ELI-ALPS Research Institute
TOWARDS THE SHARP END OF ATTOSCIENCE

Ultragyors dinamika félvezetőkben – egy kémikus nézőpontja

Csaba Janáky, PhD

2018.11.13. – SZTE

SZÉCHENYI 2020
HUNGARIAN GOVERNMENT
European Union
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INVESTING IN YOUR FUTURE

Vázlat

- Röviden az ELI-ről
- Fény-anyag kölcsönhatás határfelületeken
- Ultragyors dinamika félvezetőkben, vizsgálati módszerek
- Napelemek

Az idő rövid története

Attofizika

as 10^{-18} s

fs 10^{-15} s

ps 10^{-12} s

ns 10^{-9} s

ms 10^{-6} s

ms 10^{-3} s

Szem

10^{0} s

10^{3} s

10^{6} s

Ember

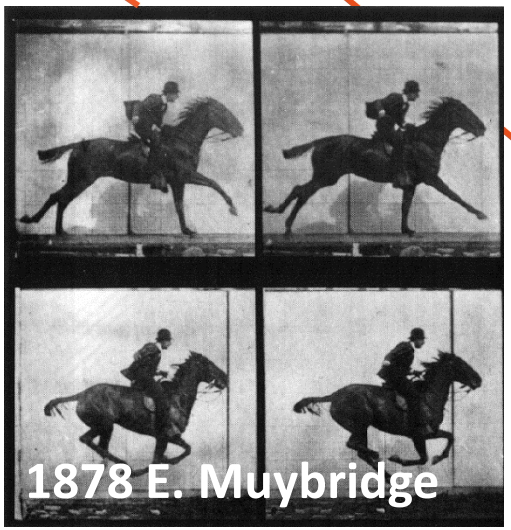
10^{9} s

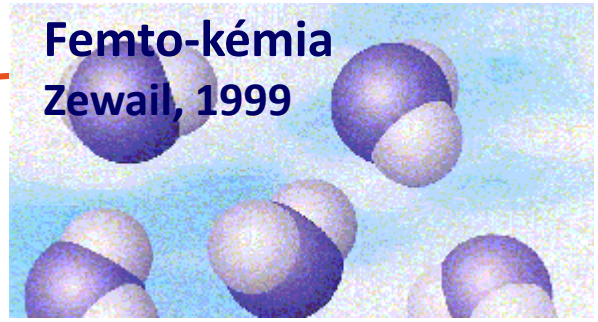
10^{12} s

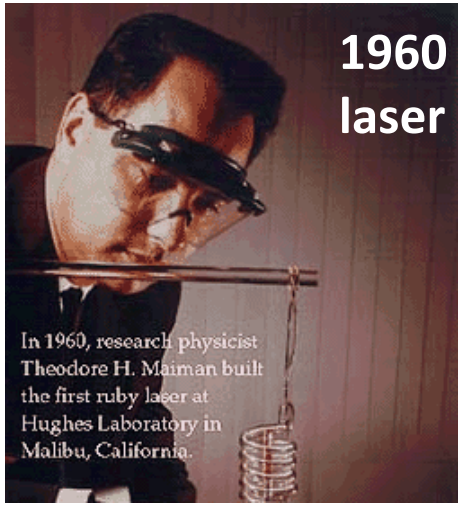
10^{15} s

Univerzum

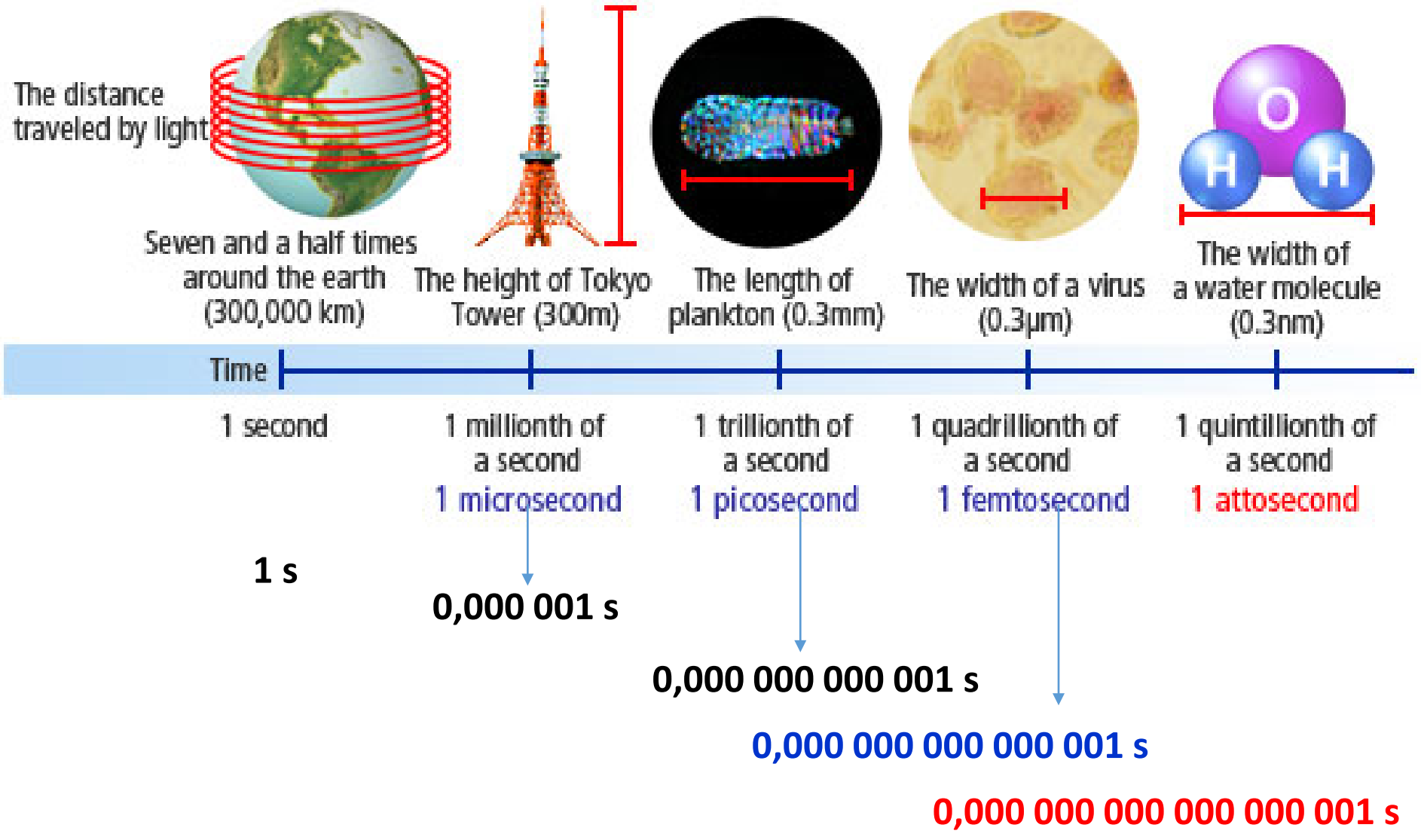
10^{18} s





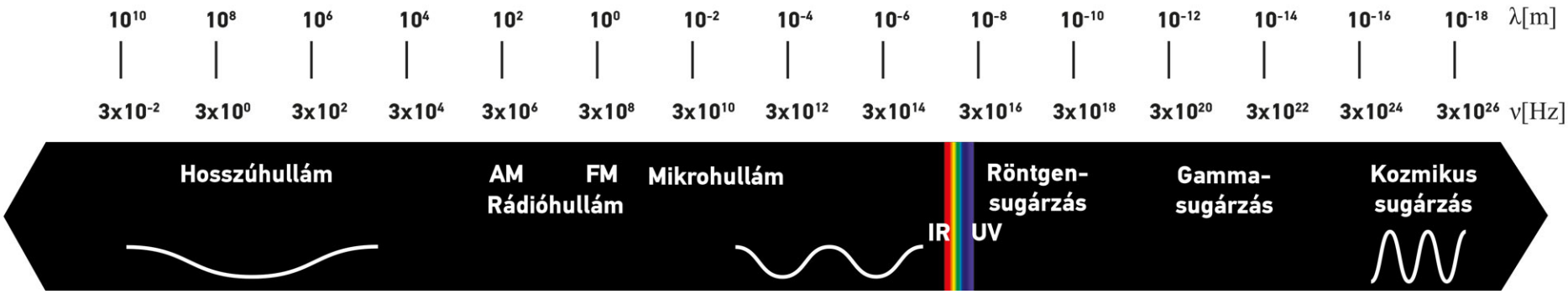


A pillanat mértéke…



Az ELI-ALPS

A lehető legrövidebb időtartamú fényimpulzusok előállítása
a lehető legszélesebb spektrális tartományon
a lehető legnagyobb ismétlési frekvenciával.



A megújított Scientific Case

1. Kutatási tevékenység szerkezete
2. Lézeres kutatás és fejlesztés
3. Másodlagos források
4. Alapkutatási tevékenység
5. Alkalmazott kutatási tevékenység
6. Ipari alkalmazások
7. A közép-infravörös lézer használatának tudományos távlatai

Research activities

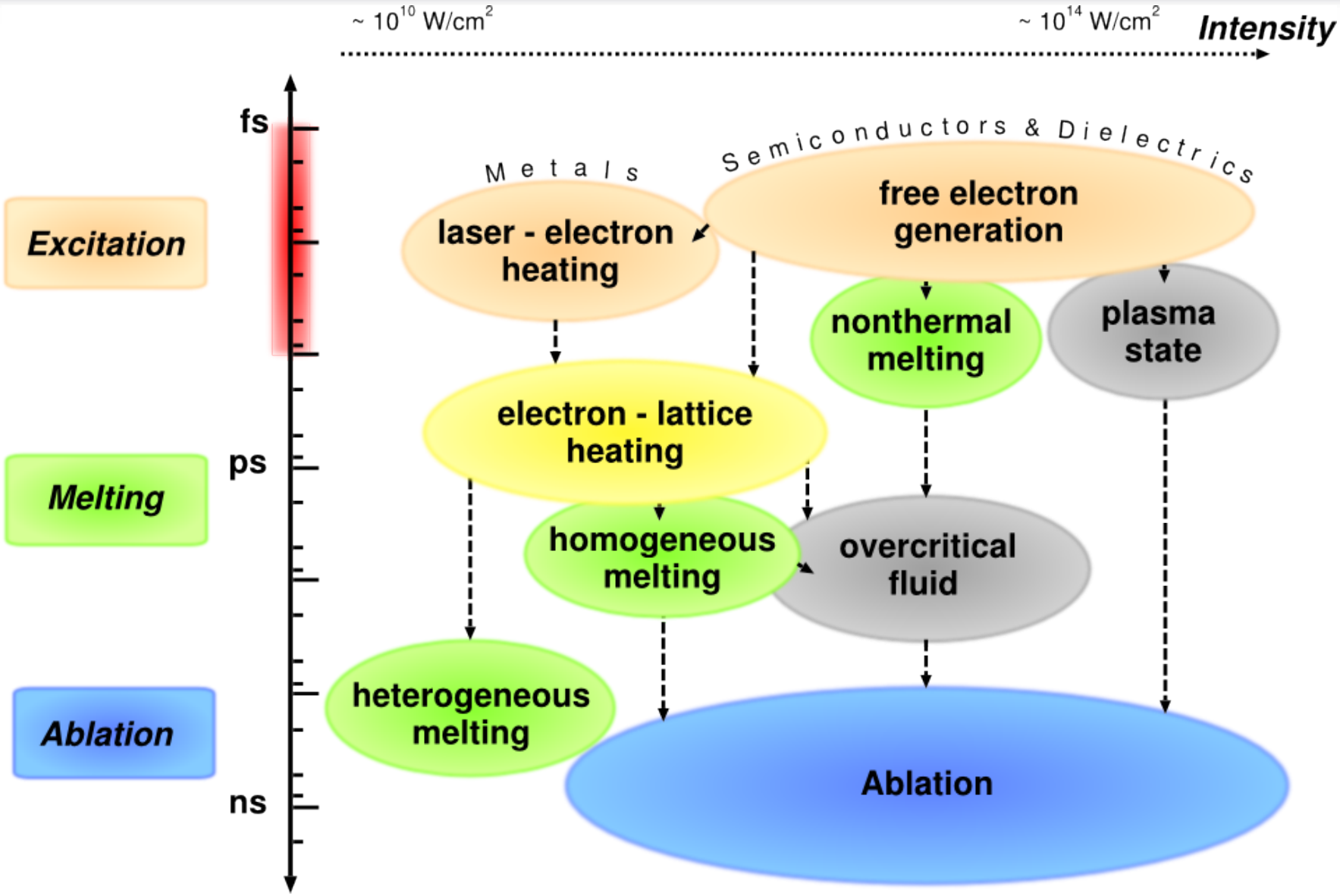
1 Laser research and development

2 Research and development of secondary sources

3 Atomic, molecular, nanophysics, cond.mat. research

4 Applied research | biomedicine, materials science

See in details: www.eli-alps.hu


~ 10^10 W/cm^2
~ 10^14 W/cm^2
Intensity
fs
ps
ns
Excitation
Melting
Ablation
Metals
Semiconductors & Dielectrics
laser - electron heating
free electron generation
nonthermal melting
plasma state
electron - lattice heating
homogeneous melting
overcritical fluid
heterogeneous melting
Ablation

Fizikai Nobel-díj 2018

Ill. Niklas Elmehed. © Nobel Media

Gérard Mourou

Prize share: 1/4

Ill. Niklas Elmehed. © Nobel Media

Donna Strickland

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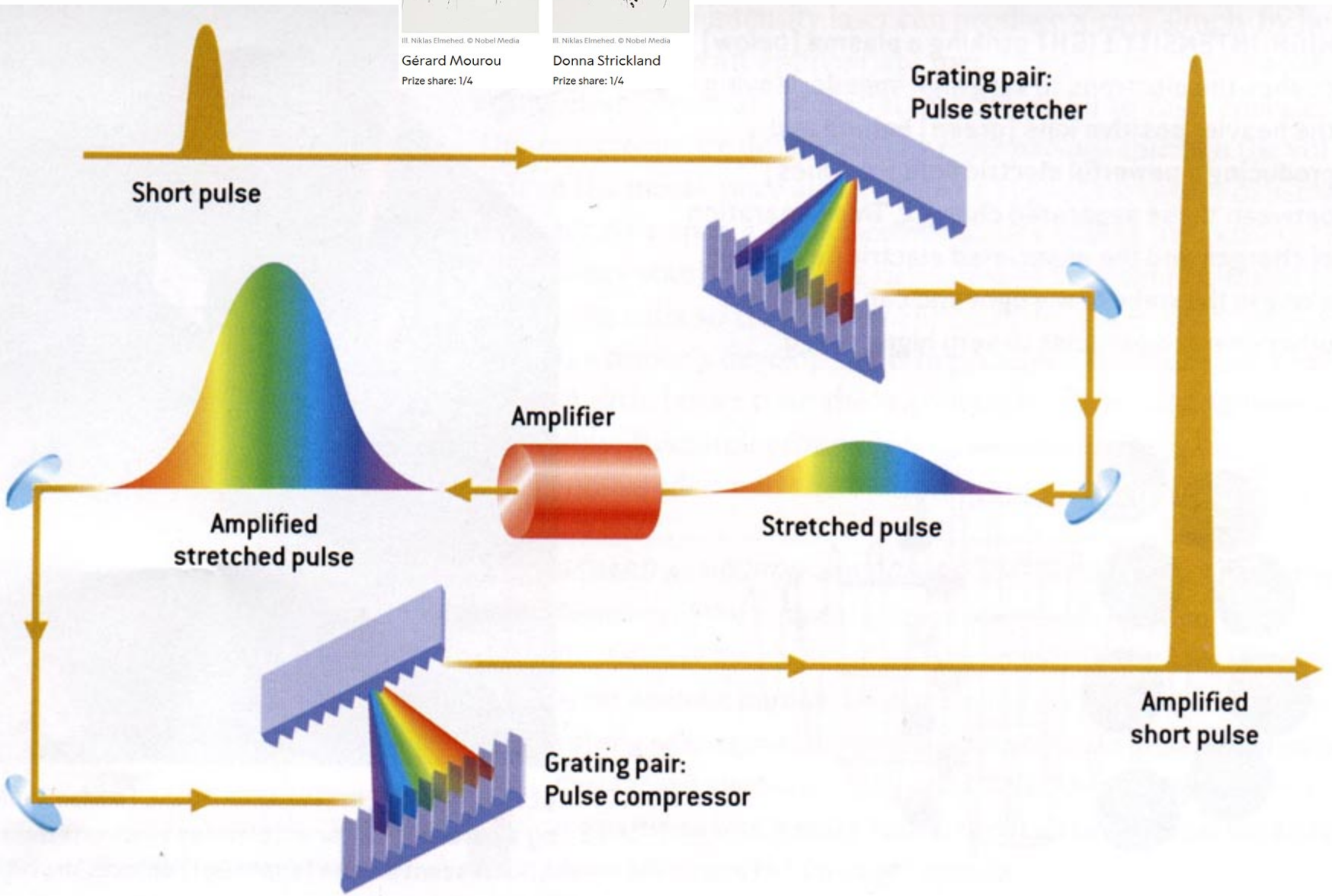
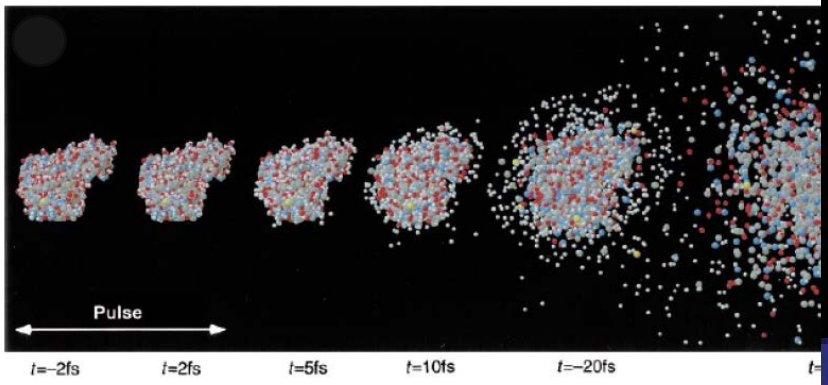


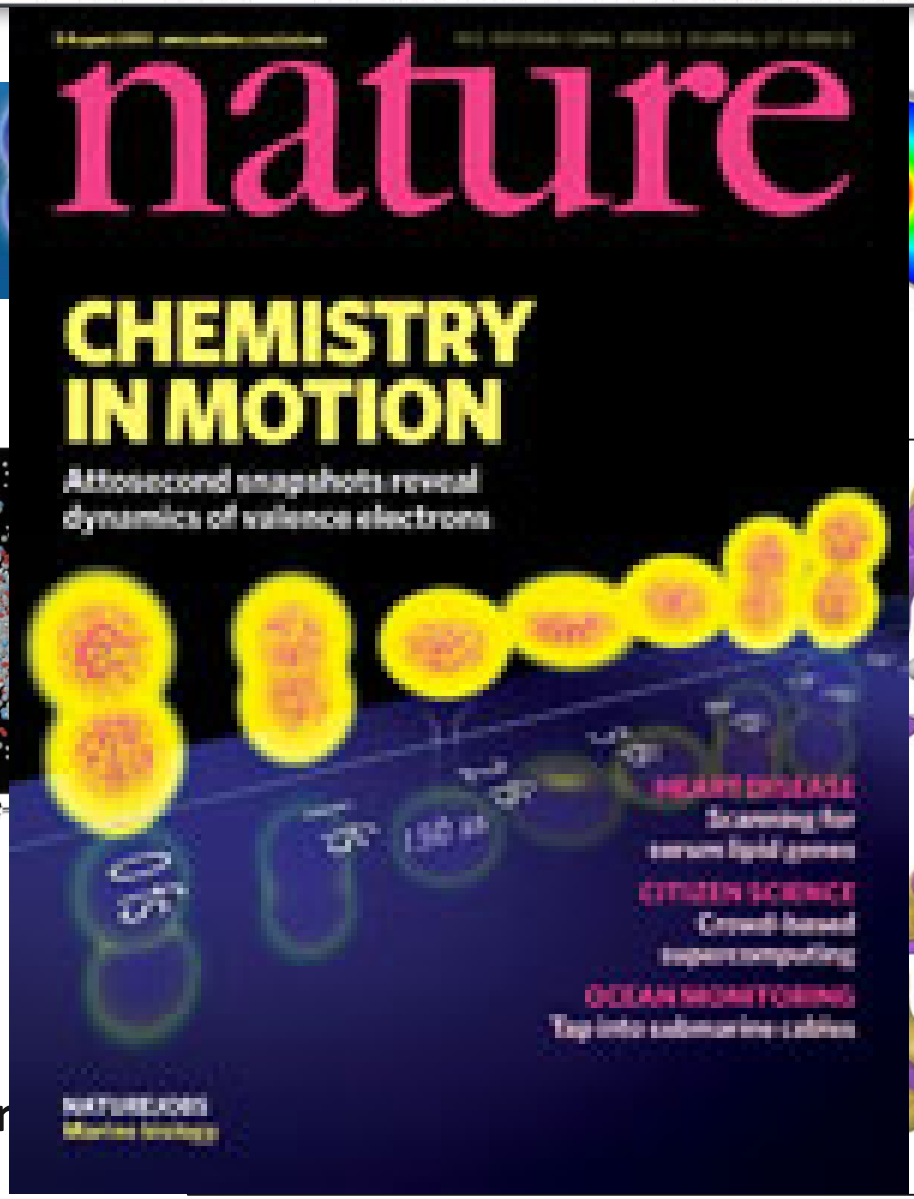
Attosecond electron dynamics

Krypton atom



Protein desintegration

Structural changes in phenyl-alar



How to harvest the energy of sunlight?

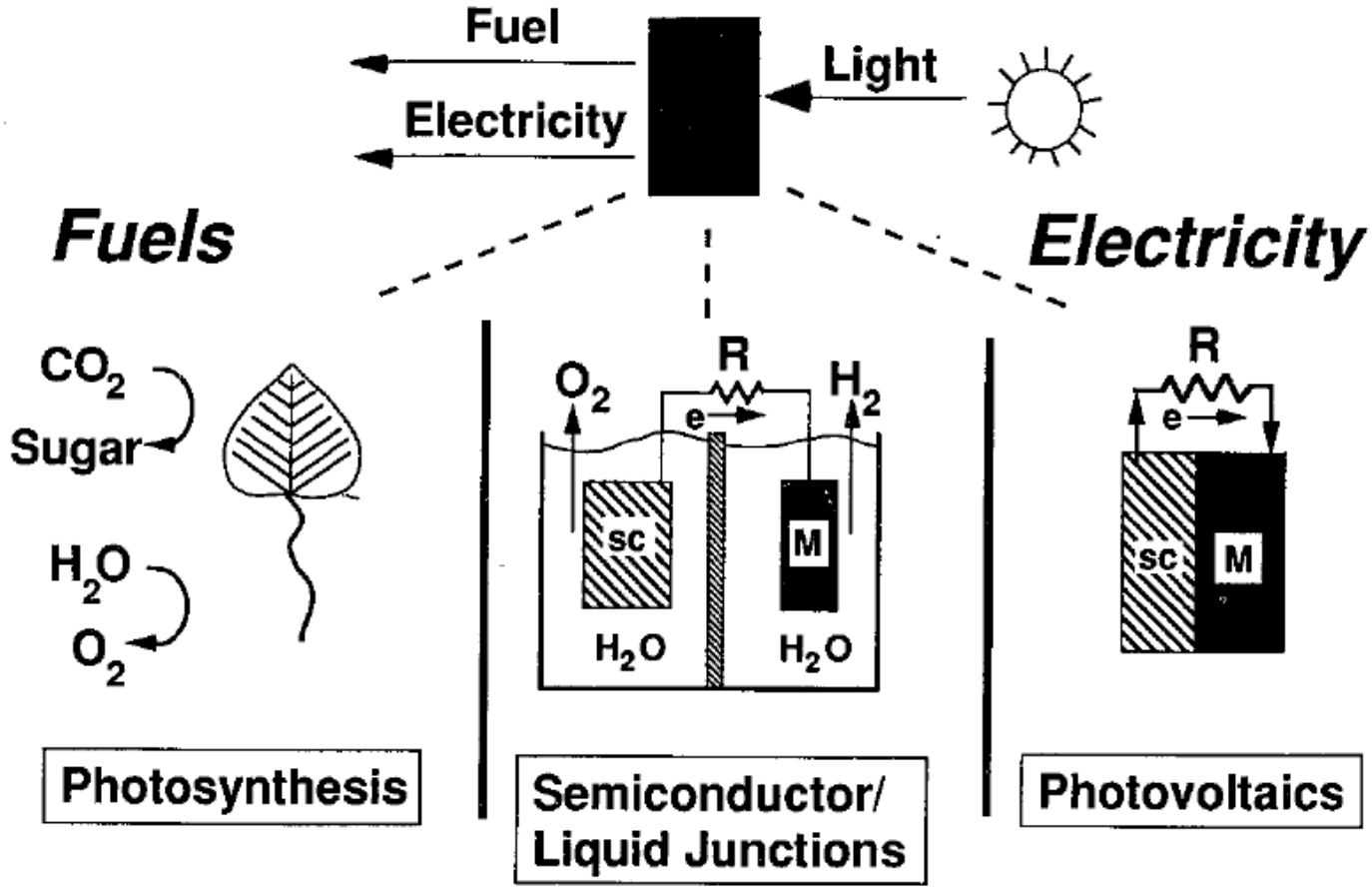
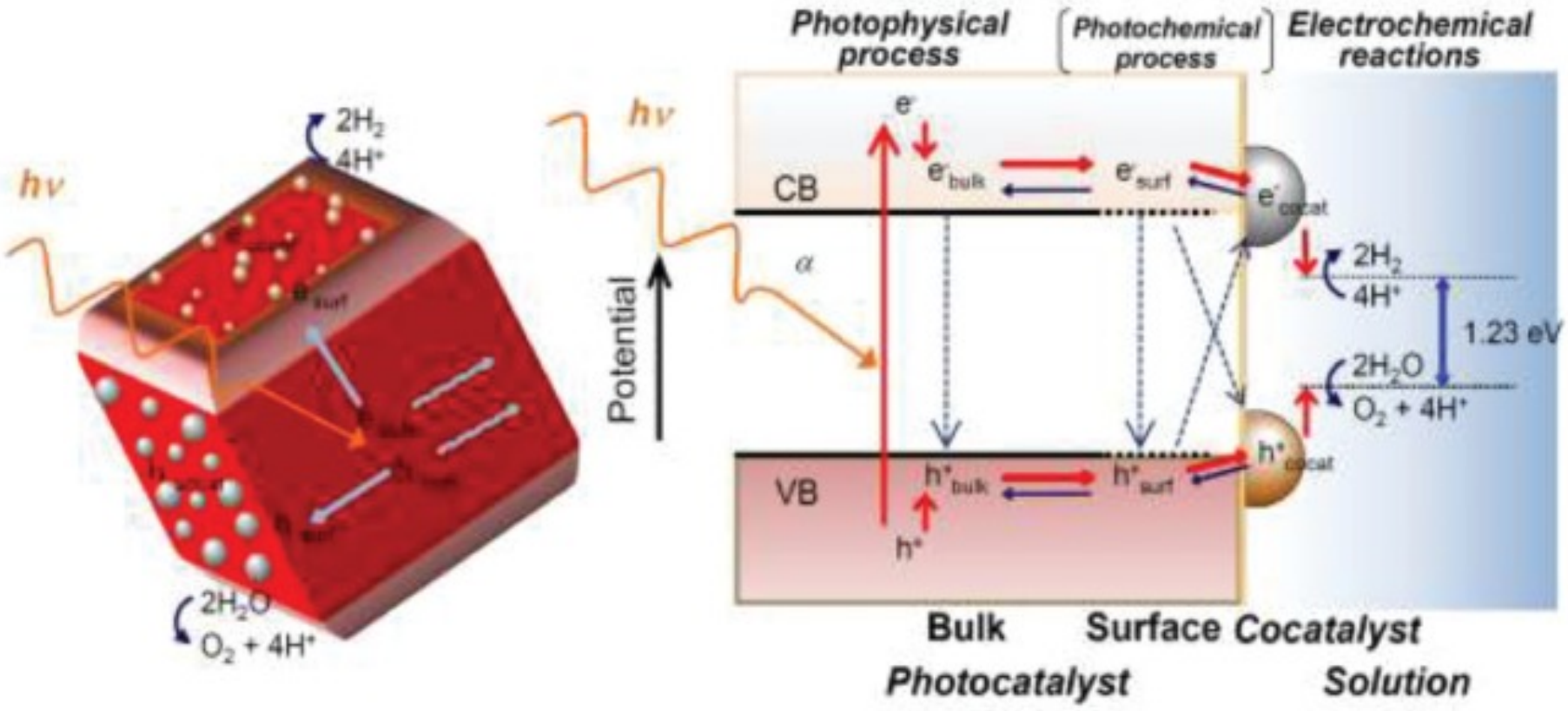


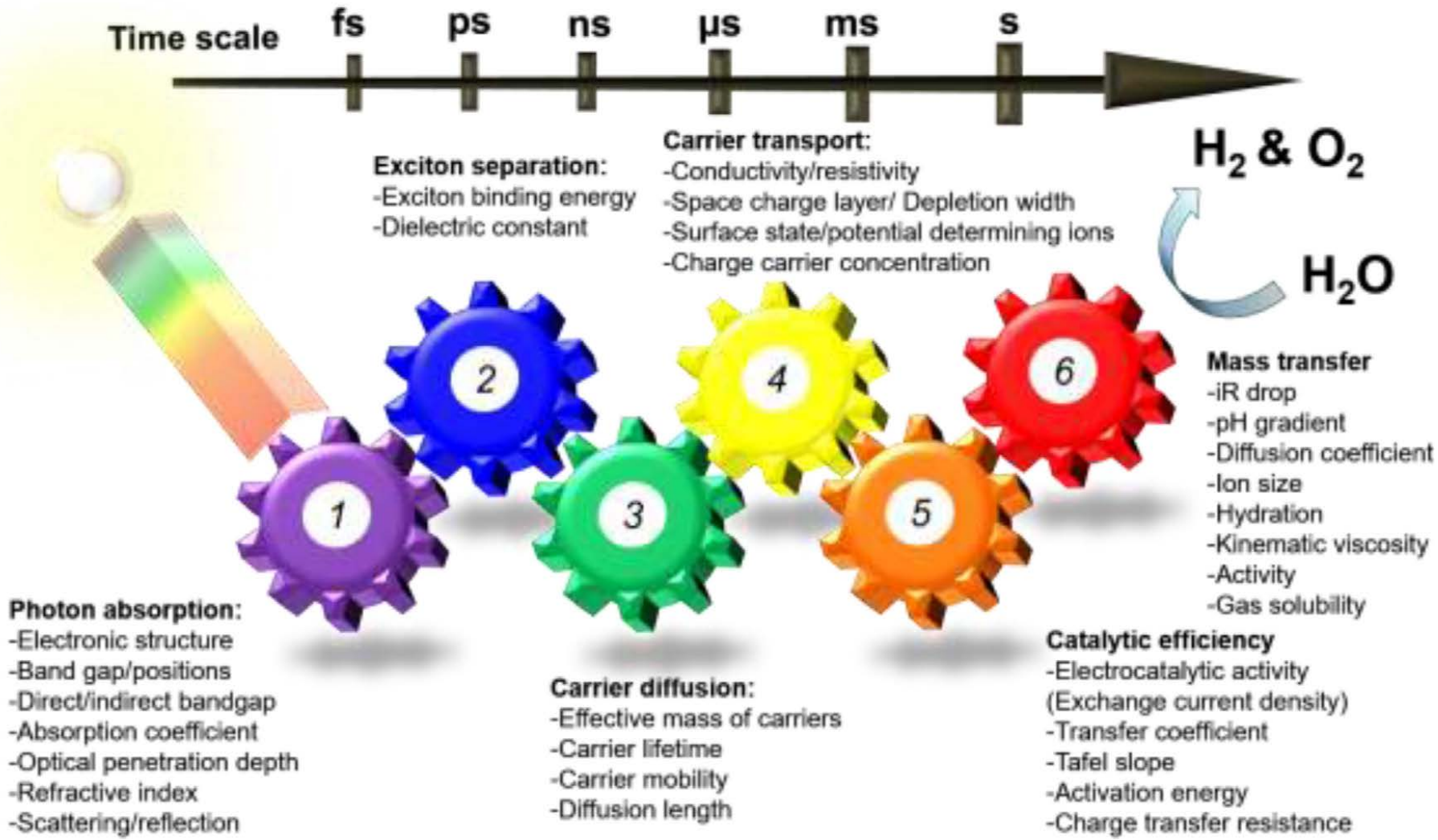
Figure 1. Methods of solar energy conversion.

There is nothing new under the sun: see Fujishima-Honda (1972)

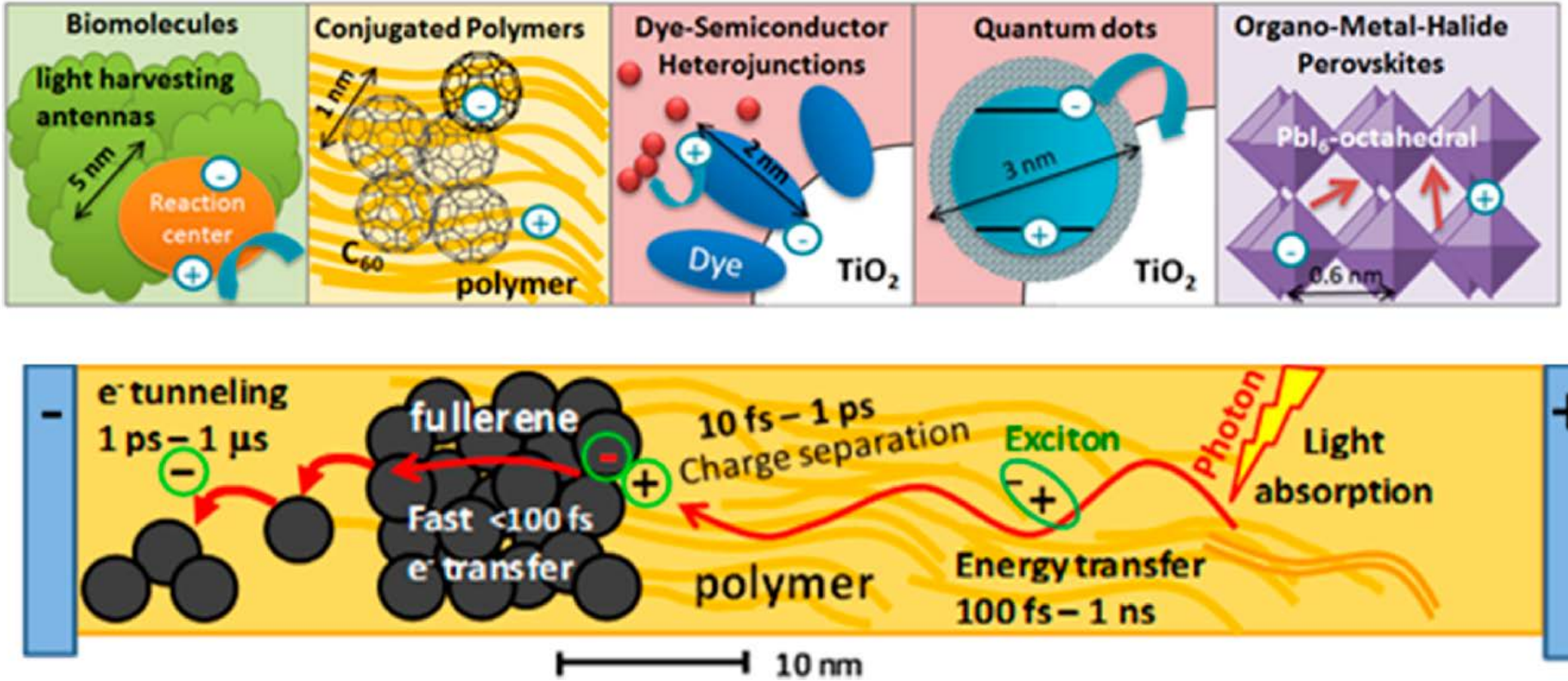
Milyen folyamatok mennek végbe megvilágításkor?



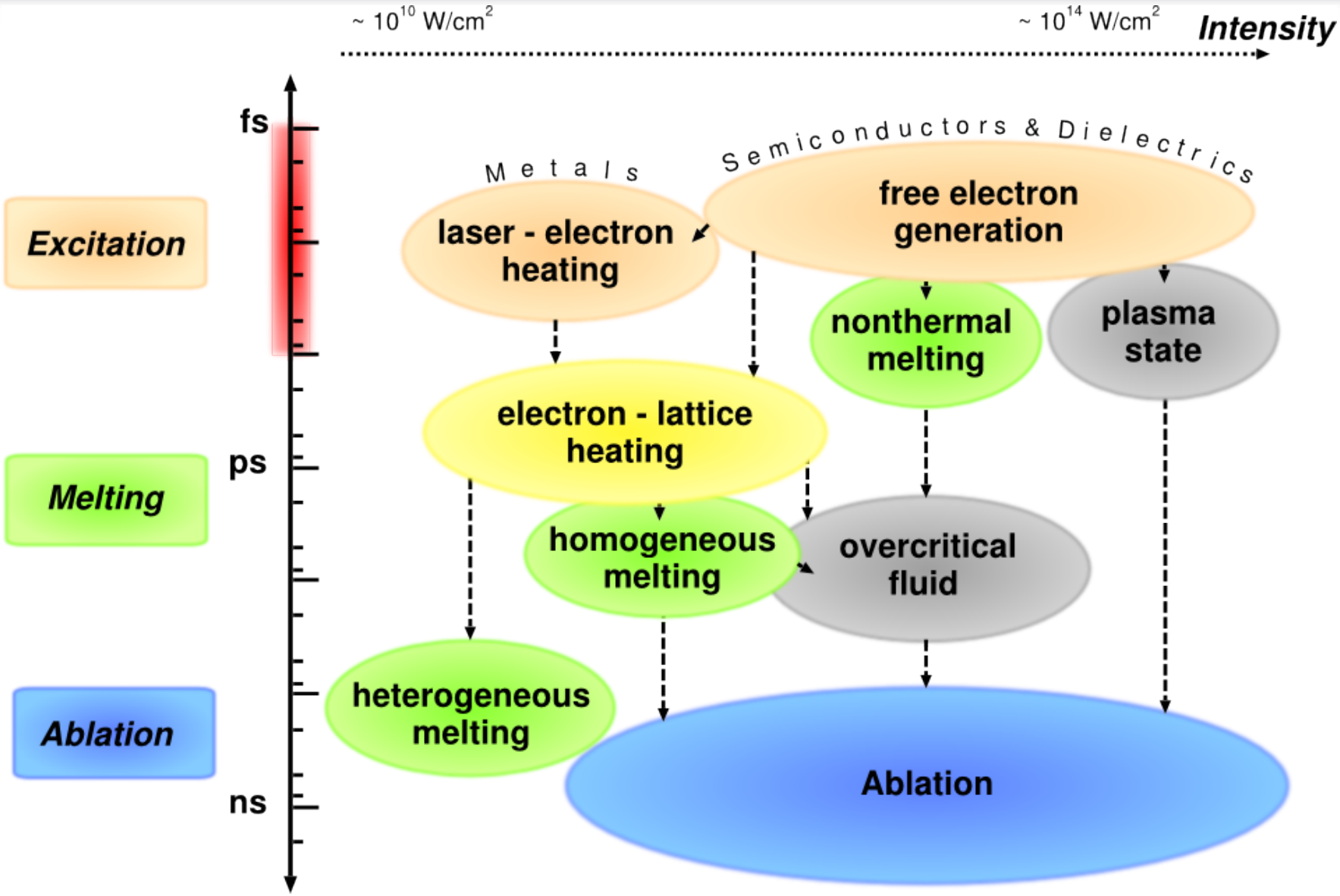
Folyamatok időskálája I.



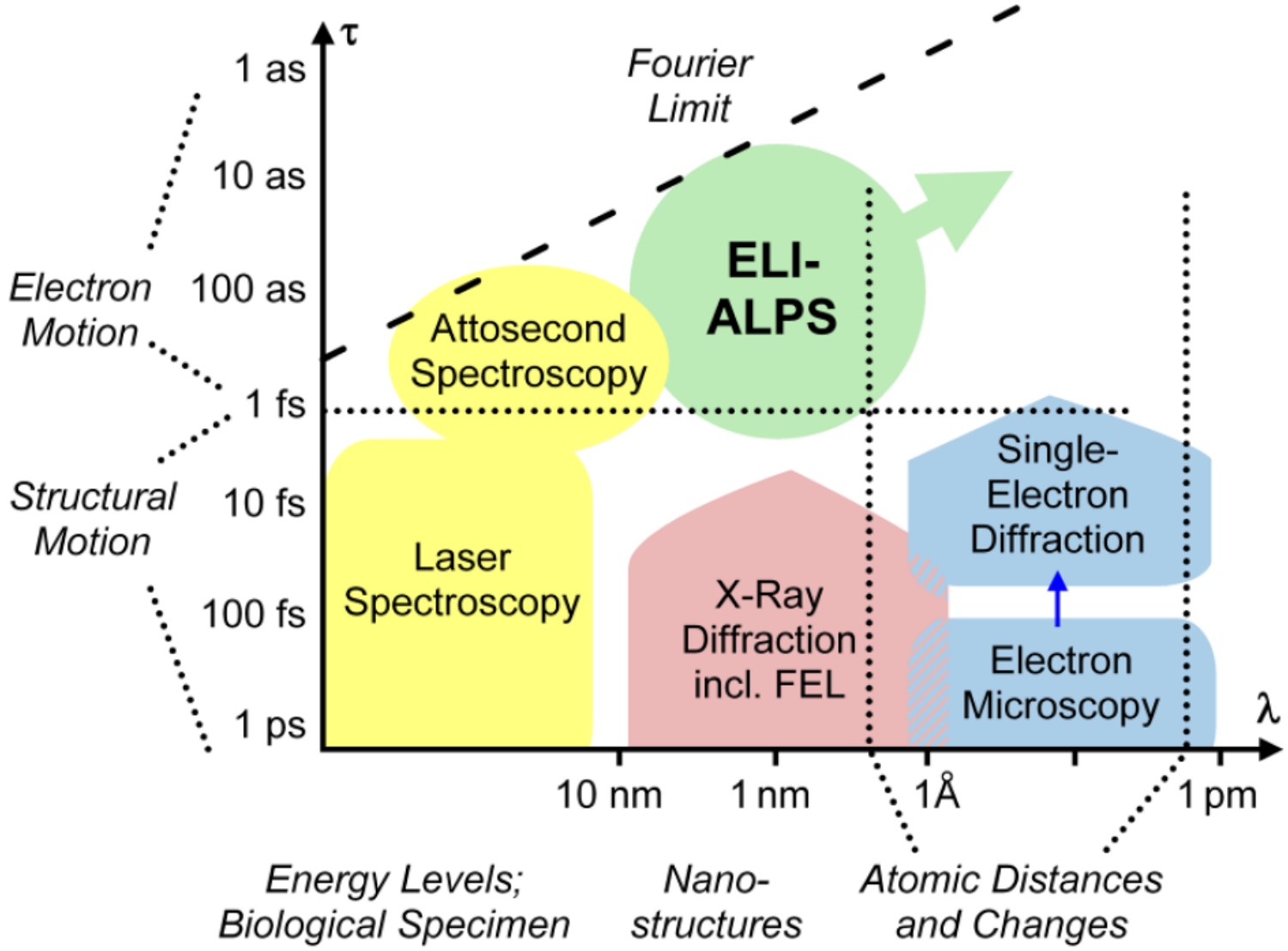
Folyamatok időskálája II.



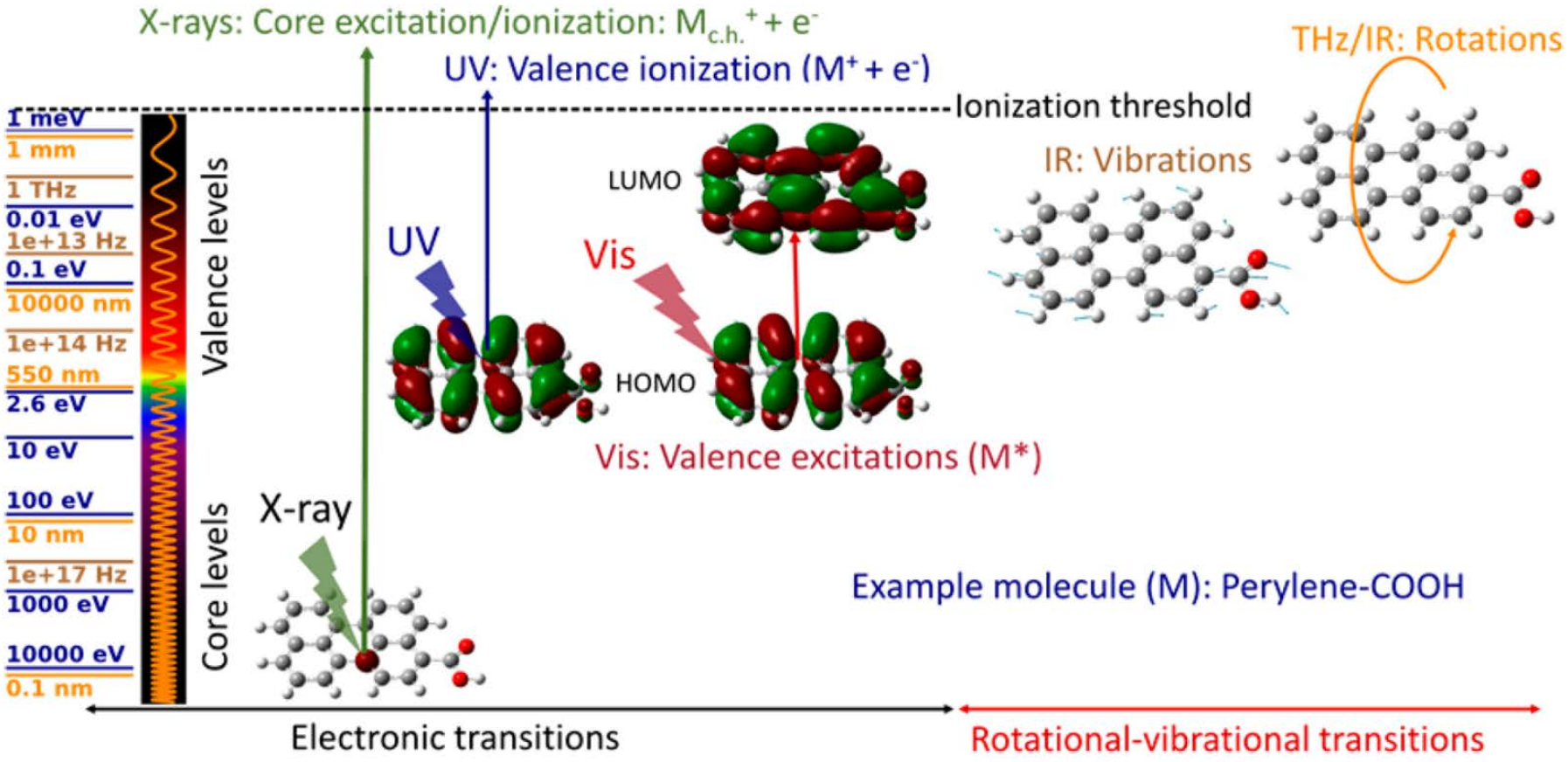
Fundamental understanding is often missing…



ELI-ALPS mission



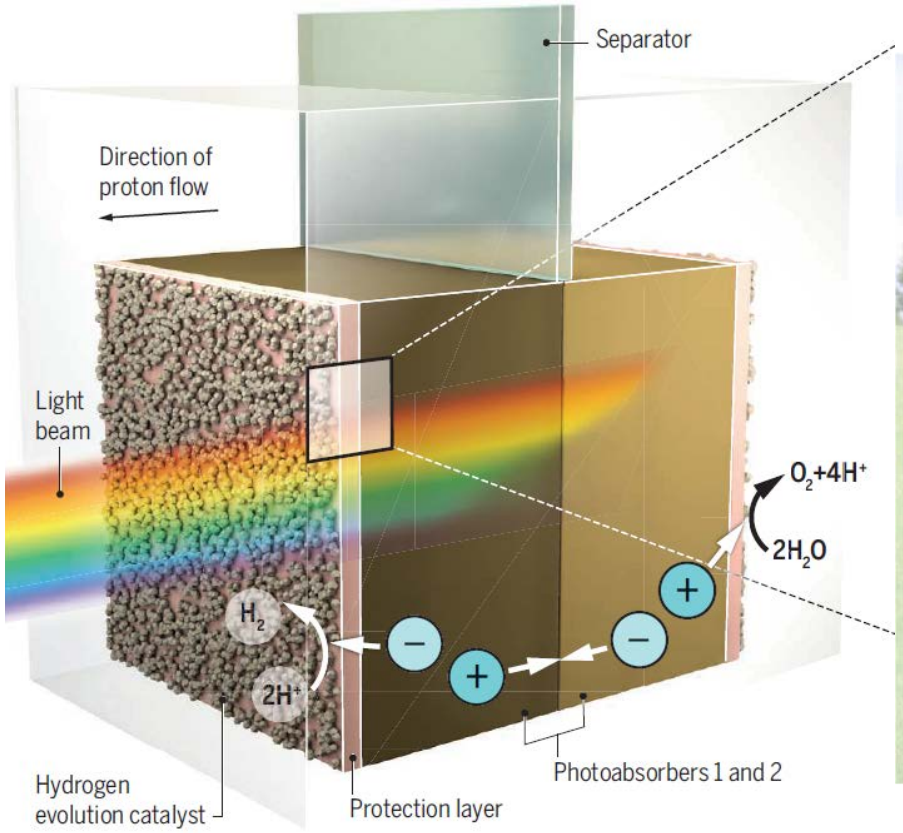
Folyamatok energetikája

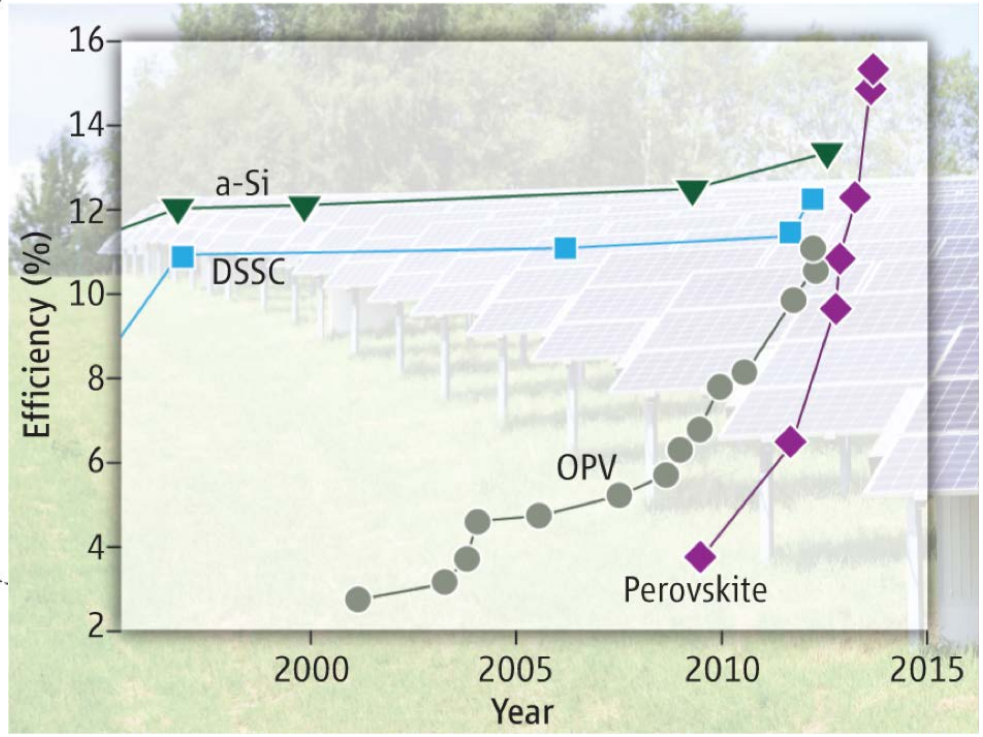


Why are these semiconductor interfaces interesting I.?

Solar energy conversion at irradiated semiconductor interfaces:

- Solid/solid interface: solar photovoltaic cells (electricity generation)
- Solid/liquid interface: photoelectrochemical cells (solar fuel generation)

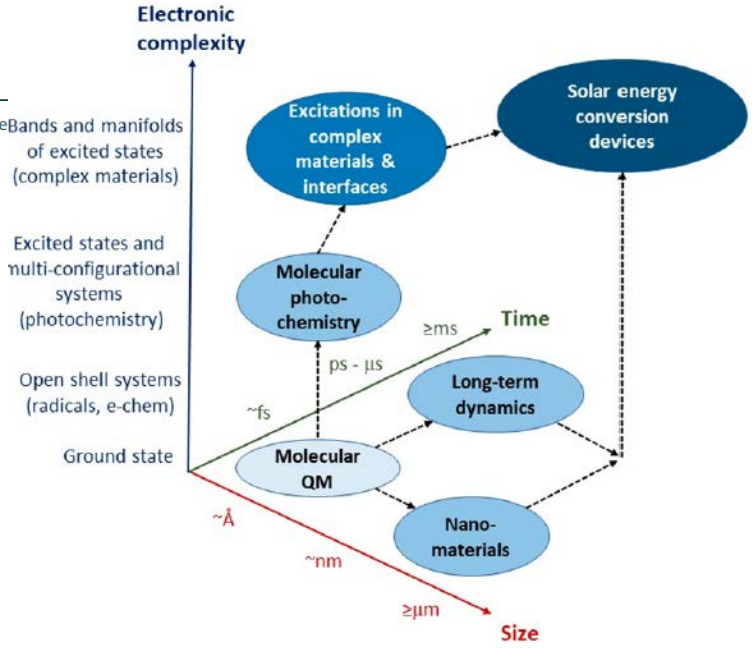




ACS Energy LETTERS

DOI: 10.1021/acsenergylett.7b00413
ACS Energy Lett. 2017, 2, 1425−1428

http://pubs.acs.org/journal/aeBands and manifolds



Current Trends in Semiconductor Photoelectrochemistry

New Insights Provided by New Techniques. It was common in most of the talks that careful materials and system engineering is of prime importance to tailor the interfacial properties of the photoelectrodes. As another common theme, it was often

> Novel in operando tools are necessary to gain better understanding of the fundamental elementary steps of photoelectrochemical processes.

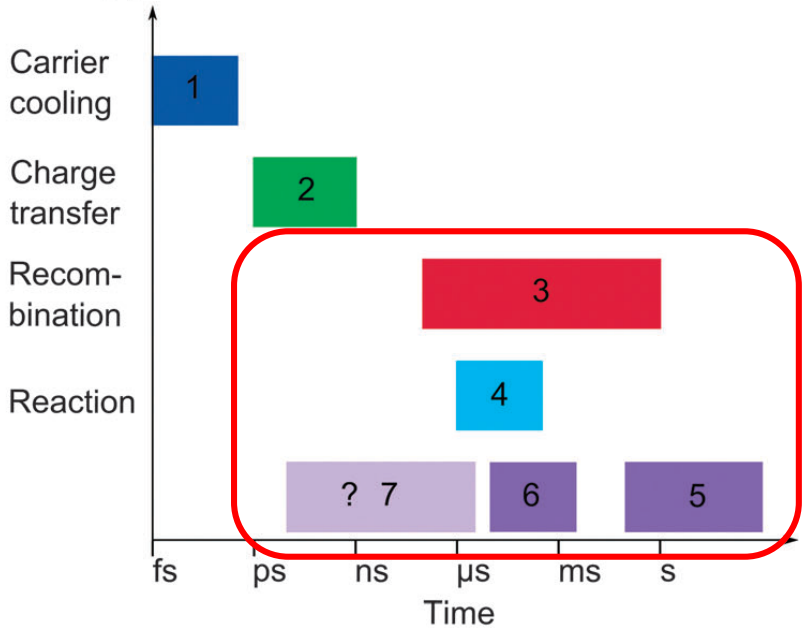
claimed that novel in operando tools are indeed necessary to gain better understanding of the fundamental elementary steps of the photoelectrochemical processes. Thus, the special lecture given by Peter Dombi, head of the Scientific Applications

Ultrafast dynamics in semiconductors I.

State-of-the-Art

The efficient conversion of clean, sustainable solar energy using photoelectrochemical and photocatalytic systems requires precise control over the thermodynamics, kinetics, and structural aspects of materials and molecules. Various photoinduced processes in semiconductors occur at distinctly different timescales. Ultrafast laser spectroscopy has been long the tool for examining mechanistic aspects of light induced processes in semiconductors as well as at semiconductor interfaces.

So far, most of the work has focused mainly on transient absorption spectroscopy, at relatively long timescales (typically ns-µs, sometimes ps), where charge transfer, recombination, and different surface reactions occur. On the other hand, much less is known about the photo-excitation process itself, carrier cooling and trapping, **which occurs at the femtosecond timescale**.



Why semiconductor nanostructures I.?

What happens with the photogenerated charge carriers ***in the semiconductors***?

We aim to understand the **peculiar conduction mechanisms** (including photoinduced charge carrier formation, exciton dissociation, recombination, etc.) in different classes of semiconductors; such as *organic semiconductors* (conjugated polymers) , different *1D and 2D inorganic semiconductors* (this latter group is also called topological insulators, such as MoS_2 and $NbSe_2$), and *organic-inorganic hybrid materials* (for example organic lead halide perovskites).

While these materials play an impressively increasing role in different practical applications, very little is known about the **fundamentals of the mechanism of (photo)conductivity** (which forms the basis of most applications) observed in these materials.

Why semiconductor nanostructures II.?

Interfacial electron transfer

There is only limited information on the charge carrier dynamics through SC/SC junctions at **well-defined surfaces and nanstructures**.

Photogenerated electrons can move and get trapped at the semiconductors surface within 100-200 fs and relax into deeper bulk traps at the 100 ps timescale. However, if the semiconductor is decorated with metal nanoparticles or films (Schottky-junction), they can intercept these electrons before they relax to the deep bulk trap states.

However, **in situ experiments were difficult so far**, because water-based solutions absorb the probe. However, special cell designs using very thin liquid films, and the high intensity output of the ELI lasers may help to overcome these difficulties.

Methodology I.: overview

Most ultrafast techniques are pump-probe approaches generally relying on a Ti:sapphire laser with an optical delay line to achieve femtosecond time resolution over a nanosecond range. The sample is photoexcited with the pump pulse and then probed a short time later.

- **visible or near-infrared (near-IR) transient absorption (TA) spectroscopy**
- **time-resolved fluorescence spectroscopy**
- **time-resolved terahertz spectroscopy (TRTS)**
- time-resolved X-ray absorption spectroscopy (TR-XAS),
- time-resolved microwave spectroscopy,
- ultrafast electron microscopy,
- femtosecond diffuse reflectance spectroscopy,
- **time-resolved two-photon photoemission (TR-2PPE),**
- time-correlated single-photon counting,
- time-resolved photoelectron spectroscopy (TRPES),
- ultrafast Kerr-gated fluorescence microscopy,
- picosecond electron paramagnetic resonance (EPR) spectroscopy,
- time-resolved resonance Raman spectroscopy

Methodology III.: transient absorption spectroscopy

Visible or near-infrared (near-IR) transient absorption (TA) spectroscopy probes interband and molecular transitions. TA is the most widely used ultrafast technique for solar fuel studies. The sample is excited by a pump pulse and the dynamics of the sample are monitored as a function of time at many wavelengths by a white-light supercontinuum probe. **This technique can be used in both transmission or reflection mode.**

Specifications

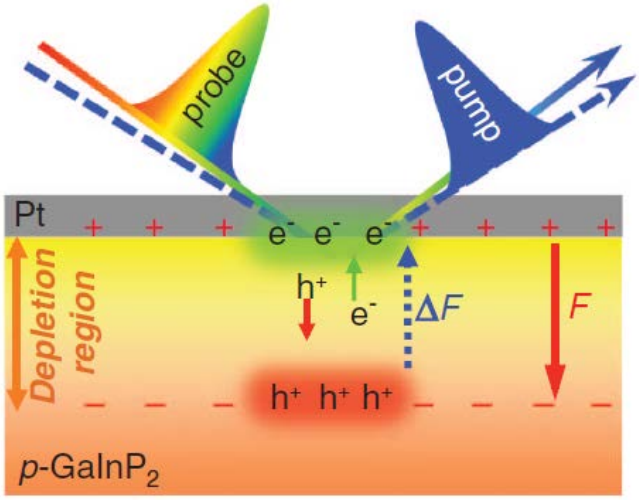
An example from Newport

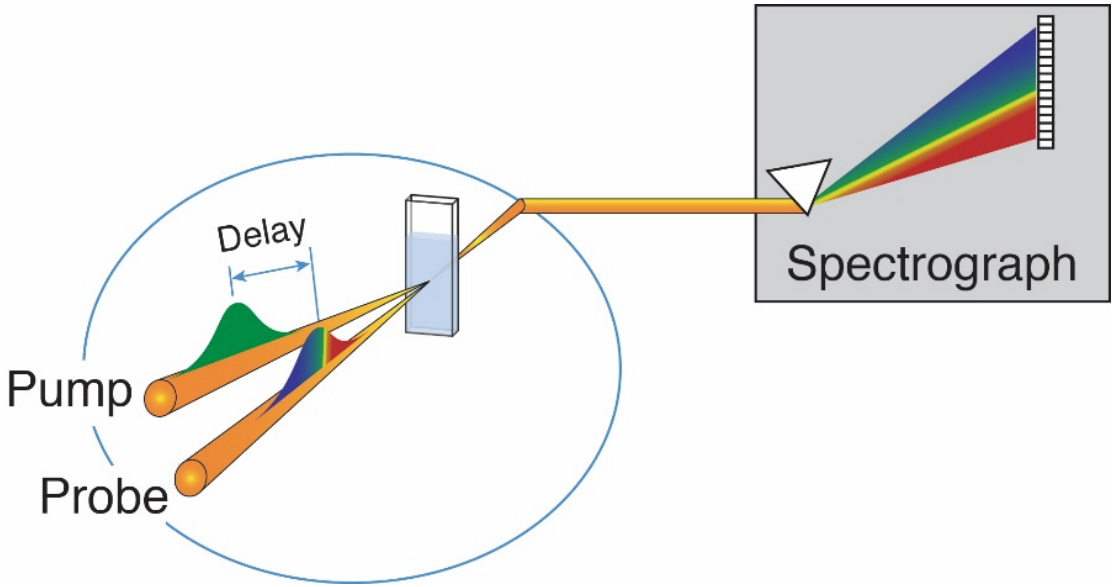
TAS Transient Absorption Spectrometer Specifications	
Probe Spectral Range	350 - 1600 nm, depending on options
Pump-Probe Delay Range	3.33 ns, standard
Pump-Probe Delay Resolution	13.3 fs standard, 2.2 fs optional
Intrinsic Time Resolution	< 10 fs
Time Resolution	1.4 times the pump or probe duration
Supported Pulse Repetition Rate	10 Hz - 8 kHz, depending on options
Spectrometer Supported Spectral Range	180 - 2900 nm
Spectrometer Supported Spectral Resolution	0.17 - 1.05 nm

Methodology IV.: transient absorption spectroscopy

Transient Absorption Spectroscopy can be used to trace the intermediate states in a photo-chemical reaction; energy, charge or electron transfer process; conformational changes, thermal relaxation, fluorescence or phosphorescence processes, etc.

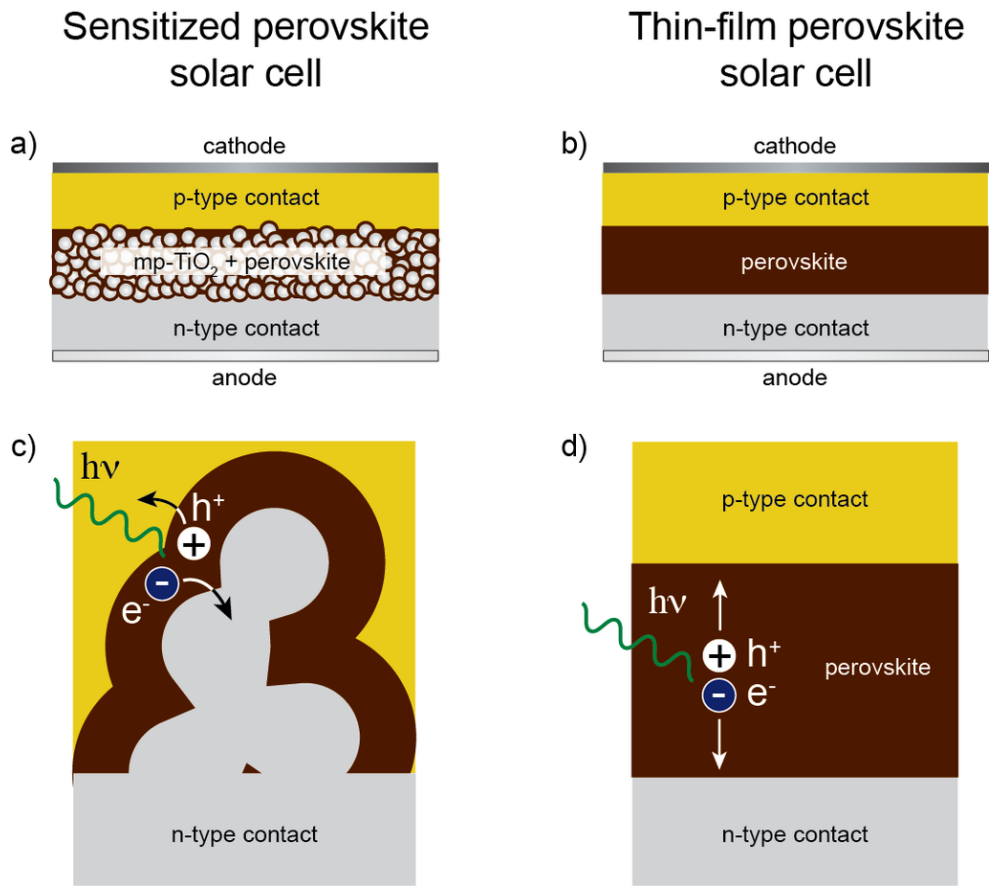
Transient absorption spectroscopy has become an important tool for characterizing various **electronic states and energy transfer processes** in nanoparticles, to locate trap states and further helps in characterizing the **efficient passivation strategies.**





Photovoltaic Solar Cells

There are multiple interface of interest and the picture gets even murkier at the nanoscale!

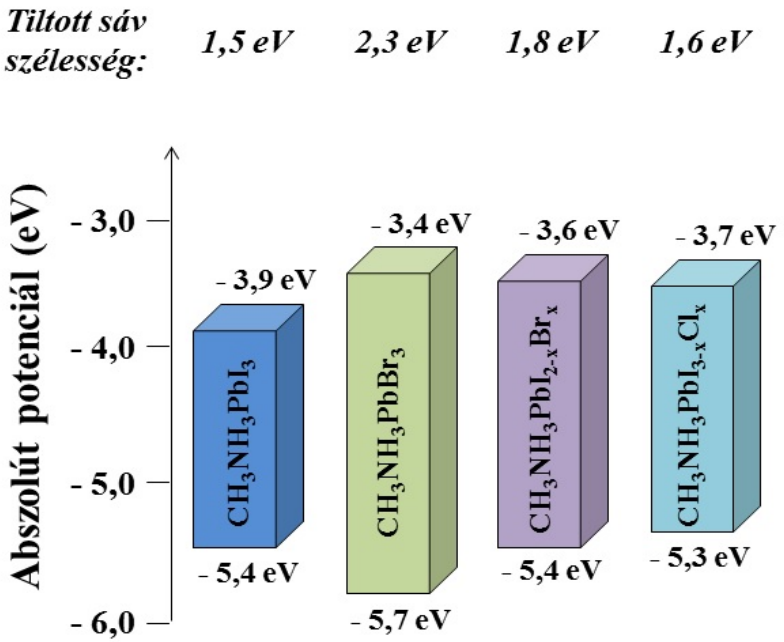


Till now we don't have experimental evidence wheter the photoexcited species are excitons or free charge carriers (+timescale!)

What are the right model systems?

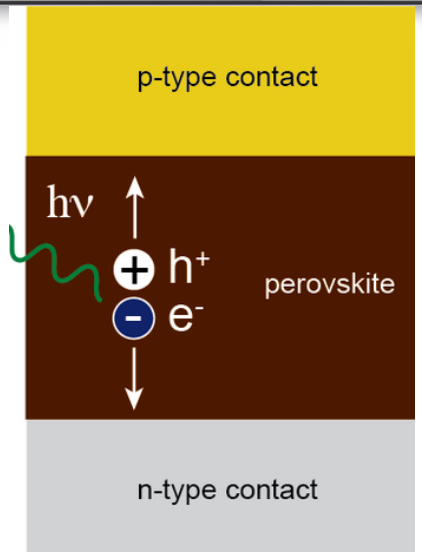
- Well-defined materials to allow to distinguish between among the various competing processes.
- Practically relevant systems shall be studied.
- Nanoscale engineering shall be possible.

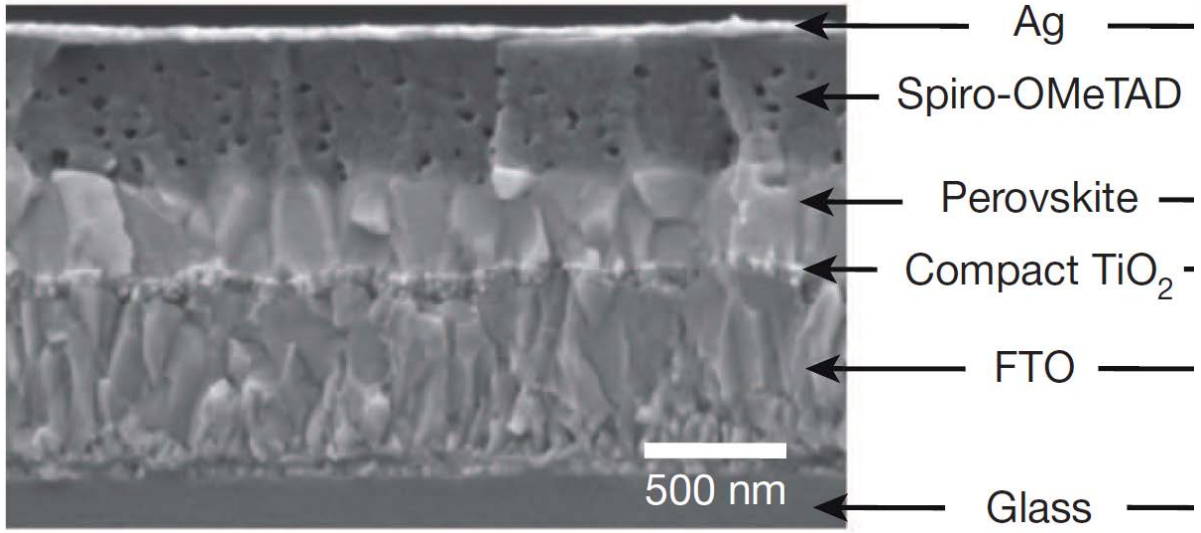
System #1 Lead halide perovskites (in collaboration with László Óvári)

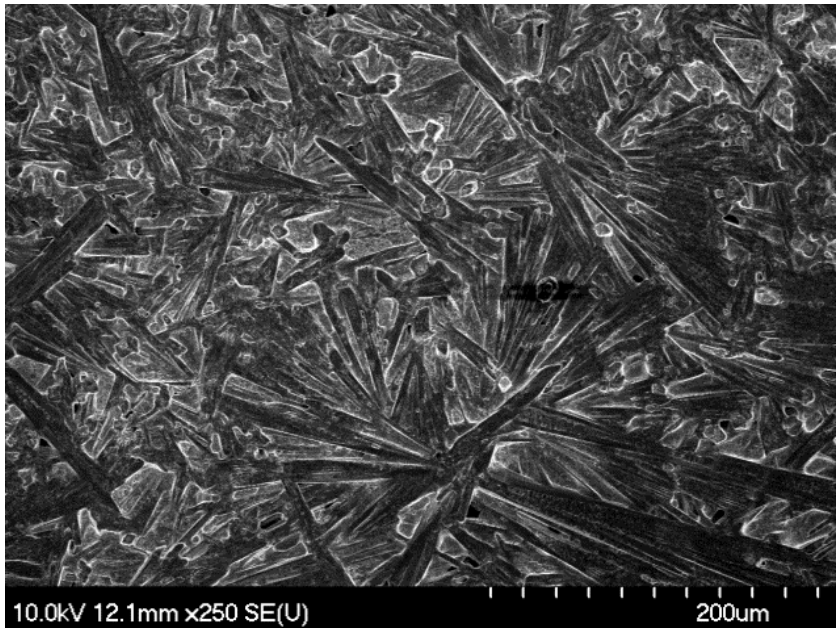


Lead halide perovskites II.
Single crystals

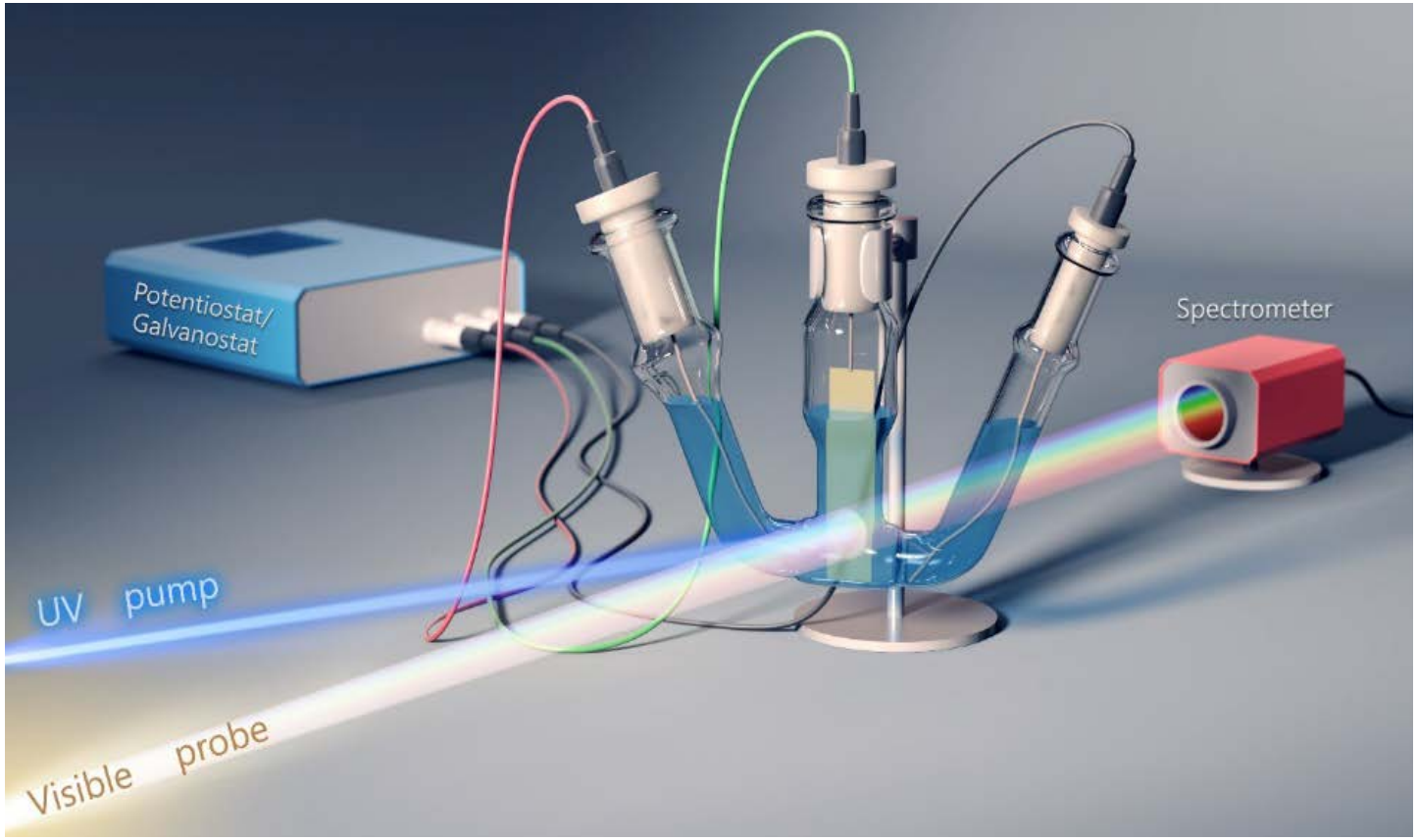
Lead halide perovskites I.







Transient absorption spectroscopy - electrochemistry



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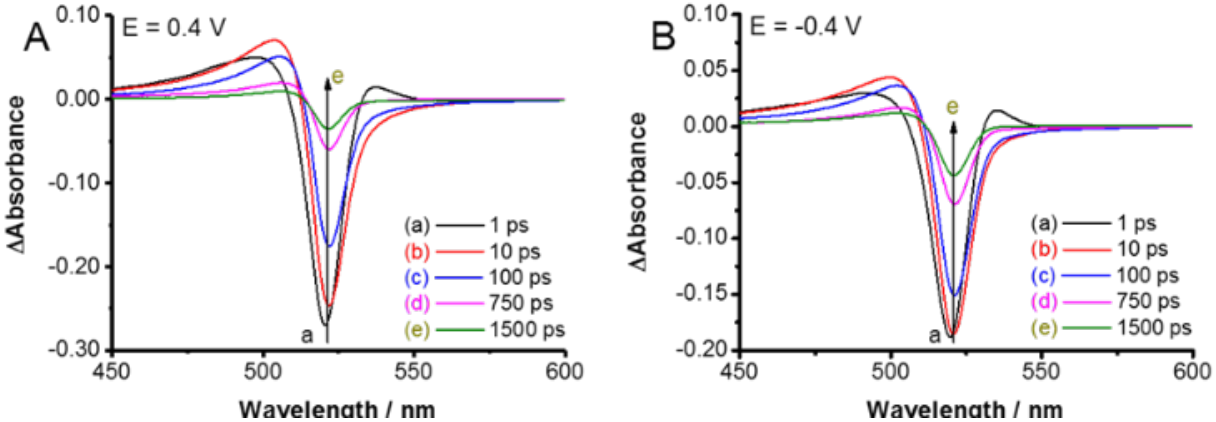
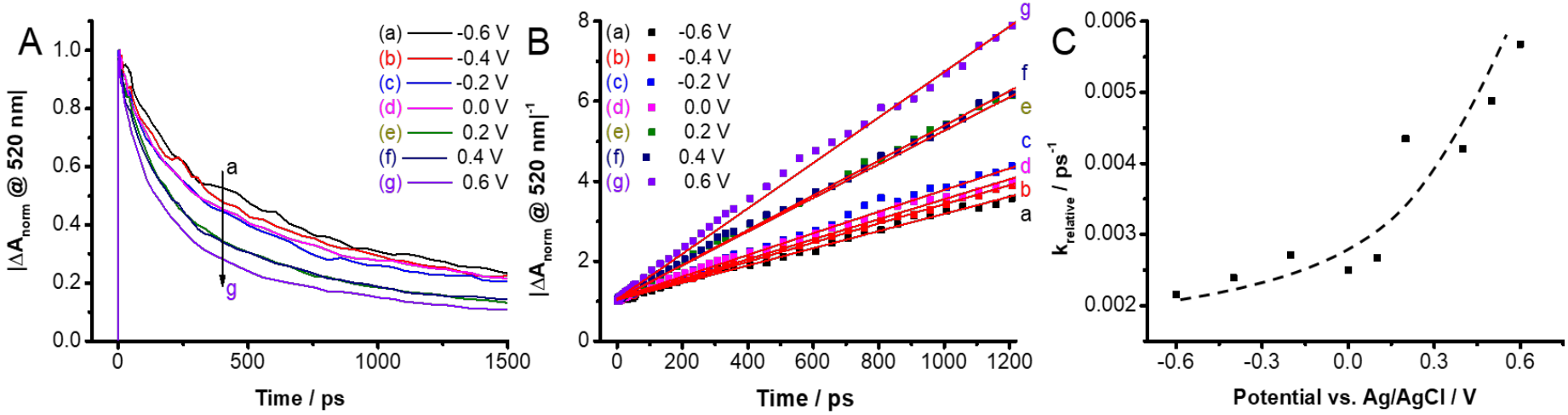
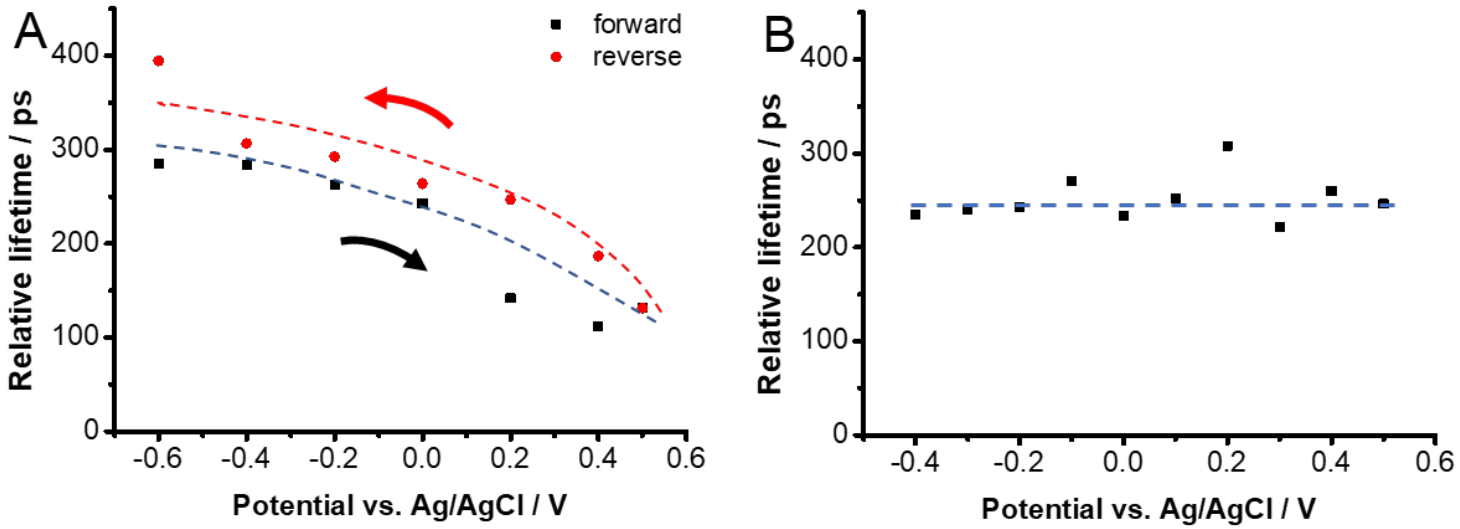
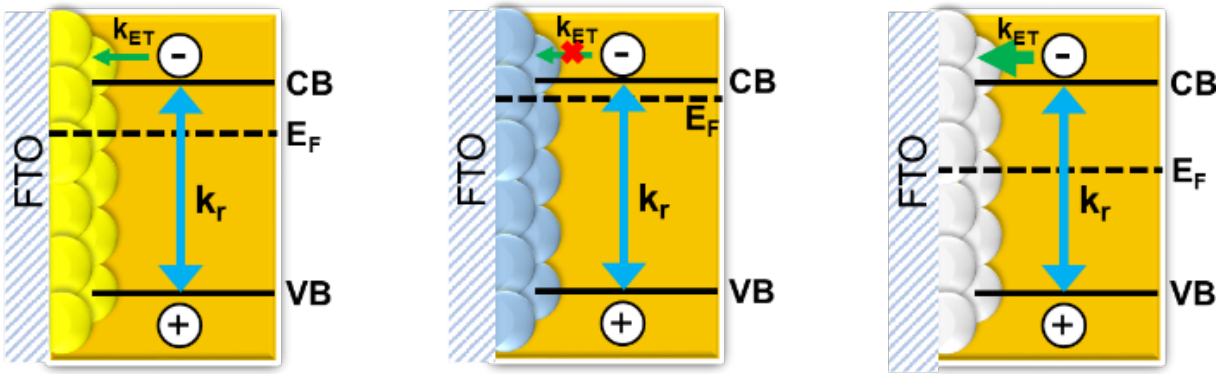




Transient absorption spectroscopy - electrochemistry





Methodology V.: Time-resolved fluorescence spectroscopy

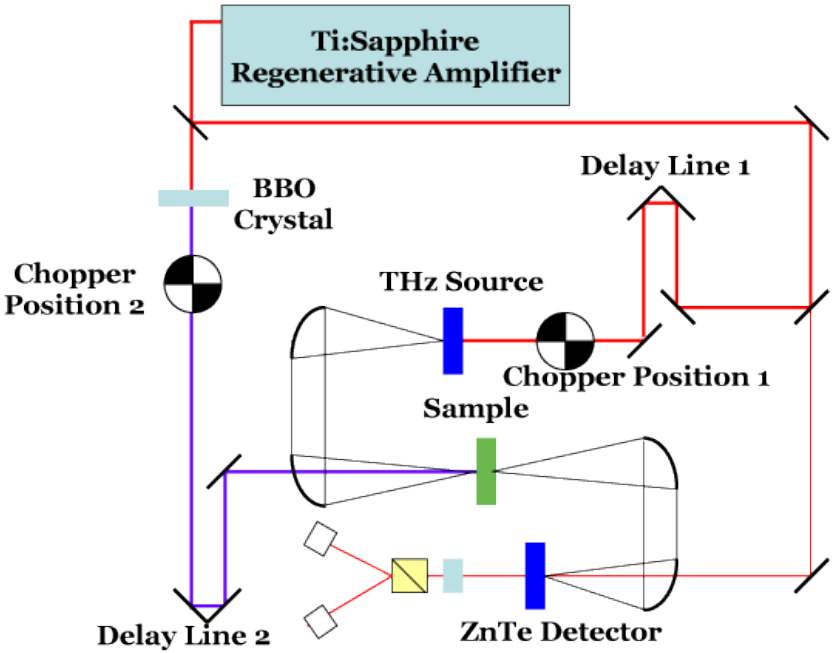
Time-resolved fluorescence spectroscopy is an extension of fluorescence spectroscopy. Here, the **fluorescence of a sample is monitored as a function of time after excitation by a flash of light**. The time resolution can be obtained in a number of ways, depending on the required sensitivity and time resolution:

- With fast-detection electronics (nanoseconds and slower)
- With Time Correlated Single Photon Counting (picoseconds and slower)
- With a streak camera (picoseconds and slower)
- With intensified CCD cameras (down to 200 picoseconds and slower)
- With optical gating (femtoseconds-nanoseconds) - a short laser pulse acts as a gate for the detection of fluorescence light; only fluorescence light that arrives at the detector at the same time as the gate pulse is detected.

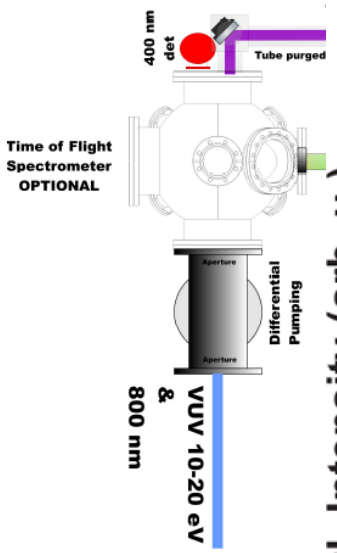
Methodology II.: Time resolved THZ spectroscopy

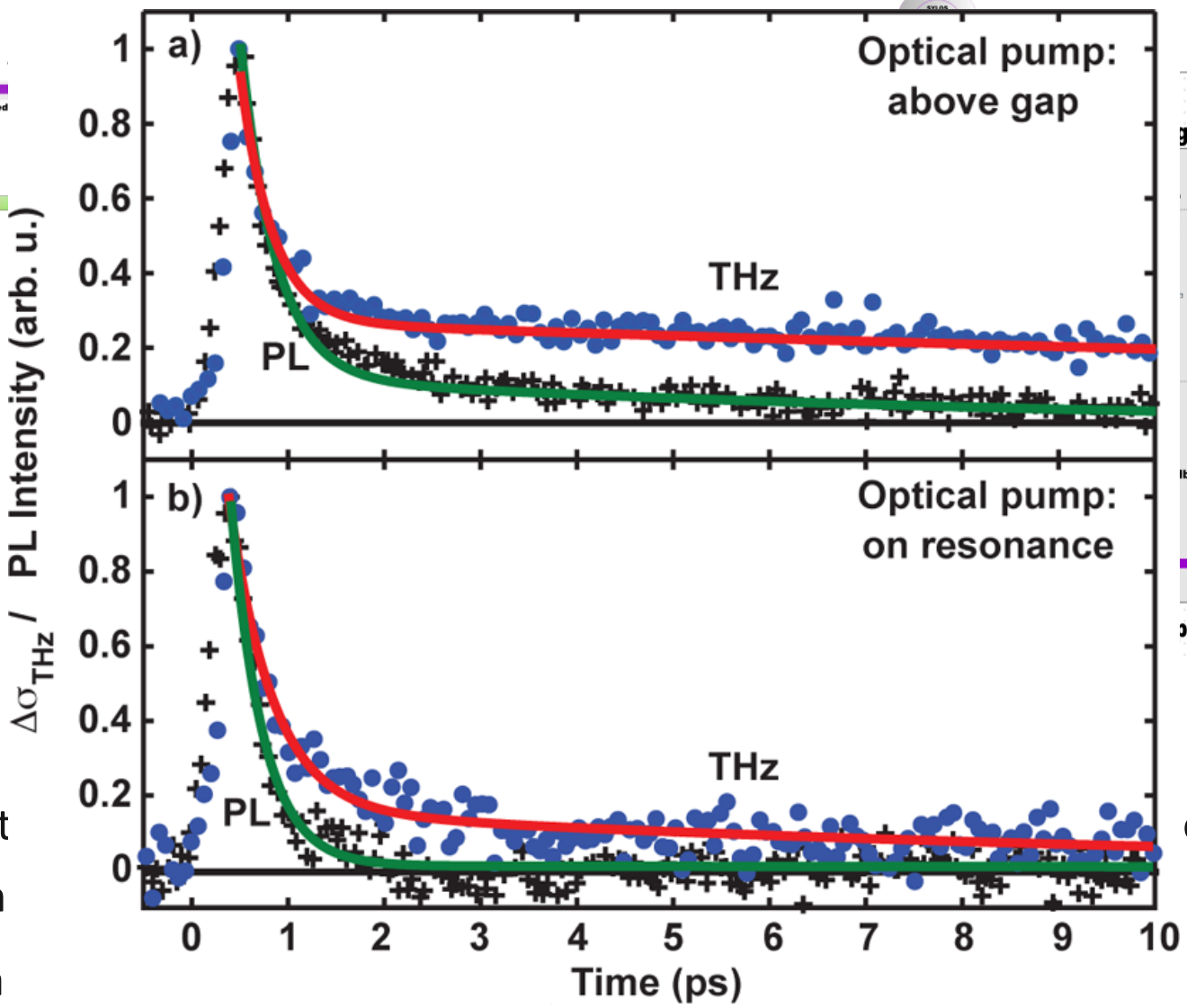
Time-resolved terahertz spectroscopy (TRTS) uses an **optical pump with a THZ probe** to measure intraband transitions TRTS is used in solar fuel research as a **noncontact probe of transient photoconductivity.** TRTS is technique which is used to study systems in which a visible excitation initiates a change in far-infrared absorption properties on a sub-picosecond timescale.

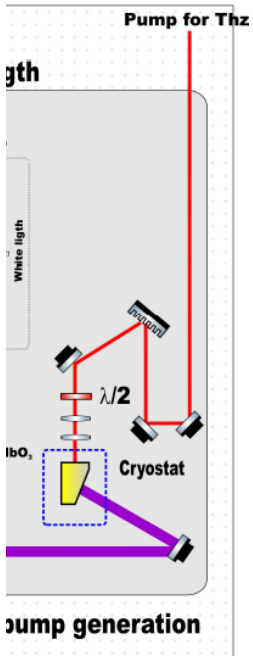
The change in the peak THz time-domain transmission is monitored as a function of the time delay between the pump and probe beams. Because the pump beam is chopped, the measured signal is the change in THz transmission observed upon photoexcitation.



Methodology III.: Combined methods are even more powerful



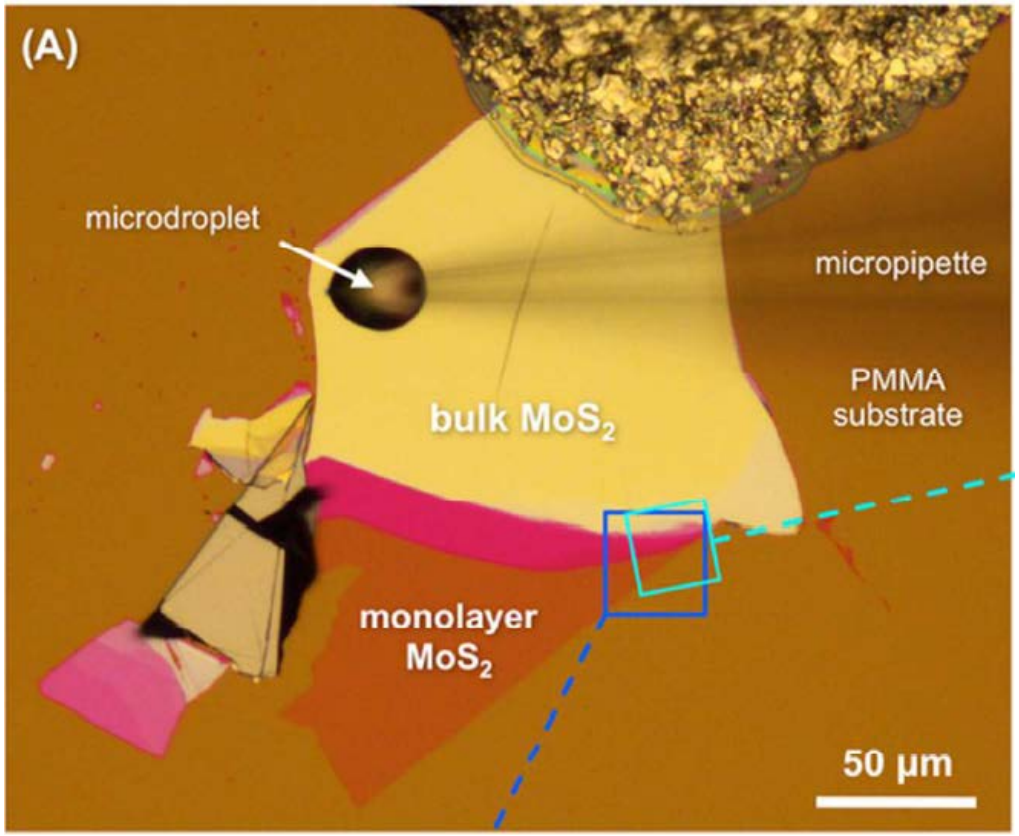




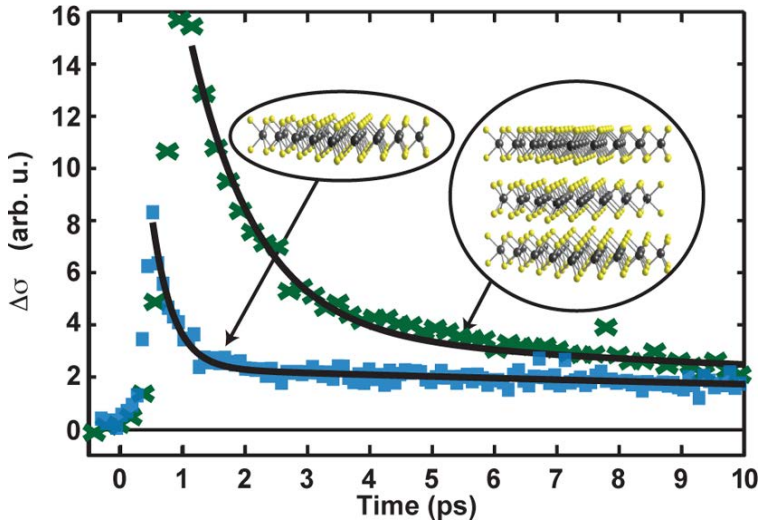
- Experiment ow to test different m
- Evolution a

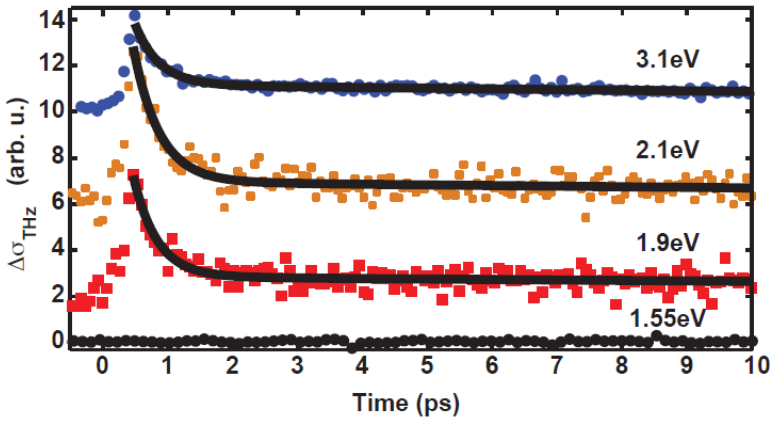
Spatially and temporally resolved THZ spectroscopy

Multispectral Imaging (MSI) system



Nano Letters 16, 2016, 2023–2032



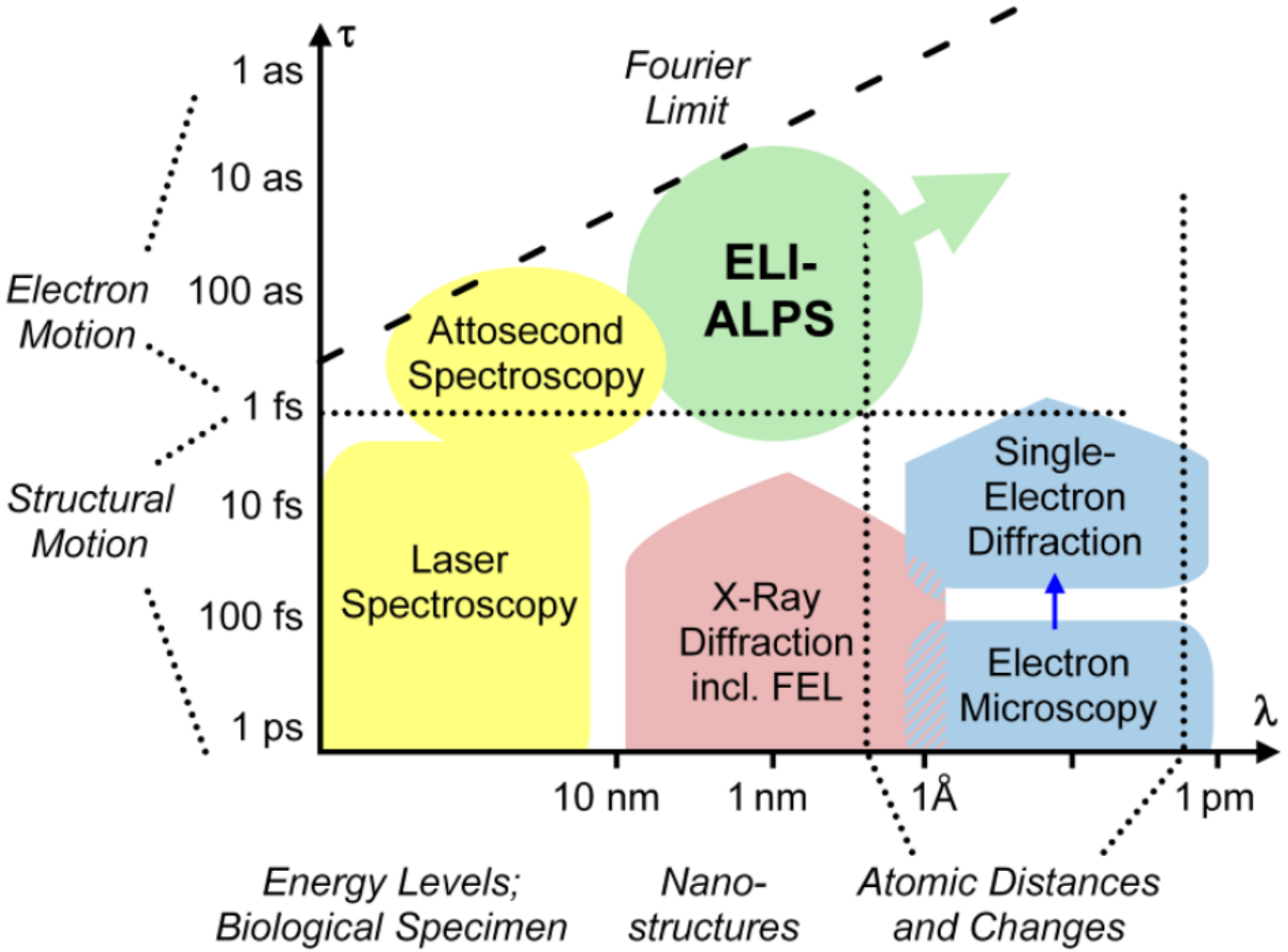


ACS Nano, 8, 2014, 11147-11153

Either spatial or temporal resolution

Technique	Probe type	Key properties measured	Typical resolution	Limitations and challenges
Scanning photocurrent microscopy (SPCM) (conventional)	Optical	Locally generated photocurrent; used to determine local quantum efficiency, minority carrier diffusion lengths, electric field distributions, and more	1–25 μm	Spatial resolution set by Abbe diffraction limit; typically limited to monochromatic light; avoiding high injection conditions and bubble formation
Near field scanning optical microscopy (NSOM)-based SPCM	Optical/physical	Similar capabilities to SPCM, but with higher spatial resolution.	10's nm–1 μm	Spatial resolution set by size of NSOM tip aperture; tip heating; interference; difficult on rough surfaces
Optical spectroscopies (Raman, UV-vis, IR, SFG)	Optical	Chemical, physical, and optical properties of photoelectrode surface	1–25 μm	Spatial resolution set by Abbe diffraction limit; long acquisition times; bubble formation
Ultrafast spectroscopies *e.g.* transient absorption spectroscopy (TA)	Optical	Lifetimes of electronic and vibrational states, interfacial charge transfer rates, and transient photoconductivity (THz)	sub ps–ns, 100 μm	Long acquisition times; avoiding high injection conditions; different detection systems for <ns, ns–μs, and μs–s
Scanning electrochemical microscopy (SECM)	Physical/electrochemical (non-contact)	Local catalytic activity and kinetic rate constants; sensitive to local opto-electronic properties in PEC systems; advanced forms of SECM for pH-sensing, corrosion analysis, and more	10's nm–100 μm	Resolution set by tip dimensions and tip–substrate distance; difficult with rough surfaces; bubble formation; challenges with light integration
Electrochemical scanning tunneling microscopy (E-STM)	Physical/electronic	Atomically resolved physical and electronic structure; video rate imaging possible	Å–nm (atomic resolution possible)	Difficult on rough surfaces; limited scan area size; poorly defined tip geometries, limited electrochemical window for STM tips
Atomic force microscopy (AFM)	Physical/electronic	Surface morphology, conductivity, capacitance, surface potentials, double layer forces, hydration layer structure	Å–5 nm (atomic resolution possible)	Difficult on rough surfaces; limited scan area size; limited electrochemical window for conductive tips

Az ELI helye ezekben a folyamatokban



THANK YOU FOR YOUR ATTENTION!

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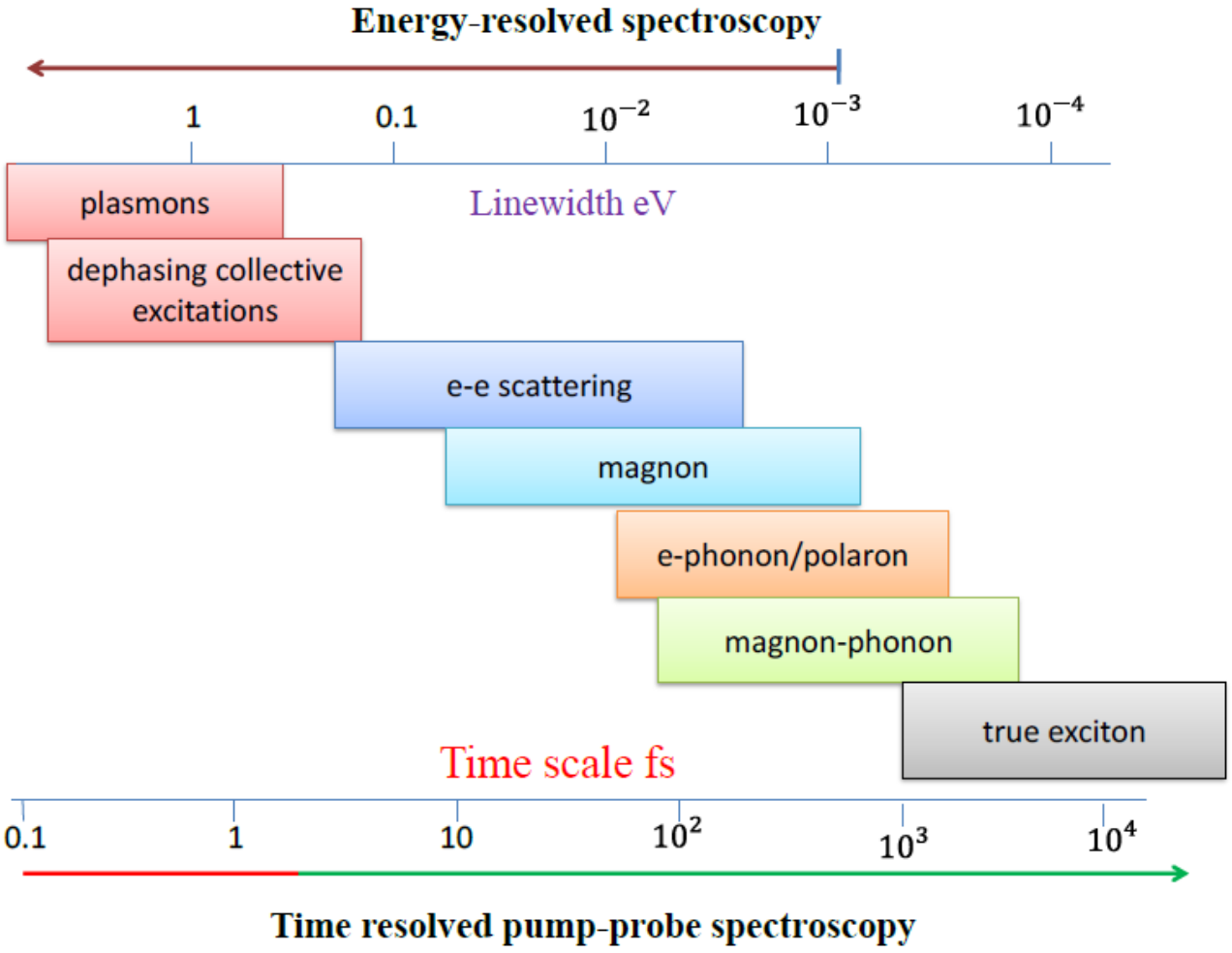
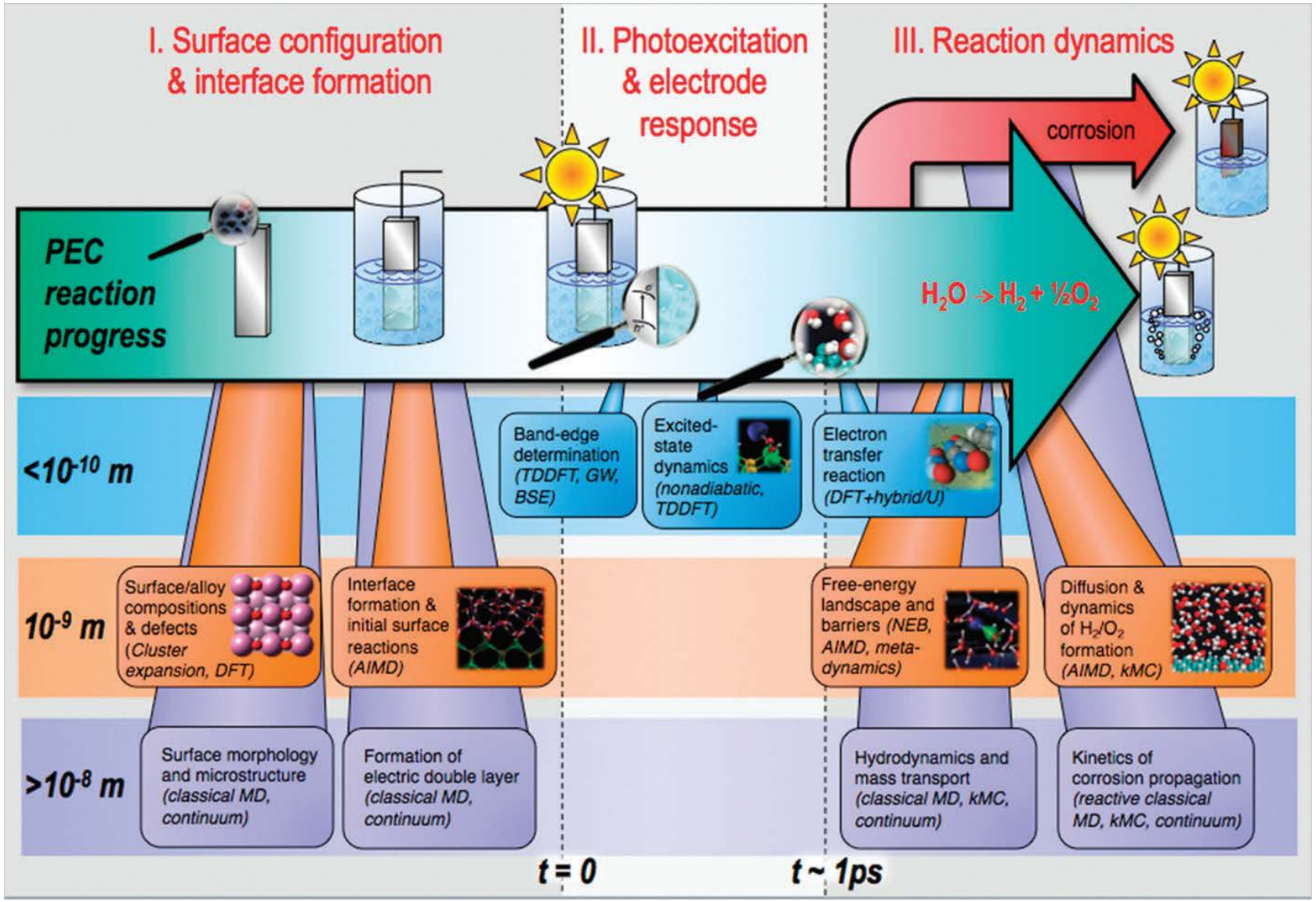
Outline


Energy-resolved spectroscopy
1
0.1
10^{-2}
10^{-3}
10^{-4}
plasmons
Linewidth eV
dephasing collective excitations
e-e scattering
magnon
e-phonon/polaron
magnon-phonon
true exciton
Time scale fs
0.1
1
10
10^{2}
10^{3}
10^{4}
Time resolved pump-probe spectroscopy


I. Surface configuration & interface formation
II. Photoexcitation & electrode response
III. Reaction dynamics
corrosion
PEC reaction progress
$H_2O \rightarrow H_2 + \frac{1}{2}O_2$
<10^{-10} m
Band-edge determination (TDDFT, GW, BSE)
Excited-state dynamics (nonadiabatic, TDDFT)
Electron transfer reaction (DFT+hybrid/U)
10^{-9} m
Surface/alloy compositions & defects (Cluster expansion, DFT)
Interface formation & initial surface reactions (AIMD)
Free-energy landscape and barriers (NEB, AIMD, meta-dynamics)
Diffusion & dynamics of H_2/O_2 formation (AIMD, kMC)
>10^{-8} m
Surface morphology and microstructure (classical MD, continuum)
Formation of electric double layer (classical MD, continuum)
Hydrodynamics and mass transport (classical MD, kMC, continuum)
Kinetics of corrosion propagation (reactive classical MD, kMC, continuum)
t = 0
t ~ 1ps