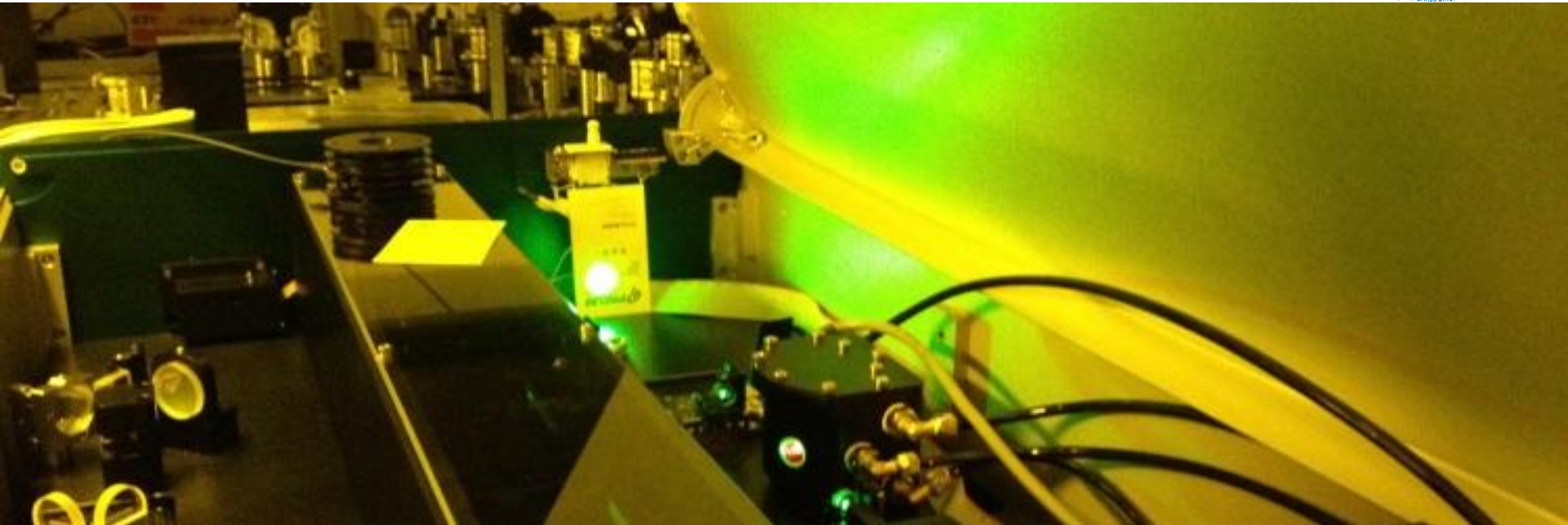
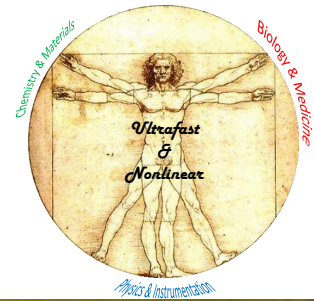


Femtosecond Spectroscopy Unit



Keshav M. Dani



OIST

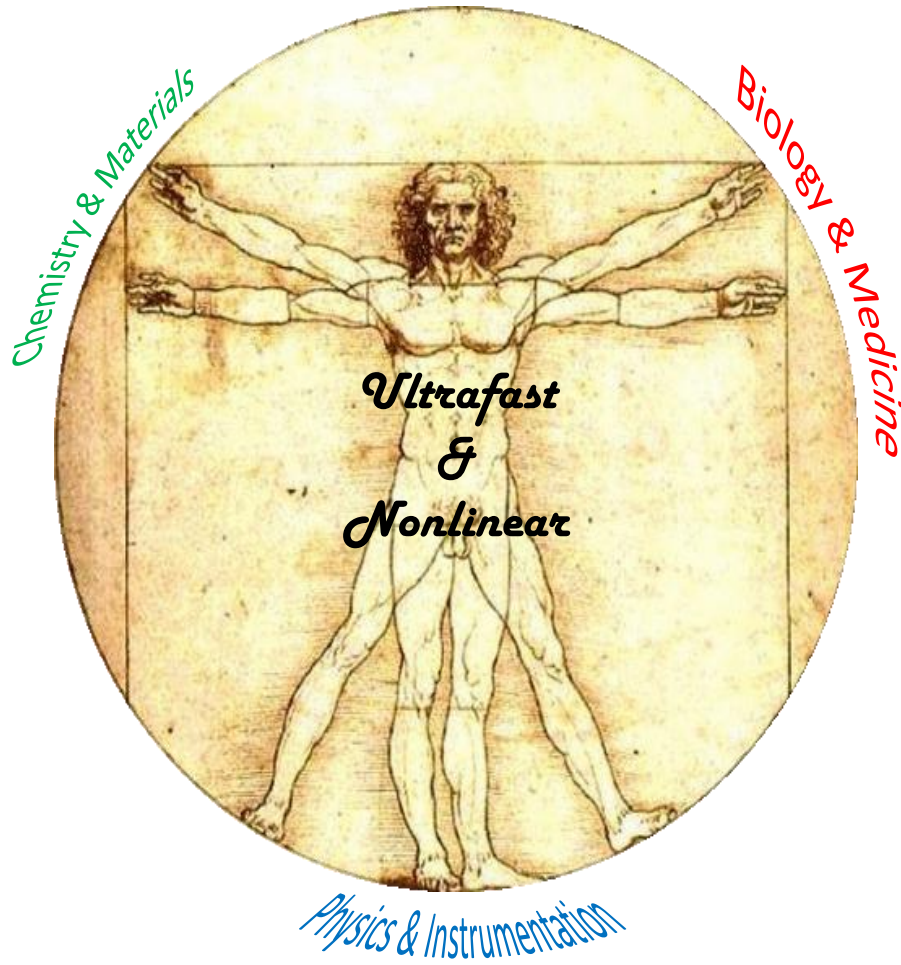
OKINAWA INSTITUTE OF SCIENCE AND TECHNOLOGY GRADUATE UNIVERSITY

Femtosecond Spectroscopy Unit

July 2013



RESEARCH INTERESTS & PROJECTS

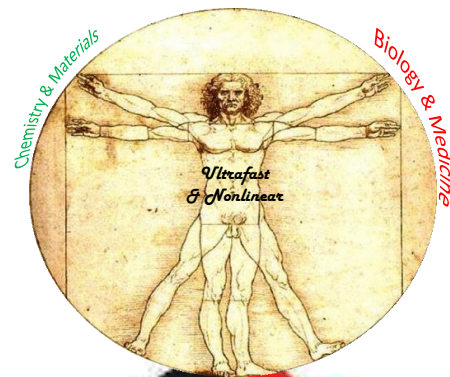


Experimental Capabilities



High Power/
Low Rep. Rate
LASER SYSTEM

HIGH ENERGY
LAB



THEORY
PROGRAM



Light Matter
Interactions, Many-
Body Correlations

MICROSCOPY
LAB

Low Power/ High
Rep. Rate
LASER SYSTEM

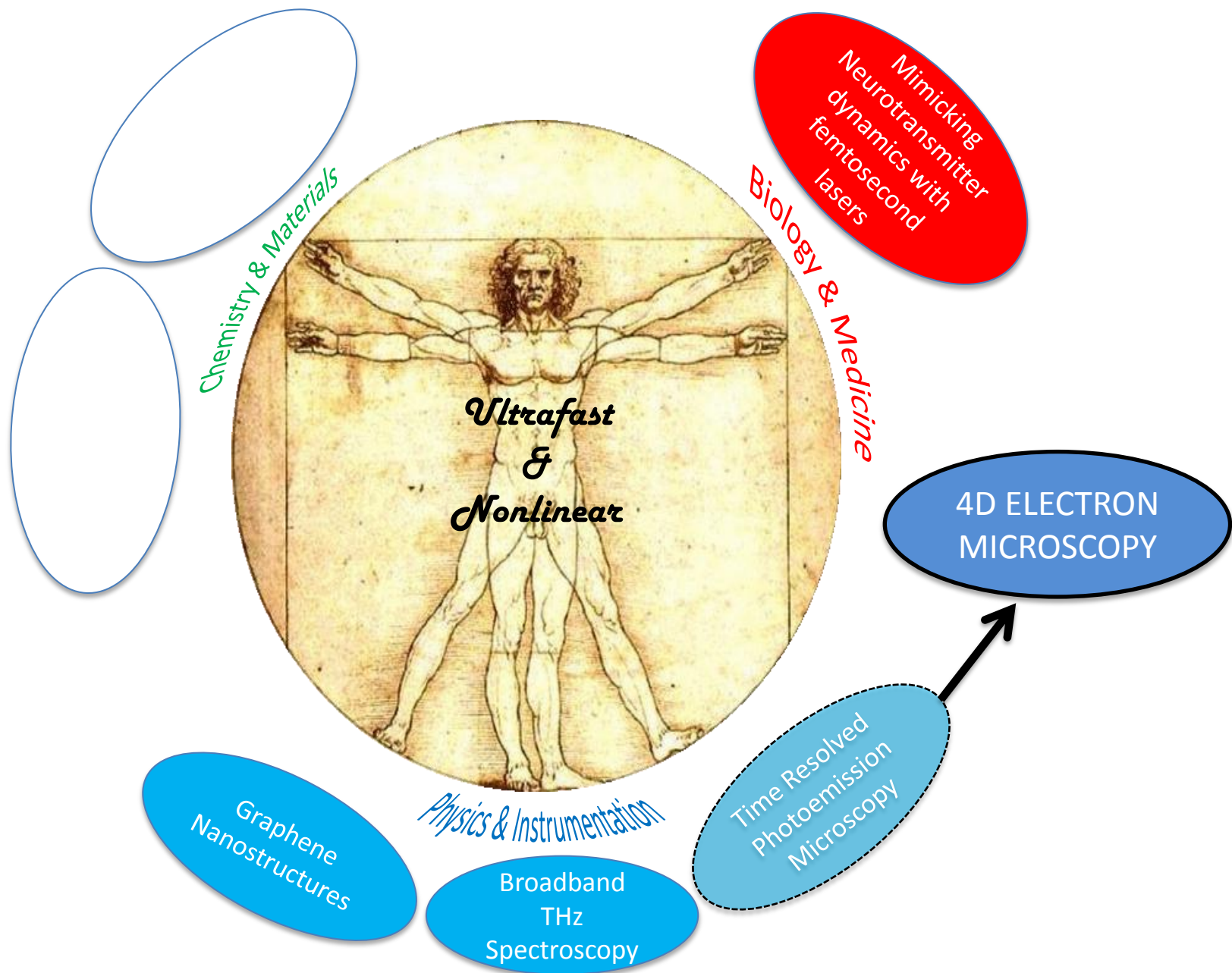
LEEM LAB



ELEC. MICROSCOPY
10nm Res., 150meV
Energy Res.



RESEARCH INTERESTS & PROJECTS



Intro to 4D Electron Microscopy

In 1959, Feynman talked of the bottomless possibilities in the field of nanotechnology.

Richard Feynman Tiny Machines



The Feynman Lecture
on Nanotechnology

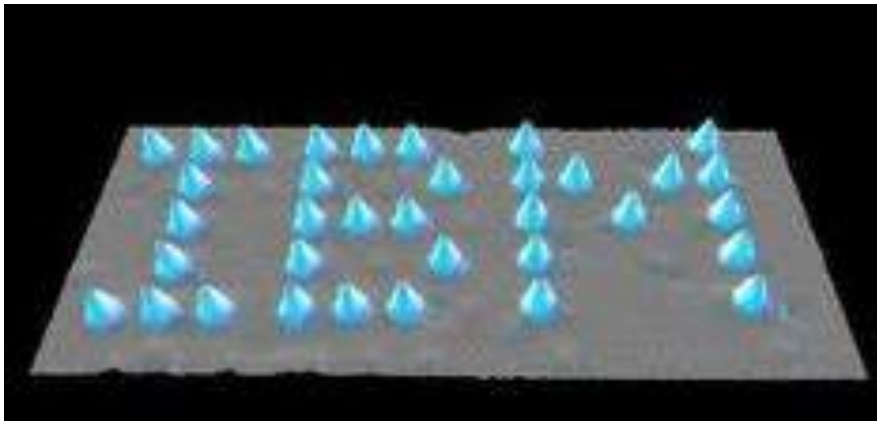
*Nanomachines: a hundred tiny hands,
submicroscopic computers*

*Nanofabrication: Arranging the atoms one by
one.*

*Nanoimaging: 100X better electron
microscopes to sequence DNAs*

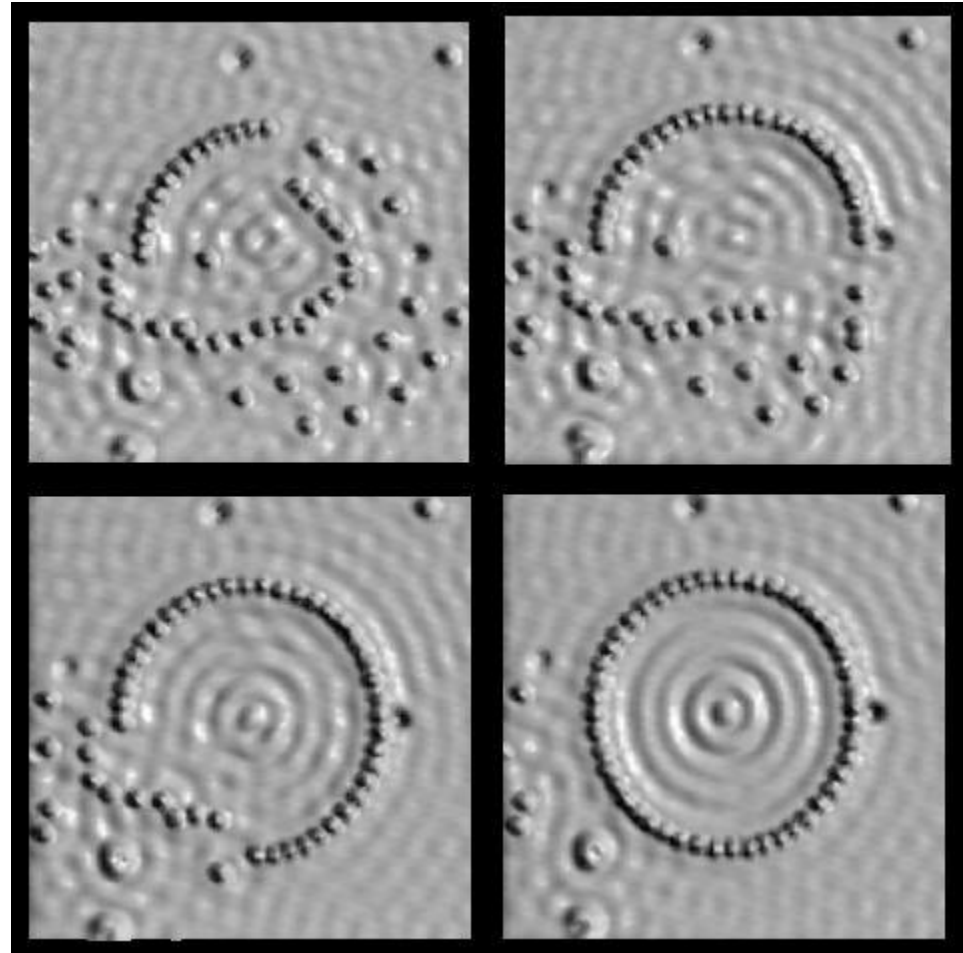
Intro to 4D Electron Microscopy

In 1989, Don Eigler at IBM wrote IBM with 35 Xe atoms using a scanning tunnelling microscope.



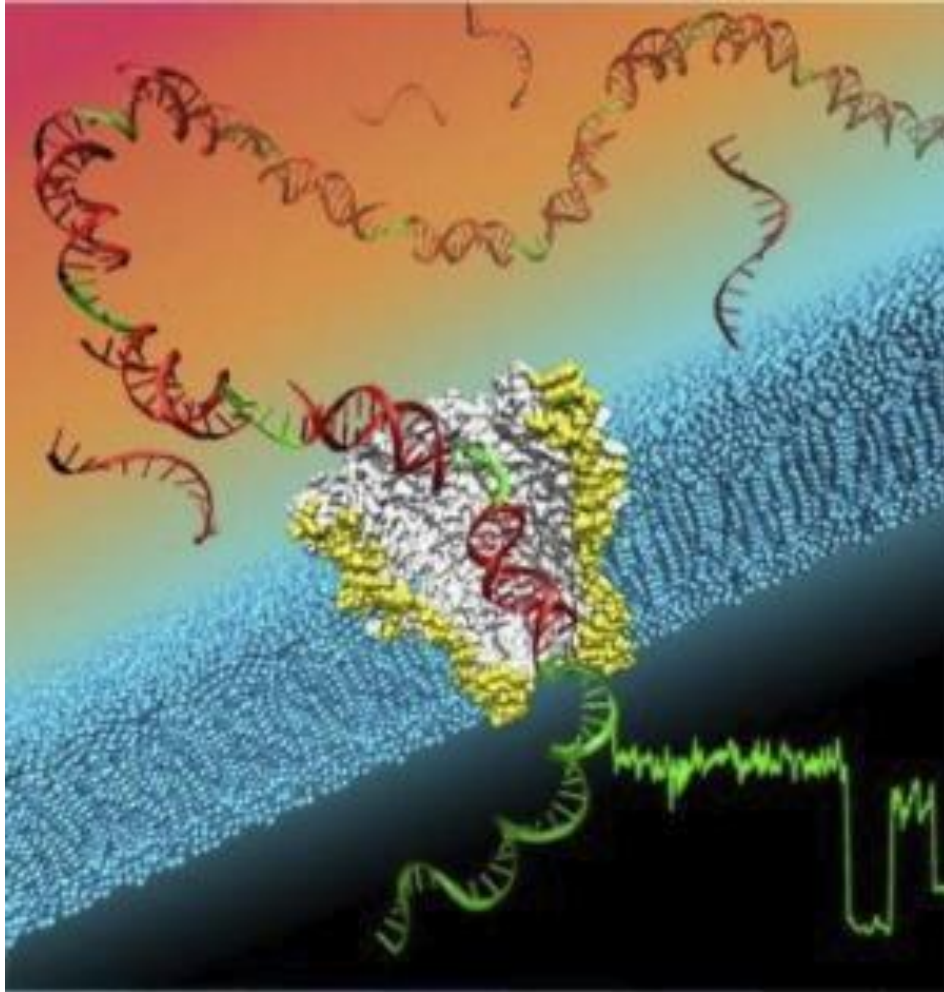
Eigler, D. *et al.* *Nature* **344**, p. 524-526 (1990)

Crommie, M., *et al.* *Science* **262**, p. 218-220 (1993)



Intro to 4D Electron Microscopy

Nanotechnology allows the rapid sequencing of DNA.



U. of Wash., 'Nanoscale DNA Sequencing Could Spur Revolution in Personal Health Care', ScienceDaily 21st Aug. 2010

Nanopore DNA sequencing with MspA. [10.1073/pnas.1001831107](https://doi.org/10.1073/pnas.1001831107)

Intro to 4D Electron Microscopy

One of the key advances in studying the nano- and later sub-nano world has been the rapid development of Electron Microscopy



E. Ruska Archives



Intro to 4D Electron Microscopy

One of the key dimensions missing from this discussion is Time!

Initial State



Final State

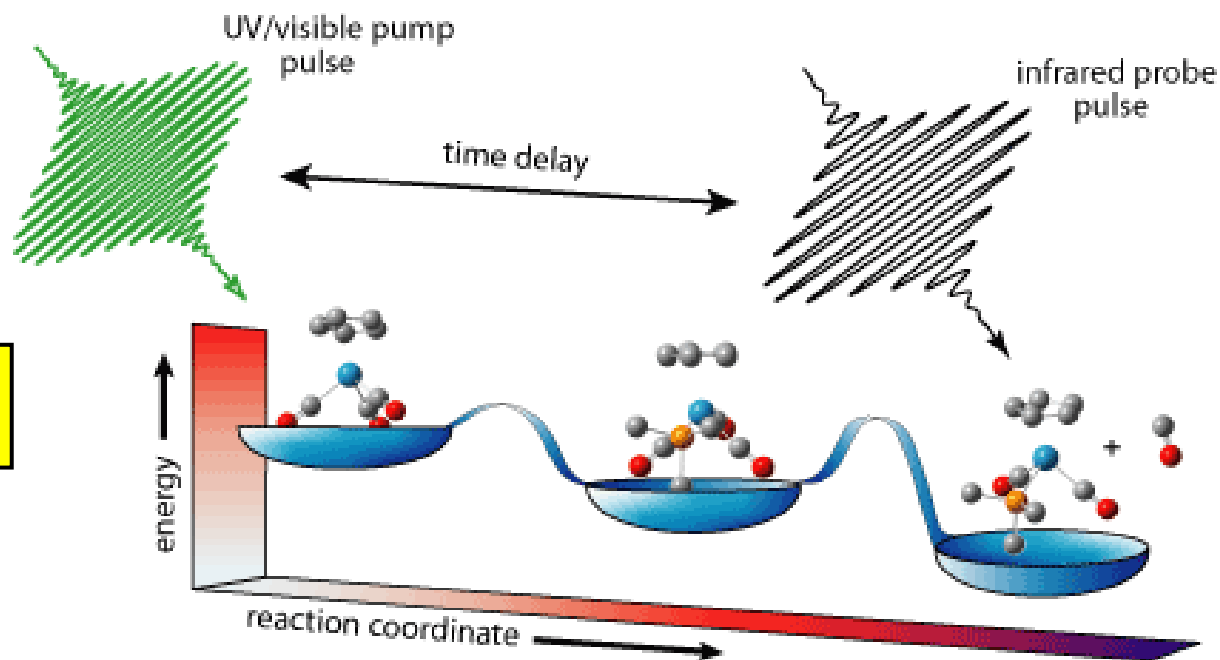
The first documented evidence of high-speed photography is in 1877, when Leland Stanford paid Muybridge to settle a bet about whether racehorses were ever airborne.



Intro to 4D Electron Microscopy

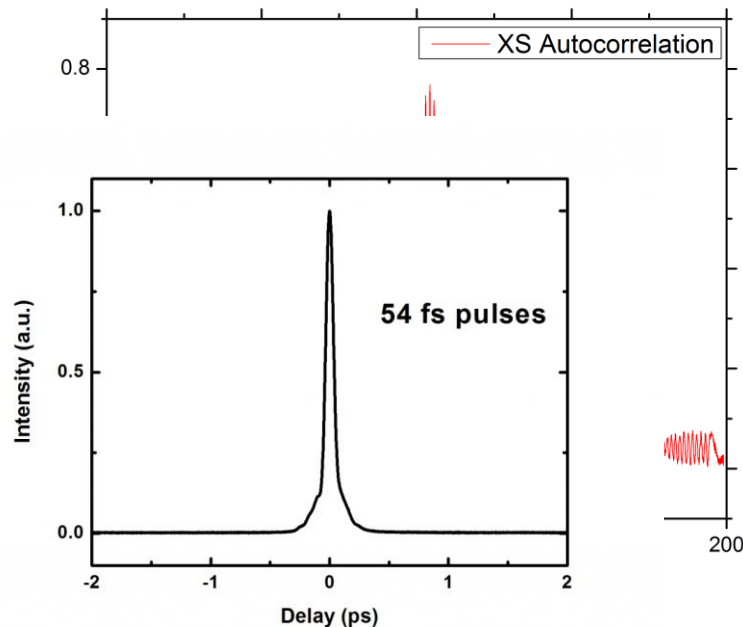
Optical pulses may not provide good spatial resolution, but they provide excellent temporal resolution!

Femto Chemistry:
Developed by A. Zewail



Intro to 4D Electron Microscopy

Over the past few decades, temporal resolution has gone from a few picoseconds to attoseconds, with applications from science to industry!



67 as pulse at UCF

Dr. Chang, UCF

High Peak Power Pulses
with Fiber Lasers

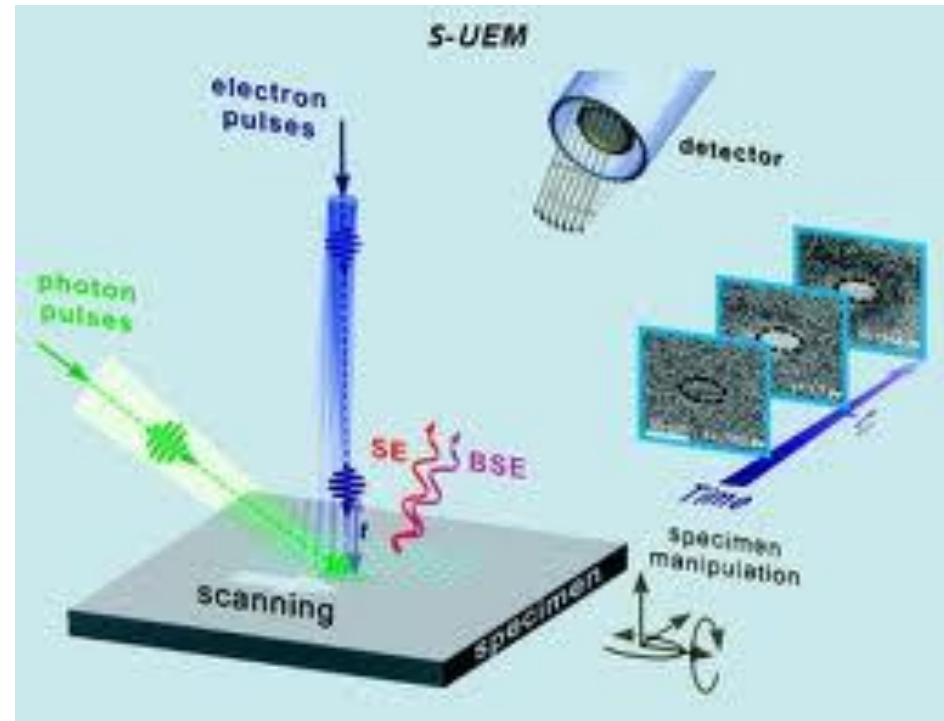
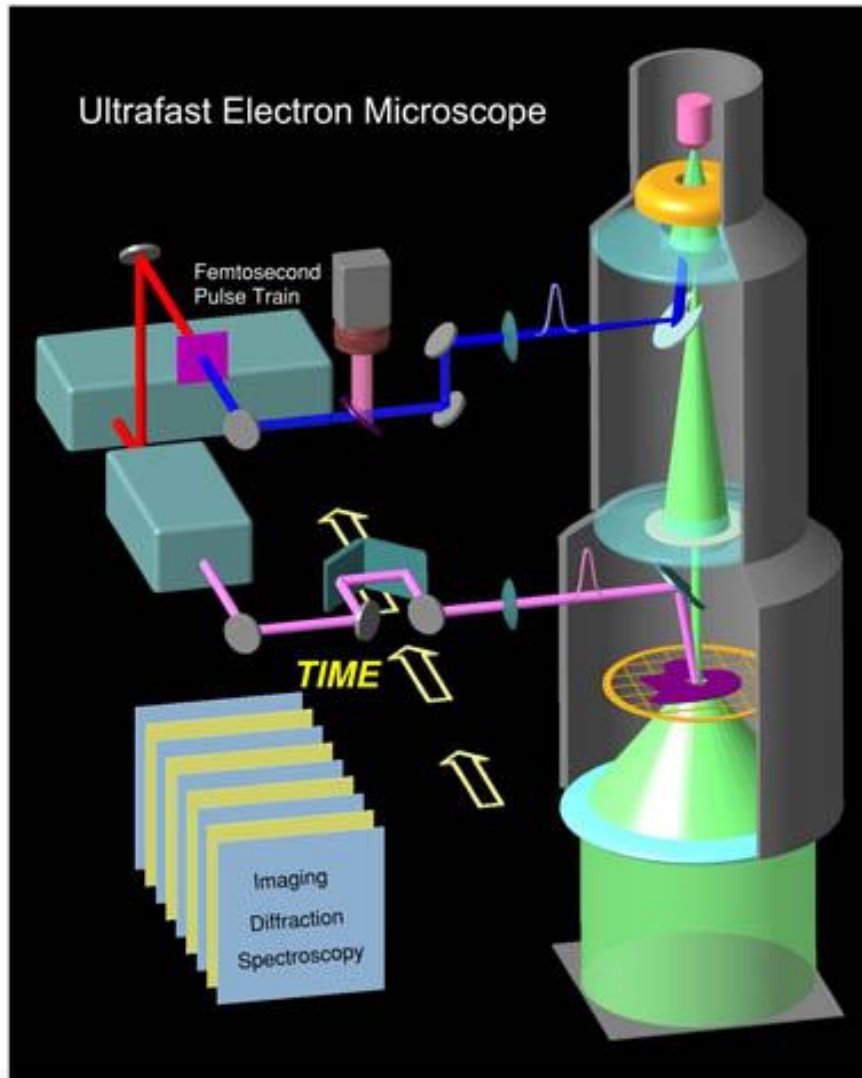
Intro to 4D Electron Microscopy

4D Microscopy: The ability to study phenomena with high temporal and spatial resolution has obvious implications.

- Single (sub) particle imaging
- Nanomechanical Motion
- Molecular Movies, Electron Videos
- Phase Transition
- Exploring new scientific domains
 - Spatial fluctuations on the femtoscale, or
 - Temporal changes in a high res. image

Intro to 4D Electron Microscopy

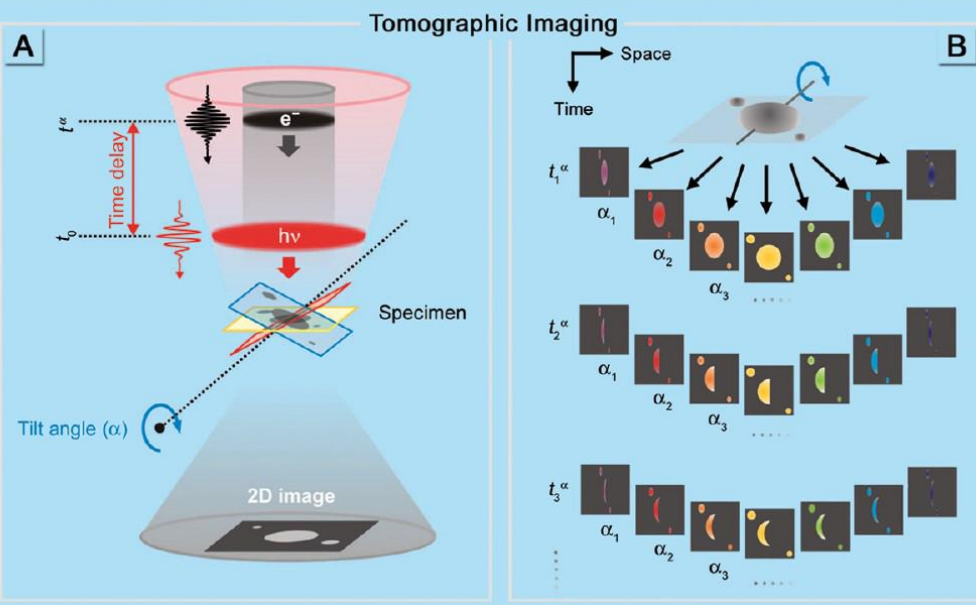
One combines Ultrafast Spectroscopy with Electron Microscopy to get both – high temporal and spatial resolution.



Lobastov, V. A. et al. Proc. Natl. Acad. Sci. U.S.A. 2005, 102, 7069.

Intro to 4D Electron Microscopy

One gets the three spatial dimensions by tilting the sample and using reconstruction algorithms.



Intro to 4D Electron Microscopy

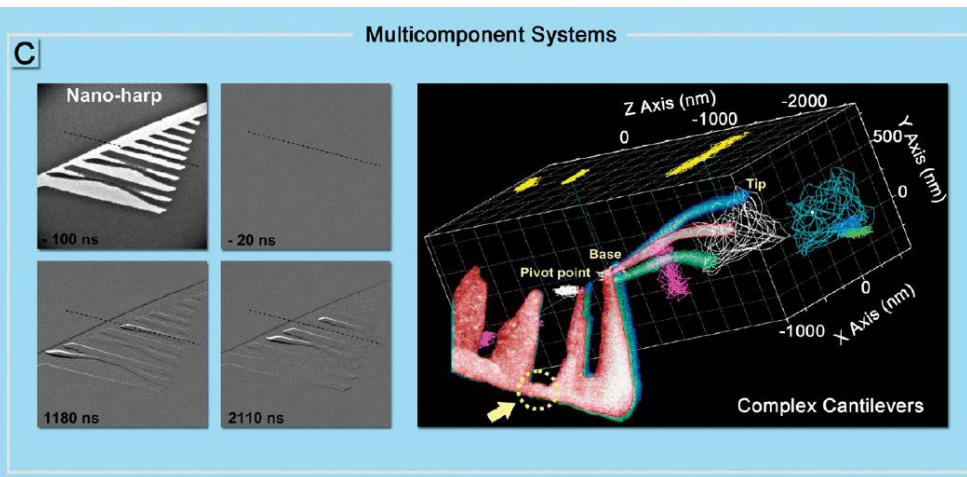
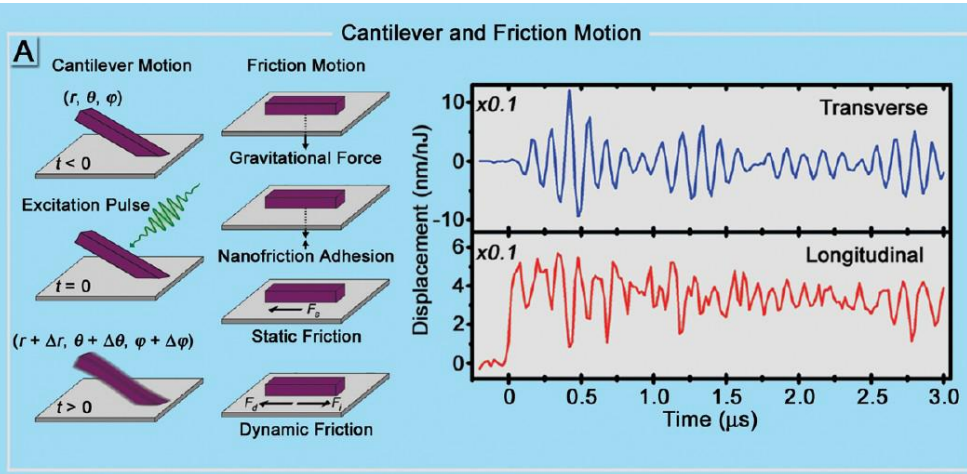
Space Charge Effect: Maintaining temporal resolution with electron packets is a challenge due to columbic repulsion between electrons.

SINGLE ELECTRON PACKETS

- Weak photoemission, so only $\sim 1\text{e/pulse}$.
- Requires many pulses to acquire image
- Requires reversible photoexcitation and relaxation to ground state
- Requires high-repetition rate lasers, hence low power in pump pulse

Intro to 4D Electron Microscopy

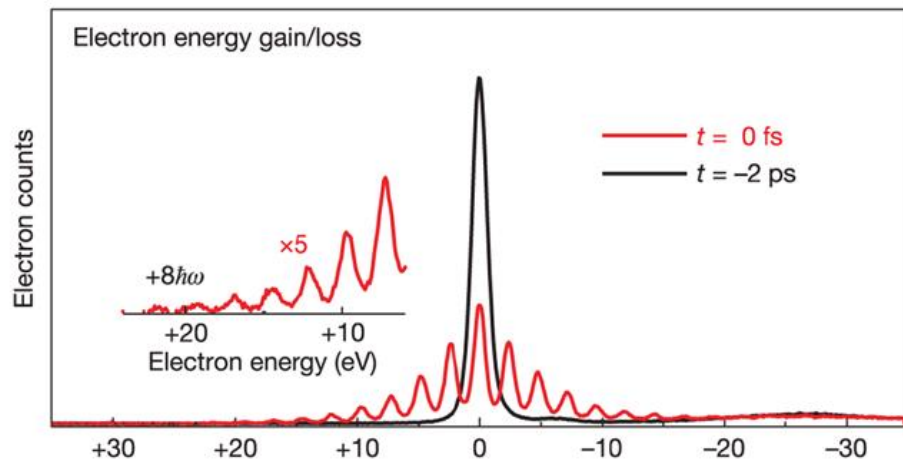
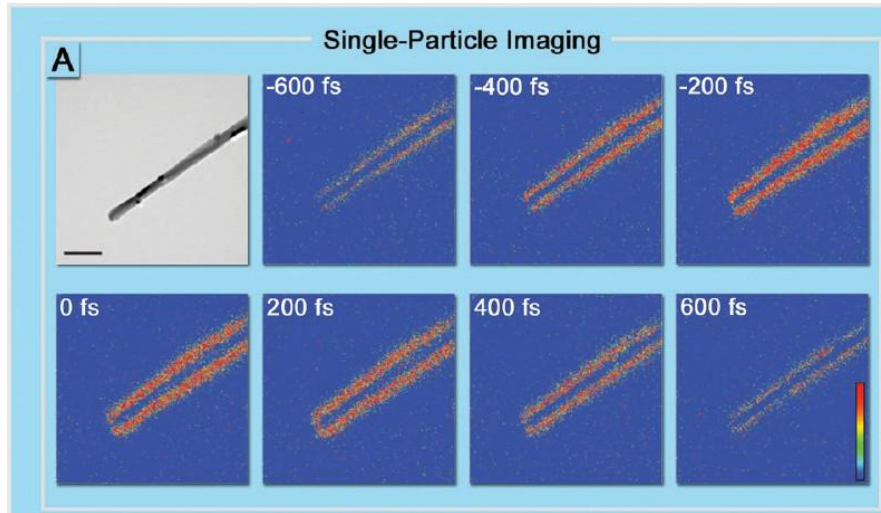
Observation of Nanomechanical motion: Nano Levers, Nano Membranes and Nano Harps!



- Cu Crystals lying on surface or fixed at one end (cantilevers)
- Extract material properties of system through mapping of cantilever motion in space over time.
- Allow the construction of nanomusical instruments where design determines pitch.
- To what nanoscale limit are classical material properties valid?

Intro to 4D Electron Microscopy

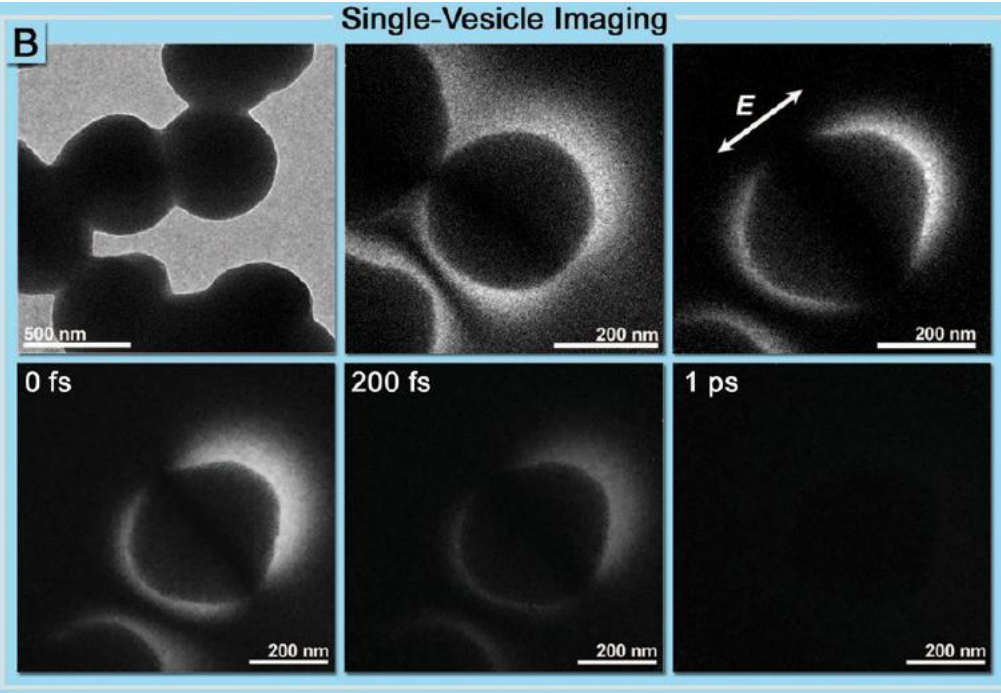
Imaging dynamics of single (sub) particles.



- Photon Induced Near-Field Evanescent Microscopy (PINEM) initiated by pump pulse
- Electrons interact with evanescent photon field and can be imaged
- Strong e-photon interaction provides high contrast images of single particles

Intro to 4D Electron Microscopy

Imaging of polarization sensitive protein vesicles with PINEM



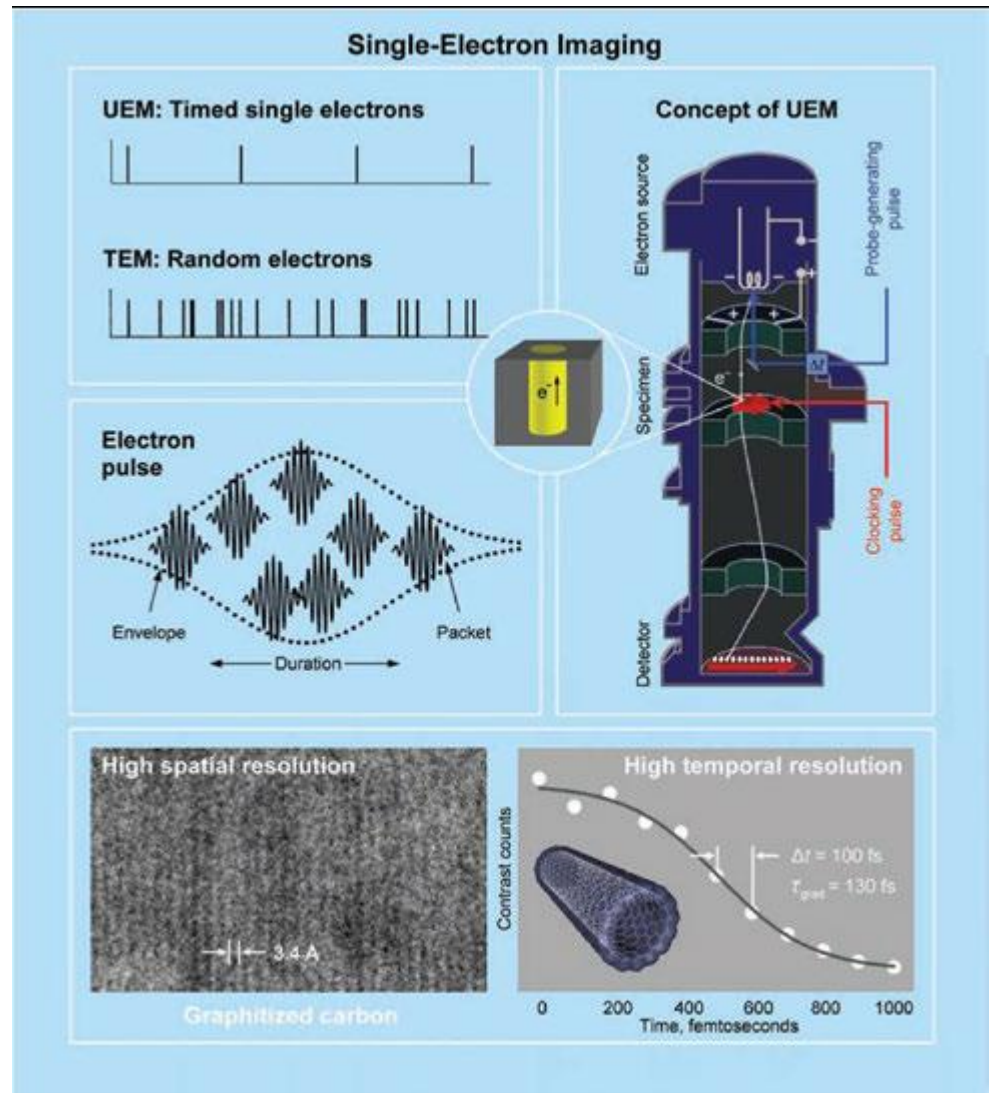
- Due to low pump absorption, high pump energies can be used to enhance PINEM contrast without damaging biological samples

Intro to 4D Electron Microscopy

The availability of the first commercial 4D Electron Microscope hopes to make the technique accessible to a large number of scientists.



TECNAI Femto UEM, FEI. Released Oct. 2013



Intro to 4D Electron Microscopy

FUTURE OUTLOOK:

MULTI ELECTRON PACKETS

- Single shot diffraction or imaging
- Access to destructible or irreversible phenomena
- Requires a large number of electrons per pulse and space-charge leaves temporal resolution in the ns
 - Recompress electron bunch using RF pulses
 - Use higher energy electrons to minimize space charge effect

LOWER ACCERLATING VOLTAGES

- Study phenomena in ambient conditions – soln cells, env. chambers
- Potentially less damage to sensitive samples

ATTOSECOND DYNAMICS

- Truly visualize electron dynamics

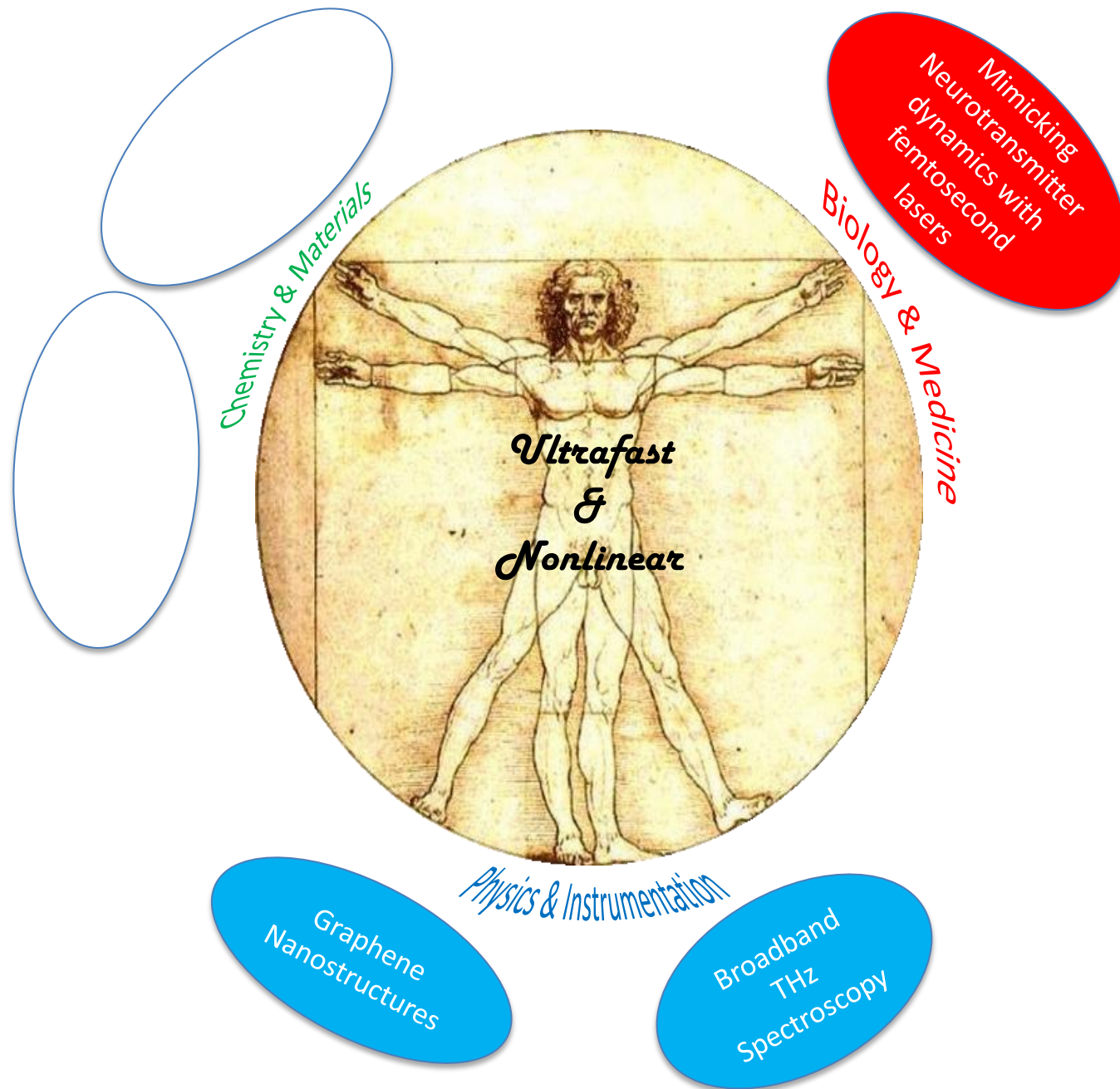


THANK YOU

ありがとうございました



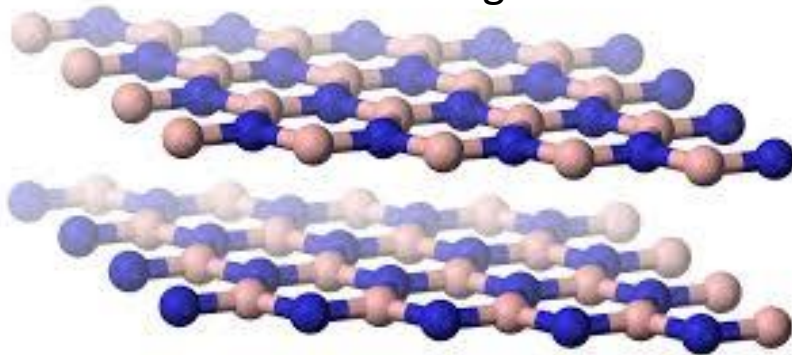
RESEARCH INTERESTS & PROJECTS



2D Materials and Heterostructures

Beyond Graphene, other two-dimensional materials exhibit a range of properties from insulating (h-BN) to semi-conducting (MoS₂) to semi-metallic (G)

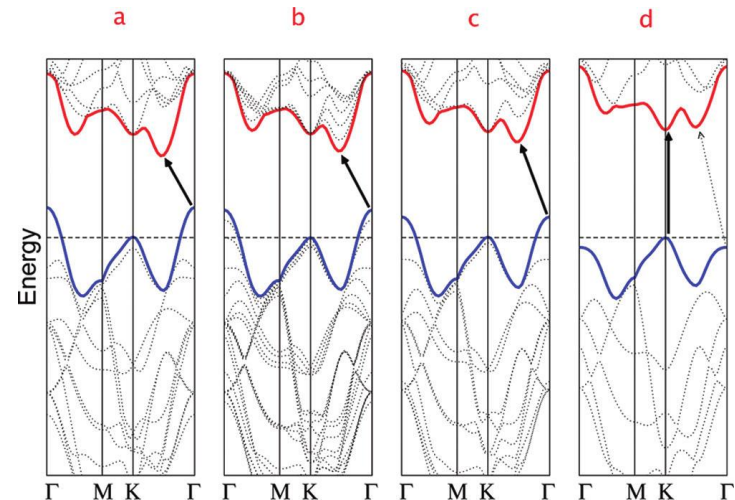
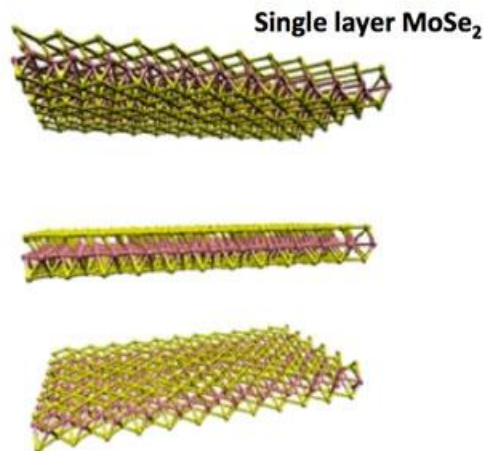
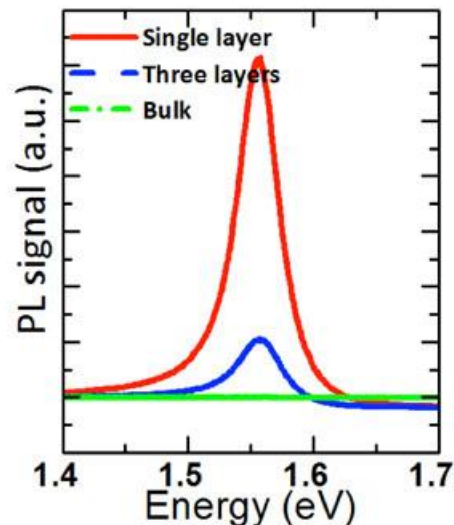
Hexagonal Boron Nitride



http://en.wikipedia.org/wiki/Boron_nitride

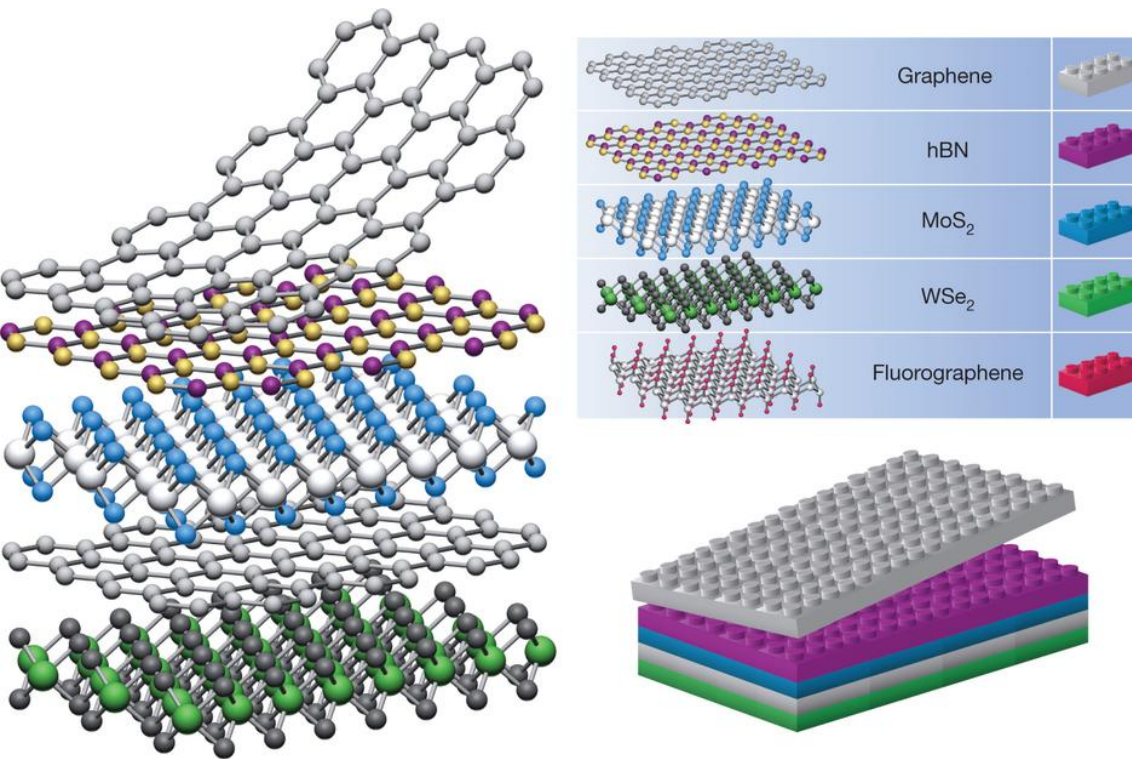


web.ics.purdue.edu

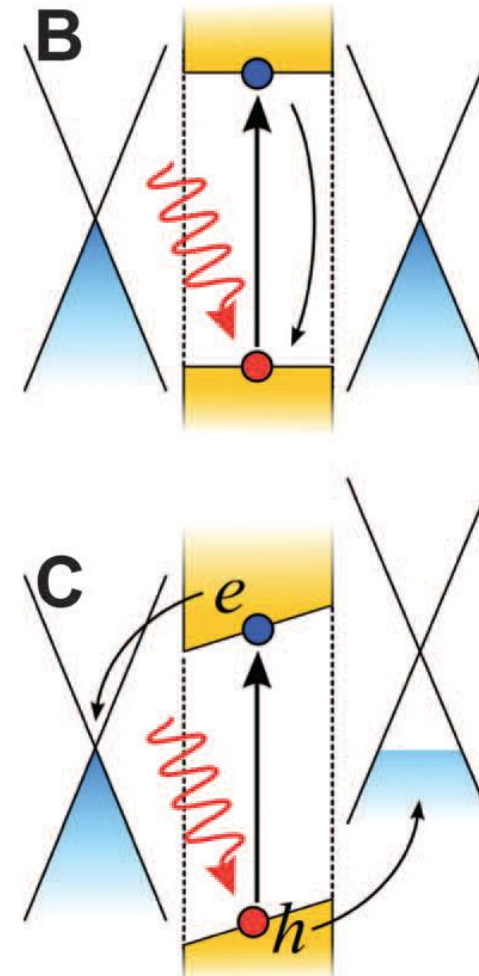


2D Materials and Heterostructures

Combining 2D materials to create heterostructures with new and novel functionality is an intriguing possibility.



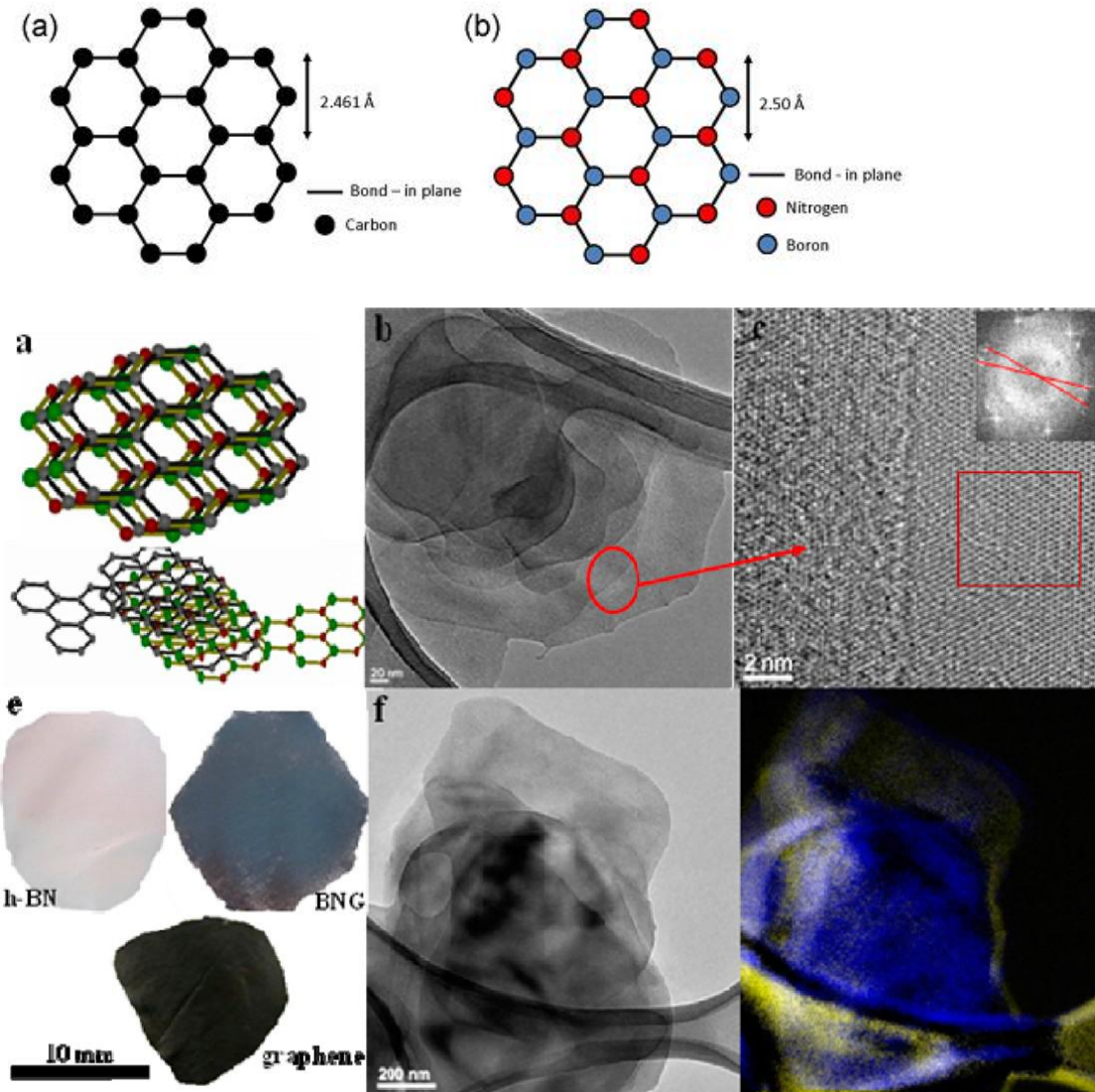
A. Geim & I.V. Grigorieva, Nature 499, 419–425 (2013)



K. Novoselov, et al, Science v340 p1311 2013

2D Materials and Heterostructures

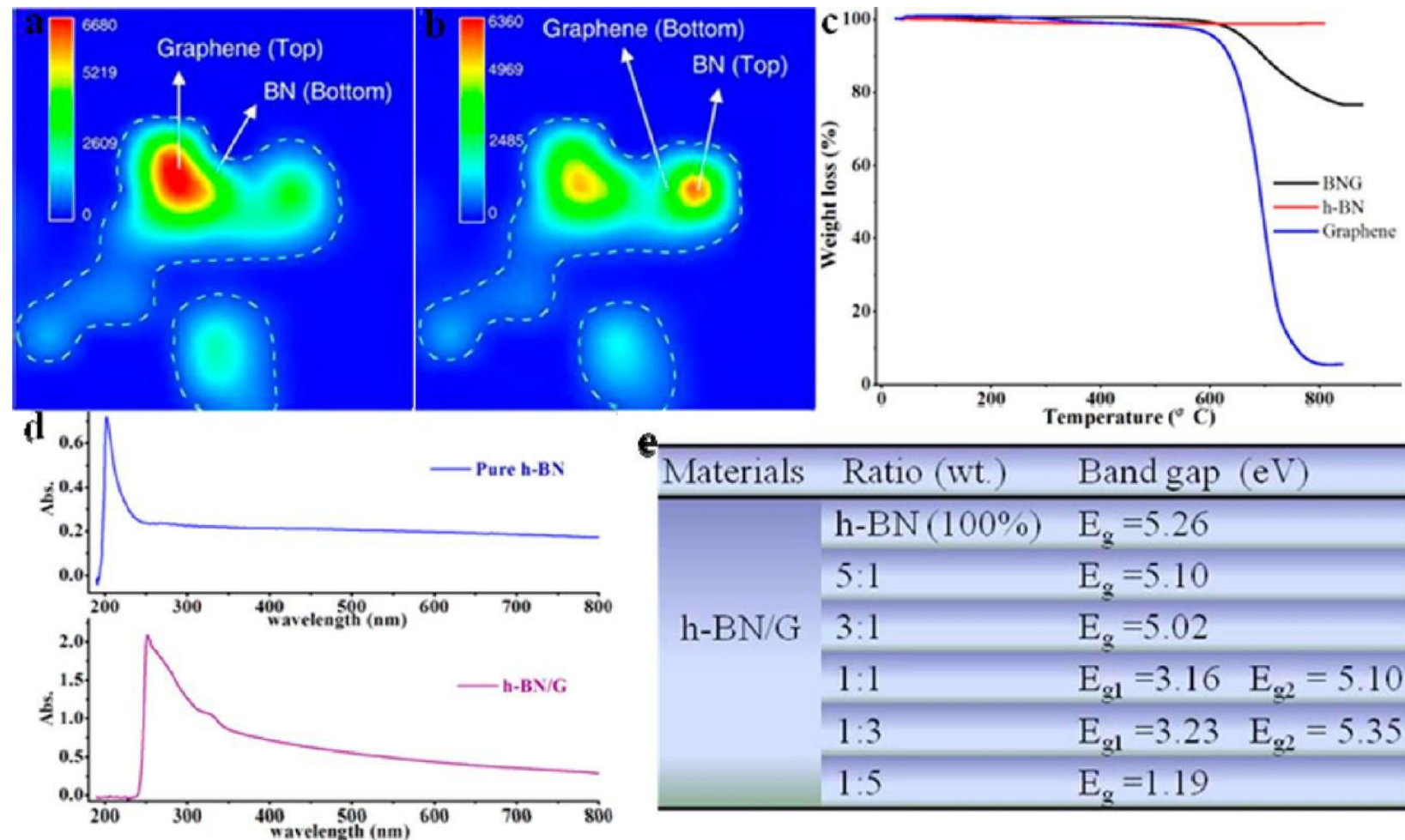
In particular, the similar crystal structures of hBN and G allow for an interesting mix of heterostructures.



- Disperse exfoliated h-BN and G layers in liquid phase
- Mix in various concentrations to create artificially stacked h-BN/G solids via Van der Waals Interaction
- These heterostructures are expected to show interesting opto-electronic properties

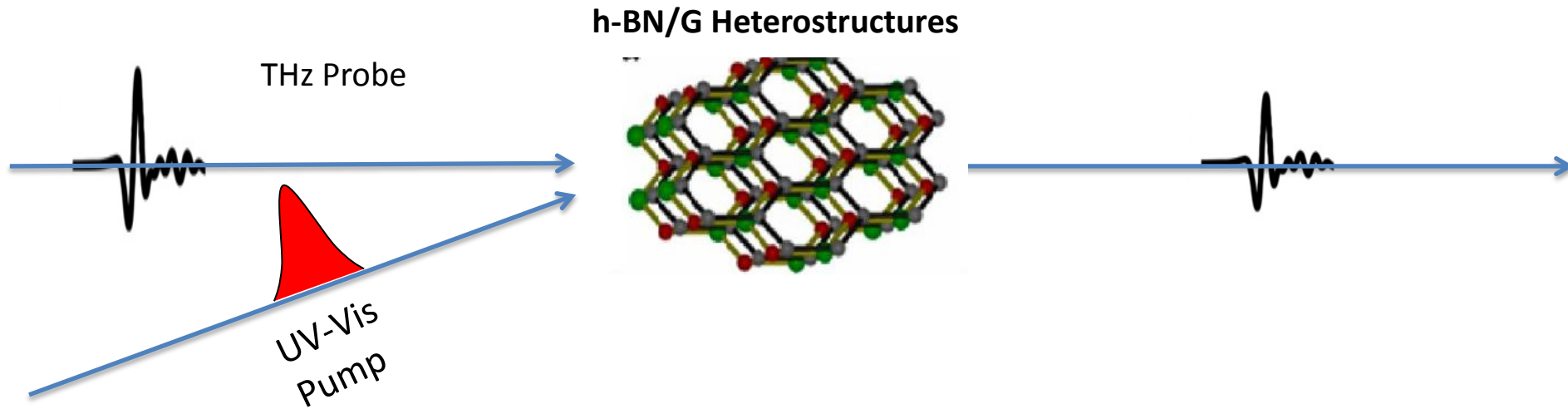
2D Materials and Heterostructures

For heterostructures with varying ratios of h-BN/G one sees the evolution of a bandgap from UV to IR.



2D Materials and Heterostructures

We then use UV/Vis pump to photoexcite carriers, and THz probe to study their transient dynamics – recombination times, carrier mobility, etc.

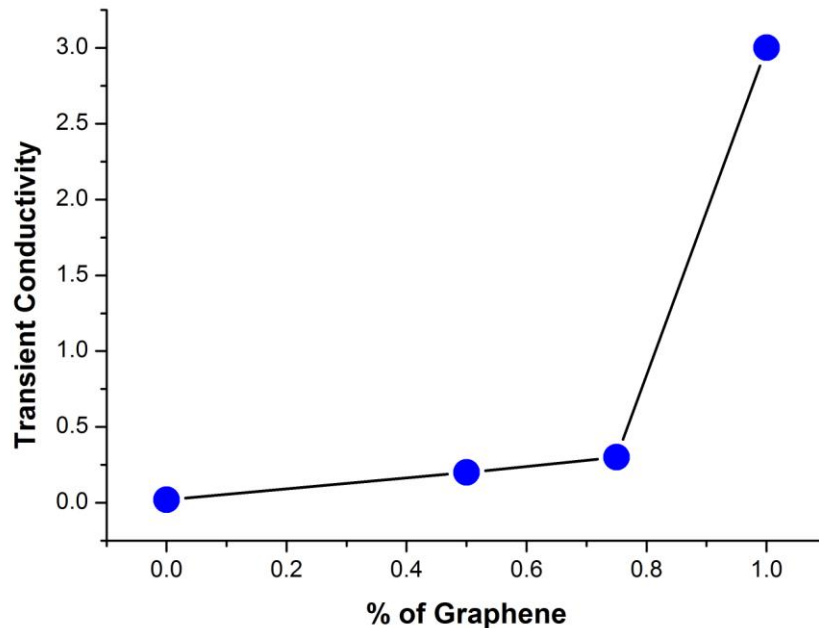
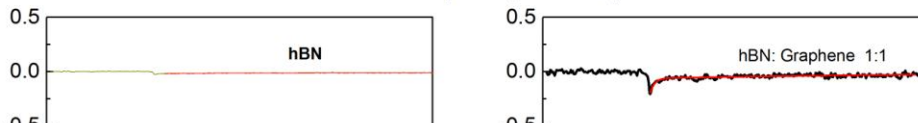


We hope to explore the opto-electronic properties of these heterostructures from a fundamental and applied perspective.

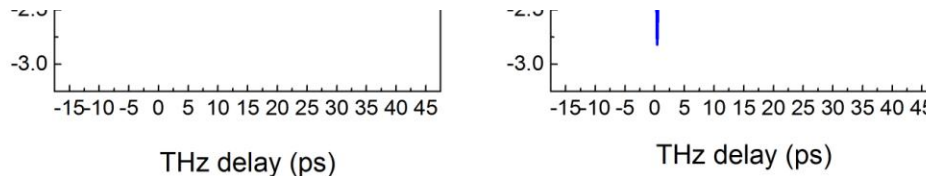
2D Materials and Heterostructures

With a $\sim 400\text{nm}$ Pump, we see the transient photoconductivity drastically drop with even a ratio of h-BN in the heterostructure.

370 nm pump-THz probe



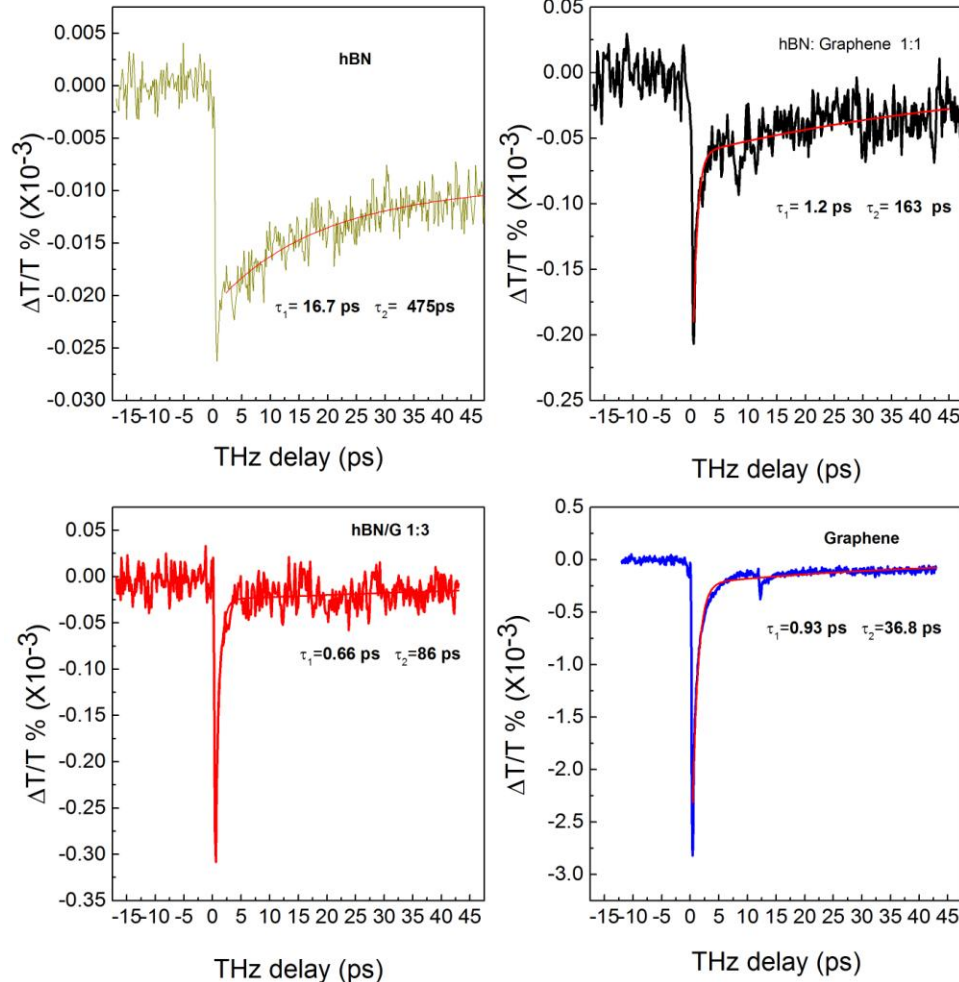
- h-BN is an insulator, G is a semi-metal
- Transient Photoconductivity not simply proportional to the percentage of Graphene in the heterostructure



2D Materials and Heterostructures

The decay dynamics suggest that the transient photoconductivity is due to the graphene flakes.

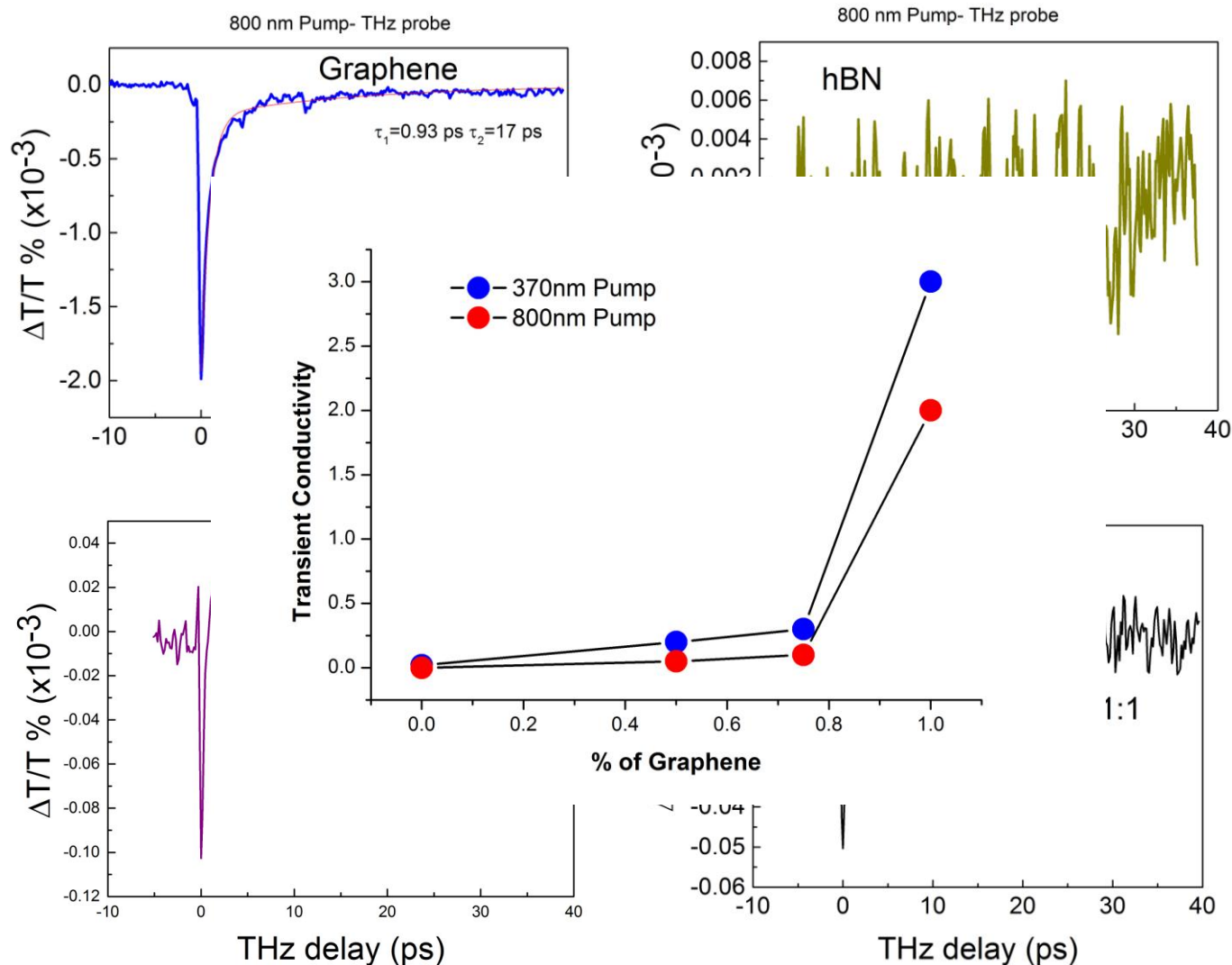
370 nm pump-THz probe



- From decay dynamics, origin of signal seems to be due to transient photoconductivity in graphene.

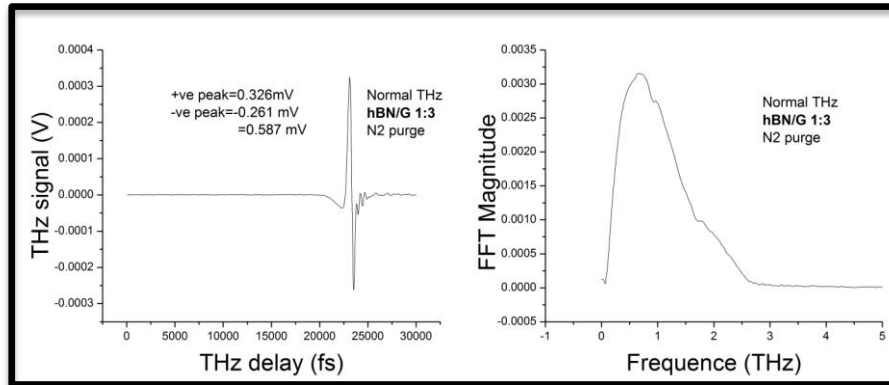
2D Materials and Heterostructures

With an 800nm pump, first we see a similar trend in the amplitude of photoconductivity – a small amount of h-BN drastically reduces conductivity.

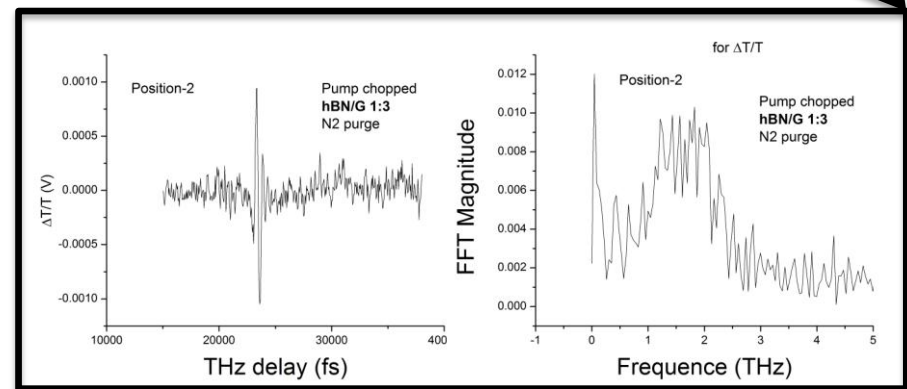
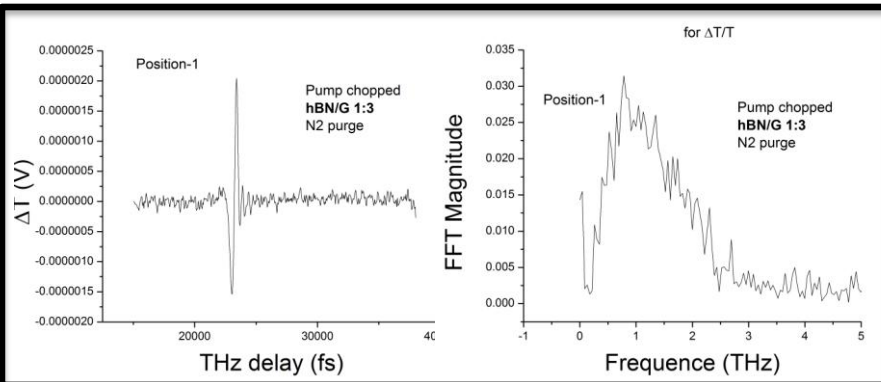
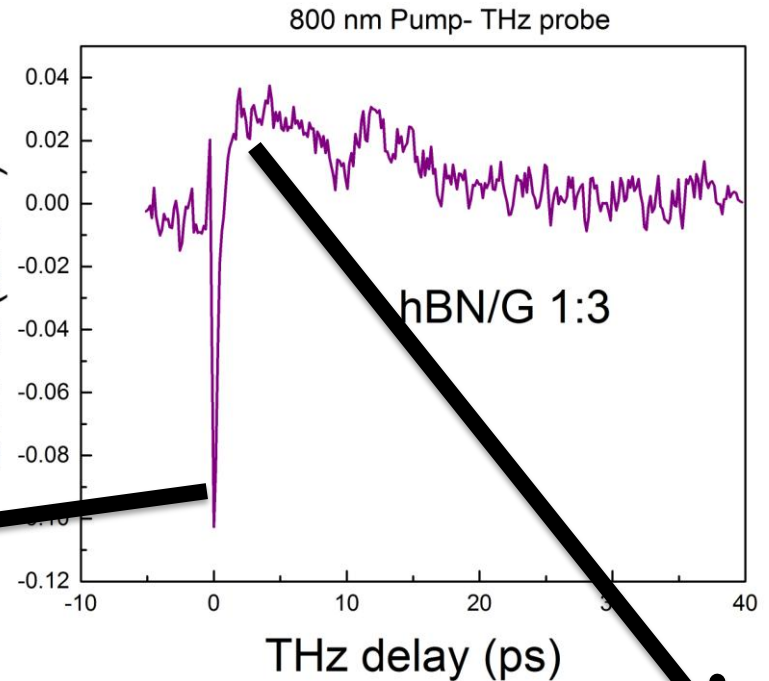


2D Materials and Heterostructures

But we also see the presence of new behavior that not seen in the pure h-BN and G phases of the heterostructure

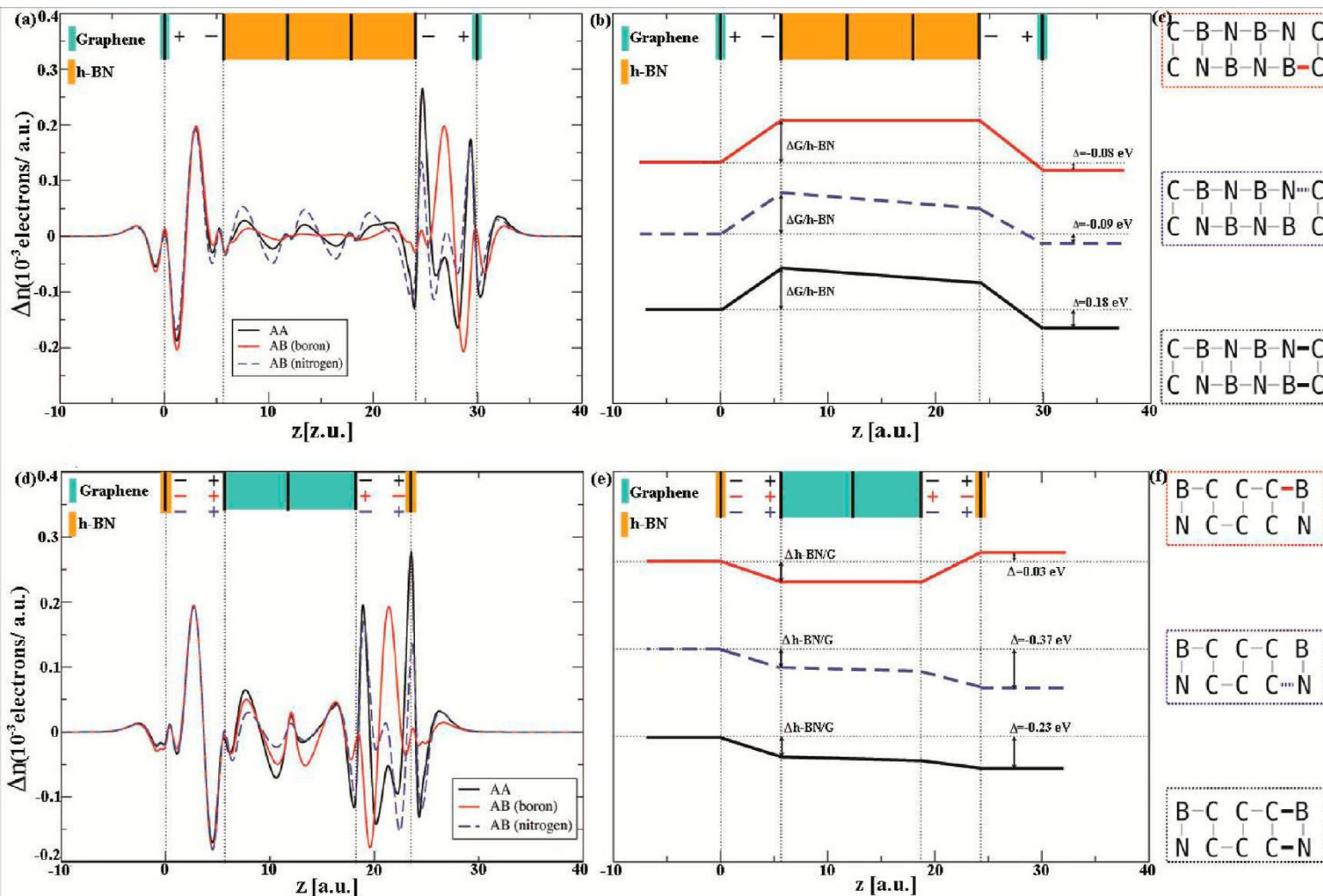


$\Delta T/T \% (\times 10^{-3})$



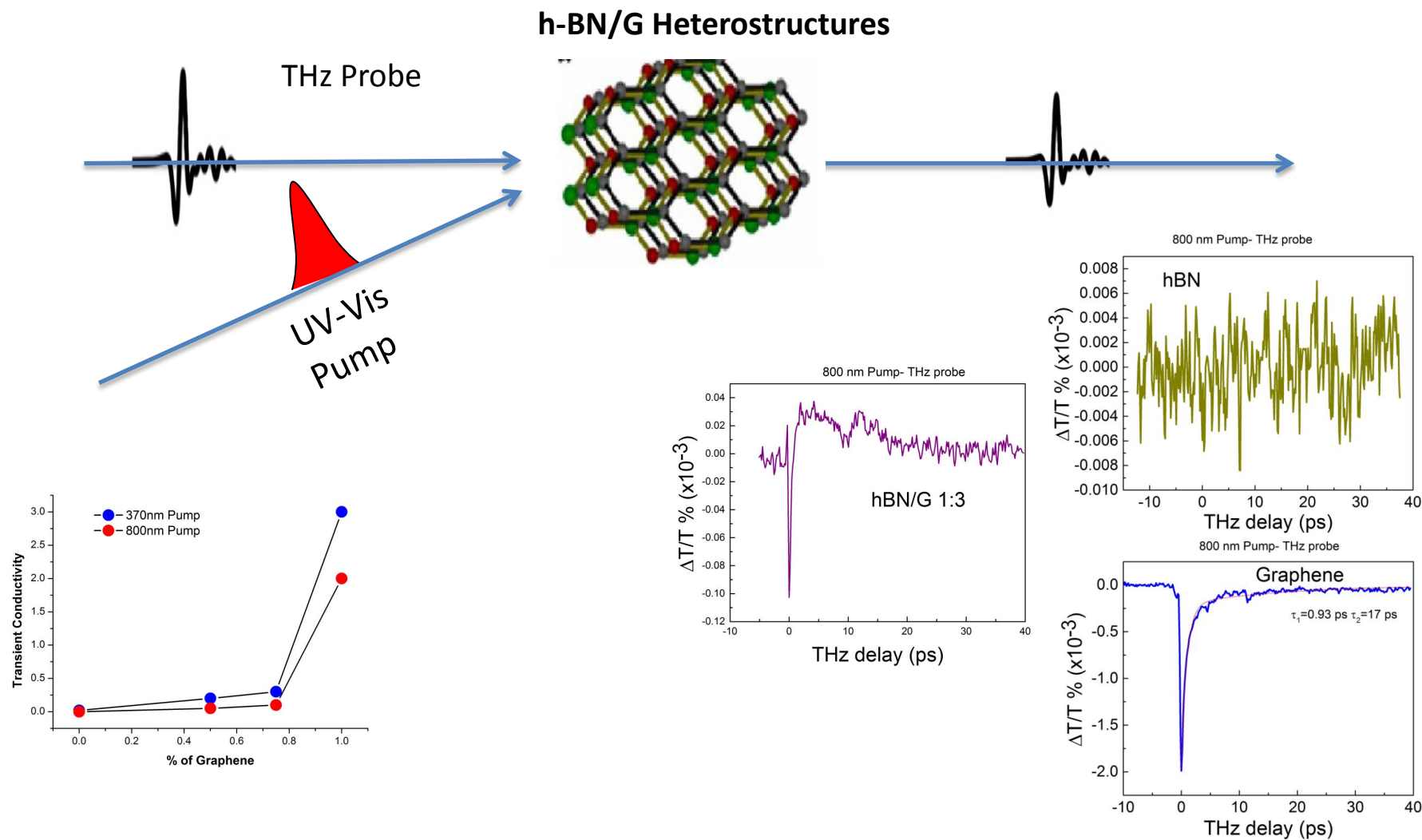
2D Materials and Heterostructures

Our best guess so far is that an induced dipole moment between the h-BN/G layers modifies the opto-electronic response as measured by the THz probe.

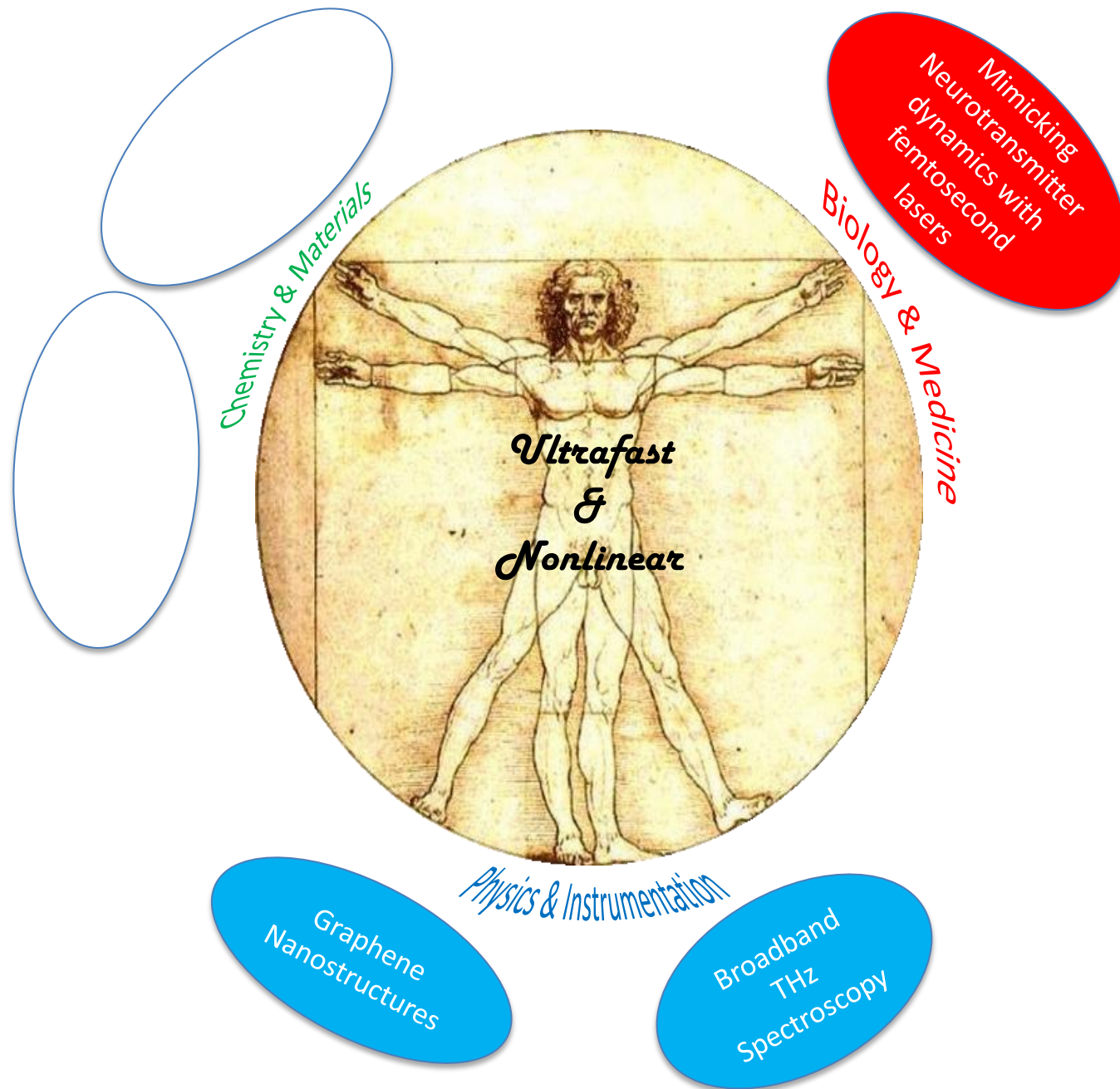


2D Materials and Heterostructures

In conclusion, we are seeing some interesting behavior in the opto-electronic response of h-BN/G heterostructures! We don't quite know why yet!



RESEARCH INTERESTS & PROJECTS





Otago Univ., NZ



Wickens Unit
**NEUROBIOLOGY RESEARCH
UNIT**



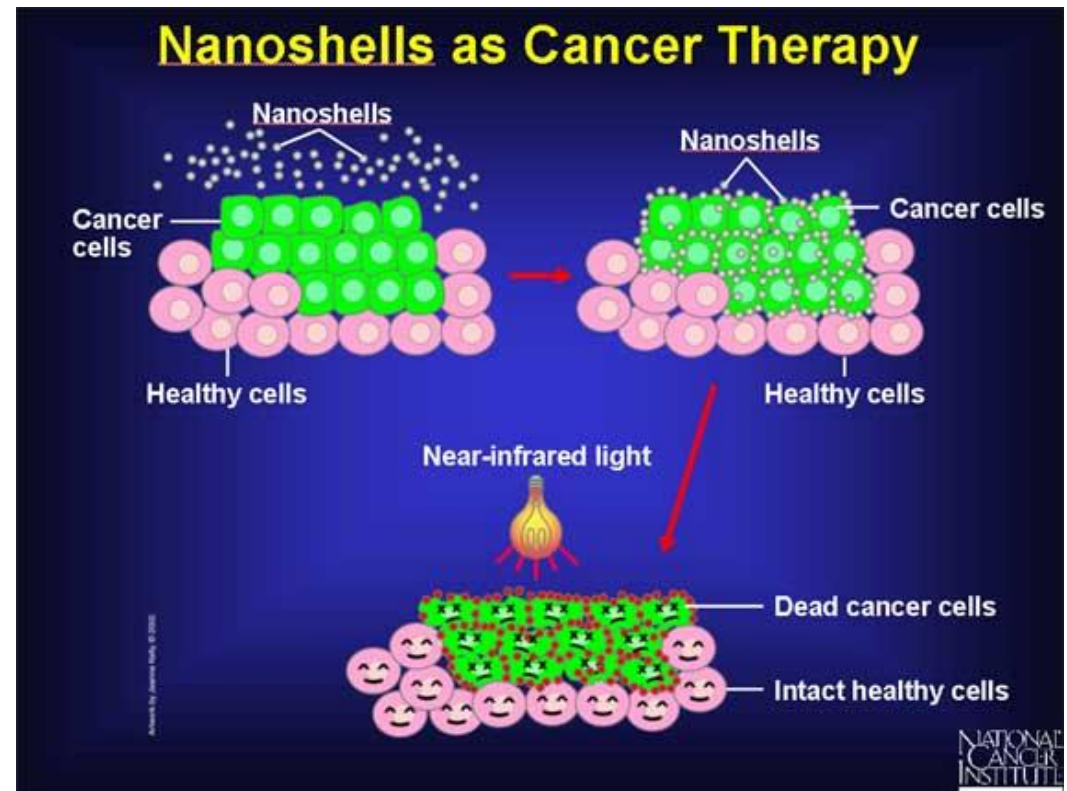
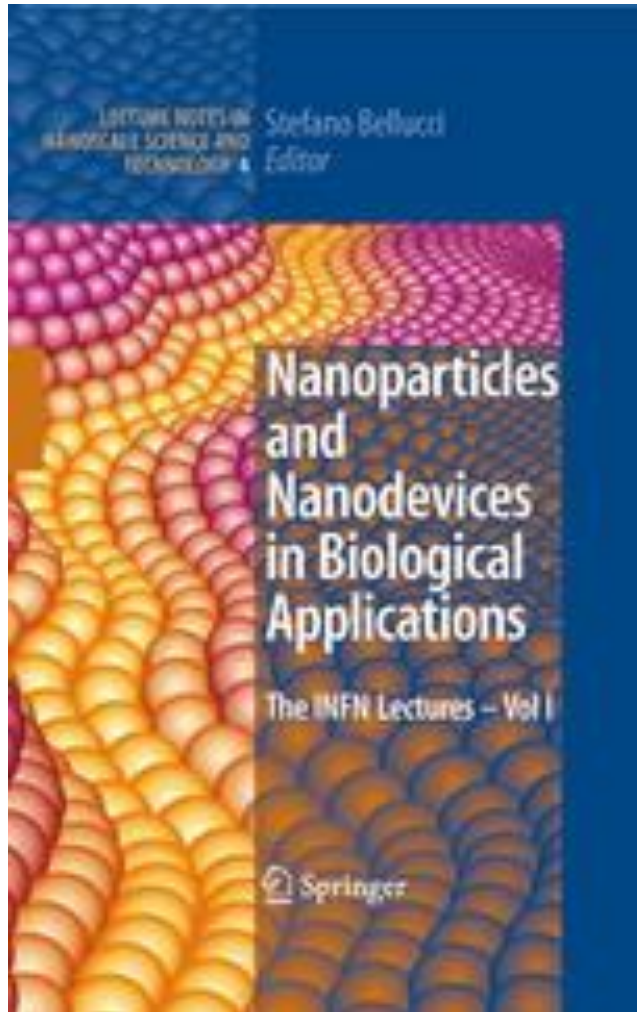
Dani Unit
**FEMTOSECOND
SPECTROSCOPY UNIT**

Mimicking Neurochemistry with Femtosecond Pulses

Takashi Nakano, Catherine Chin, Eng Wui Tan, Pete Hale, John Reynolds, Jeff Wickens, Keshav M. Dani

Mimicking Neurotransmitter Dynamics

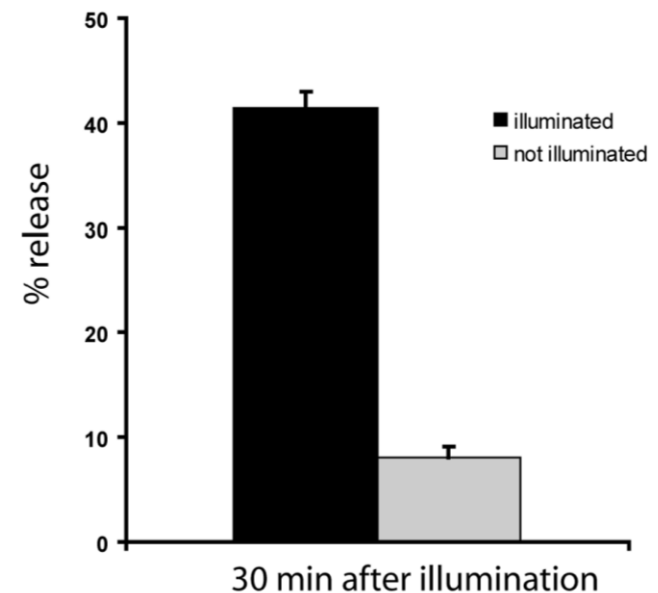
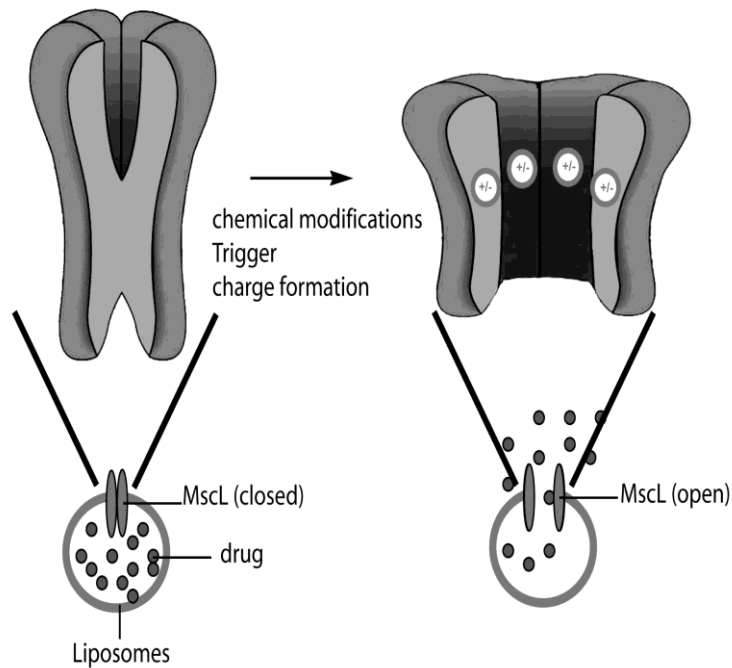
With the development of sophisticated tools in nanotechnology, there is a recent push to develop nanoscale biocompatible tools to interact with living organisms.



The first steps in this process have been to develop nanoscale drug delivery systems that respond to an external stimulus.

Mimicking Neurotransmitter Dynamics

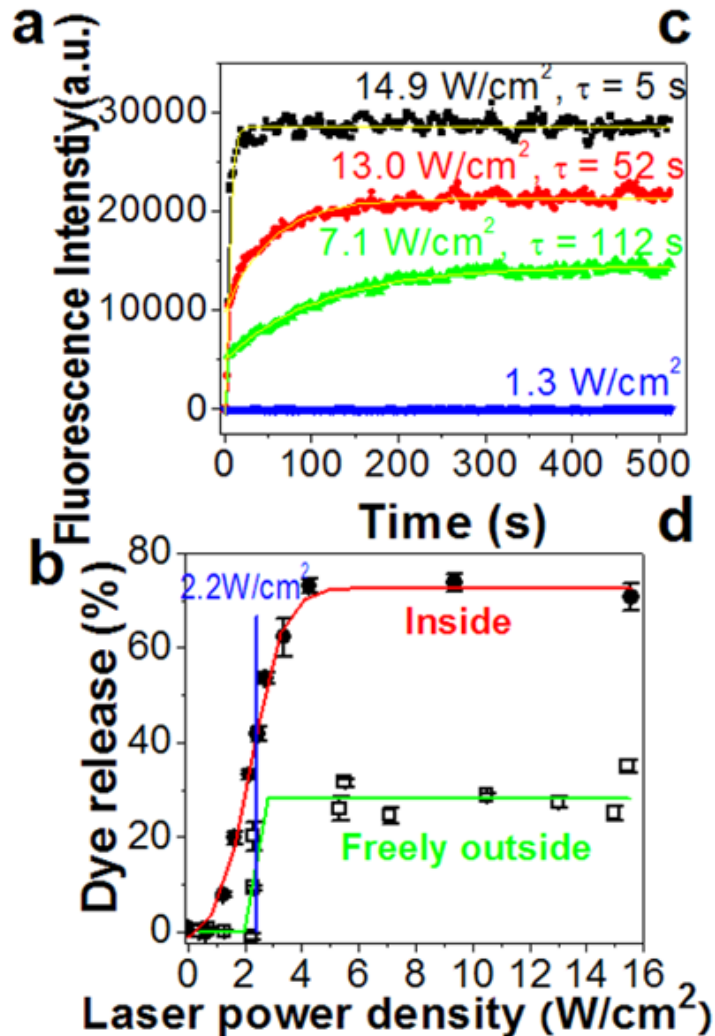
For example, over the past few years, a variety of targeted, nanoscale drug delivery systems have been suggested and demonstrated to attack cancerous cells.



Chemical or Light Stimulation

Mimicking Neurotransmitter Dynamics

Over the past few year, a variety of targeted, nanoscale drug delivery systems have been suggested and demonstrated to attack cancerous cells.



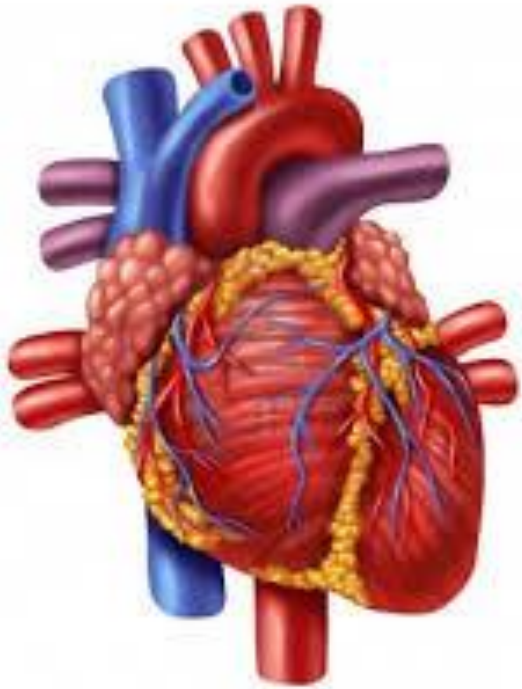
In general, these results attempt to only:

- Achieve single-shot release and permanently alter or destroy the delivery system
- Operate on much slower timescales - typically minutes or days, and few seconds at best.

Mimicking Neurotransmitter Dynamics

The next stage in the evolution of artificial nano-systems is to *mimic* biofunctionality!

I) Biofunctionality is rhythmic

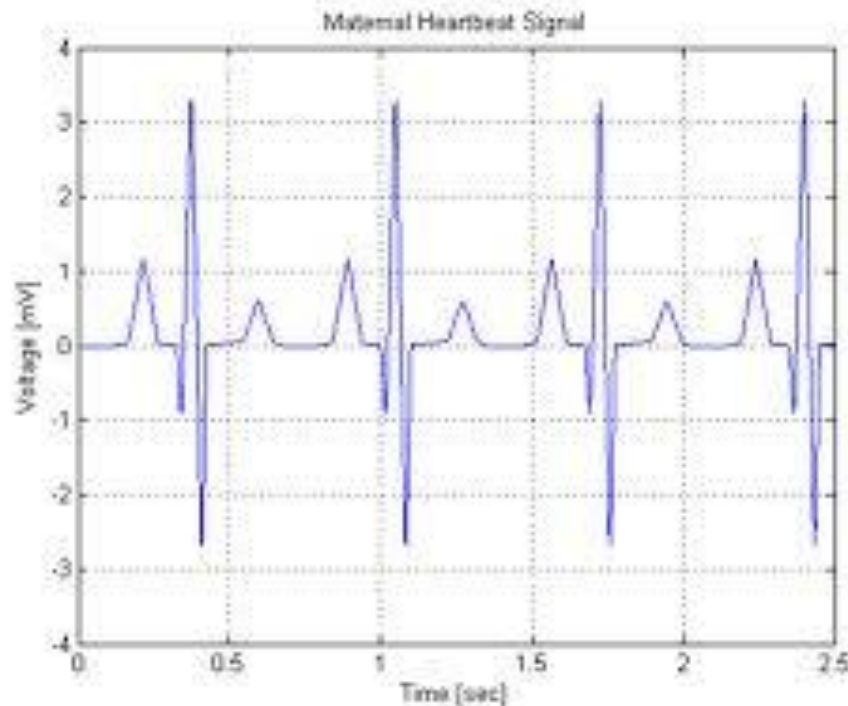


- Repeated, rhythmic operation! Pulsatile operation!
- Non-destructive triggering!

Mimicking Neurotransmitter Dynamics

The next stage in the evolution of artificial nano-systems is to *mimic* biofunctionality!

II) Temporal control is essential

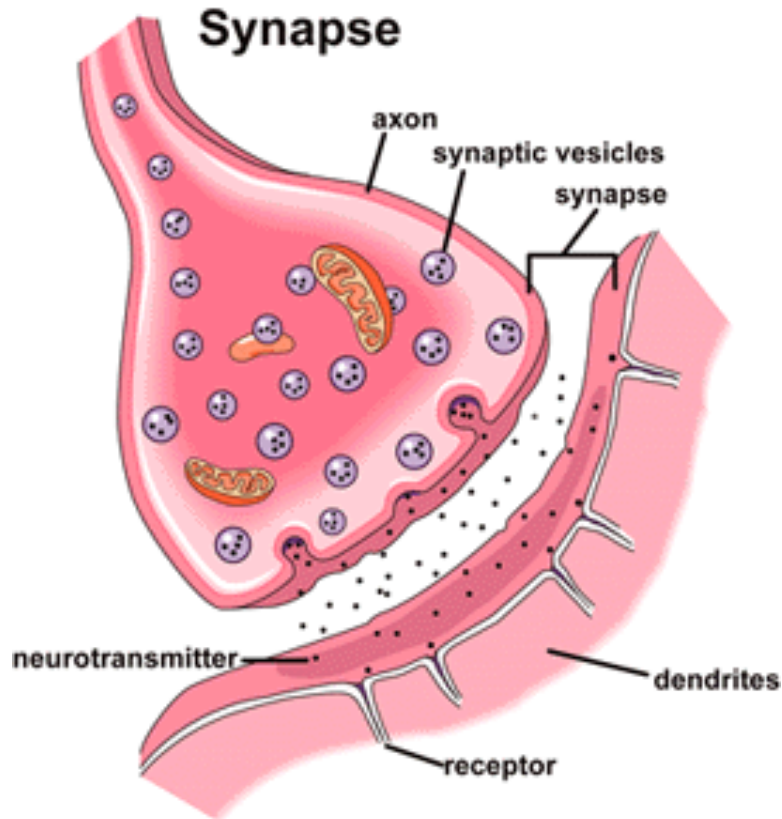


- Biorhythms follow specific temporal rhythms –
 - subsecond thought processes
 - heartbeats per minute
 - daily sleep cycles
 - ageing processes.
- Functionality critically depends on the temporal profile of the rhythm!

- Temporal control over rhythmic operation
 - ranging from milliseconds to minutes to hours to days
 - Control over each event, as well as frequency of events

Mimicking Neurotransmitter Dynamics

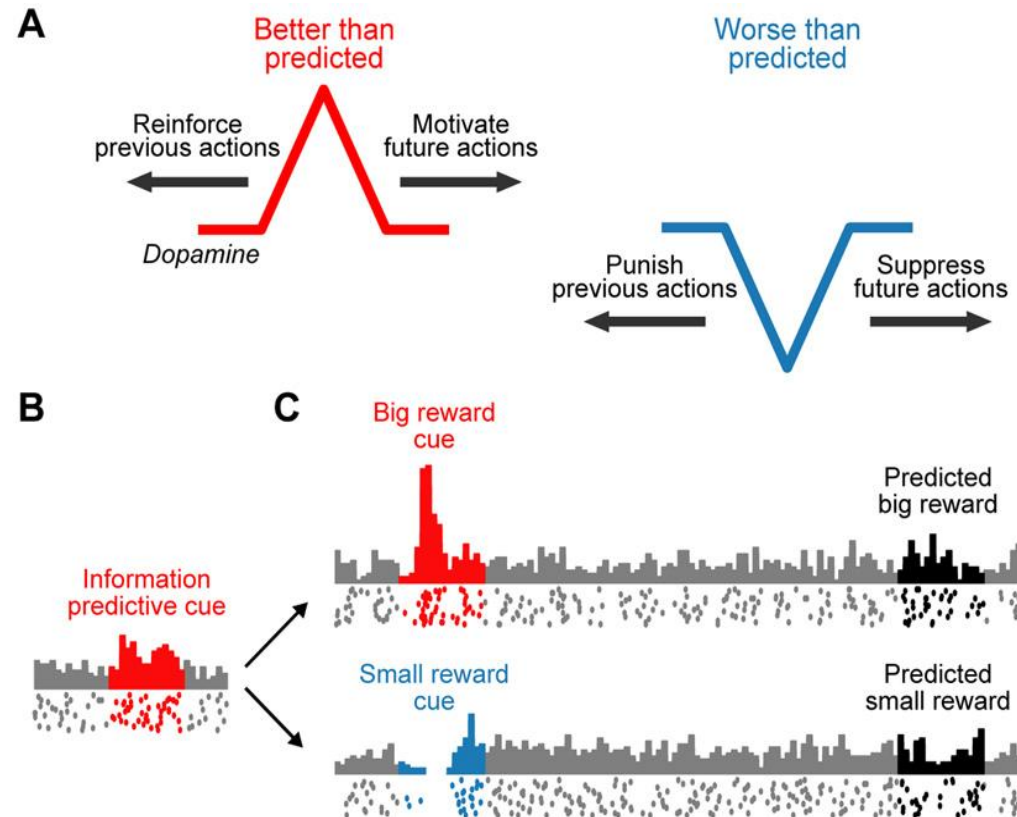
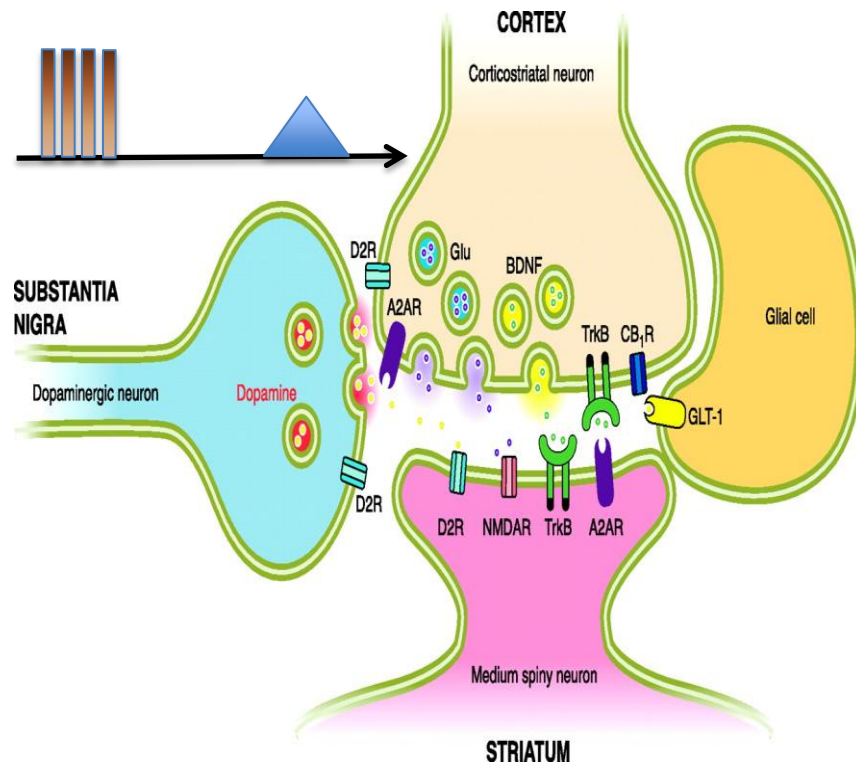
A neuron communicates with the next one by releasing a neurotransmitter at its 'end terminal', which may then trigger the next neuron.



The efficiency of this 'communication' changes, can be changed over time, thus allowing for 'learned behavior', 'memory', etc.

Mimicking Neurotransmitter Dynamics

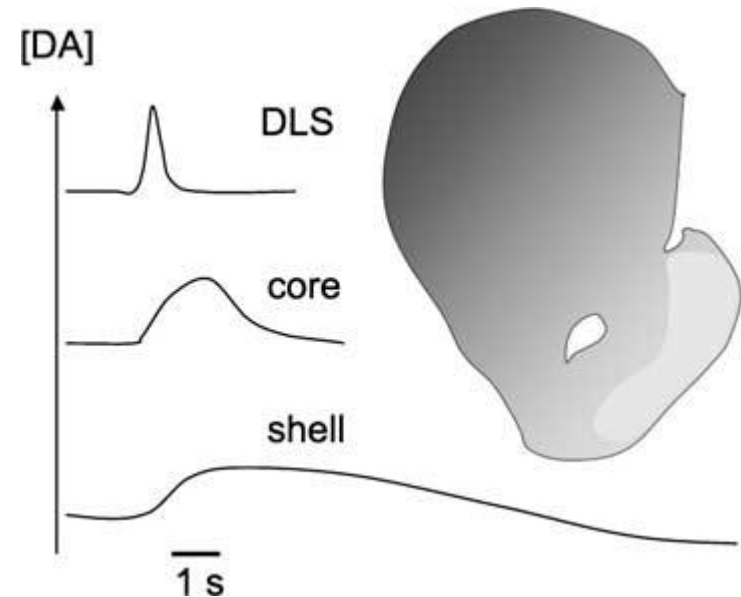
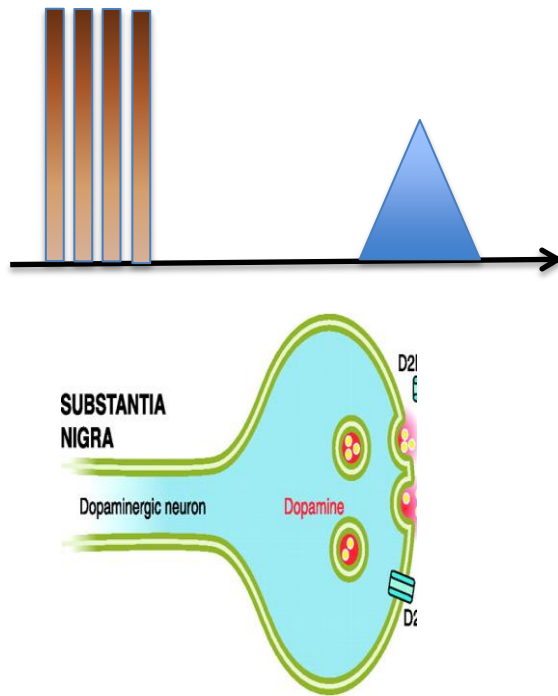
A particular way to control this efficiency is through a neuromodulator like Dopamine.



Via this mechanism, dopamine neurons and dopamine release plays a crucial role in learning behavior and a variety of neurological diseases, e.g. Parkinsons.

Mimicking Neurotransmitter Dynamics

The release profile of dopamine is crucial in modulating brain functions and varies from region to region in the brain.

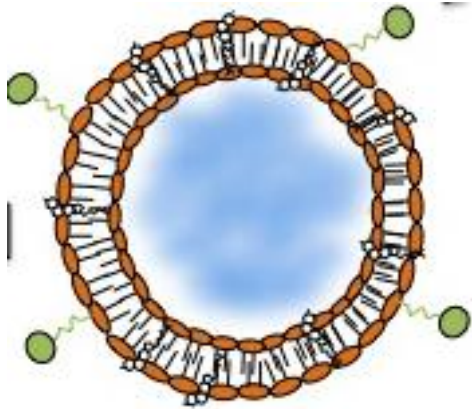


Mimicking the dopamine release profile on demand would be a crucial step in the study of brain & learning behavior, and in addressing neurological diseases.

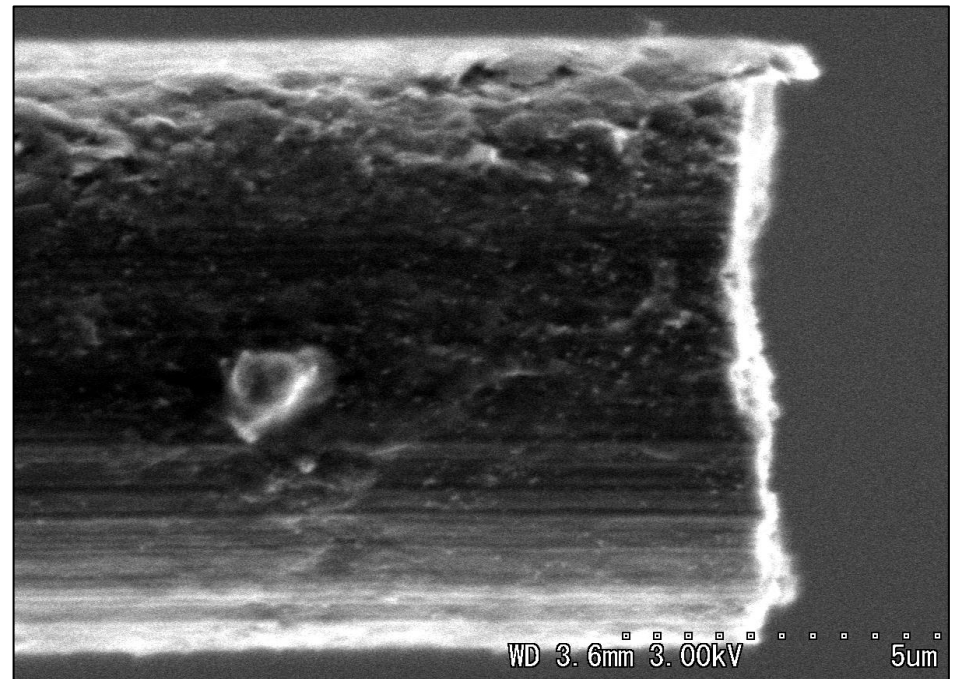
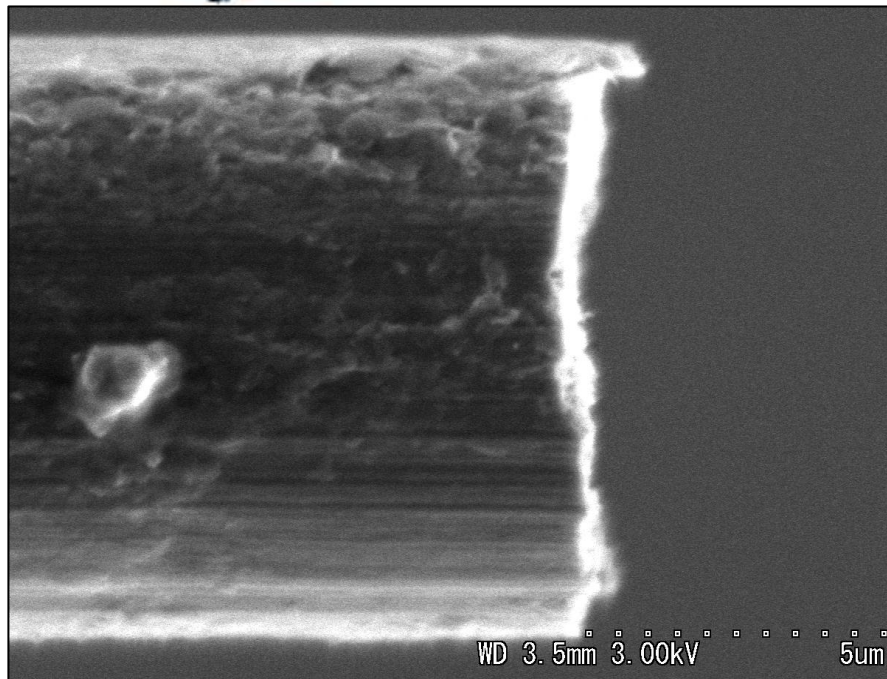
Thereby, we need a method for an on-demand sub-second, repeatable dopamine delivery mechanism with nanomolar concentrations.

Mimicking Neurotransmitter Dynamics

We make dopamine filled liposome structures, tether them to Au nanoshells and fix them to a carbon fiber for repeated, sensitive measurements

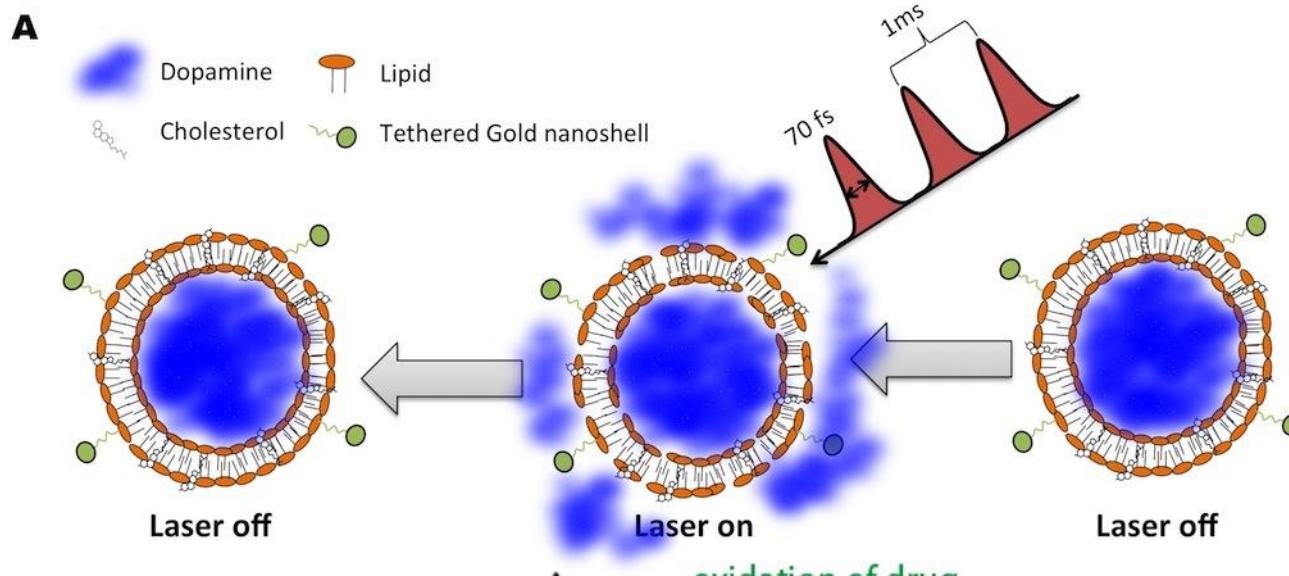


- We synthesize liposomes structures packed them with dopamine.
- We tether Au nanoparticles to the liposome structures
- We stick the structures to a carbon fiber for repeated, sensitive measurements



Mimicking Neurotransmitter Dynamics

To cause dopamine release, we expose the liposome structures to femtosecond pulses with sub-second exposure times.

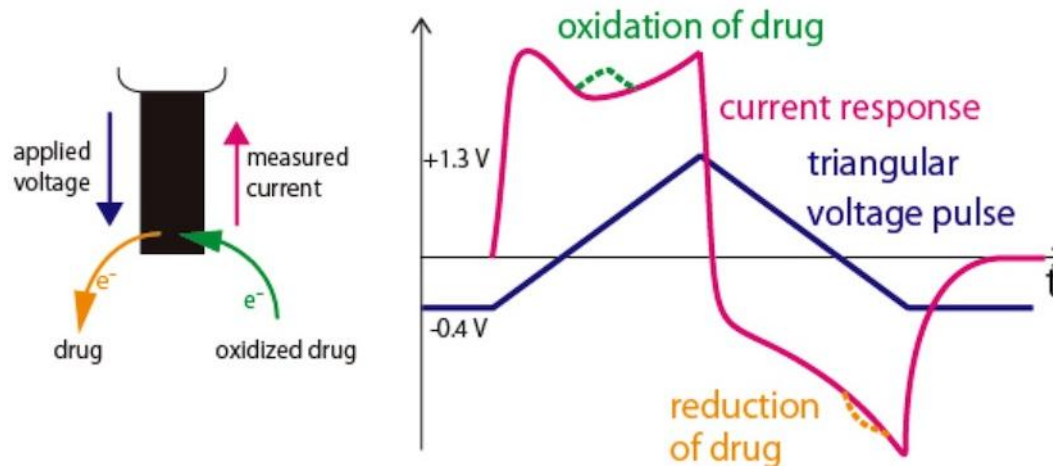


- We stimulate the liposome structures attached to the carbon fiber with a train of femtosecond pulses
- The pulses are 70fs flashes, 1 ms apart, with an energy of 2-3mJ/cm² per pulse

Mimicking Neurotransmitter Dynamics

To measure the dopamine release, we use a sensitive Fast Scan Cyclic Voltammetry technique.

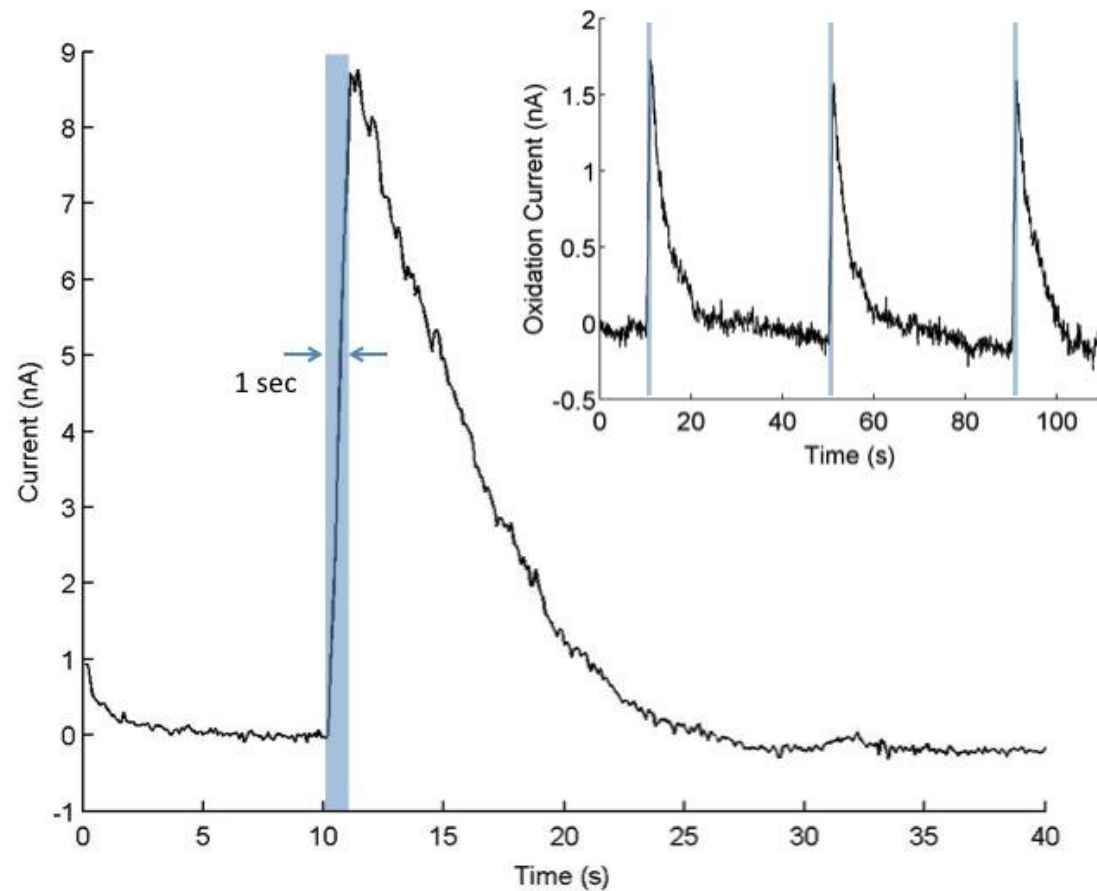
B



- Using the same carbon fiber as an electrode, we achieve very sensitive measurements.
- We send a voltage pulse down the carbon fiber, which oxidizes any dopamine in the near-by environment.
- The oxidation current gives us a measure of the dopamine quantity

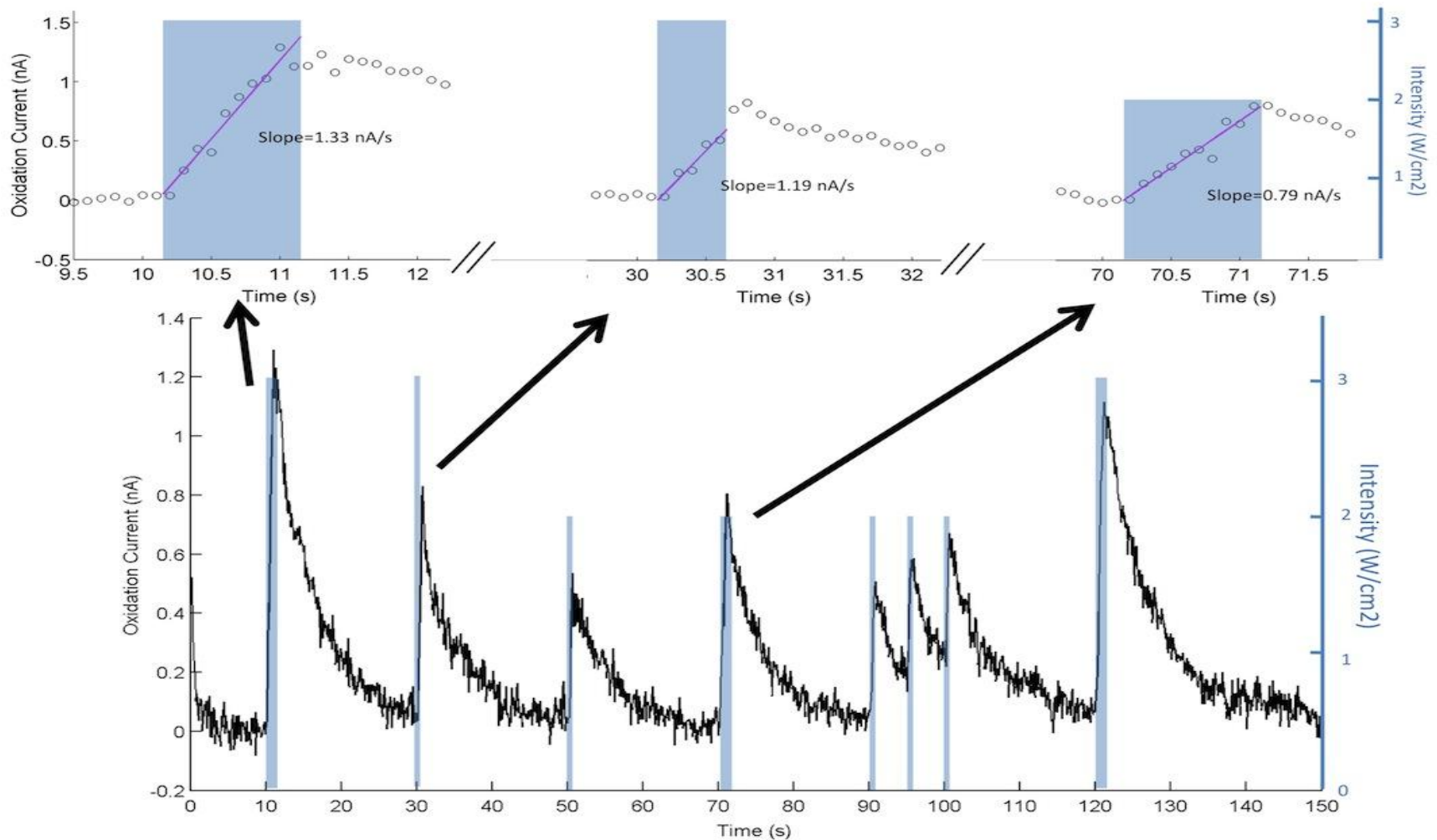
Mimicking Neurotransmitter Dynamics

We see a rapid increase in dopamine concentration during the application of the laser pulse-train, and a decay determined by the diffusion time in the solution.



Mimicking Neurotransmitter Dynamics

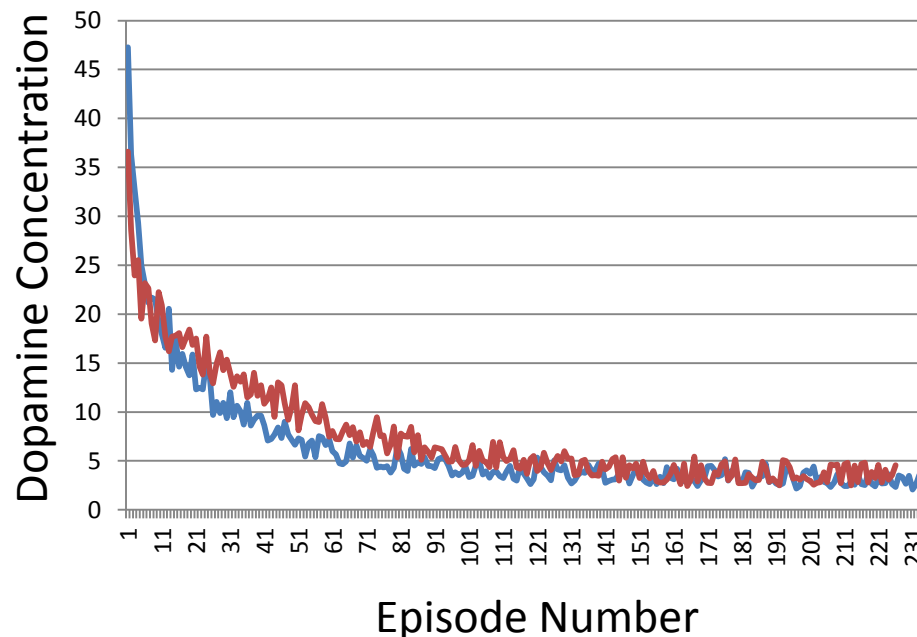
By varying the pulse energy and exposure time, we generate a dopamine delivery profile of choice, thereby mimicking the appropriate neurotransmitter dynamics!



Mimicking Neurotransmitter Dynamics

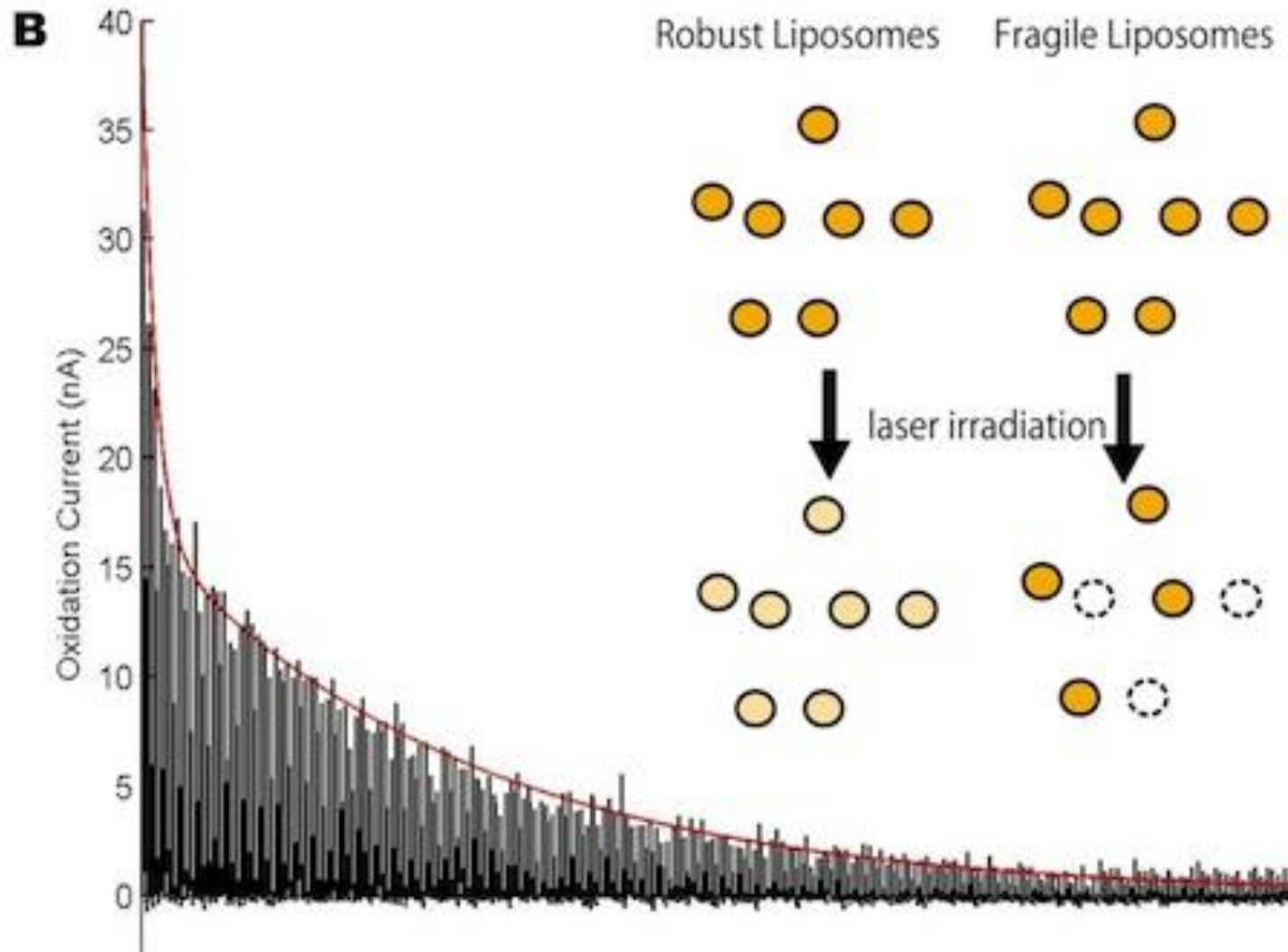
On long timescales, we see a bi-exponential fit to the data implying two mechanisms of release: a fast rapid process, and a slow repeatable process.

- Dopamine released by destroying liposomes
 - Fast process, with large release of dopamine at early time
 - Small fraction of liposomes participating
- Dopamine released due to laser induced permeability of liposomes
 - Slow, repeatable process over time
 - Most liposomes fall in this category



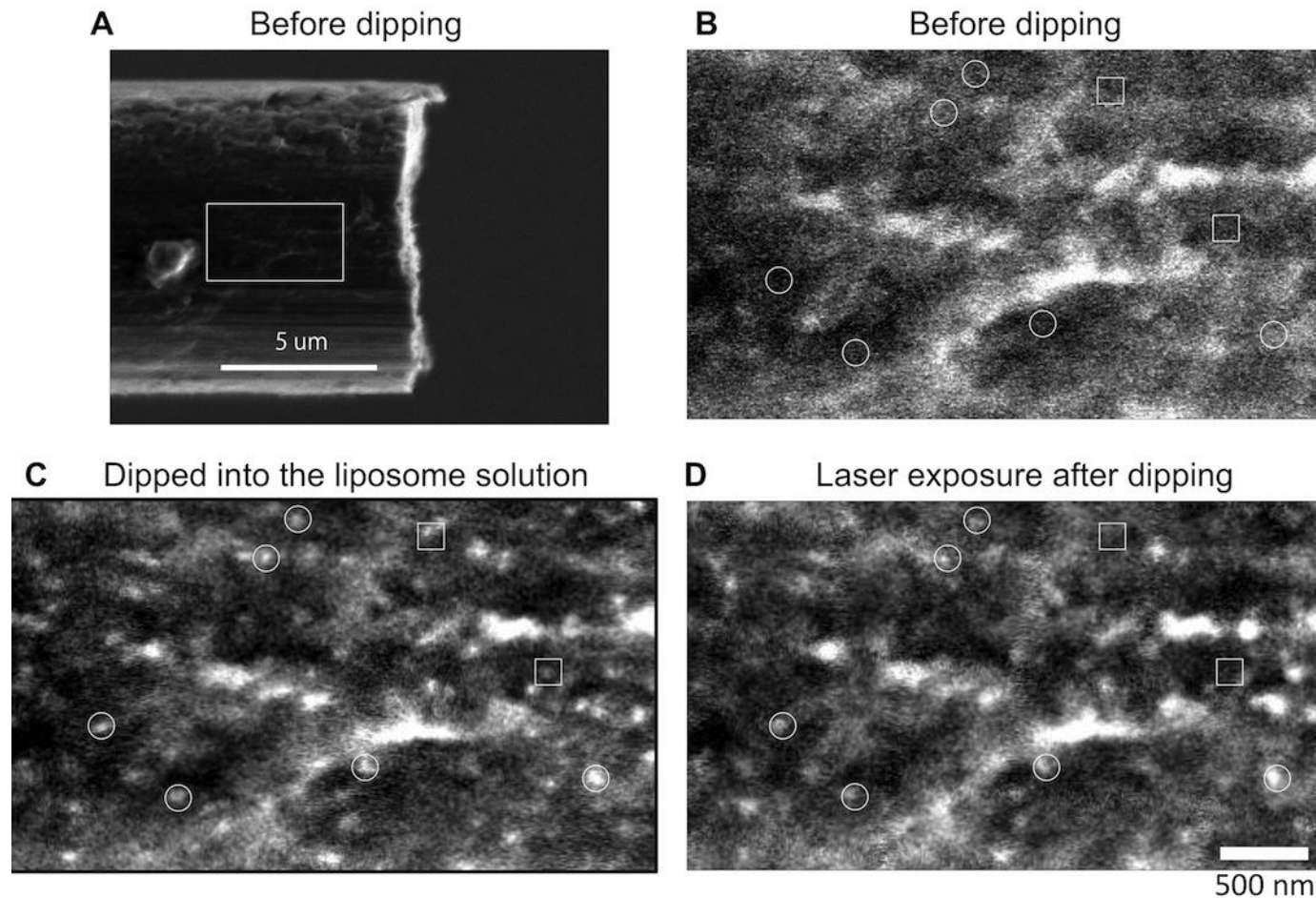
Mimicking Neurotransmitter Dynamics

By fitting our data, we get that ~20% fragile ones that are destroyed, and ~80% robust ones that repeatedly release dopamine.



Mimicking Neurotransmitter Dynamics

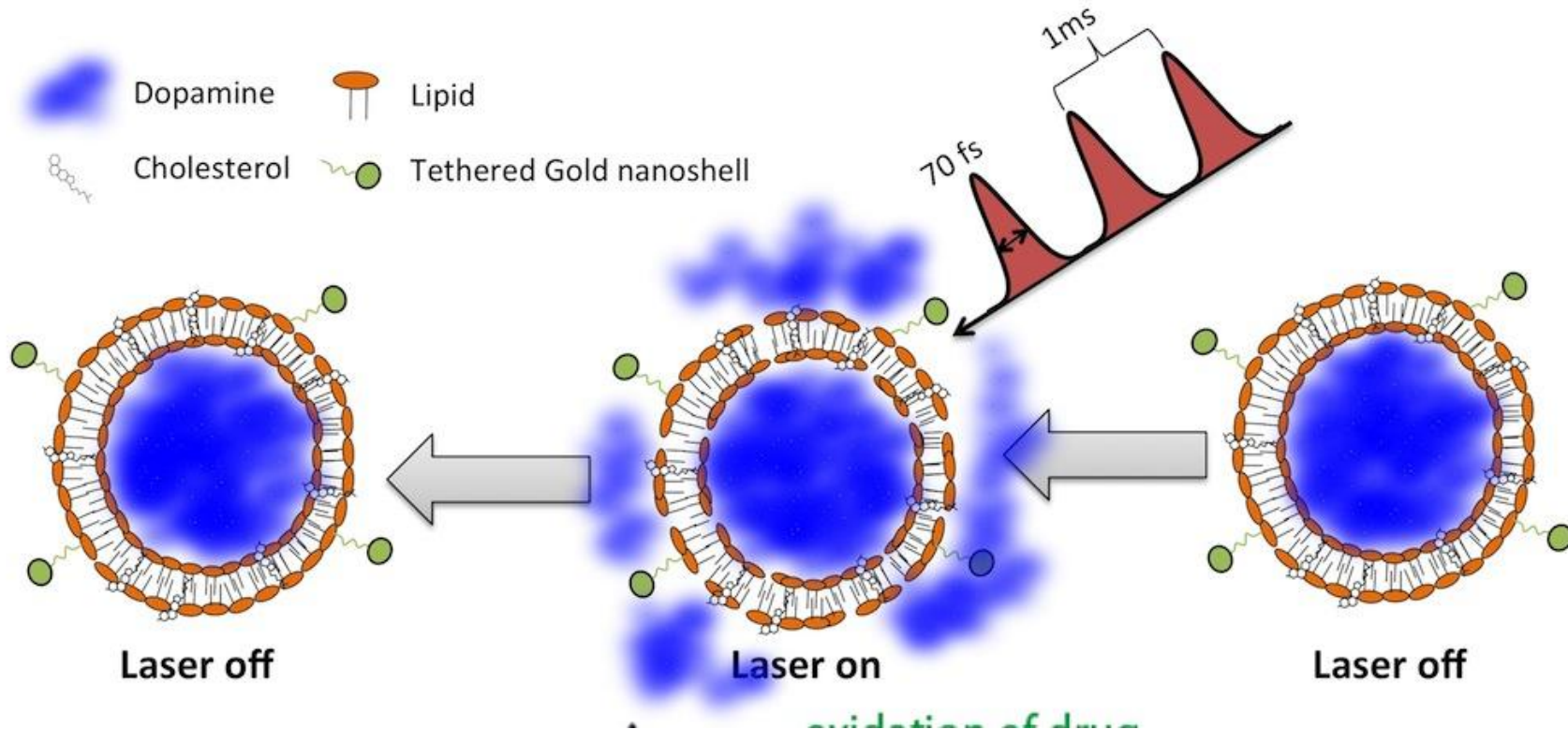
An electron microscope image confirms the robustness of ~80% of liposomes after multiple laser exposures.



Mimicking Neurotransmitter Dynamics

Here, we demonstrate a nanoscale, biocompatible system to mimic neurofunctions – *subsecond, pulsatile* release of neurochemicals *on demand*!

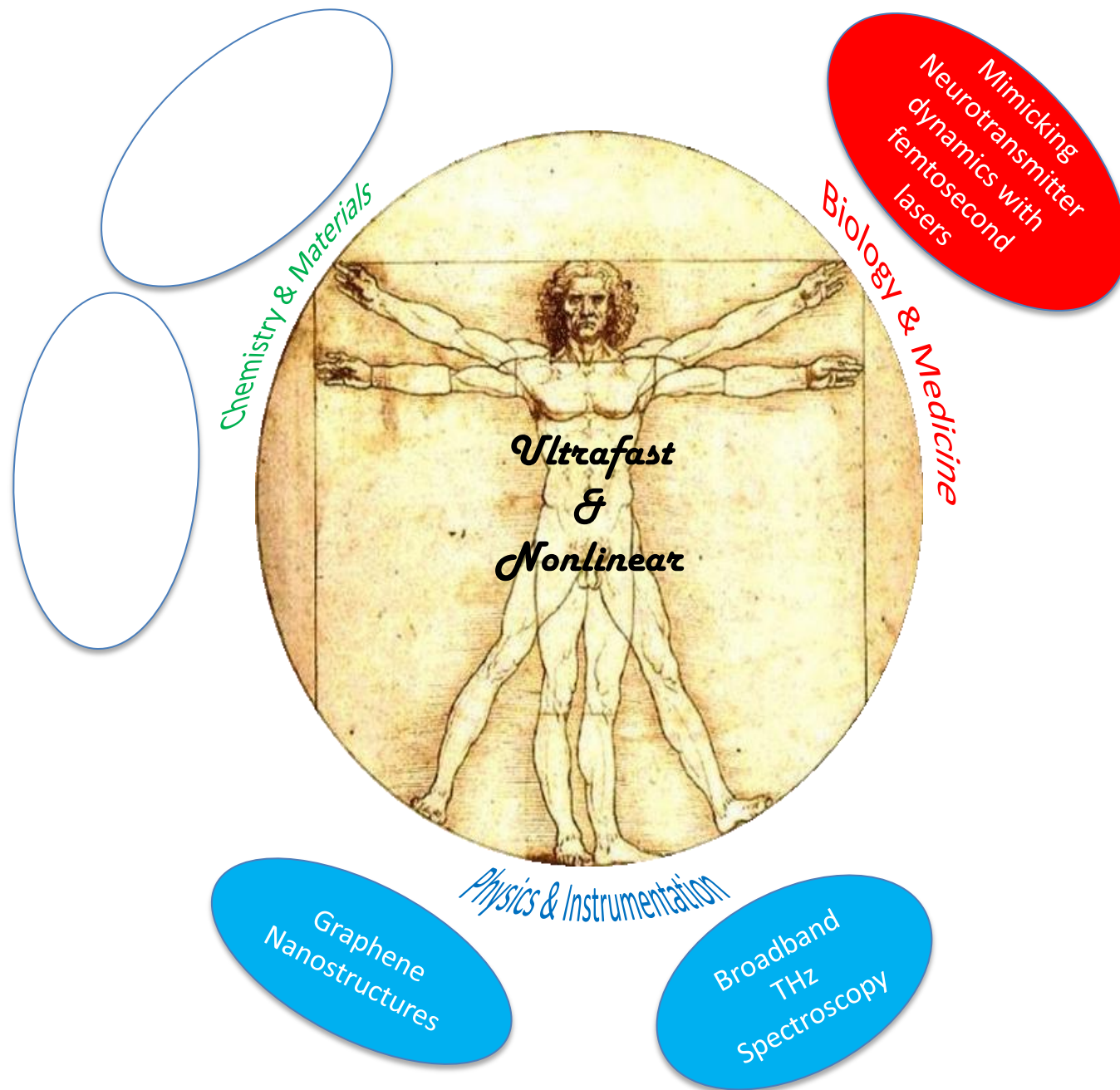
A



Mimicking Neurotransmitter Dynamics

- **Developments in laser technology:**
 - fiber lasers, access deeper portions in the brain, multi-location stimulation
- **Multi-Channel Operation:**
 - Tune nanoshell response to different wavelengths of light
- **Neural Prosthesis:**
 - Replace 'broken' neurons with these artificial structures
- **'Dopamine factories'** to liposomes to prevent depletion of dopamine

RESEARCH INTERESTS & PROJECTS





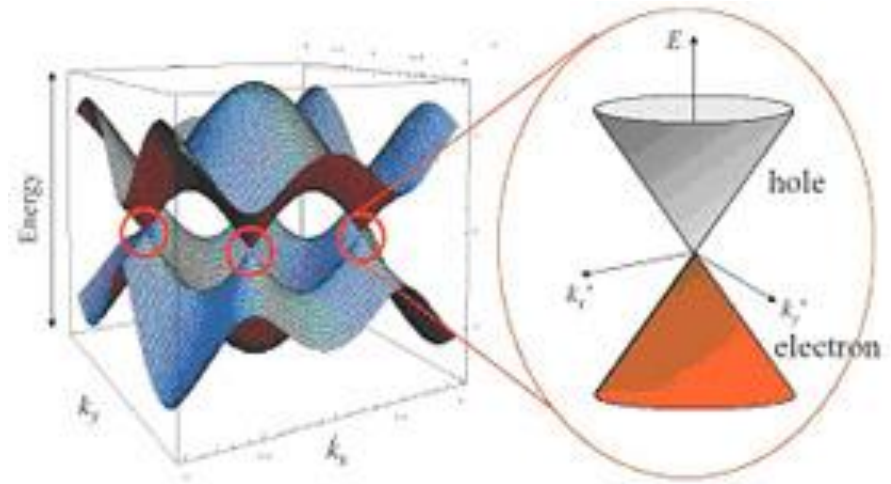
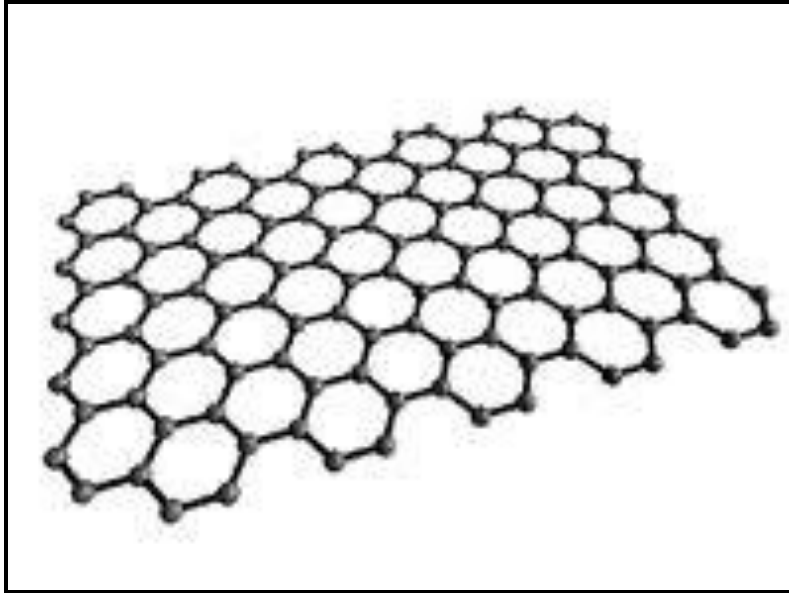
Dani Unit

Optical Selection Rules allow manipulation of unique states in graphene nanostructures

Eleftheria Kavousanaki, Rico Pohle, Keshav M. Dani

Optical Selection Rules in Graphene Nanostructures

Graphene, a recently isolated allotrope of carbon, demonstrates a linear-energy momentum dispersion.



$$\varepsilon = \hbar v_F \kappa$$

$$\varepsilon = \sqrt{(m_0 c^2)^2 + (pc)^2} \approx pc$$

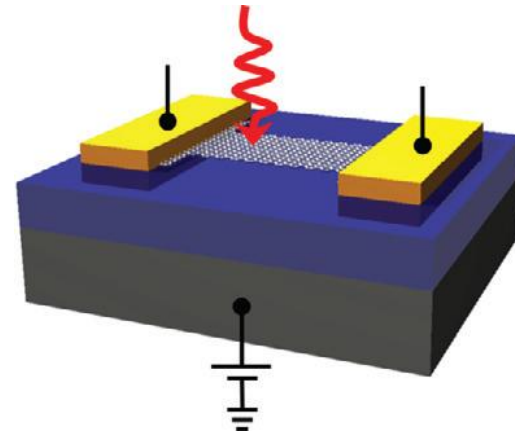
Optical Selection Rules in Graphene Nanostructures

The high conductivity and transparency of graphene suggest its utility as a transparent conductor for applications in touchscreen, photovoltaics, etc.

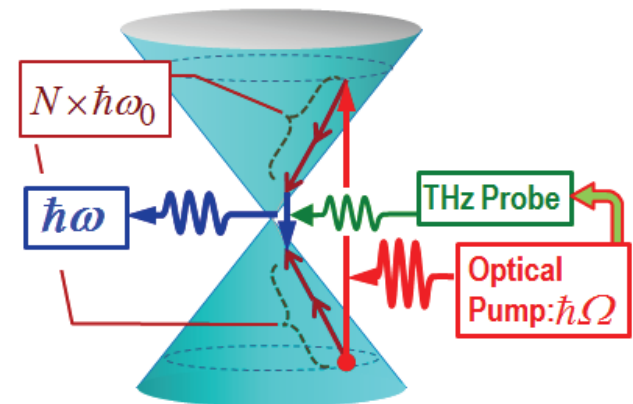
Touch Screen Devices



Bae, S, et al. *Nat. Nano.* **4**, 574-578 (2010)



Xia, F, et al. DOI: 10.1038/NNANO.2009.292

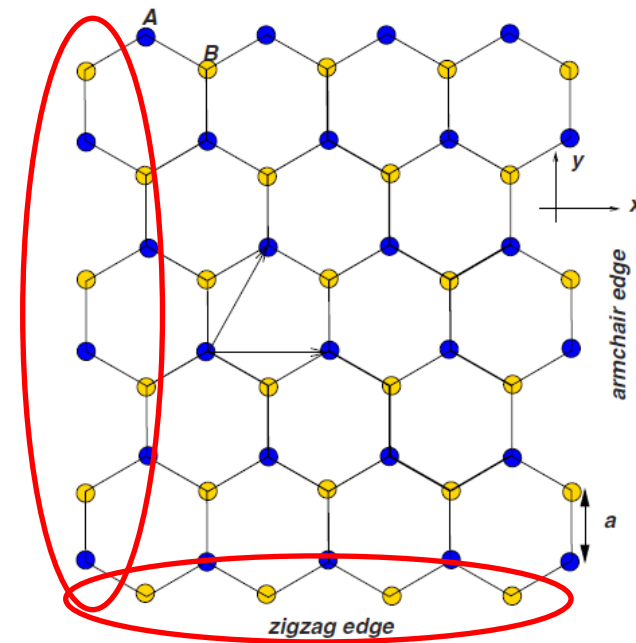


Ryzhii, et al. *APL* **101**, 083114 2007

Optical Selection Rules in Graphene Nanostructures

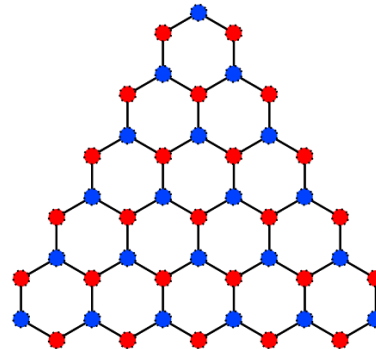
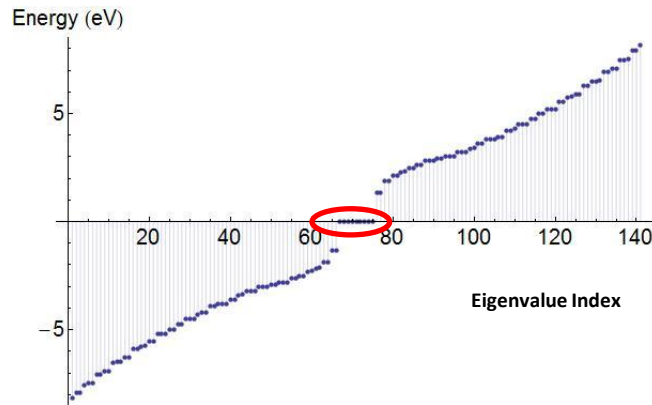
Depending on the 'edges' of the graphene nanostructures, one gets unique and exotic optical properties, e.g. half-filled states at the Fermi Level.

- ARMCHAIR EDGES
- ZIG ZAG EDGES

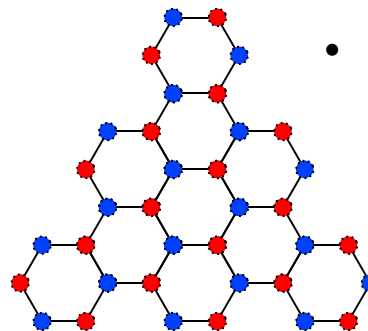
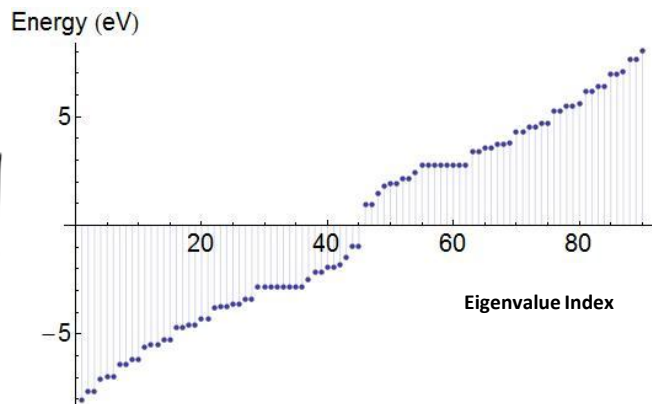


Optical Selection Rules in Graphene Nanostructures

In Triangular zigzag quantum dots, one expects half-filled states at the Fermi Level.

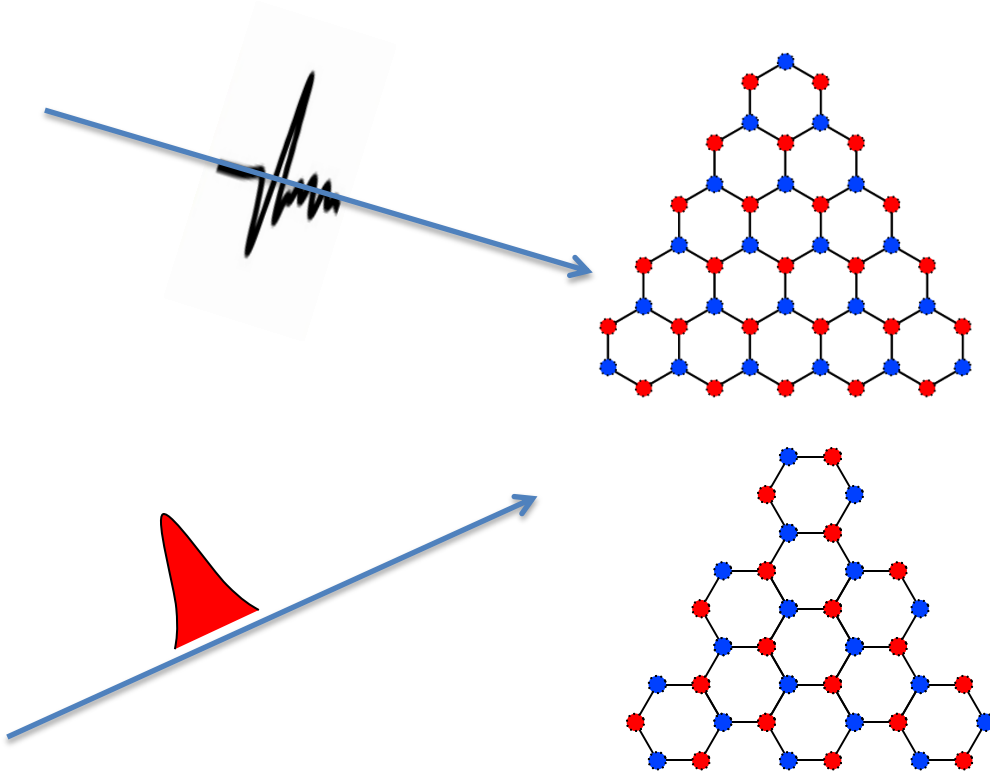


- Zero energy states
- Half-filled fermi level
- Magnetism at Room Temperature



Optical Selection Rules in Graphene Nanostructures

We would like to investigate the optical properties of these graphene nanostructures, and explore ways to manipulate these exotic states with light.



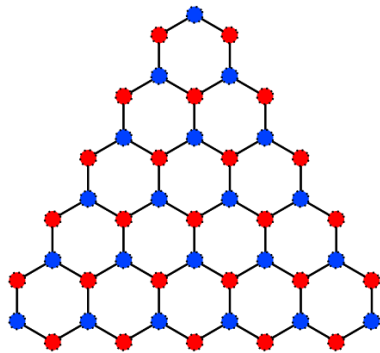
- Optical Selection Rules
- Non-linear Optical Properties
- Manipulating zero energy states

Optical Selection Rules in Graphene Nanostructures

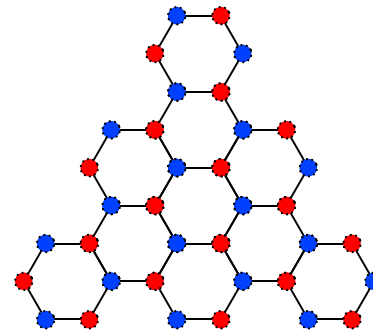
We use the standard Tight-Binding Hamiltonian with nearest neighbor hopping to calculate the eigenstates of the system.

■ Tight-binding Hamiltonian

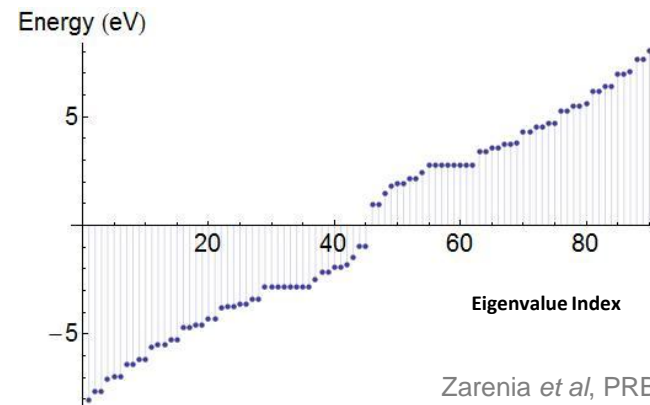
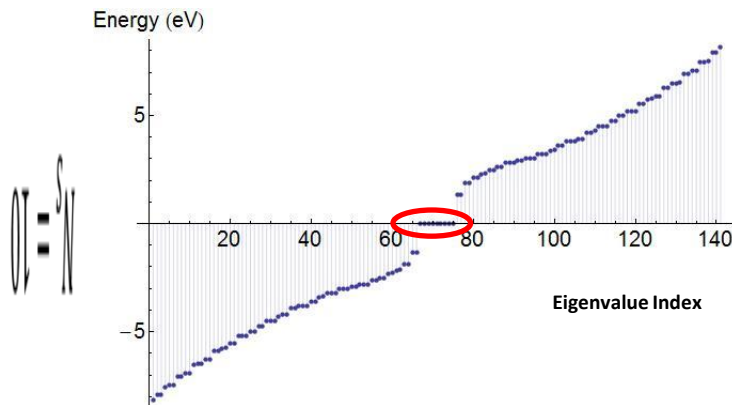
$$H = -t \sum_{\langle i,j \rangle, \sigma} (a_{\sigma,i}^{\dagger} b_{\sigma,j} + \text{H.c.})$$



ZIG ZAG DOT



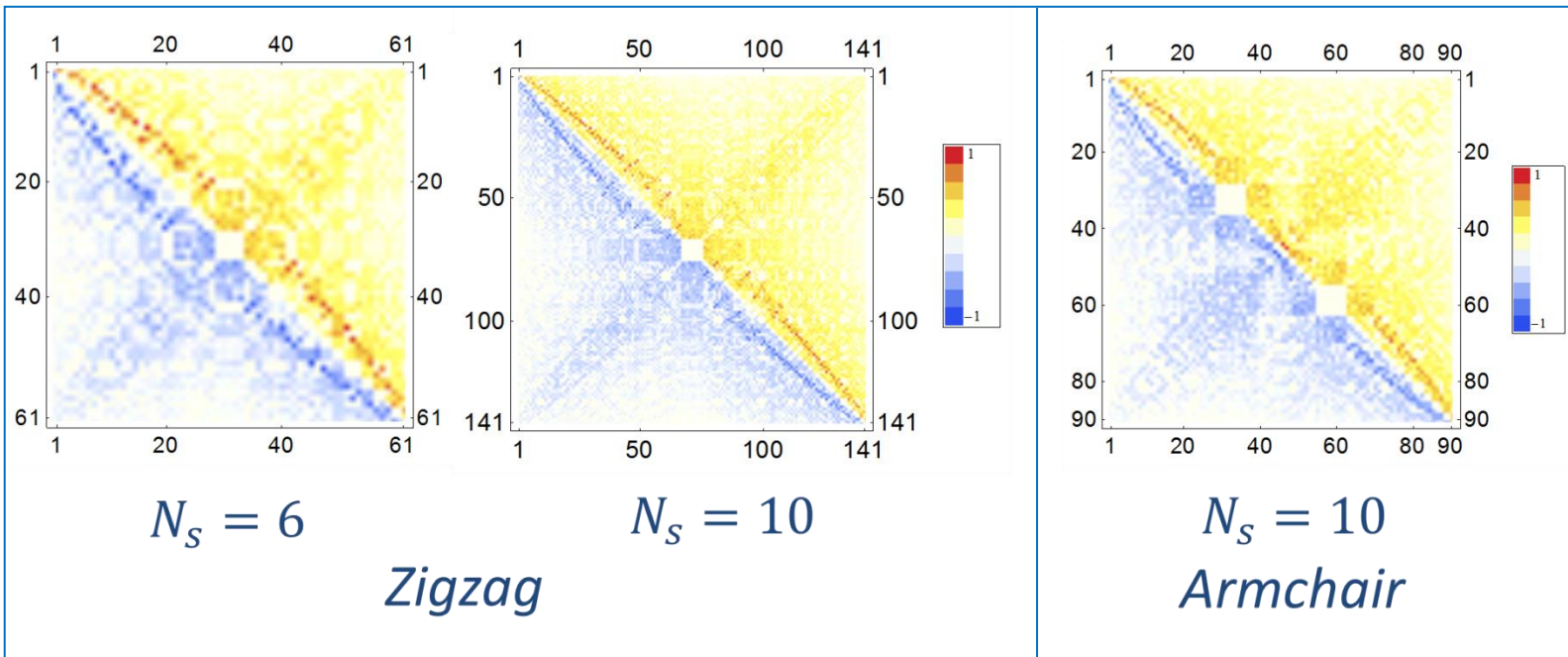
ARMCHAIR DOT



Optical Selection Rules in Graphene Nanostructures

This then allows us to calculate the dipole matrix element and linear absorption of the system.

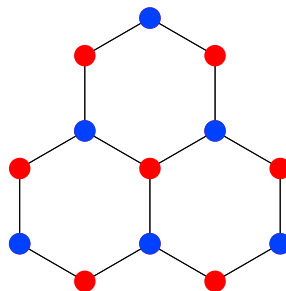
$$f_{nm} = \frac{2}{m_e} \frac{|\langle \varphi_n | p | \varphi_m \rangle|^2}{E_n - E_m}$$



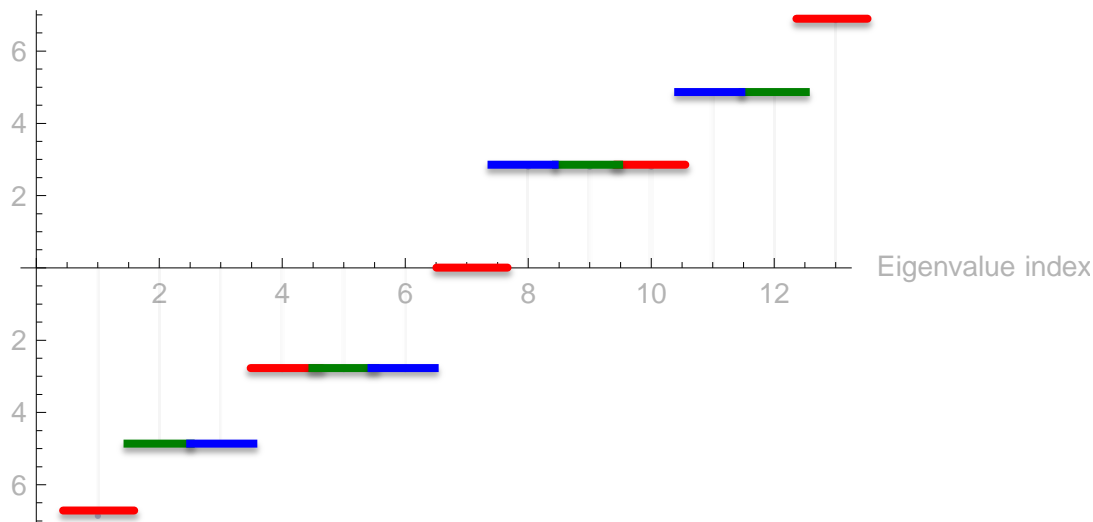
Optical Selection Rules in Graphene Nanostructures

Utilizing the discrete rotational symmetry in the system, we classify eigenstates based on the eigenvalue of the discrete rotational operator.

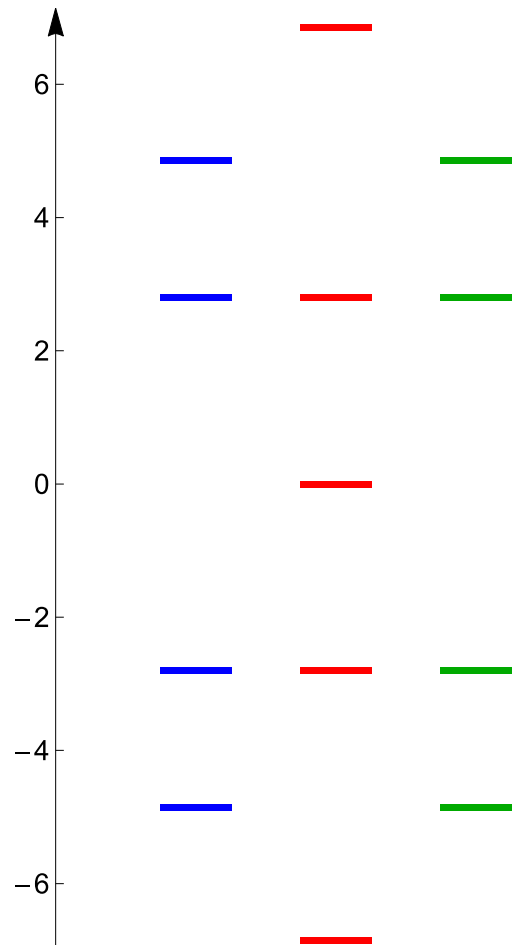
$$R|\phi_n\rangle = e^{i\psi_n}|\phi_n\rangle$$



Energy (eV)



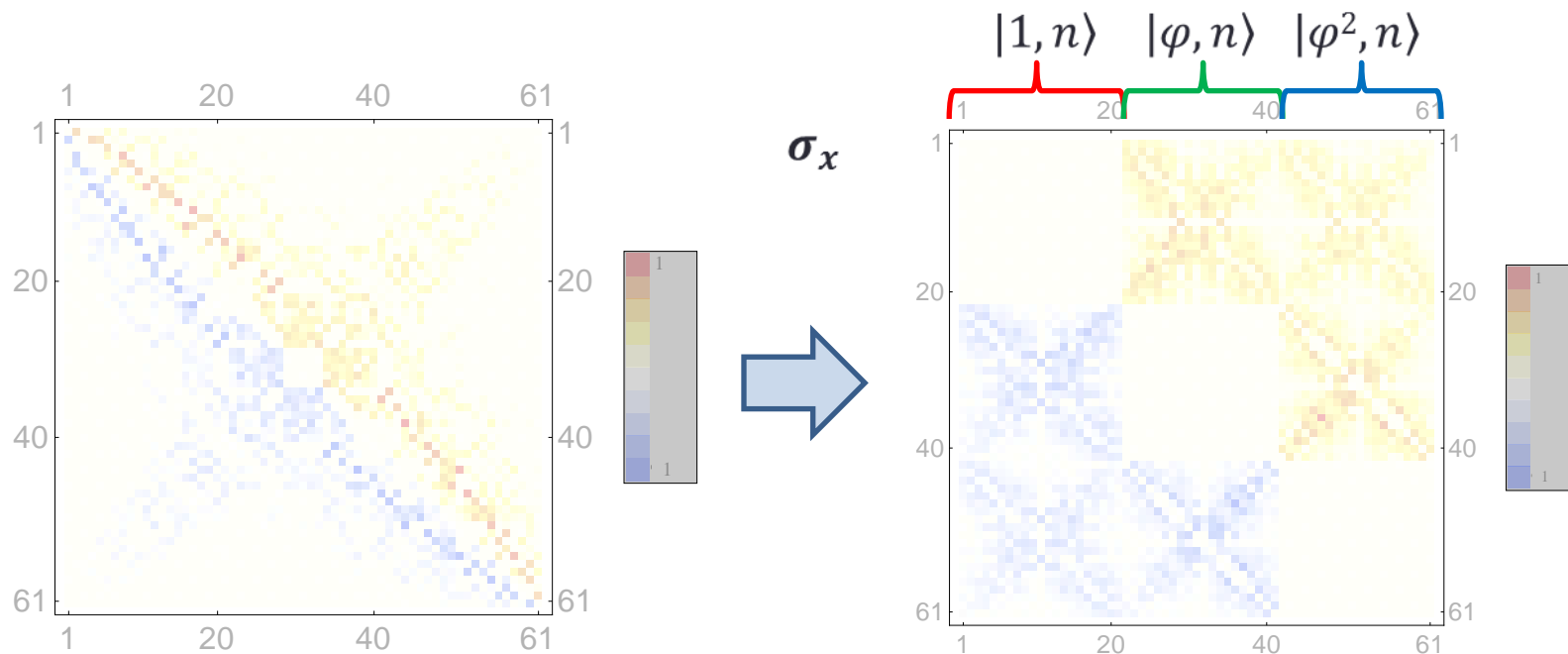
Energy



$$\psi_1 = -\frac{2\pi}{3} \quad \psi_2 = 2\pi \quad \psi_3 = \frac{2\pi}{3}$$

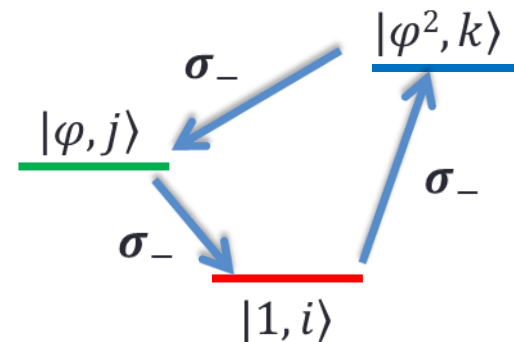
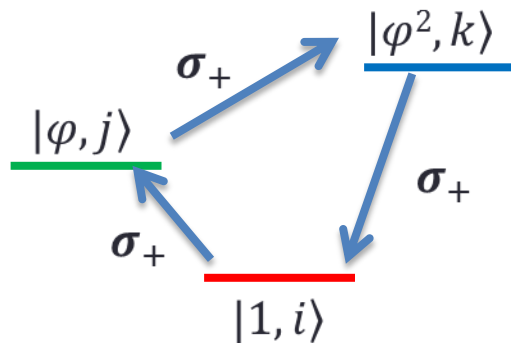
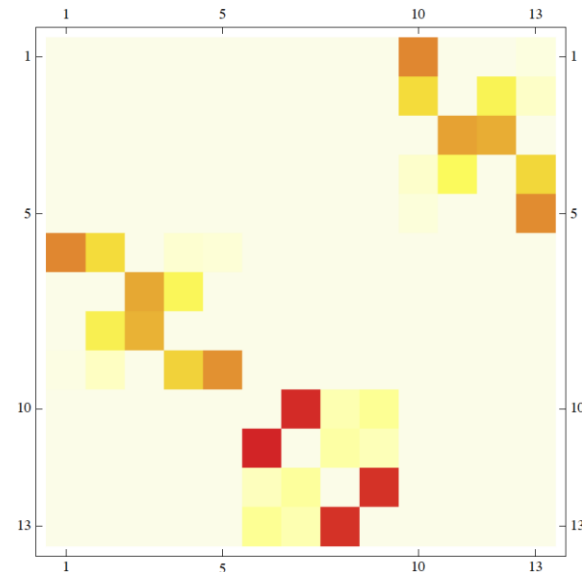
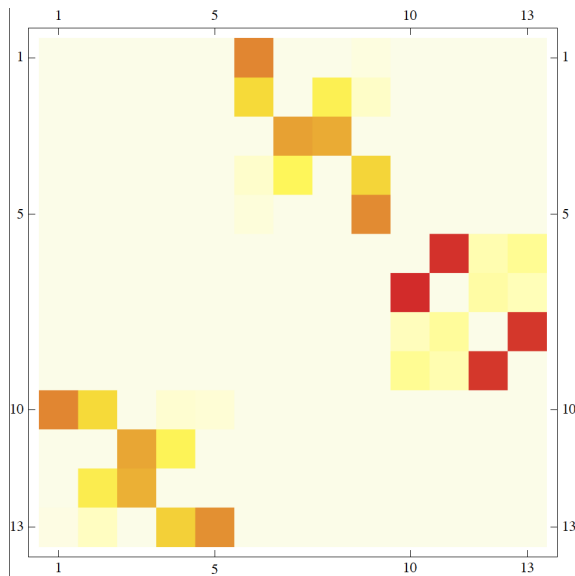
Optical Selection Rules in Graphene Nanostructures

The Dipole Transition Matrix takes on a much simpler structure in the modified basis.

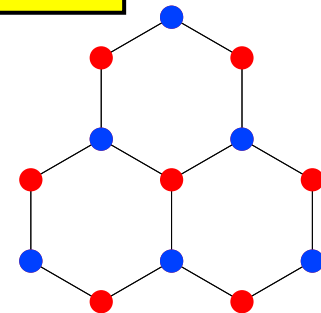
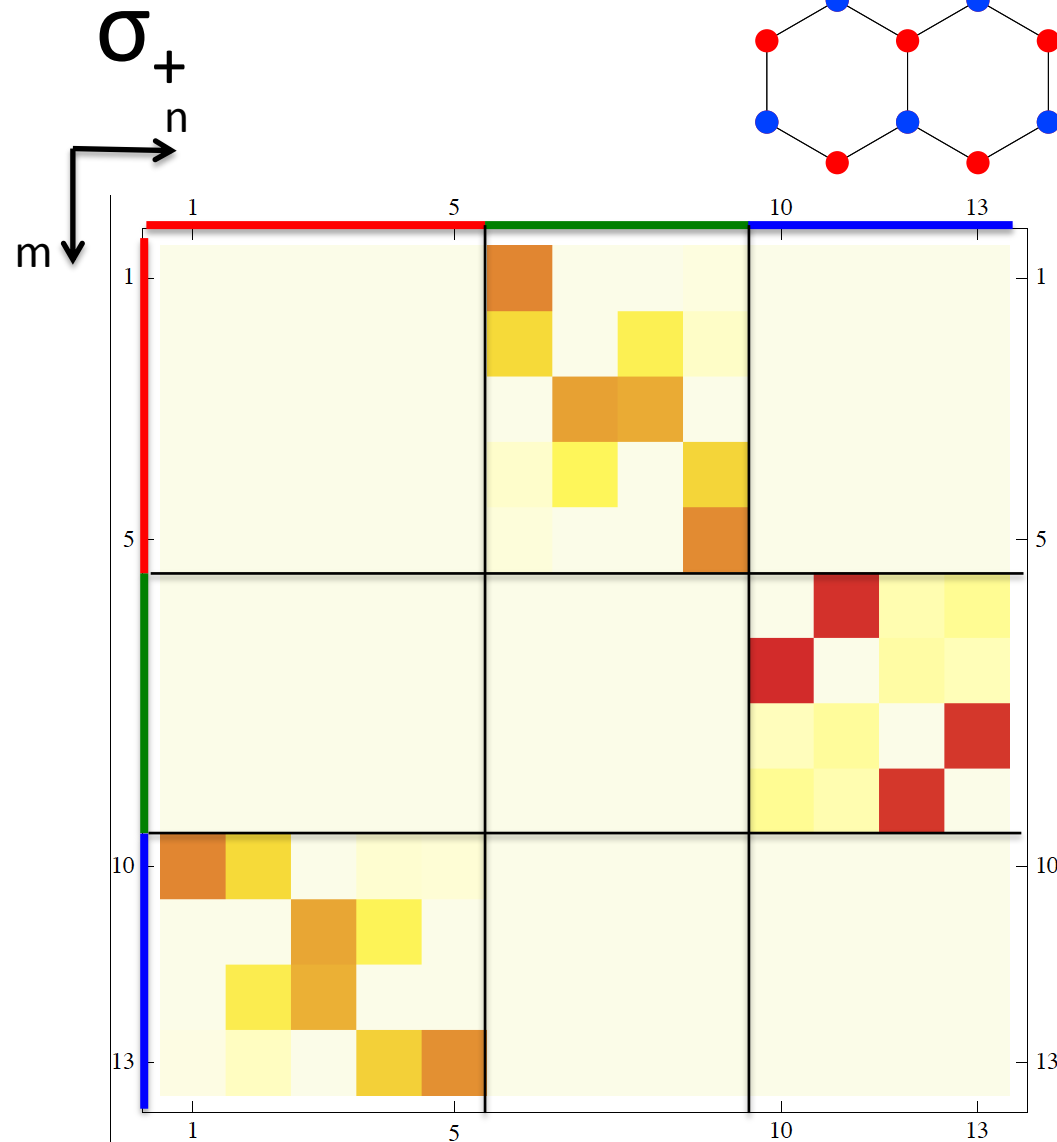
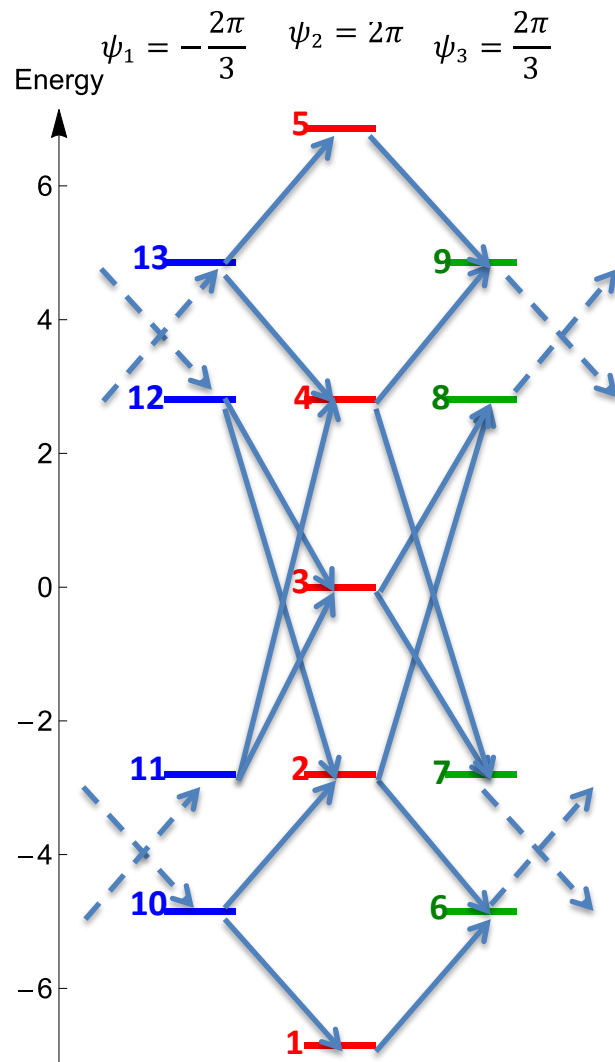


Optical Selection Rules in Graphene Nanostructures

In particular, using $\sigma+$ and $\sigma-$ light, gives clear optical transition rules.

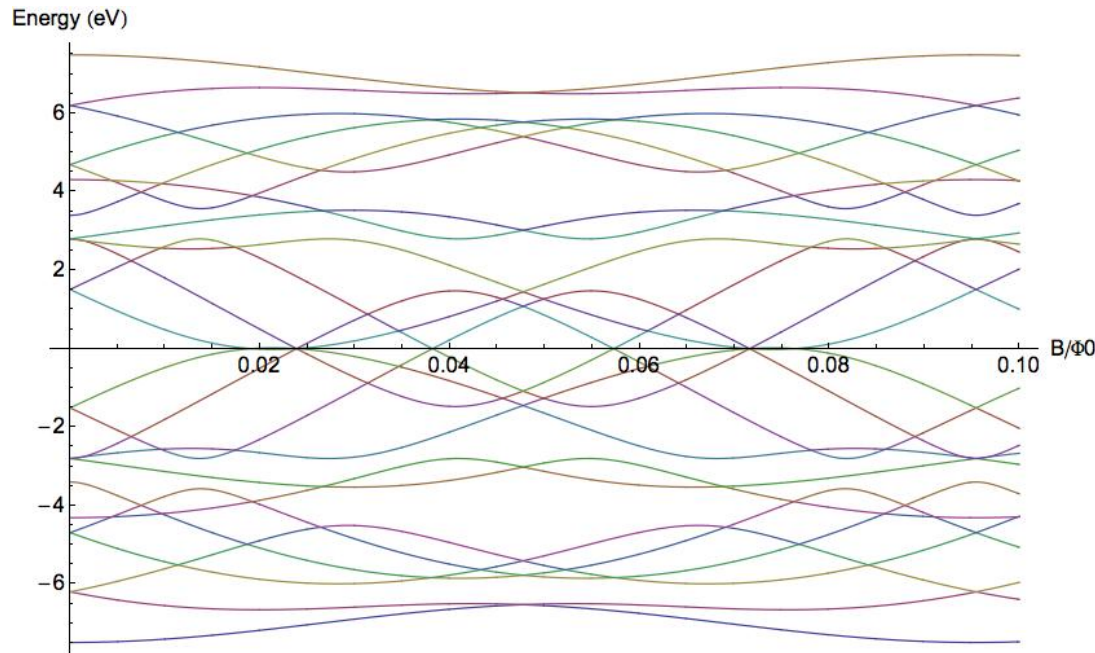


Optical Selection Rules in Graphene Nanostructures



Optical Selection Rules in Graphene Nanostructures

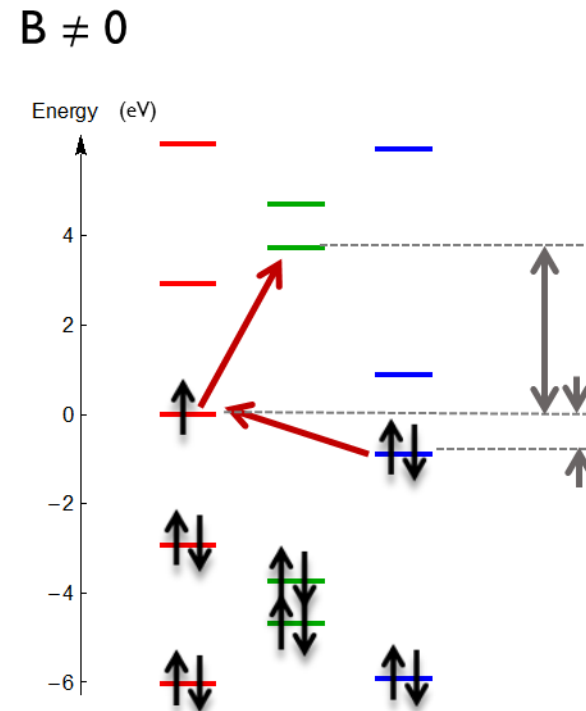
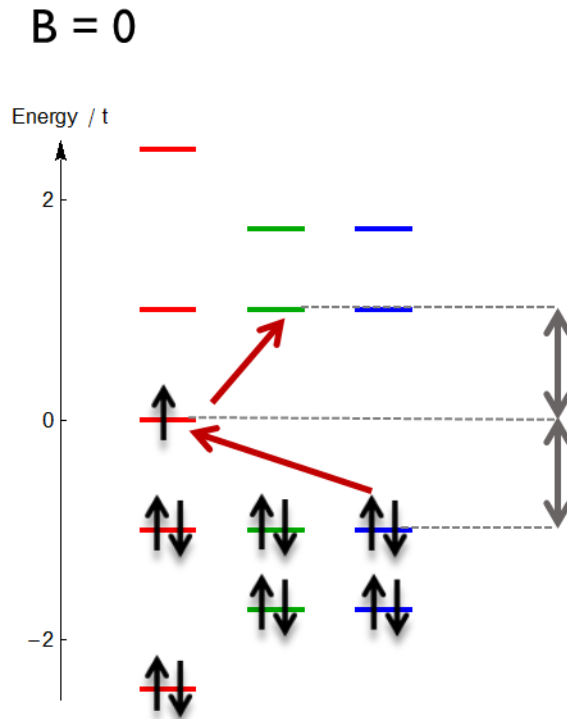
Optical Selection Rules survive in a B-field, and suggest ways of probing and manipulating the zero-energy states optically.



- Zero energy states don't move
- Breaks the degeneracy between different rotational eigenstates

Optical Selection Rules in Graphene Nanostructures

Optical Selection Rules survive in a B-field, and suggest ways of probing and manipulating the zero-energy states optically.

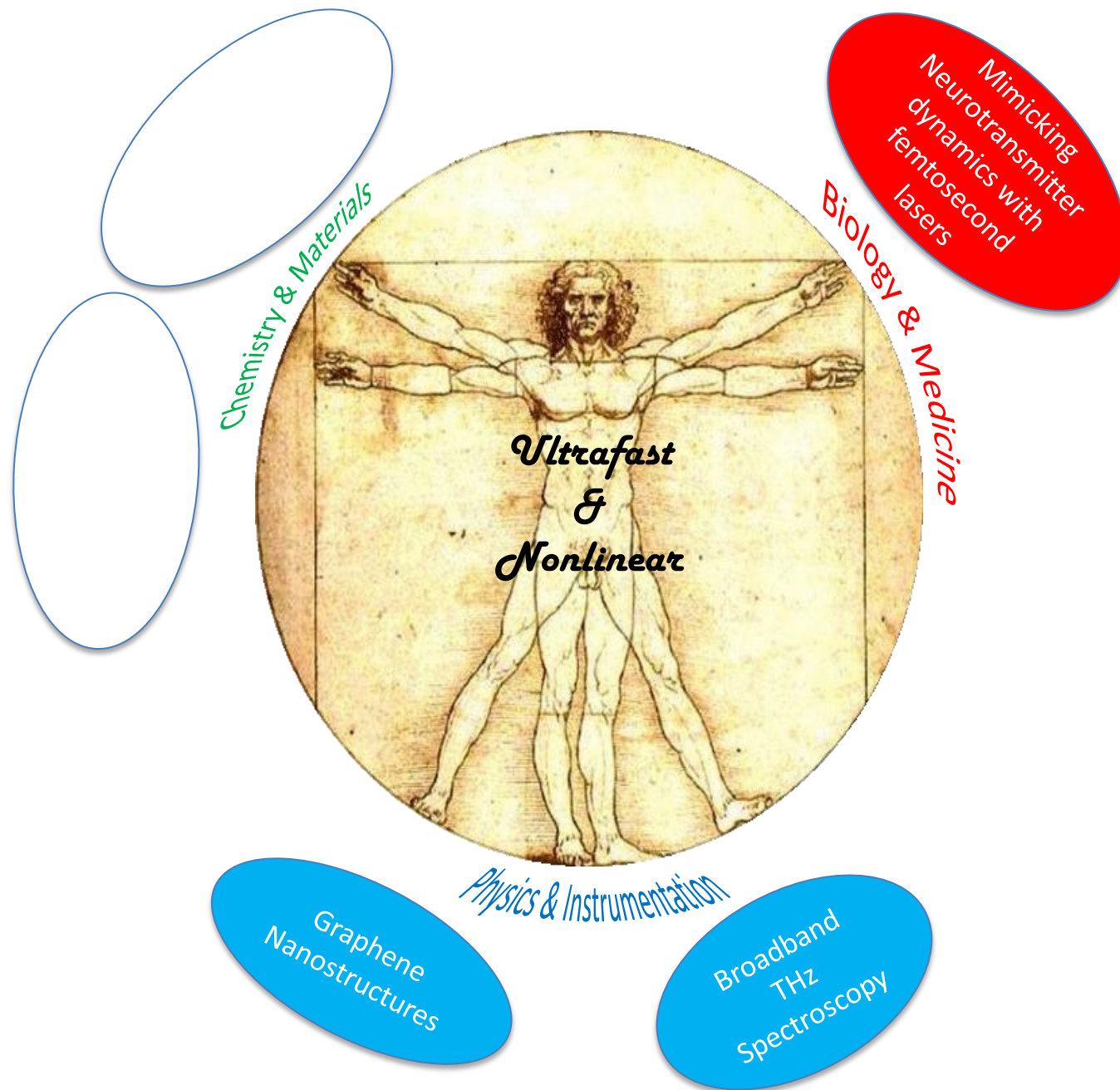


Optical Selection Rules in Graphene Nanostructures

In conclusion:

- Graphene quantum dots display optical selection rules based on their rotational symmetries
- These selection rules survive in the presence of a magnetic field
- They suggest ways of specifically manipulating and accessing the zero-energy states, and other interesting electronic states of the system

RESEARCH INTERESTS & PROJECTS



Femtosecond Spectroscopy Unit



THANK YOU

Strong Partnerships with:

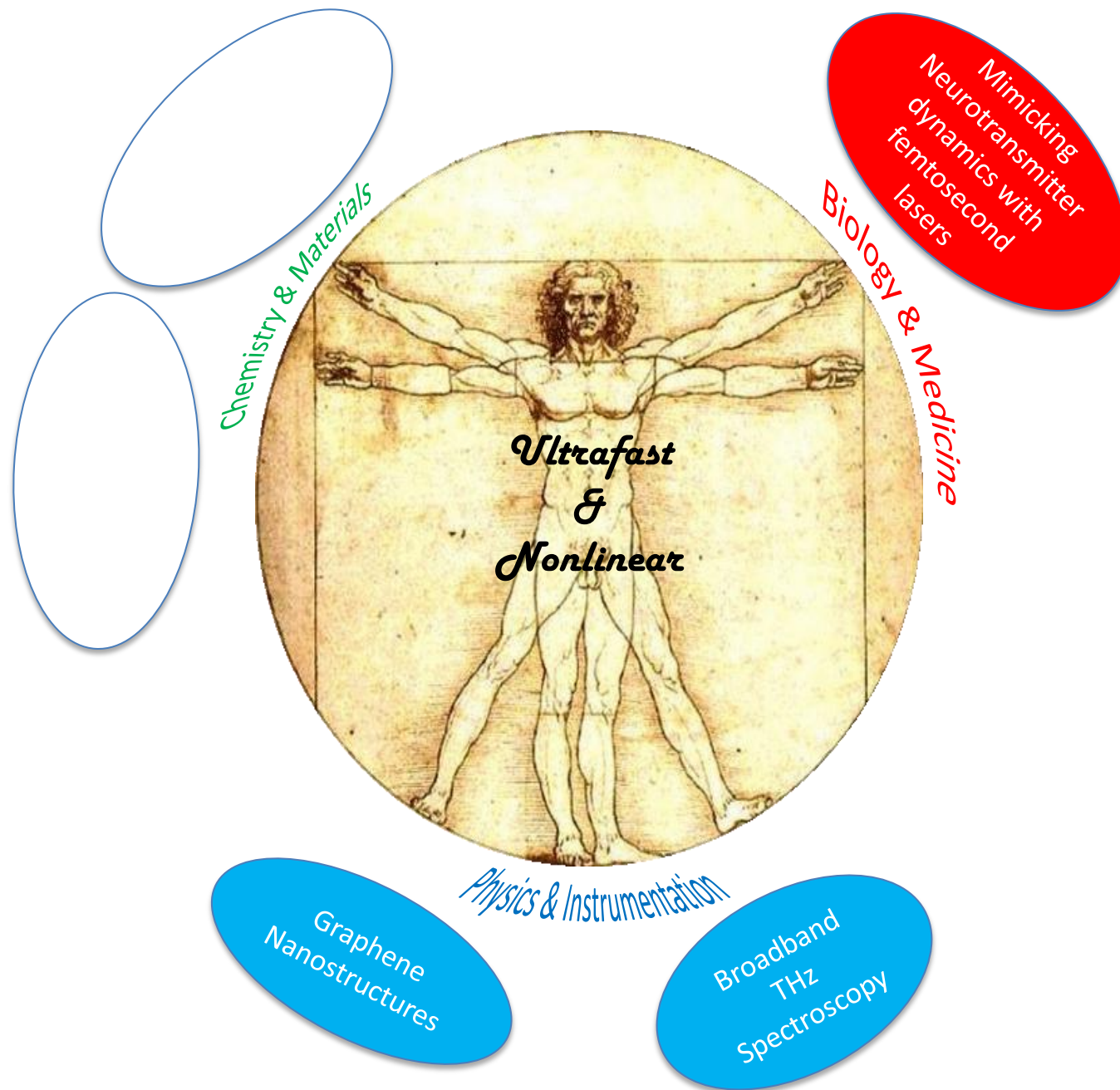
Ecole Normale Supérieure, Paris, France
Technical University, Berlin, Germany
Rice University, Texas, USA
Southern Illinois University, Illinois, USA
Los Alamos National Lab, USA

Partnerships within OIST:

Wickens Unit – Mimicking Neurodynamics
Sowann Unit – Magnetic Nanoparticles
Qi Unit – Organic Electronics
Shannon Unit – Graphene Nanostructures

<https://groups.oist.jp/fsu>

RESEARCH INTERESTS & PROJECTS





Tignon Group



Dani Unit

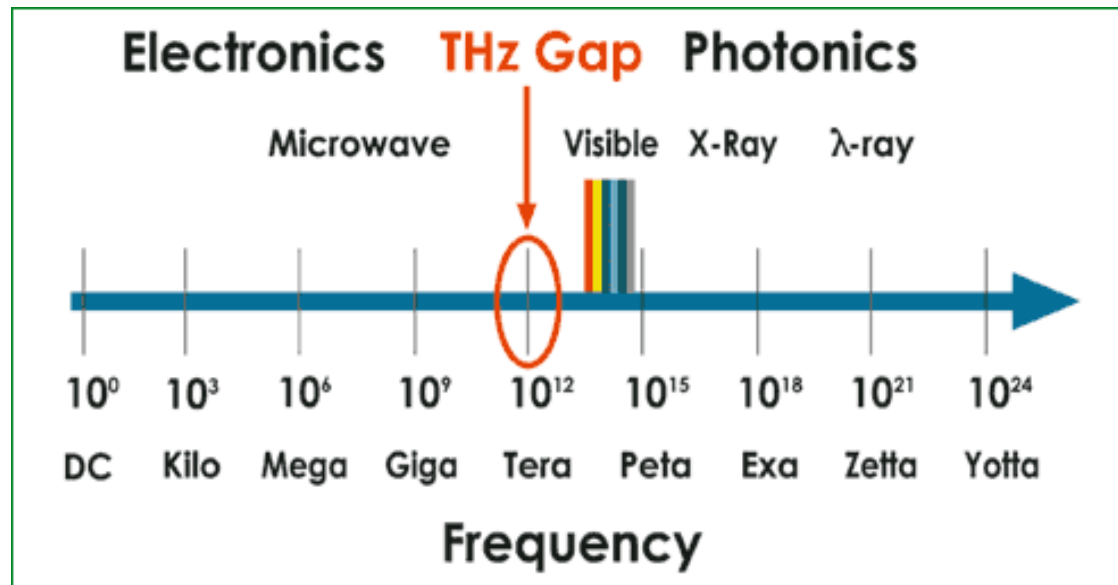
Ultrabroadband THz Generation with Interdigitated Photoconductive Antennas

Pete Hale, Catherine Chin, Julien Madeo, Sukhdeep Dhillon, Juliette Mangeney, Matthieu Baillergeau

Ultrabroadband THz Generation

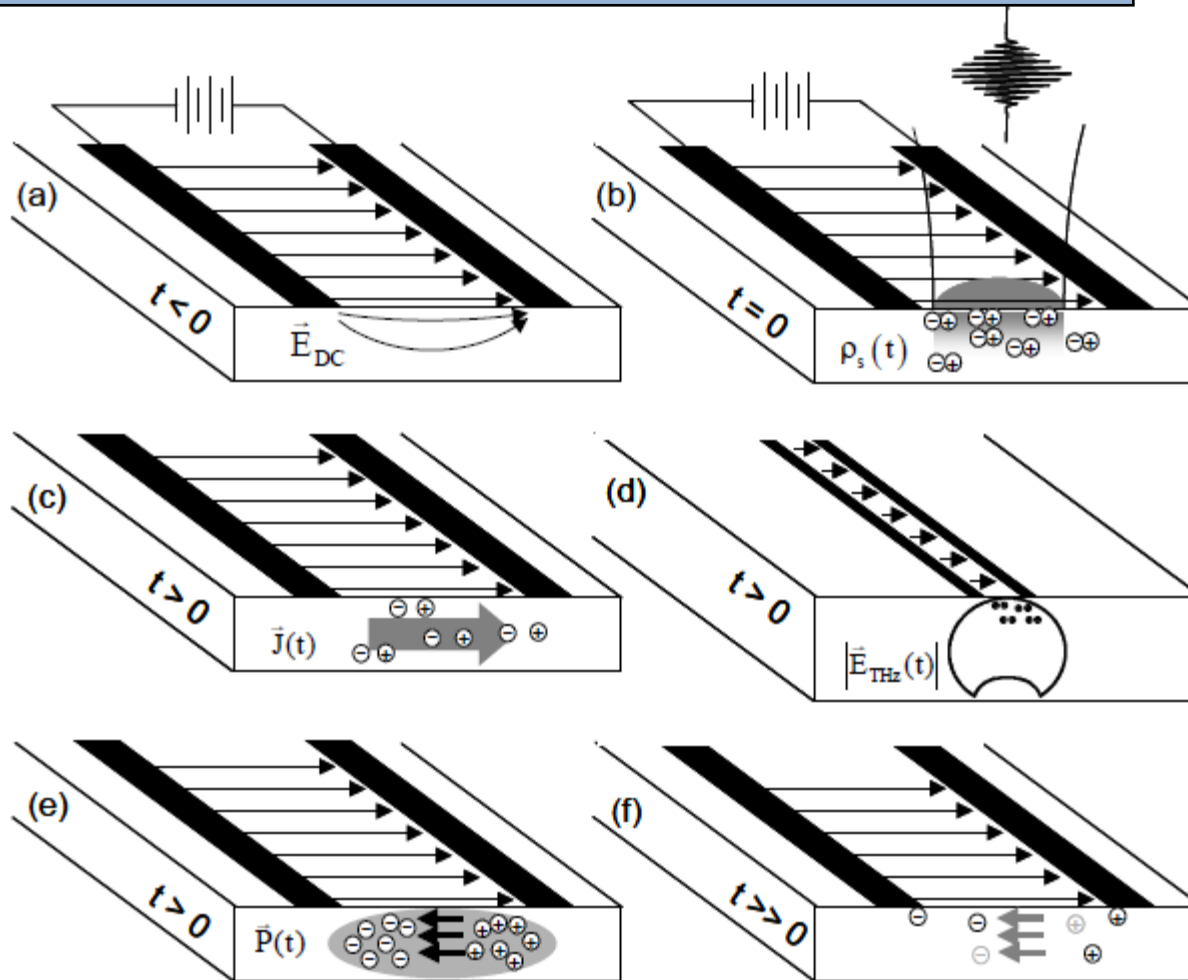
The THz 'gap' lies between electronics and optics and needs to be accessed by a hybridized method encompassing both fields!

- Terahertz measurements, traditionally 0.1 THz - 3 THz
 - Corresponds to 3 mm - 100 μm
 - 0.4 meV – 12 meV
- Low energy spectrum



Ultrabroadband THz Generation

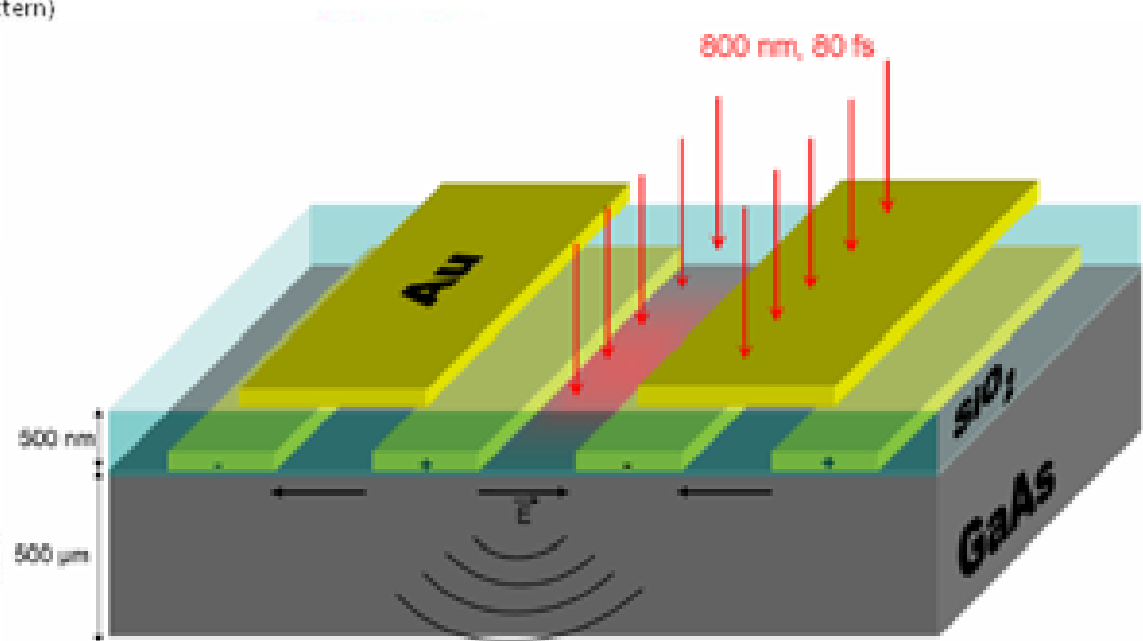
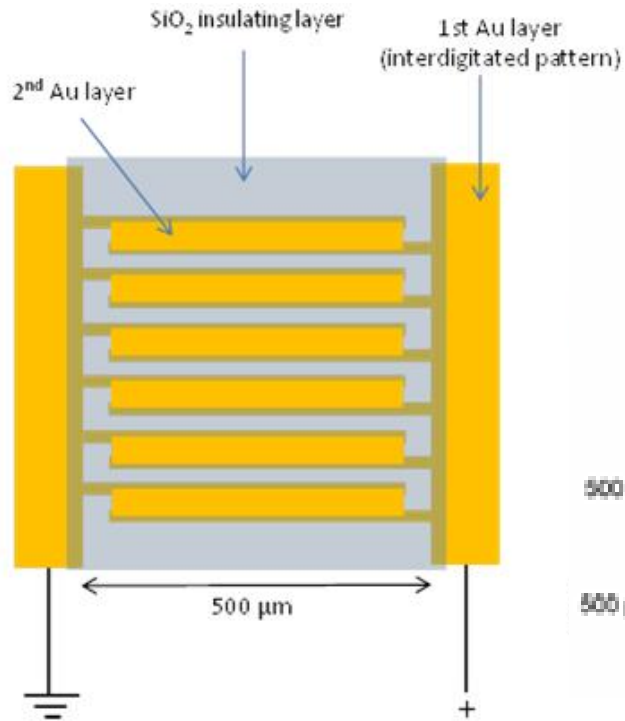
We use photoconductive antennas to generate THz in this project.



The accelerating current (i.e. charge) emits an electromagnetic wave which is at the THz frequency due to the material and experimental parameters in play.

Ultrabroadband THz Generation

Our antennas are inter-digitated allowing for larger spot sizes and higher excitation powers.

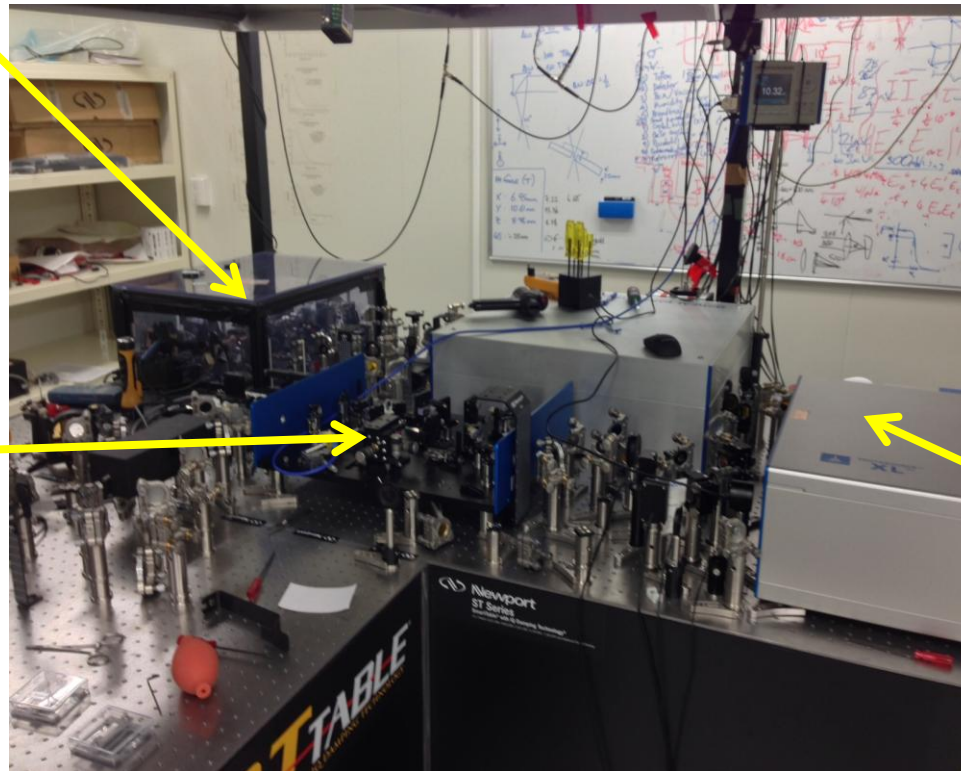


Ultrabroadband THz Generation

Our setup consists of a high power, high rep-rate commercial oscillator, a fiber based short-pulse kit and a home-built THz setup.

THz TDS

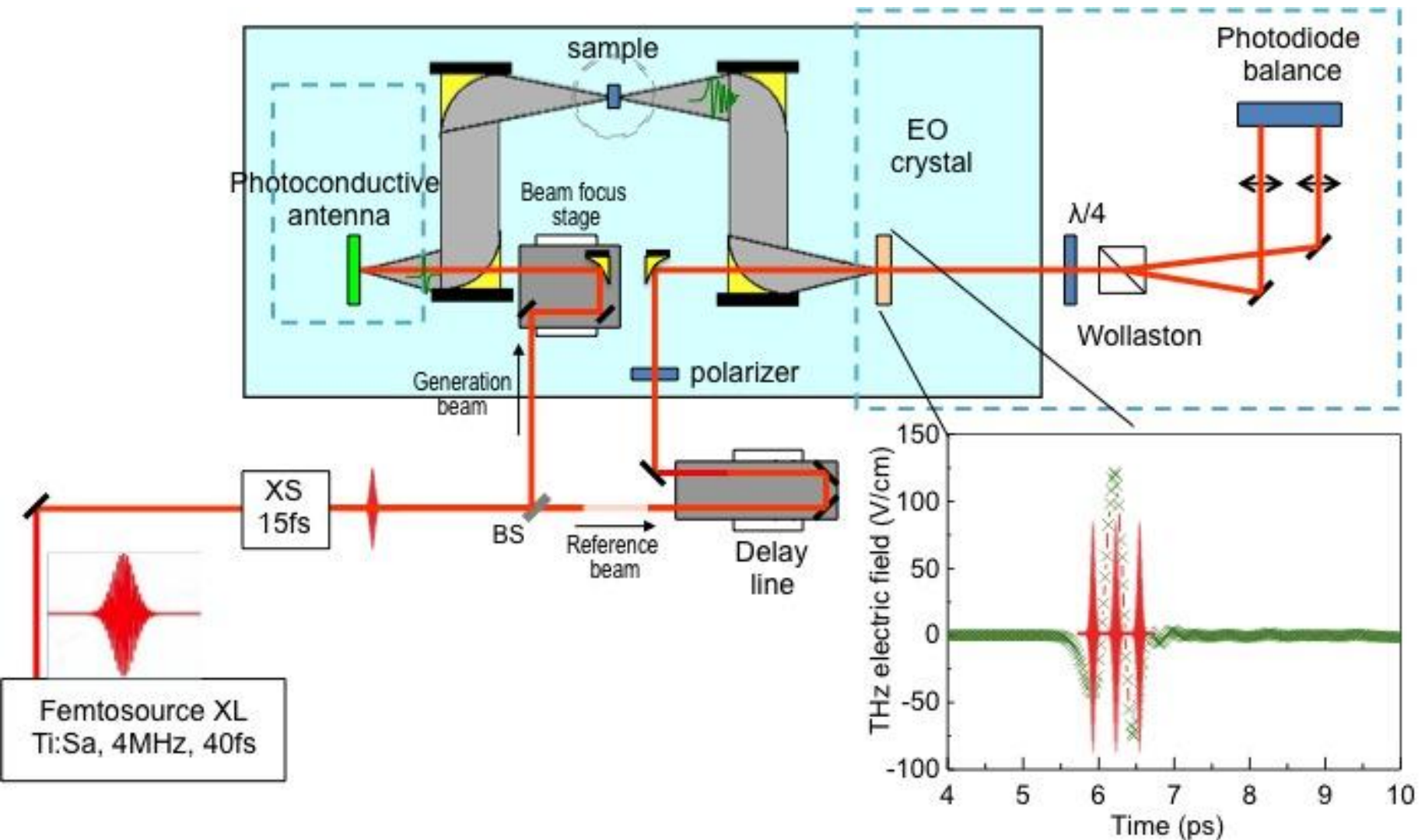
XS:
15 fs
4 MHz
200nJ/pulse



XL:
45 fs
4 MHz
650nJ/pulse

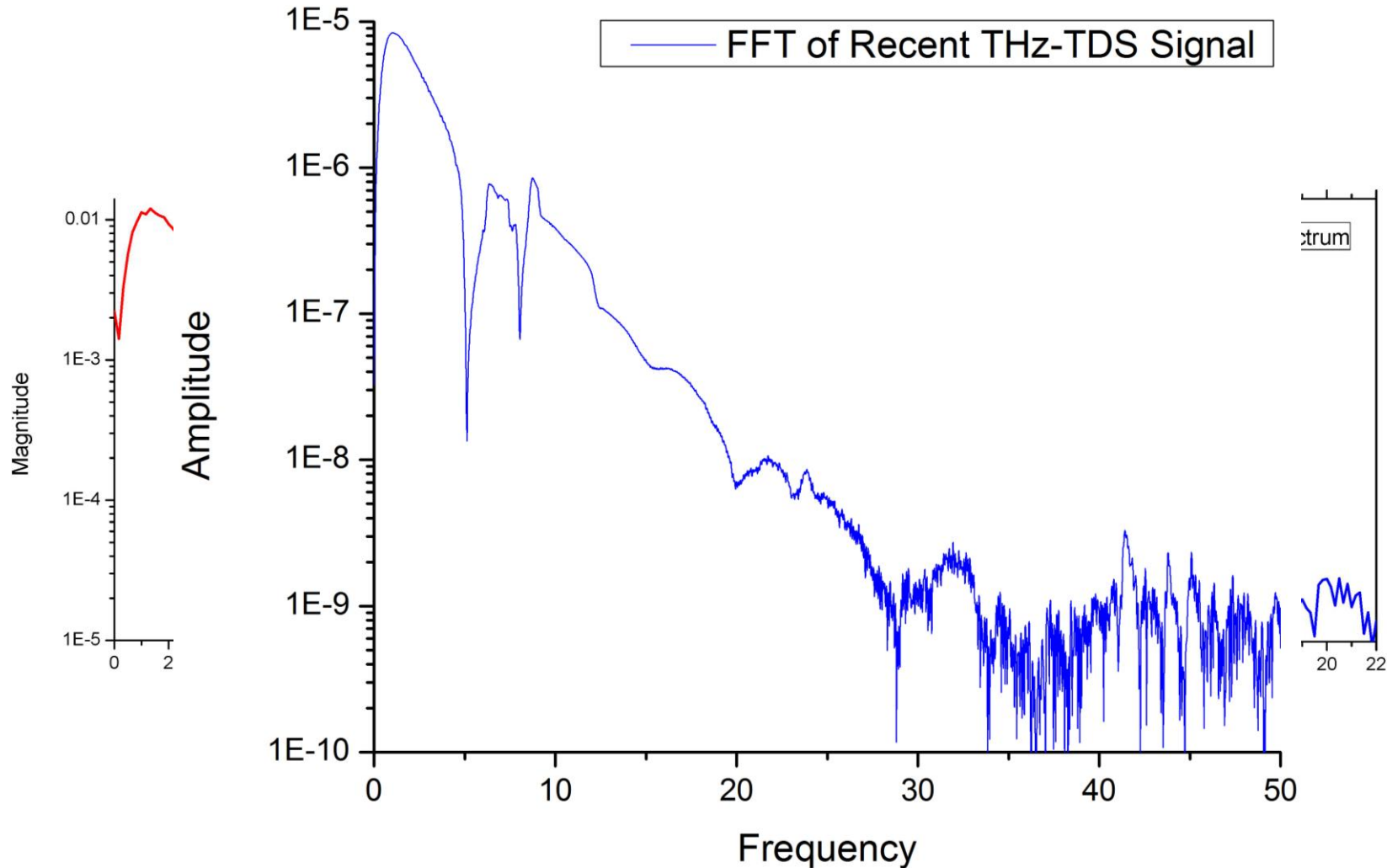
Ultrabroadband THz Generation

We believe the key characteristics of our THz setup are: short pulses, high power, high rep. rate & inter-digitated antennas.



Ultrabroadband THz Generation

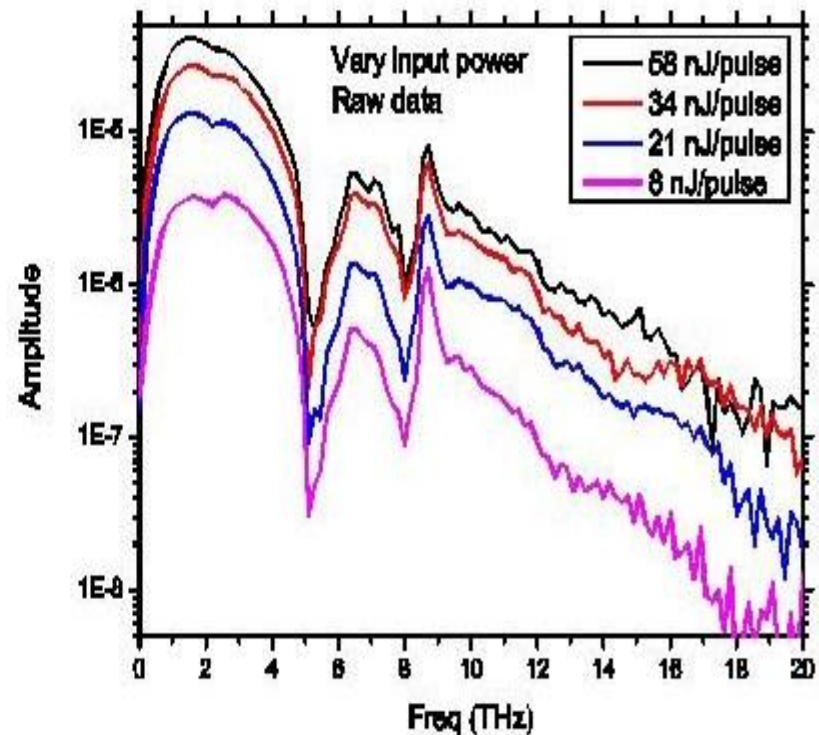
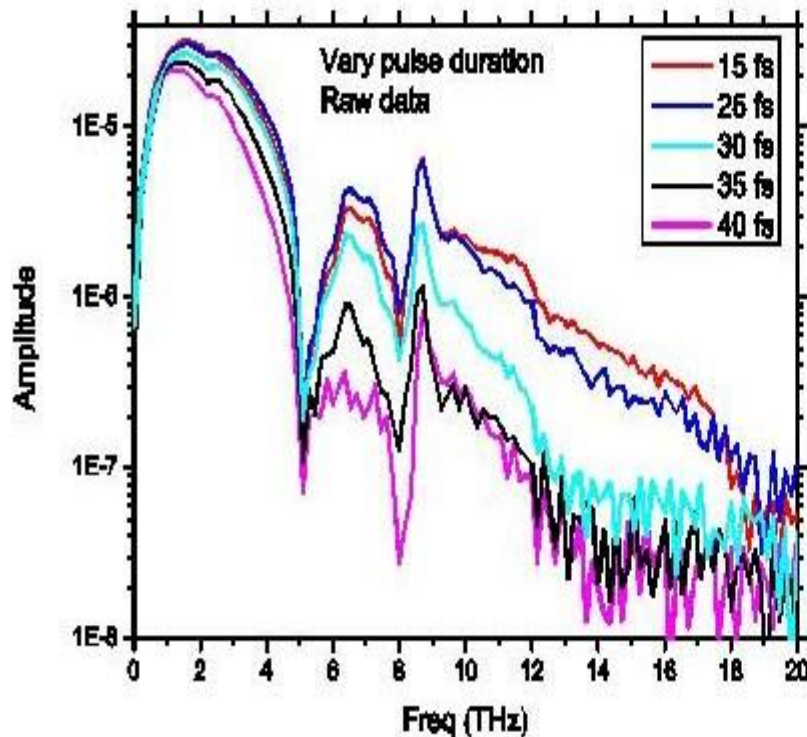
We have produced ultrabroadband THz pulses in the time domain with our system.



However, getting the right alignment, laser stability, and good measurement conditions remains a challenge (and sometimes a mystery)!

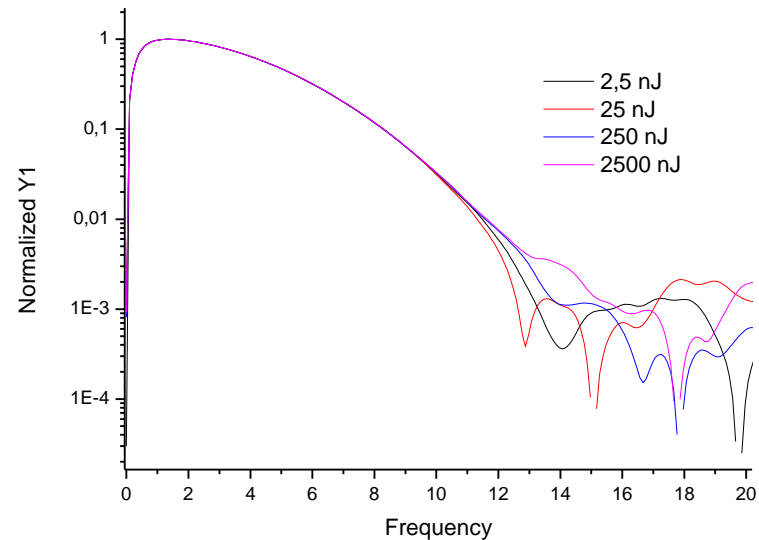
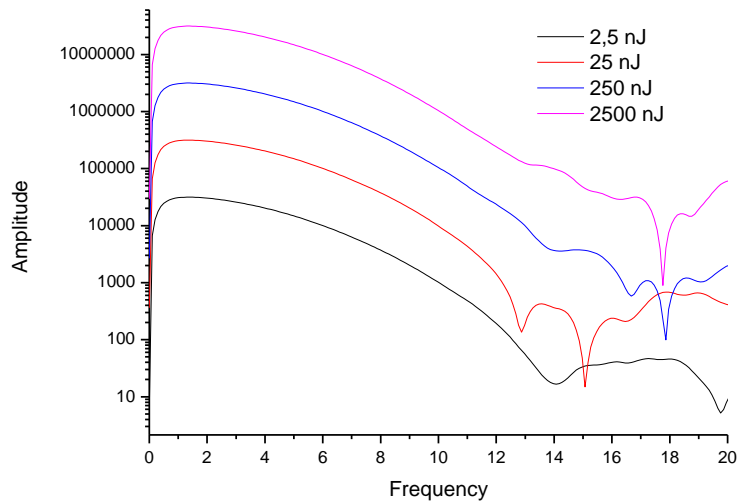
Ultrabroadband THz Generation

High power and short pulses are certainly crucial to producing ultrabroadband THz pulses.



Ultrabroadband THz Generation

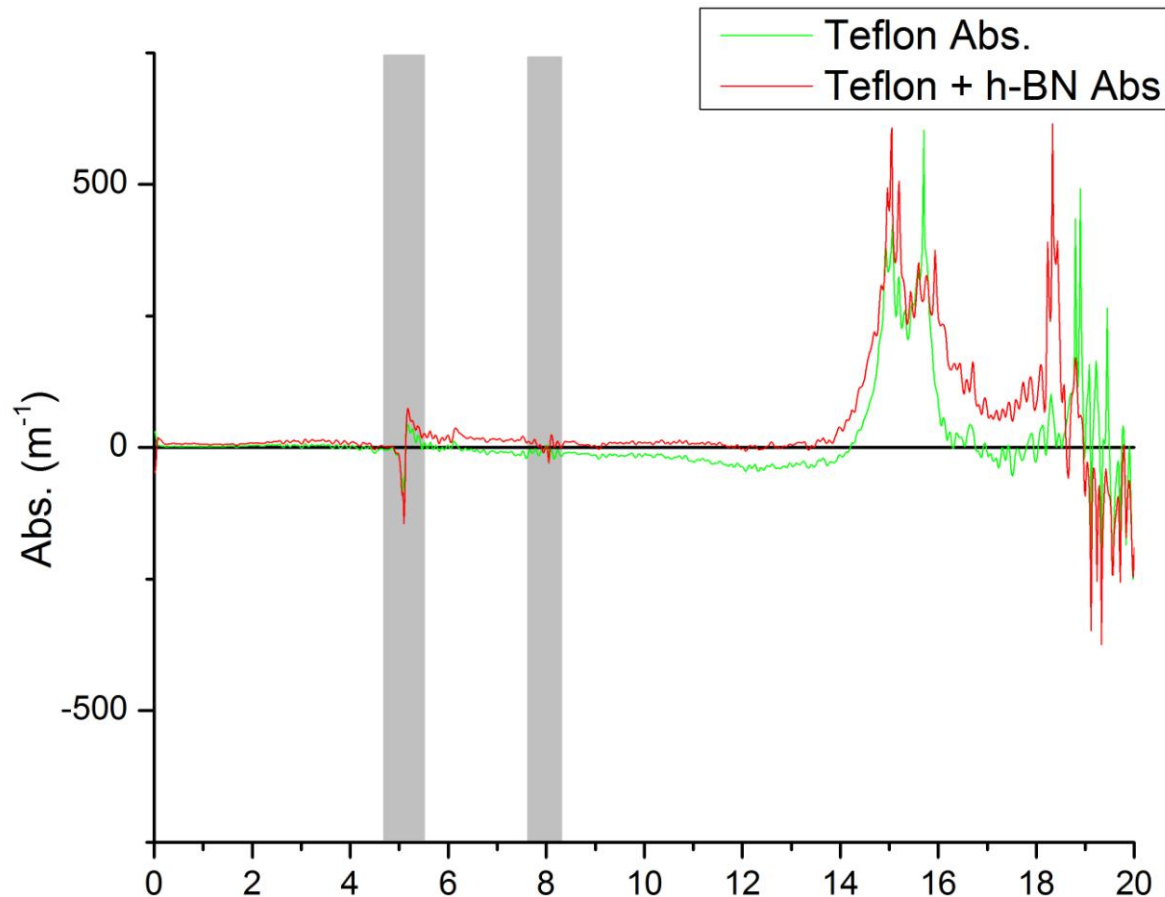
Quick simulations seem to suggest that high power simply gives you more signal, which then is higher than the noise threshold.



We are still in the process of trying to understand the mechanism and optimize (make easier) the process of getting a broadband signal.

Ultrabroadband THz Generation

In the meantime, we are also trying to THz-TDS with the system.



Further work needs to be done to optimize our TDS capabilities at high frequencies or focus on samples at lower frequencies!

RESEARCH INTERESTS & PROJECTS

