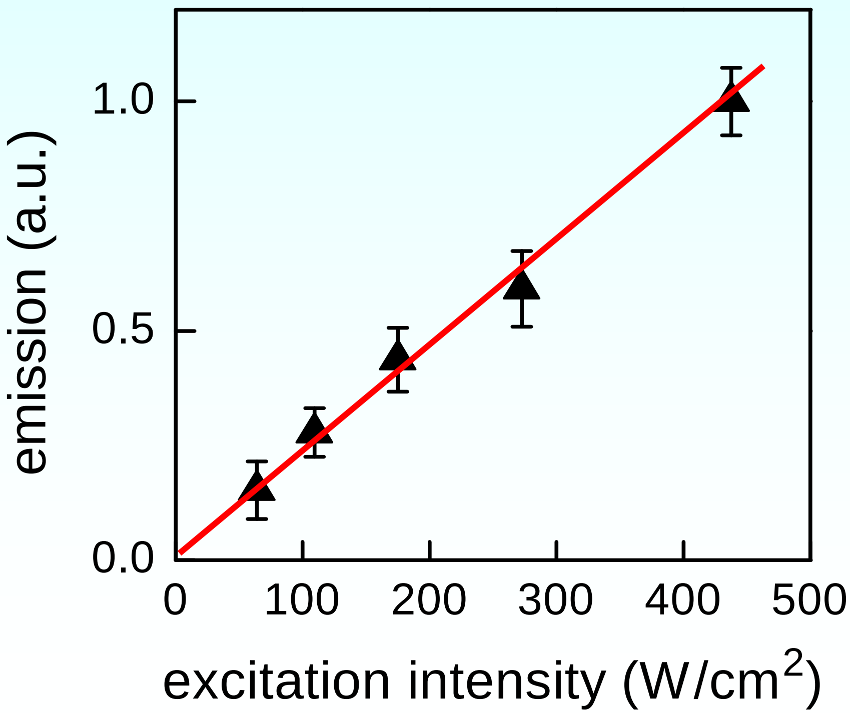
Studying extrinsic effects at the single nanotube level

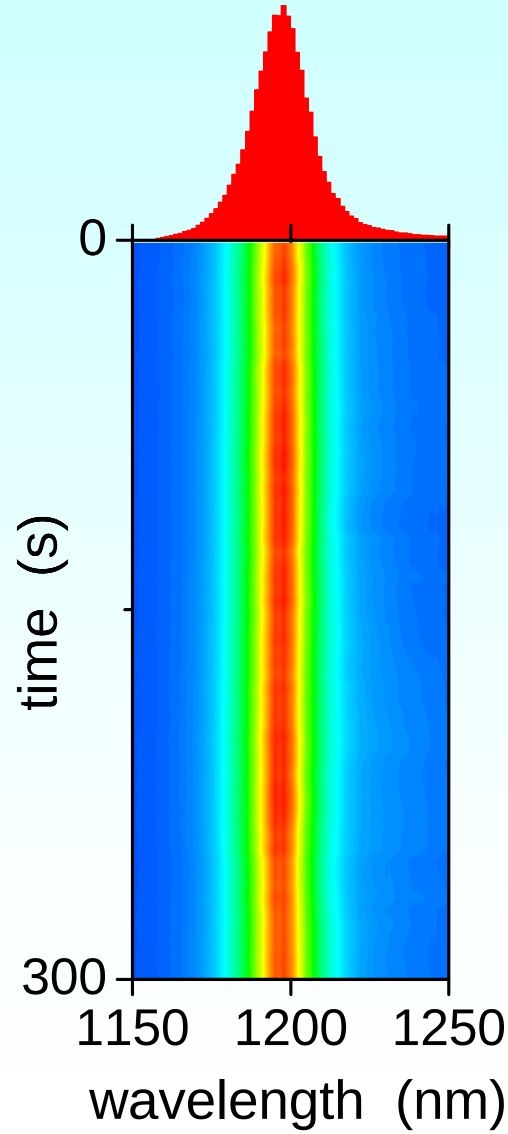
Fluorescence quenching by sidewall chemical reactions

L. Cognet et al., ***Science 316,*** 1465 (2007)

Single Nanotube Fluorescence Stability







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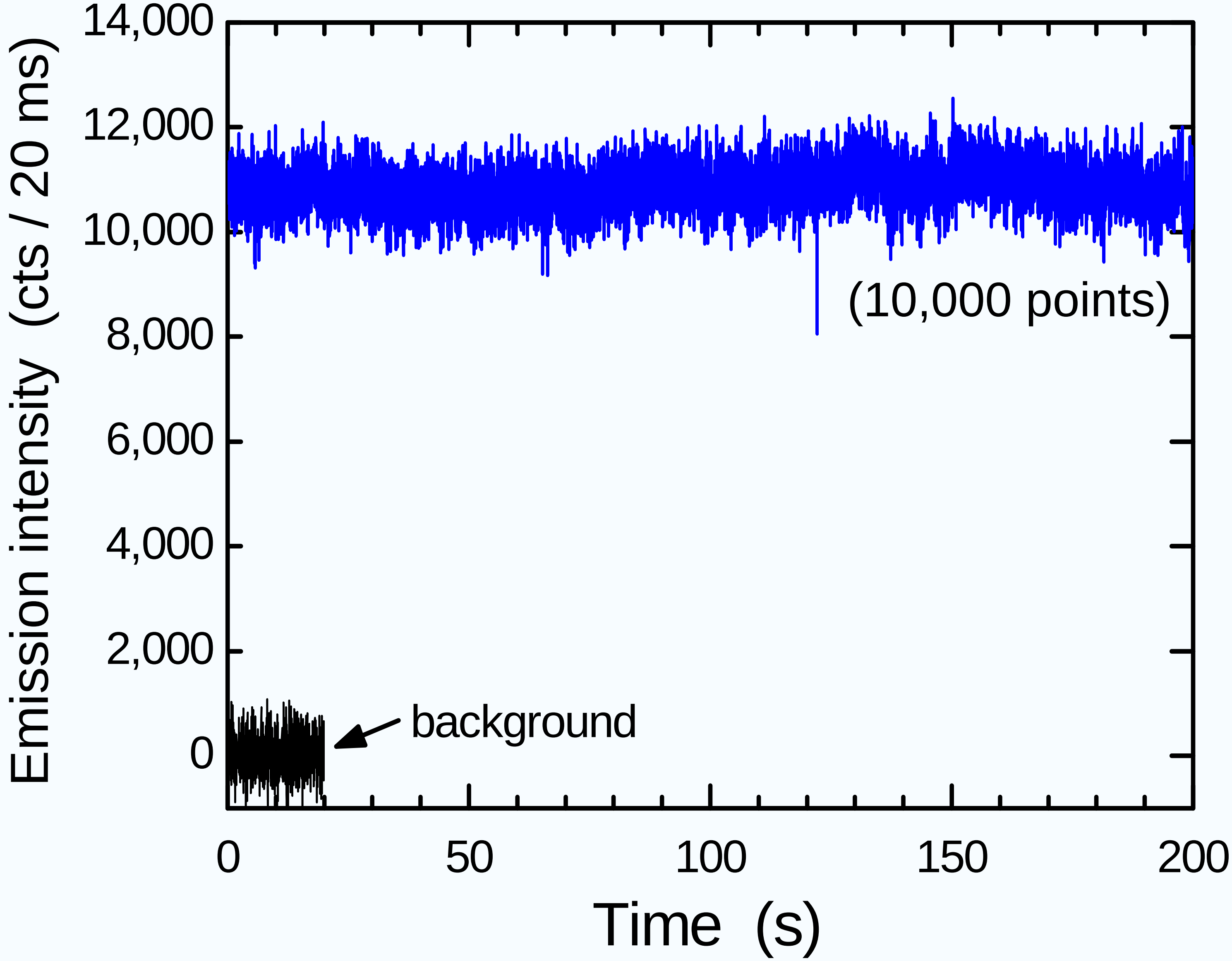
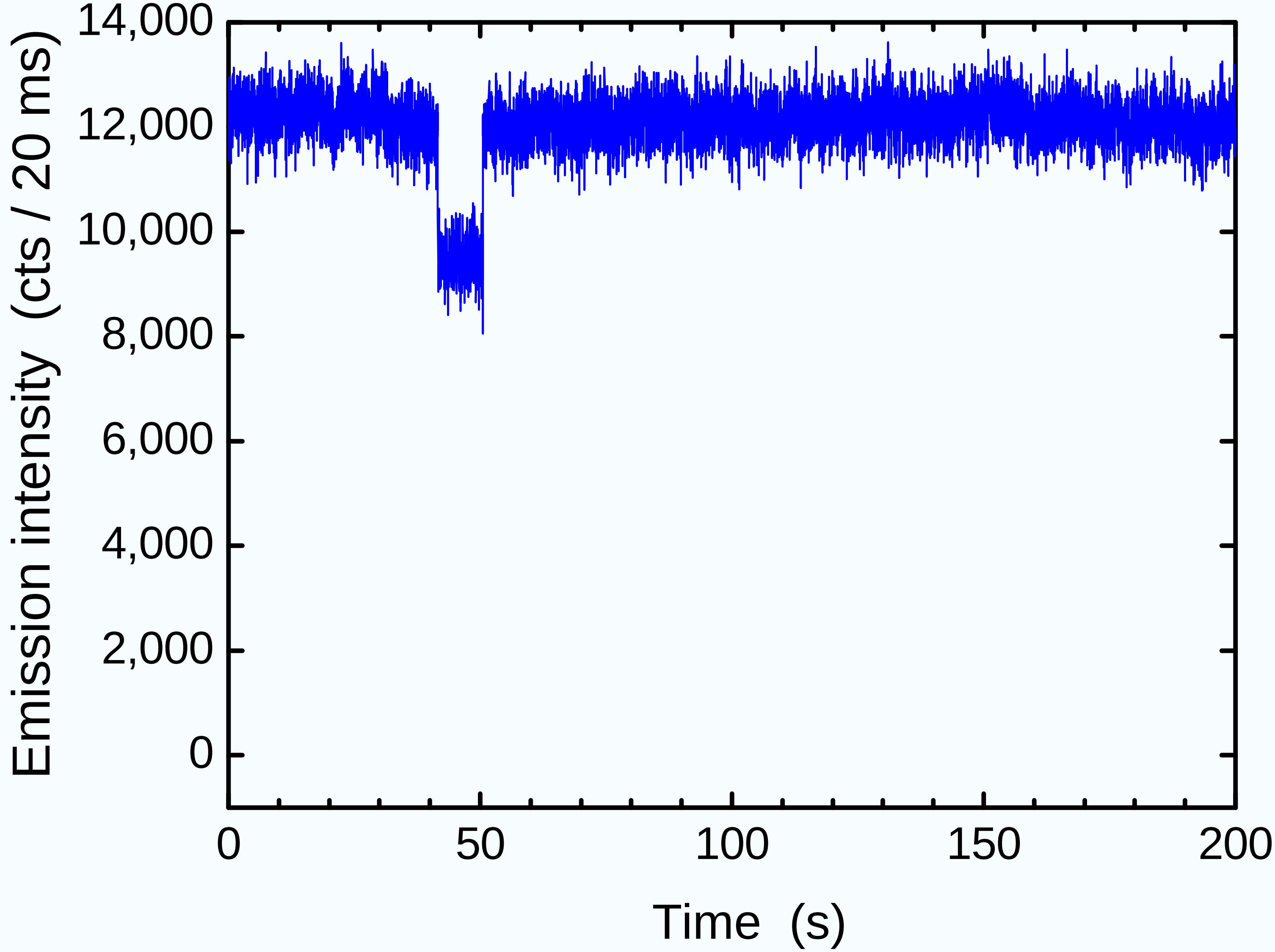
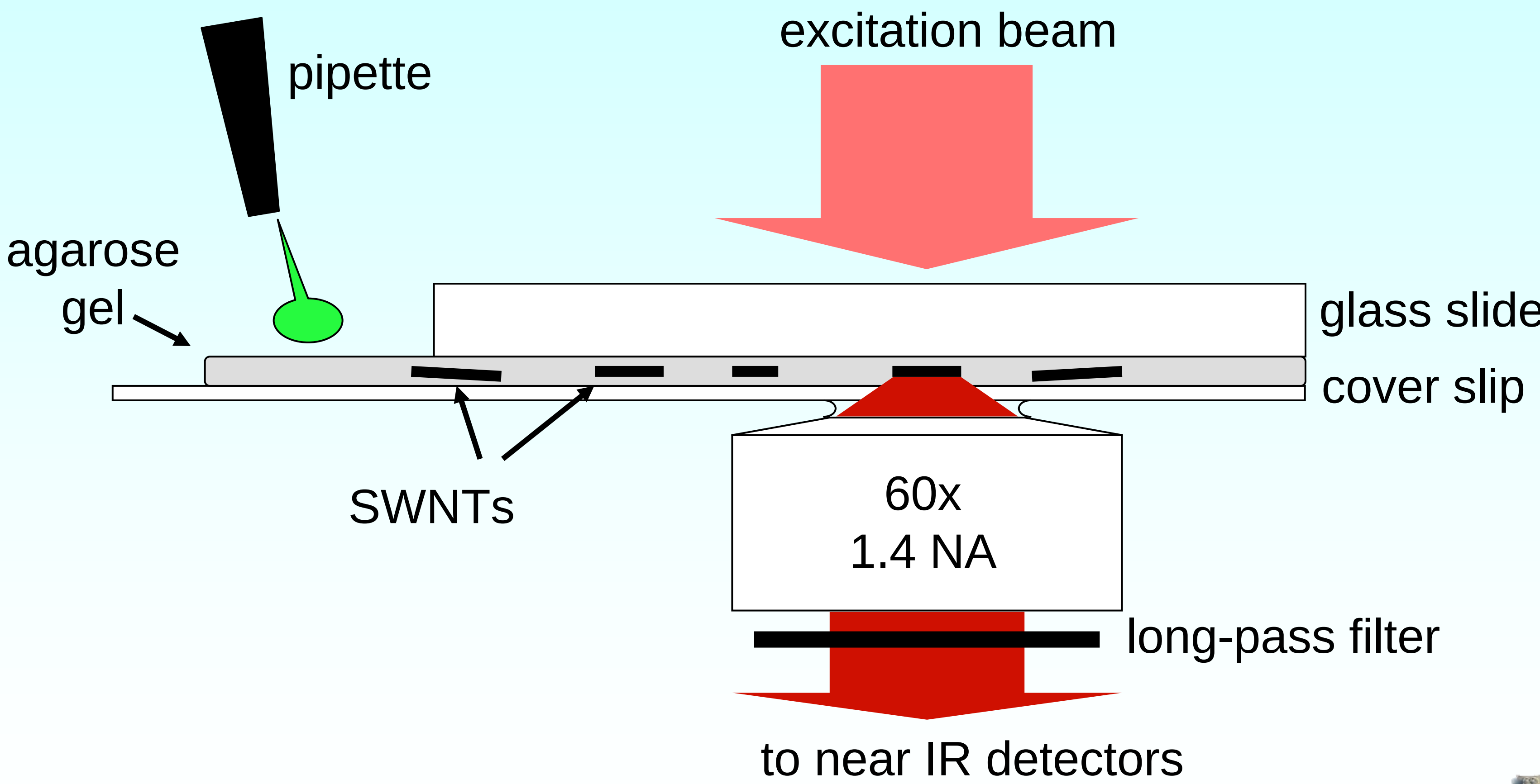
Single Nanotube Fluorescence at pH 7



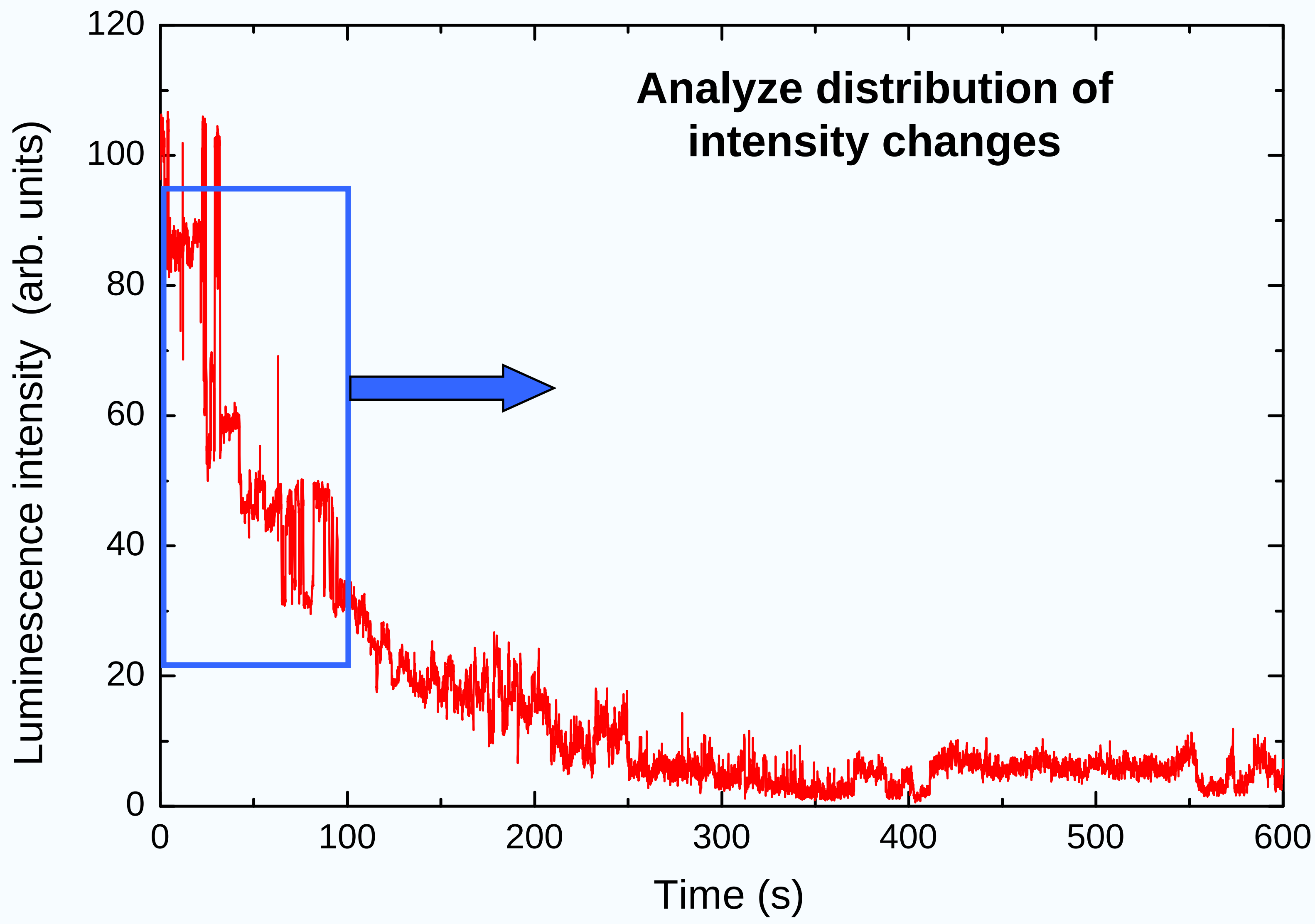
Single Nanotube Fluorescence at pH 7



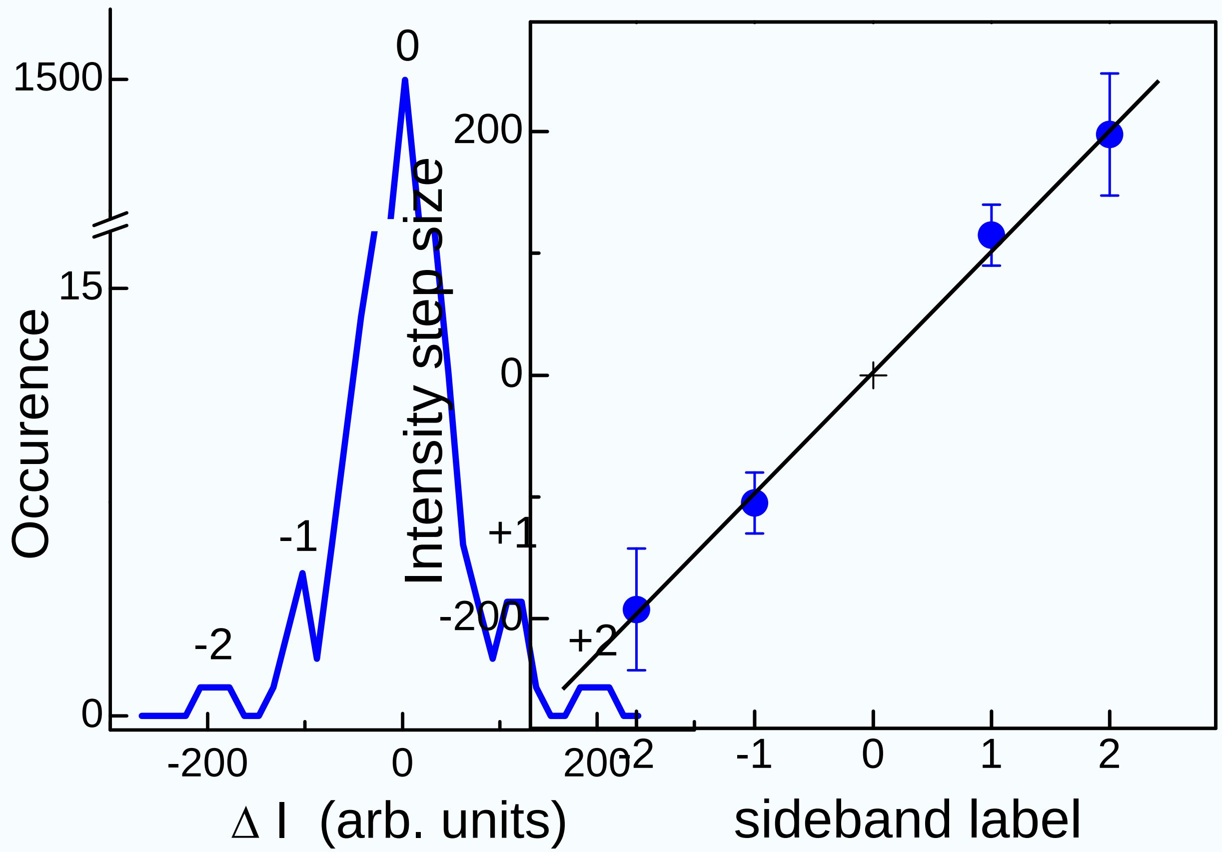
Measurement of Single Nanotube Reactive Quenching



Acid Quenching of Single Nanotube Fluorescence

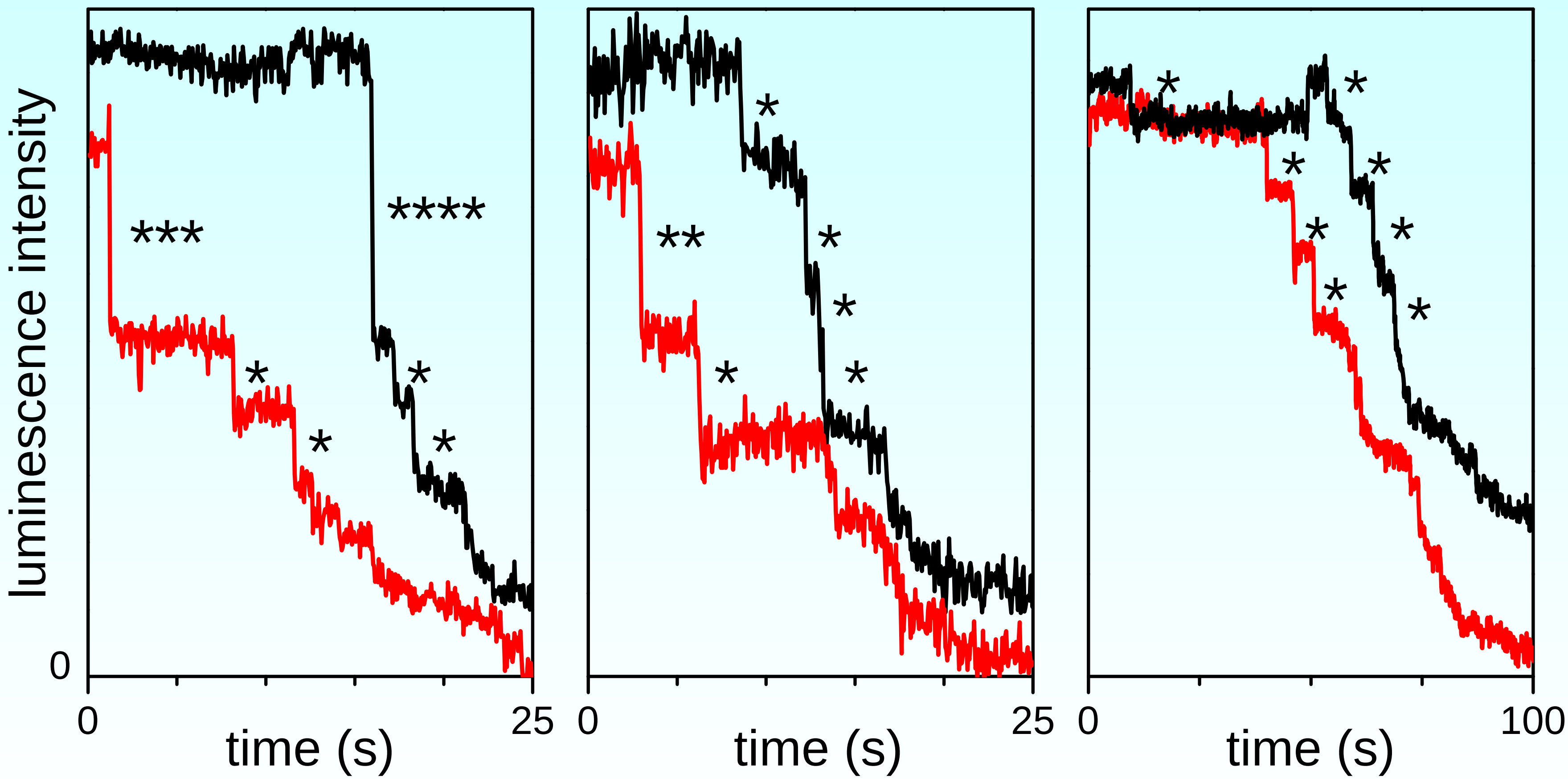


Distribution of Fluorescence Intensity Changes



Irreversible Quenching is also Stepwise

diazonium sidewall derivatization reaction



Steps are uncorrelated in time within a single nanotube

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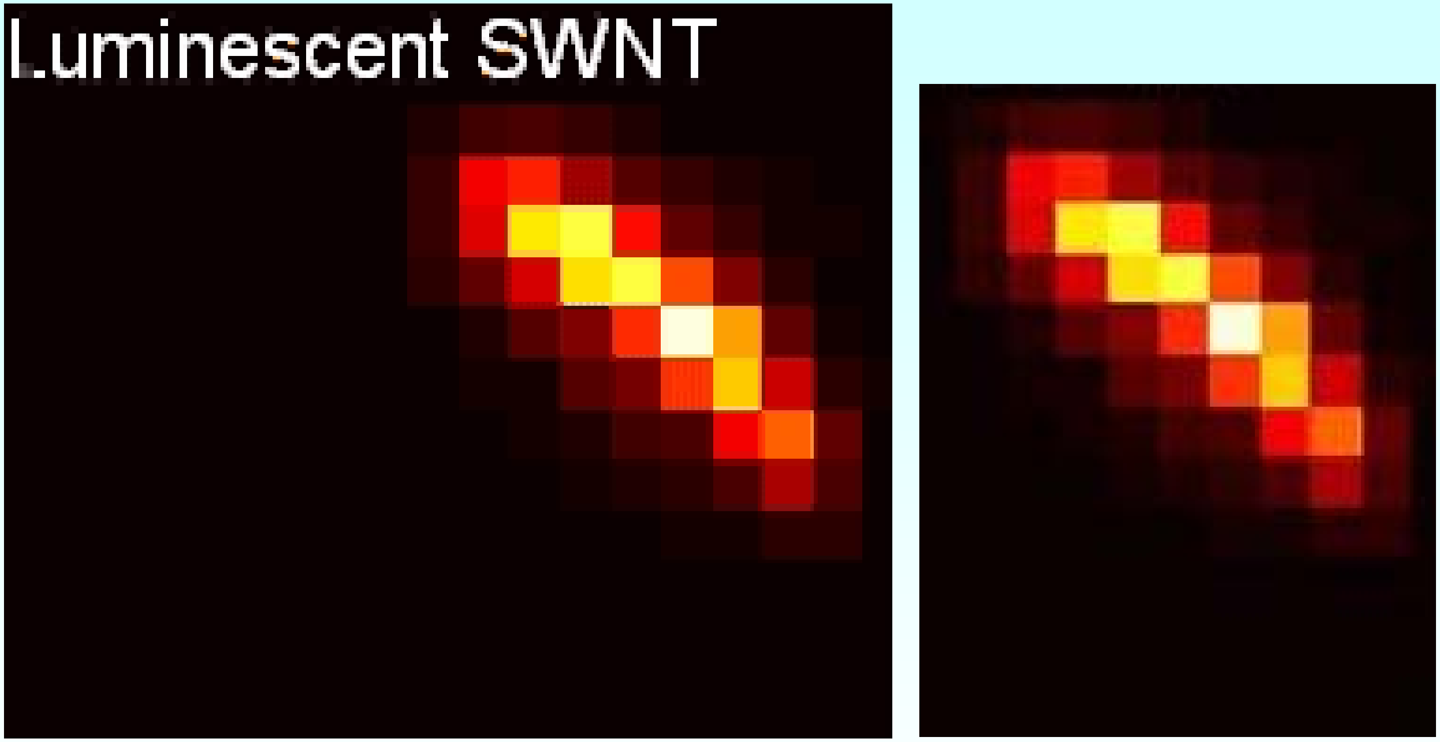
Local Changes in Emission Intensity



50 ms / frame

Steps are uncorrelated in position within a single nanotube (resolution = 670 nm)

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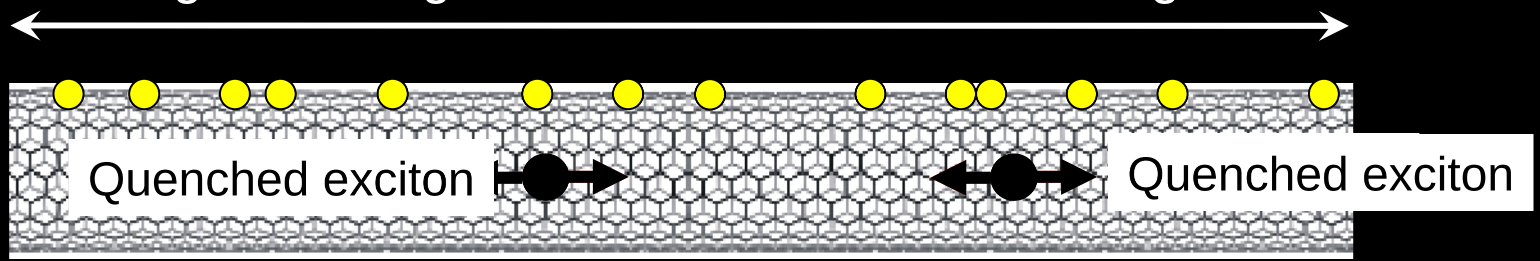
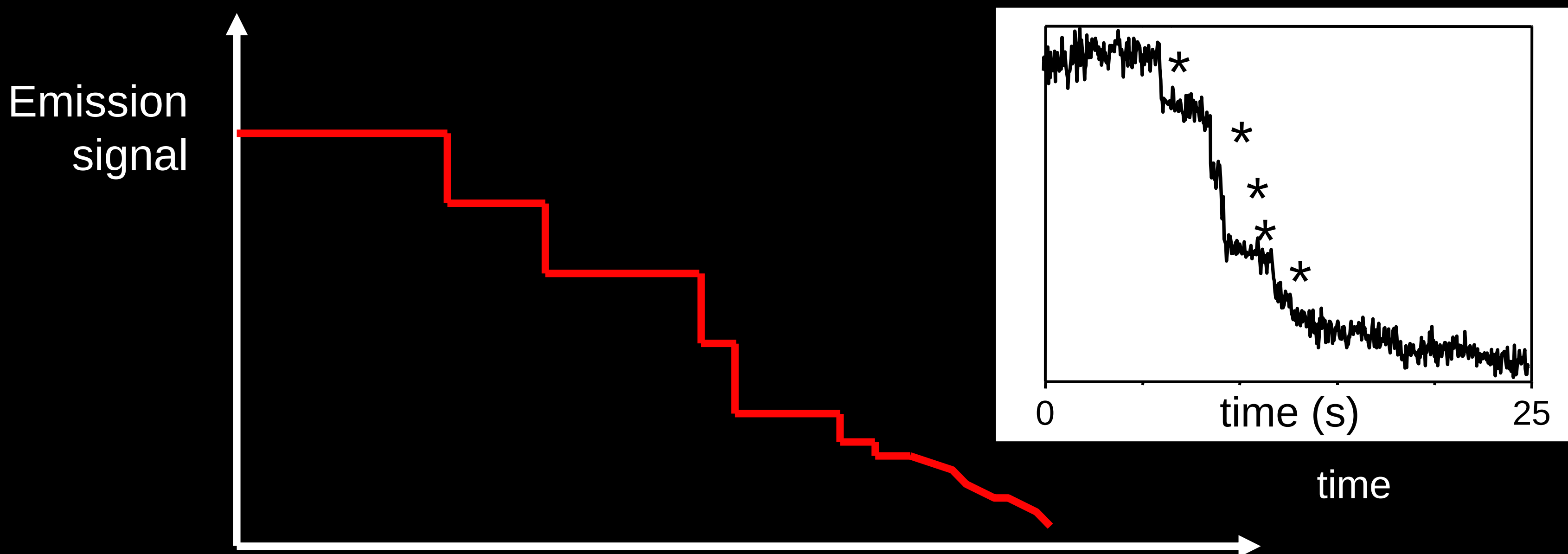
Model of Excitonic Quenching

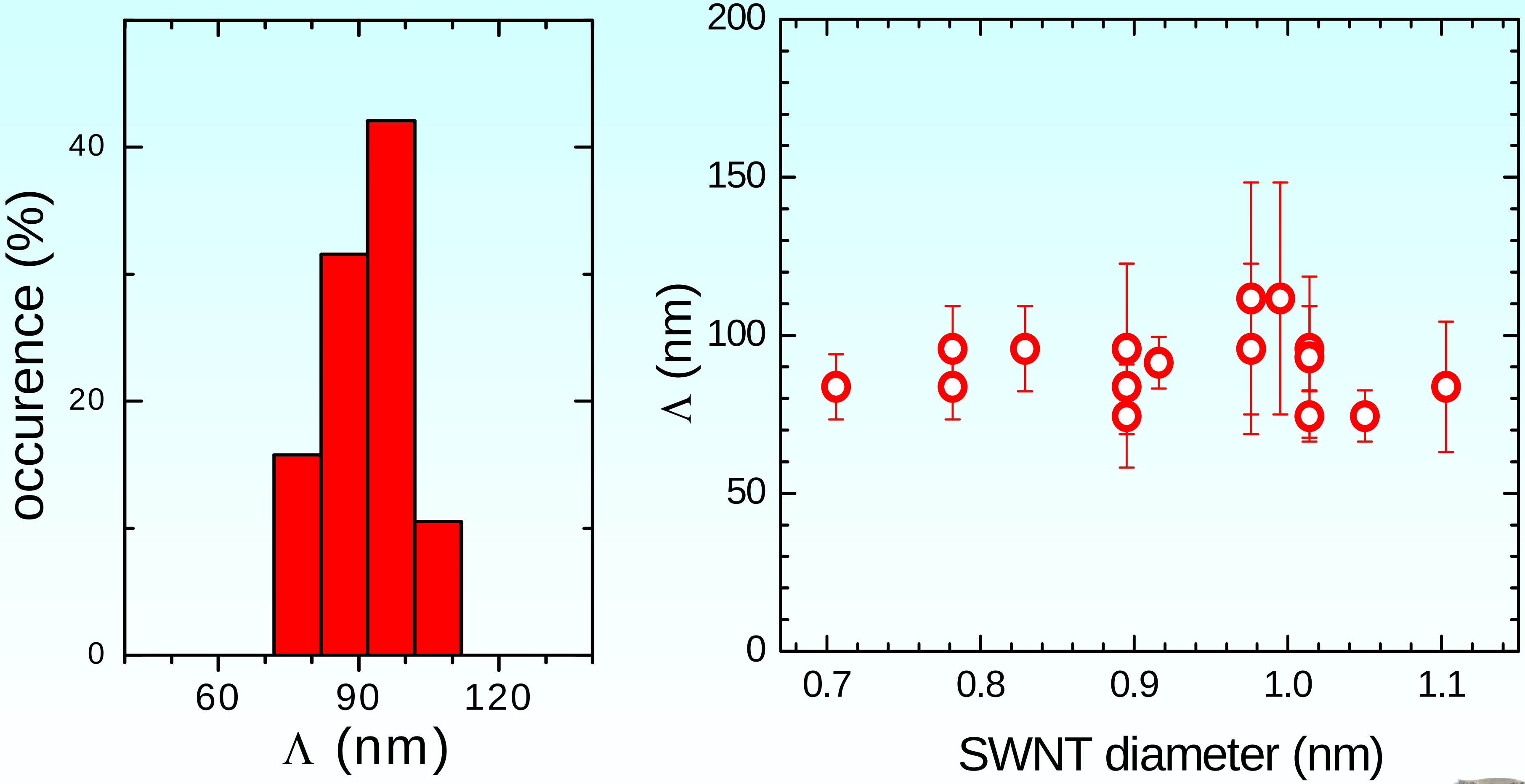
segment imaged in one diffraction-limited region



Fluorescent portion of the SWNT



Consistent Exciton Excursion Ranges



excursion range Λ = 90 nm

Findings

- An exciton visits ~10,000 carbon atoms during its intrinsic lifetime
- Each efficient quenching site can darken ~50 to 100 nm of the nanotube
- Fluorescence quantum yield is the most sensitive probe of SWNT condition

Conclusions

- Fluorimetry provides the best combination of:
  Sensitivity
  Convenience
  Detailed information on structures & condition

- Quantitative fluorimetric analysis of SWNT samples is nearly at hand

Co-Workers

My lab

Sergei Bachilo
Dmitri Tsyboulski
John-David Rocha
Tonya Leeuw
Laurent Cognet (Univ. of Bordeaux)

Collaborators

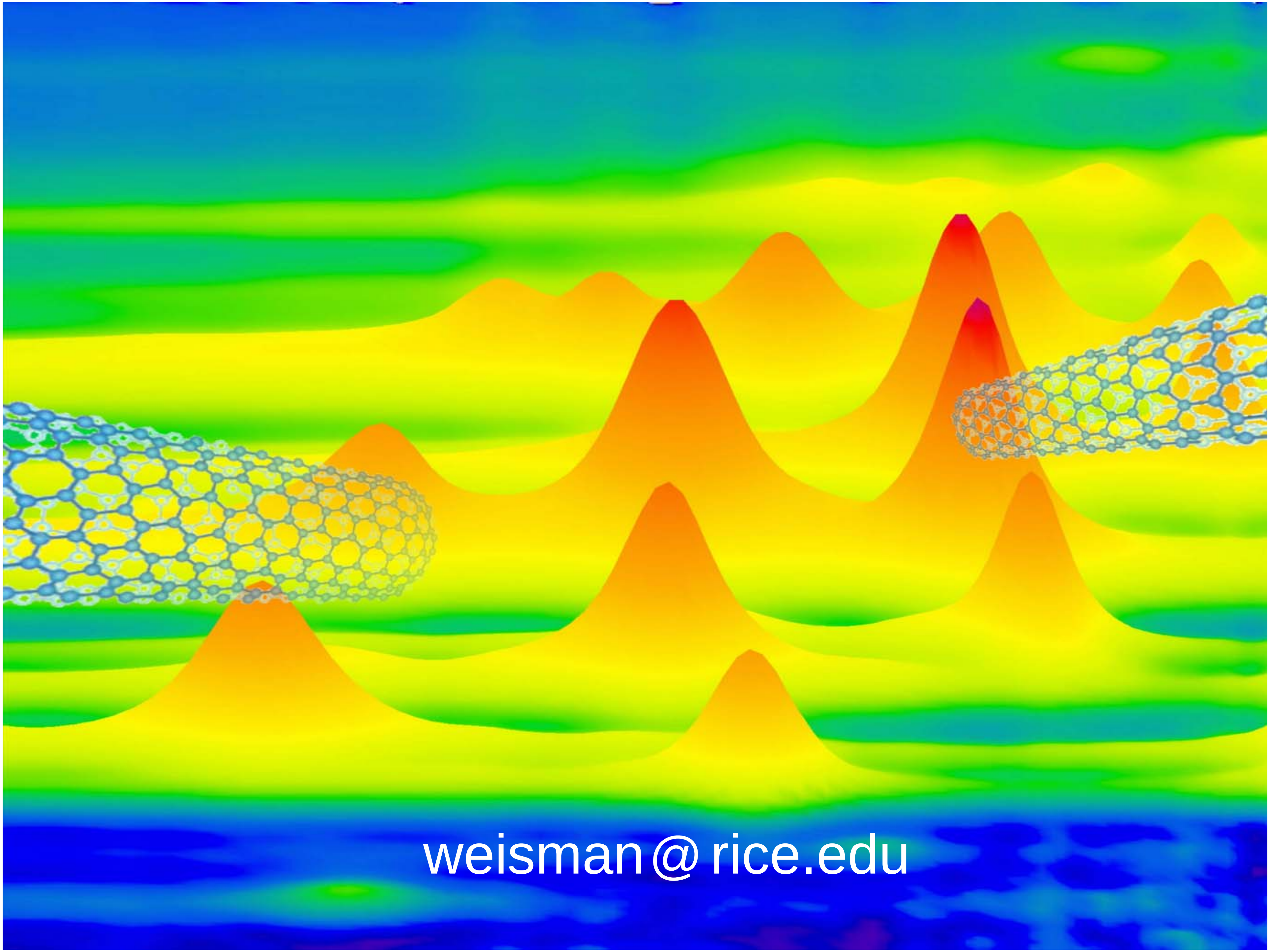
Dell Doyle, James Tour (Rice)

Support

NSF Center for Biological and Environmental Nanotechnology

Welch Foundation

Applied NanoFluorescence, LLC


weisman@ rice.edu