

Core Level Spectroscopies

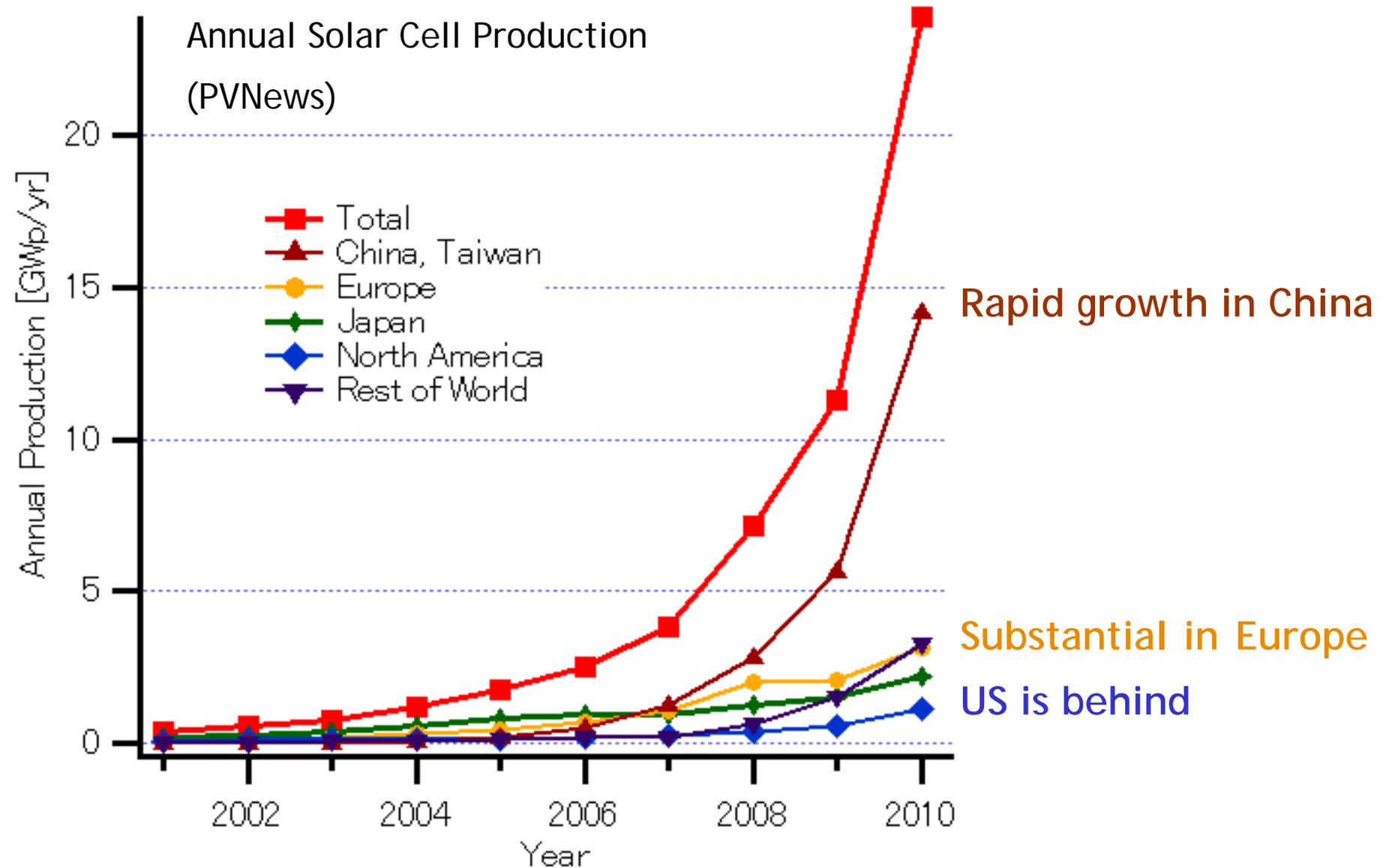
F. J. Himpsel, Univ. Wisconsin Madison

Lecture II: Case studies

1. **Photovoltaics and OLEDs**
2. **Two- and one-dimensional systems**
3. **Semiconductor surfaces and interfaces**
4. **Magnetic nanostructures**
5. **Immobilization of biomolecules at surfaces**
6. **In-situ, in-operando spectroscopy**
7. **A recent development: ultrafast**

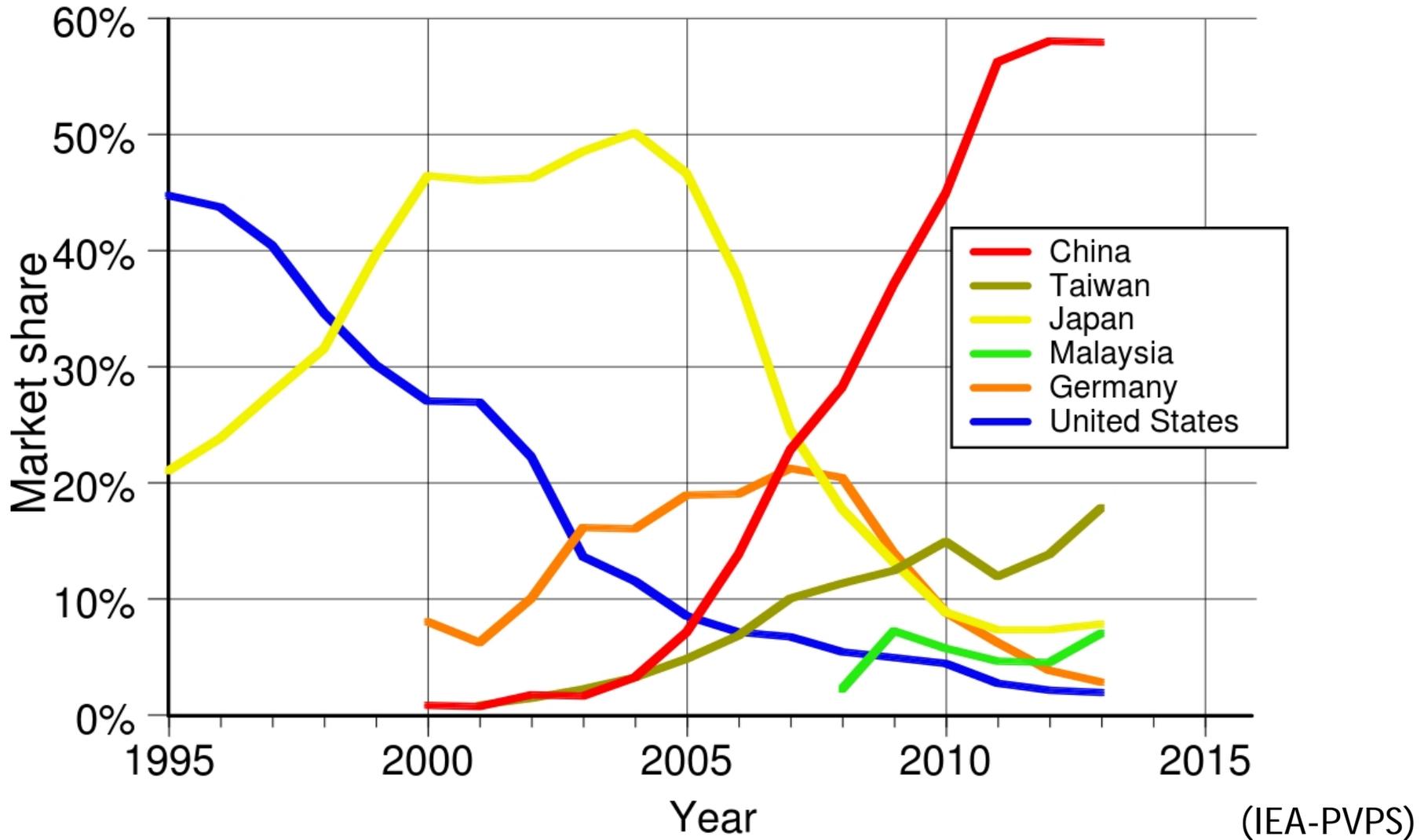
1. **Photovoltaics** and OLEDs
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Solar Cell Production Rises Exponentially, but from a Small Base

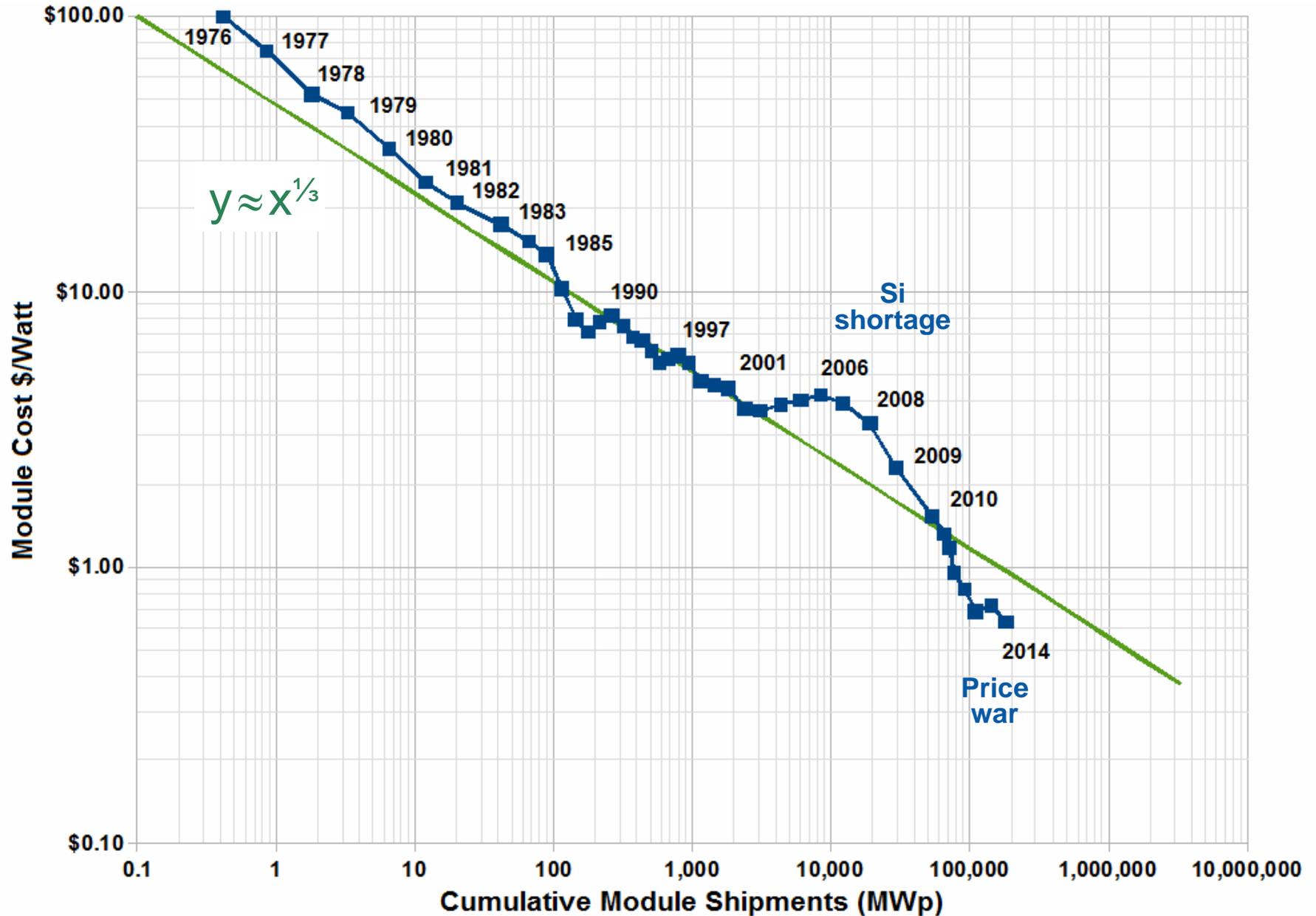


China Took the Lead

Market Share of Photovoltaic Cells



Silicon Solar Cells Dominate, Cost Decreasing like $(\text{Volume})^{-1/4}$



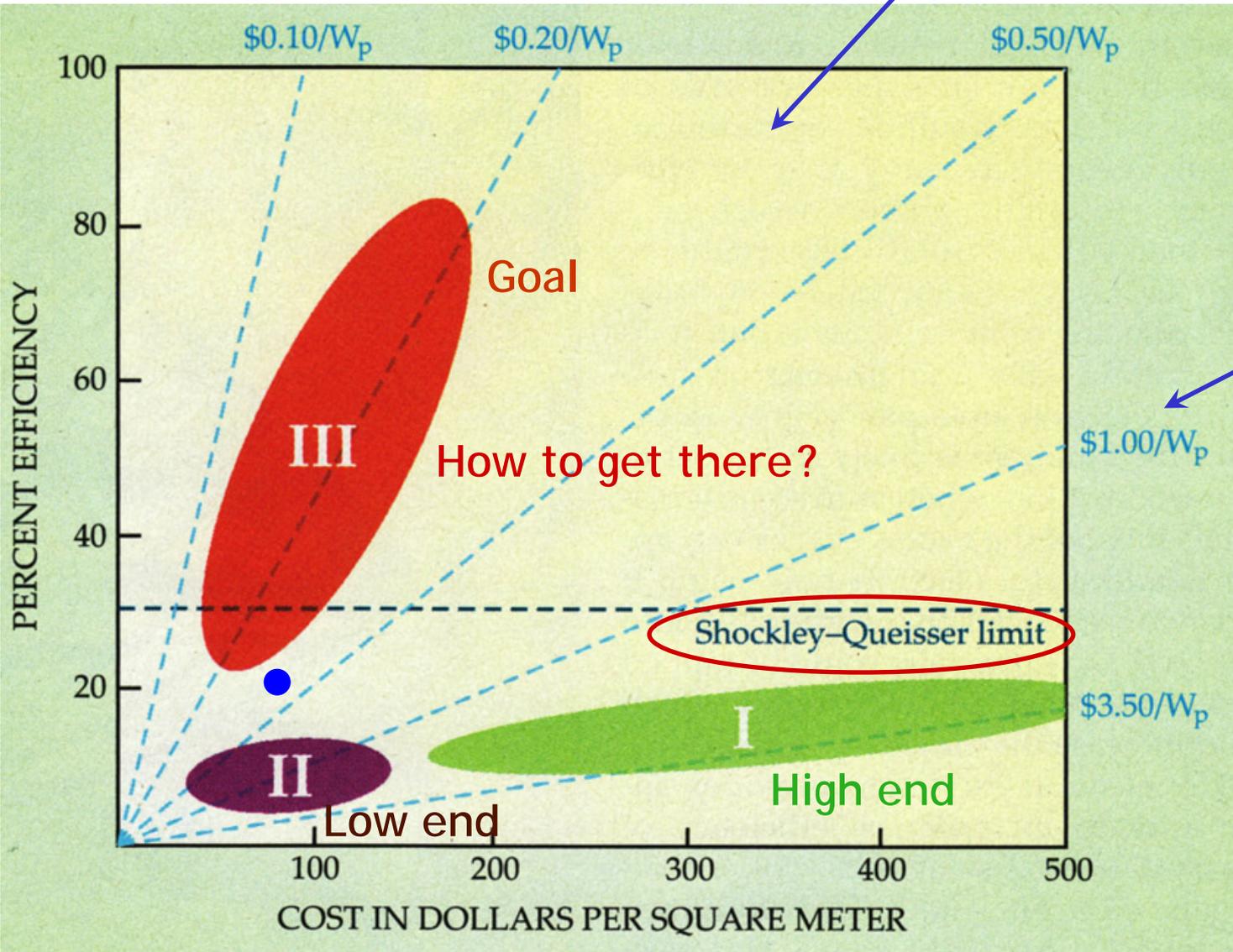
Economics of Solar Cells

**Today the price of the panels is only $\approx 1/4$ of the total cost.
The rest is for the support structure, labor, converter, ...**

- ⇒ Reduce the panel size by higher efficiency**
- ⇒ Design support for solar cells into buildings**
- ⇒ Reduce financial, legal hurdles (Solar City)**

Efficiency vs. Cost

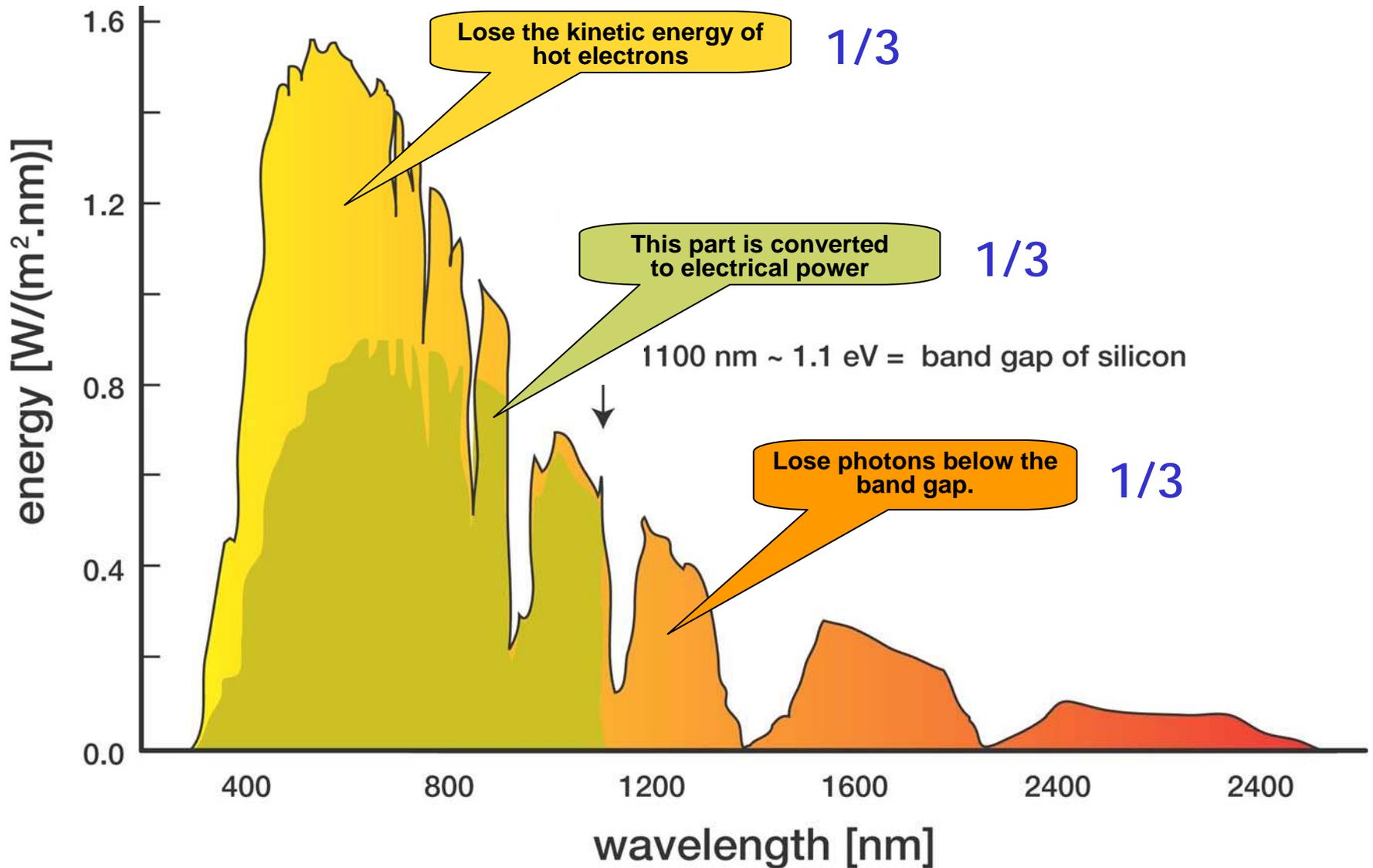
\$ 0.3/W now (for silicon cells)



1 \$/W then

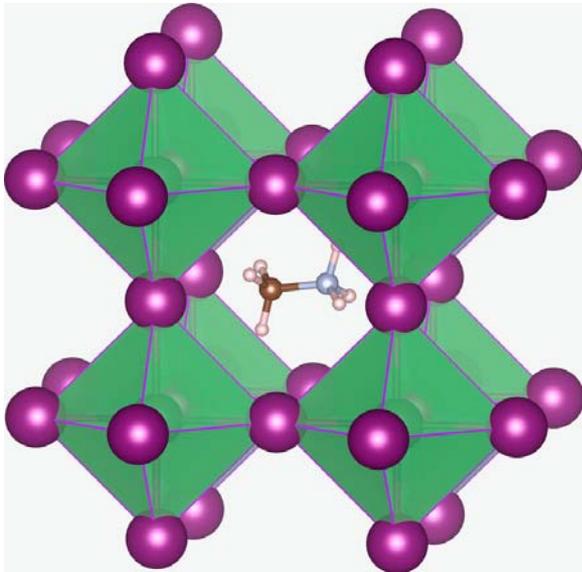
33% Limit for a Single pn Junction (Shockley-Queisser)

⇒ Need Multiple Junctions in Series (Tandem Cells)



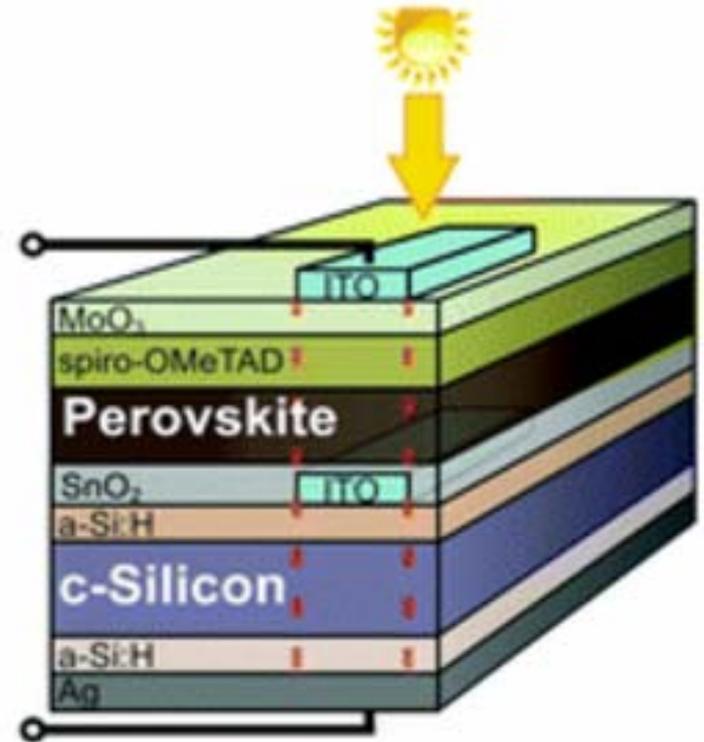
Perovskite-on-Silicon Tandem Cell

Perovskite



Halogen (Pb inside)

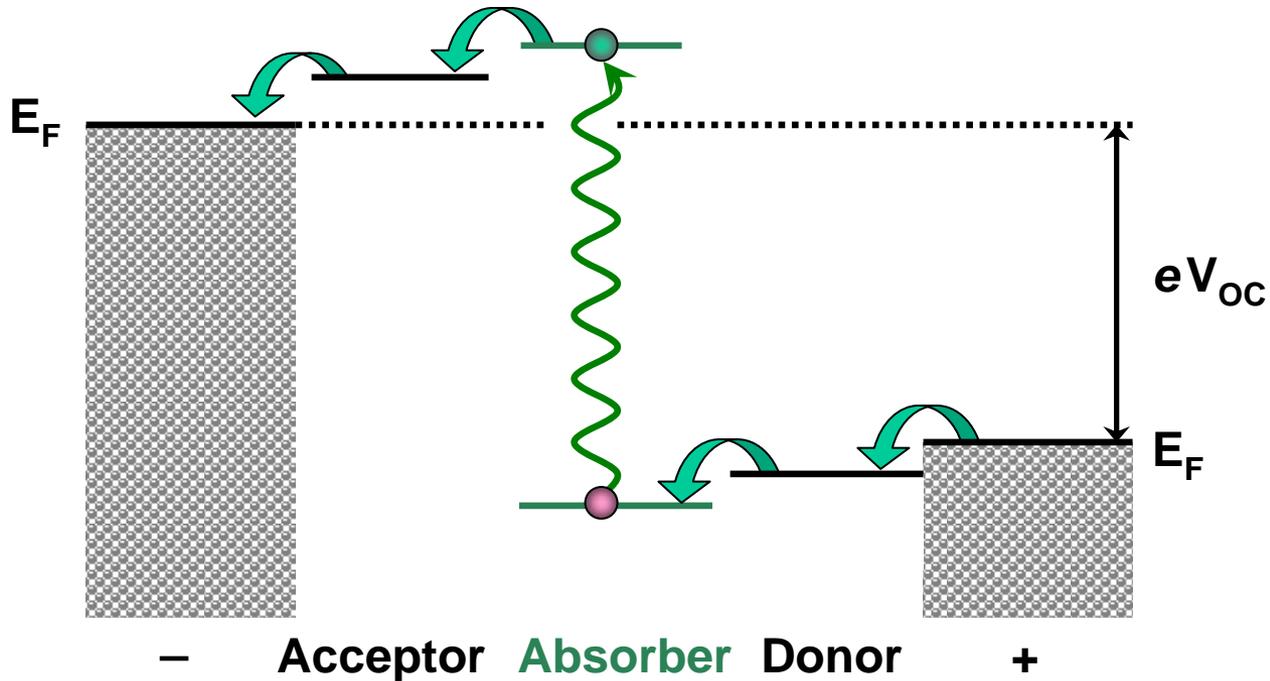
Methylammonium
molecule (center)



Energy Environ. Sci. **9**, 81 (2016)

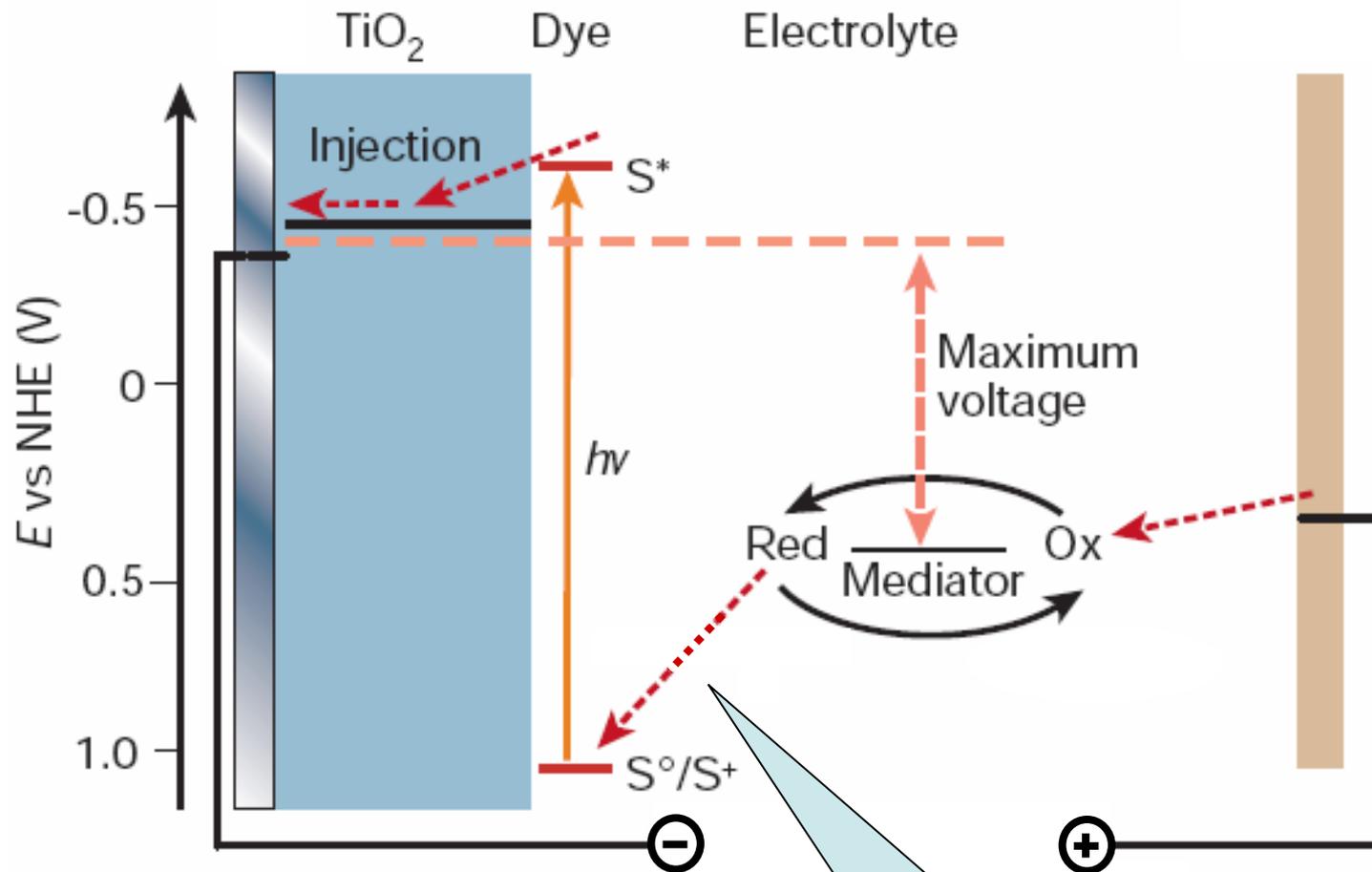
The Physicists View: Focus on the Essentials

4 Levels, 3 Materials



Small energy drop: Large voltage
Large energy drop: Large current } **Maximize power = $V \cdot I$**

Dye-Sensitized Solar Cells Combine 3 Materials

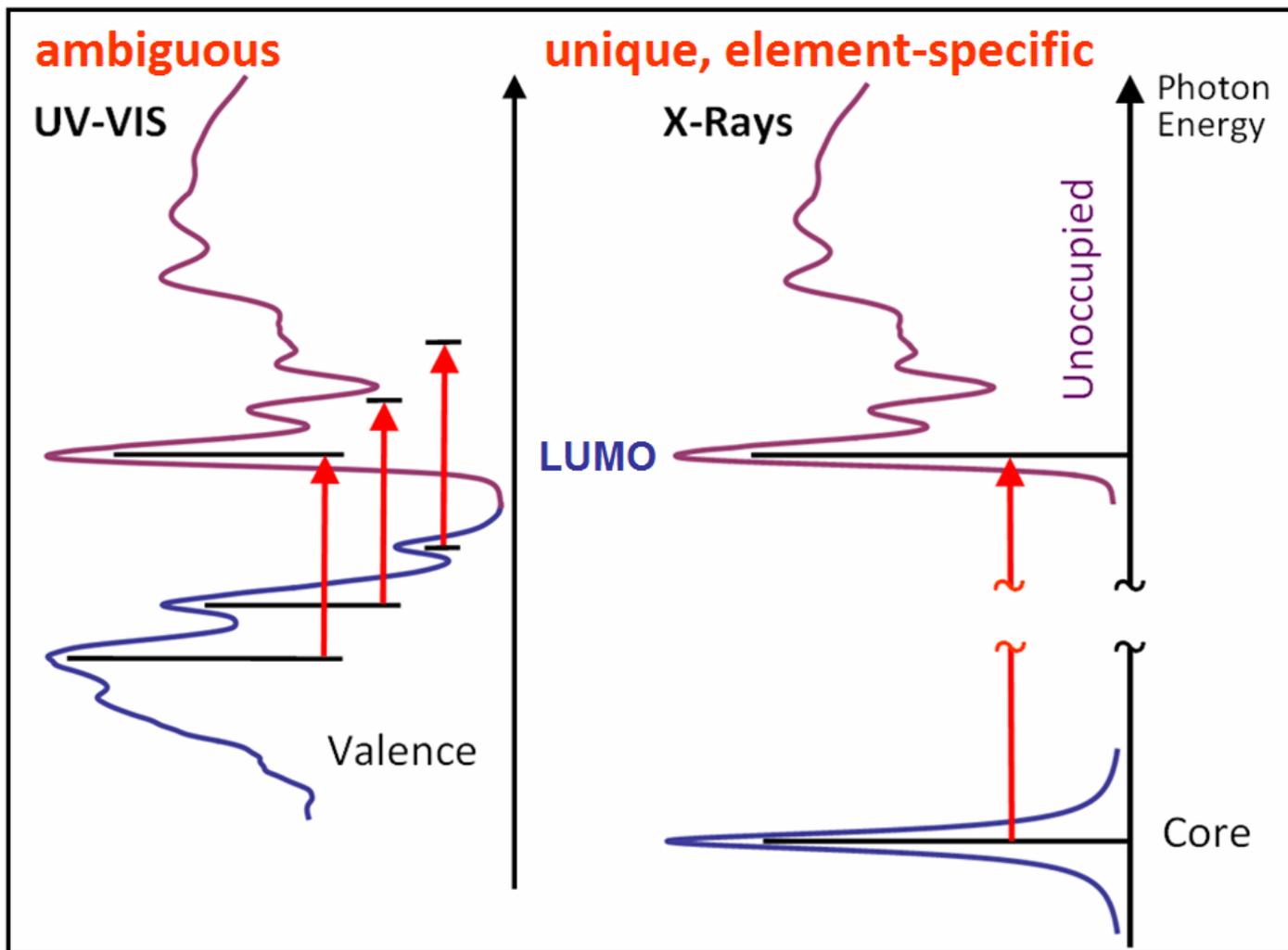


Nature **414**, 338 (2001)

J. Phys. Chem. C **112** (2008)

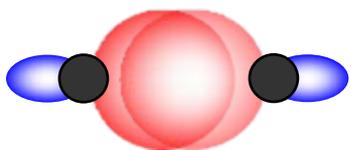
Lose half the voltage

Energy Levels from Absorption Spectroscopy

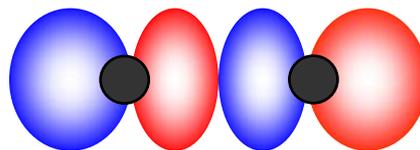


σ and π Orbitals in Organic Molecules

σ -bond:

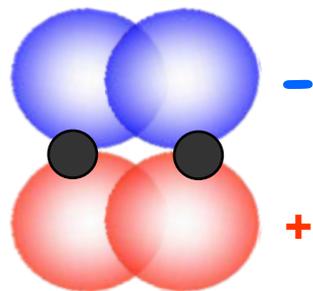


σ orbital

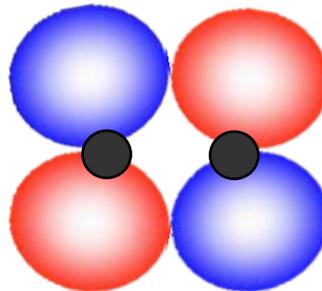


σ^* orbital

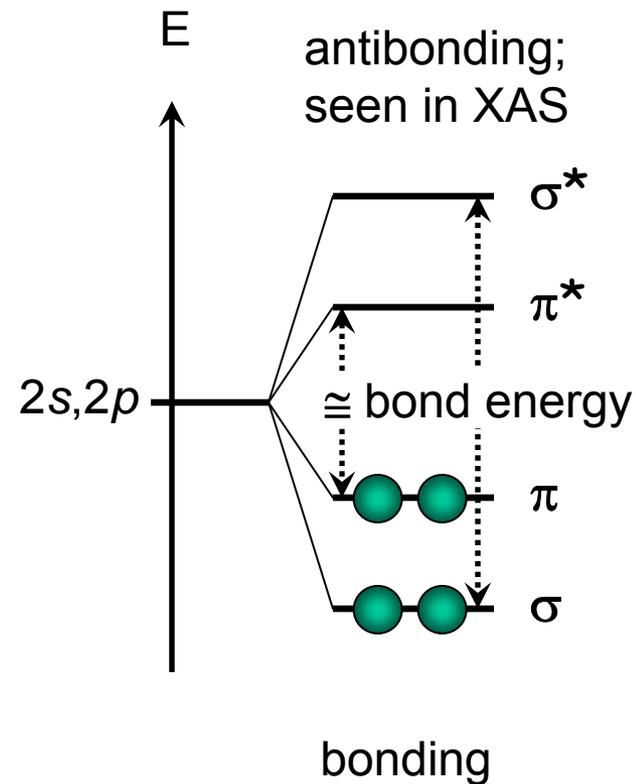
π -bond:



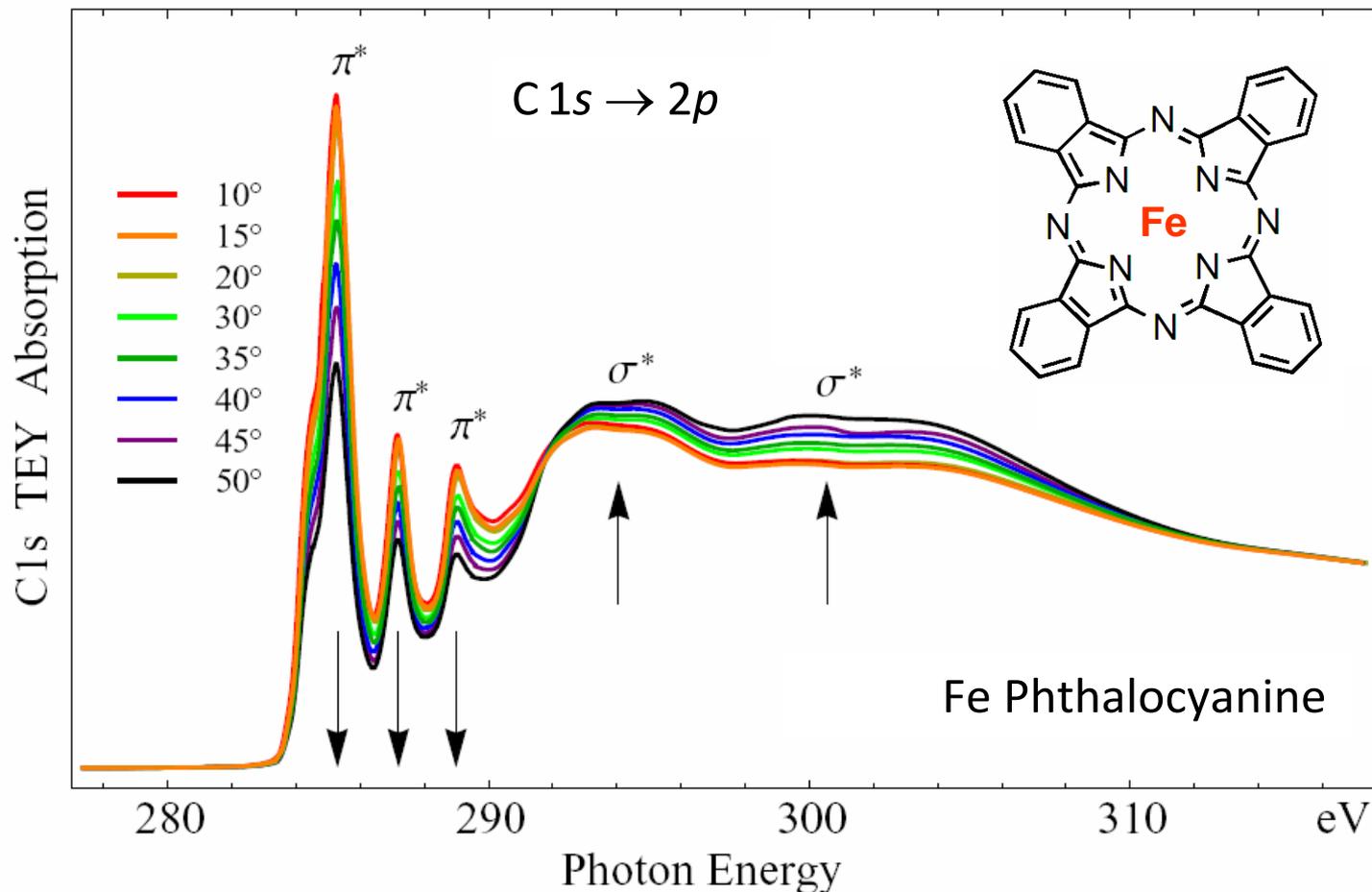
π -orbital



π^* -orbital



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



Assigning Orbitals to Atoms (Experiment)

Inverse photoemission (IPES):
Total density of states

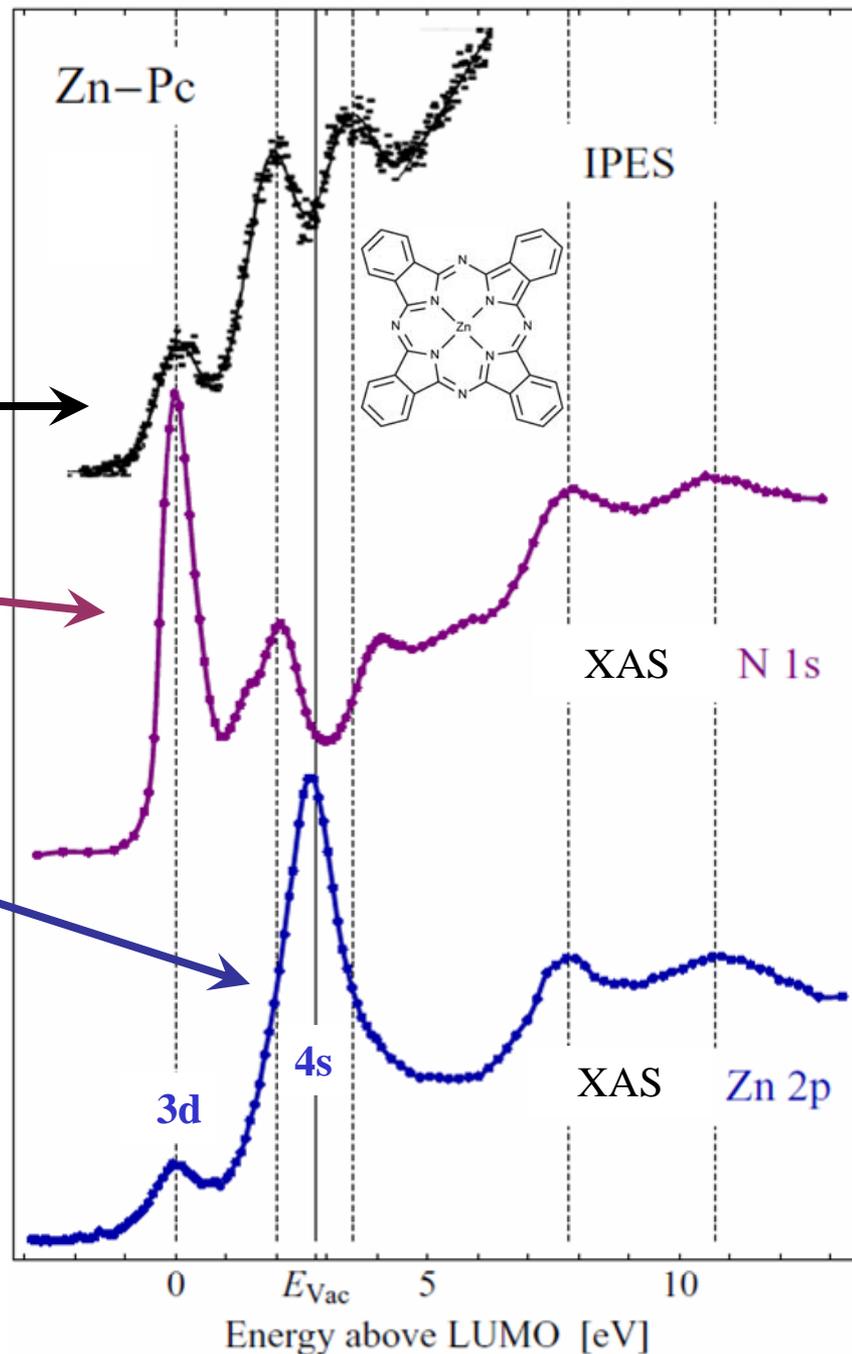
XAS, N 1s edge:
Density of N 2p states

XAS, Zn 2p edge:
Density of Zn 3d,4s states

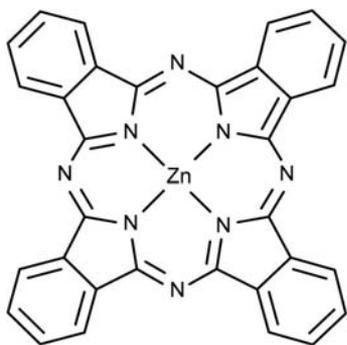
The C1s edge contains many peaks, because there are many inequivalent C atoms (compare the previous slide).

XAS: J. Chem. Phys. **134**, 204707 (2011)

IPES: Org. Electron. **3**, 53 (2002)

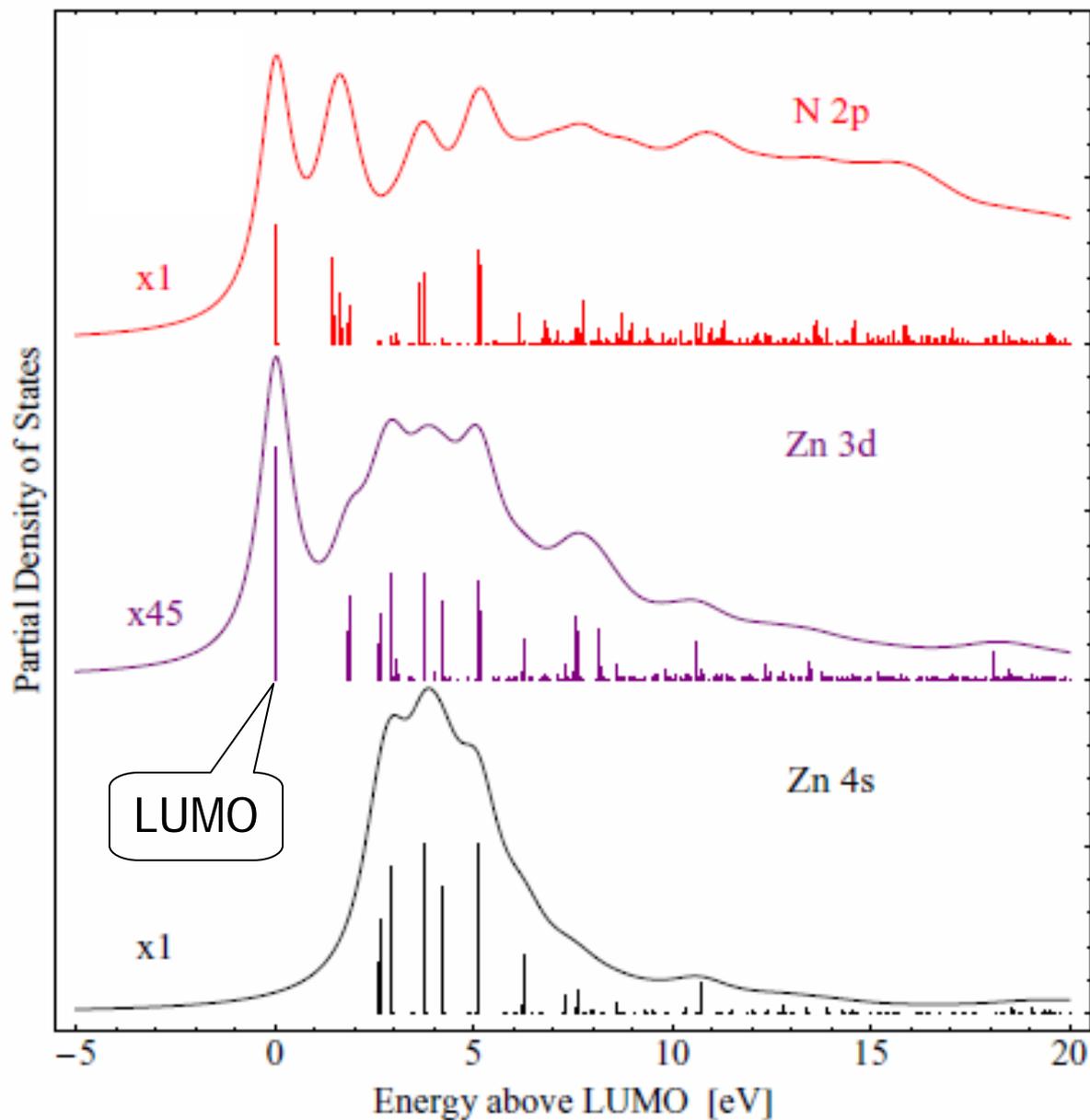


Assigning Orbitals to Atoms (Theory)

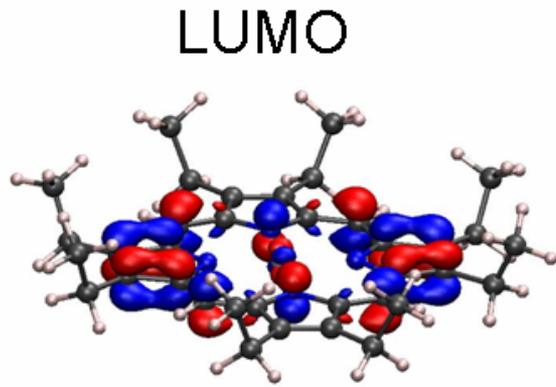


Levels get very dense at higher energies.

The two features in the Zn2p spectrum correspond to transitions into Zn3d and Zn4s orbitals.



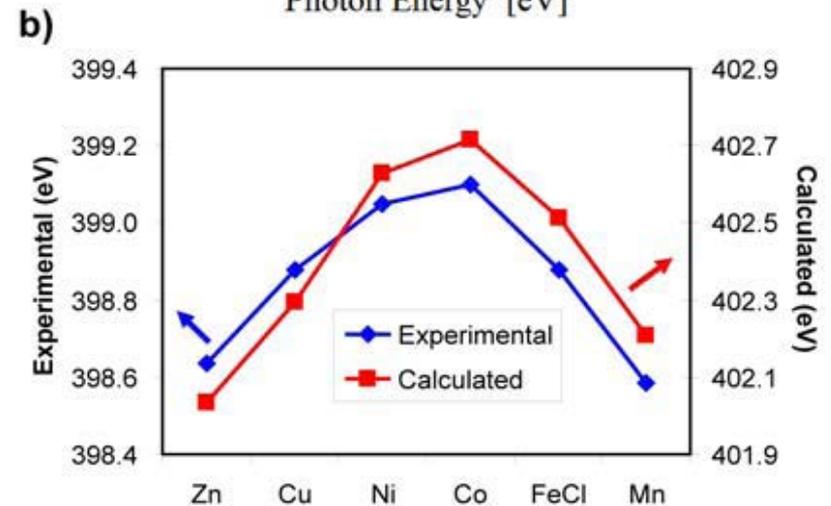
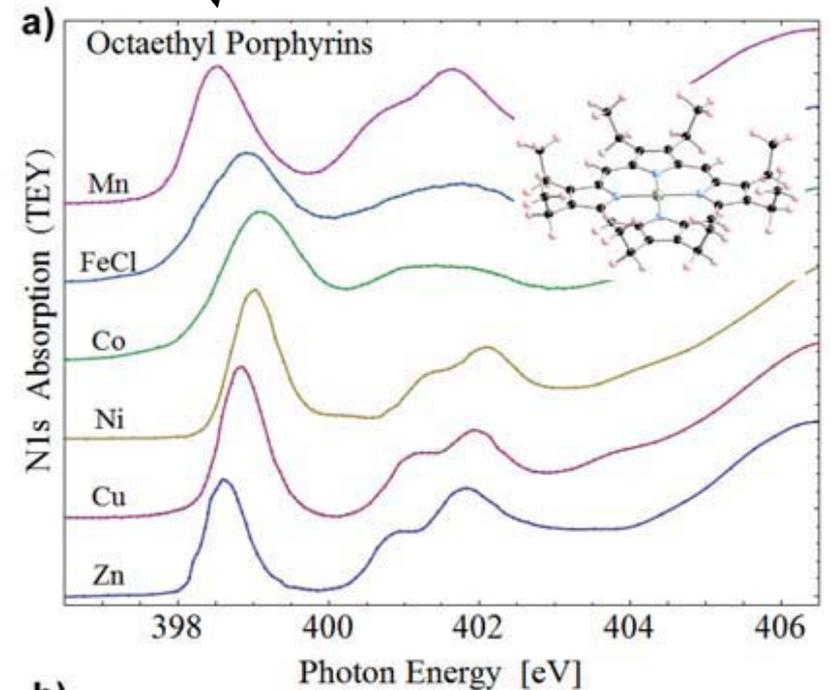
Tailor the Molecules by Varying the Central Metal Atom



(mostly at the N atoms)

Explain the origin of the shift at the N1s edge from theory.

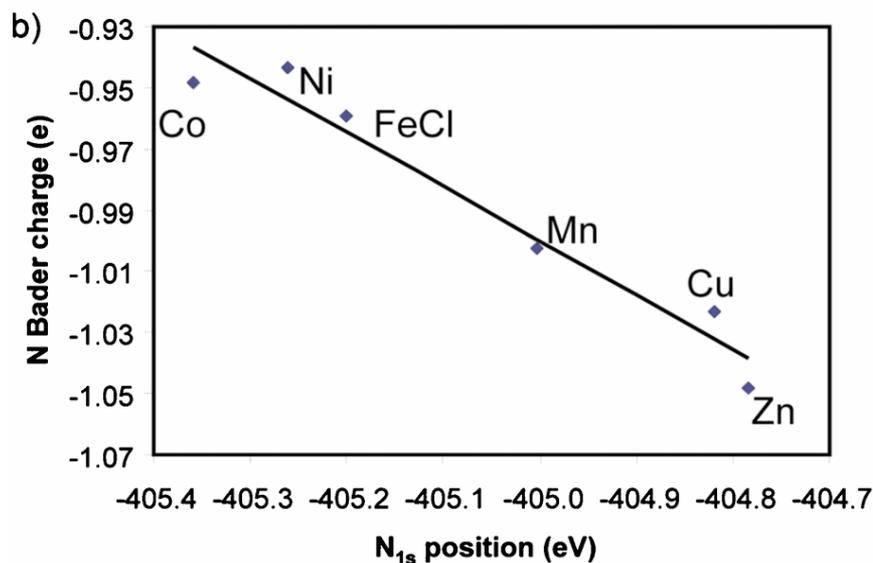
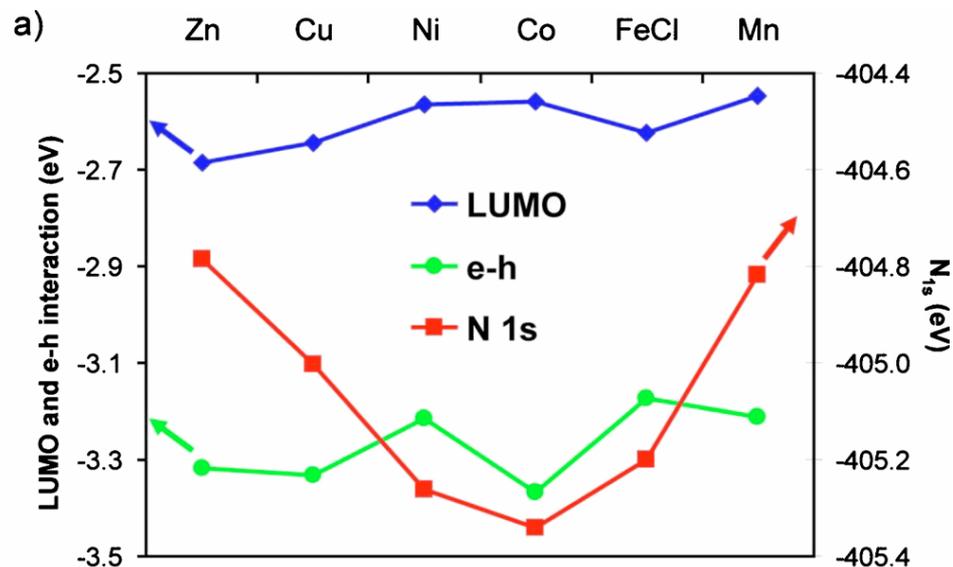
J. Chem Phys. **133**, 151103 (2010)



Three Contributions to the N1s Transition Energy in XAS

- 1) Initial state (core level)
- 2) Final state (LUMO)
- 3) Electron-hole interaction

The shift of the $N1s \rightarrow LUMO$ transition is dominated by the chemical shift of the $N1s$ level. It is proportional to the charge transfer from the metal to the nitrogen cage.

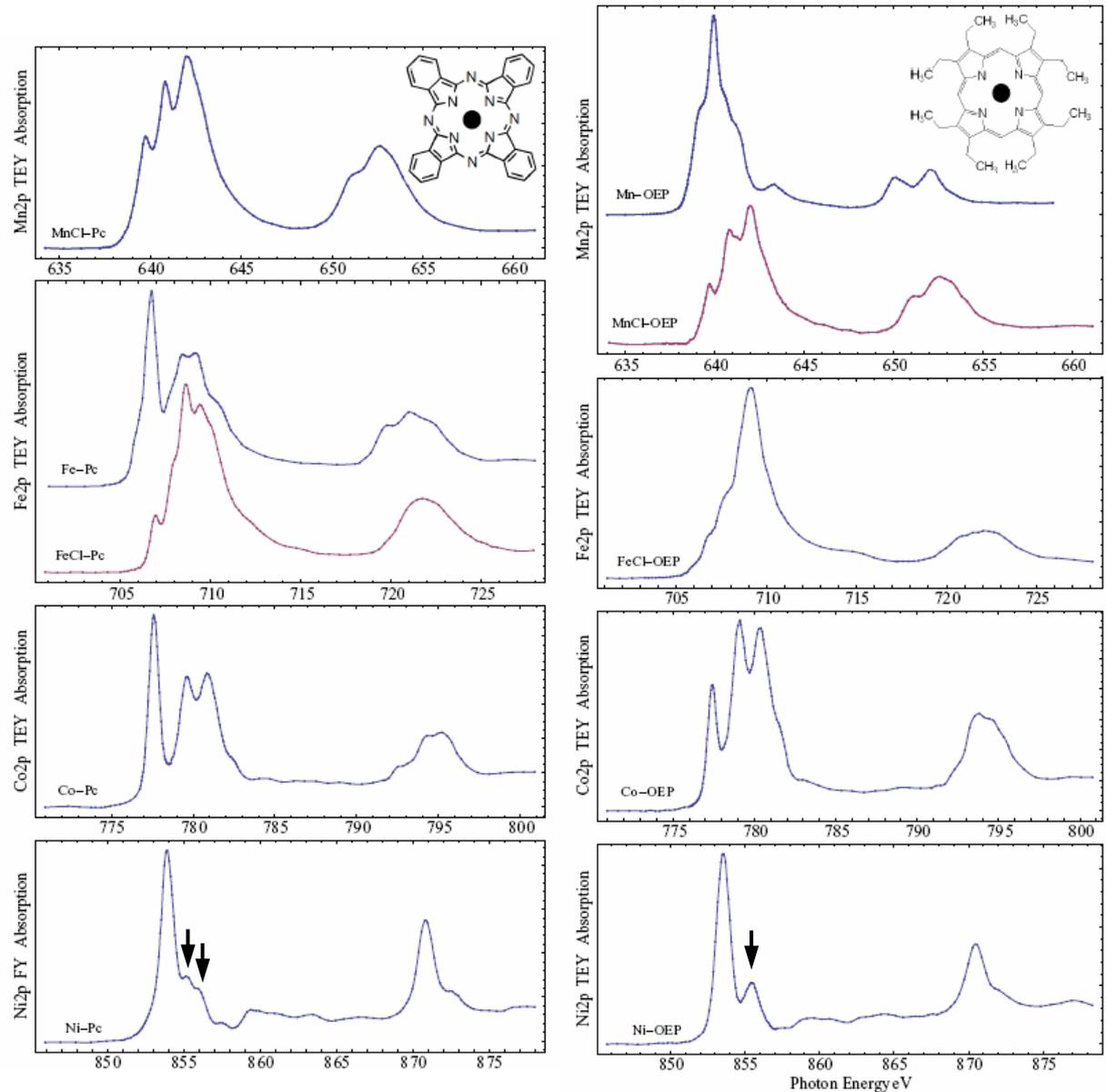


The 2p Edge of the Central Metal Atom

Obtain oxidation state and ligand field from the multiplet structure.

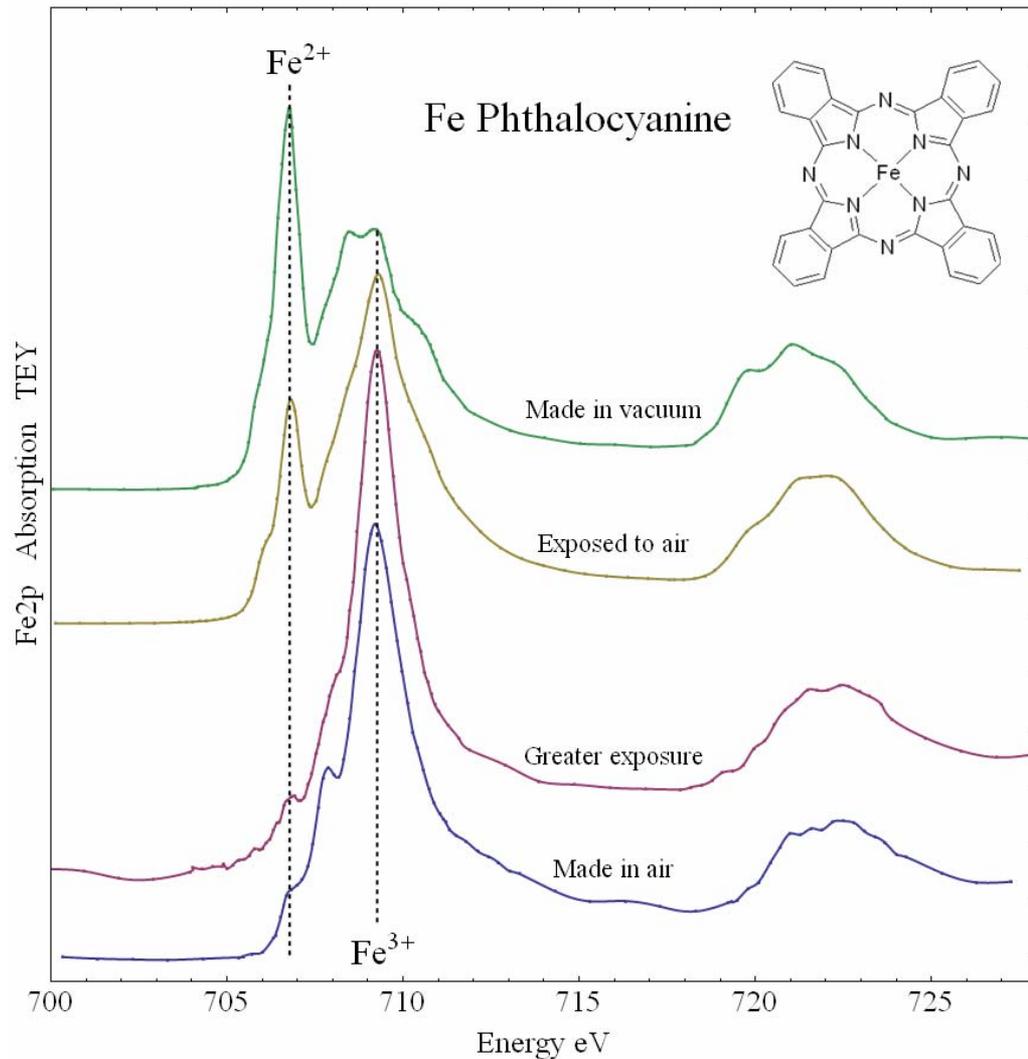
Systematics for the 3d transition metal series:
Only 2+ for Co, Ni, but
2+ and 3+ for Fe, Mn.

Easy switching of the oxidation state is important in metalloproteins (heme, PS2), as well as in catalysis.



J. Chem. Phys. **131**,
194701 (2009).

Fe-Phthalocyanine Oxidizes in Air from 2+ to 3+

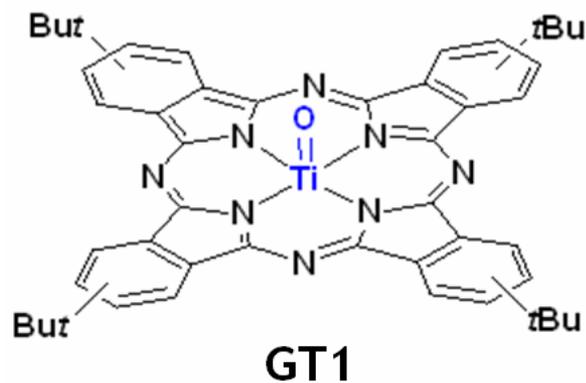
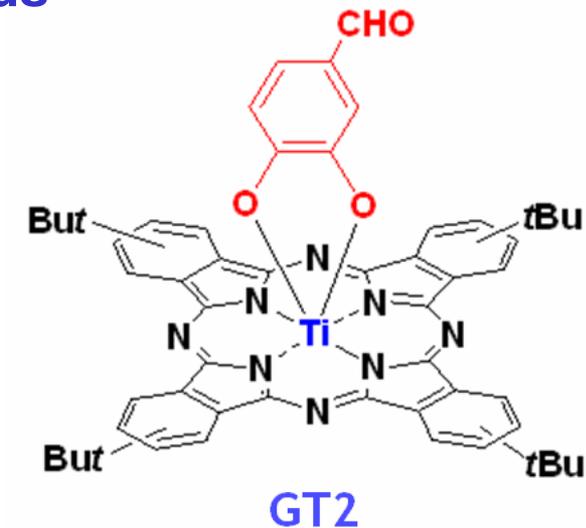
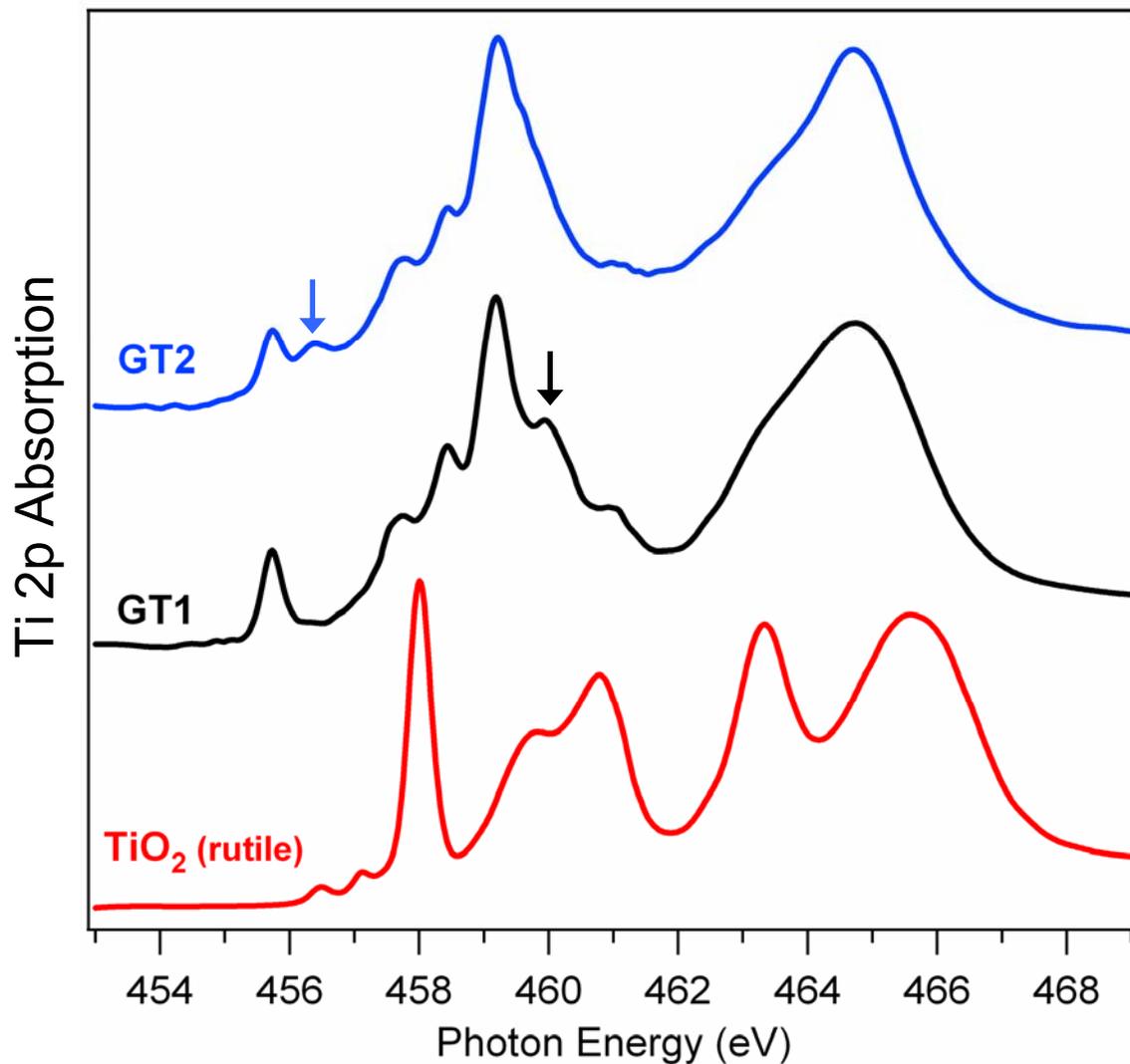


J. Chem. Phys. **131**,
194701 (2009).

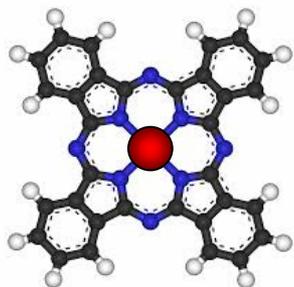
**Need a three-dimensional cage to stabilize Fe²⁺.
Find axial ligands (analogous to the heme).**

Adding Axial Ligands to Ti Phthalocyanine

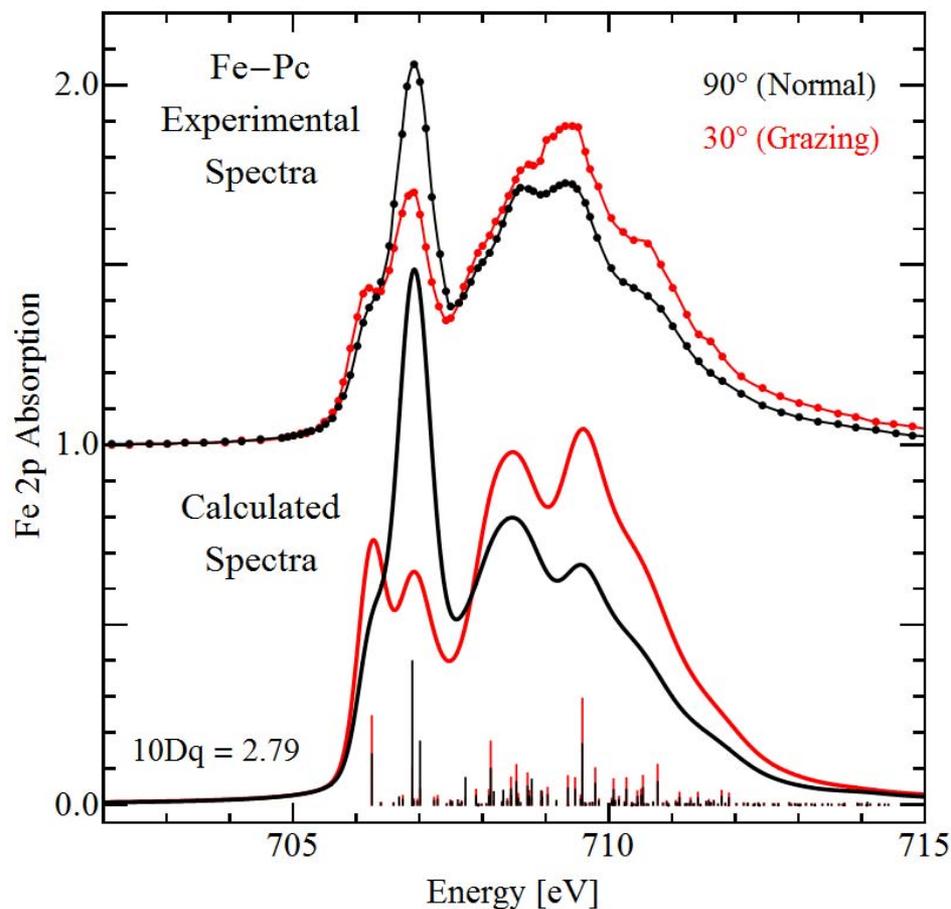
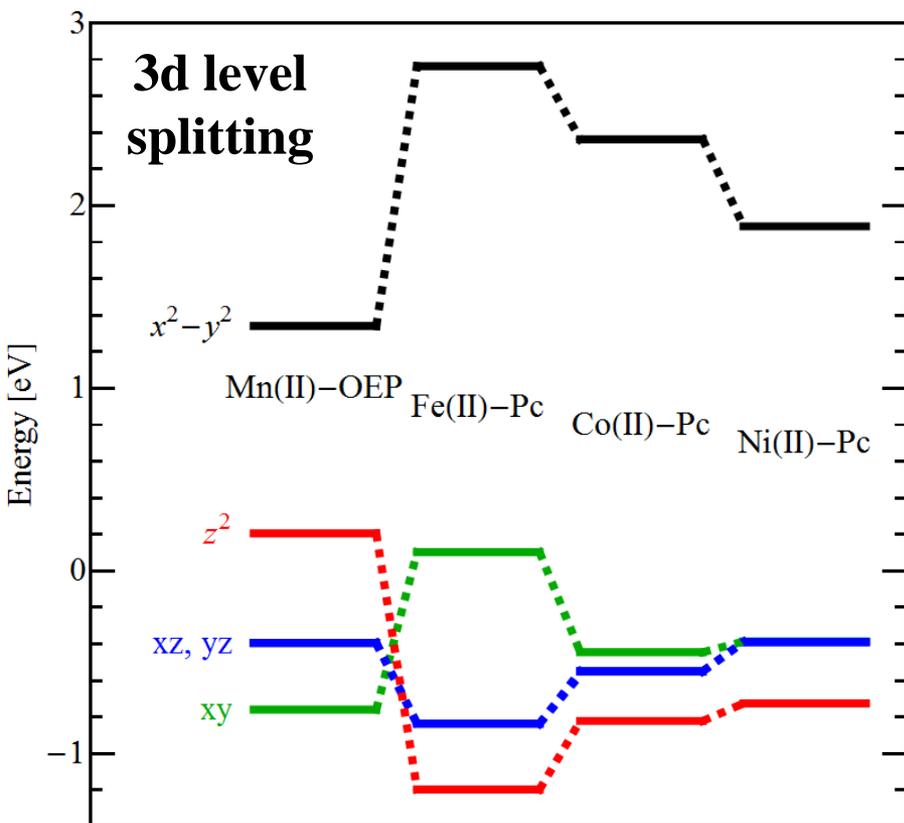
All in the Ti^{4+} oxidation state, only different ligands



Systematics of the Ligand Field Splitting

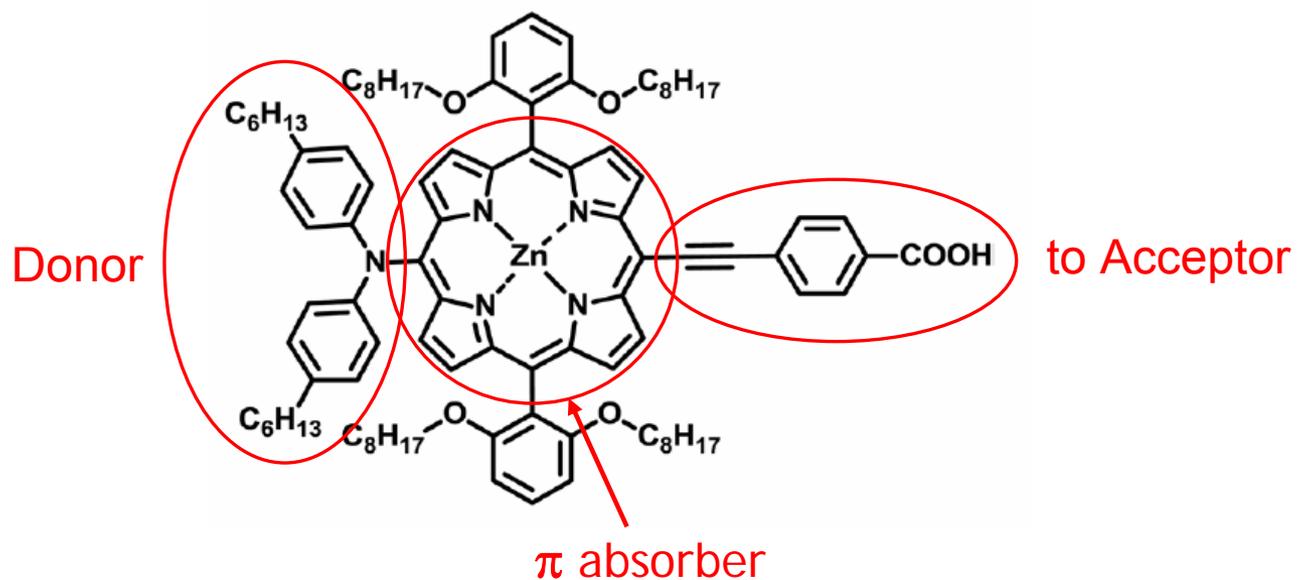


Does the
ligand field
help separating
charges?



J. Chem. Phys. **140**, 114706 (2014).

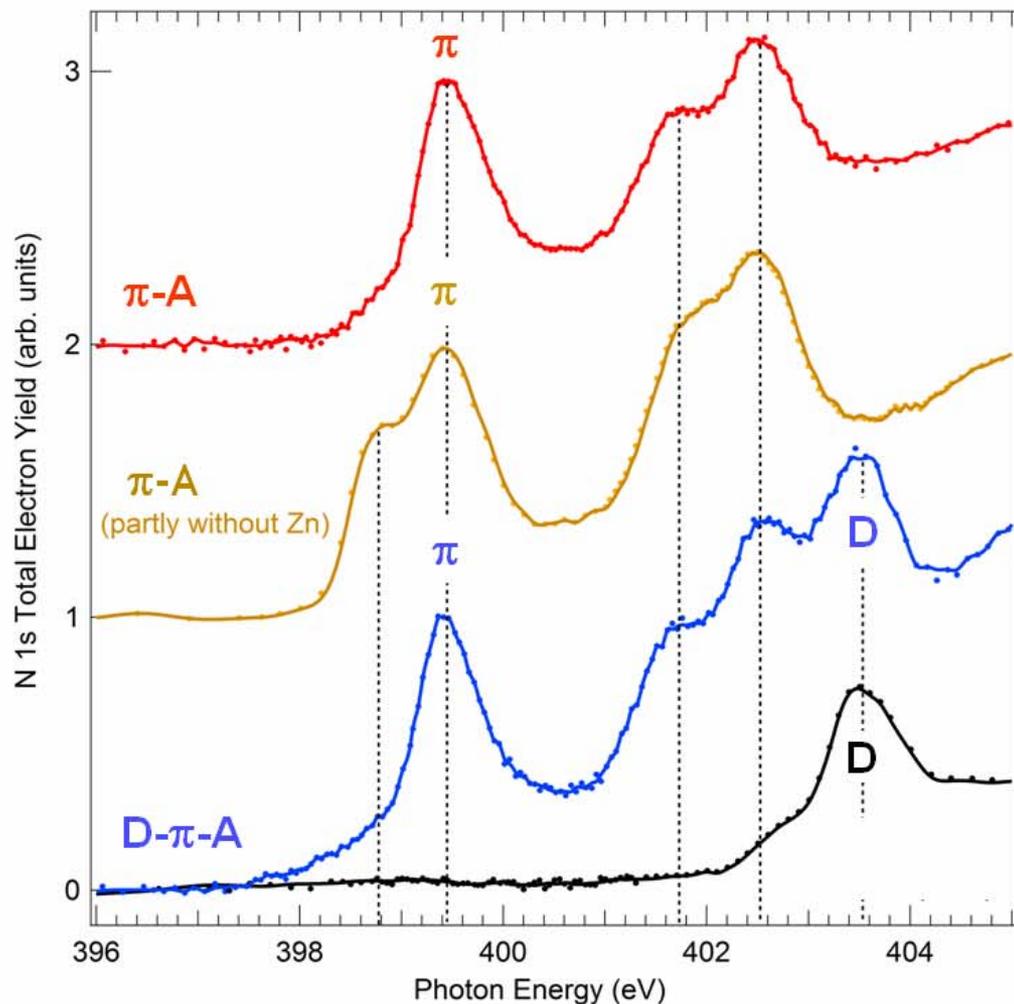
Combine the 3 Components of a Solar Cell in One Molecule with Atomic Perfection



Set a record for the efficiency of dye-sensitized solar cells (12.3%).

Science **334**, 629 (2011)

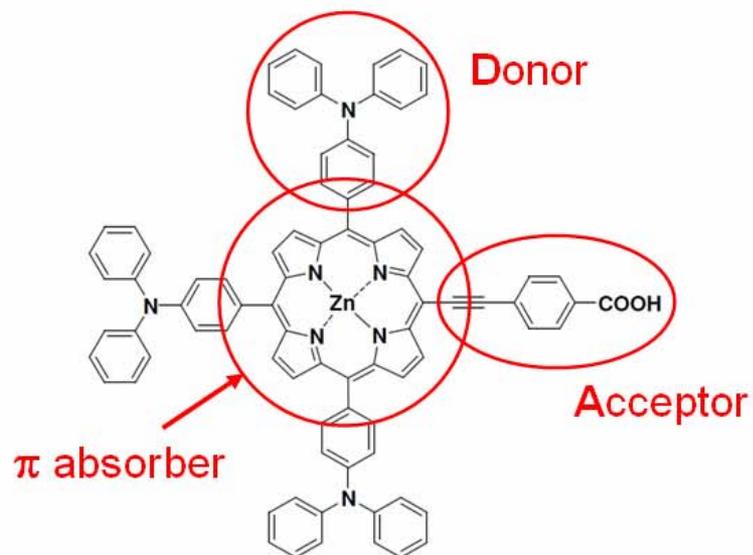
D- π -A Complexes



This led to improved synthesis.

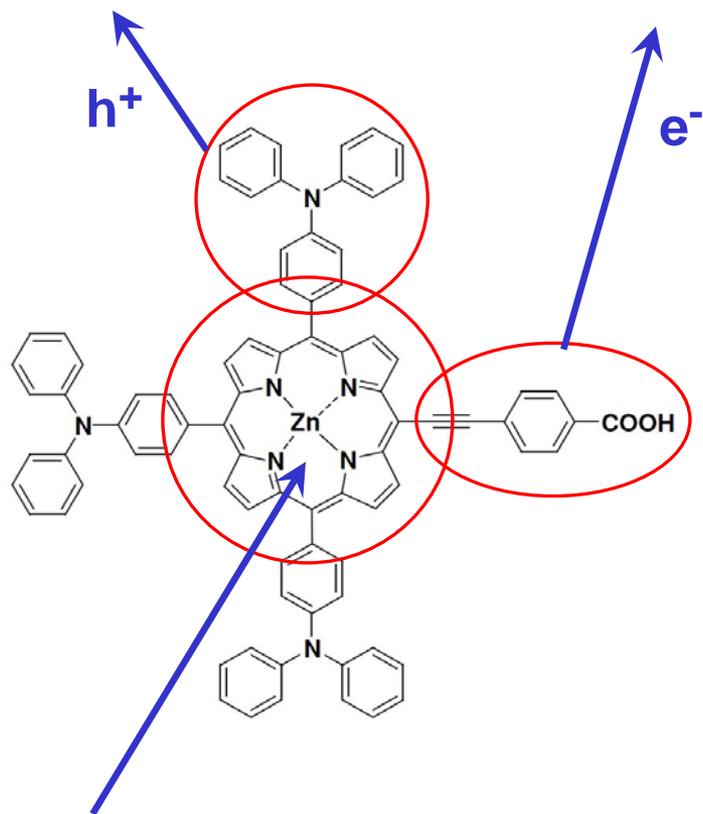


Weak point in the synthesis identified by theory (missing Zn atom).



Beyond Energy Levels: when and where are Carriers Lost ?

Probe the presence of carriers along their way out, looking at specific atoms with X-rays.



Pump the center with visible.

“Heroic” experiments demonstrate proof of principle (1 spectrum / day).

X-ray lasers hopefully will make it mainstream.

More on this at the end of the lecture.

Computational Screening of Molecules for Tandem Cells

Connect two dye molecules with an asymmetric molecular wire (=diode). Molecular complexes are atomically perfect. That would solve the main problem with tandem cells: their defective interfaces.

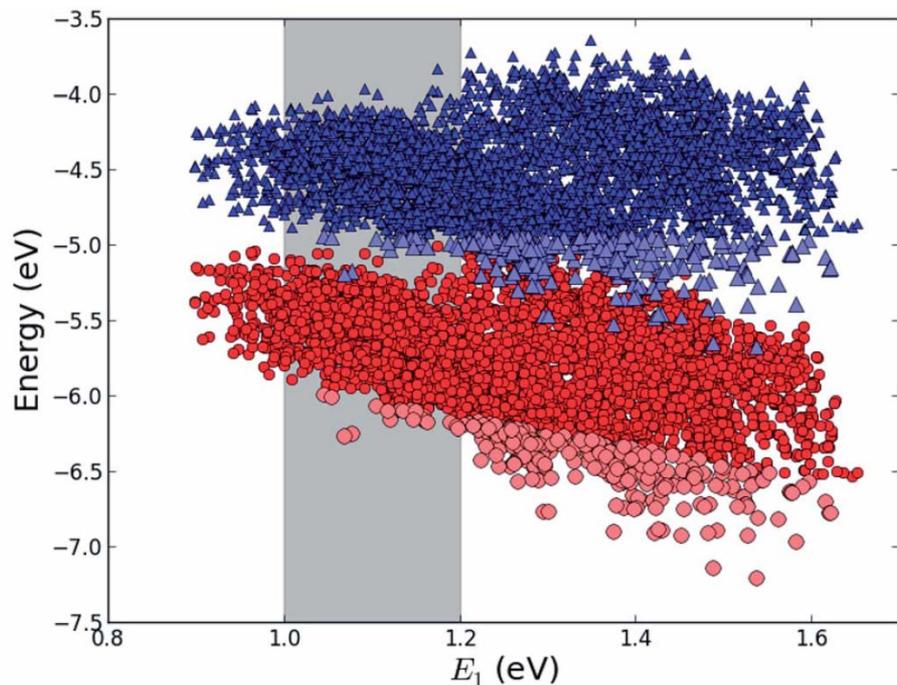
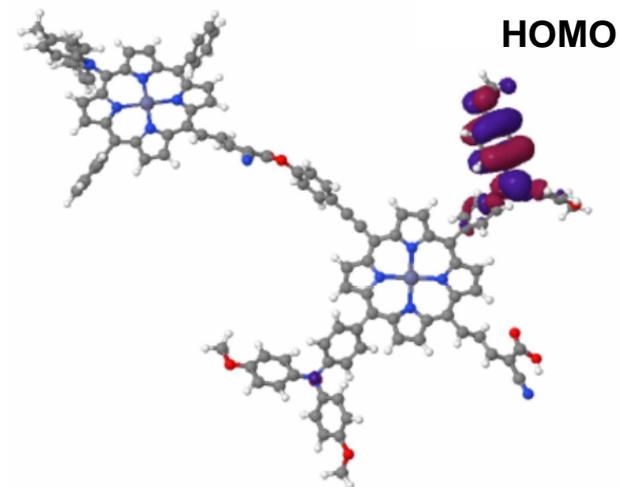
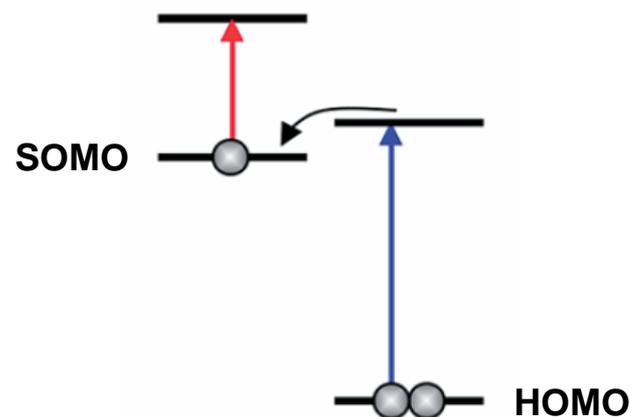


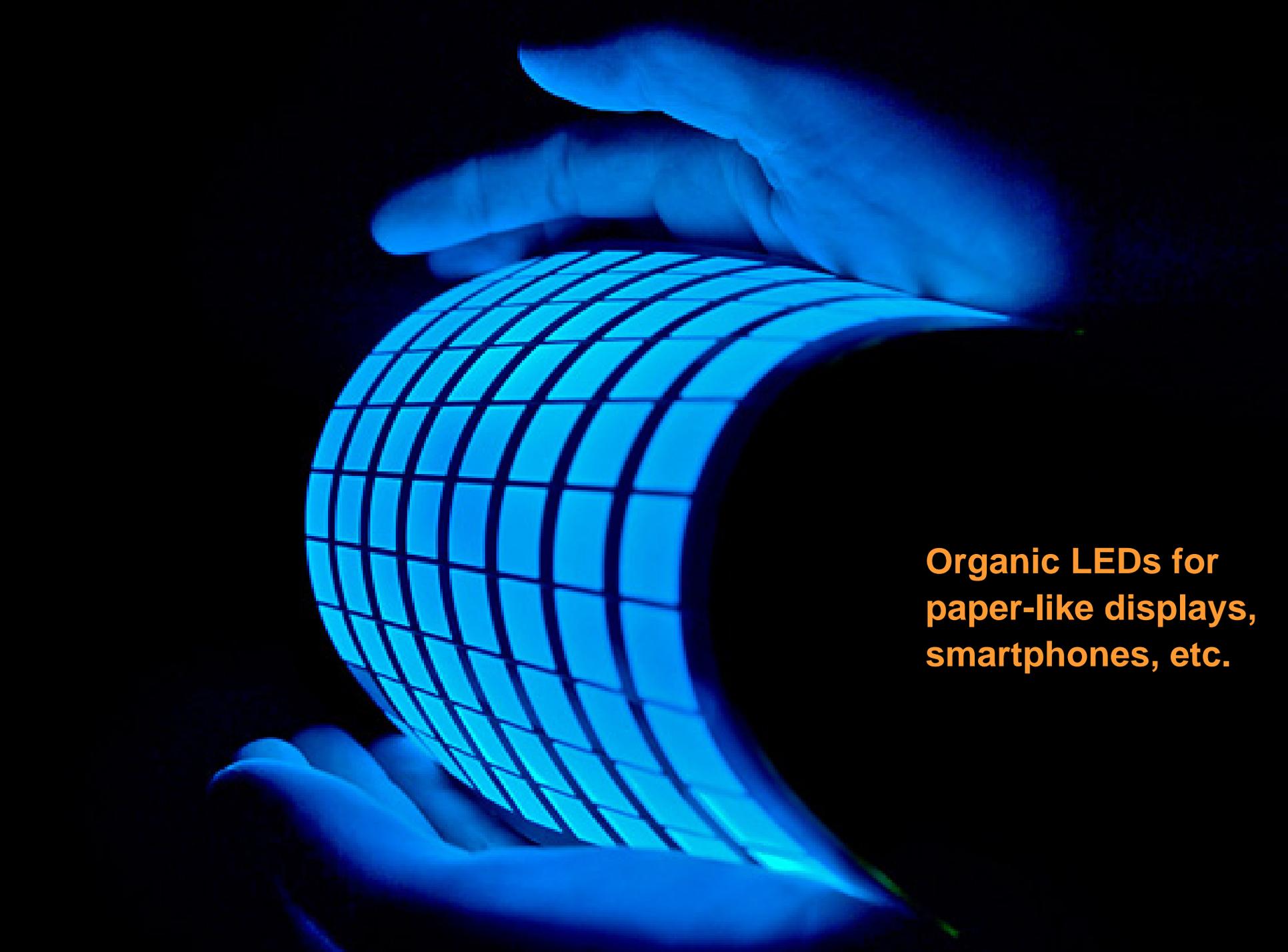
Fig. 2 E_{HOMO} (red circles) and $E_{\text{HOMO}} + E_1$ (blue triangles) for all 5000+ porphyrins in our database^{22,23} plotted against the lowest optical transition energy, E_1 .



Summary: Solar Cells

- Need to improve the efficiency to reduce overall cost. Tandem cells are the way to go (at least theoretically).
- Tailor the energy levels of donor, dye, and acceptor. Screen many molecules/solids computationally. Measure the energy levels of the best candidates.
- A dream experiment:
Follow the electrons/holes in real time through a solar cell.
Pump with visible light, probe atom-specific via core levels.

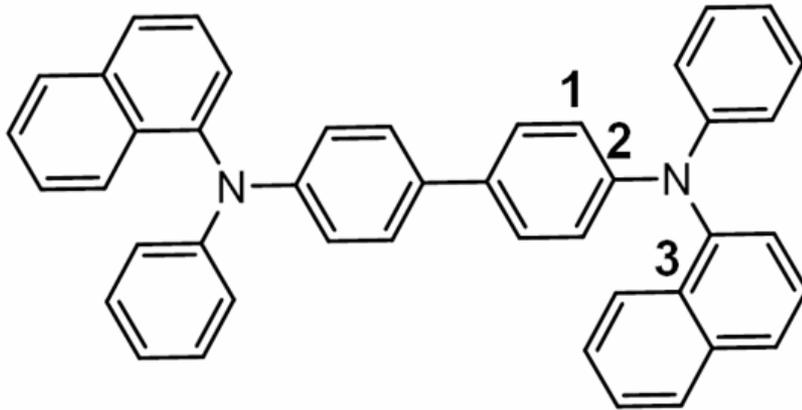
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**Organic LEDs for
paper-like displays,
smartphones, etc.**

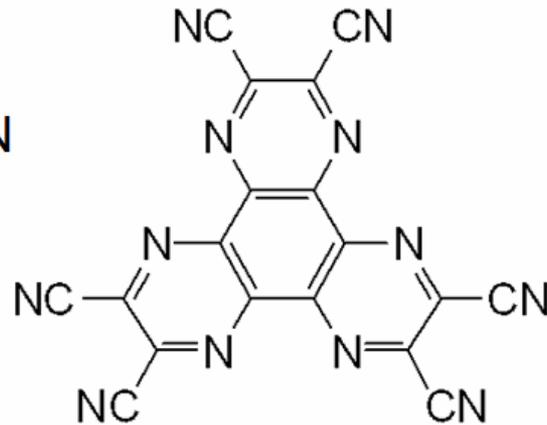
Prototypical Molecules for OLEDs

NPD



Electron Donor

HAT:CN

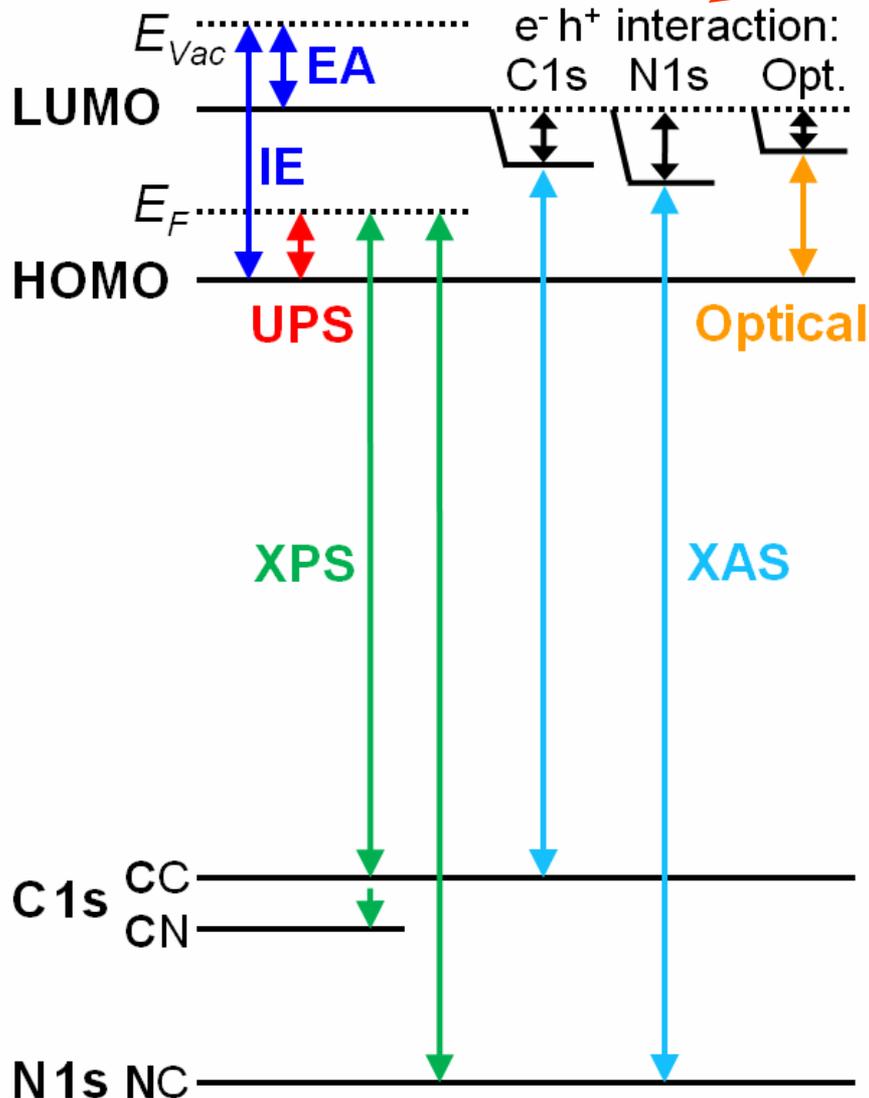


Electron Acceptor

Energy Levels in OLEDs

The most important energy levels for OLEDs are HOMO and LUMO. The HOMO is easily obtained by ultraviolet photoelectron spectroscopy (UPS). One might think that the LUMO could simply be obtained by adding the photon energy for the HOMO-LUMO transition from optical absorption. But the excited electron in the LUMO binds to the hole in the HOMO and forms a hydrogen-like exciton. The exciton binding energy needs to be added to the photon energy to obtain the HOMO-LUMO gap. Likewise, a core exciton is formed between a core hole and an electron in the LUMO. The exciton binding energy is difficult to determine from experiment or theory alone. A theoretical treatment requires complicated codes (Bethe-Salpeter equation or TDDFT). Here we consider a simpler way to obtain it by combining experiment with a one-electron ground-state calculation.

Multi-Technique Approach to Determine Exciton Binding Energies



Calculate IE and EA



$$\text{LUMO} = \text{HOMO} + (\text{IE} - \text{EA})$$

$$E_{\text{ex}}(\text{Opt}) = (\text{IE} - \text{EA}) - E_{\text{Optical}}$$

$$E_{\text{ex}}(1\text{s}) = (\text{IE} - \text{EA}) - (E_{\text{XAS}} + E_{\text{XPS}} - E_{\text{UPS}})$$

$$\text{HOMO} = E_{\text{UPS}} < 0 \quad E_{\text{XPS}} < 0$$

Avoids calculating core levels and electron-hole binding energies.

XAS Data and their Energy Level Diagram

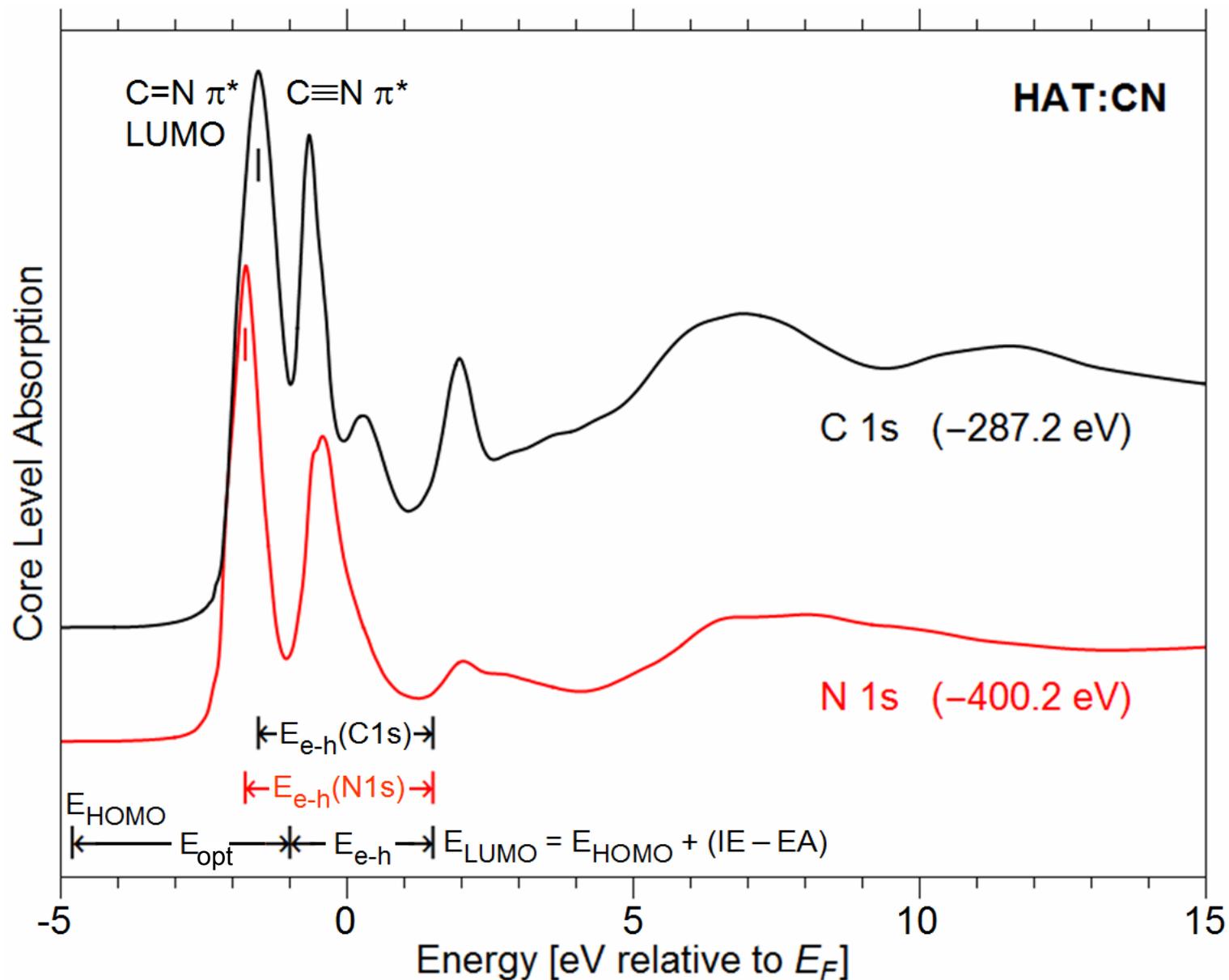


Table 3. Binding Energies^a E_{e-h} of the Valence and Core Excitons (in eV)

e-h binding	NPD	HAT:CN
E_{e-h}	1.7	2.5
E_{e-h} (C 1s)	3.2	3.0
E_{e-h} (N 1s)		3.2

^aThese binding energies are all with an electron in the LUMO.

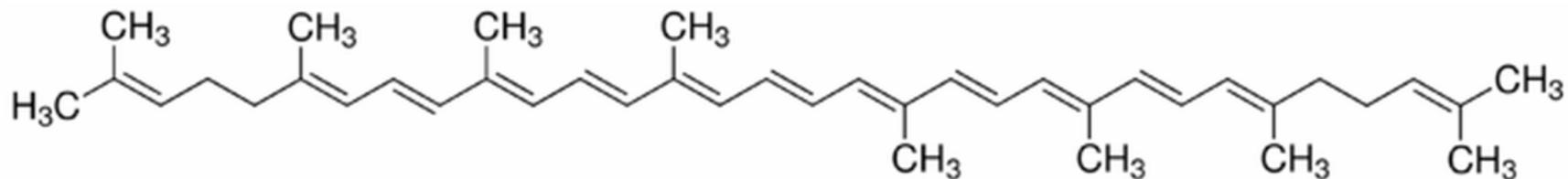
Excitons play an important role in organic electronics. Their binding energy is significant, and their mean free path is much longer than that of charged carriers. In organic photovoltaics, excitons carry the energy of the absorbed photons to the boundary between the electron acceptor and donor, where they break up into electrons and holes. In photosynthesis, excitons carry the energy absorbed by the chlorophyll to the proteins of Photosystem II, where the chemical reaction takes place.

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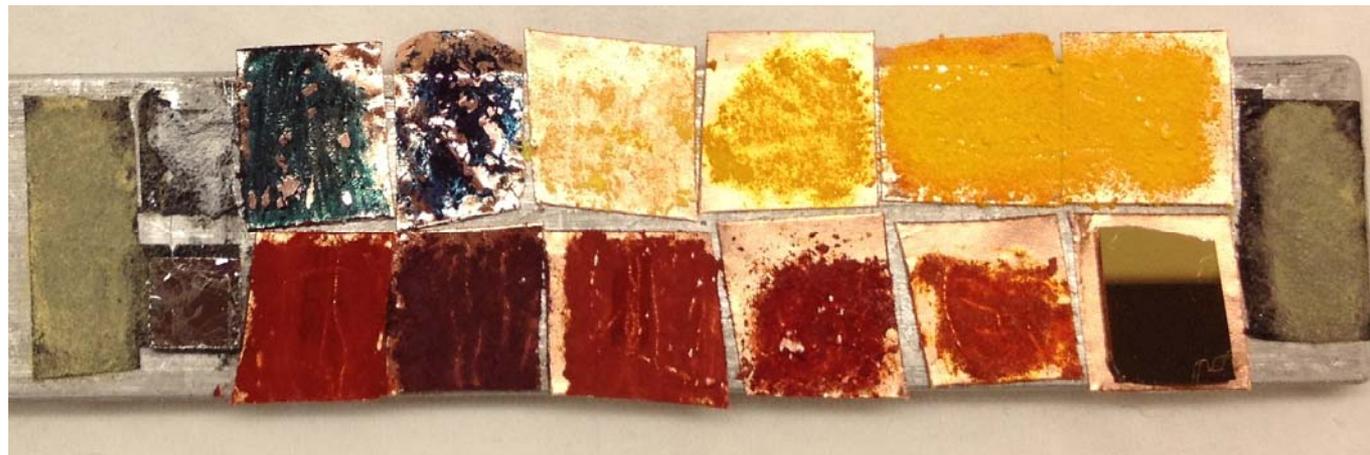
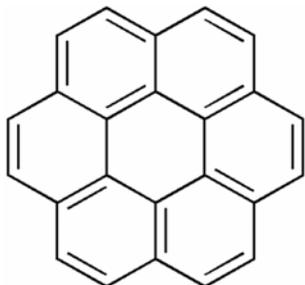
Energetics of Conducting Molecular Wires and Dots

The ultimate nanowire: a chain of atoms (here a chain of π -bonded C atoms)

Lycopene, a molecular wire

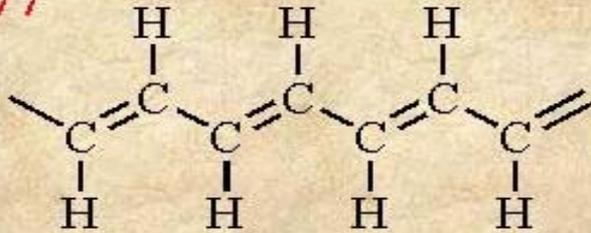


Coronene, a molecular dot



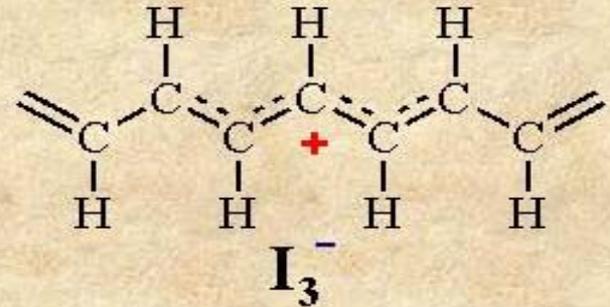
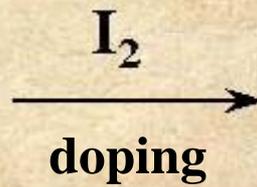
Conducting Polymers

1977



Polyacetylene (PA)

$$\sigma = 10^{-9} \text{ S/cm}$$



$$\sigma = 38 \text{ S/cm} = 38 \frac{1}{\Omega\text{cm}}$$

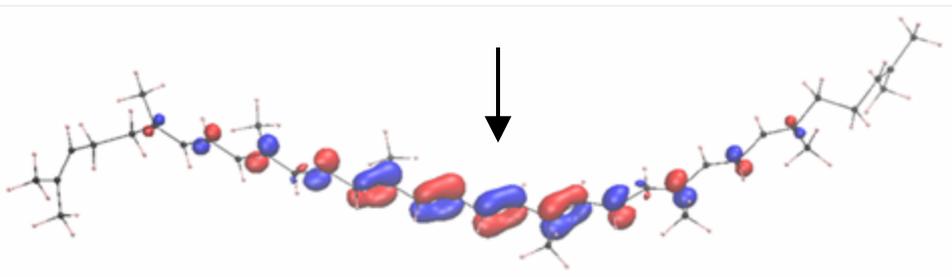
$\sigma = \text{Conductivity}$

Nobel Prize in Chemistry 2000
Shirakawa, McDiarmid, Heeger

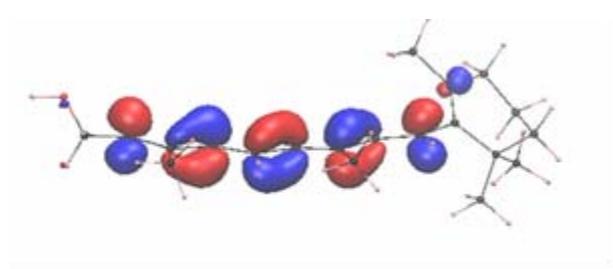
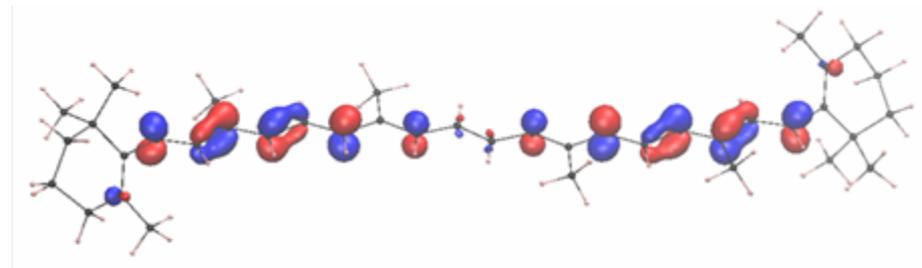
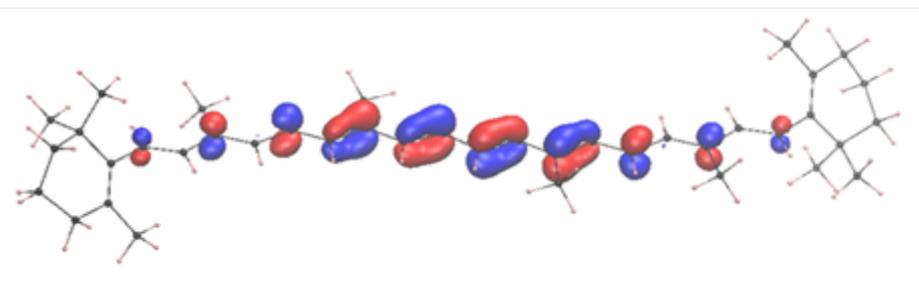
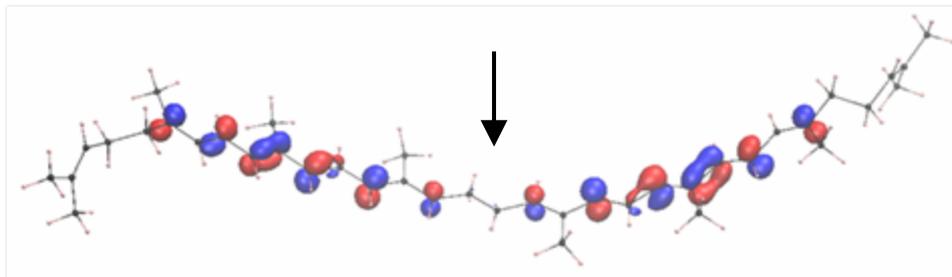


Wave Functions of Molecular Wires: Vibrating Strings

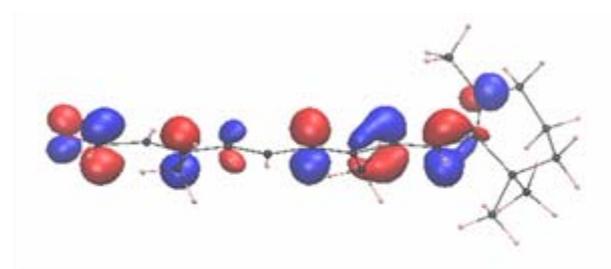
Maximum



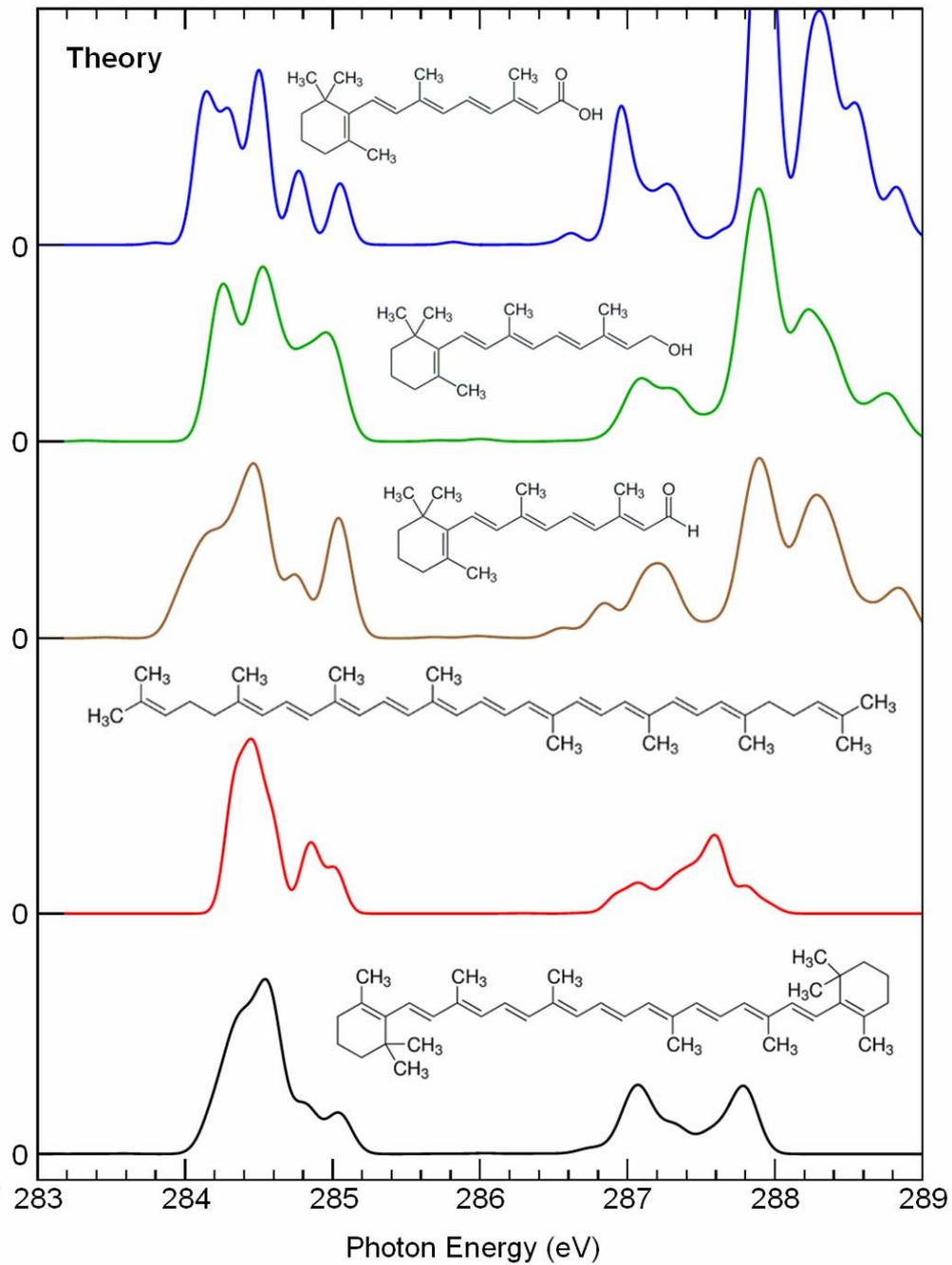
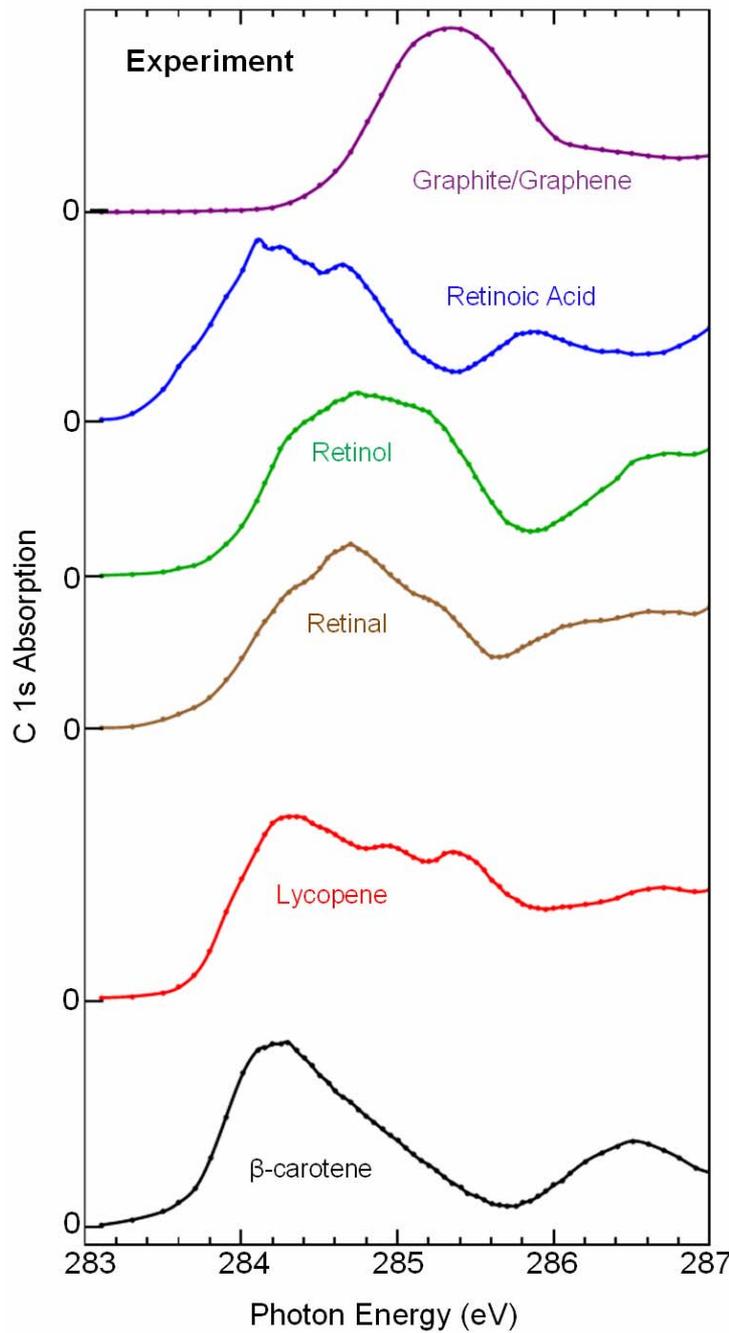
Node



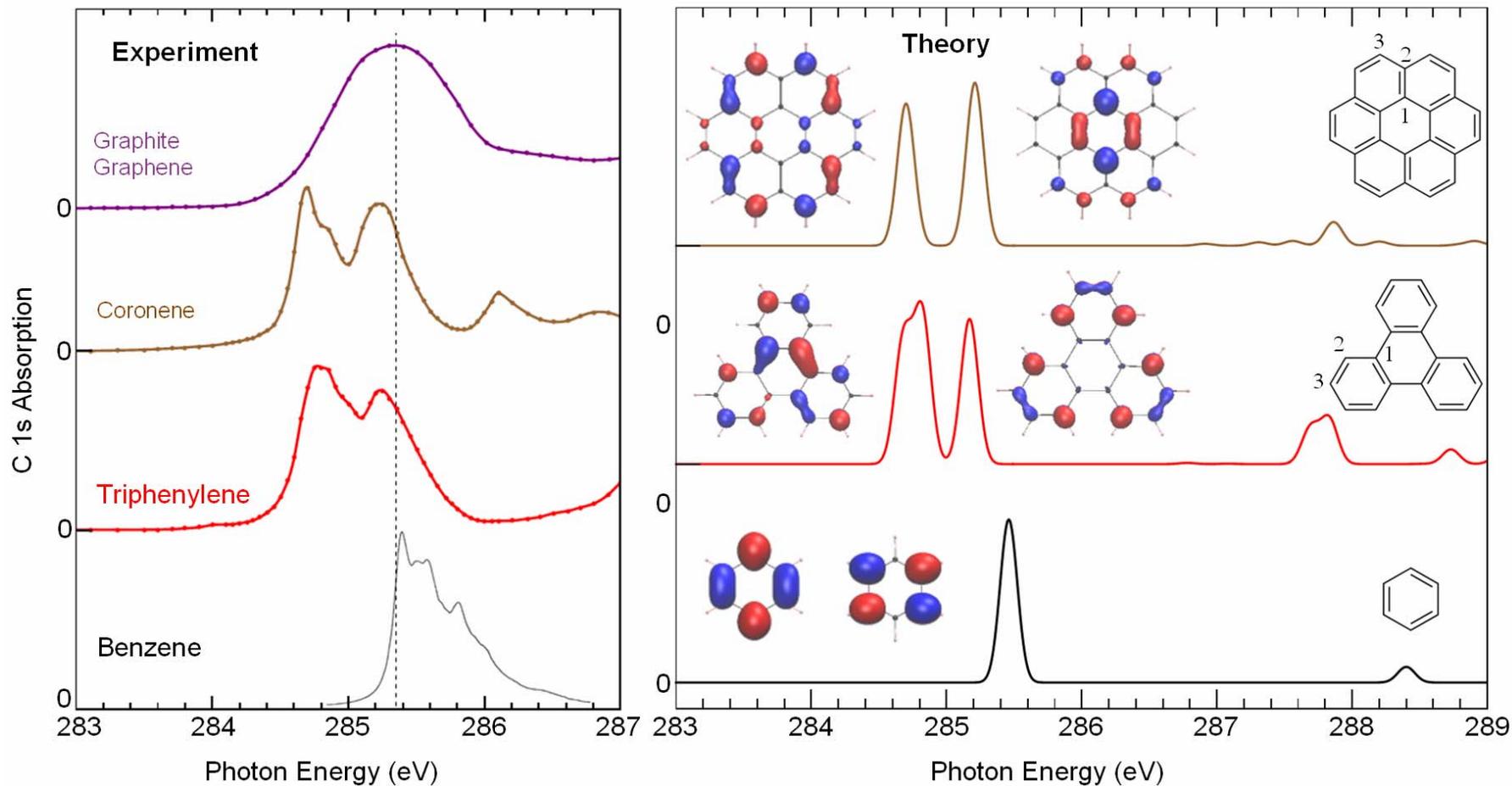
LUMO



LUMO+1

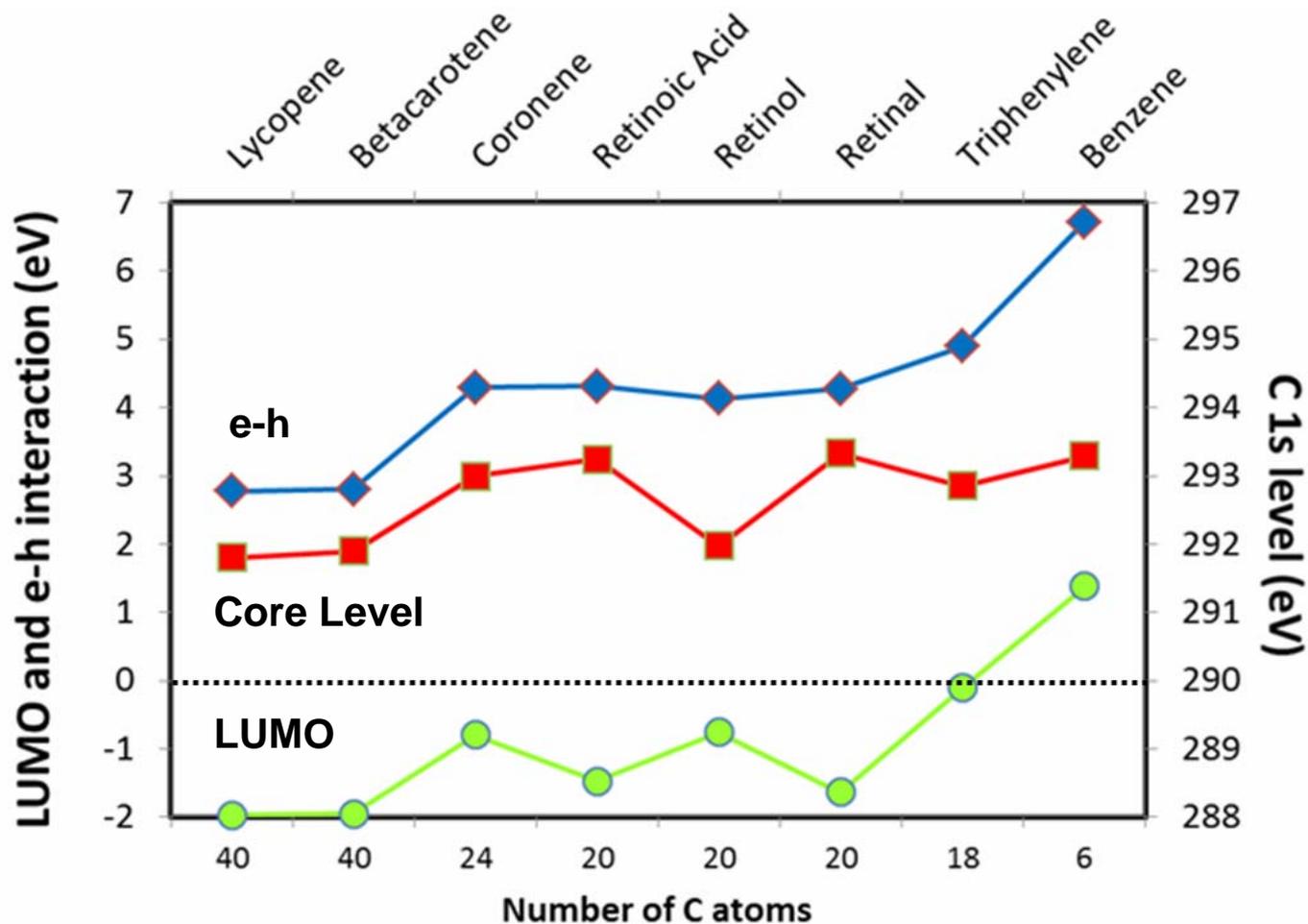


2D Molecular Quantum Dots: Modes of a Drum



Sawtooth shape due to excitation of atomic vibrations in addition to electronic states.

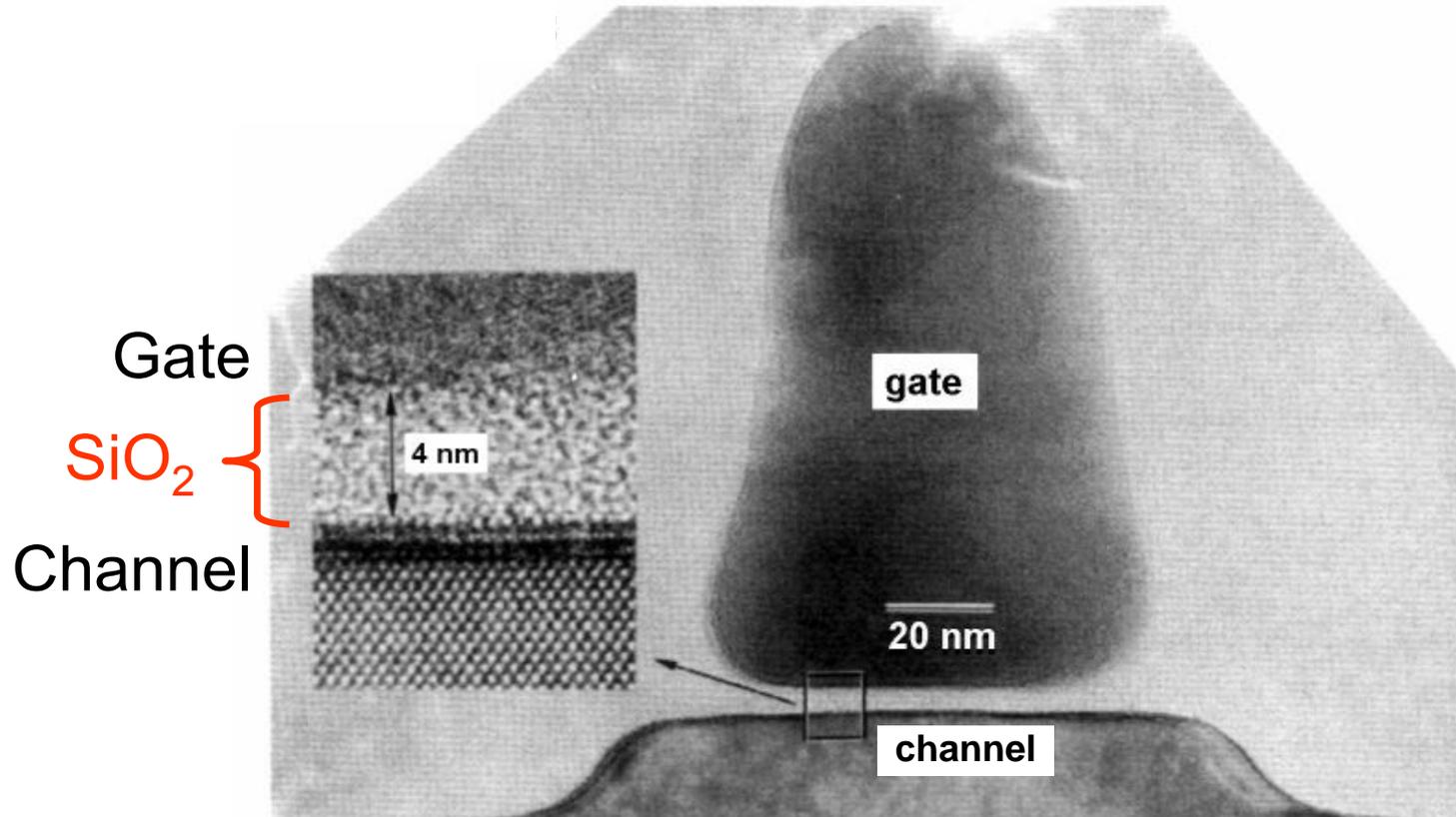
Energetics of Molecular Wires and Dots from Theory



Size of the molecule is the most relevant parameter, not dimensionality.

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The Field Effect Transistor (FET)



Moore's law of Si technology keeps getting challenged, leading to frequent innovations. One part remained unchanged for 40 years: the SiO₂ dielectric between channel and gate. The reason for its longevity was the **electronic perfection of the Si/SiO₂ interface**. It contains only 1 electrically-active defect among more than 10⁵ interface atoms, even though the SiO₂ is amorphous.

After 40 years of downscaling, the gate oxide became so thin that electrons tunneled through it, creating an **untolerable leakage current**. SiO₂ was replaced by “**high k oxides**” which could be thicker at the same capacitance.

Intel's Transistor Technology Breakthrough Represents Biggest Change to Computer Chips In 40 Years

Intel Producing First Processor Prototypes With New, Tiny 45 Nanometer Transistors, Accelerating Era of Multi-Core Computing

IBM Advancement to Spawn New Generation of Chips

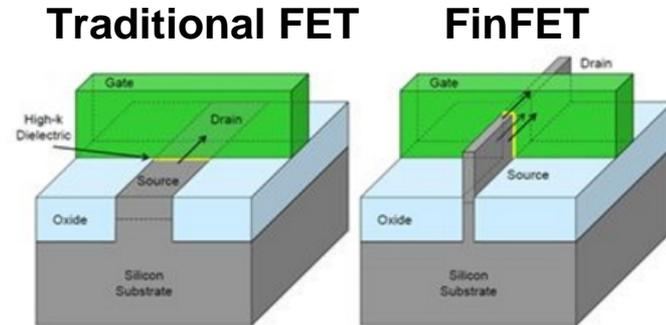
First fundamental change to basic transistor in forty years

YORKTOWN HEIGHTS, NY - 27 Jan 2007: IBM (NYSE: IBM) today announced it has developed a long-sought improvement to the transistor – the tiny on/off switch that serves as the basic building block of virtually all microchips made today.

Working with AMD and its other development partners Sony and Toshiba, the company has found a way to construct a critical part of the transistor with a new material, clearing a path toward

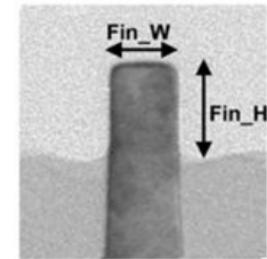
But in the end, **SiO₂ still survived at the interface** between Si and the high-k oxides, because those have poor interfaces with Si.

The latest generation of transistors have a channel shaped like a shark fin and a wrap-around gate. Both increase the capacitance.



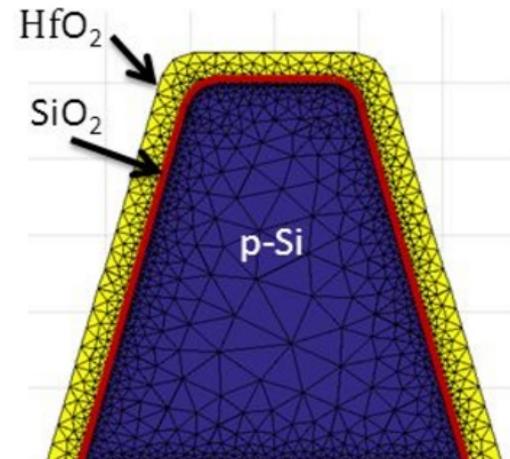
Intel Corp.

- High-k gate dielectric for thin equivalent oxide thicknesses (sub 2nm)
- Thin SiO₂ layer at interface between high-k dielectric and substrate (1nm)

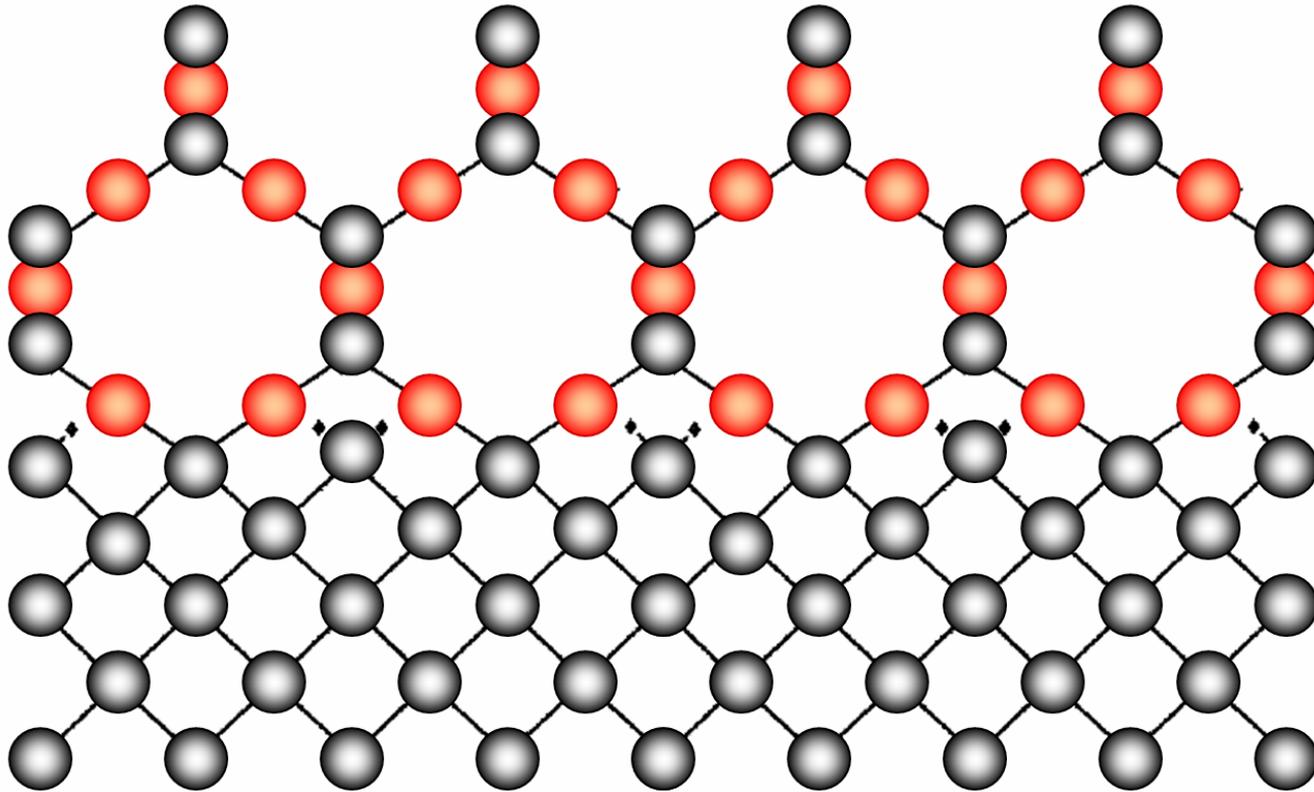


$$W_{\text{eff}} = 2 \times \text{Fin}_H + \text{Fin}_W$$

Despite the introduction of HfO₂ as gate dielectric the interface to Si is still formed by **1 nm of SiO₂**:



The Si/SiO₂ Interface

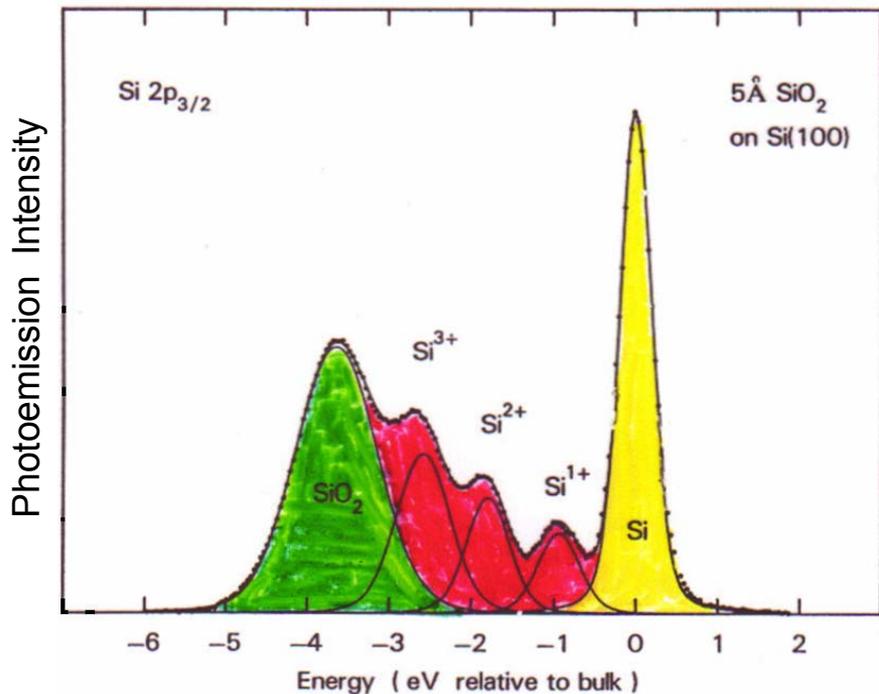


J. Vac. Sci. Technol. **19**, 395 (1981)

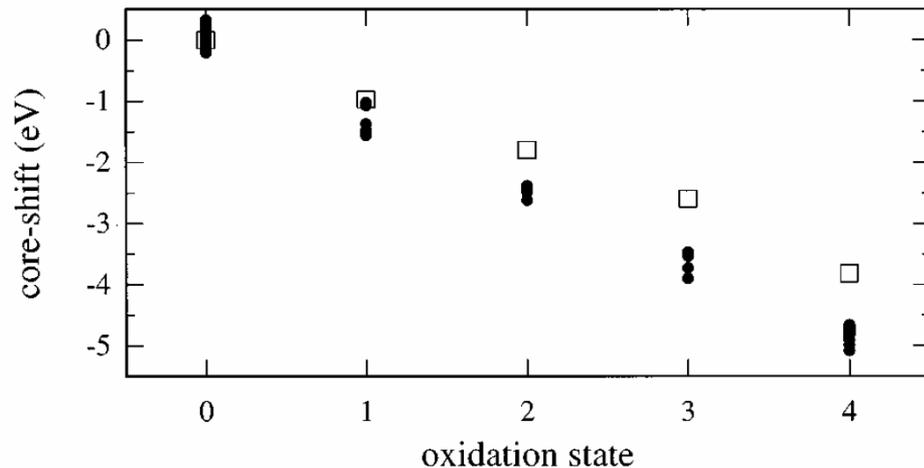
The simplest model of the Si/SiO₂ interface is a nearly lattice-matched connection to a crystalline form of Si/SiO₂. It shows that there are about **twice as many bonds coming from the Si side as from the SiO₂ side**. That leaves half of the interface Si atoms with broken bonds. The real surface is less abrupt, and SiO₂ is amorphous.

Intermediate Oxidation States of Si at the Si/SiO₂ Interface

A gradual transition from Si to SiO₂ avoids broken bonds by going through intermediate oxidation states (in red below). They are unstable in the bulk and exist only at the interface. Each oxidation state gives rise to a distinct core level shift (see the next slide). This trend is reproduced by density functional theory.



PRB **38**, 6084 (1988)

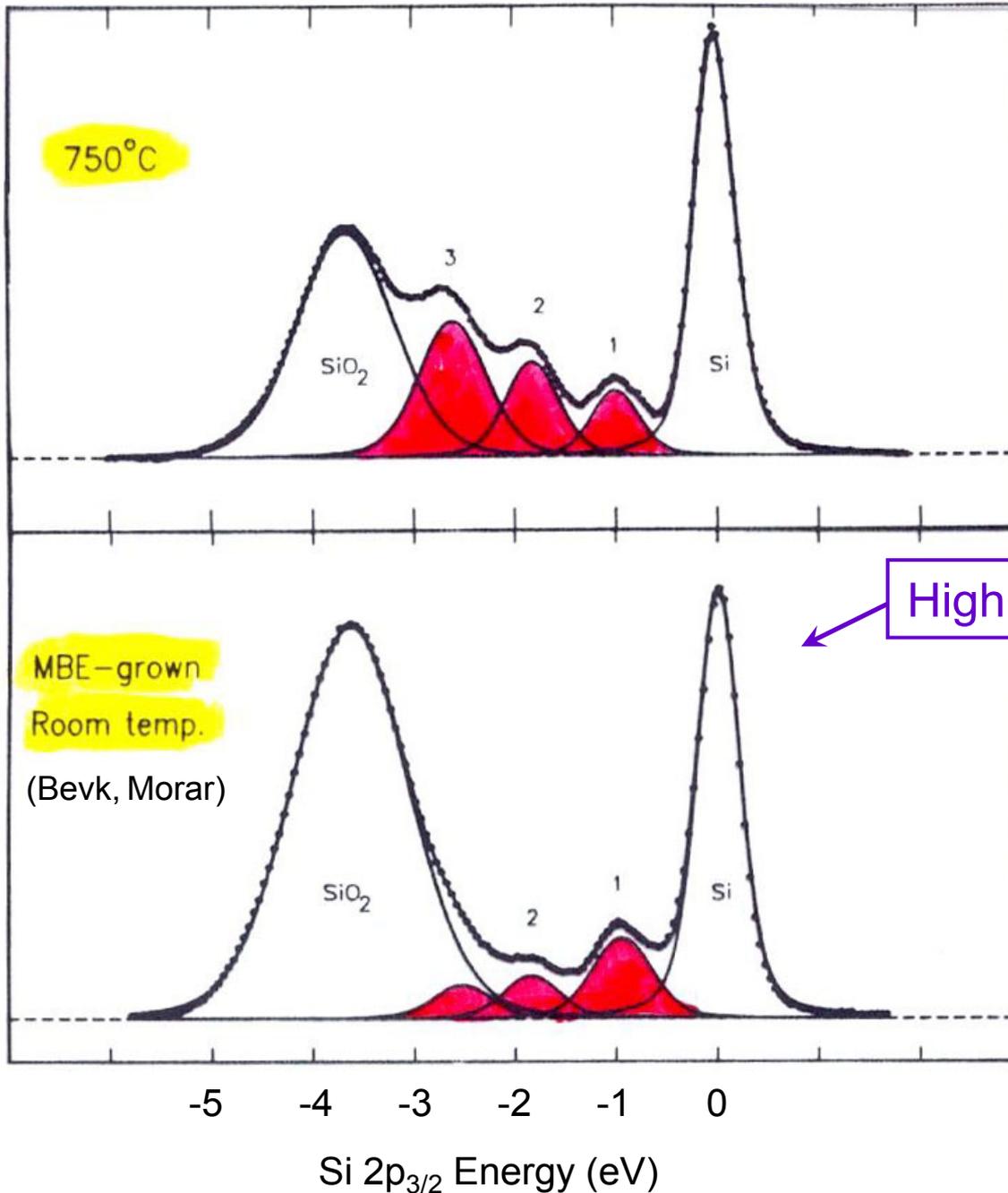


Calculated Si2p core level shifts (full circles) versus experimental shifts (open squares). Multiple circles represent different structures.

PRB **53**, 10942 (1996)

Optimization of the Interface

The areas under the peaks represent the areal density of Si atoms for each oxidation state.

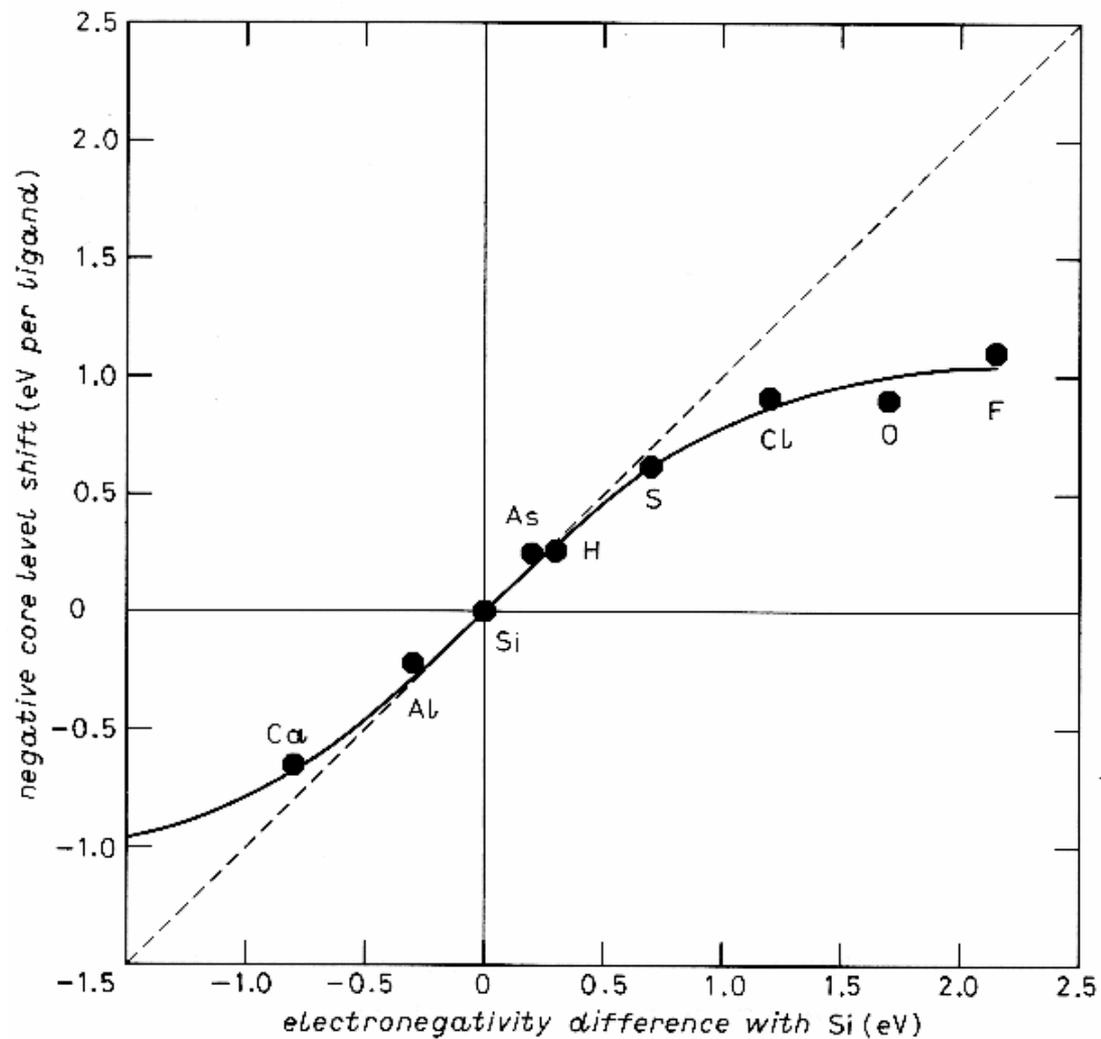
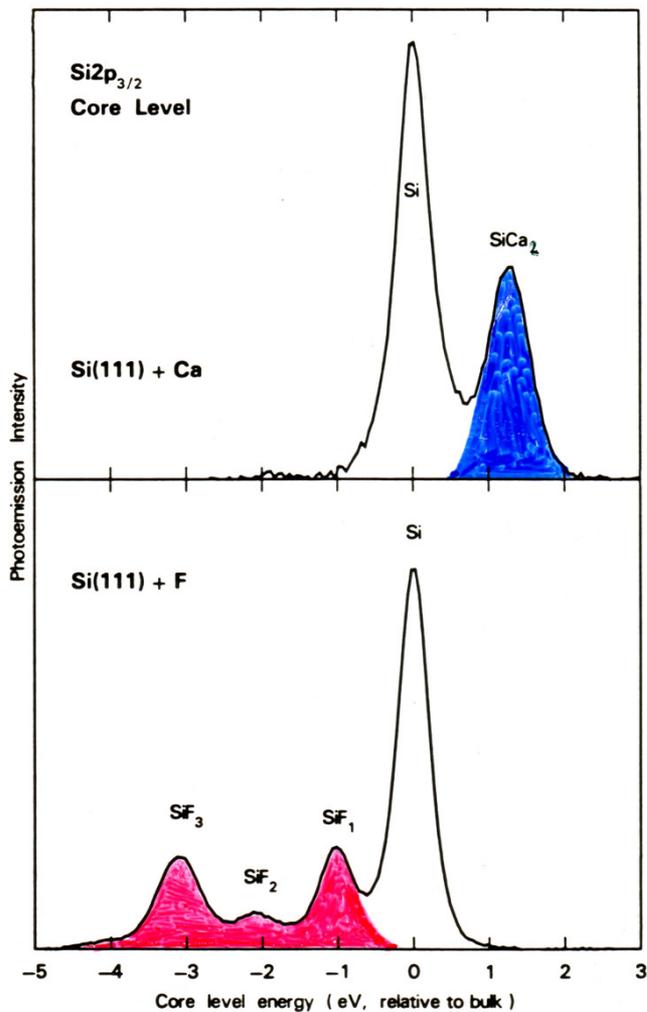


High electrical quality

Low temperature oxidation of a flat surface produces a more abrupt interface. Such spectra are widely used for systematically optimizing the interface preparation.

Si(100) is the preferred substrate for electronic devices, since it tends to form higher quality interfaces.

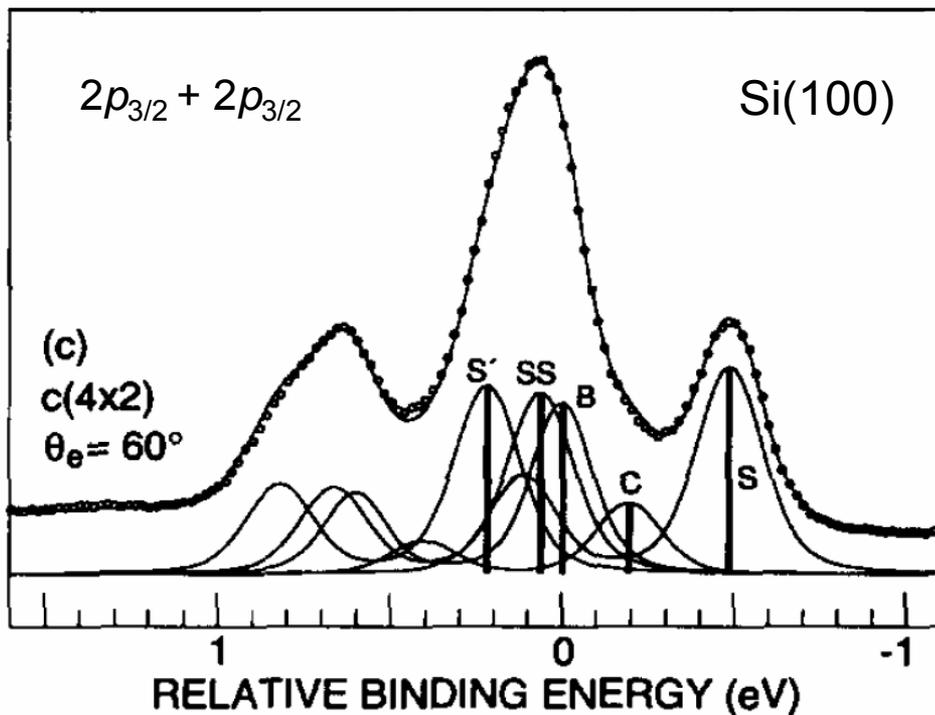
Core Level Shift vs. Charge Transfer for Si



FJH et al., Enrico Fermi School on "Photoemission and Absorption Spectroscopy of Solids and Interfaces with Synchrotron Radiation", North Holland (Amsterdam 1990), p. 203.

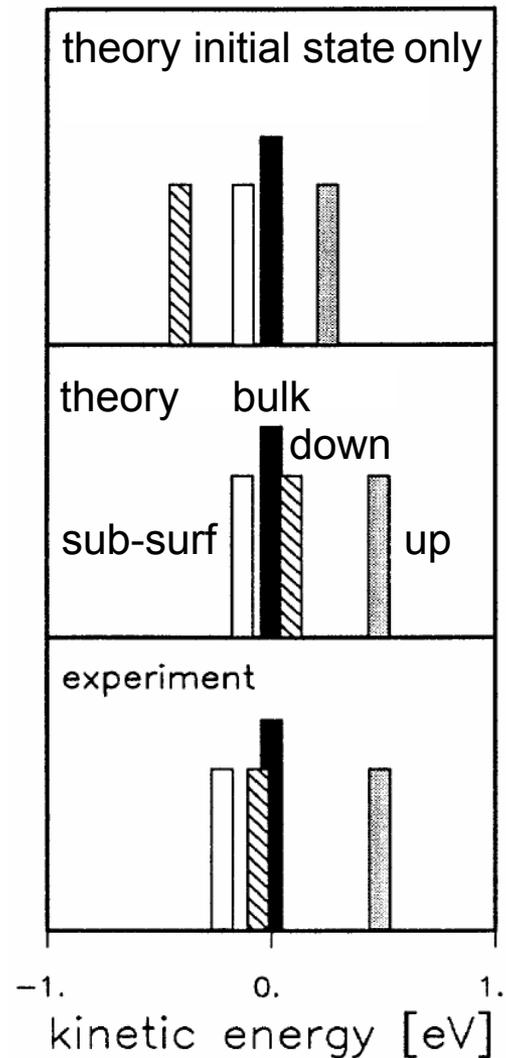
Initial vs. Final State Core Level Shifts at Clean Si Surfaces

Surf. Sci. **287/288**, 529 (1993)

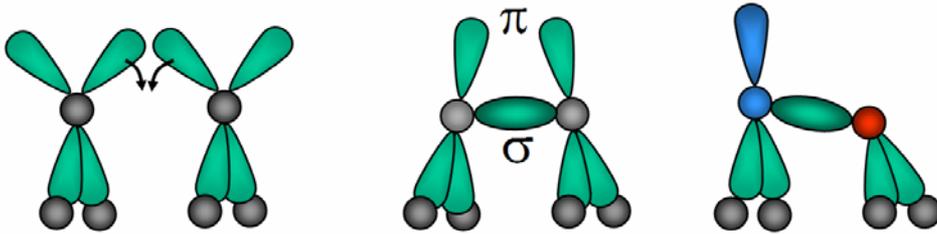


In addition to the chemical shift due to charge transfer in the ground state one has to consider dielectric screening in the final state. That reduces the binding energy. This reduction is larger at the surface where surface states increase the dielectric constant (see next slide).

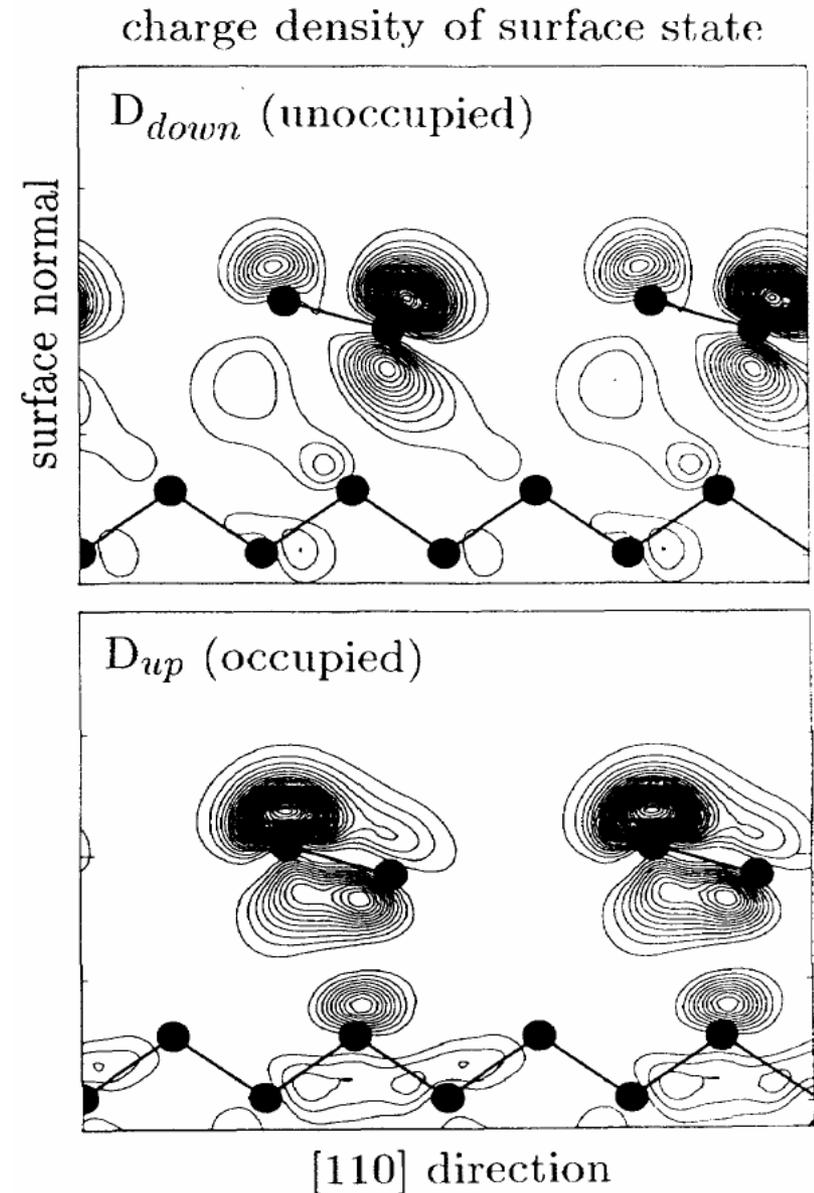
PRL **71**, 2338 (1993)



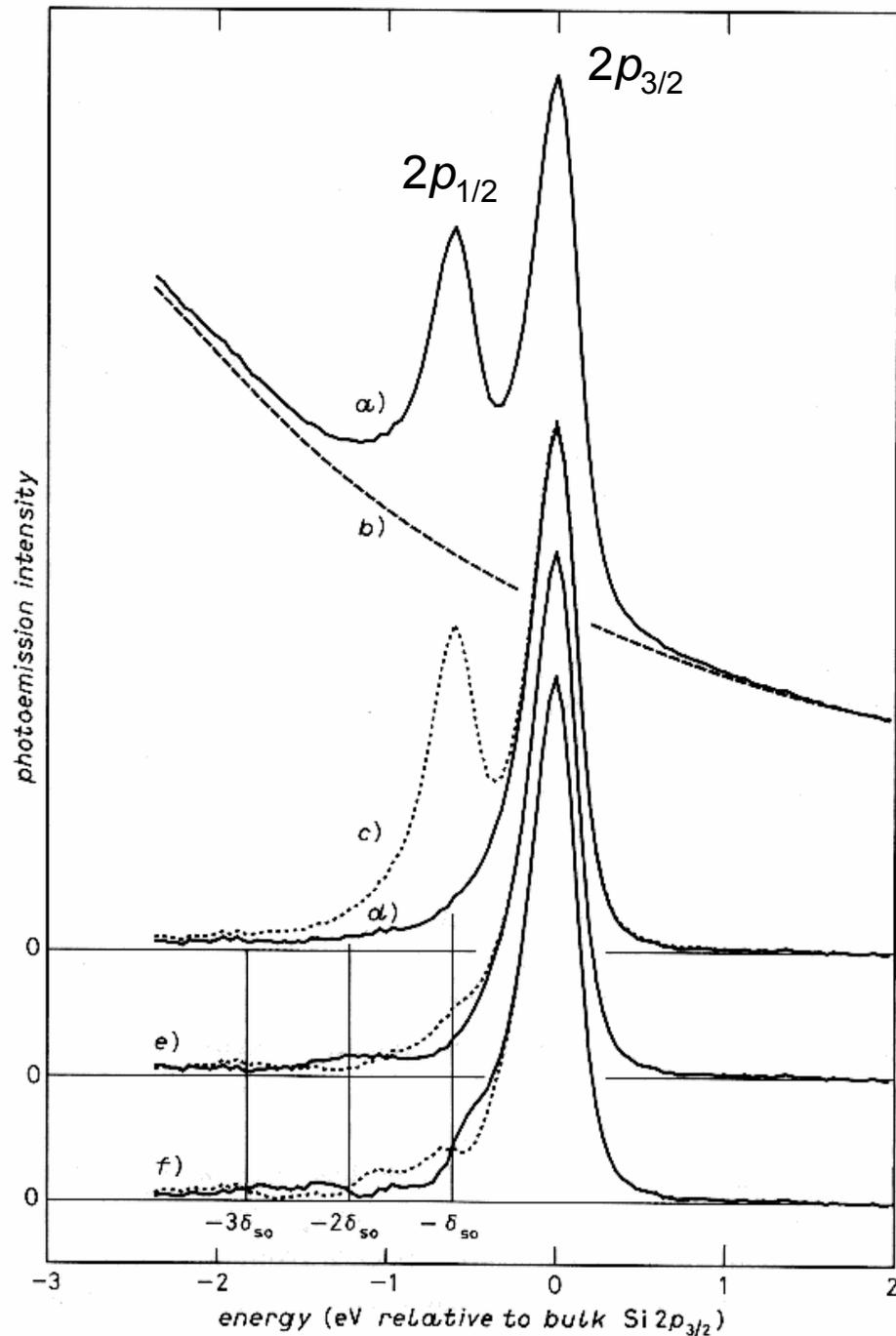
Asymmetric Dimer Structure of the Clean Si(100) Surface



All Si surfaces are highly-reconstructed, since directional covalent bonds are broken. These are desperate to reconnect. They even form π -bonds which are unstable for Si (in contrast to carbon). An additional up-down motion of the dimerized atoms at the surface converts two half-filled π -orbitals into a filled and an empty orbital.



Separating the Si $2p_{1/2}$ and Si $2p_{3/2}$ Contributions



To untangle the overlapping Si $2p_{1/2}$ and $2p_{3/2}$ spectra it is useful to apply the following routine:

First, subtract the secondary electron background, obtained from taking the same scan with lower photon energy.

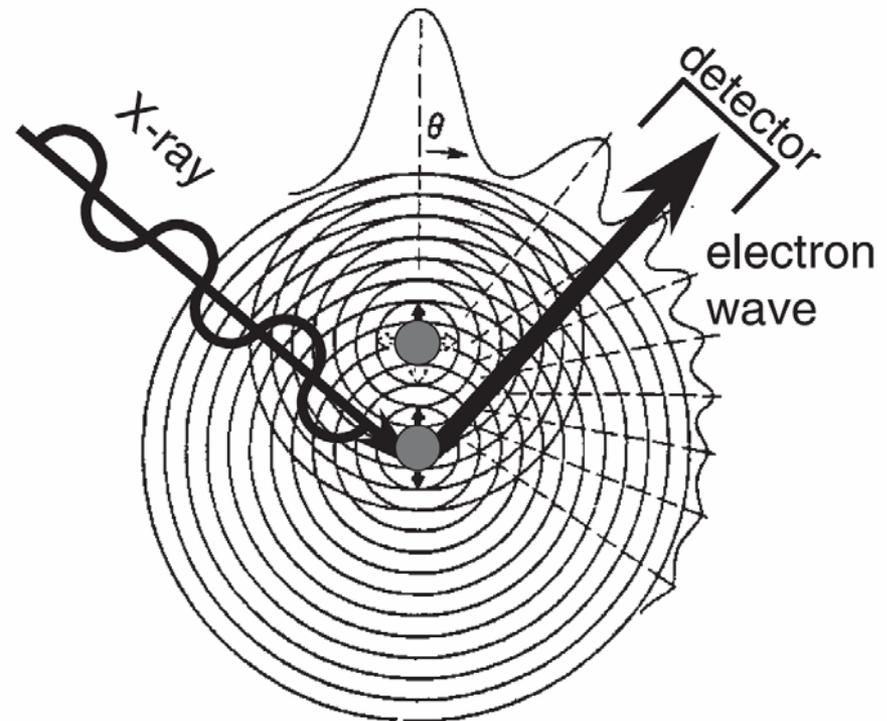
Then subtract the $2p_{1/2}$ contribution by an iterative scheme, starting from the right. This can be done for every spin-orbit splitting δ_{so} and branching ratio R . These are known properties of the Si atom, but they need to be fine-tuned to remove residual oscillations on the left side of the spectrum. Details of the procedure are given in the reference on the slide about core level shift vs. charge transfer.

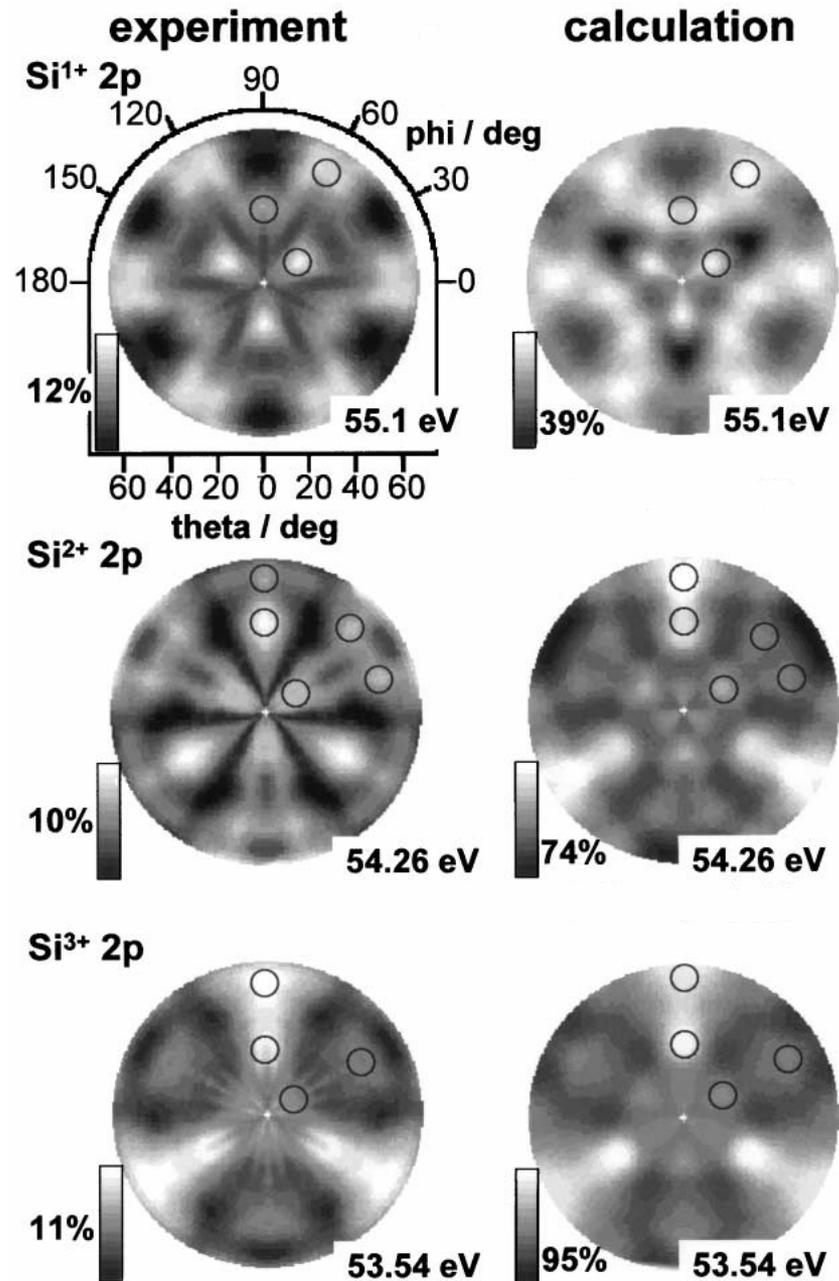
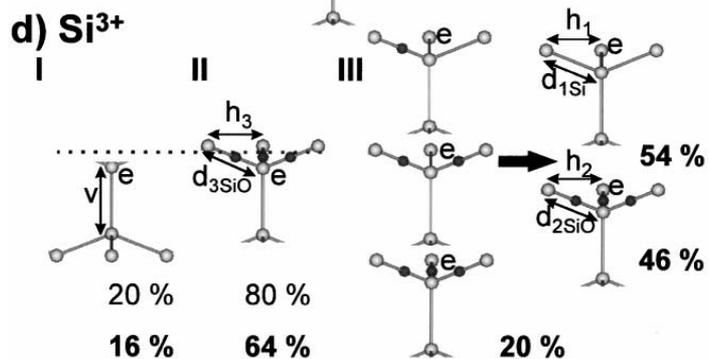
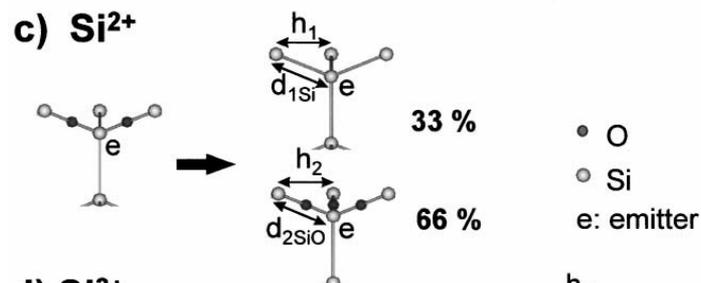
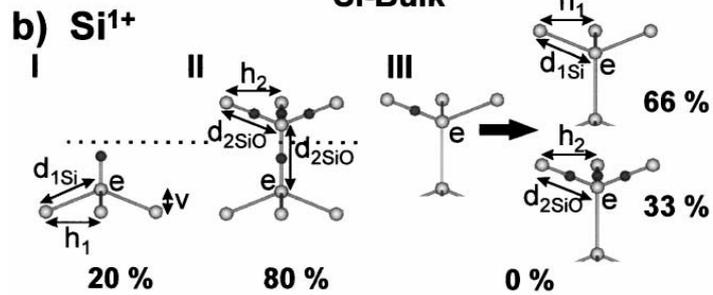
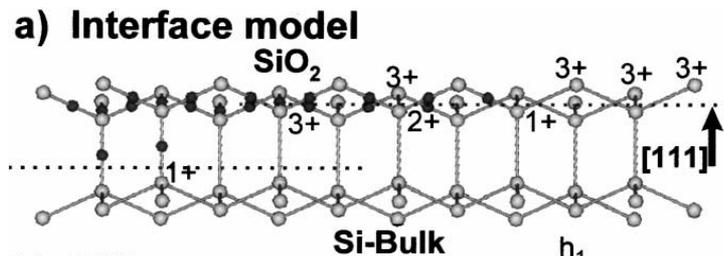
Atom-Specific Structure Determination at the Si/SiO₂ Interface

It is possible to obtain structural information about atoms in the neighborhood of a Si atom with a specific oxidation state. For this purpose the momentum distribution of the Si2*p* photoelectron intensity is measured and simulated by multiple scattering calculations similar to those used in low energy electron diffraction (LEED).

Photoelectron Diffraction (PhD):

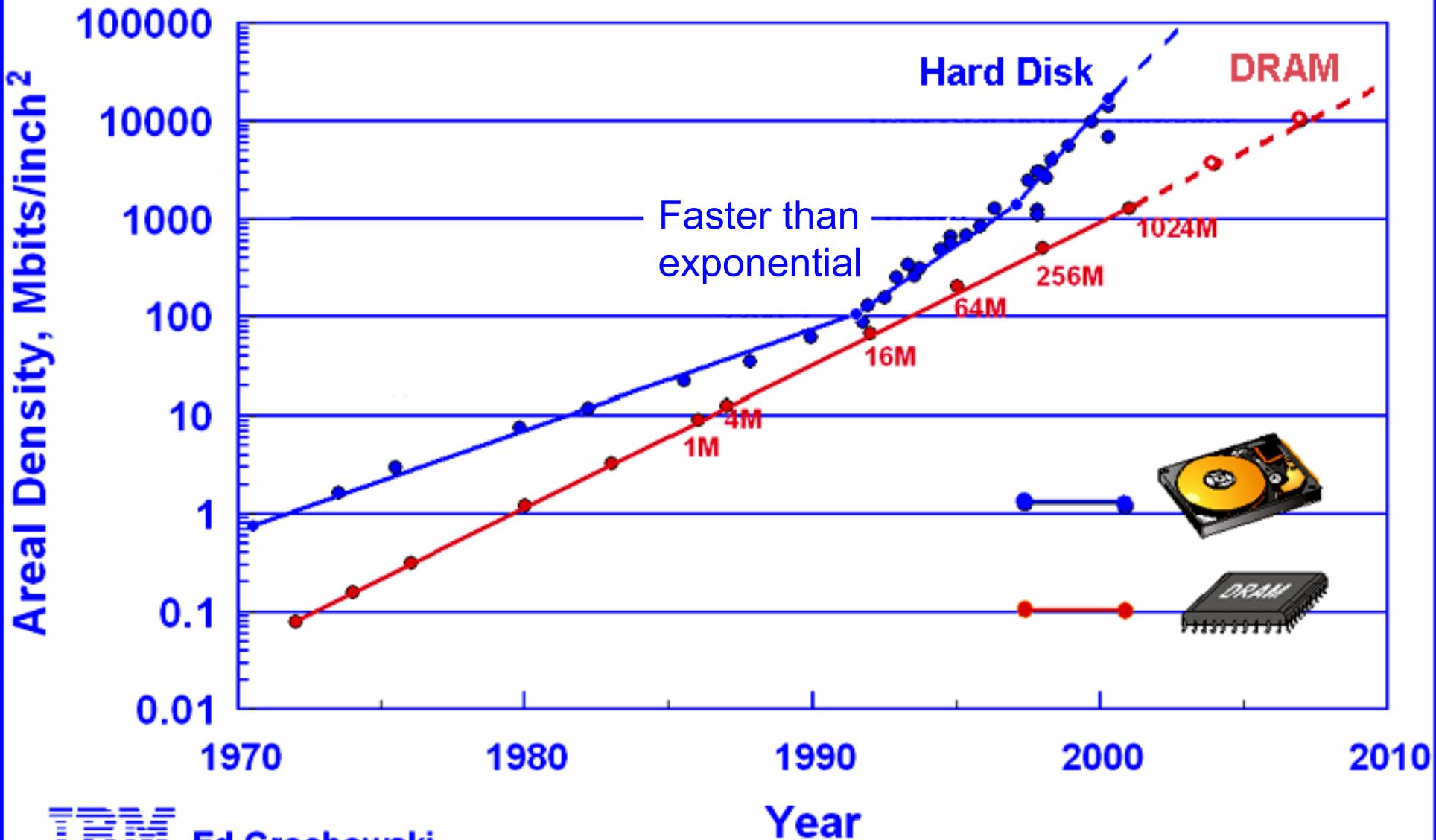
The spherical wave of a photoelectron emitted from a specific core level serves as reference wave, while the waves scattered by neighboring atoms create the object wave.



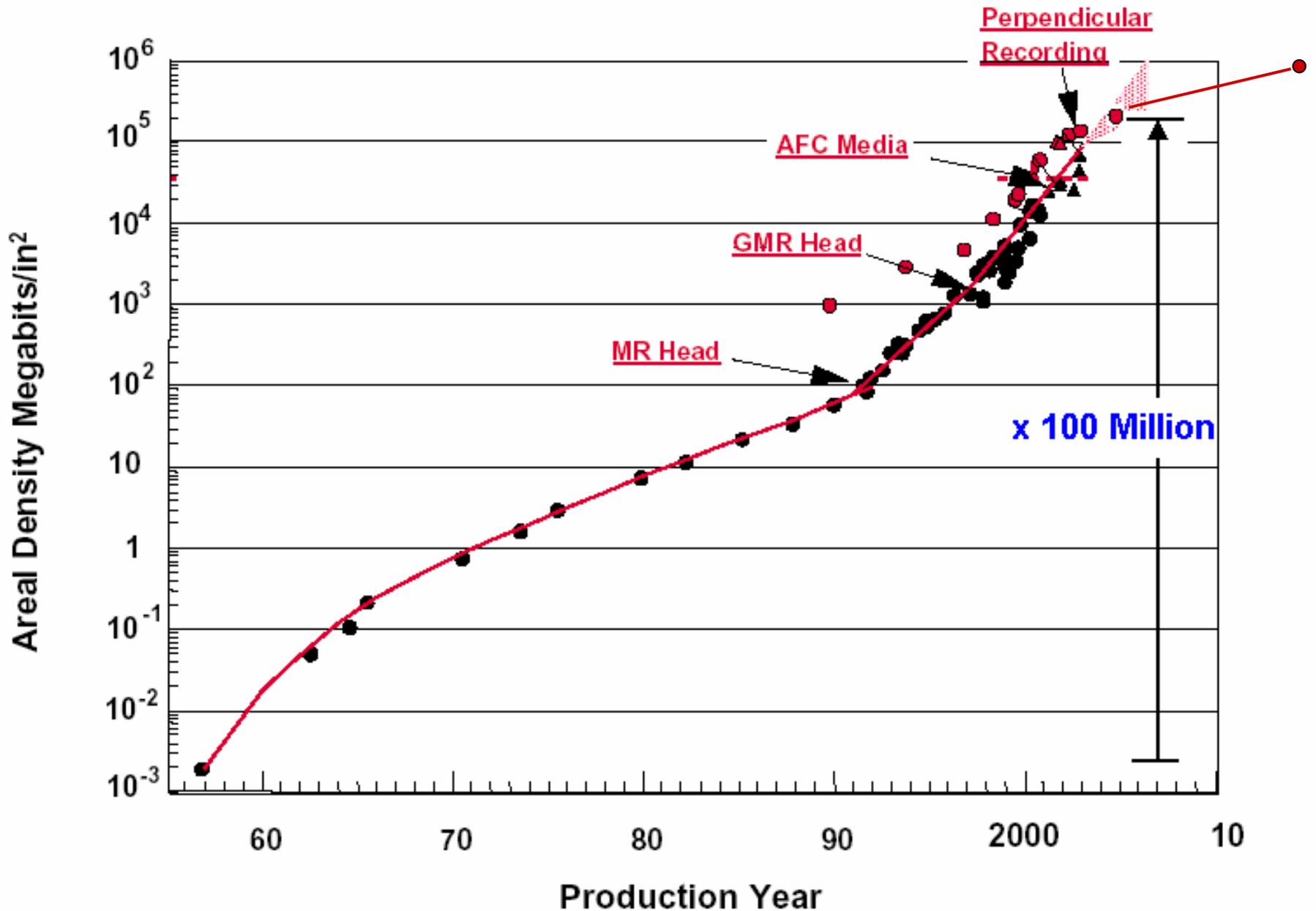


1. **Photovoltaics and OLEDs**
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7. **A recent development: ultrafast**

Data Storage Density



Magnetic Data Storage: Rapid Changes



GMR and TMR Reading Heads

General principle:

- Two ferromagnetic layers separated by a nonmagnetic layer.
- For $B = 0$ they have opposite magnetization (180°).
- An external B-field forces them parallel (0°).
- The switch from opposite to parallel spin polarizers reduces the electrical resistance.
- Maximum small field sensitivity at the switching point (90°).

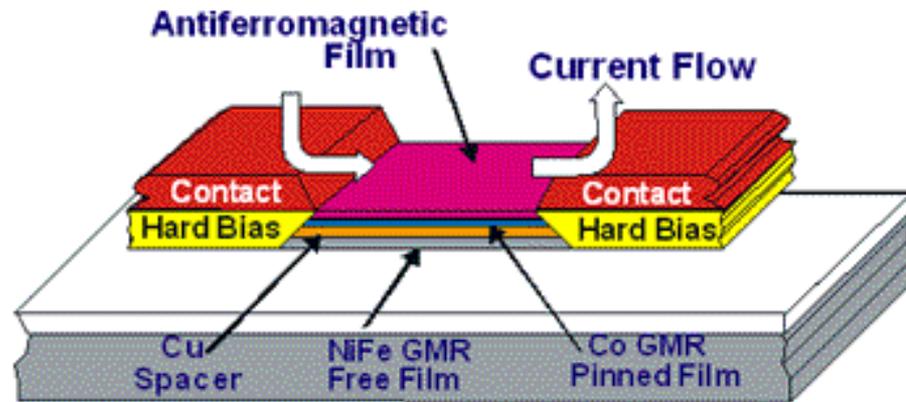
Implementation:

- GMR = metallic spacer (Physics Nobel Prize 2007)
- TMR = insulating spacer (current technology)

GMR vs. TMR

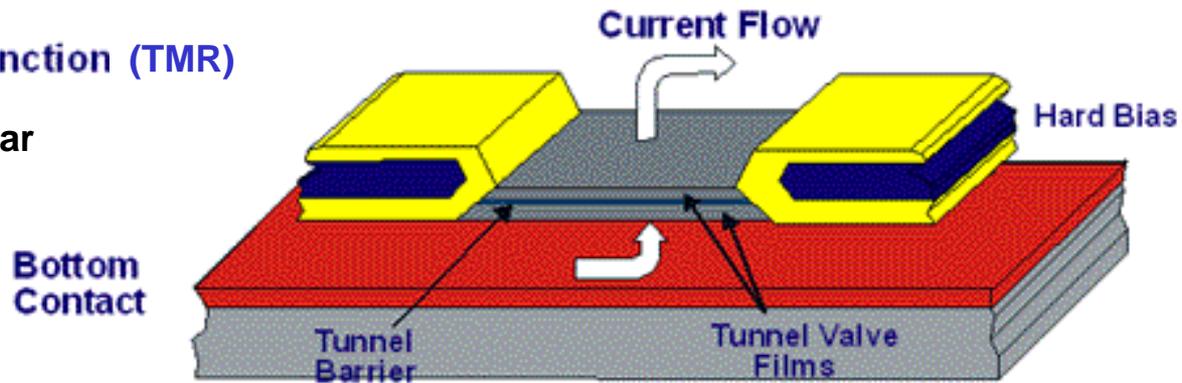
Spin Valve (GMR)

Current in plane (CIP)



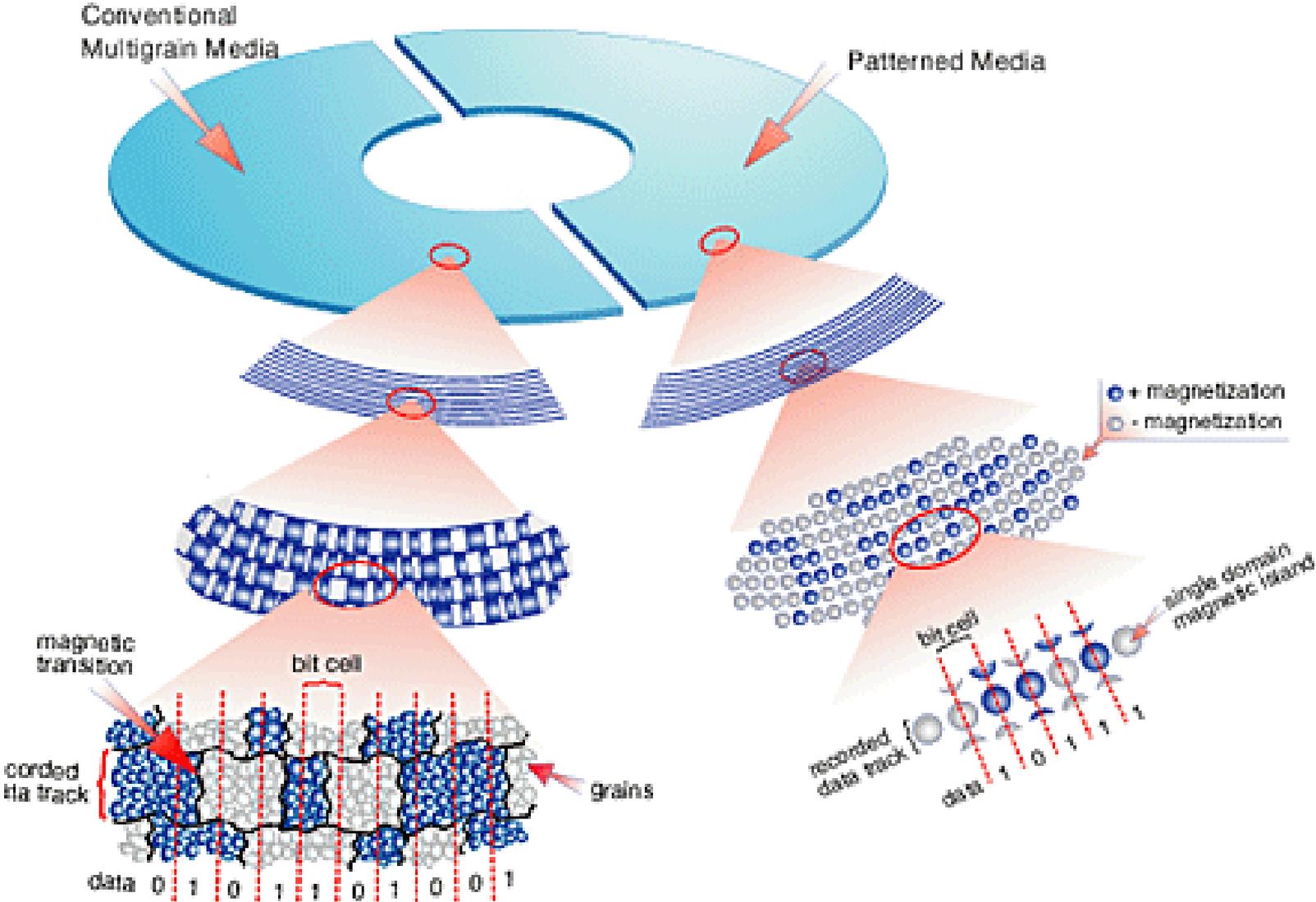
Magnetic Tunnel Junction (TMR)

Current perpendicular to the plane (CPP)

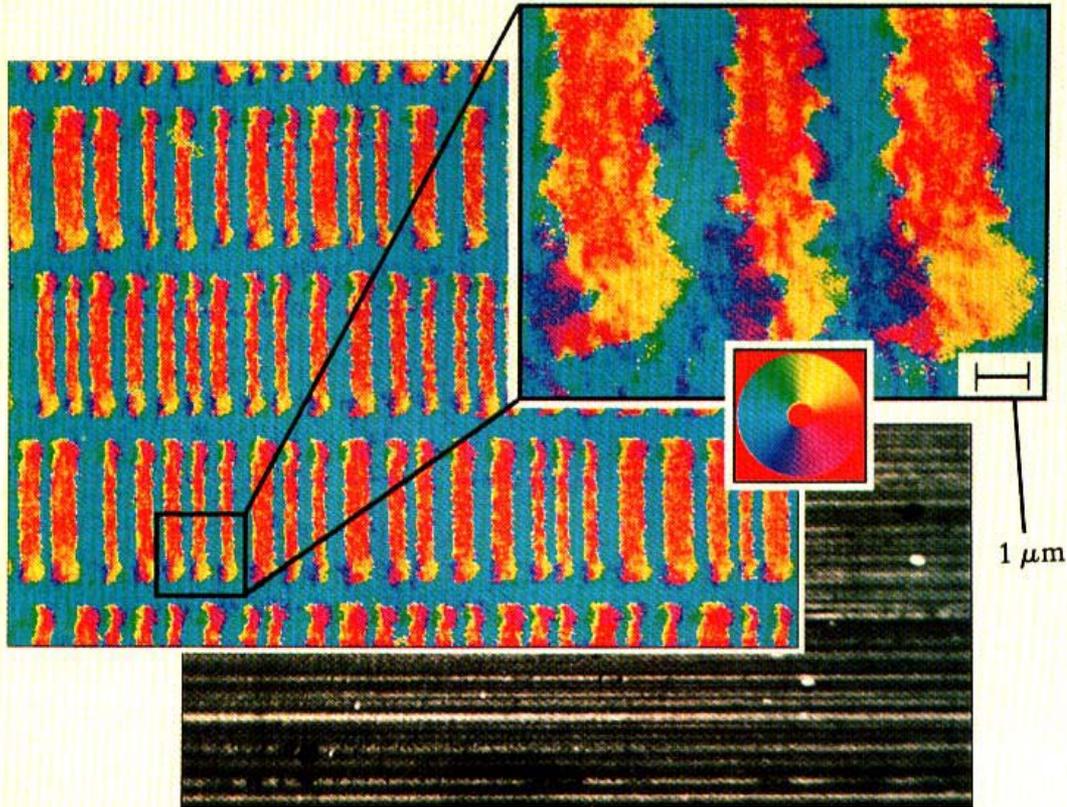


TMR has replaced GMR in hard disk reading heads. The response is larger with the current perpendicular to the interfaces. They act as spin filters. The “Hard Bias” films set the proper magnetization direction.

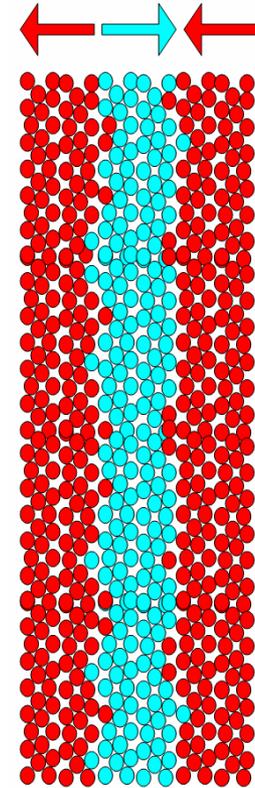
The Ultimate Storage Medium: One Particle per Bit



Magnetic Microscopes are Crucial for Analyzing the Magnetic Patterns in Reading Heads and Storage Media

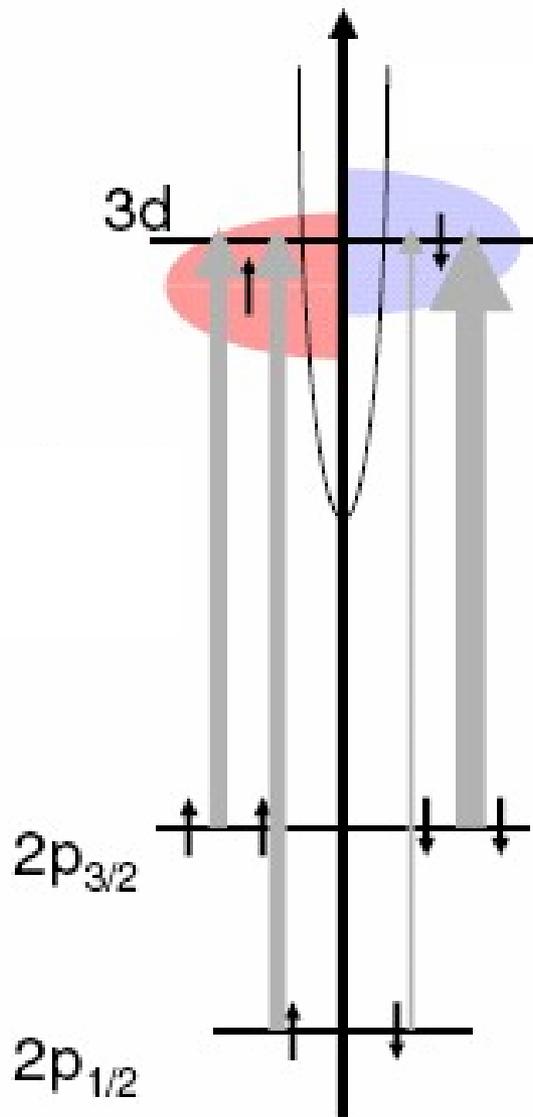


Magnetic image of stored bits on a hard disk, obtained with a spin-polarized electron microscope
(J. Unguris)



Schematic structure of magnetic bits on a hard disk. They are composed of 10 nm CoPtCr particles.

Magnetic Circular Dichroism (MCD or XMCD)

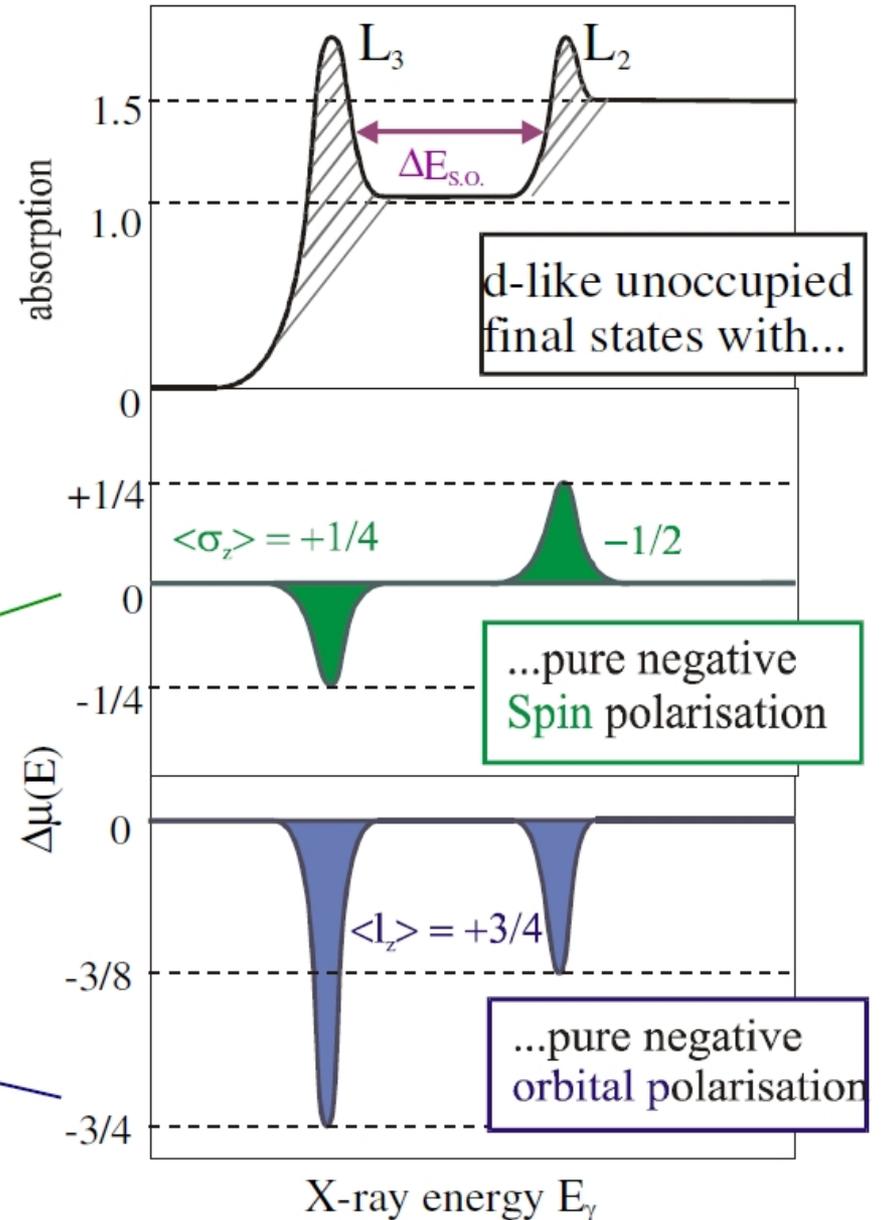


Use dipole selection rules for circularly-polarized X-rays to preferentially excite spin-polarized valence states from unpolarized core levels. The helicity of the X-rays is switched from parallel to anti-parallel (relative to the magnetization). The difference spectrum then provides magnetic contrast in X-ray microscopes (Lecture 1, Section 6).

A similar method for obtaining magnetic contrast in antiferromagnets uses linearly-polarized light rotated by 90° .

Orbital vs. Spin Magnetic Moment

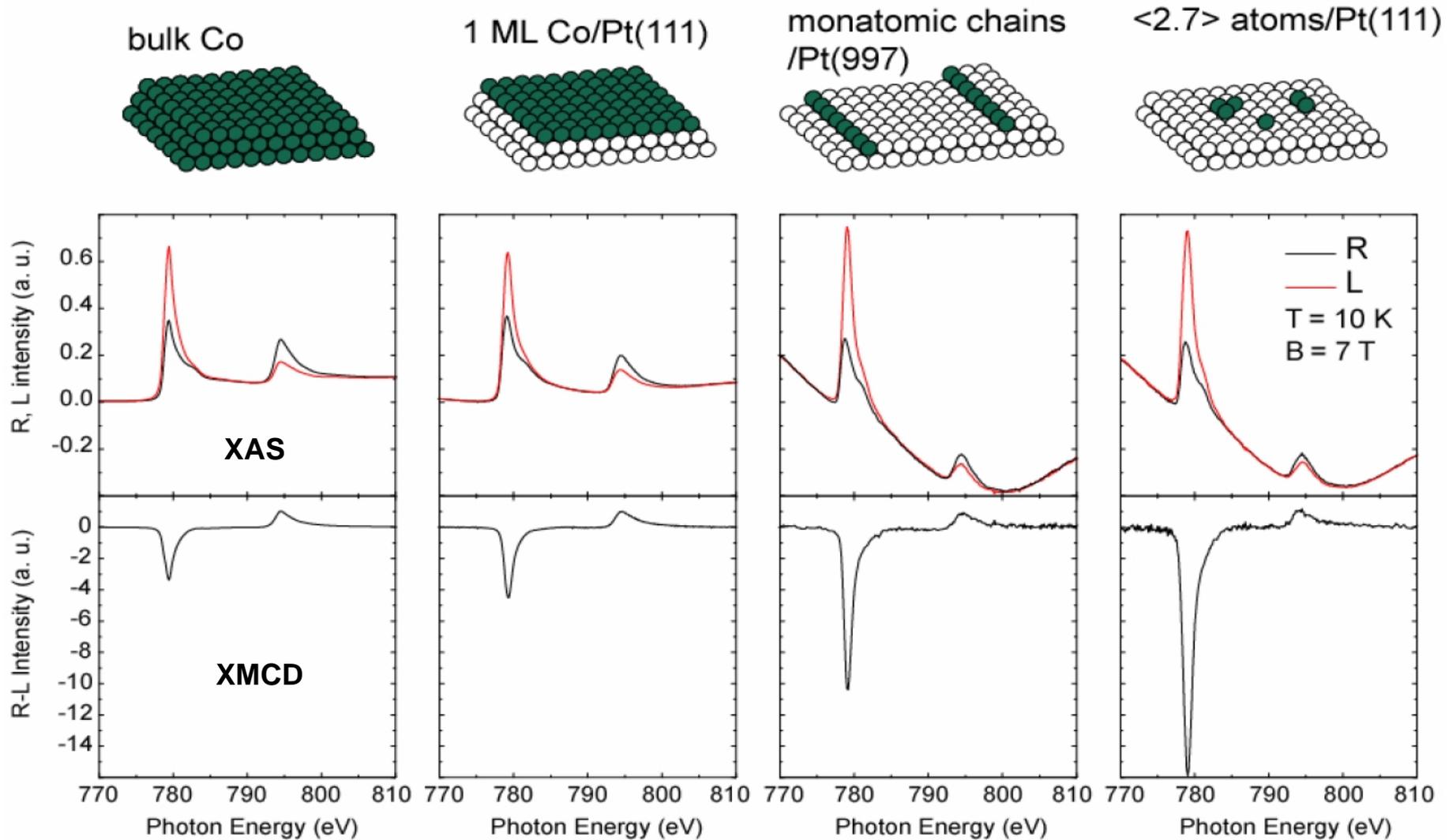
difference spectra
 $\Delta\mu = \mu^+ - \mu^-$
 schematically



Sum rules:
 Fit the experimental spectrum by a weighted addition of both contributions to obtain spin and orbital moments

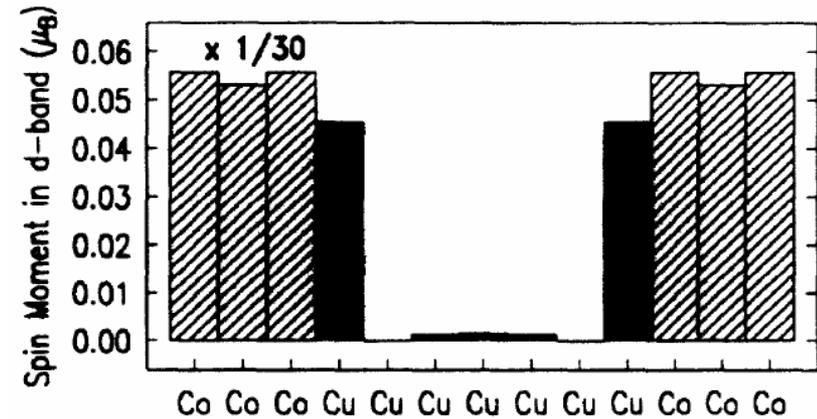
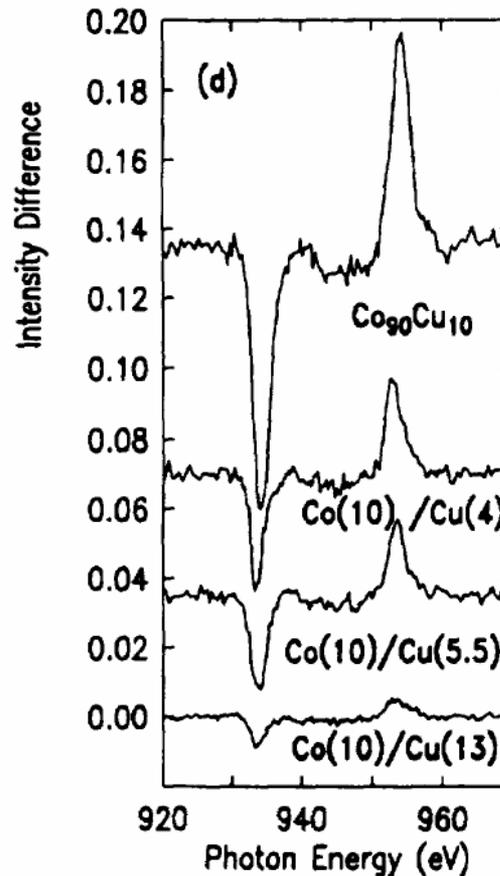
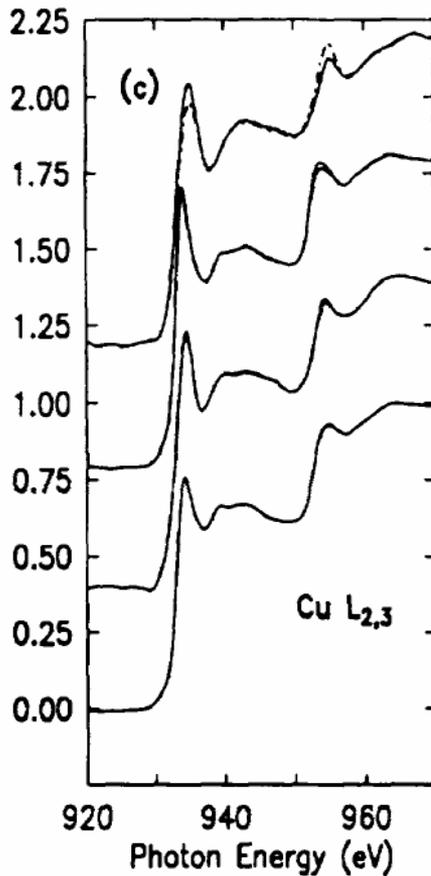
(B. Mesler)

Magnetic moments from 3D to 0D



- The magnetic moment increases (max. in atoms, Hund's rule)
- The Curie temperature decreases (fewer neighbors)

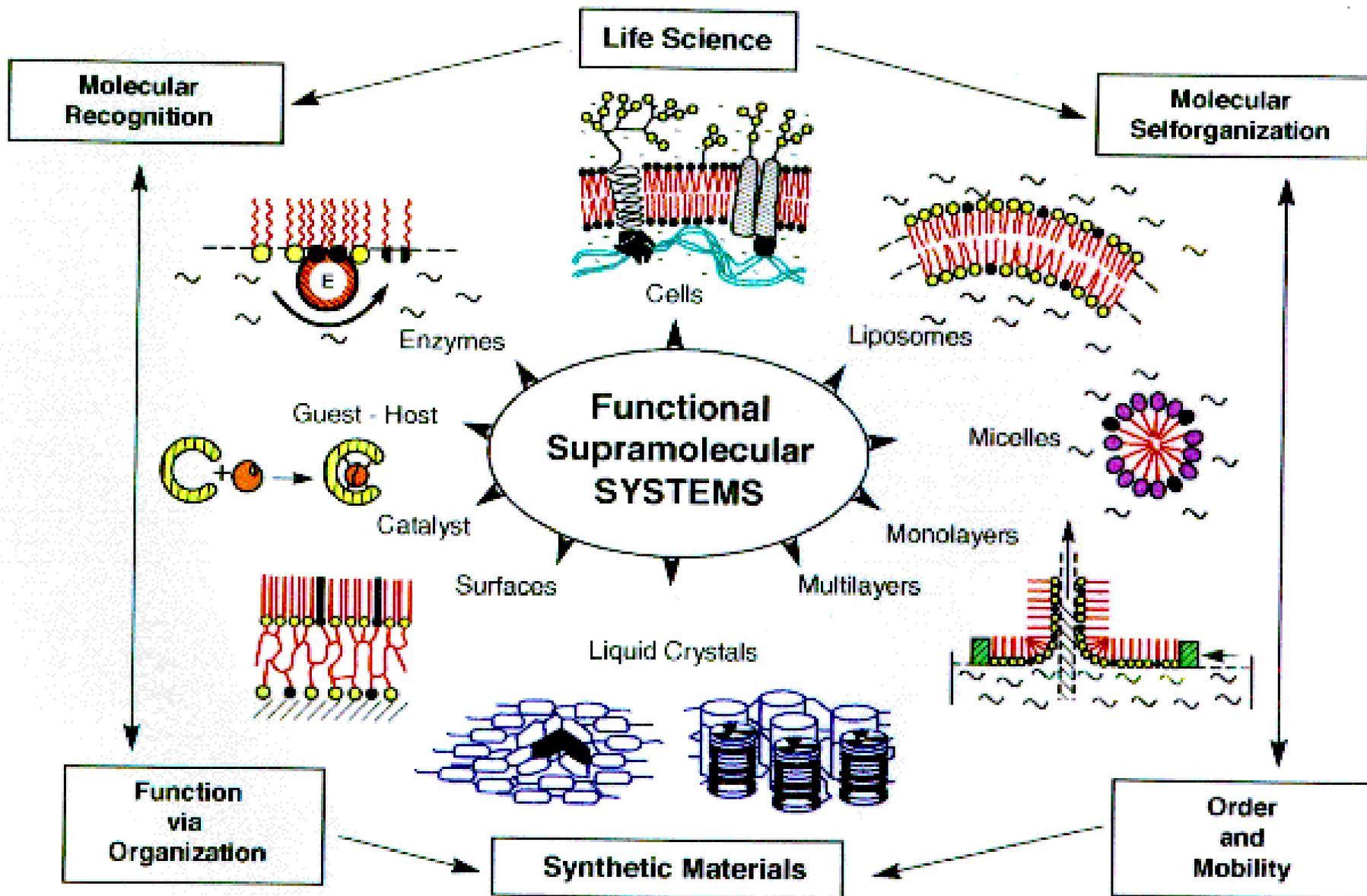
Element-Specific Magnetization in CoCuCo multilayers



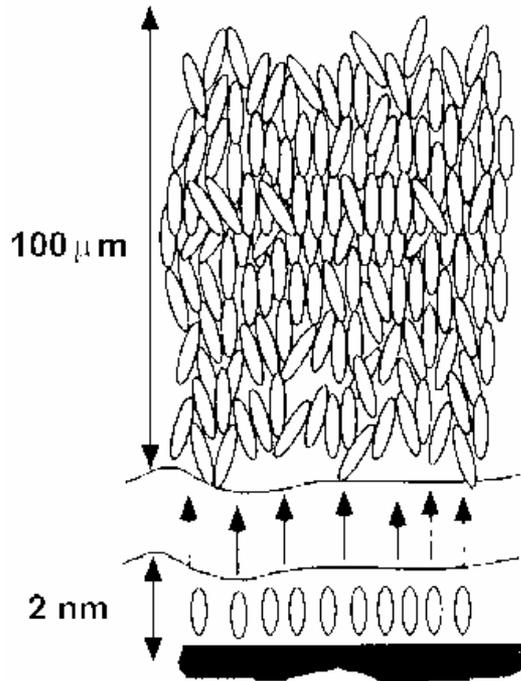
- Measure the magnetic moments of Cu and Co separately at their $L_{2,3}$ edges.
- Surprisingly, Cu acquires a magnetic moment by hybridization with the Co 3d states.
- This induced magnetism is restricted to the interface layer.
- Similar layers were used in GMR reading heads.

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Natural Biomolecule Assemblies

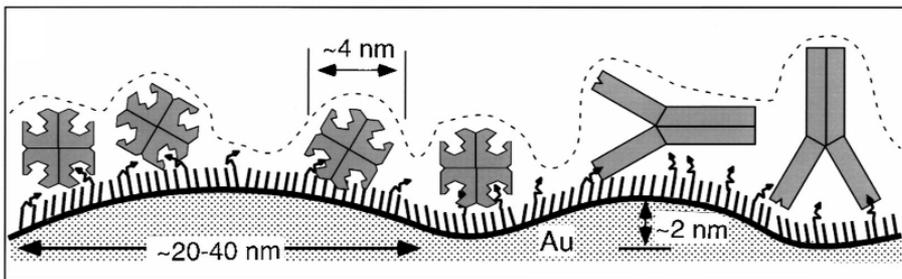


Liquid Crystals as Biosensors



A monolayer of liquid crystal molecules at the interface determines the orientation of the whole 100 μm film, leading to **amplification factors of $>10^4$** .

This effect has been used to **detect proteins and/or viruses** by attaching antibodies to the surface of a sensor which has been made bio-compatible by alkane thiols. A virus attaches itself to its antibodies. A virus scrambles the orientation of the liquid crystal which can be read out optically in the field.

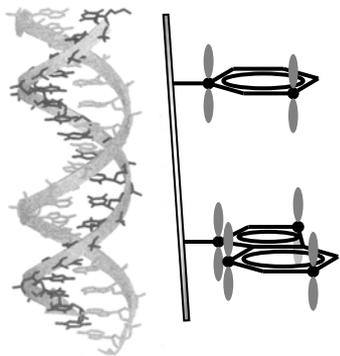


Immobilization of biomolecules at surfaces is used in **DNA and protein microarrays**.

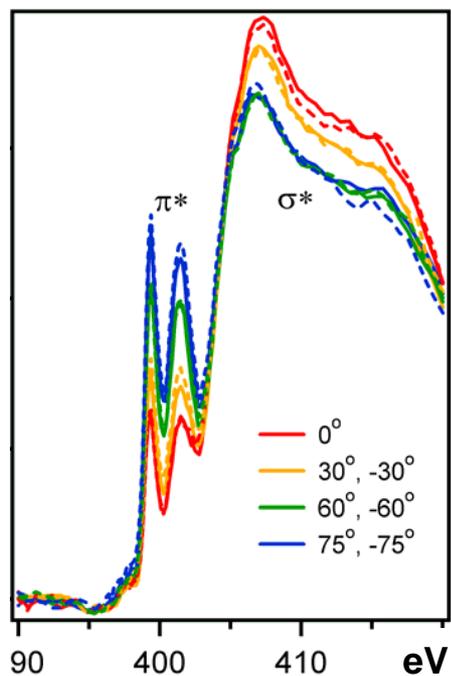
The N1s Edge Targets Key Orbitals of Biomolecules

DNA:

π^* orbitals of the nucleotide bases

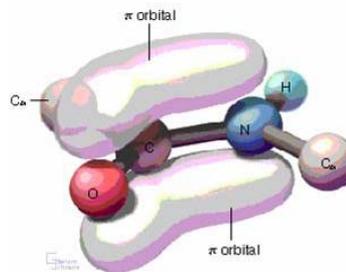


Oriented DNA

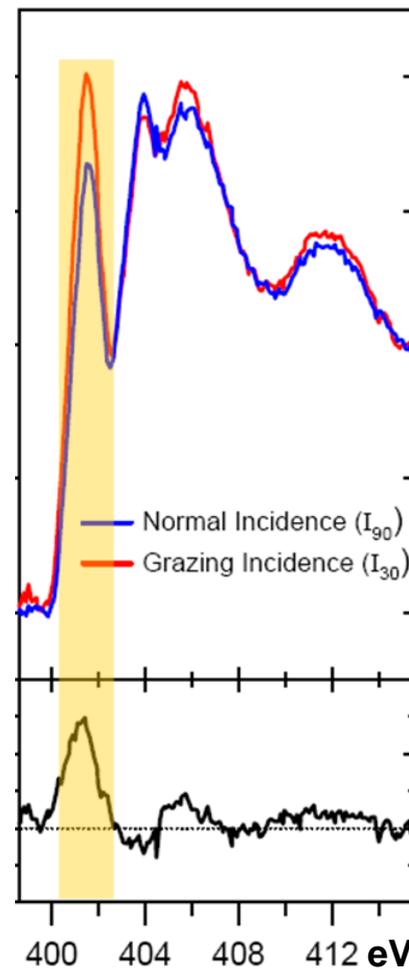


Proteins:

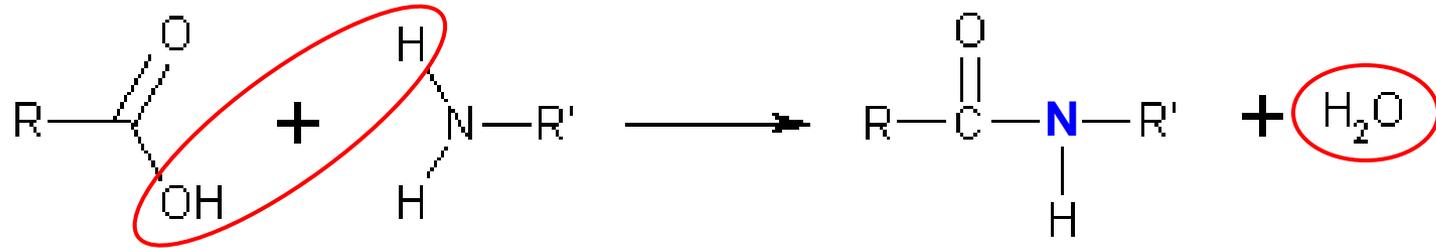
Peptide bond between amino acids



Oriented RNase A

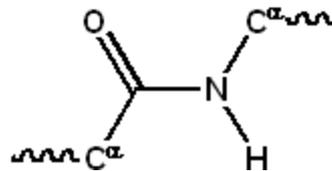


The Peptide Bond Connecting Amino Acids in Proteins



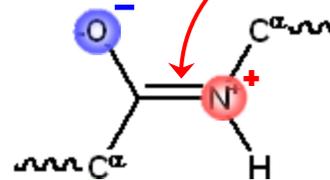
Two amino acids react.

A nitrogen atom bridges them.



covalent

+

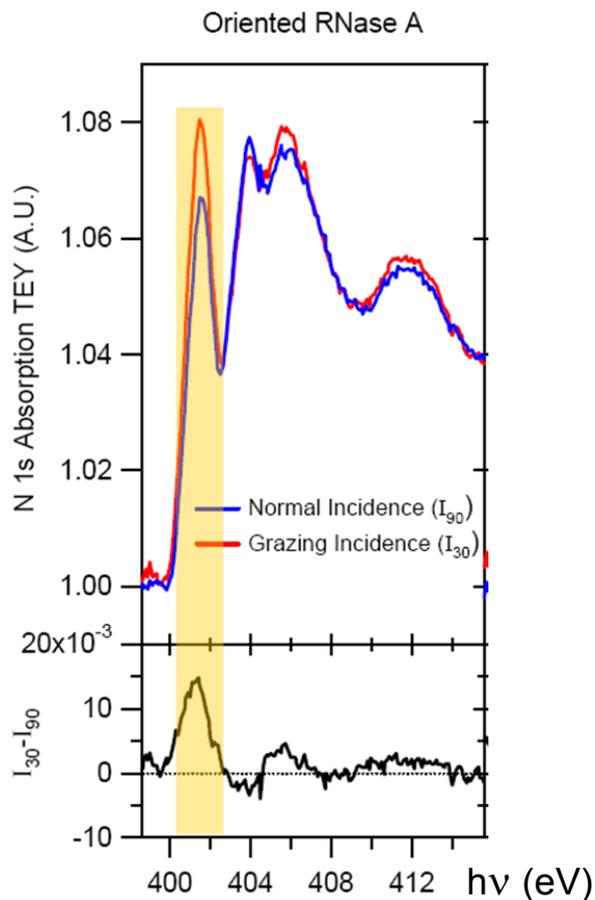


(zwitter)-ionic

See the π^* orbital of this double bond at the N1s edge.

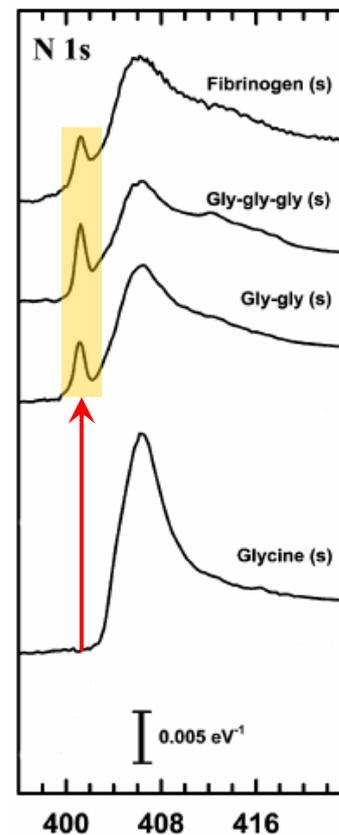
Signature of the Peptide Bond at the N1s Edge

The π^* of the peptide bond is the largest N 1s peak.



Langmuir **22**, 7719 (2006)

Need a dimer to establish the π^* peptide bond orbital.

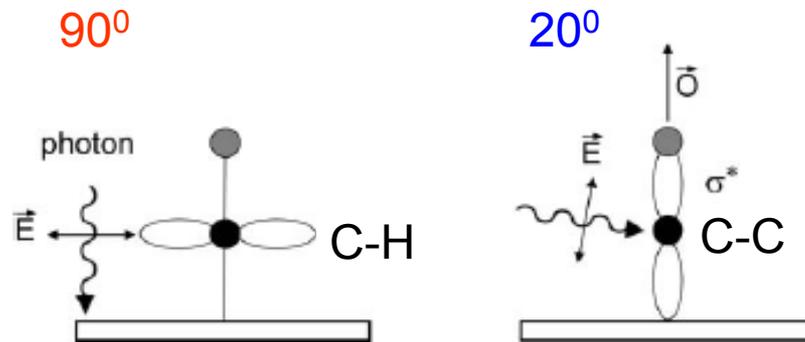


J. Phys. Chem. A **107**, 6144 (2003)

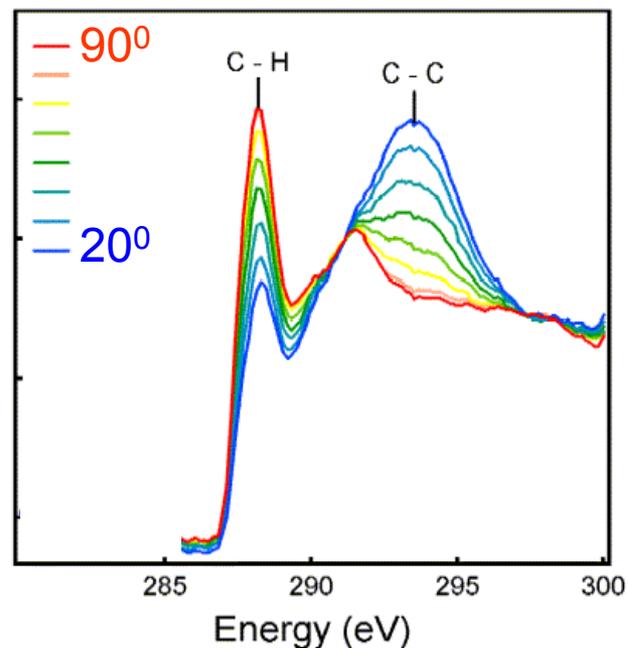
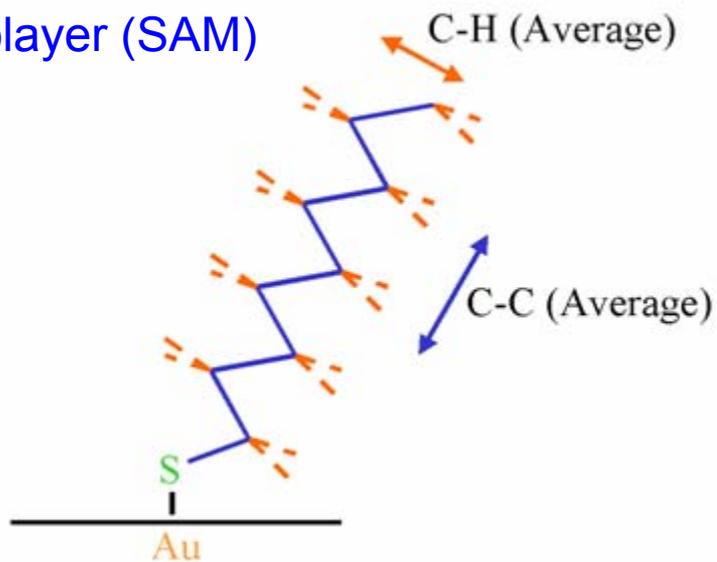
Molecular Orientation from Polarization-Dependent XAS

Dipole selection rules:

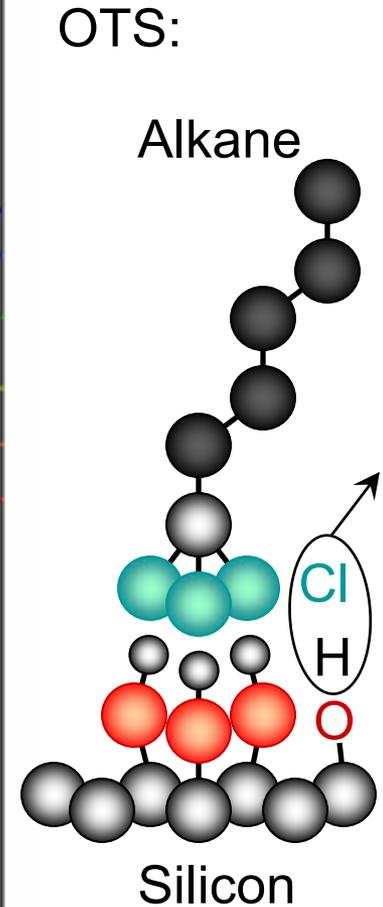
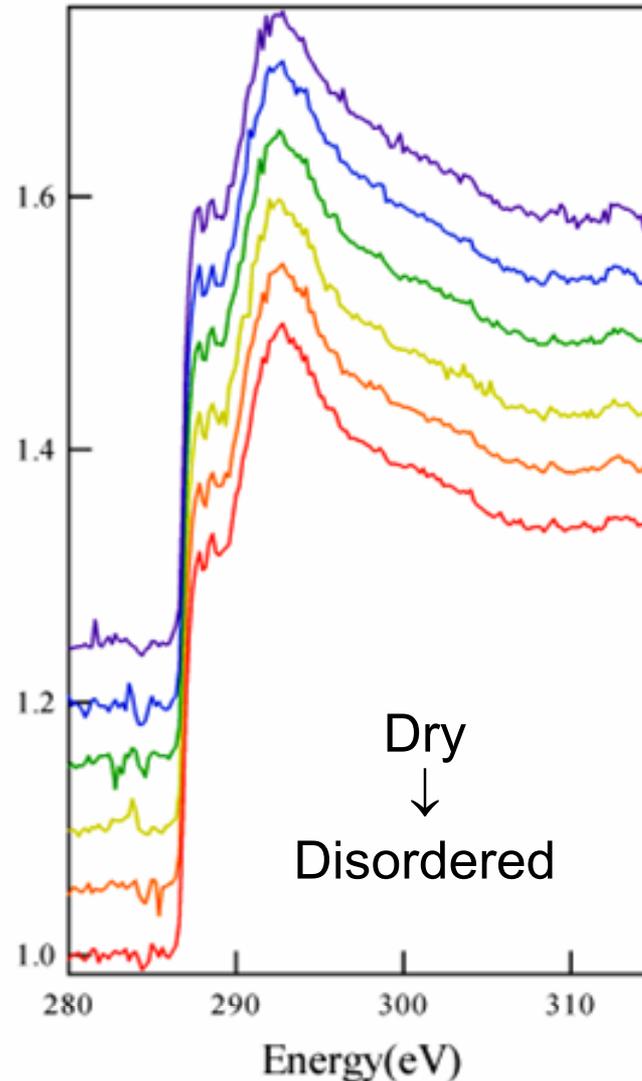
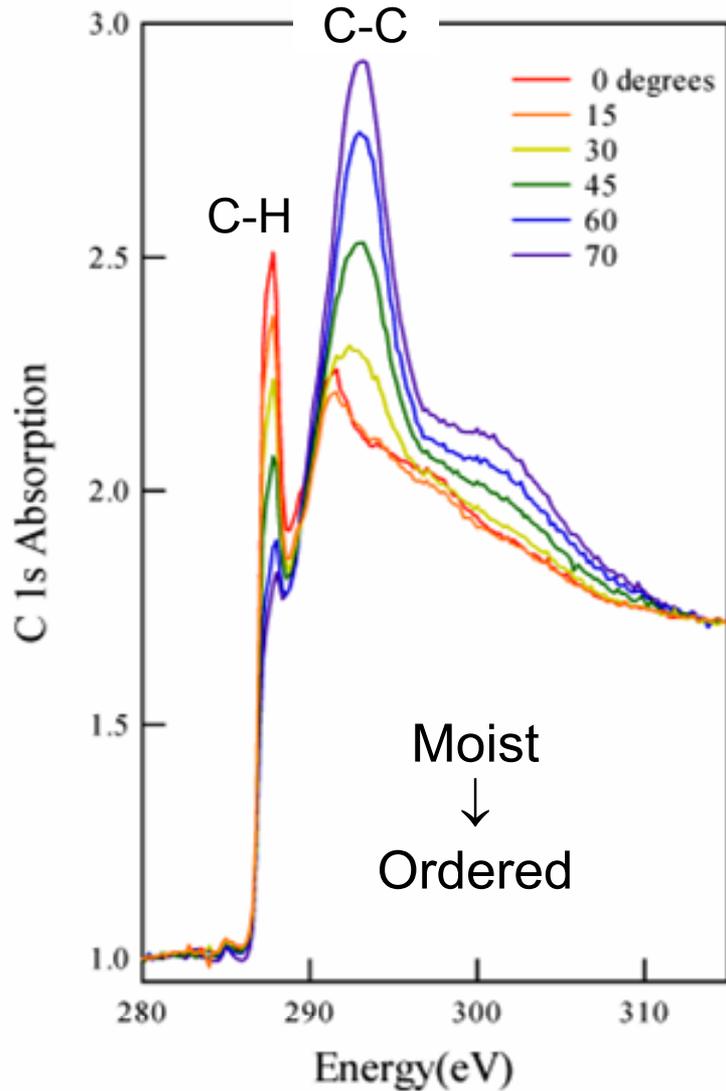
- $l \rightarrow l \pm 1$, here $s \rightarrow p$
- Electric field vector \vec{E} parallel to the orientation of the molecular orbital



Self-assembled monolayer (SAM)



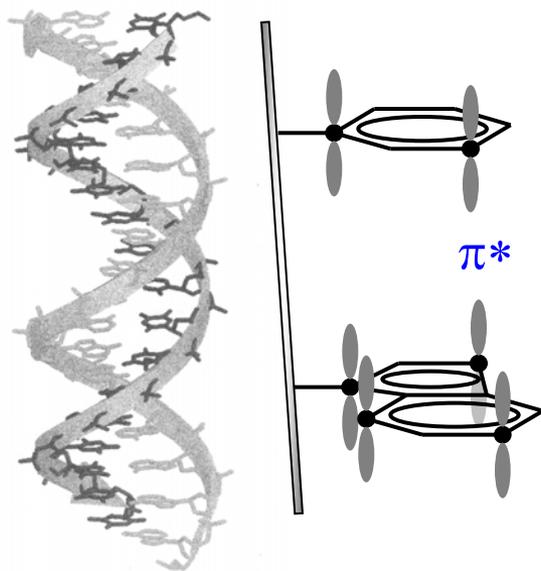
Attaching Alkanes to Silicon via Siloxane Chemistry



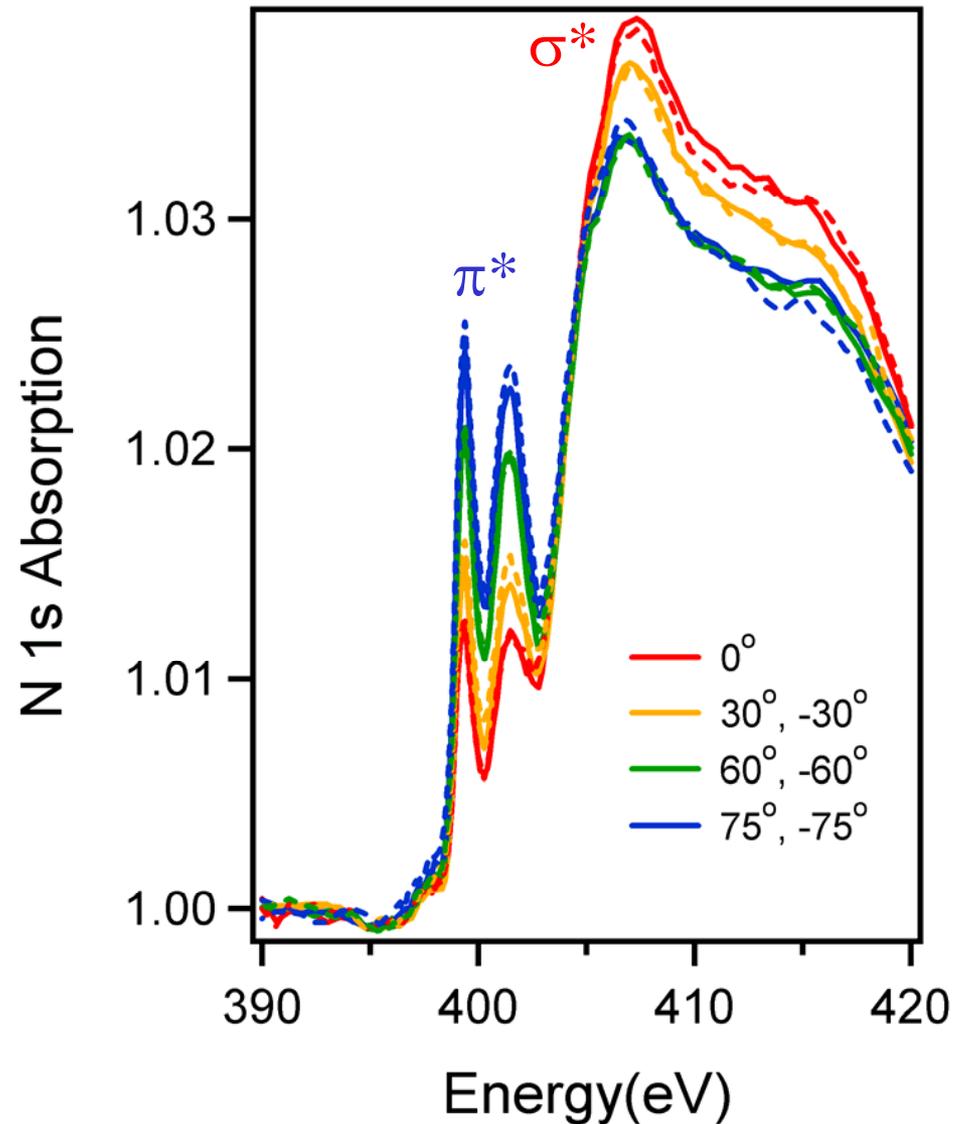
Preparation is Critical

Langmuir **18**, 1250 (2002)

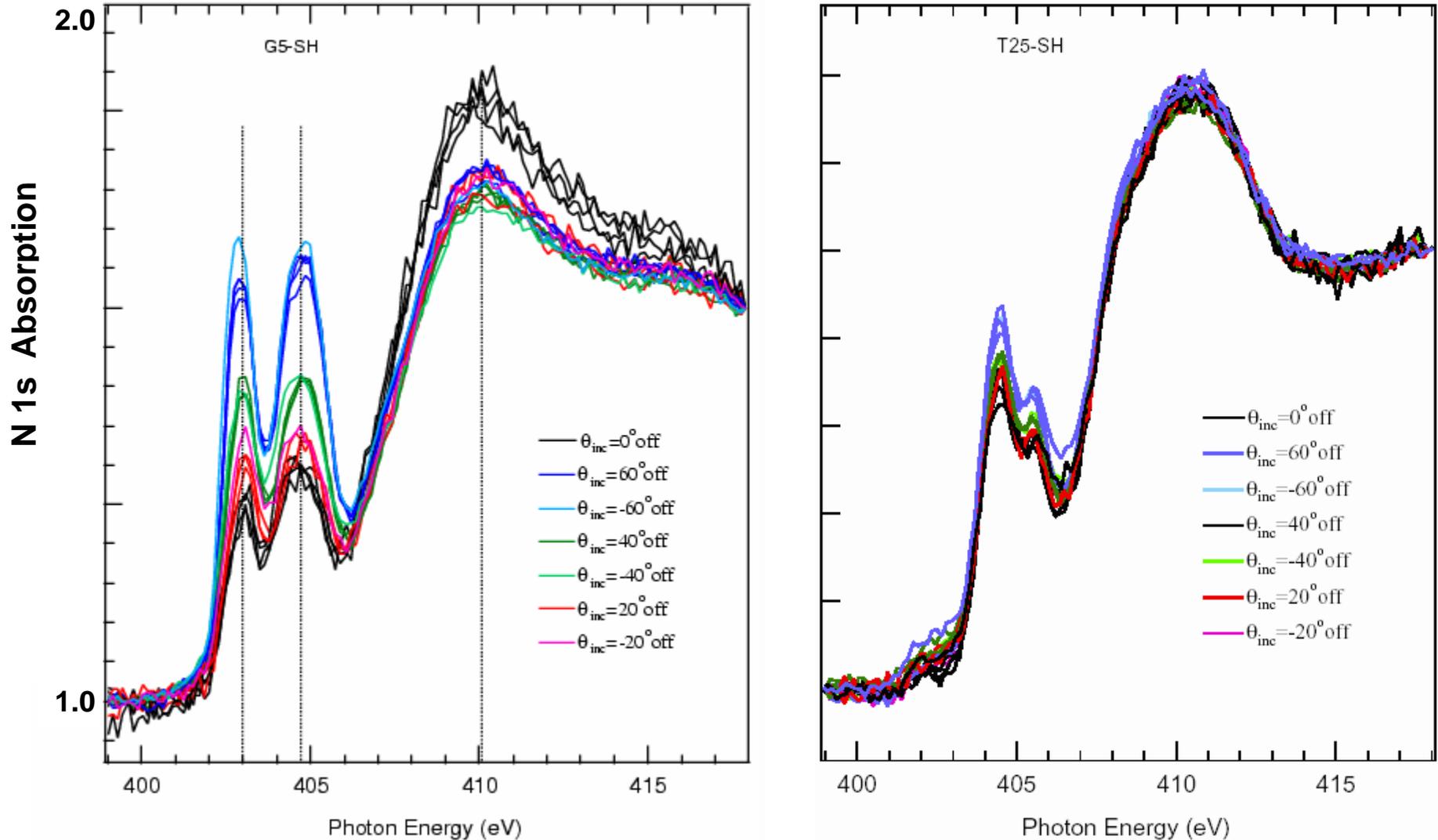
Orbital Orientation of DNA at a Surface



- All $N2p \pi^*$ orbitals are parallel to the axis of the double-helix.
- Selective excitation from the $N1s$ core level eliminates the orbitals located at C atoms.

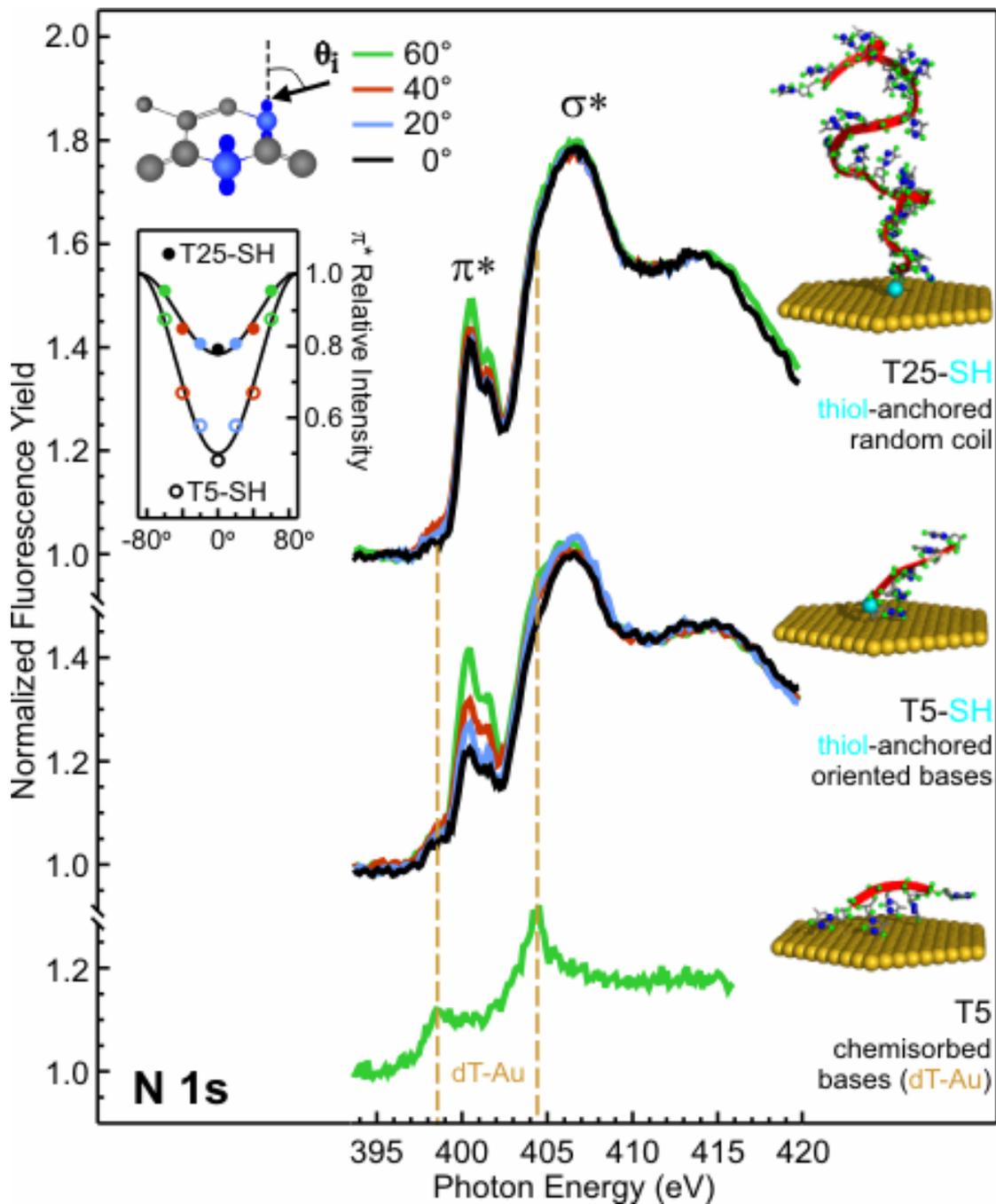


Short DNA Oligomers are Better Oriented



Fluorescence detection improves signal/background (100% , versus 4% for electrons in the previous slide)

Orientation of DNA attached to Au via Thiol Chemistry (DNA Chips)

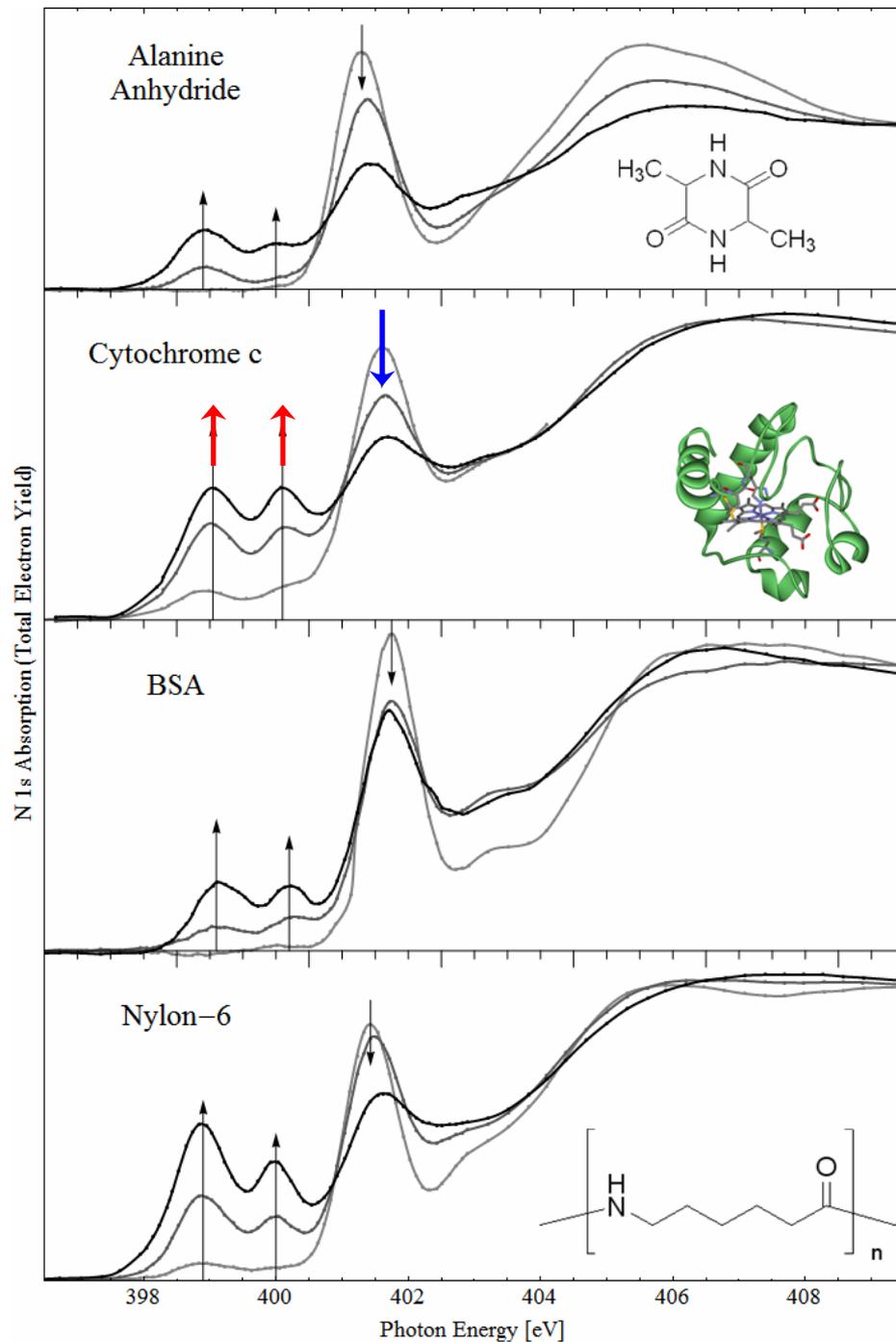


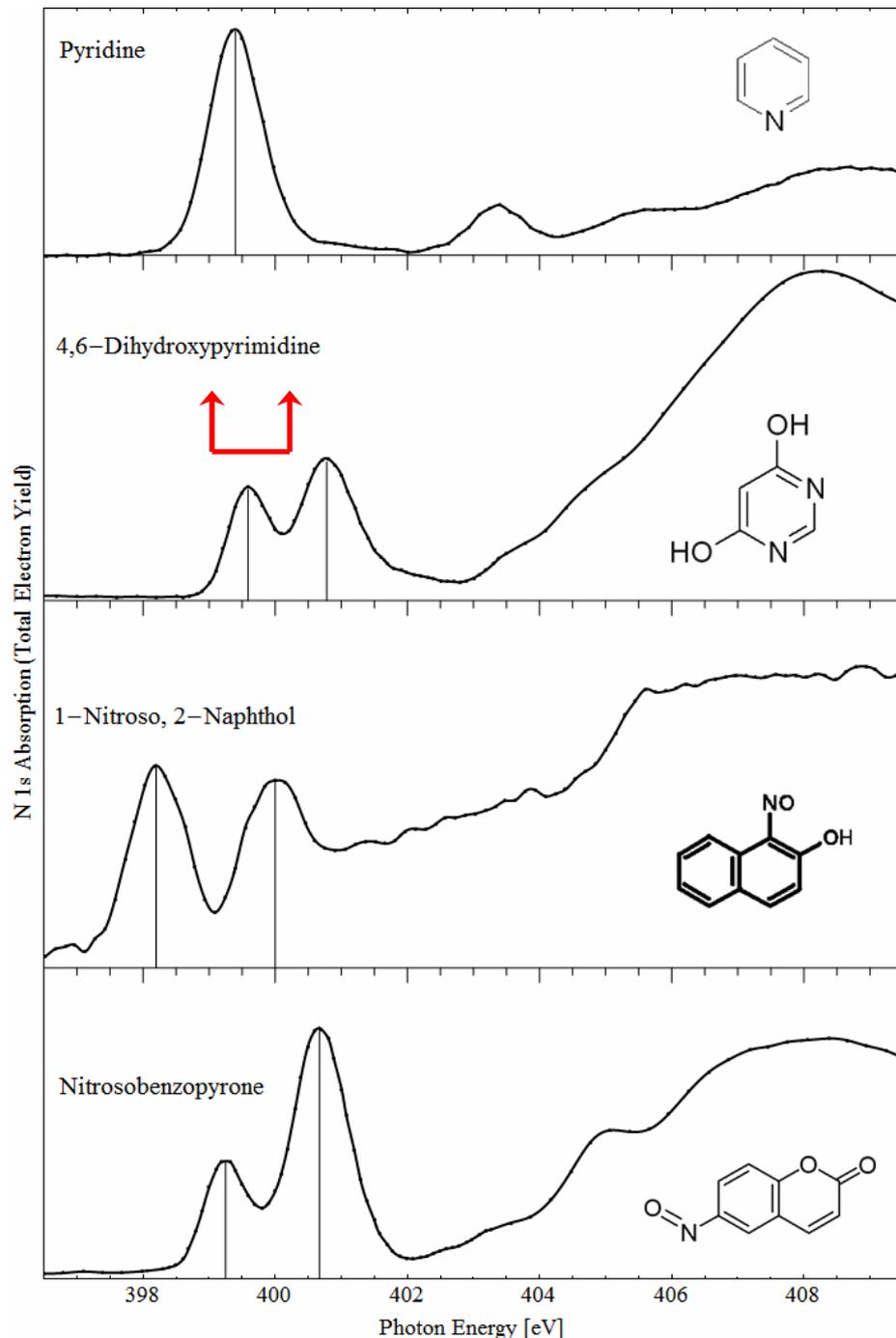
Single-stranded DNA needs to be accessible to hybridization with the target DNA.

Radiation Damage of the Peptide (Amide) Bond

- The π^* peak of the peptide bond weakens.
- A new π^* doublet appears.
- Universal (small and large proteins, amide polymers, such as nylon)

J. Chem. Phys. **135**, 044702 (2011)





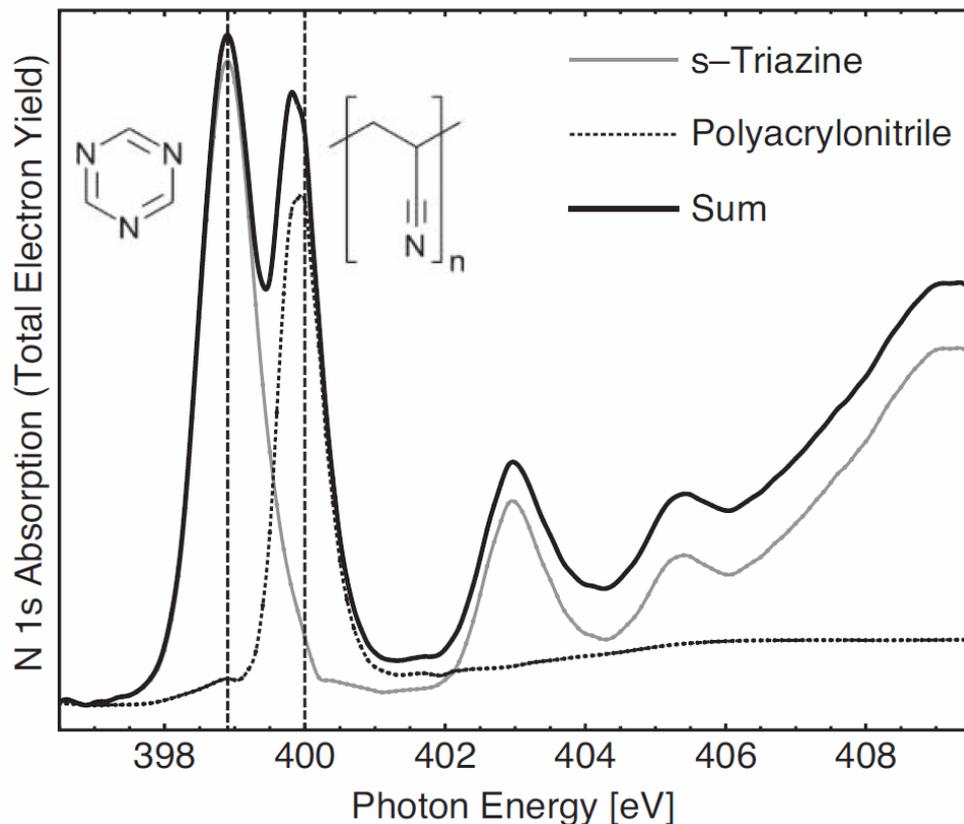
Identify the Reaction Product(s) Using Reference Molecules

Model compounds for fingerprinting:

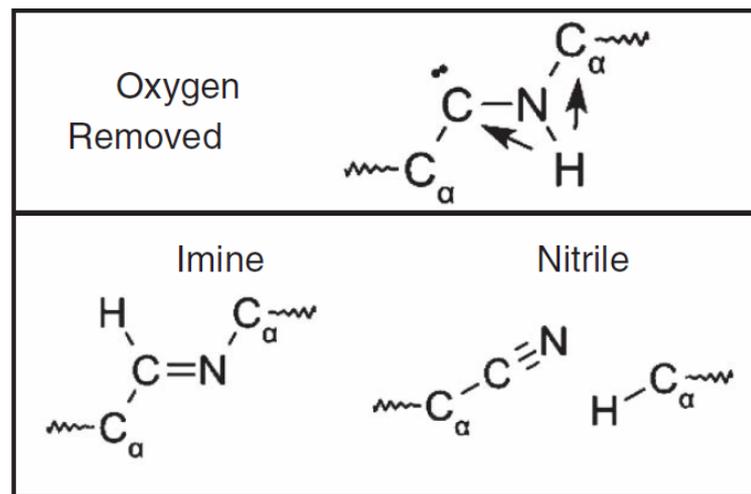
- Imine (top two panels)
 - Nitroso (bottom two panels)
 - Nitrile (not shown)
- Symmetric imines have a single π^* near the position of the lower peak.
 - An asymmetric imine has a doublet similar to that of the **broken peptide bond**, but it is shifted in energy.
 - The splitting is too large in nitroso and too small in nitrile groups.
 - Tested many more molecules.

Two Reaction Products and a Model of Bond Breaking

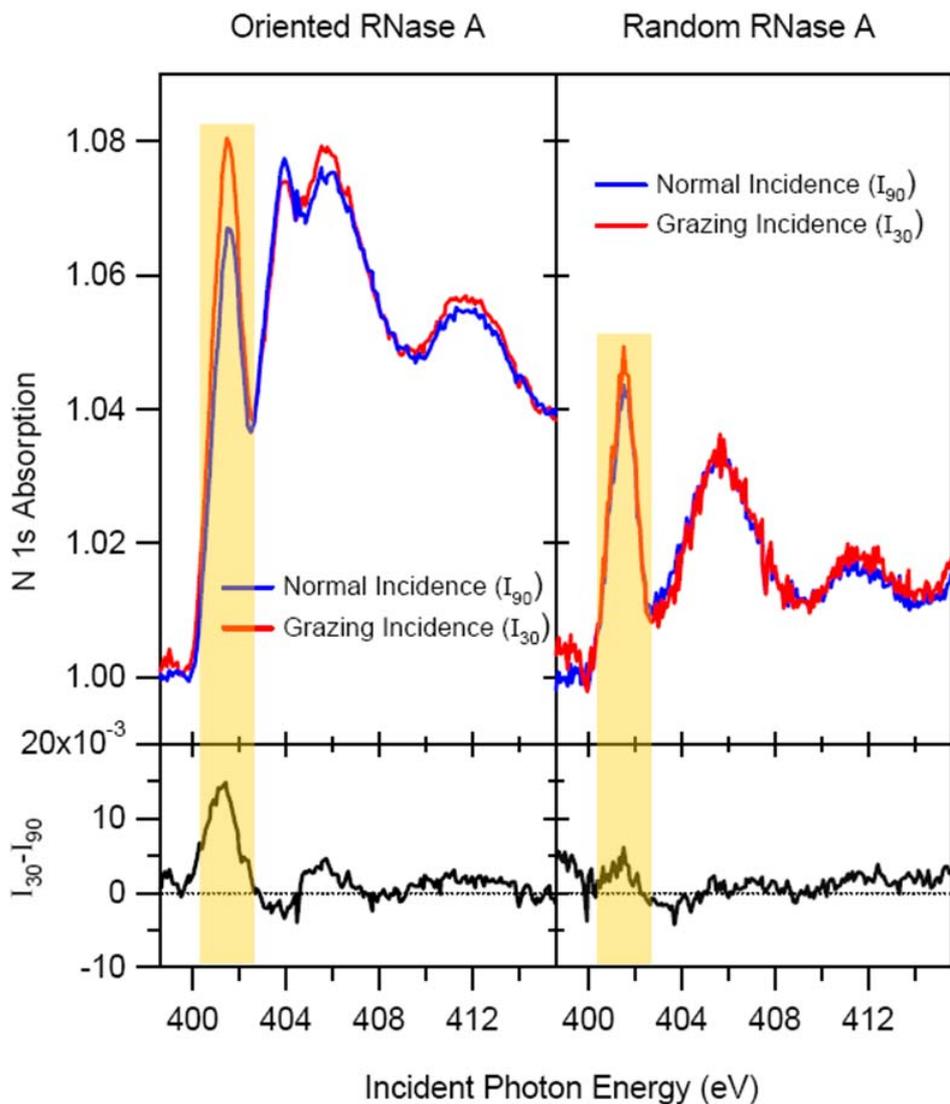
The final analysis yields two products for the photochemical breaking of the peptide bond: imine and nitrile. They explain the radiation-induced peaks (vertical dashed lines below). These can be modeled by a sum of an imine and a nitrile spectrum.



Results at the O1s edge suggest a de-oxygenation as initial step of the photochemical reaction. There are two options for the amino hydrogen to heal the broken C=O bond, indicated by two arrows. These lead to imine and nitrile as products.

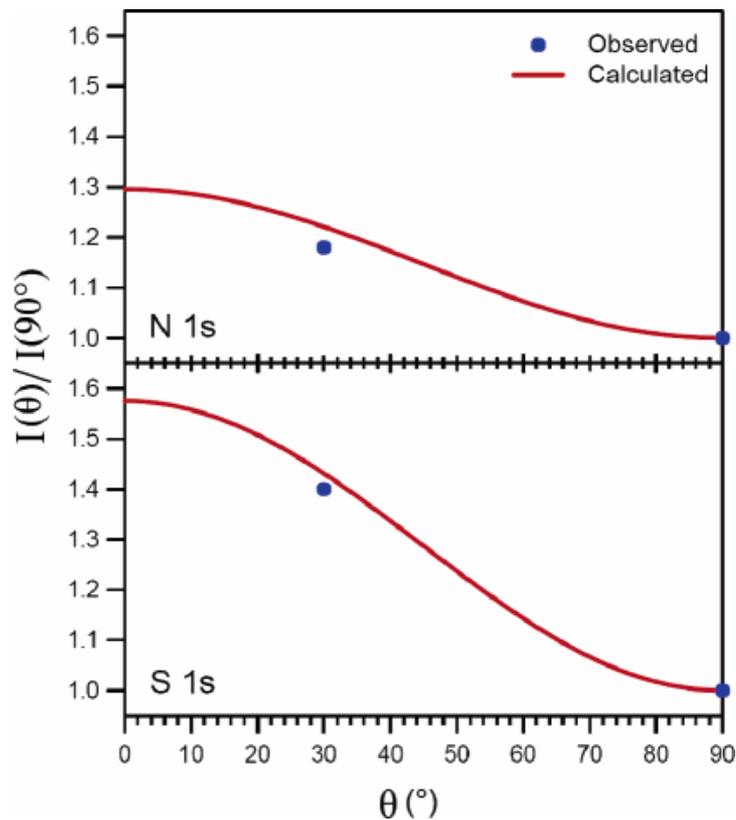


Toward Larger Biomolecules: RNase A with 124 Amino Acids



Langmuir **22**, 7719 (2006)

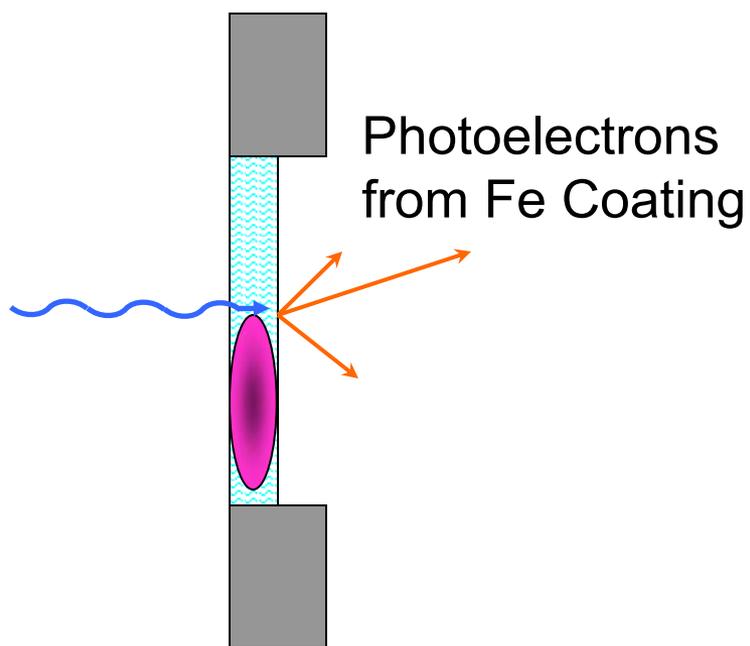
As the number of inequivalent N atoms increases, it helps to consider the sulfur 1s edge, since S is present only in a few amino acids. That leads to stronger polarization dependence.



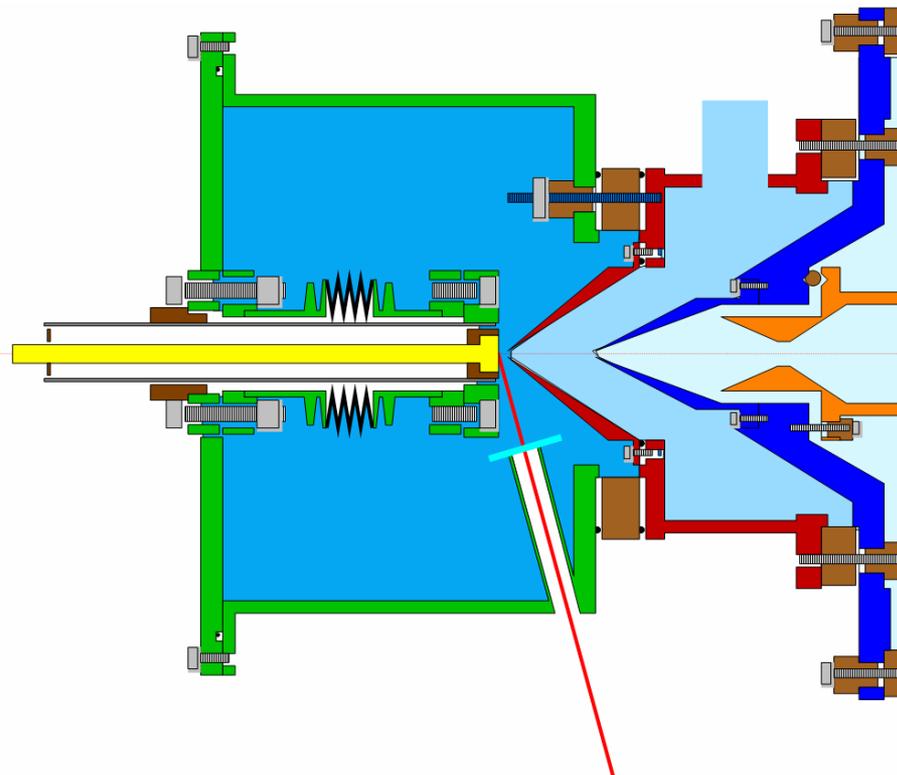
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“Wet” XAS and XPS

XAS: Wet cell with Si_3N_4 windows



XPS: Differential pumping of water vapor



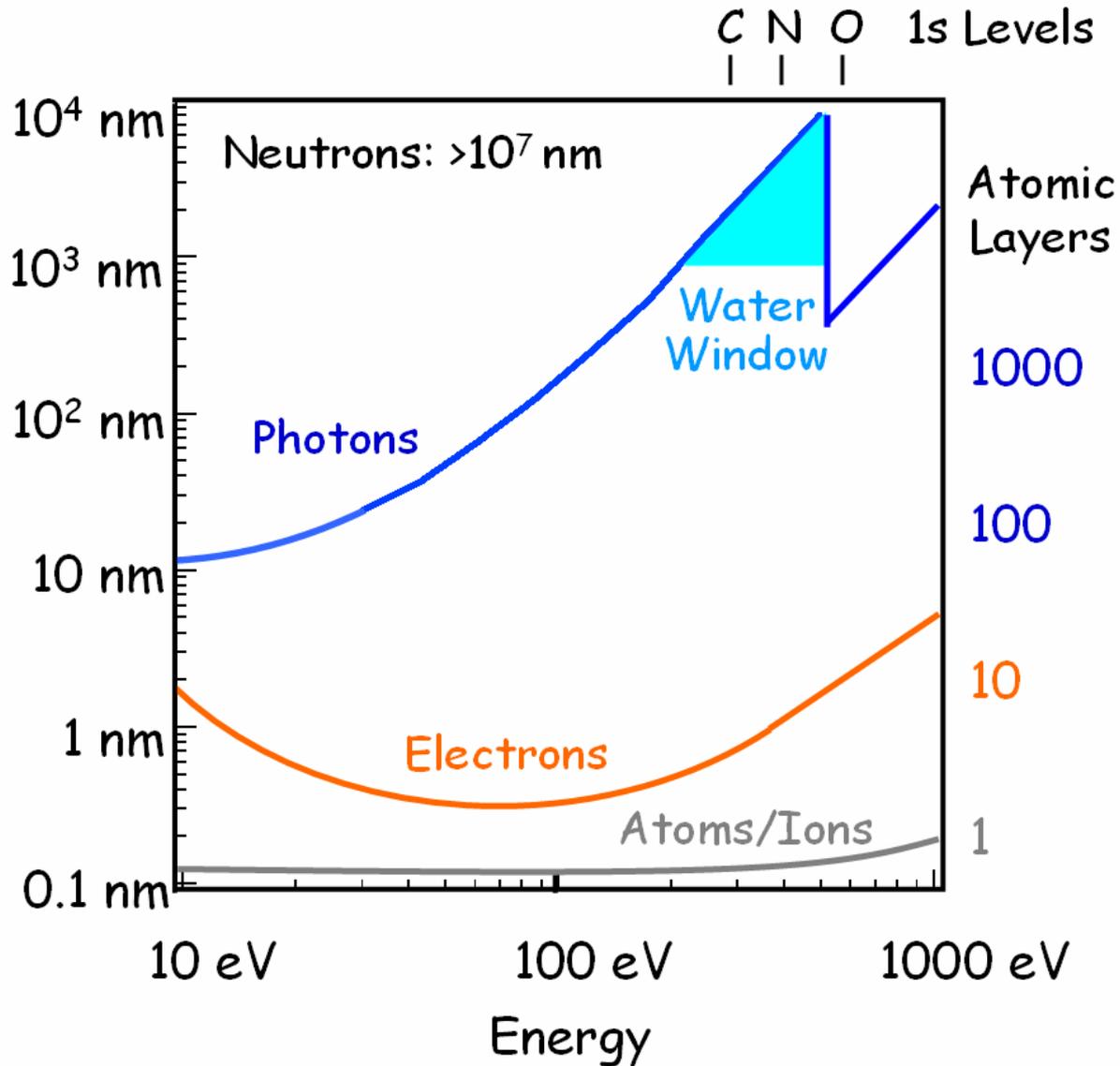
Reviews:

J. Chem. Phys. **119**, 10467 (2003)

Surface Science Reports **63**, 169 (2008)

Adv. Mater. **27**, 1512 (2015)

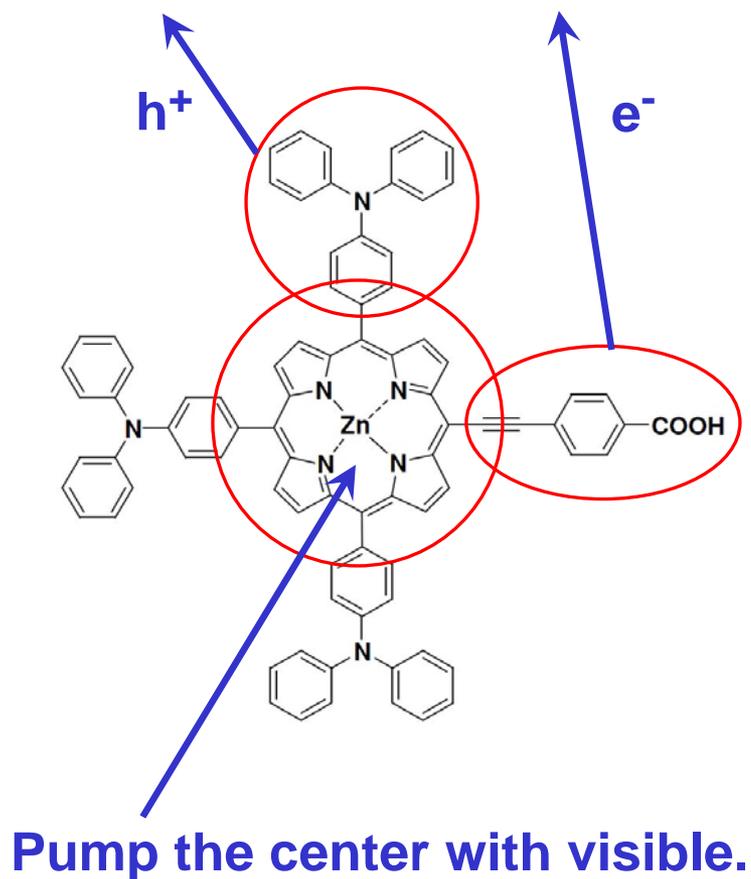
Probing Depths of Various Particles



1. **Photovoltaics and OLEDs**
2. **Two- and one-dimensional systems**
3. **Semiconductor surfaces and interfaces**
4. **Magnetic nanostructures**
5. **Immobilization of biomolecules at surfaces**
6. **In-situ, in-operando spectroscopy**
7. **A recent development: ultrafast**

Beyond Energy Levels: Lifetimes vs. Charge Transfer Rates

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

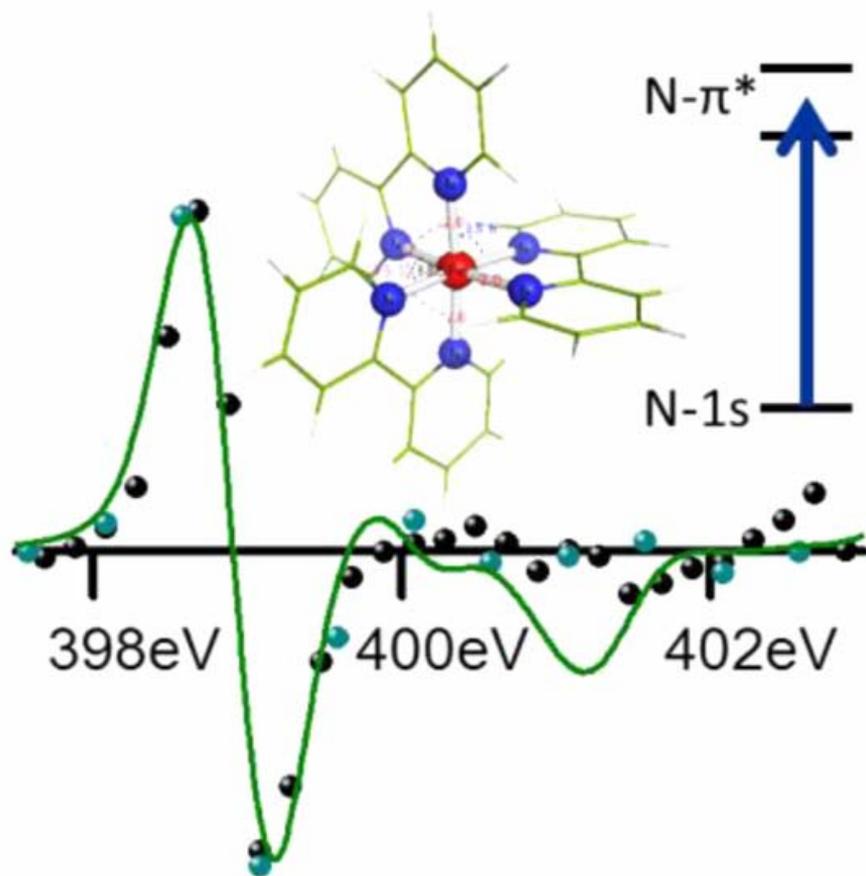


In solar cells, the lifetimes of the charge carriers affect the photocurrent dramatically. It is crucial to find out where carriers are lost: inside a molecule or across an interface?

Add time as extra variable (fs-ns). Ultra-fast techniques are used already in the UV/vis regime, such as nonlinear optics, transient absorption, and 2-photon photoemission.

Need an atom-specific X-ray probe to locate carriers within atomic distances. “Heroic” experiments look promising. But it will take X-ray lasers with high repetition rate (MHz) and small energy per pulse to make this concept practical.

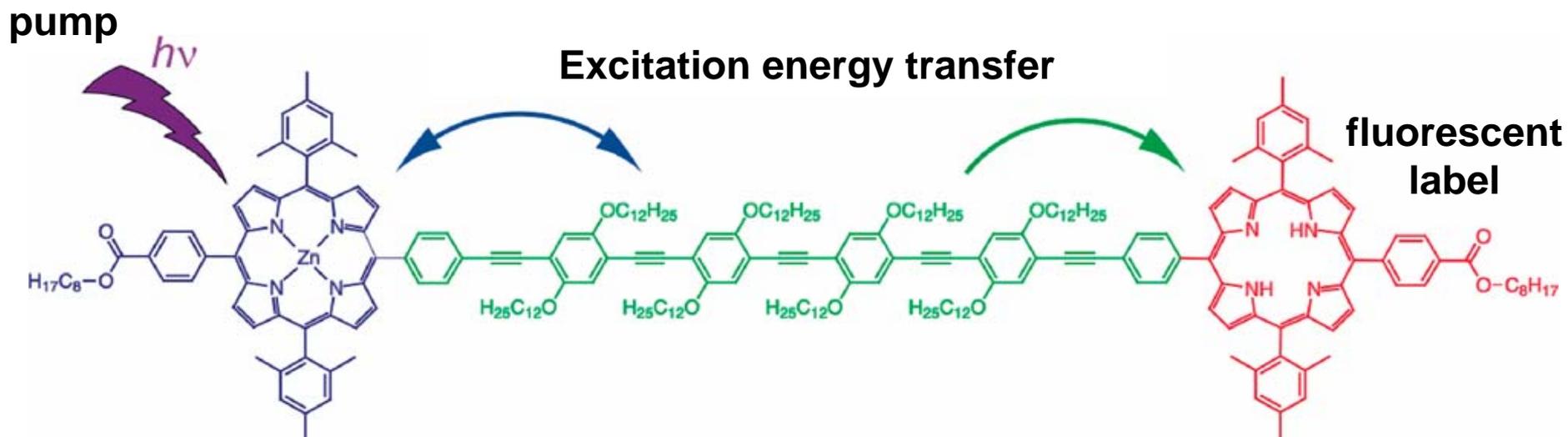
“Heroic” Proof-of-Principle Experiments (≈ 1 spectrum / day)



Pump the central **Fe** atom with visible light. That flips its spin.

Probe the resulting changes in the **N1s** absorption spectrum. The **N1s** \rightarrow π^* transition energy changes slightly. Use this to find out when carriers electrons arrive at the N atoms.

Propagation of Carriers along a Molecular Wire (UV/Visible)



Vary the length of the connecting molecular wire
to find the individual transfer rates.
Make models of rate constants.

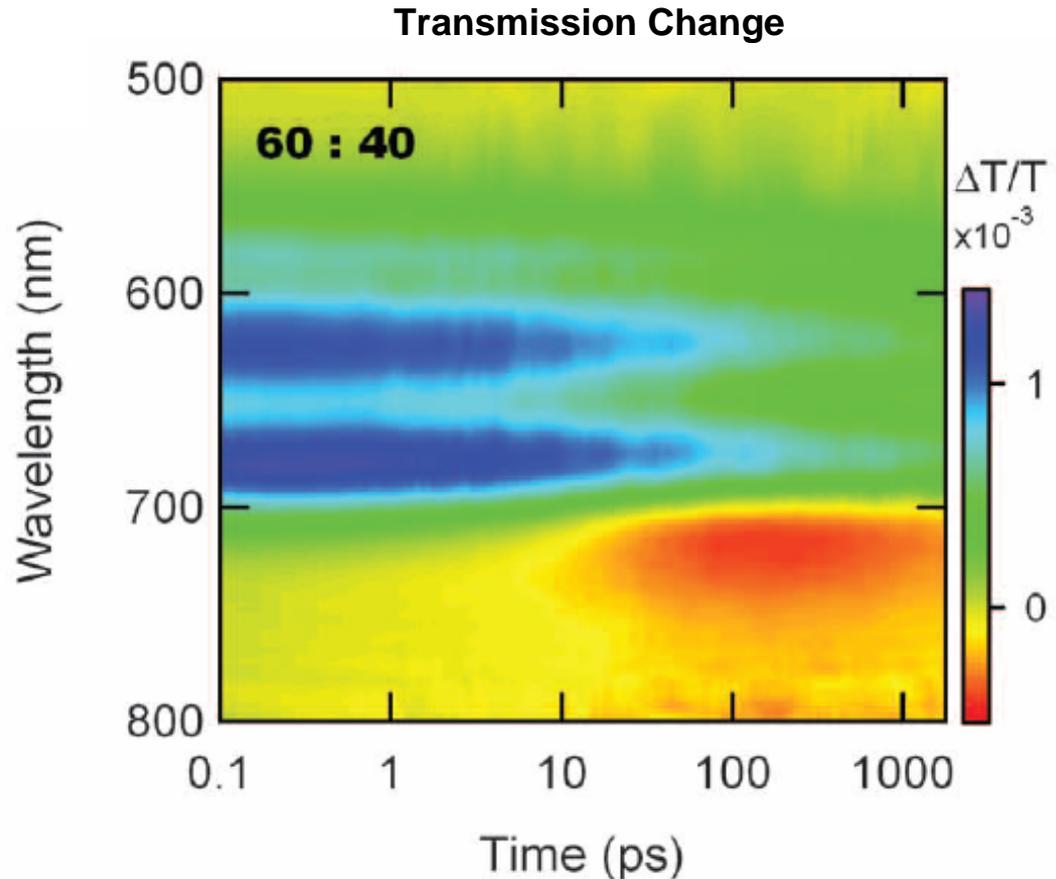
Transient Absorption in the UV/Visible (Standard Tool)

**Bleaching by depopulation
of the ground state.**

**Extra transitions starting
from excited states.**

**Time constants: ps ... μ s
The longer the better.**

Science **343**, 512 (2015)



But where are the carriers lost? At impurities, interfaces, ...?

Need atom-specific data from soft X-rays (sharpest core levels).