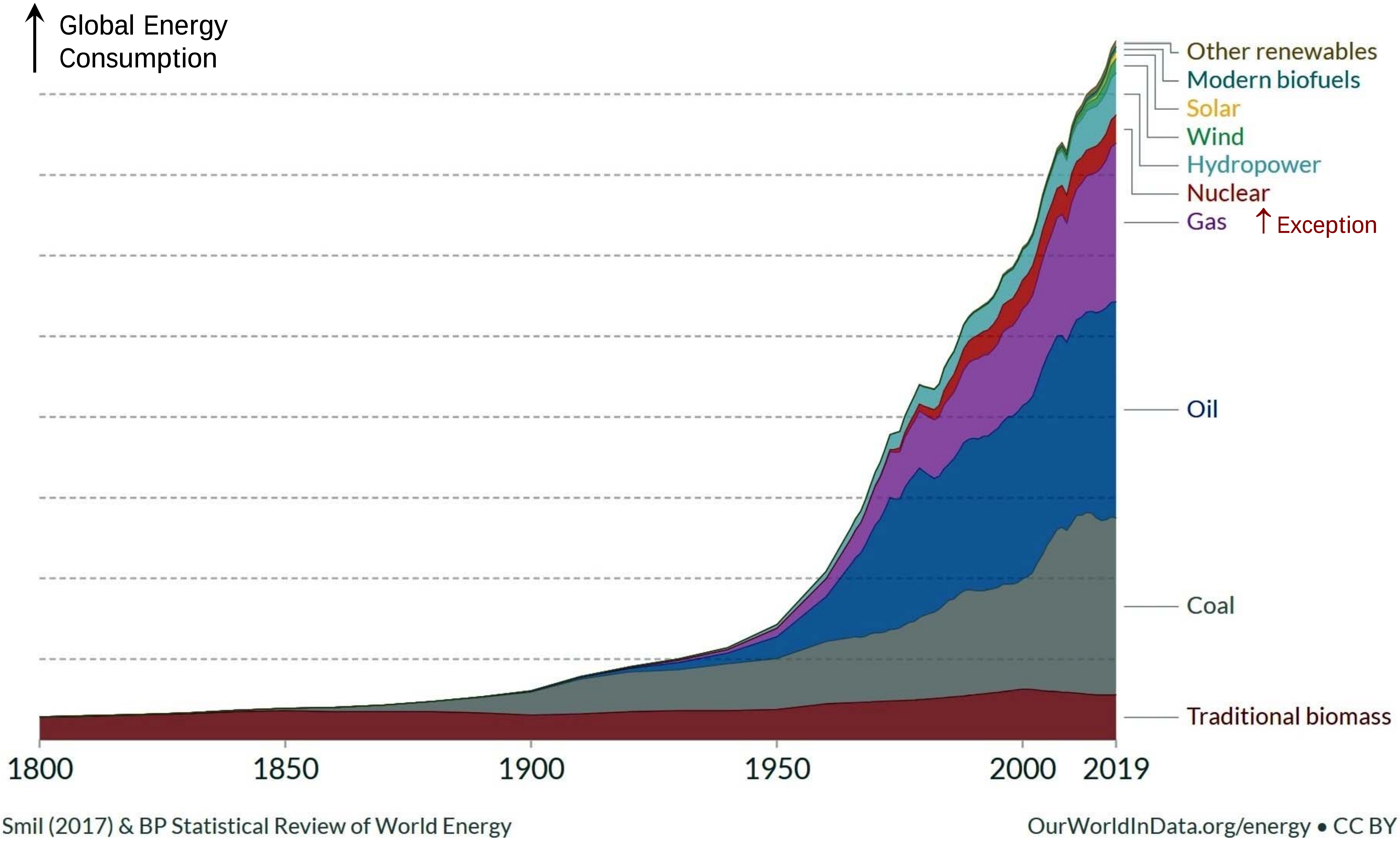
Designing New Materials for Solar Energy Conversion

- Global outlook on clean energy, including economics
- Using X-rays to tailor the energy levels in solar cells
- A dream: Follow the fate of charge carriers in real time

F. J. Himpsel, University of Wisconsin Madison

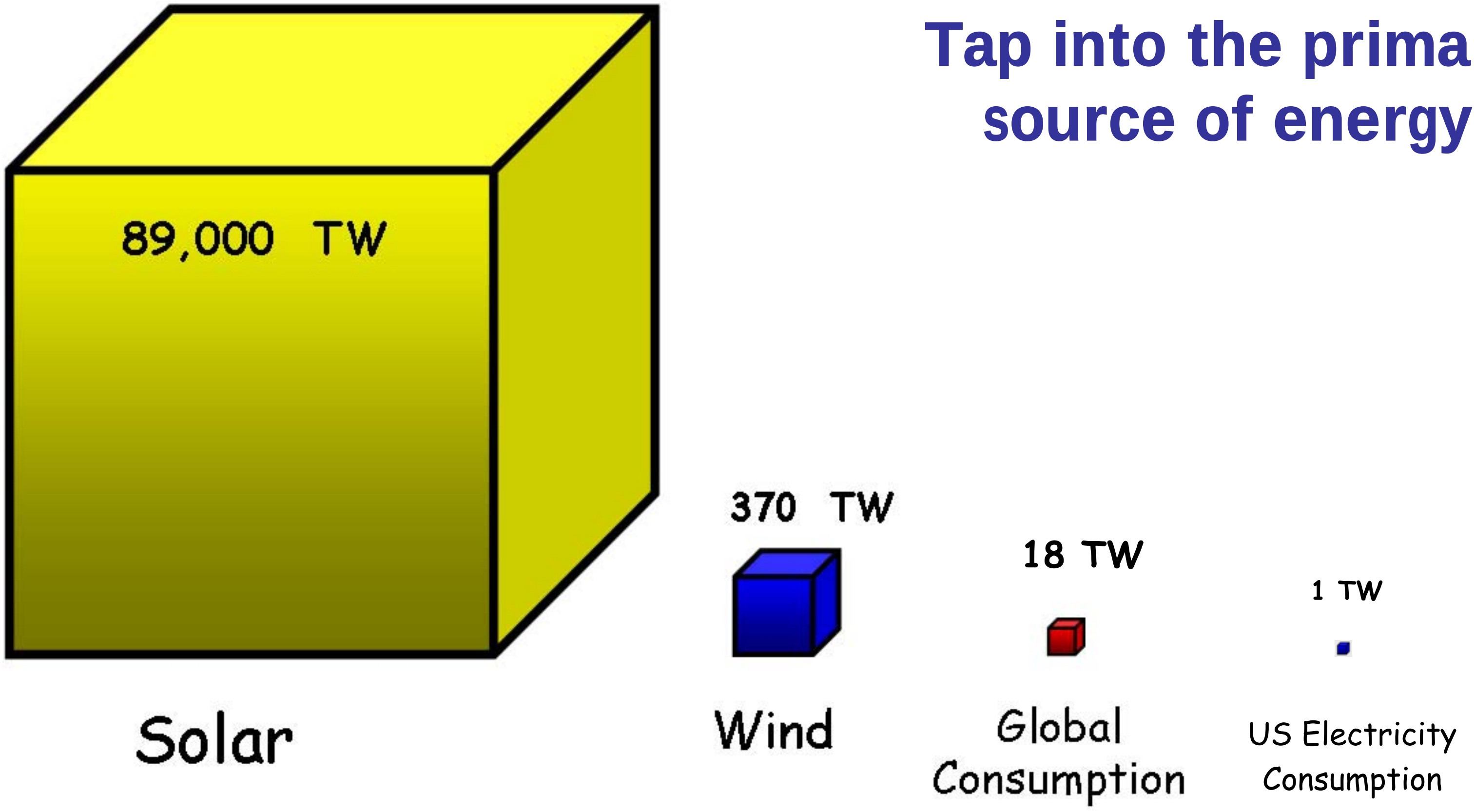
Most of our energy originates from the Sun



Smil (2017) & BP Statistical Review of World Energy

OurWorldInData.org/energy • CC BY

Tap into the primary source of energy



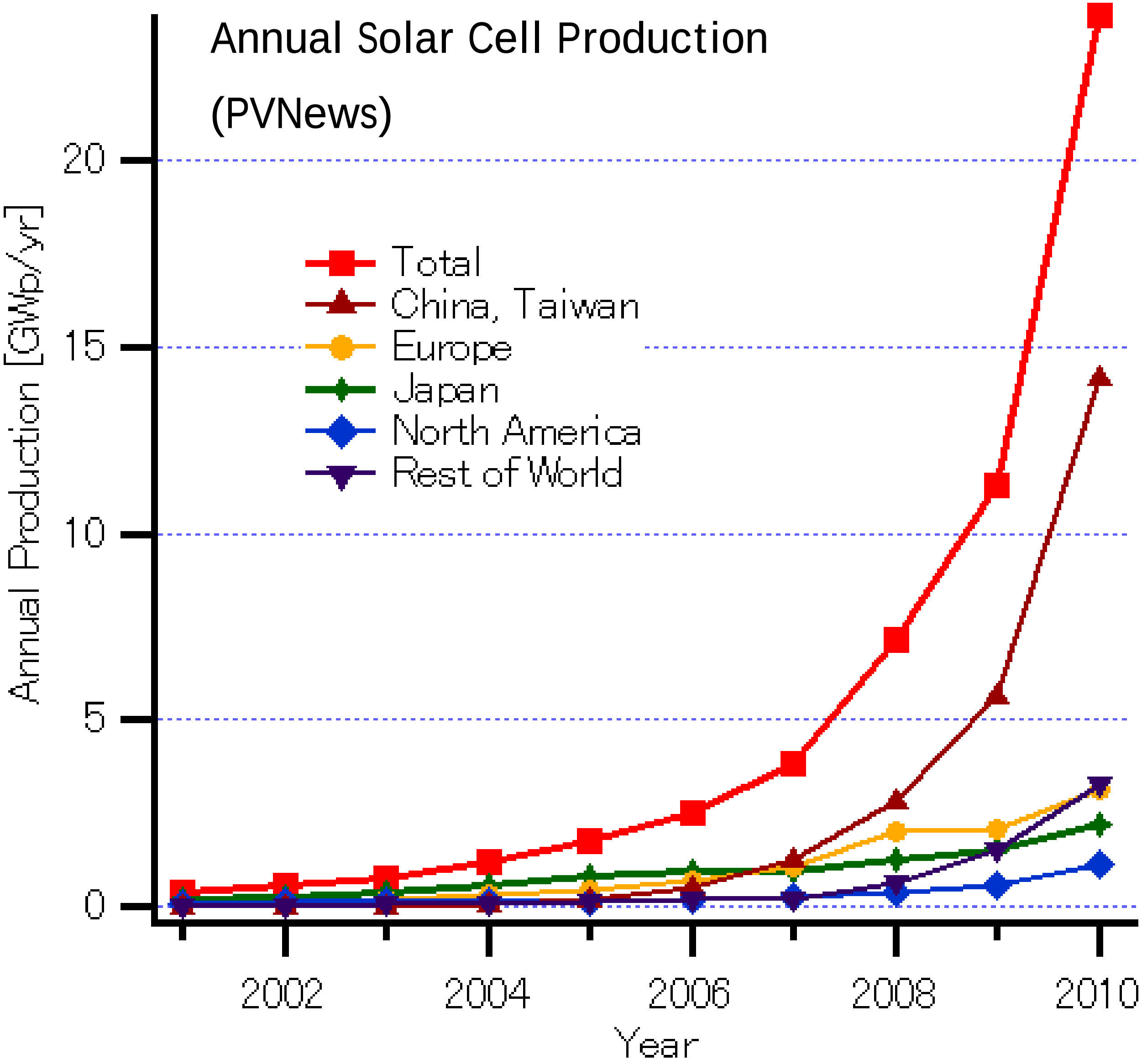
Willie Sutton, a notorious bank robber, was asked why he keeps robbing banks. The answer: Because that's where the money is.

Use the same logic for pursuing solar energy.

Convert solar energy
to the three dominant forms of energy

- **Heat:** low-tech
- **Fuel:** atomic, molecular scale (photo-electro-catalysis)
- **Electricity:** nanometer, picosecond scales (photo-voltaics)

Solar cell production rose quickly, but from a small base

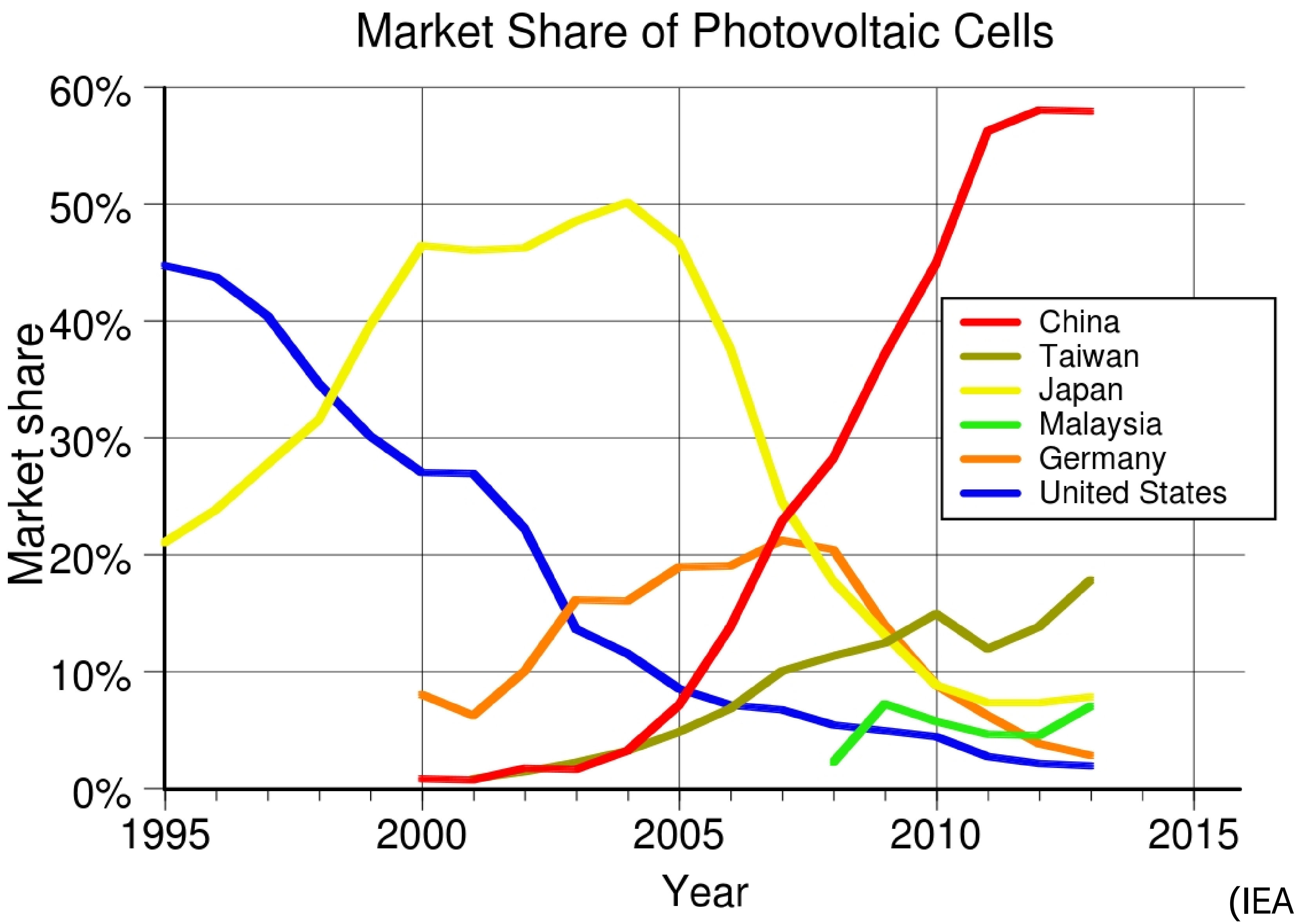


Rapid growth in China

Substantial in Europe

US is late

China took over



(IEA-PVPS)

$100\times100\ (\mathrm{miles})^2$ of solar cells could produce all the electricity for the US

$1\ \mathrm{kW/m^2}$	Incident solar power
× ¼	Useful daylight
× 0.20	Efficiency of a solar cell
$\times\ 2.6\cdot10^{10}\ \mathrm{m^2}$	$100\times100\ (\mathrm{miles})^2$
= 1.3 TW	
≈ 1 TW	Electric power generated in the US

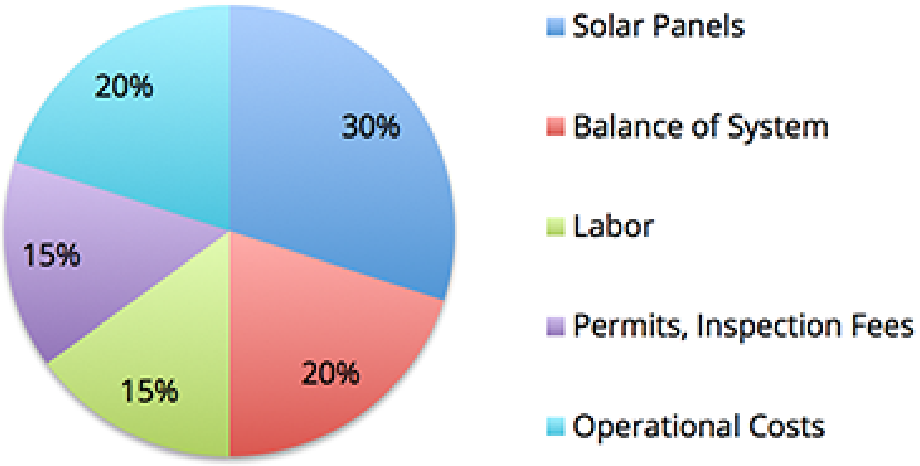
0.7 TW could also be generated by all the rooftops in the US (NREL)

How much would it cost ?

0.5 $/W Price of solar panels (modules) per Watt

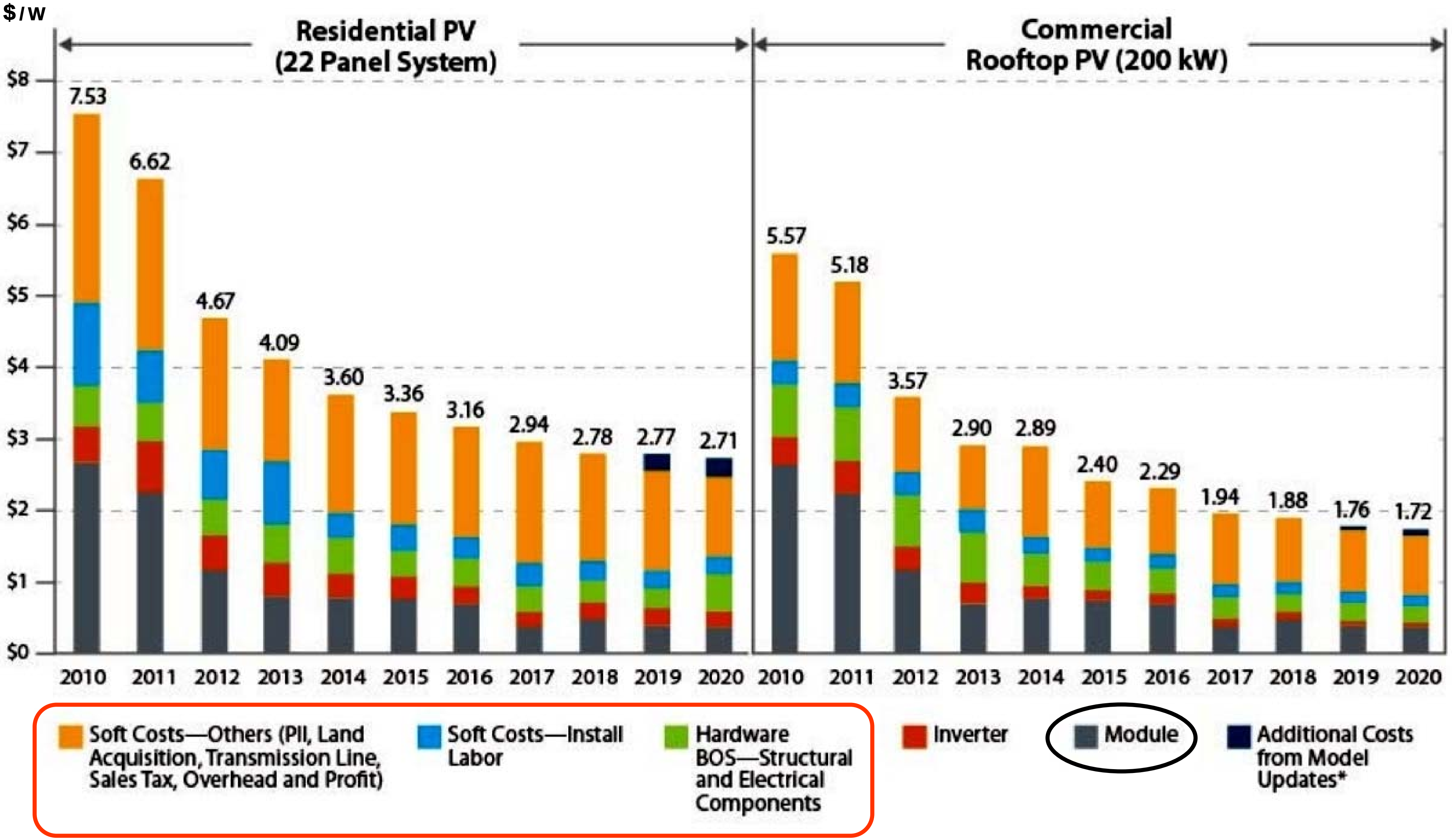
× 1 TW Electric power generated in the US

= 0.5 T$ (compare the US GDP of ca. 20 T$)



Solar panels make up only a fraction of the cost (falling rapidly).

Total cost of solar installations, breakdown by NREL



These costs increase with the area of the installation

Economics of solar energy

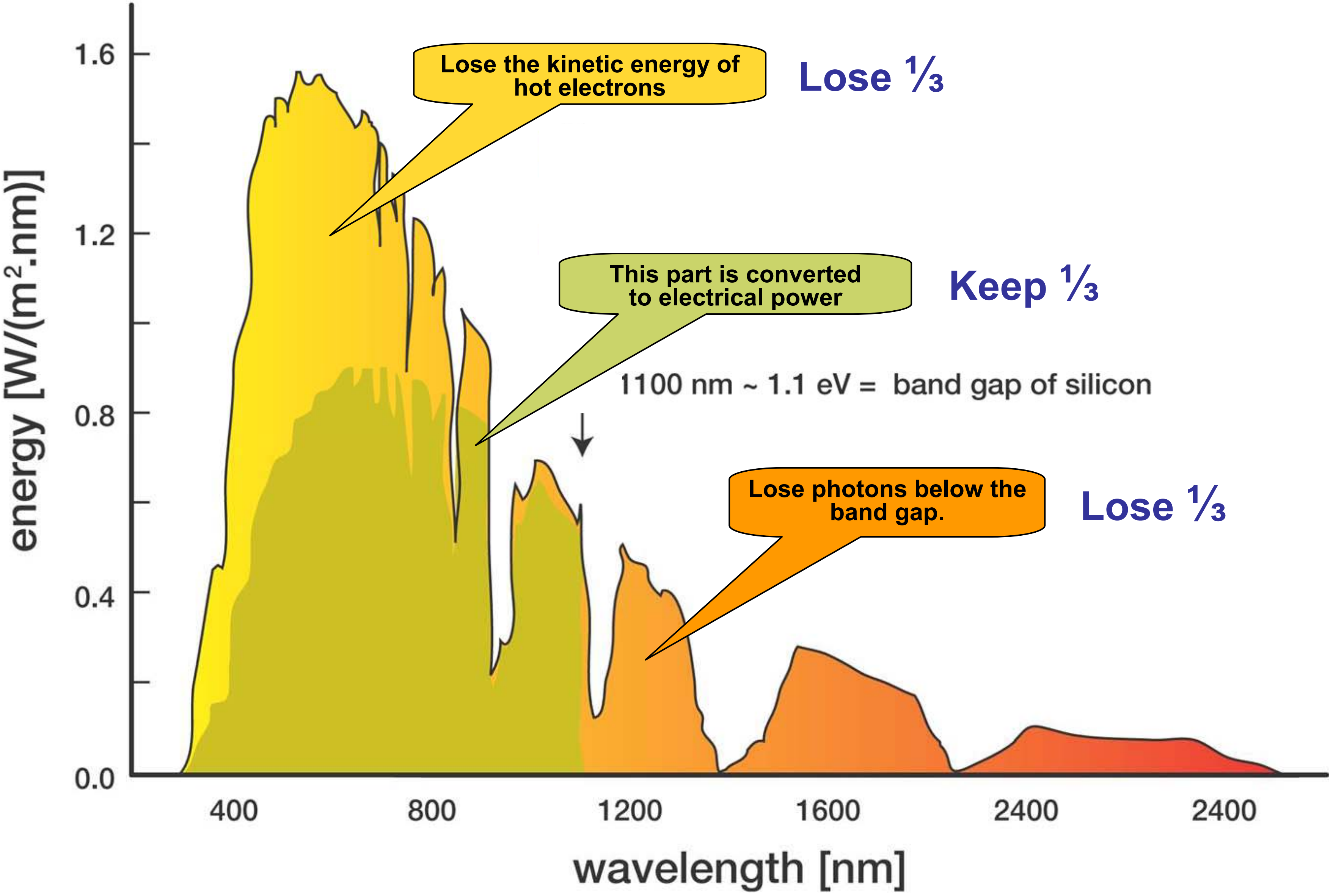
Solar panels make up only a fraction of the total cost

Major costs increase with the area of the installation

- ⇒ Reduce the area via higher efficiency of solar cells
- ⇒ Design support for panels into buildings
- ⇒ Reduce legal hurdles, create incentives

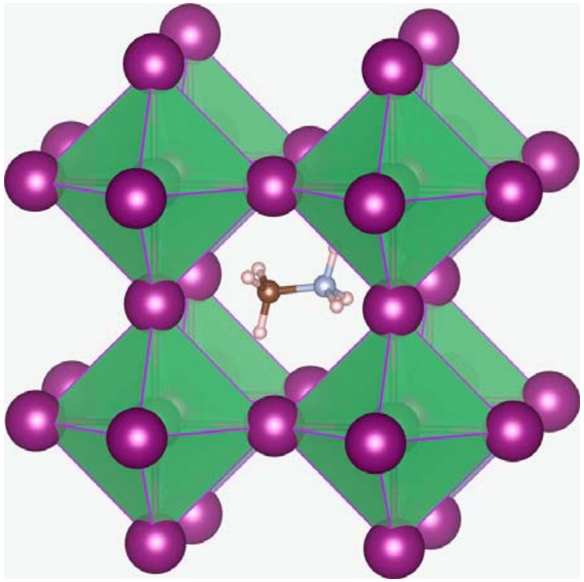
Efficiency limit of 33% for a single junction

Use multiple junctions in series: tandem cells



Perovskite-on-silicon tandem cell

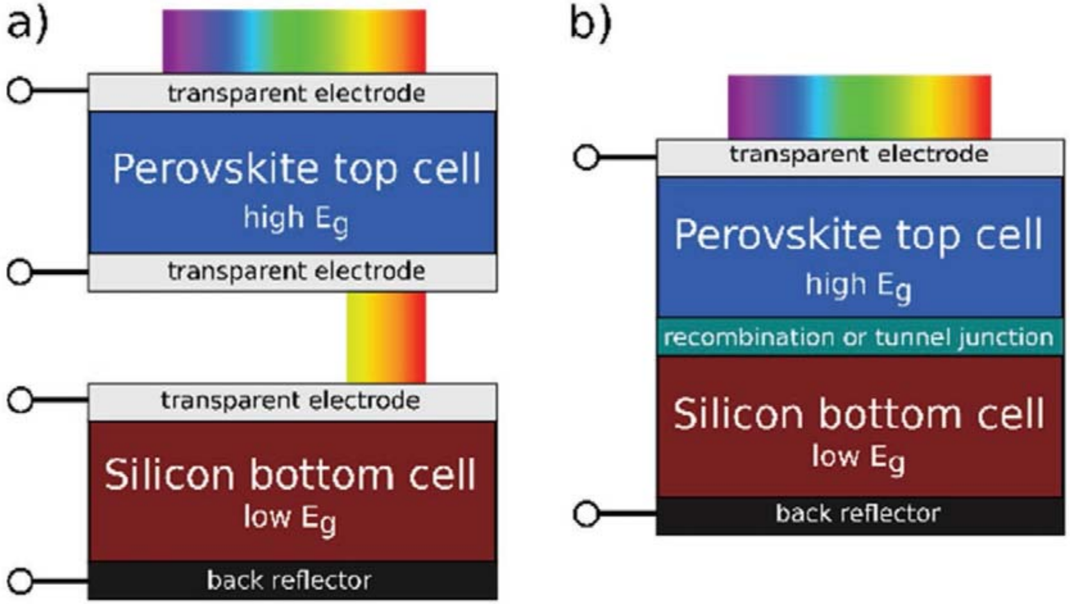
Perovskite



Halogen cage (Pb inside)

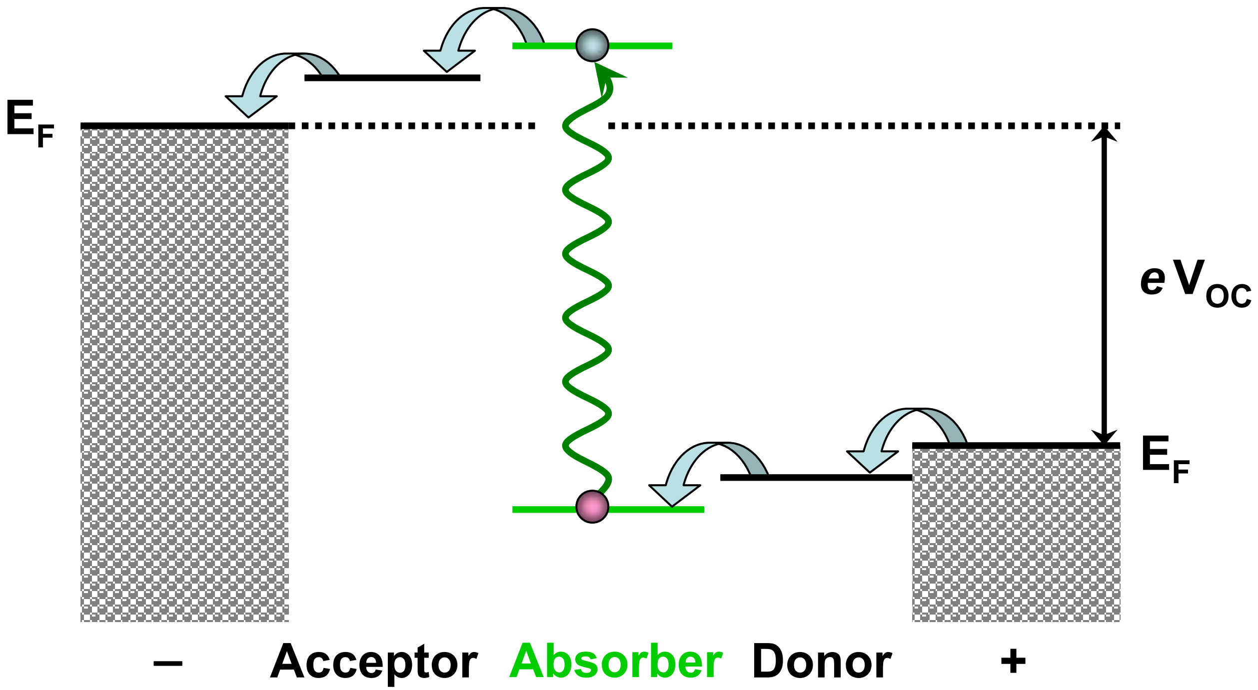
Methylammonium outside

Tandem configurations



Werner et al., Adv. Mater. Interfaces **5**, 1700731(2018)

Design a solar cell from scratch:
Utilize 4 energy levels, 3 materials

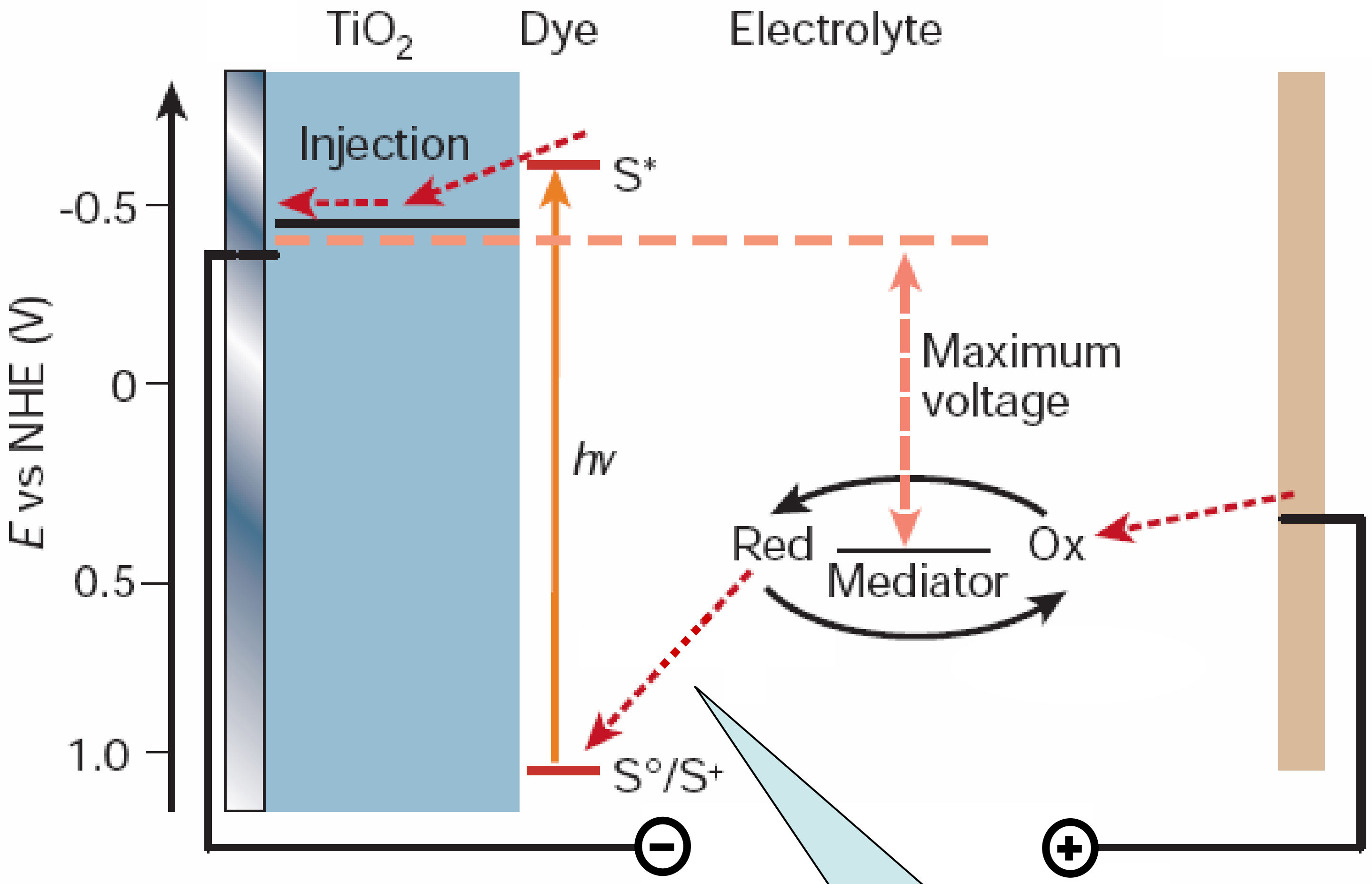


Small energy drop: Large voltage

Large energy drop: Large current

Want both for maximum power

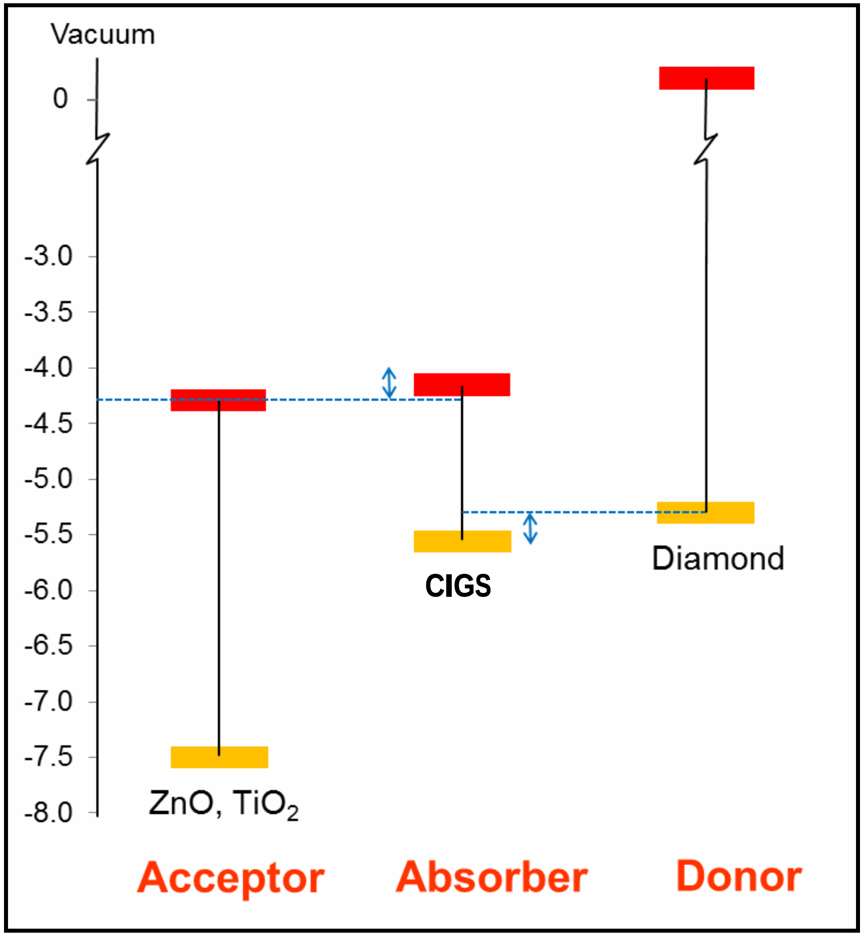
Dye-sensitized solar cells combine 3 materials

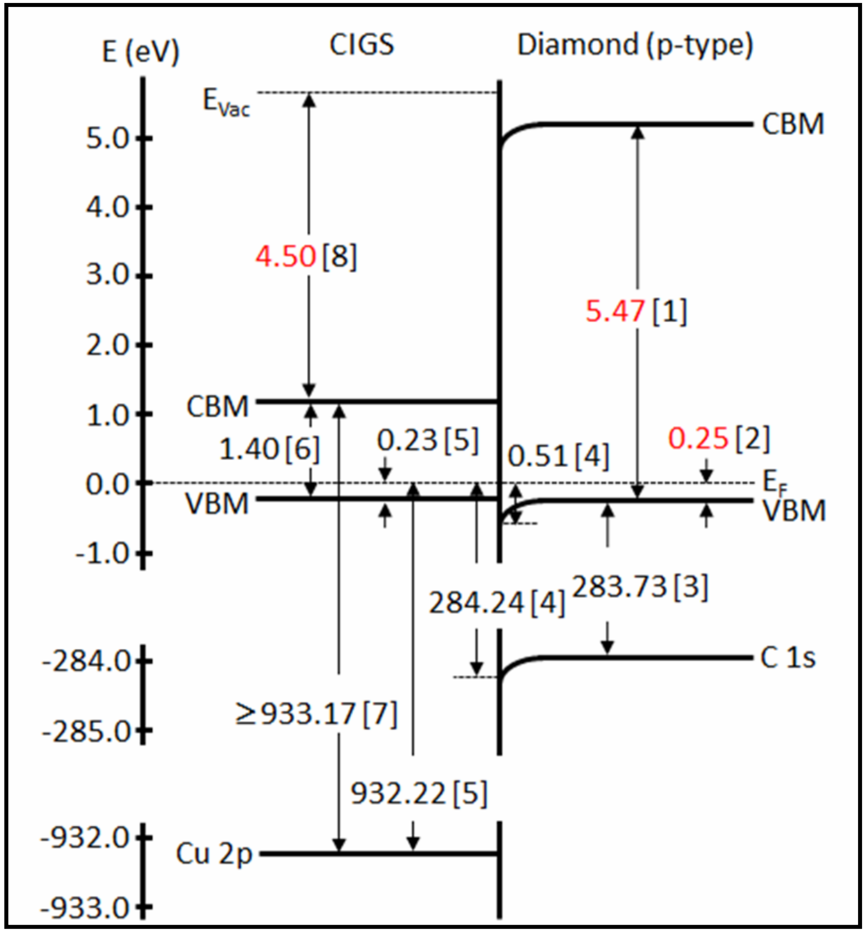


Lose half the voltage to fill holes quickly

Grätzel, Nature **414**, 338 (2001)
J. Phys. Chem. C **112** (2008)

Measure energy levels with synchrotron techniques





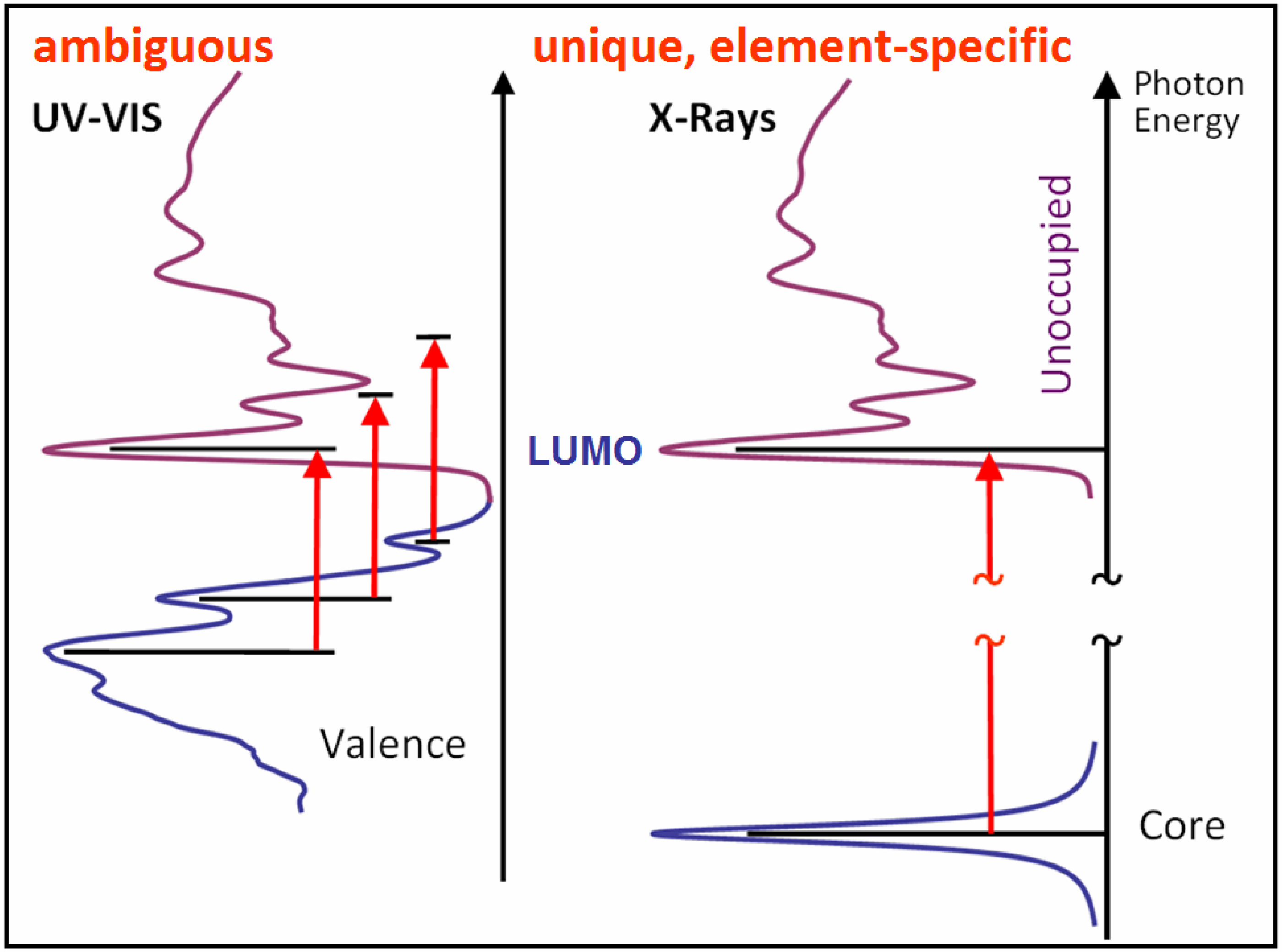
Diamond film as inert, transparent electron donor material

Energy levels from spectroscopy (XAS, XPS, UPS, optical, electrical)

Collaboration with Uppsala (growth, optical), UC Davis (HAXPS), LBL (synchrotron), UC Berkeley (theory)

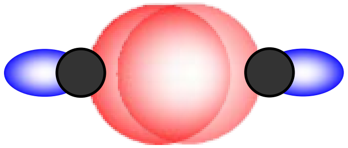
Kapilashrami et al., J. Appl. Phys. **116**, 143702 (2014)

Energy levels from absorption spectroscopy

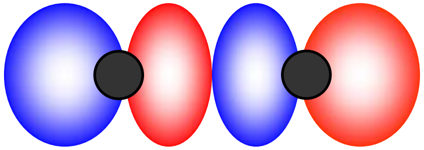


σ and π orbitals in organic molecules

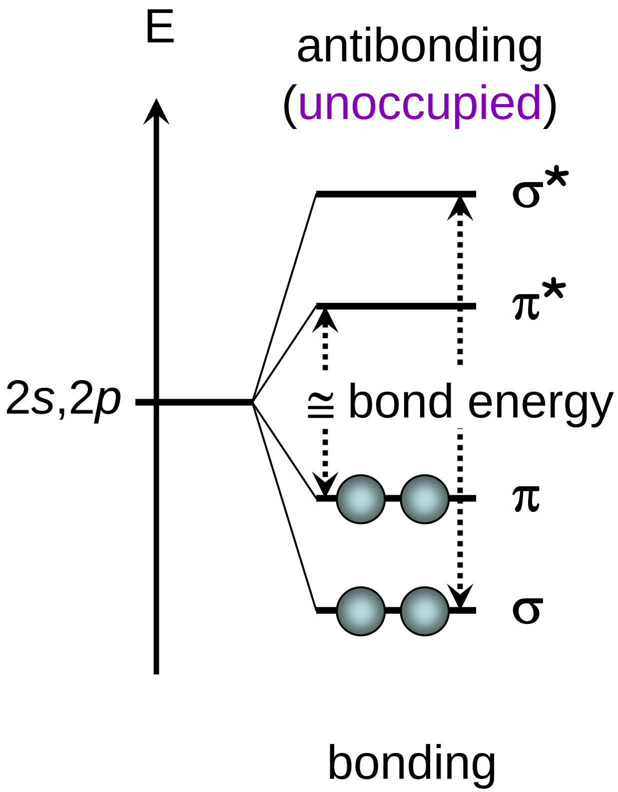
σ-bond:



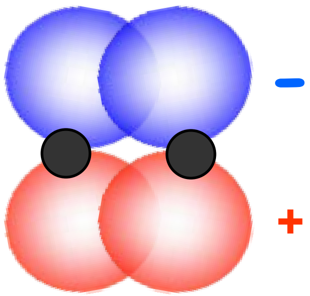
σ orbital



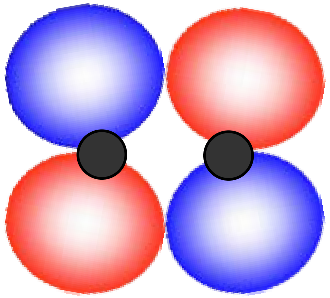
σ* orbital



π-bond:



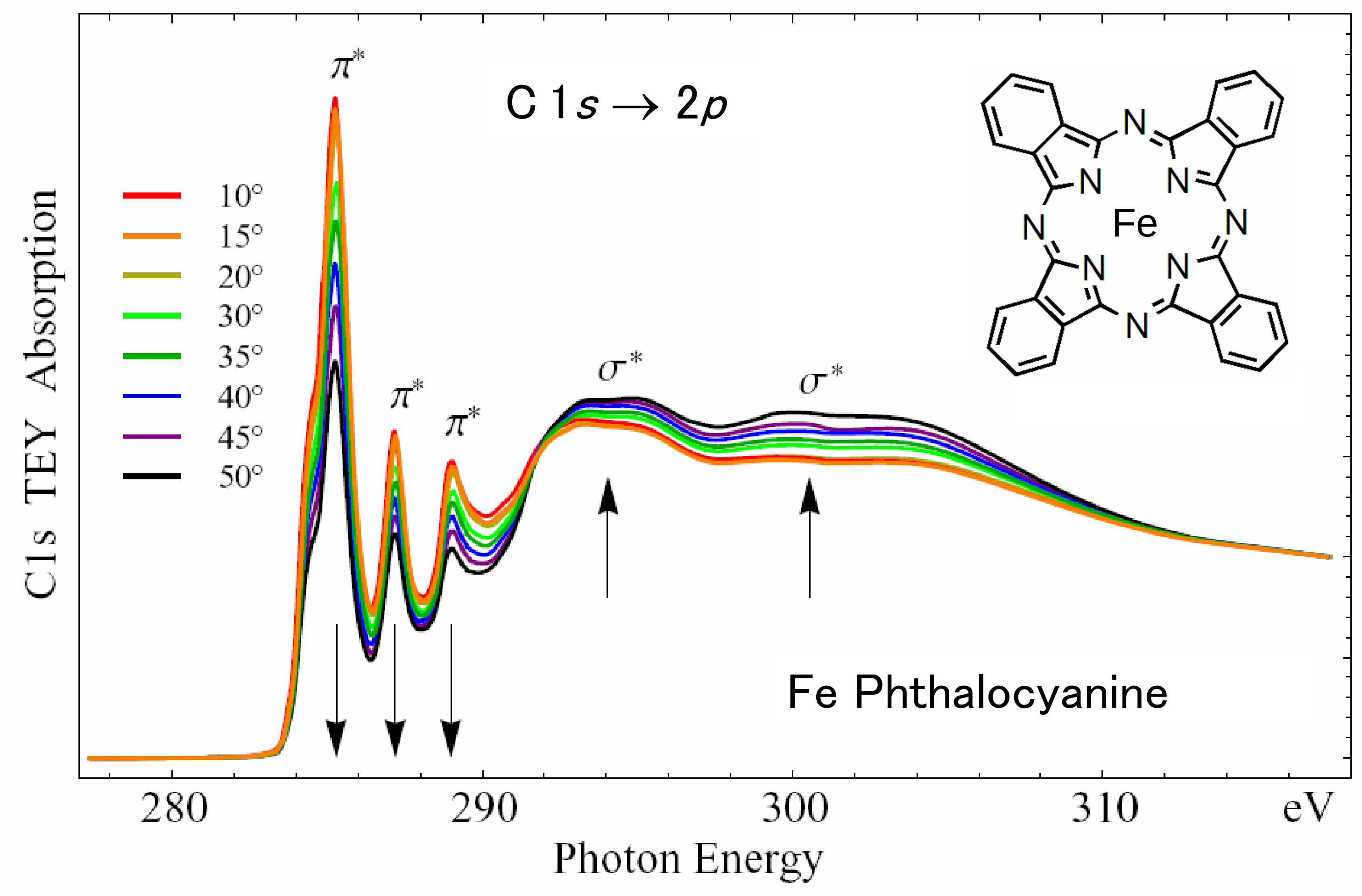
π-orbital



π*-orbital

Orientation of molecular orbitals via polarized x-rays

Distinguish π^* orbitals (perpendicular to the molecule) from σ^* orbitals (in-plane)



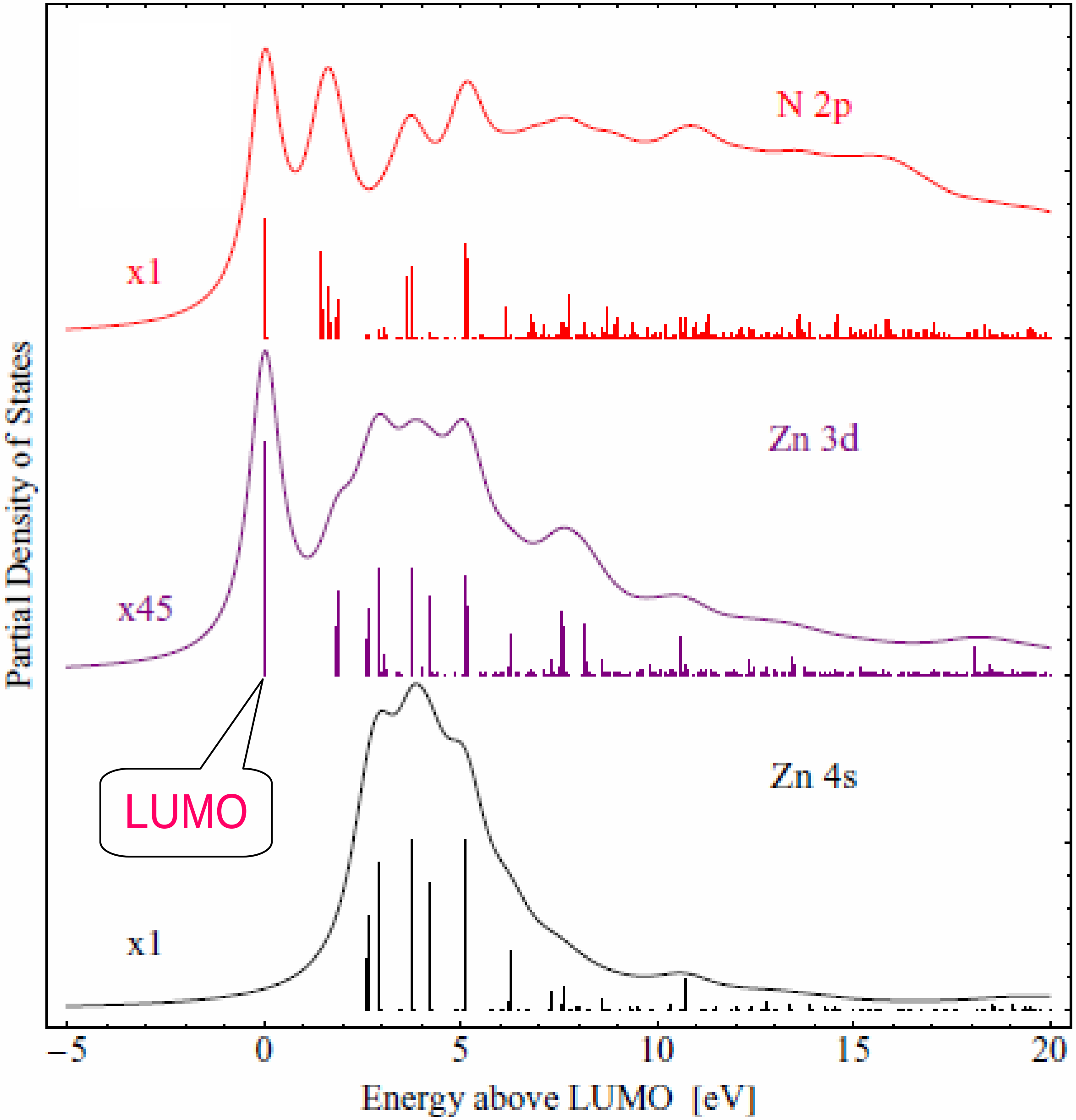
Cook et al., J. Chem. Phys. **131**, 194701 (2009)

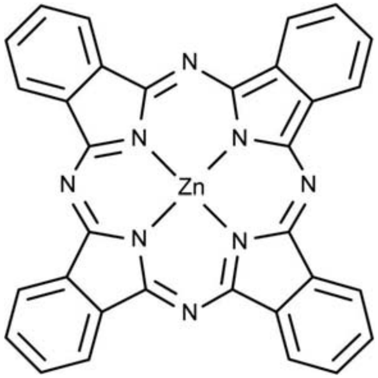
Calculate energy levels, wave functions

Levels get very dense at higher energies.

Electrons quickly trickle down to the LUMO.

Focus on the LUMO.

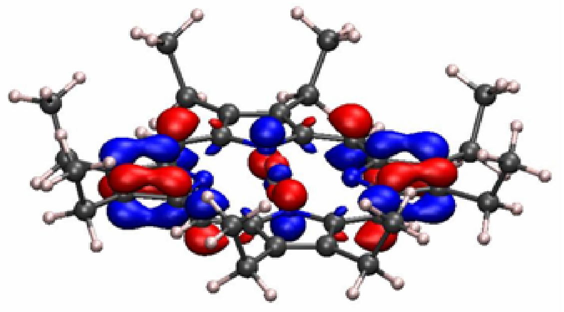


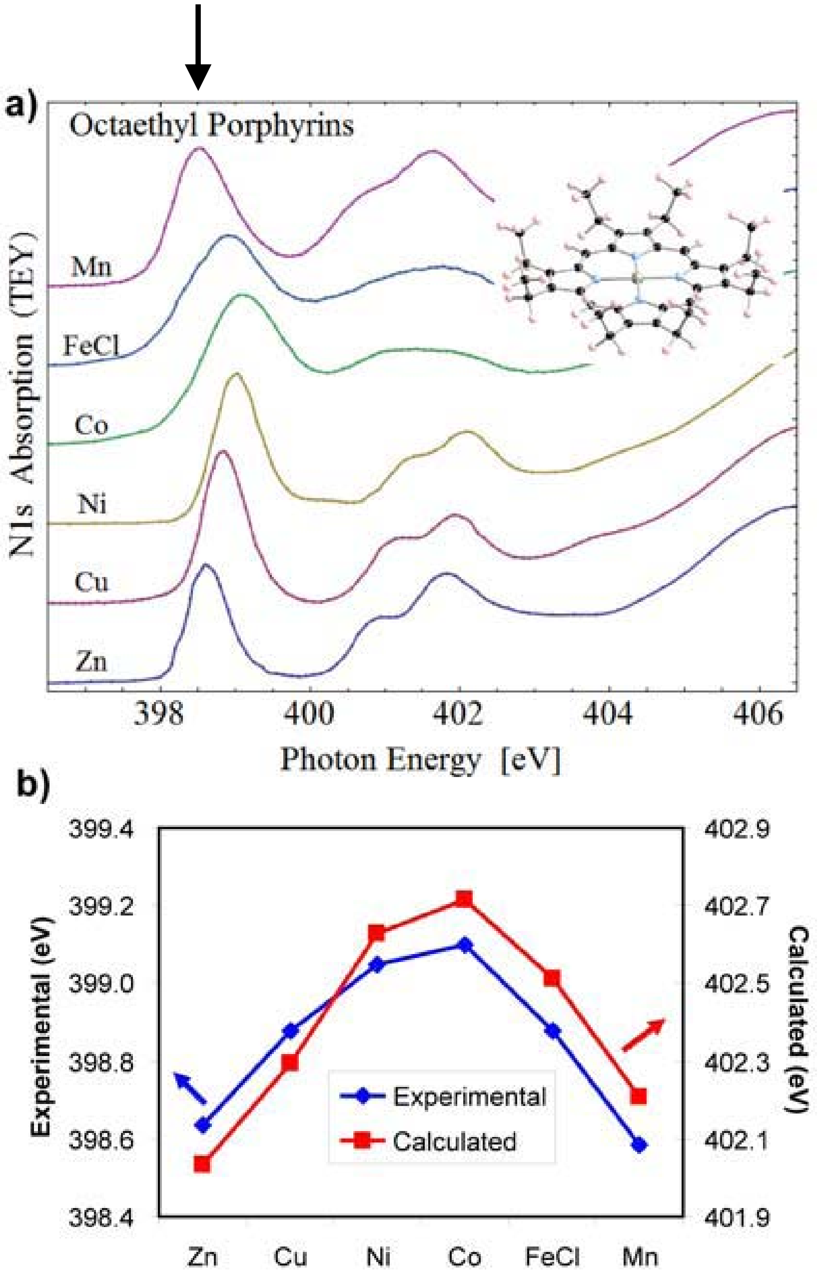


Cook et al., J. Chem. Phys. **134**, 204707 (2011)

Systematics: N1s → LUMO transition in porphyrins

LUMO (mostly at N)

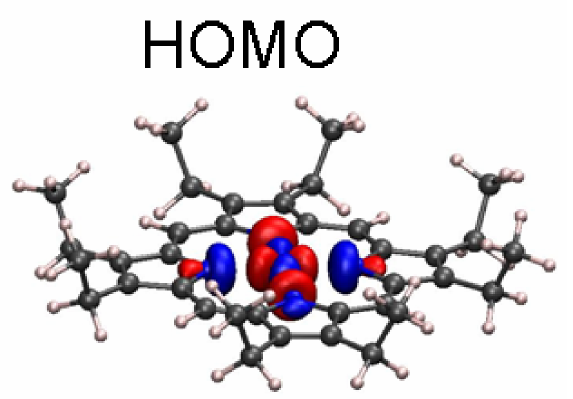




The N 1s core level shift is due to electron transfer from the metal to the surrounding nitrogens. It tracks the metal electronegativity.

Garcia-Lastra et al., J. Chem Phys. **133**, 151103 (2010)

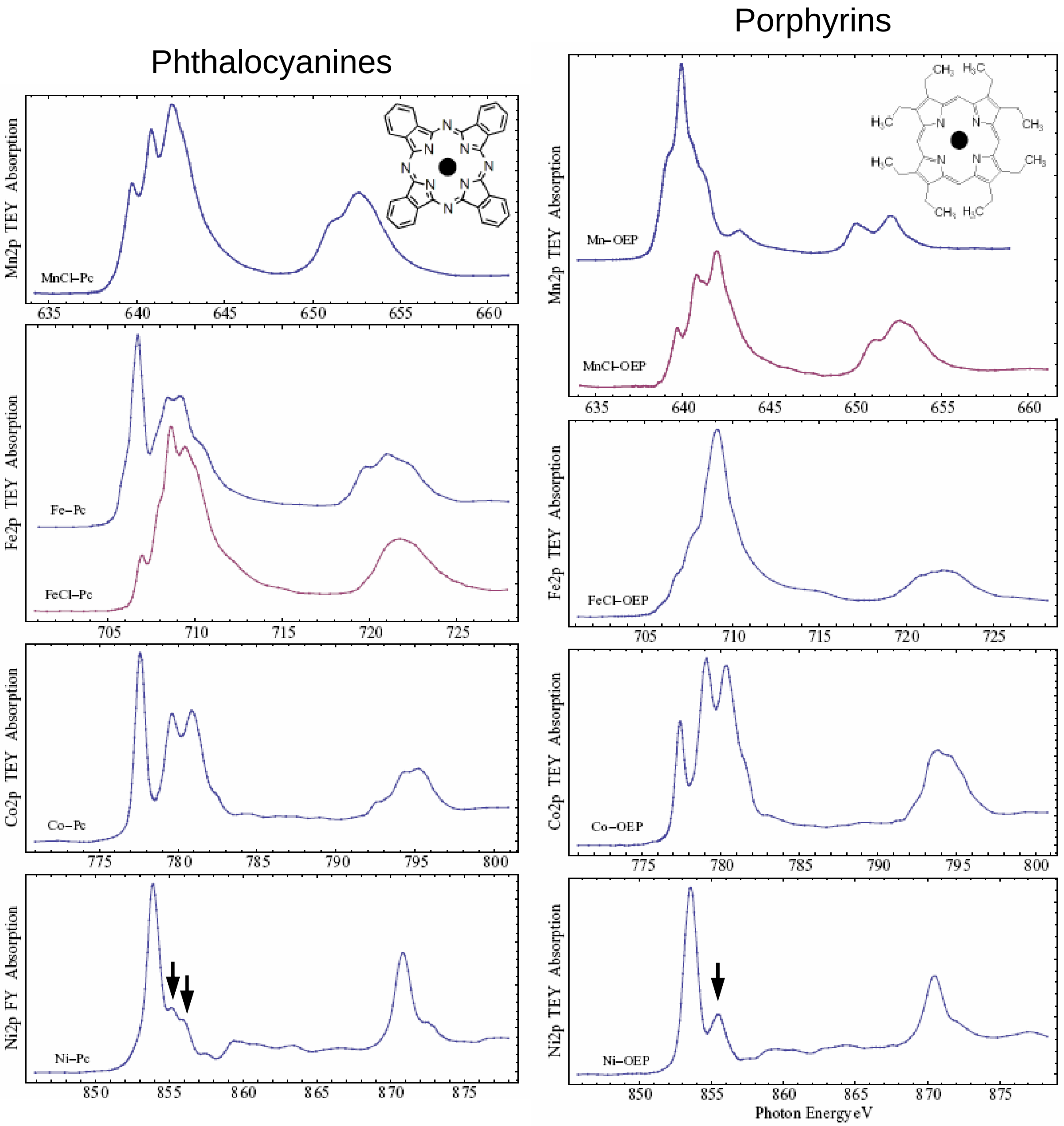
Systematics: Metal 2p → 3d transitions at the metal atom



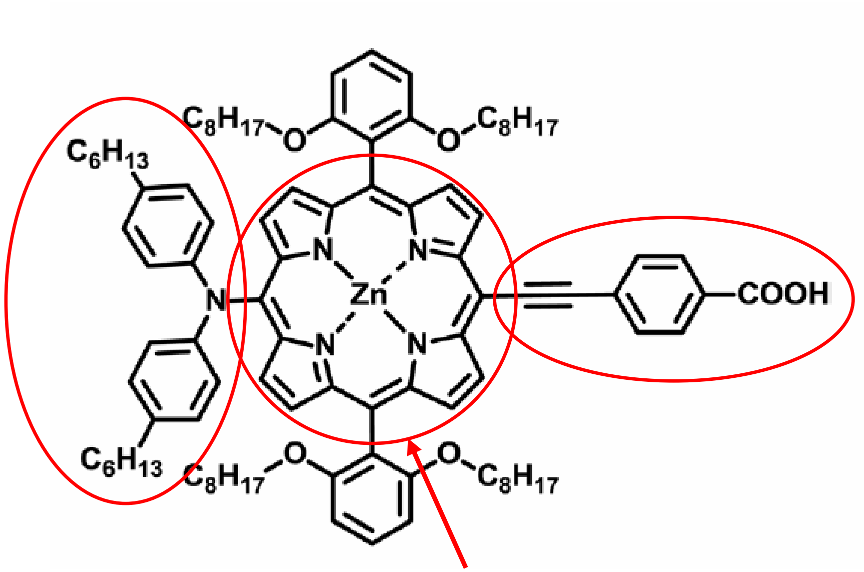
The multiplets reveal the oxidation state and the ligand field

Fe, Mn are stable in both the 2+ and 3+ oxidation states . That facilitates charge separation

Cook et al., J. Chem. Phys. **131**, 194701 (2009)



Combine the three components of a solar cell in one molecule with atomic perfection



Donor

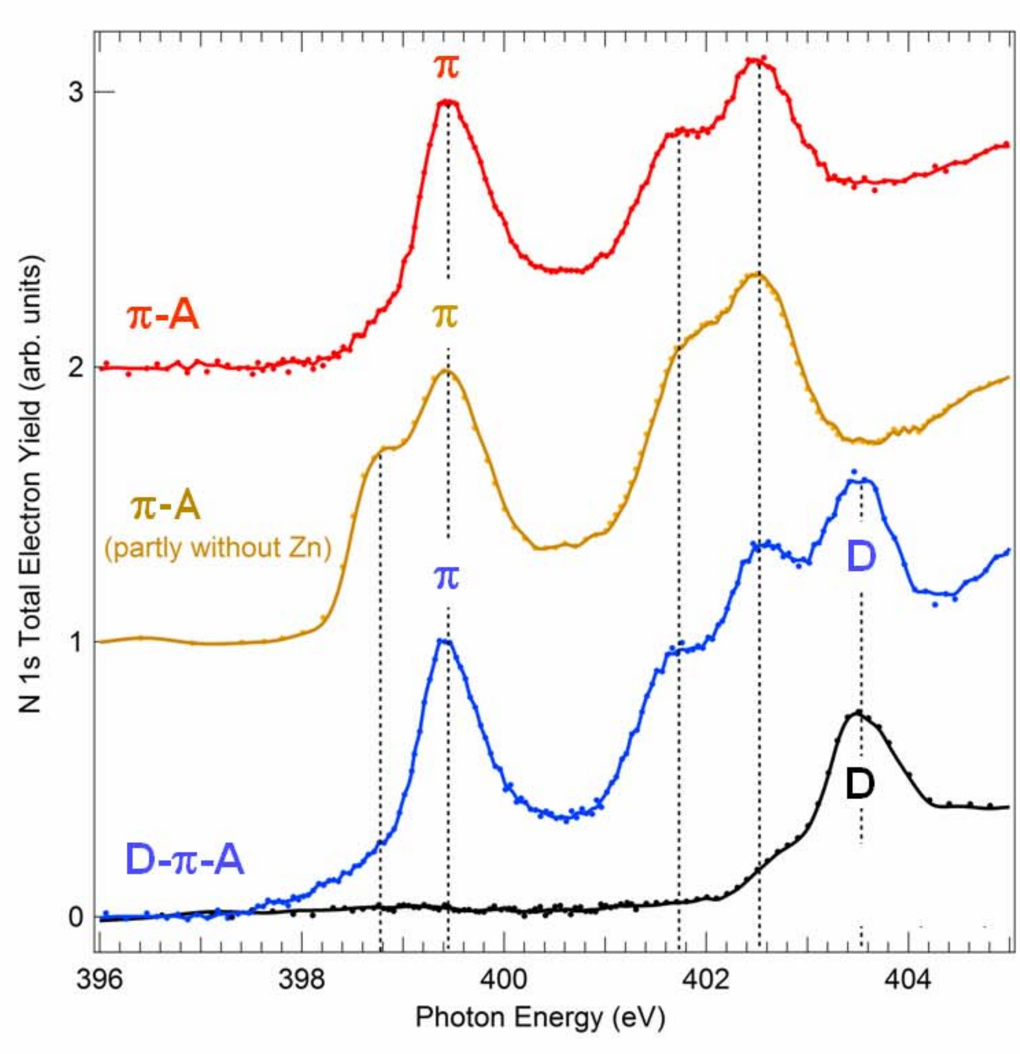
to Acceptor

π absorber

Achieved efficiency record for dye-sensitized solar cells (12.3%)

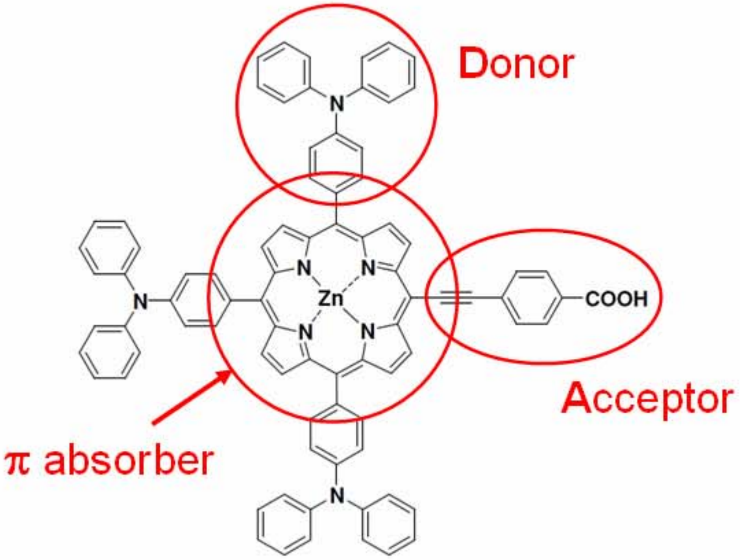
Grätzel group: Yella et al. Science **334**, 629 (2011)

D–π–A (donor–π–acceptor) complexes



This led to improved synthesis.

Weak point in the synthesis identified by theory (missing Zn atom).



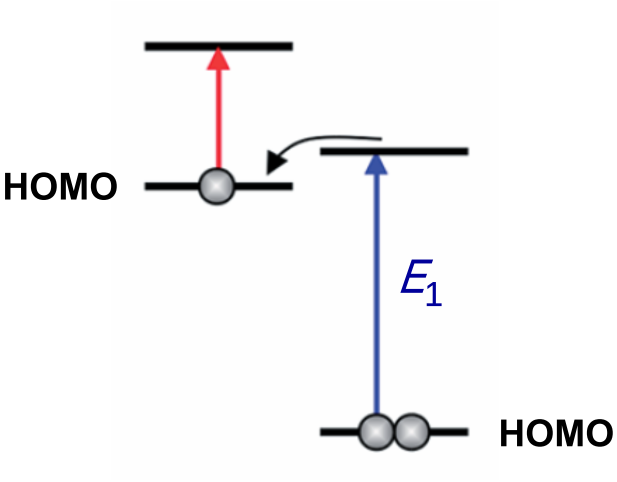
Collaboration with U. Autonoma Madrid (synthesis), U. San Sebastian (spectroscopy), LBL (theory)

Zegkinoglou et al., J. Phys. Chem. C **117**, 13357 (2013)

Design tandem cells with atomic precision?

Connect two dye molecules with an asymmetric molecular wire (=diode). Molecular complexes are atomically perfect.

It would solve the main problem of tandem cells: defects at interfaces.



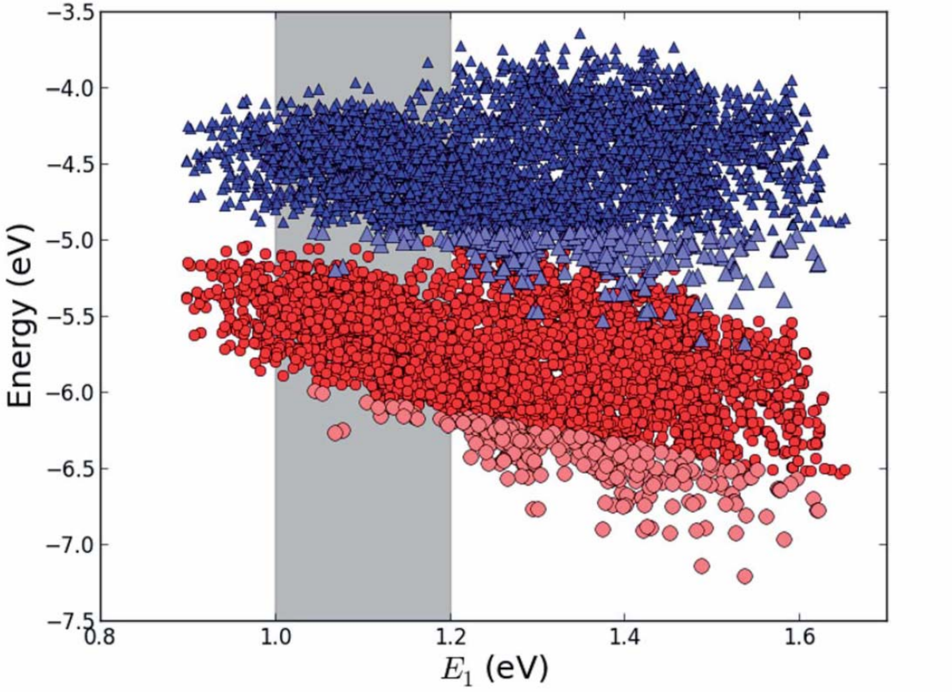
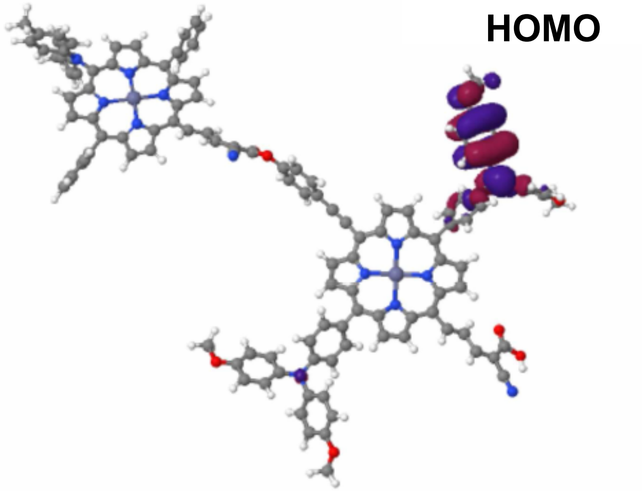


Fig. 2 E_{HOMO} (red circles) and $E_{\mathrm{HOMO}} + E_1$ (blue triangles) for all 5000+ porphyrins in our database[22,23] plotted against the lowest optical transition energy, E_1.

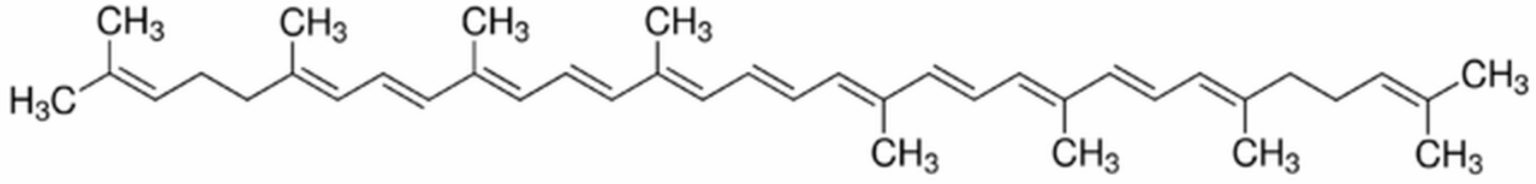


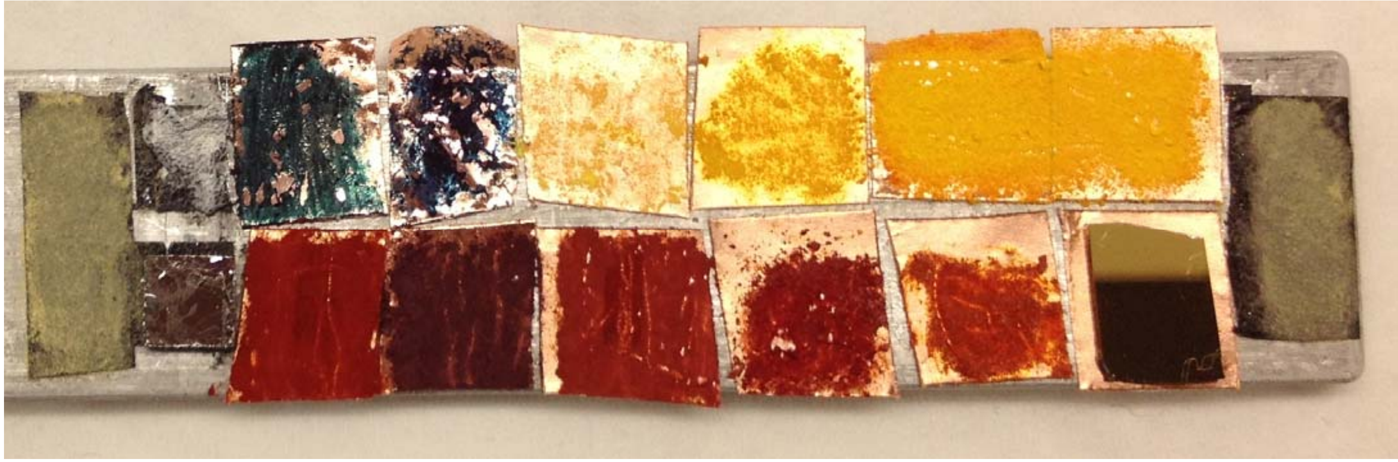
Ørnsø et al., Chemical Science **6**, 3018 (2015)

Molecular wires

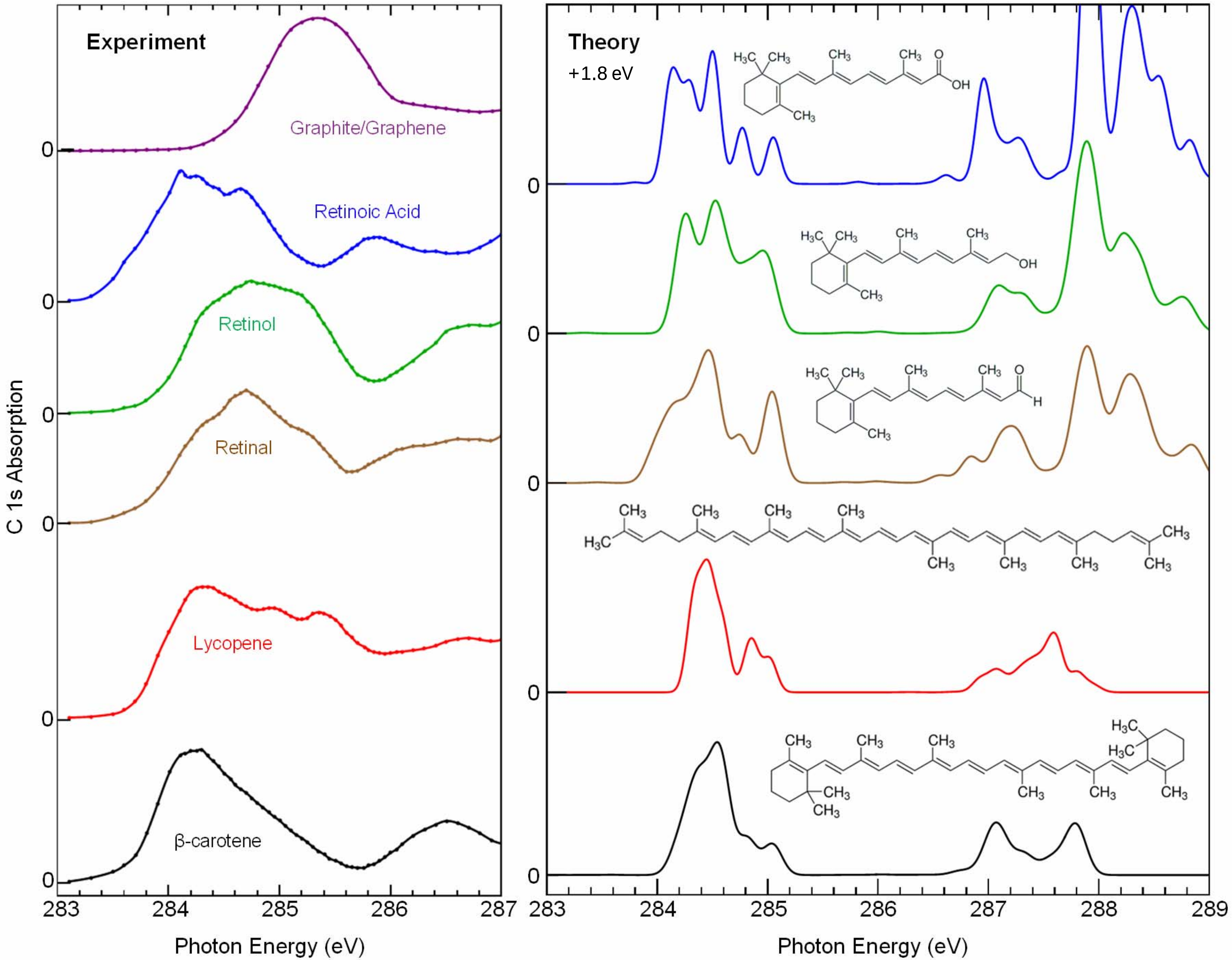
Lycopene

A single chain of overlapping π-orbitals forms a molecular wire



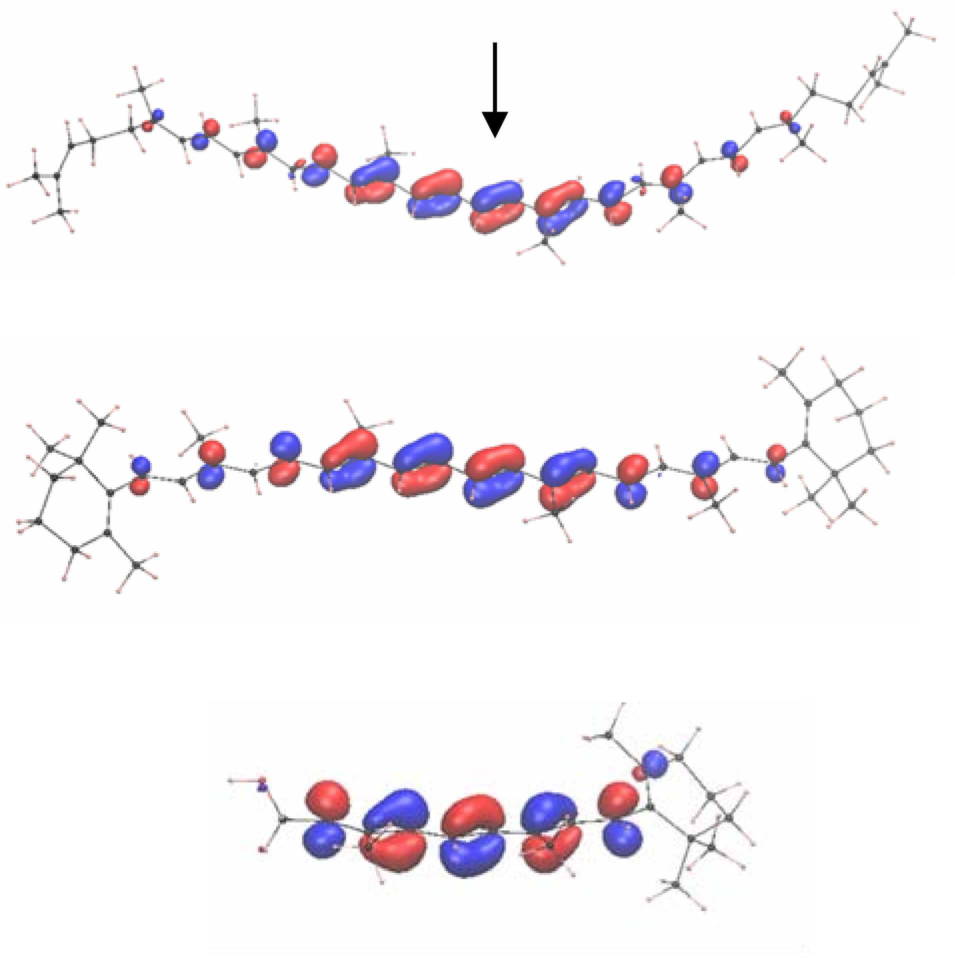


Garcia-Lastra et al., J. Phys. Chem. C **120**, 12362 (2016)


Experiment
Graphite/Graphene
Retinoic Acid
Retinol
Retinal
Lycopene
β-carotene
C 1s Absorption
0
283
284
285
286
287
Photon Energy (eV)
Theory
+1.8 eV
288
289
H3C
CH3
O
OH
H
Photon Energy (eV)

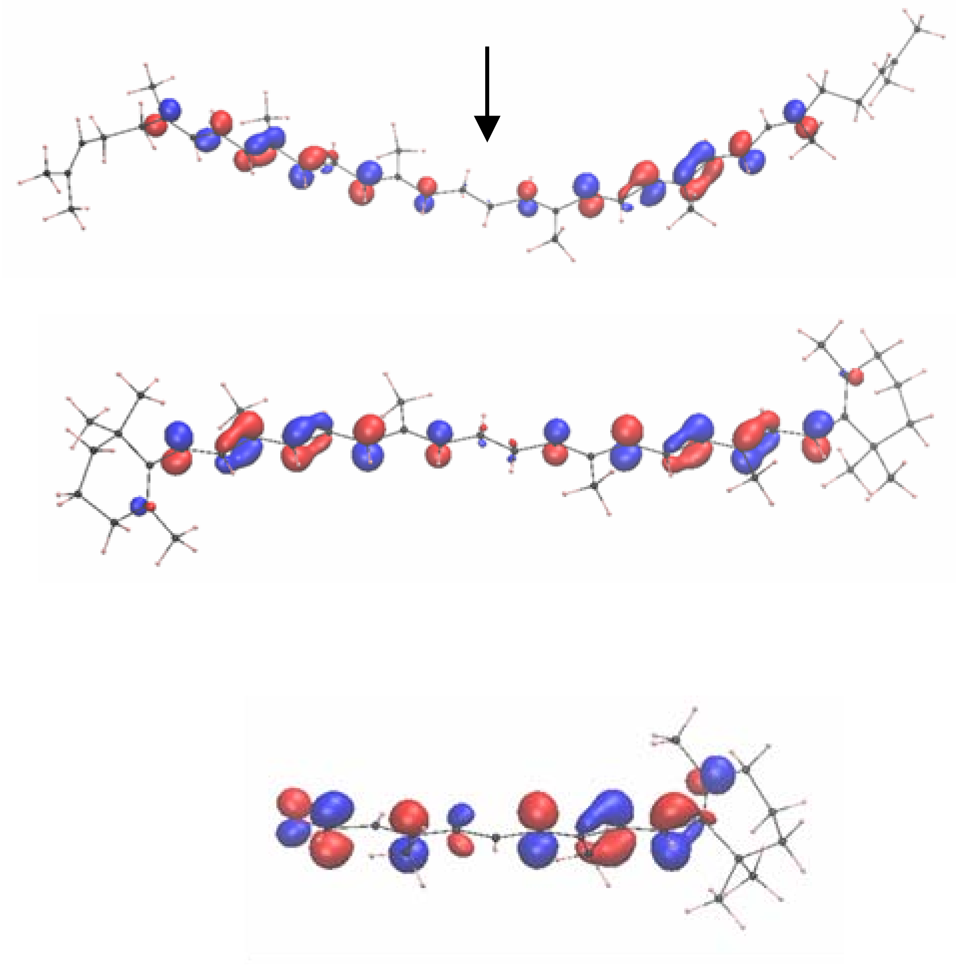
Wave functions of molecular wires: vibrating strings

Maximum



LUMO

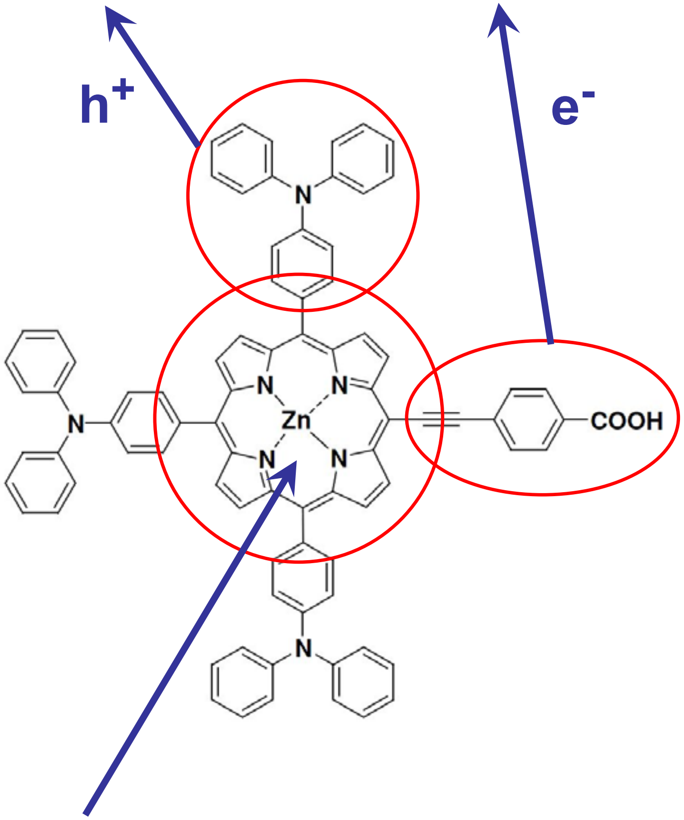
Node



LUMO+1

Beyond energy levels: lifetimes vs. loss rates

Probe the carriers along their way out with X-rays.



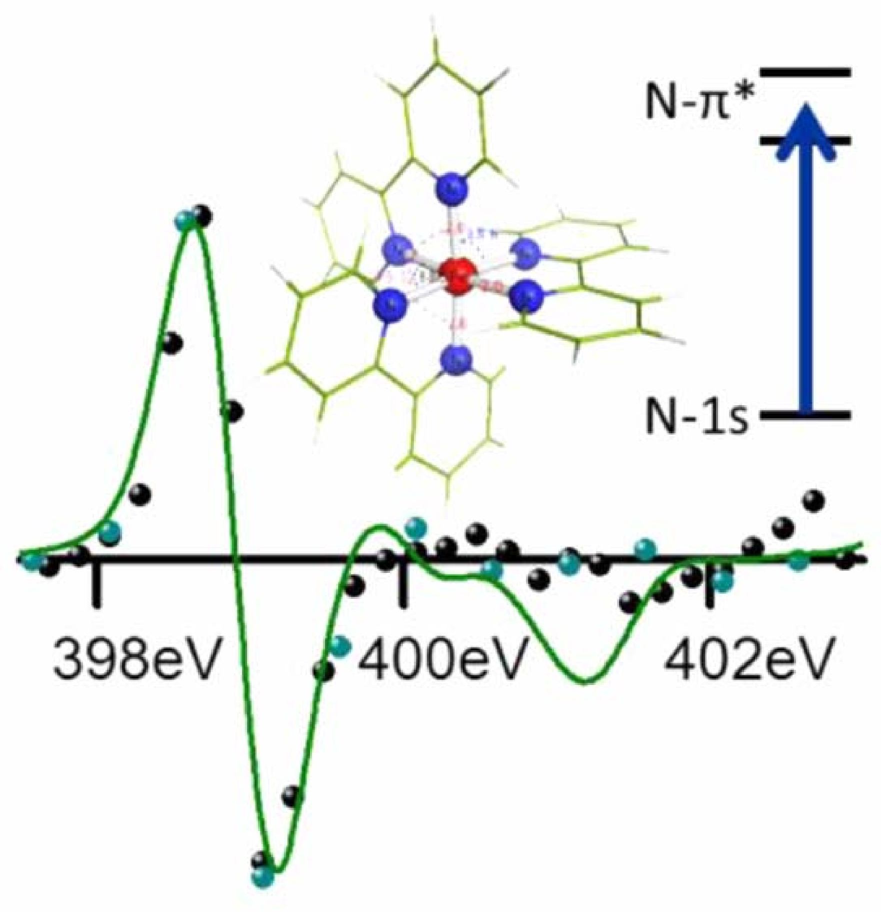
Pump the center with visible.

The lifetimes of the charge carriers affect the photocurrent dramatically. When and where are carriers lost? (inside a molecule, across a device)

Add time as variable (fs-ns). Already used in the UV/Vis (nonlinear optics, transient absorption, two-photon photoemission)

Need element-specific X-ray probes. “Heroic” experiments demonstrate proof of principle. Use free-electron lasers to make it mainstream

“Heroic” demonstration experiments (1 spectrum / day)



Small energy shift causes derivative shape.

Pump the central Fe atom with visible light.

Probe the resulting change in the N 1s → π* absorption.

Find out when hot electrons arrive at the N cage.

Then look at the surrounding C atoms, then at the electron acceptor, …

Van Kuiken,…, Huse, J. Phys. Chem. Lett. **7**, 465 (2016).
Cordones,..., Schoenlein, J. Phys. Chem. Lett. **12**, 1182 (2021).

See also:
Santomauro,…, Chergui, Structural Dynamics **4**, 044002 (2017).
Fondell,…, Föhlisch, Structural Dynamics **4**, 054902 (2017).

Transient absorption in the UV/Visible (standard tool)

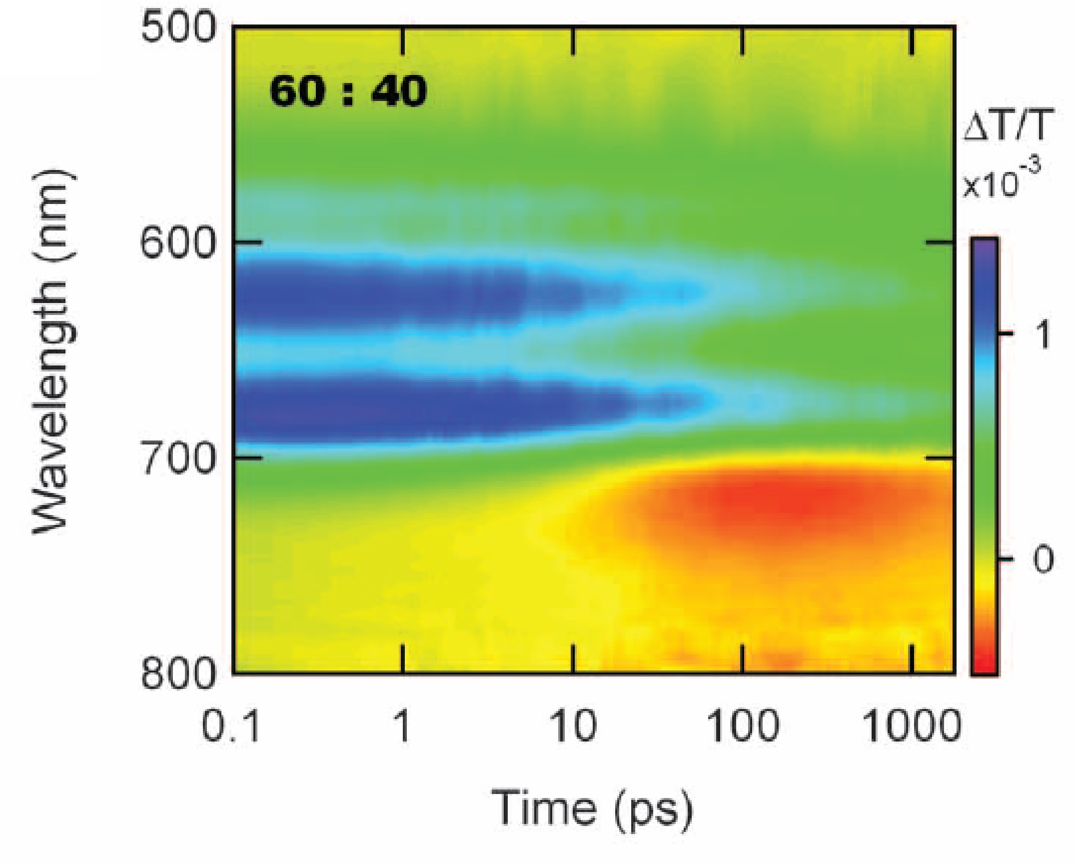
Bleaching by depopulation of the ground state

Extra transitions starting from excited states

Time constants: <ps → µs
Longer for better devices

Gelinas et al., Science
343, 512 (2015)

Change in transmission after pump



Where are the carriers lost? At impurities, interfaces?

Use element-specific core levels to identify the location

Messages

- Improve the efficiency of solar cells

  Use tandem cells, but simplify them

- Tailor the energy levels

  Use spectroscopy + computational screening

- A dream experiment:

  Follow electrons/holes across a solar cell

  Pump with visible light, probe with soft X-rays

  Low pulse energy (non-destructive) + high rep-rate (data rate)

Backup Slides
(same sequence as the talk)

What to do when the Sun does not shine?

There are many ways to store energy, but no clear winner:

- Batteries, pumping water uphill, storing molten salts, …

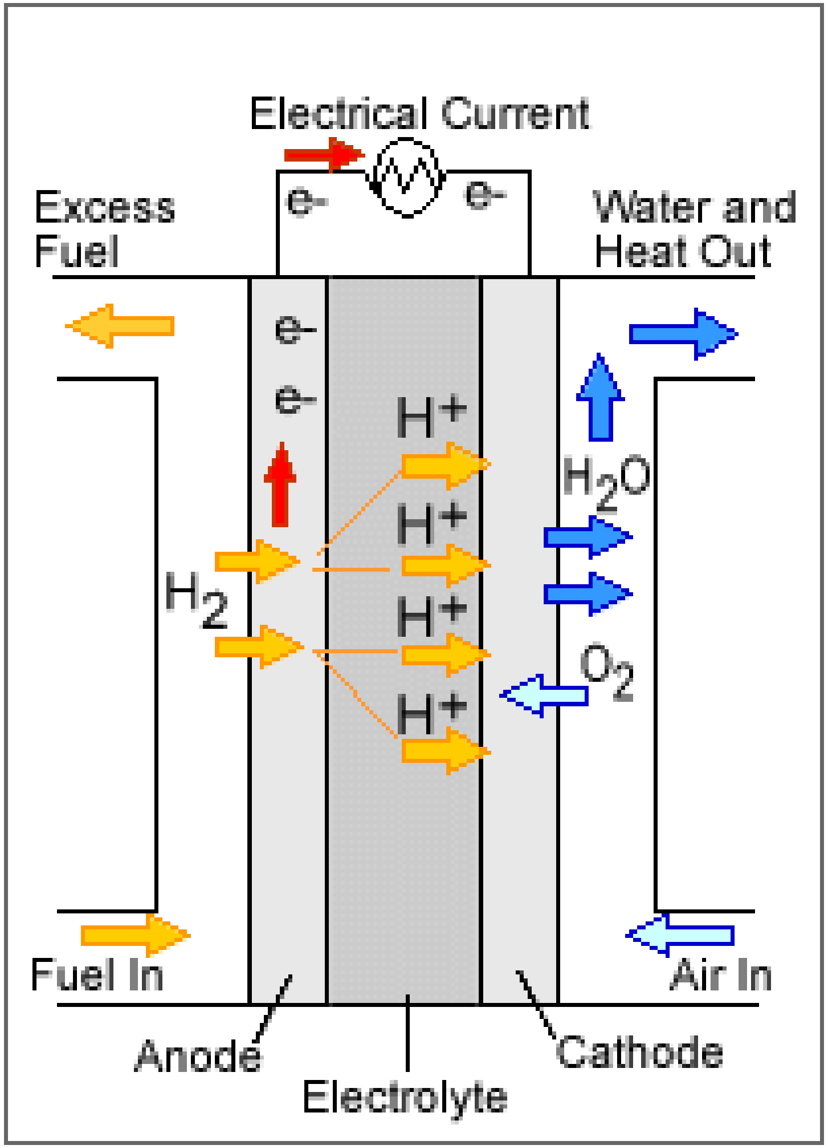
For the time being:

- Store conventional fuel, use it in a backup generator:
  - Large scale: Gas-fired power plant (Archimede project in Sicily)
  - Small scale: Fuel cell (“Bloom box” etc.)

My favorite for the long term:

- Convert solar energy to fuel during the day
- Convert fuel to electricity via fuel cells at night (or during winter)

Fuel cell



A fuel cell converts fuel directly into electricity without generating heat. That why its efficiency reaches 60% (versus 25% for a diesel generator).

The Apollo program used fuel cells for electric power. When the oxygen tank of Appollo 13 exploded, the crew sent the famous message: “Houston we’ve had a problem.“

Fuel cells are commercially available as backup generators.

Practical solutions

Solar power nicely complements conventional power plants.

- It peaks during the day when the demand is biggest:
  Air conditioning, work place, …
  Power companies have excess power at night (lower rates!)

- Transients can be made up by fast-ramping power plants:
  Natural gas, stored hydroelectric, …

- Use a central control system for managing renewable power:
  Predict power fluctuations via accurate weather predictions
  and prepare for any type of glitch (including a solar eclipse).

Location, location, location

As in the housing market, the location has a strong influence on the true cost of solar (or wind) power:

- **Amount of sunshine (or wind)**
- **Distance between power plant and user:**

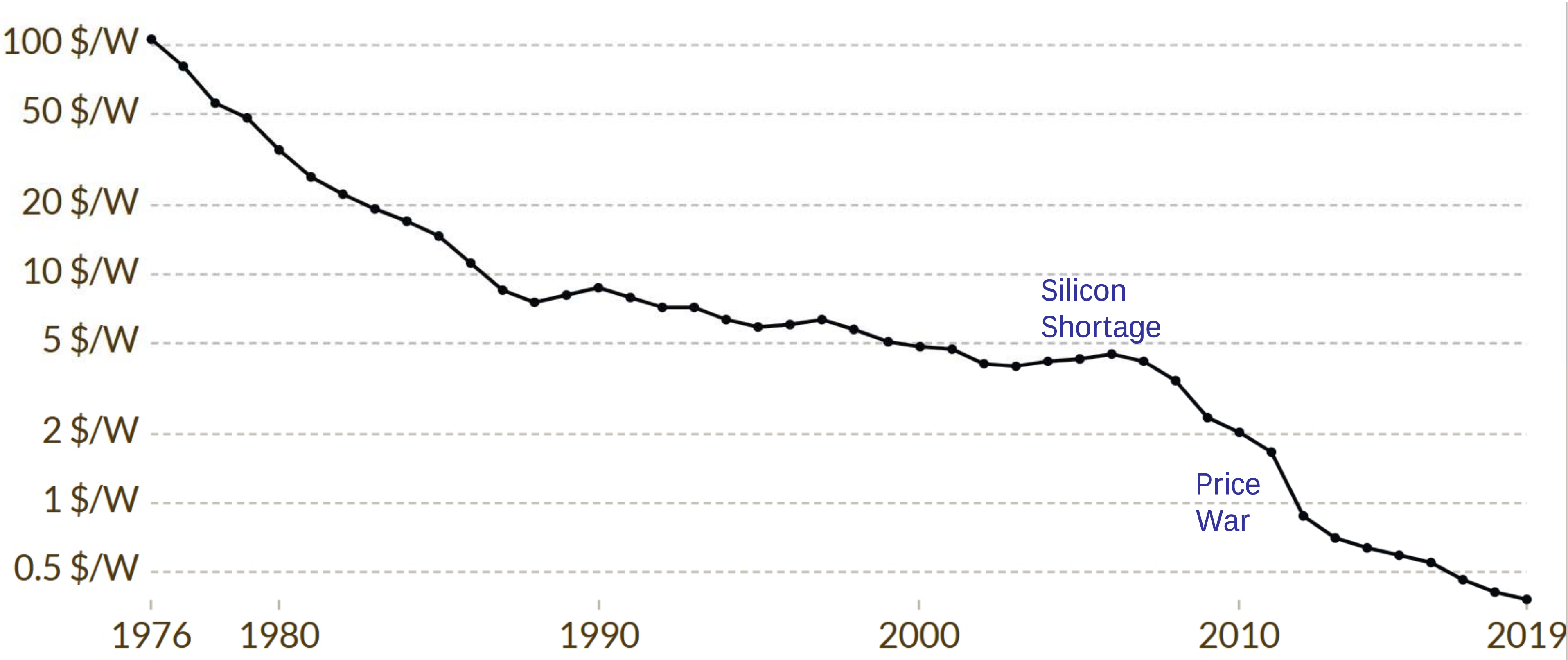
  Long-distance power transmission is costly and lossy
- **Trade-off between utility scale PV power plants, community solar, individual solar**

Examples:

Northern Germany has wind, southern Germany sunshine

Wind power in west Texas, big cities in the east

Price history of silicon solar modules

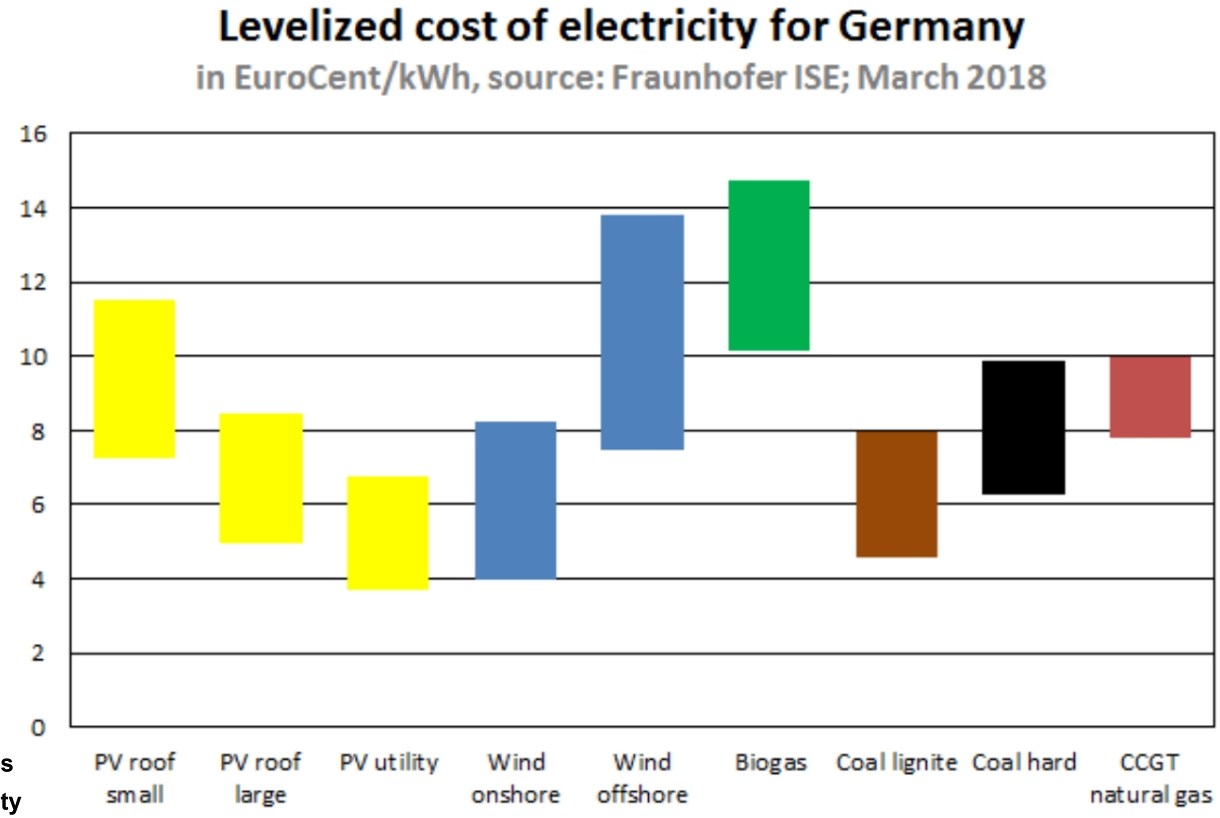


Source: LaFond et al. (2017) & IRENA Database

OurWorldInData.org/energy • CC BY

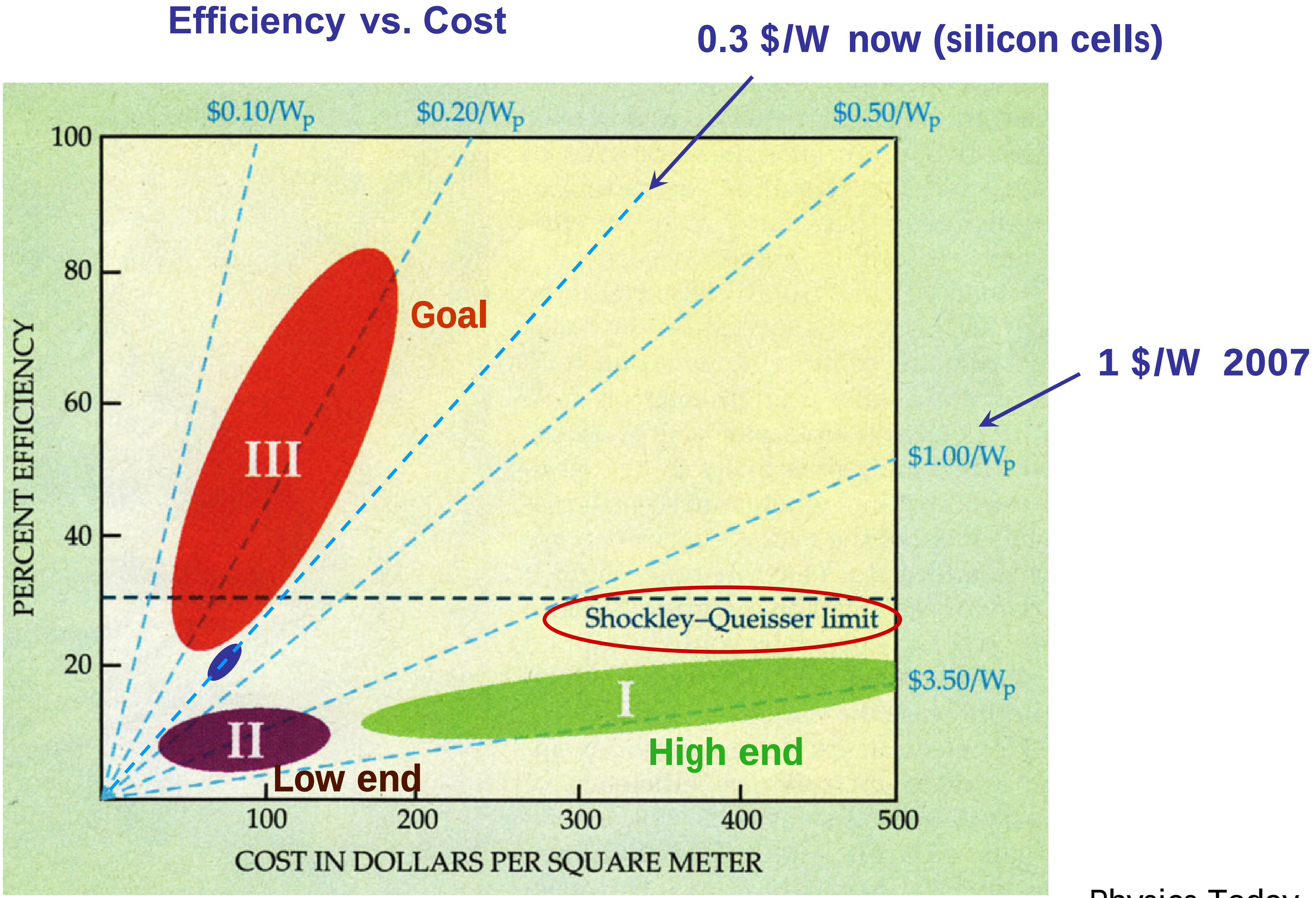
Cost comparison with fuels is tricky

- Solar energy is free, fuels are not: $/kW vs. $/kWh
- To get $/kWh, divide by the lifetime of a solar cell. Want long lifetime, short energy payback time.
- Comparisons use levelized cost, which includes the initial investment, lifetime, and fuel cost.

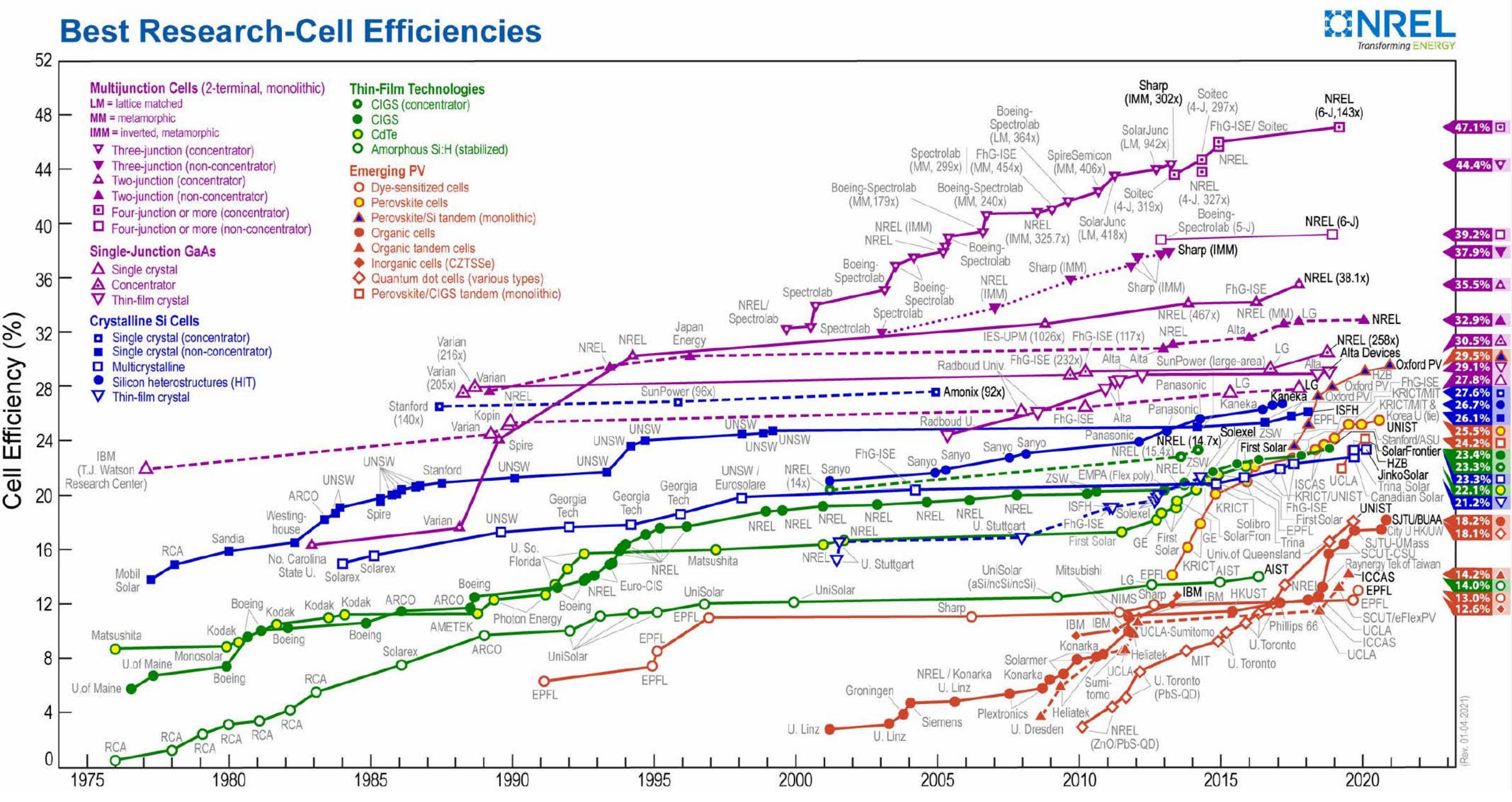


PV = Photovoltaics
= Solar to Electricity

Efficiency vs. Cost



Physics Today
March 2007

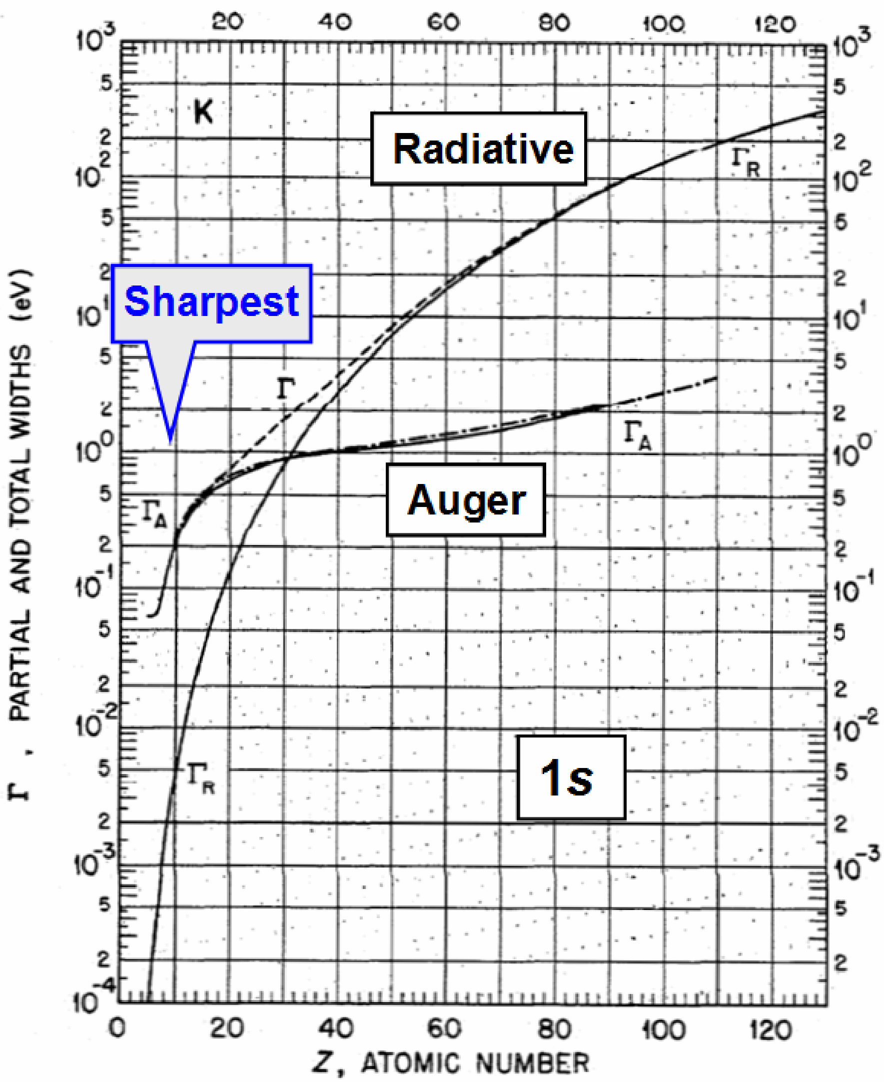


Silicon solar cells are getting close to their practical efficiency limit (≈25%).

Need to capture the full solar spectrum via multi-junctions (tandem cells). Achieved ≈45% in very complex structures. Simplify them.

Core level width from lifetime broadening

The sharpest core levels have ≈10-1500 eV binding energy.

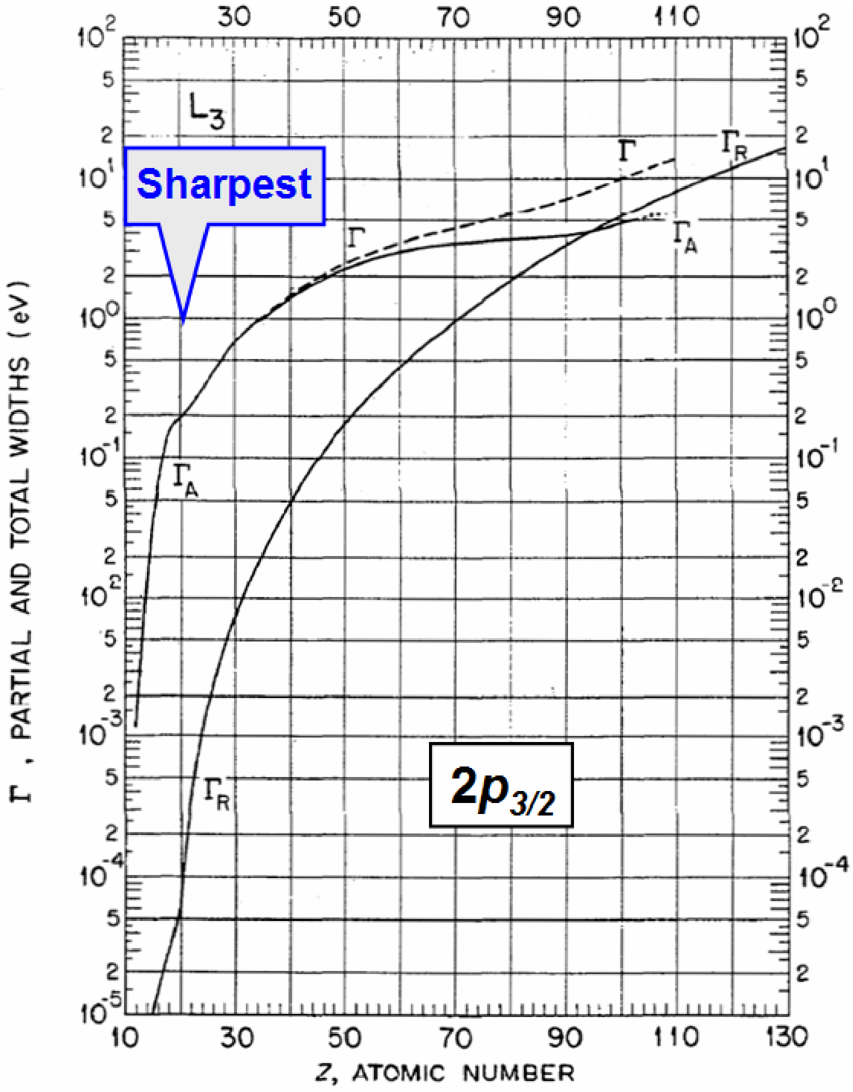

Radiative

Sharpest

Auger

1s

FIGURE 1. Theoretical partial and total atomic level widths for K shell. Γ_A = Auger width, Γ_R = radiative width, Γ = total width.


Sharpest

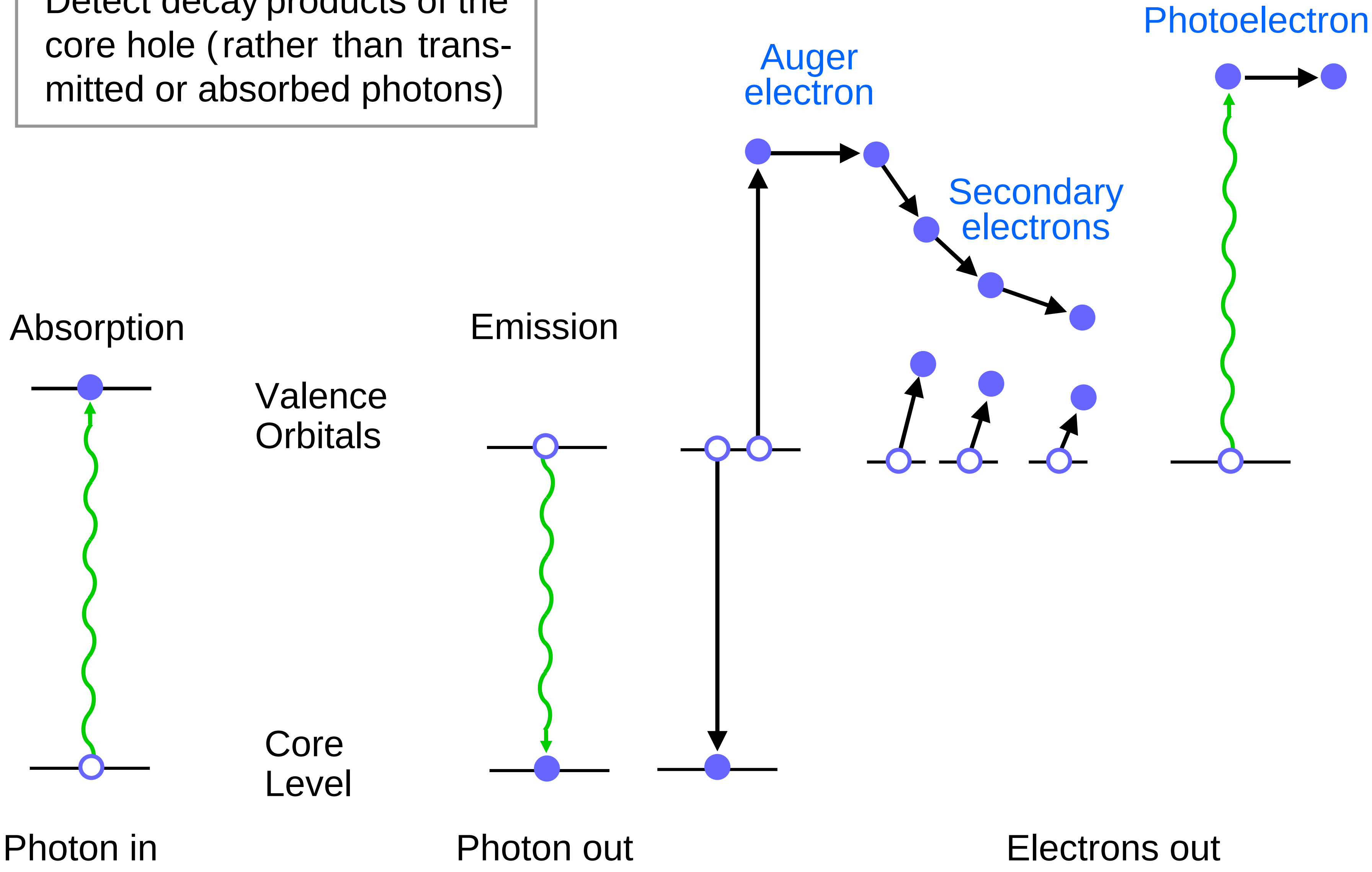
$2p_{3/2}$

FIGURE 4. Theoretical partial and total atomic level widths for L_3 subshell. Γ_A = Auger width, Γ_R = radiative width, Γ = total width.

Journal of Physical and Chemical Reference Data **8**, 329 (1979)

Decay processes after X-ray absorption

Detect decay products of the core hole (rather than transmitted or absorbed photons)



Photoelectron

Auger electron

Secondary electrons

Absorption

Emission

Valence Orbitals

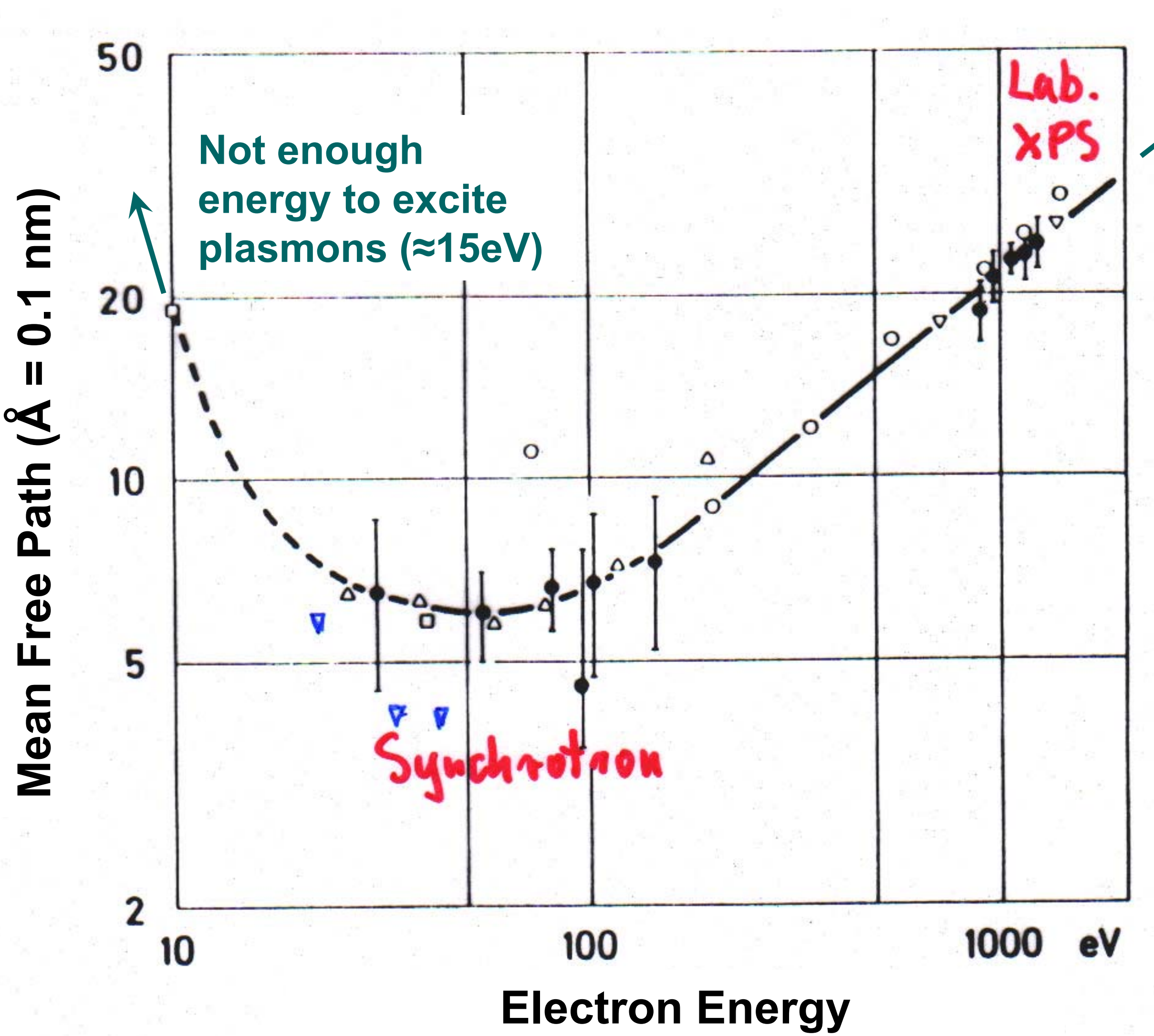
Core Level

Photon in

Photon out

Electrons out

Probing depth of electrons



Not enough energy to excite plasmons (≈15eV)

Fast electrons travel farther

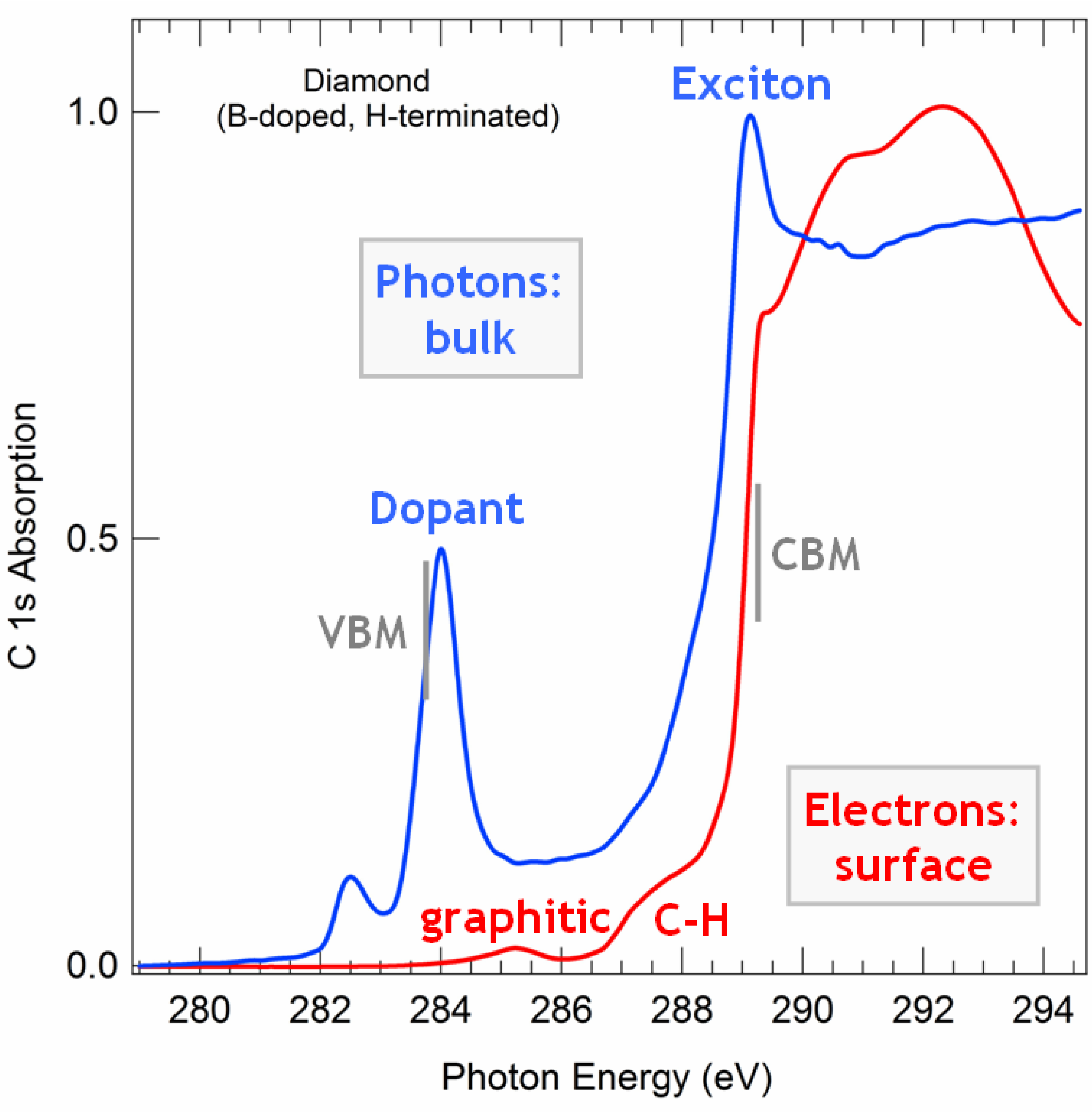
▽ Si

● ○ Ge

□ GaAs

NIST database: https://www.nist.gov/srd/nist-standard-reference-database-71

Vary the probing depth by detecting photons vs. electrons



Zegkinoglou et al.
J. Phys. Chem C
116, 13877 (2012)

Probing depths of various particles