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Seeing chemical interactions and dynamics with time-resolved X-ray spectroscopy

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XVIII School on Synchrotron Radiation “Gilberto Vlaic”: Fundamentals, Methods and Applications
21 September-1 October 2026, Muggia (Trieste), Italy

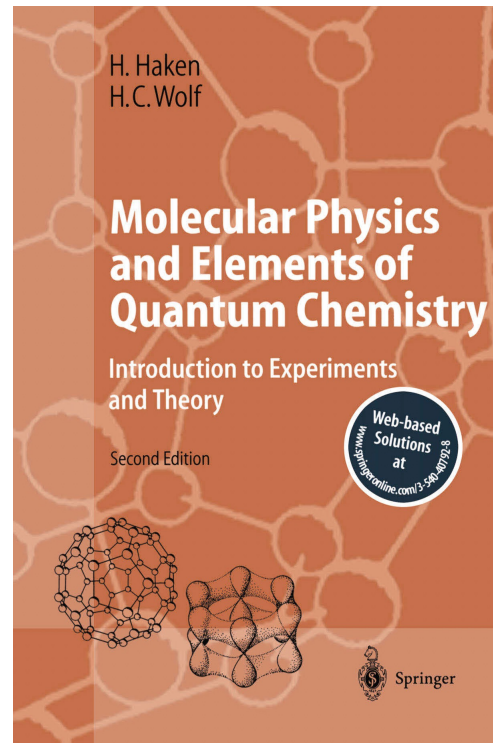
Outline

- A broadly accessible science motivation
- Some basics (throughout)
- Specific examples (from our research at XFELs)

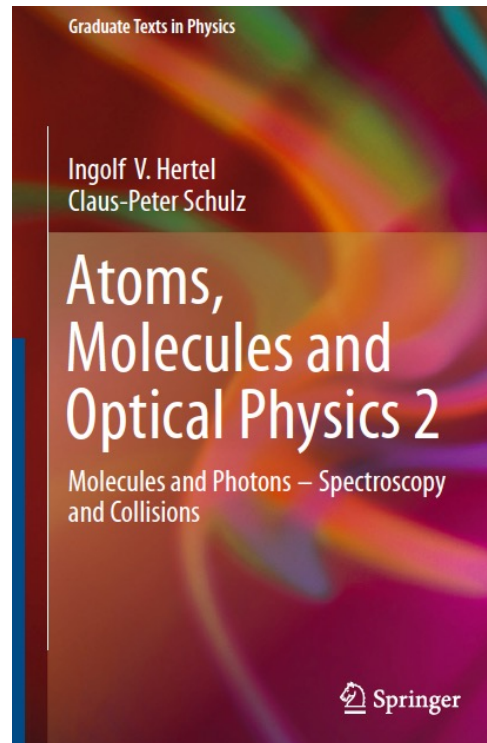
Discussions!

Text book recommendations

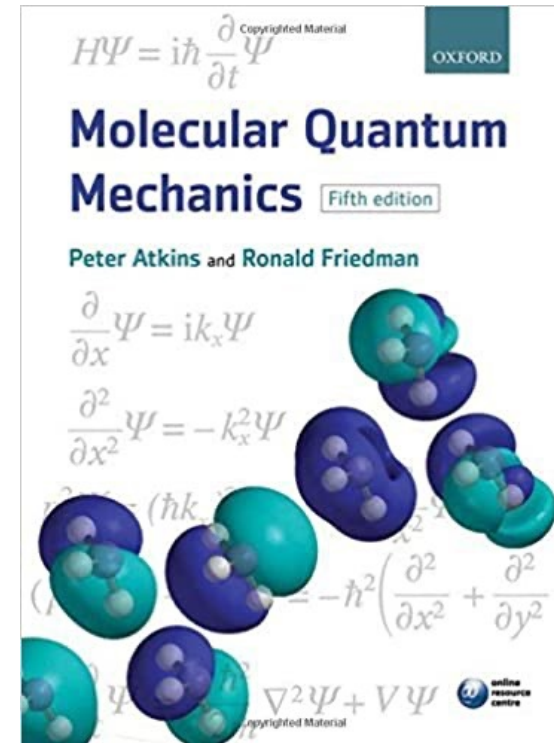
Haken/Wolf



Hertel/Schulz



Atkins/Friedman



A science case that motivates time-resolved X-ray spectroscopy

Oil pumpjack and flaring



On Lake Maracaibo (Venezuela), Gaby Oraa/Bloomberg/Getty Images

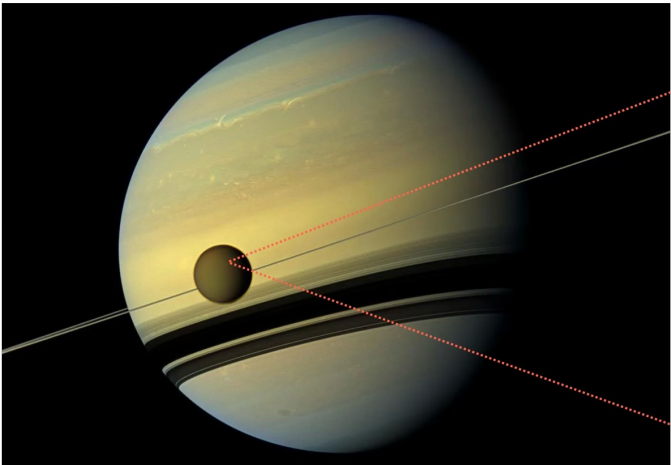
Green vegetables



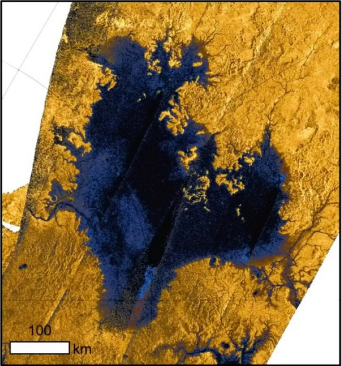
Red oak

Kaewpradup et al., Scientific Reports 15, 5282 (2025)

Titan, Saturn's largest moon



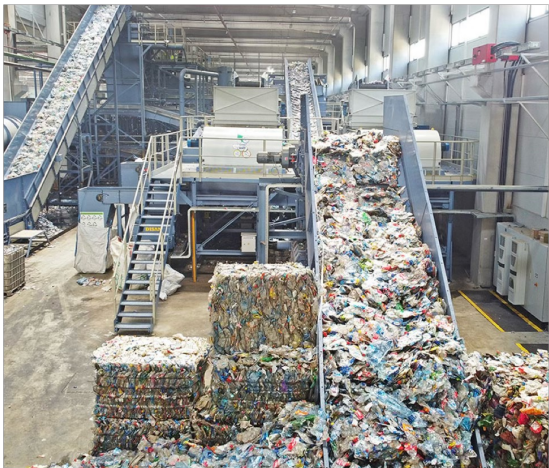
Methane see (-180 °C)



Cassini-Huygens project (NASA, ESA, ASI)

Credits: NASA/JPL-Caltech/Space Science Institute

Chemical re(up)cycling



Herbold Meckesheim

Drug development

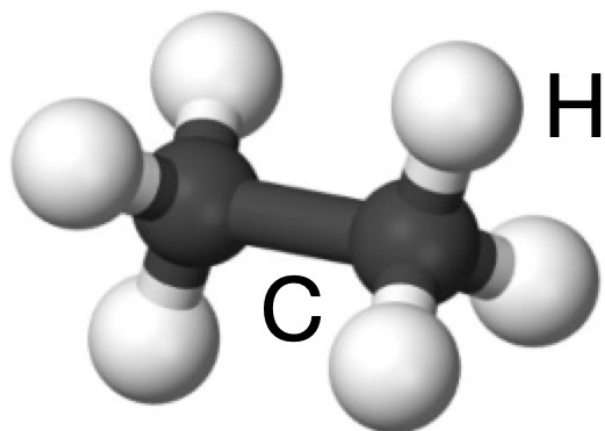


Getty Images

Alkanes, a form of hydrocarbons

4.3 eV

100 kcal/mol, 440 kJ/mol



Alkane

Very stable C-H bonds (strong, non-polar bonds with low polarizability), in abundant and stable molecules

→ (Photo)catalytic C-H activation

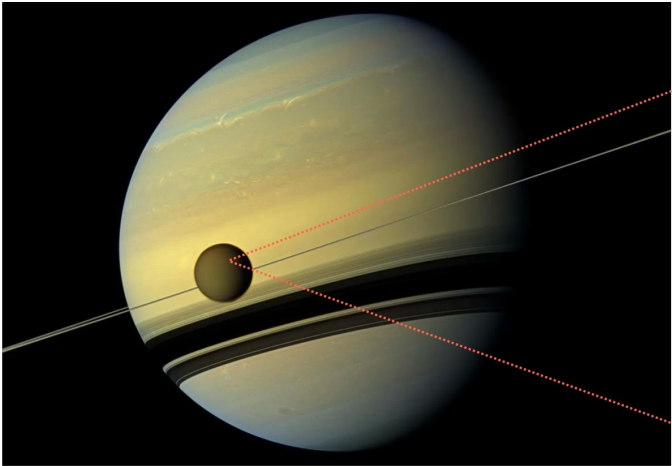
A science case that motivates time-resolved X-ray spectroscopy

Oil pumpjack and flaring



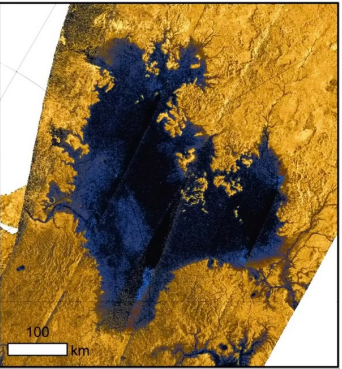
On Lake Maracaibo (Venezuela), Gaby Oraa/Bloomberg/Getty Images

Titan, Saturn’s largest moon



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Drug development



Getty Images

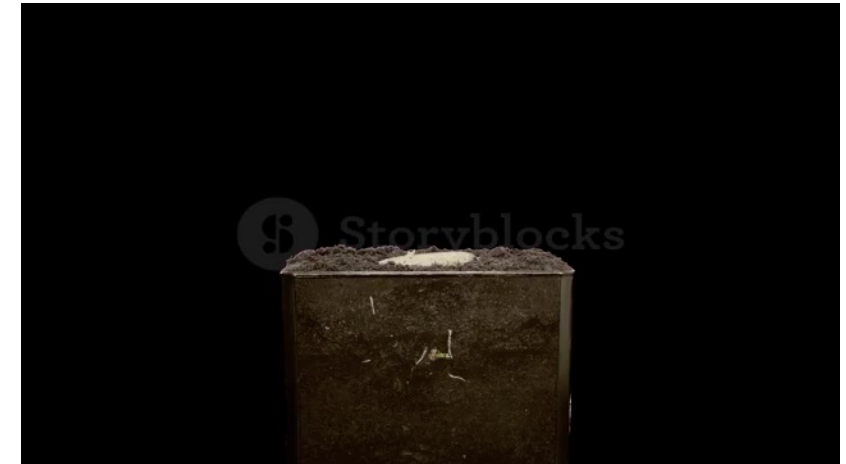
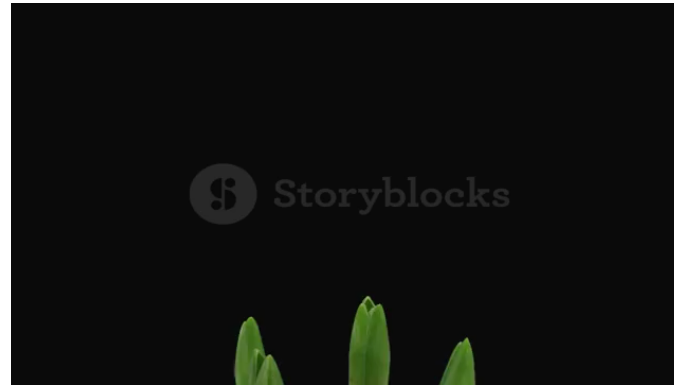
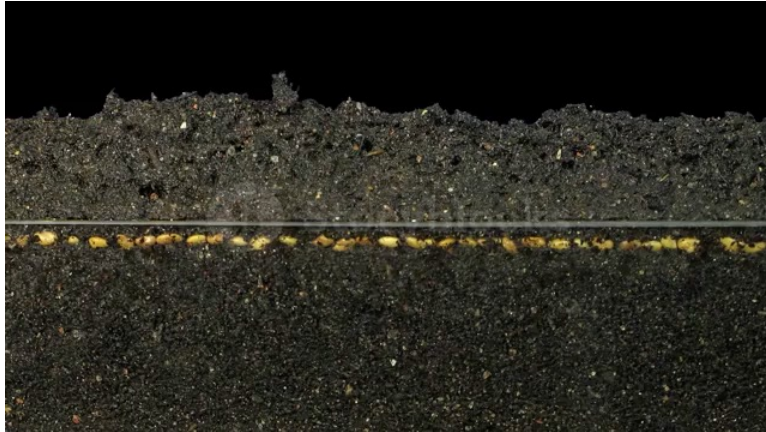
Green vegetables



Kaewpradup et al., Scientific Reports 15, 5282 (2025)

Chemical synthesis, transformations, bond engineering

Biology, chemistry and physics at action



Photosynthesis: Capture, convert, store energy of the sun (with water and CO_2) in the form of chemical bonds, and make organic material.

Learn to rearrange bonds

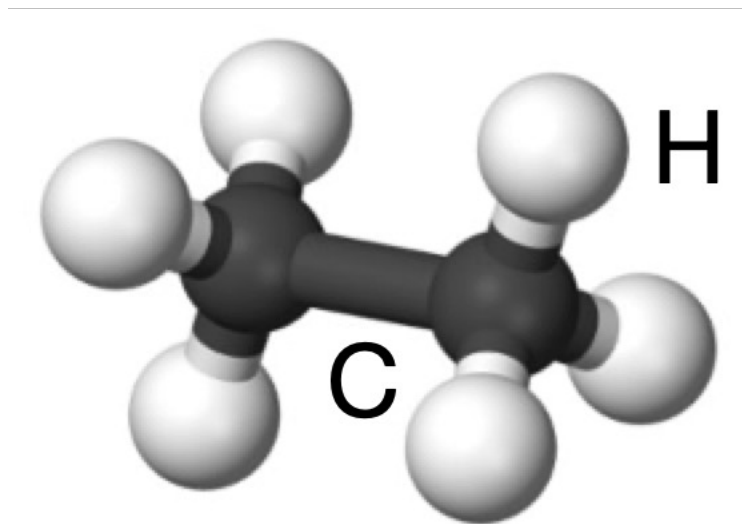
Characterize molecules in weird bonding
configurations

Induce and make use of weak interactions

Alkanes, a form of hydrocarbons

4.3 eV

100 kcal/mol, 440 kJ/mol



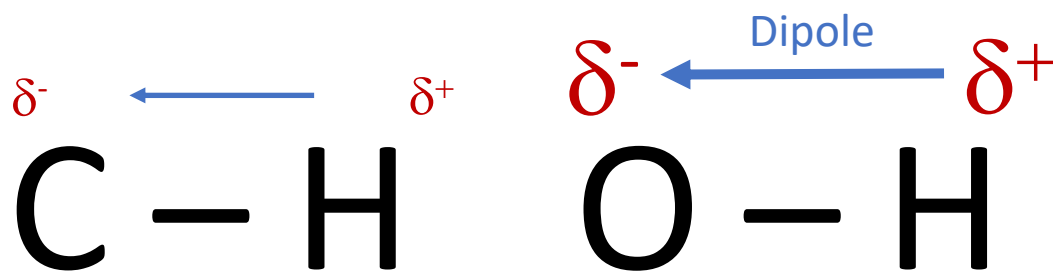
Alkane

*O-H bonds are easier to break
Strength = 110 kcal/mol!?*

Why are C-H bonds so hard to break?

The C-H bond

What's the fundamental difference between C-H and O-H bonds?



Electronegativity of the elements

6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98	1 H 2.20
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www.sciencenotes.org

Bond	Average dipole moment (wrt to H-Cl)
C-H	0.4
N-H	1.2
O-H	1.4
F-H	1.6

*Catalytic methane to methanol
conversion is a big thing!*

H_2^+ – (Some) essentials of molecular physics

Orbital interactions

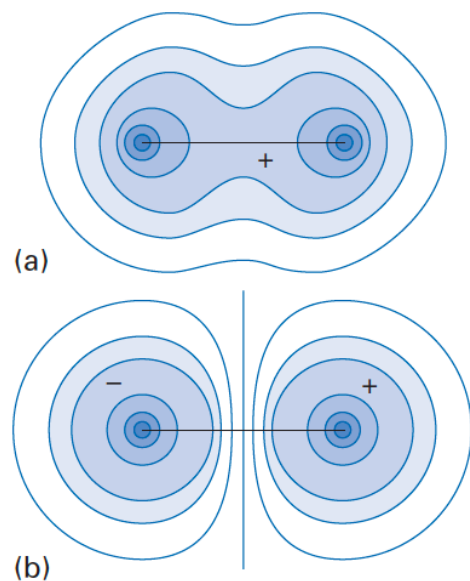


Fig. 8.6 Contour diagrams of the (a) bonding and (b) antibonding orbitals (1σ and 2σ , respectively) of the hydrogen molecule-ion in the LCAO approximation.

Orbital energies

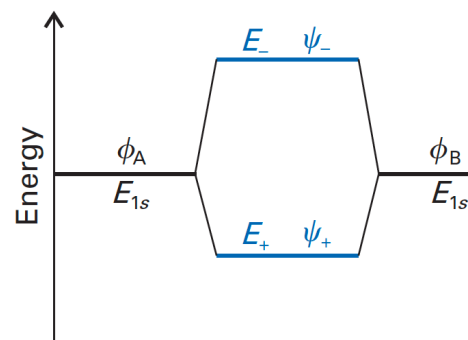


Fig. 8.11 The molecular orbital energy level diagram of the hydrogen molecule-ion in the LCAO approximation. Note that the 2σ -orbital is slightly more antibonding than the 1σ -orbital is bonding.

Potential energies

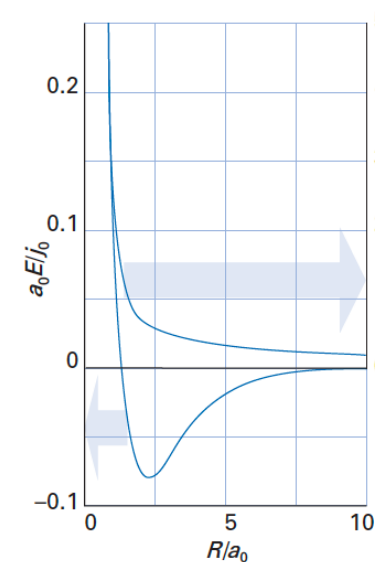
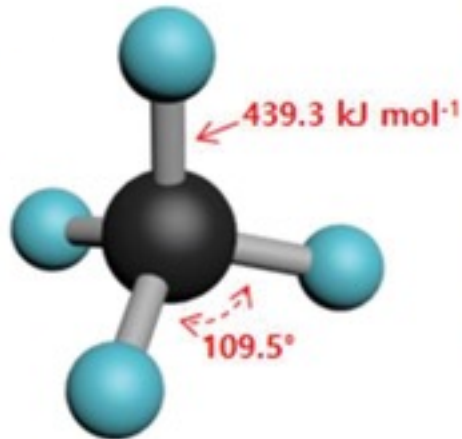


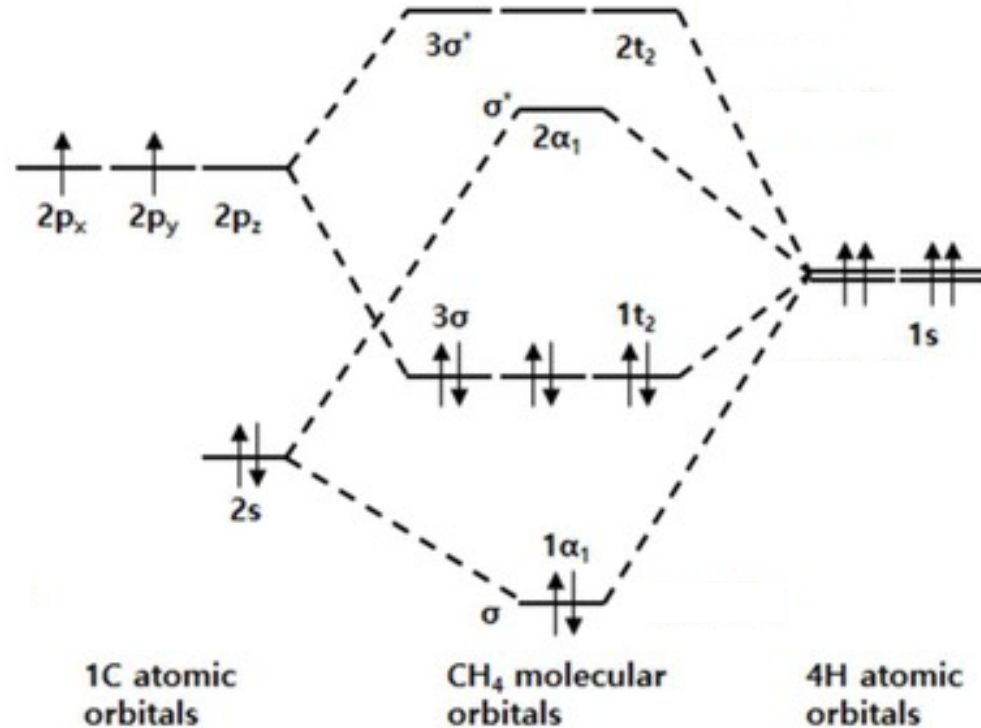
Fig. 8.12 The calculated molecular potential energy curves of the two lowest energy molecular orbitals of the hydrogen molecule-ion within the LCAO approximation. Note the change in scale between the bonding and antibonding curves.

The C-H bond (alkanes, hydrocarbons)

Methane (CH₄)



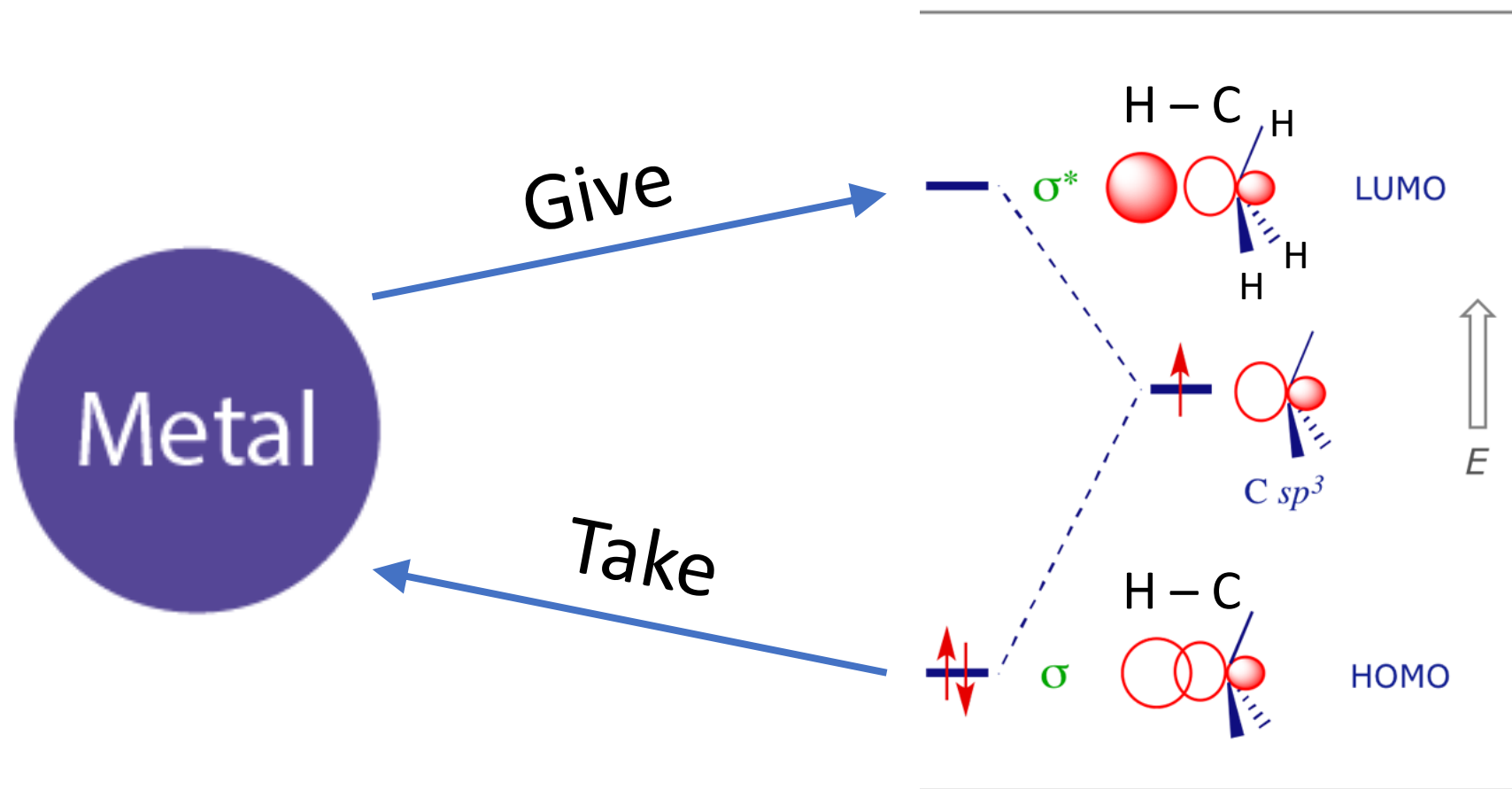
Energy of the MO



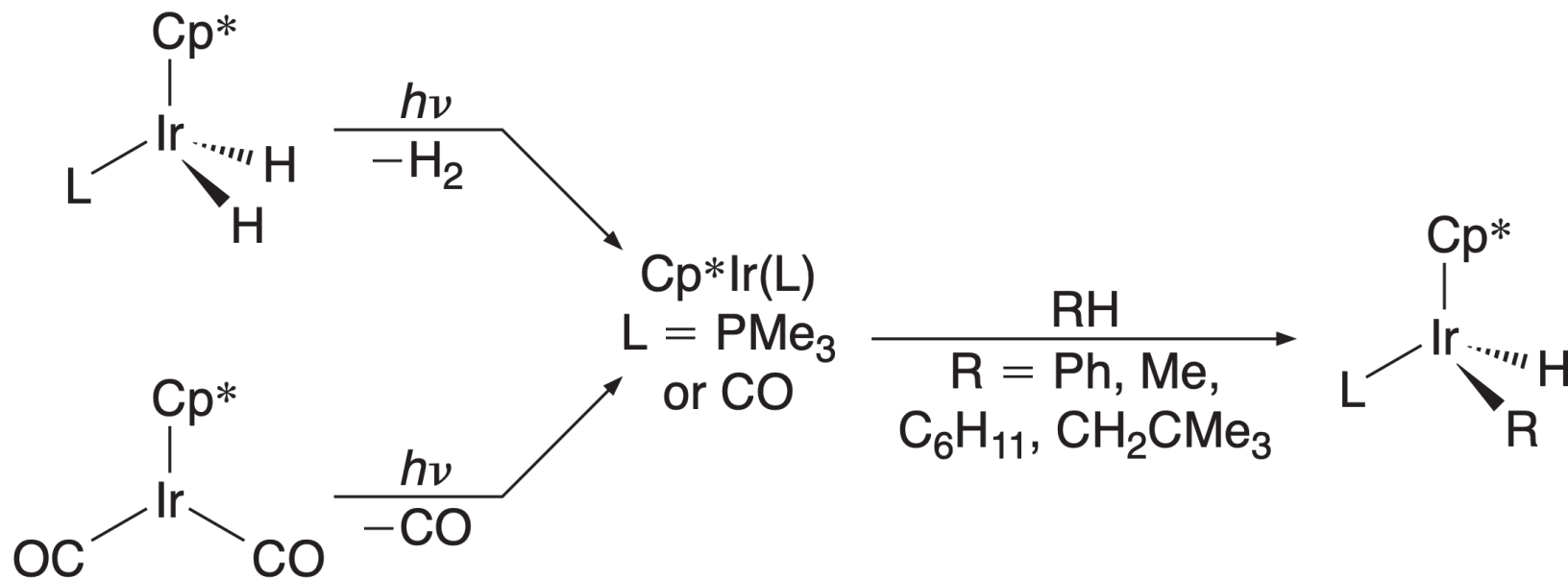
What can we do to break a C-H bond?

The C-H bond (alkanes, hydrocarbons)

What can we do to destabilize that particular interaction?



Photochemical C-H bond activation

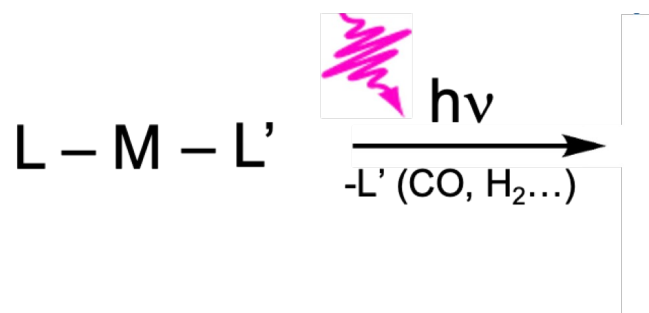


Discovered by Bergmann, Graham (1982)

Photochemical C-H bond activation with metal complexes

Ultrafast photochemistry

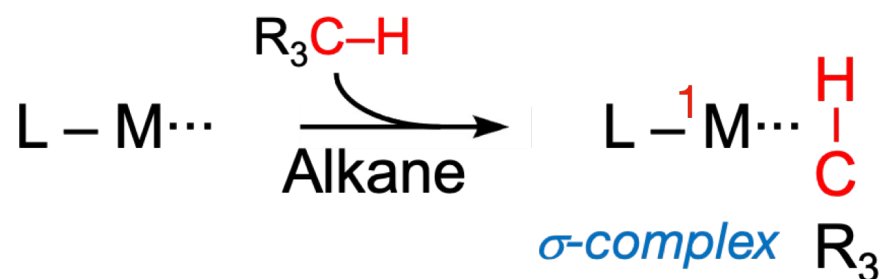
< 1 ps



*Excited-state and
dissociation dynamics*

Alkane association

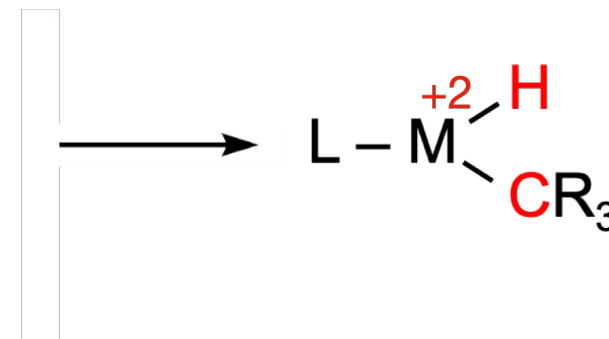
1-10 ps



*Triggered ground-state reactions
Ligand substitution*

C-H activation

1-10 ns



*Oxidative addition
reactions*

Discovered by Bergmann and Graham (1982)

Janowicz, Bergman, *J. Am. Chem. Soc.* **104**, 352 (1982), Hoyano, Graham, *J. Am. Chem. Soc.* **104**, 3723 (1982)

John F. Hartwig, *Organotransition Metal Chemistry: From Bonding to Catalysis* (2010)

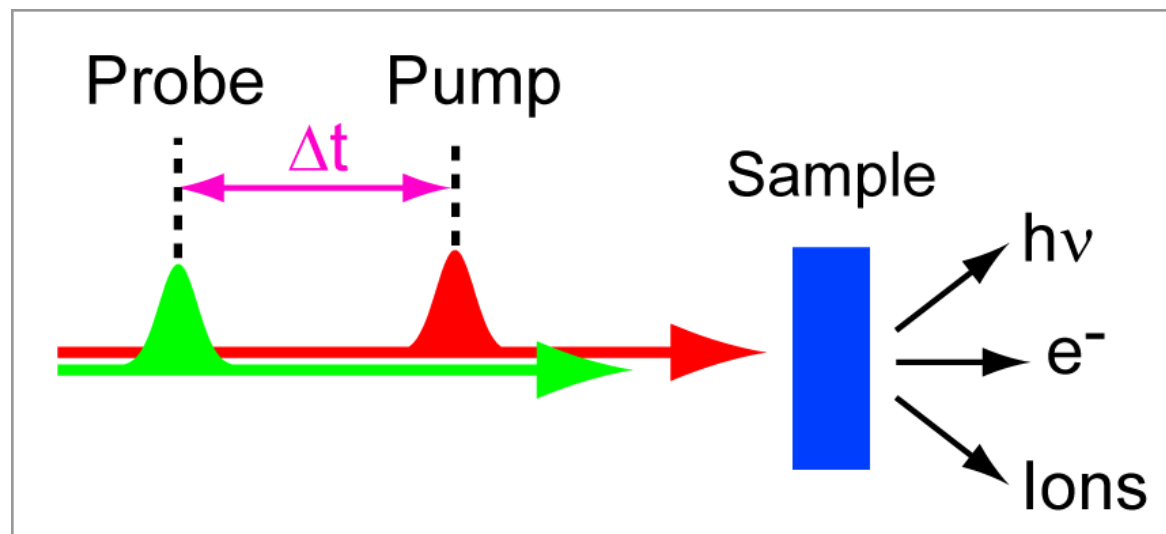
Outline

- Probing fast processes (pump-probe spectroscopy)
- Probing molecular orbitals (energies, interactions)
- Probing excited-state and dissociation dynamics
- Probing ligand association and bond activation

Specifically at the metal (elemental, chemical site and orbital specific X-ray spectroscopy)

Pump-probe spectroscopy

To catch (characterize) short-lived transient intermediates



With femtosecond optical and X-ray pulses to resolve in time (and space) transient configurations and reaction intermediates

Molecular dynamics: Short pulses and wavepackets

Common Blackbird (*Turdus merula*) • male, song

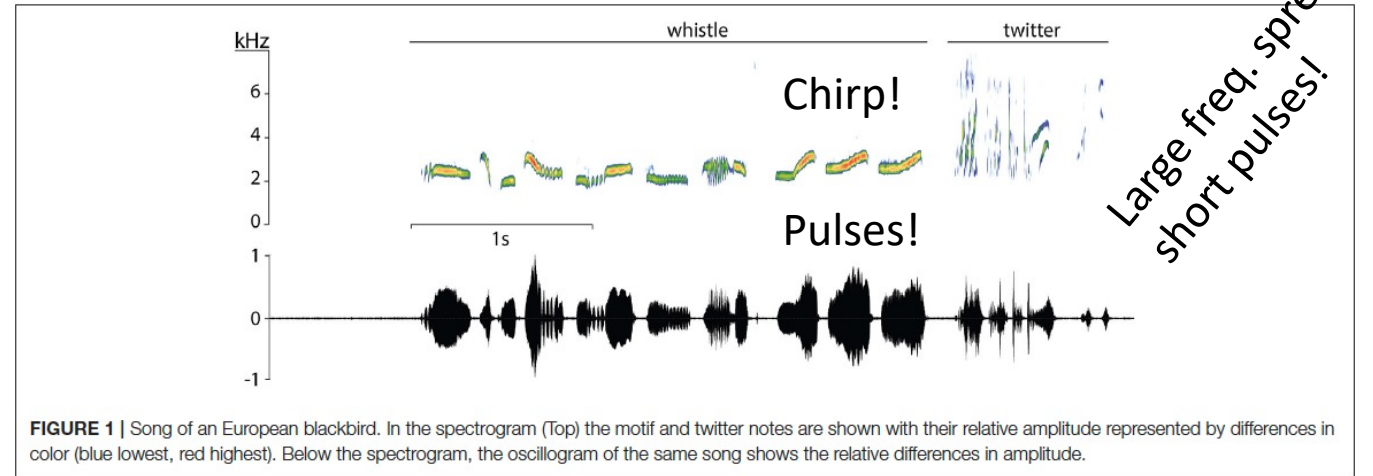


<https://www.hifi-online.net> (880 Hz)



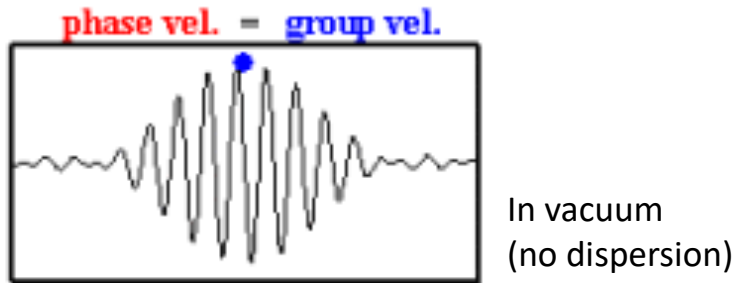
<https://www.xeno-canto.org/130204>
<https://www.deutsche-vogelstimmen.de/amsel/>

to twitter, to chirp



Sierro et al., *Frontiers in Ecology and Evolution* 5, **68** (2017).
doi: 10.3389/fevo.2017.00068

Wavepackets (sound, light, nuclei, electrons)



Rick Trebino, Georgia Tech

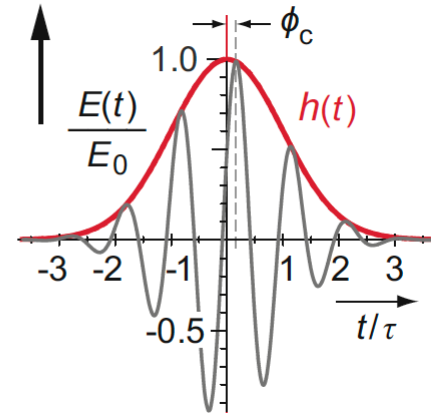
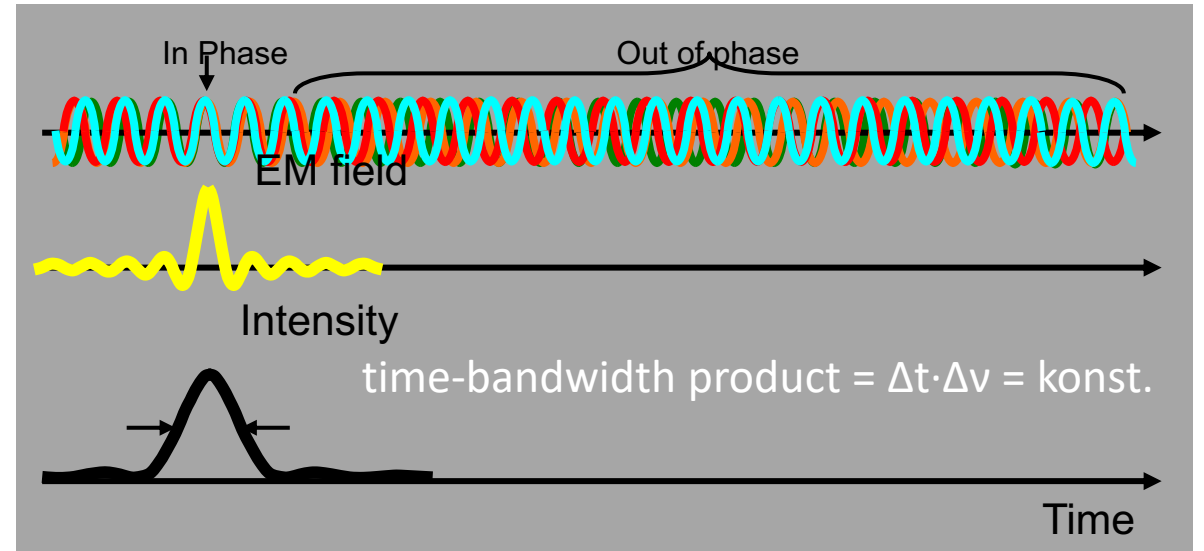
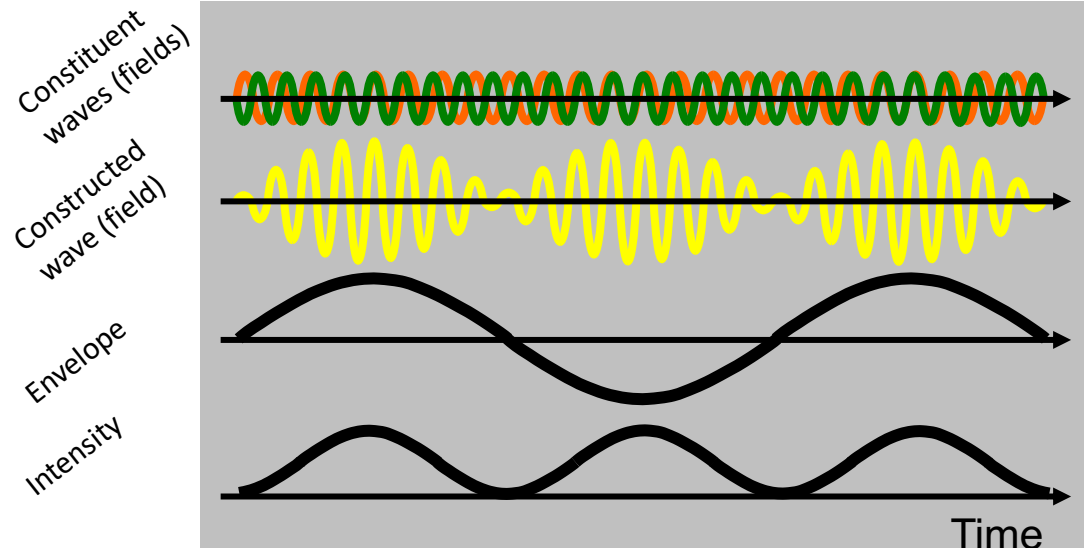


Fig. 1.24 Evolution of the electric field (*grey*) and its envelope (*red*) for a short, Gaussian pulse

Short (fs) light cycles $\rightarrow$ short (fs) pulses

Hertel/Schulz

Many waves (many fields)



But wait a second: How do we make short pulses?

By forming wavepackets = “packets of light”!

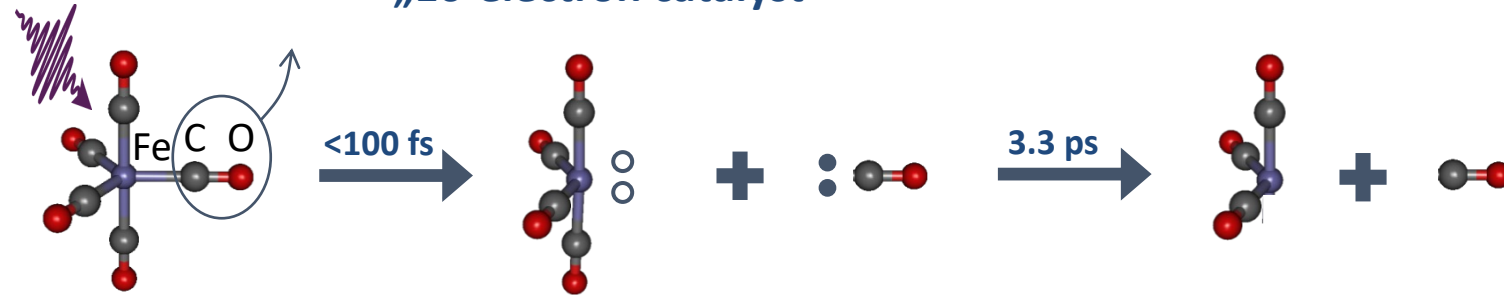
- Wavepacket = localizing wave energy in space and time
- Sound waves → Sound bursts, twitter – Sound pulse
- Light waves → “Light packet” – Light pulse
- Nuclear wavefunctions → Nuclear wavepacket (femtoseconds)
- Electron wavefunction → Electronic wavepacket (attoseconds)

Dissociation of a relatively simple molecule

Gas-phase to start with

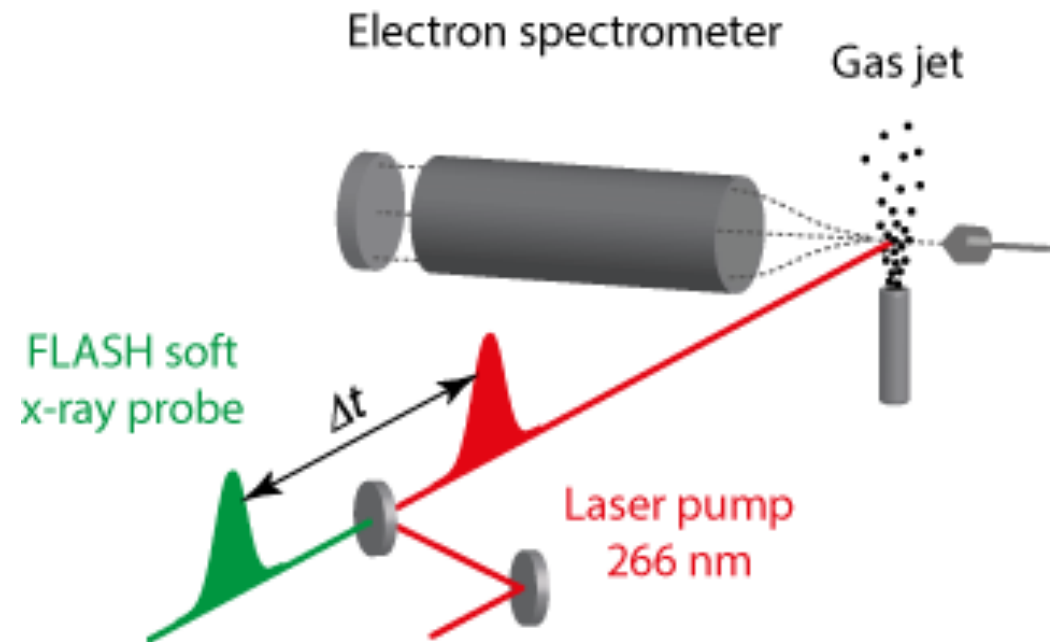
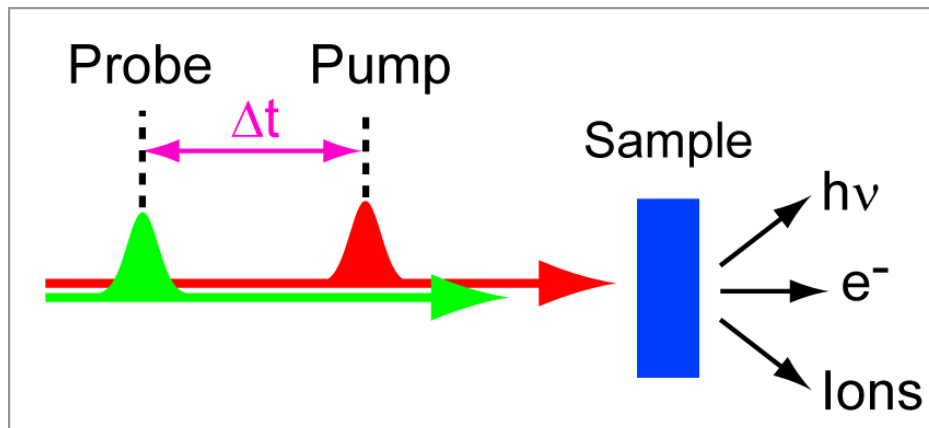


„16-electron catalyst“

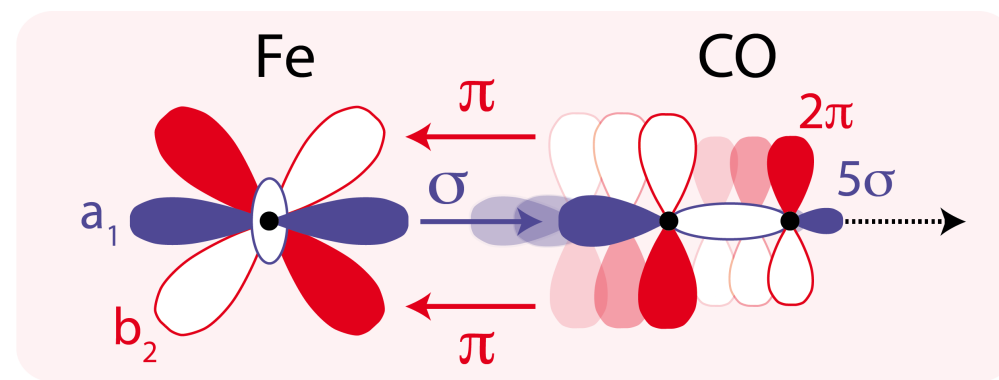
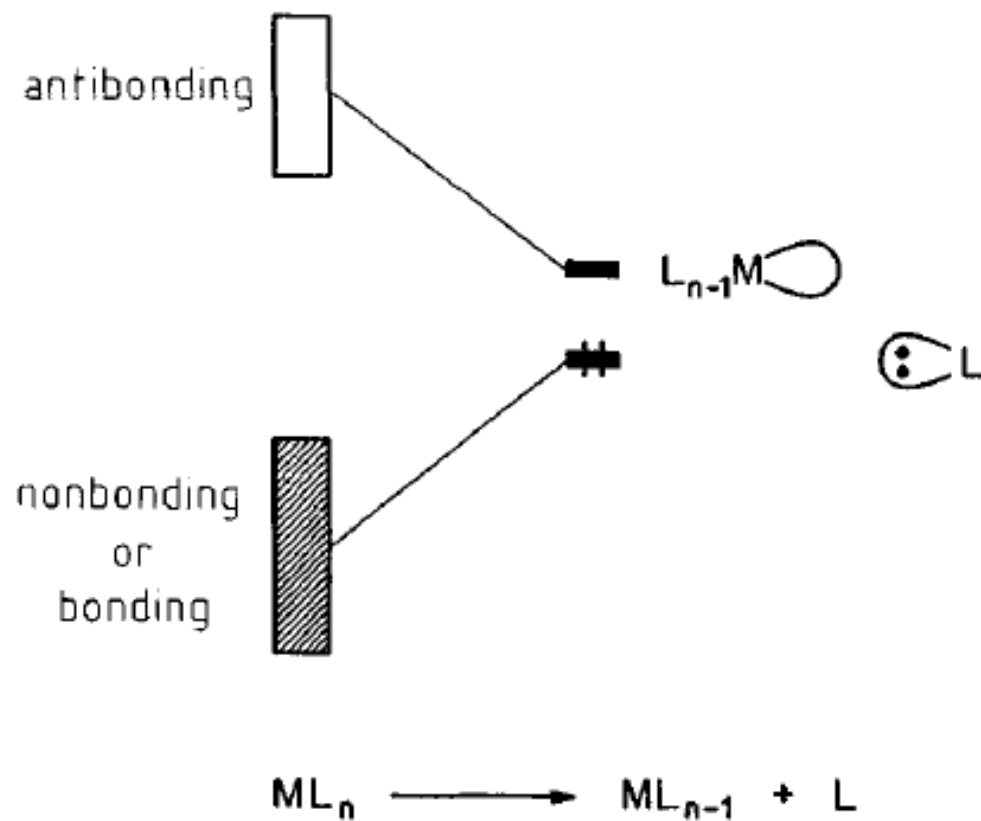


MLCT excitation

Time-resolved photoelectron spectroscopy



Testing fundamental notions of orbital interactions

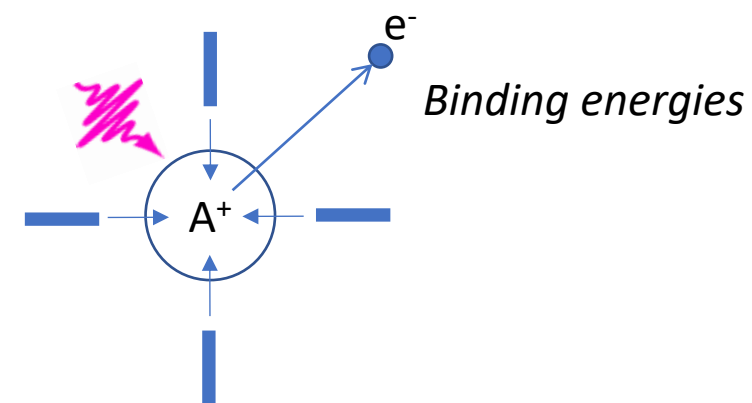
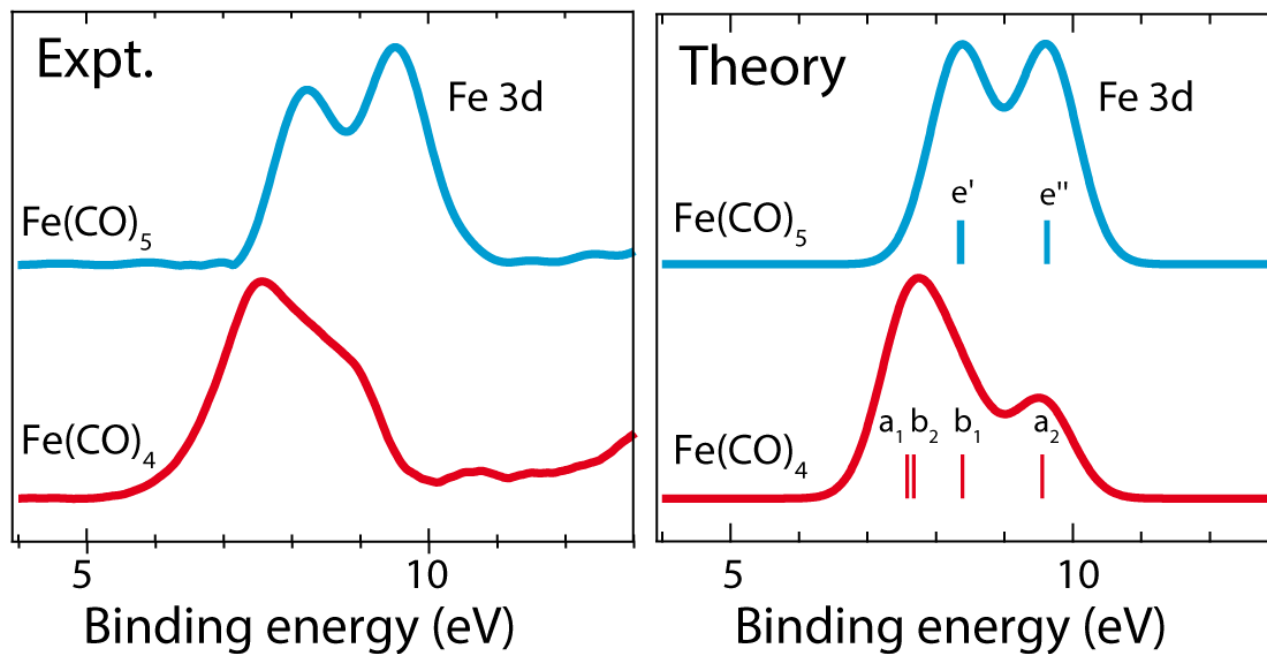


M-L bonding (σ/π , charge at M)

Testing fundamental notions of orbital interactions

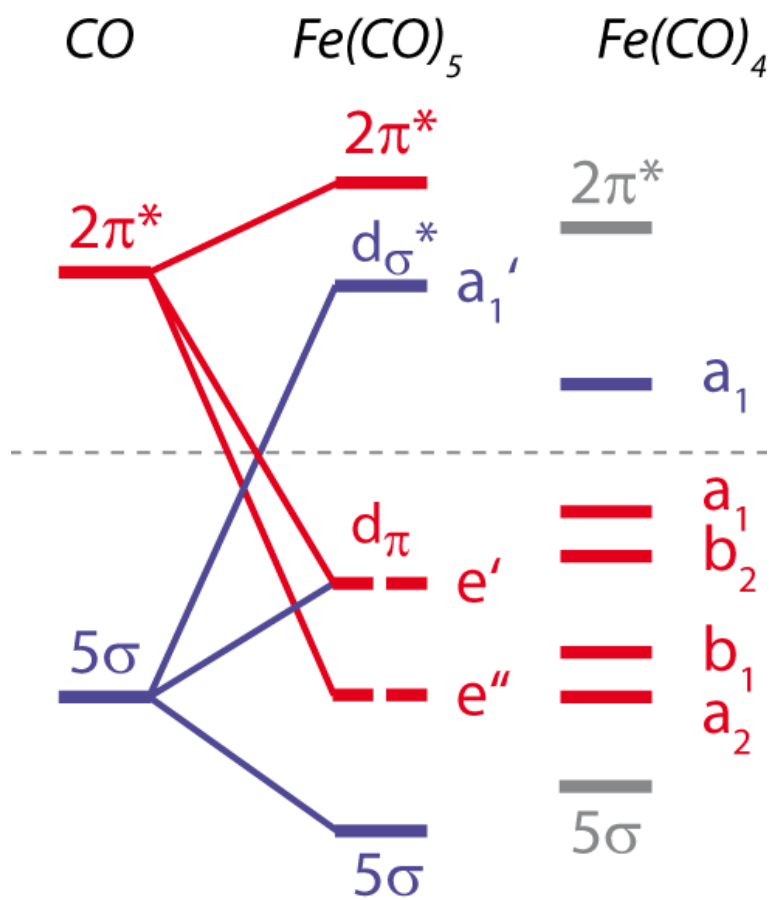
Free atom Fe $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2 \rightarrow$ Fe in a molecule Fe $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$

Time-resolved valence XPS at FLASH XFEL (gas-phase) + QC calculations



Plus or minus "hole effects"...

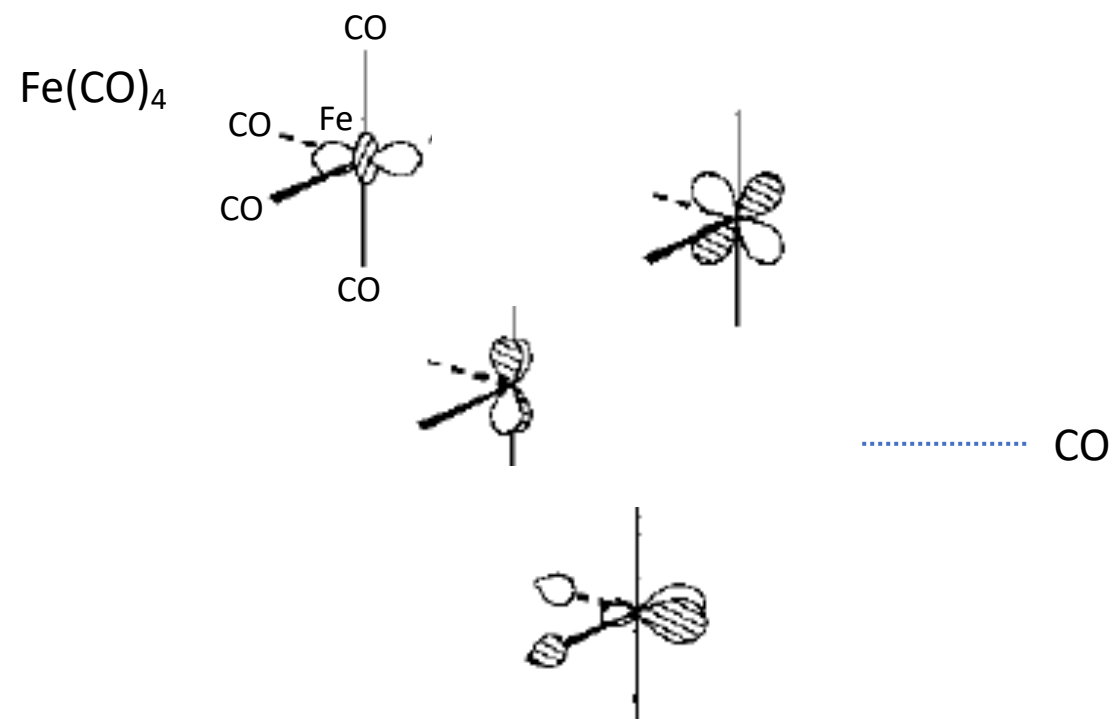
Testing fundamental notions of orbital interactions



M-L bonding (σ/π , charge at M)

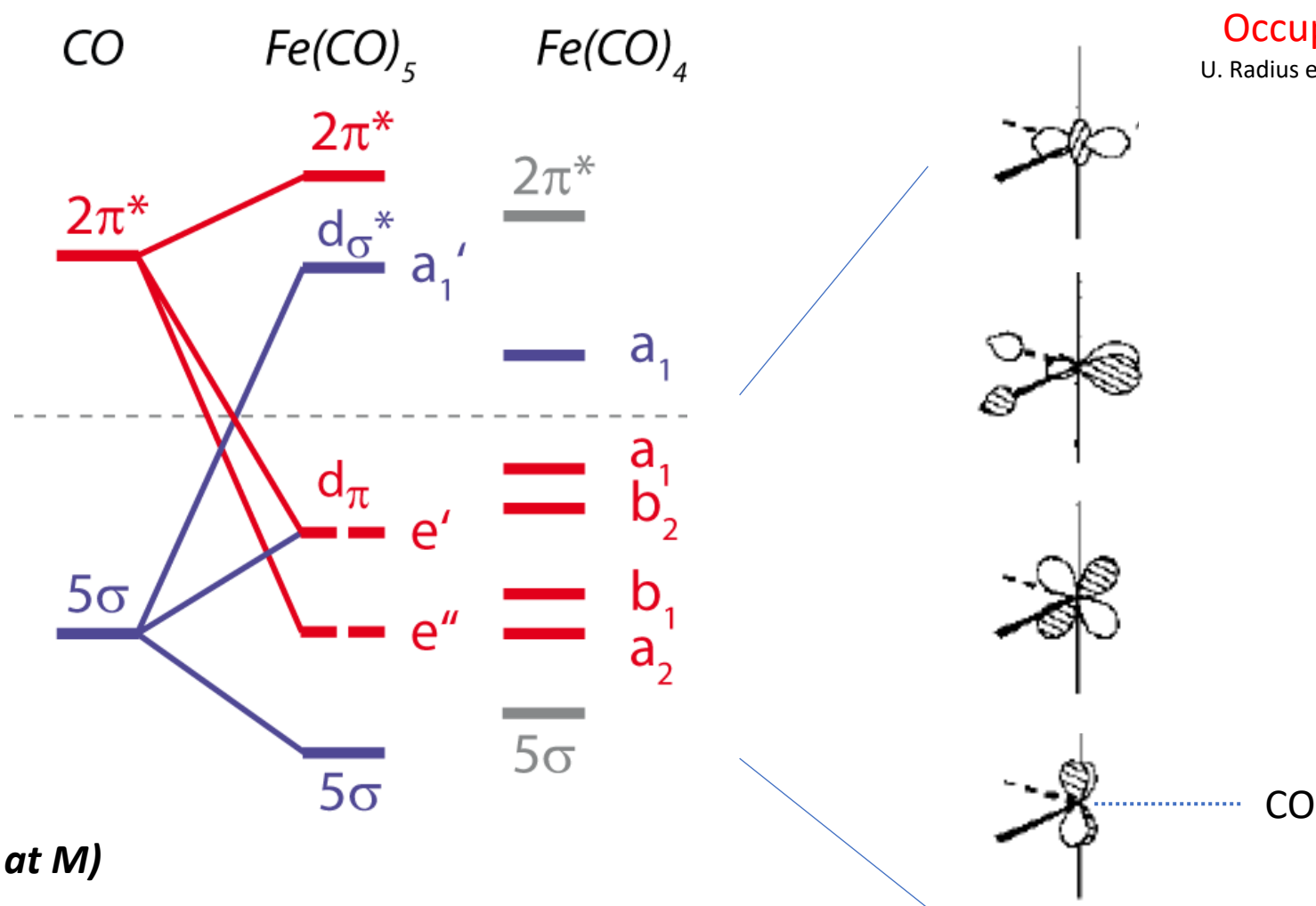
Occupied MOs of Fe(CO)₄

U. Radius et al., Inorg. Chem. **37**, 1080 (1998).



Which (occupied) orbital (drawing) corresponds to which orbital energy level?

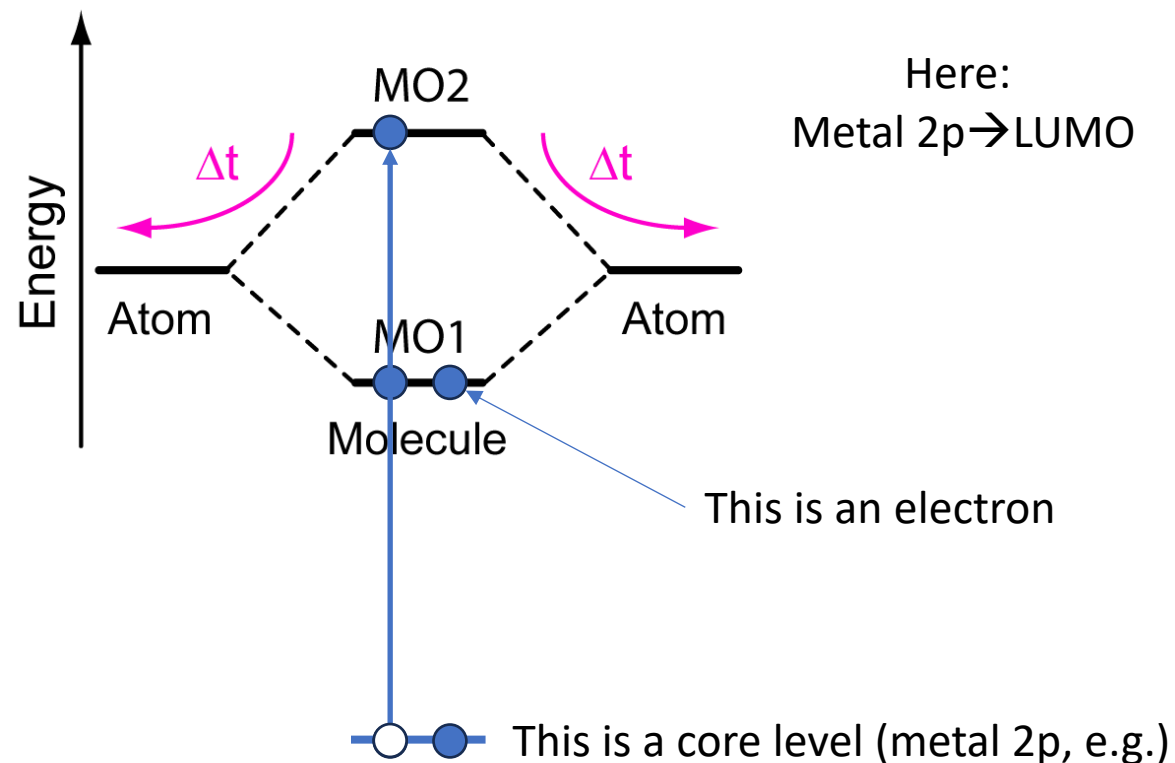
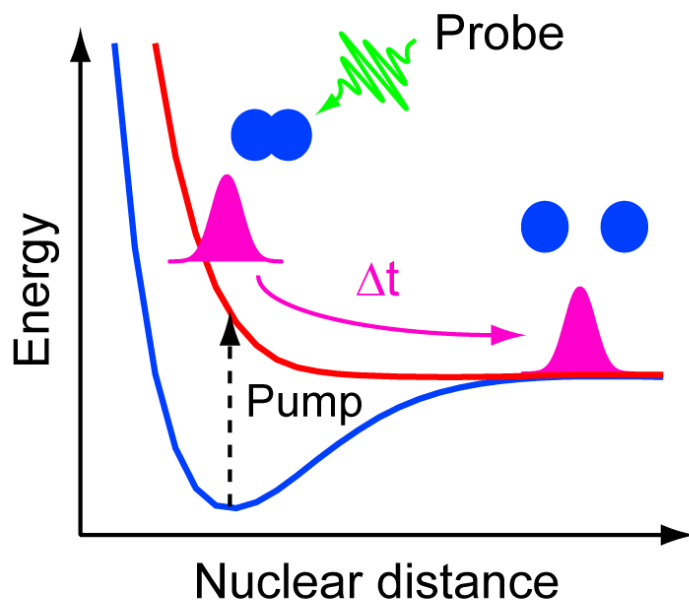
Testing fundamental notions of orbital interactions



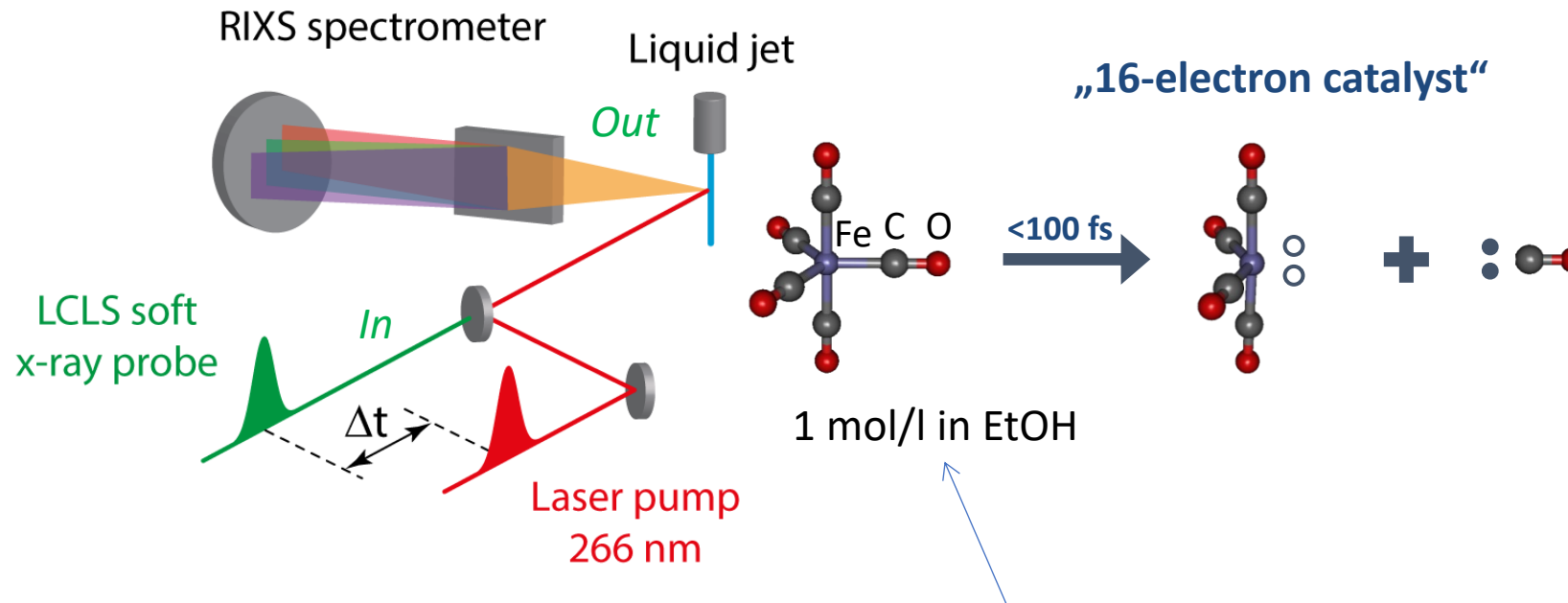
Mapping valence electron rearrangements

How do we now probe the unoccupied orbitals?

With XAS (and RIXS)!

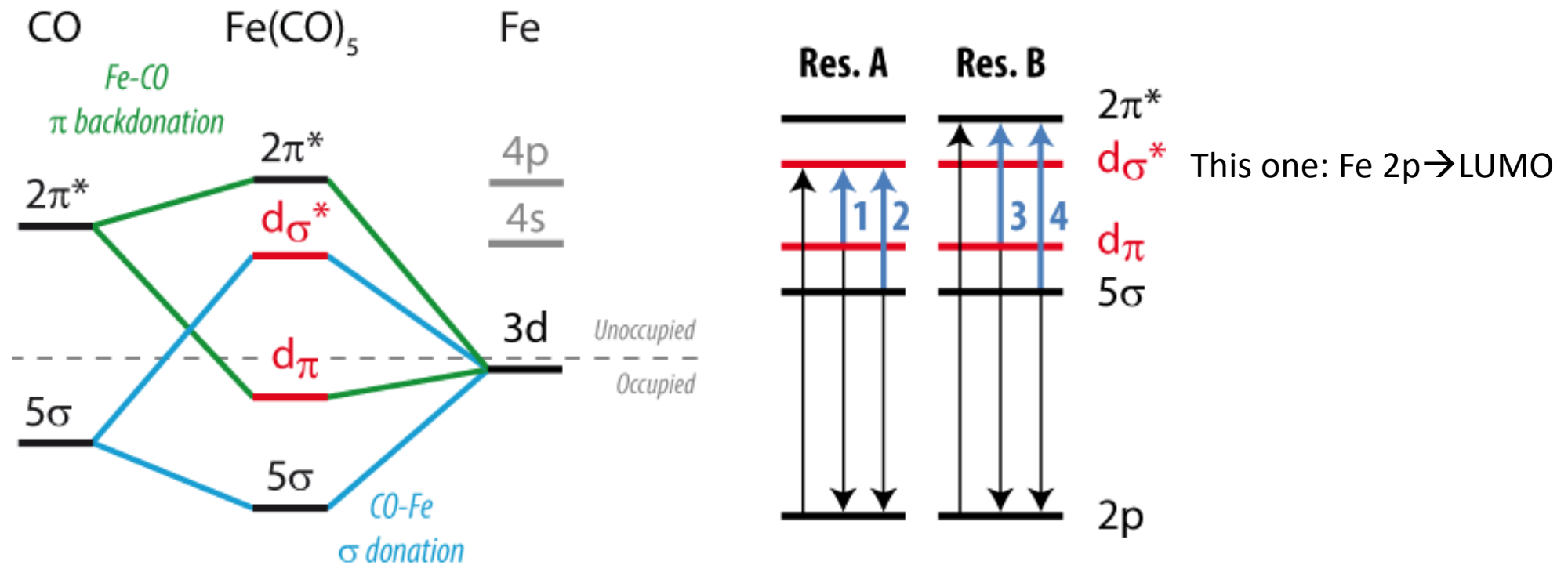


Time-resolved RIXS* at LCLS

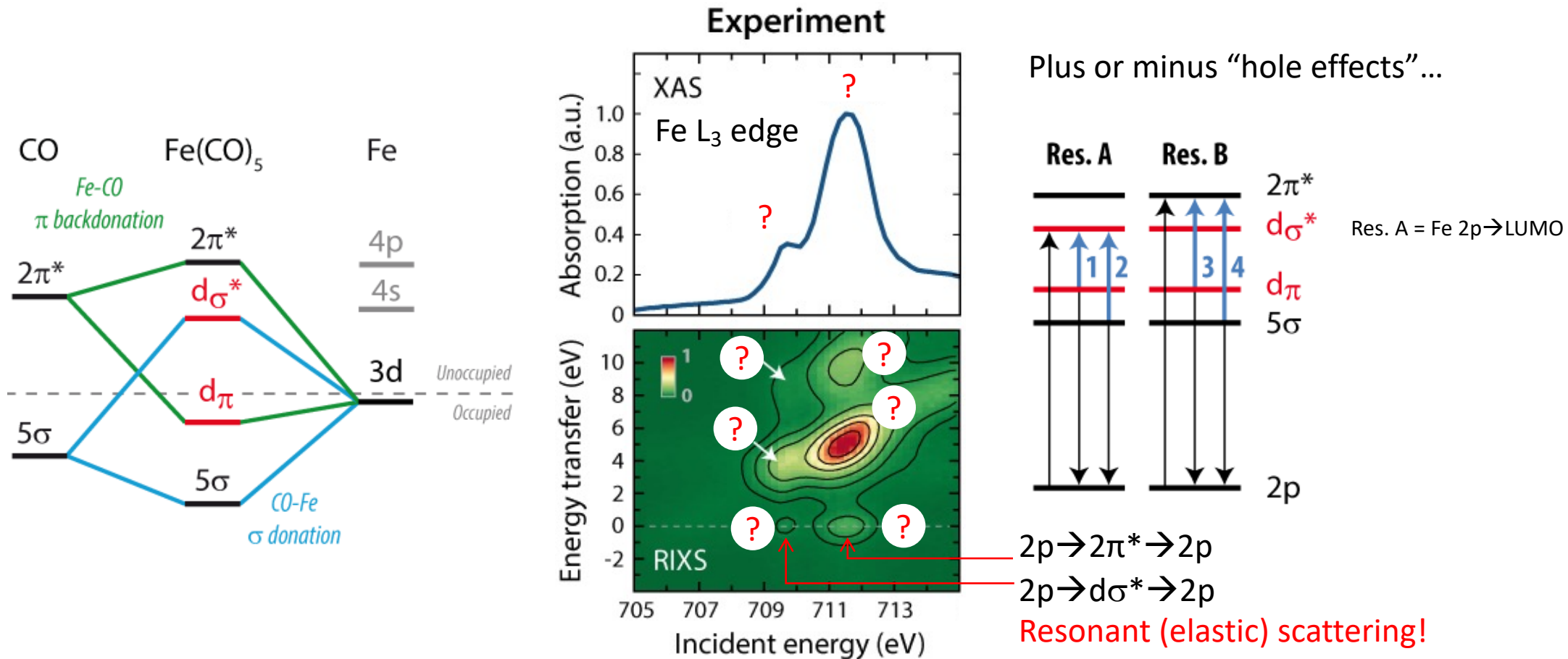


*Resonant Inelastic X-ray Scattering

RIXS of Fe(CO)₅

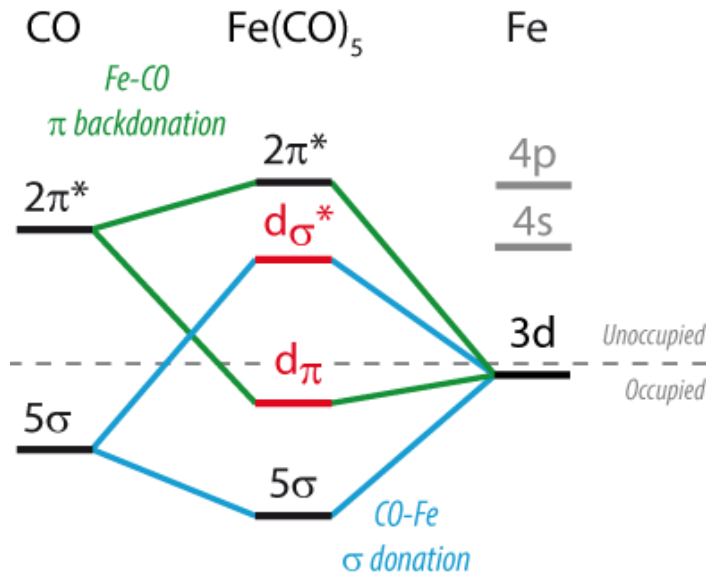


You do the job: Assign the features!

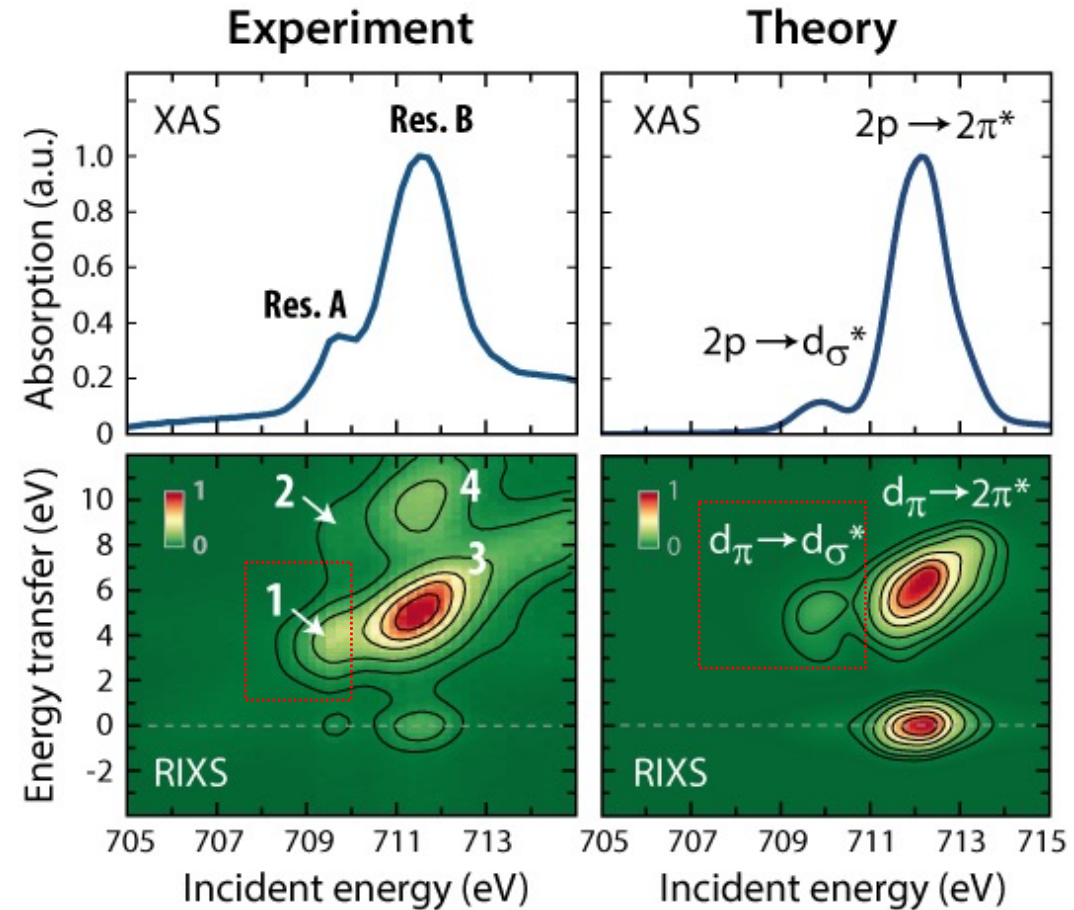


RIXS of Fe(CO)₅

5σ not included (transitions 2 and 4 missing)!



Let's focus on these transitions because they involve the frontier orbitals HOMO and LUMO!

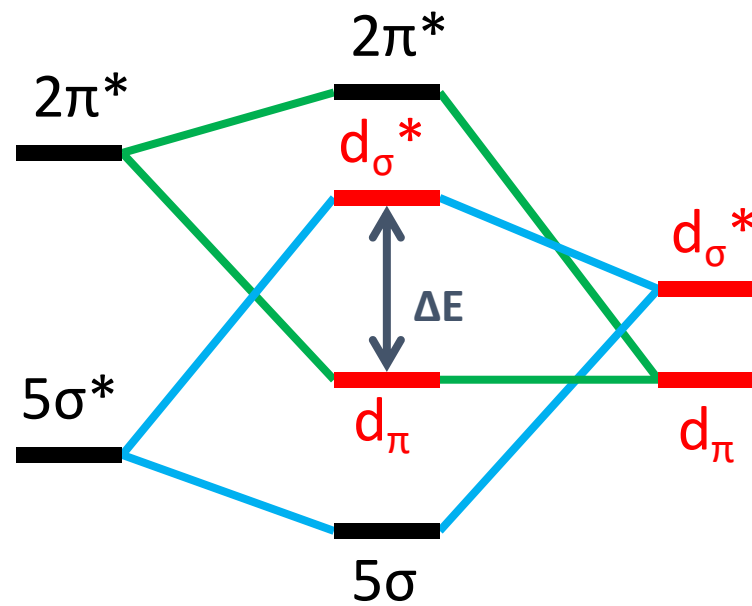


Book chapter in „X-Ray Free Electron Lasers“ by J. Yano, V. Yachandra, U. Bergmann (Eds.), *Royal Society of Chemistry Energy and Environment Series*, Ph. Wernet (2017).

CO

Fe(CO)₅

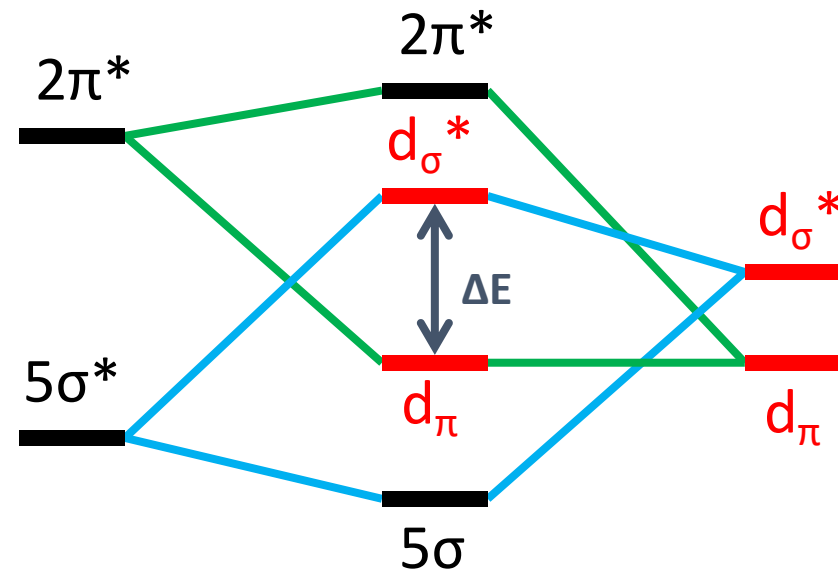
Fe(CO)₄



CO

Fe(CO)₅

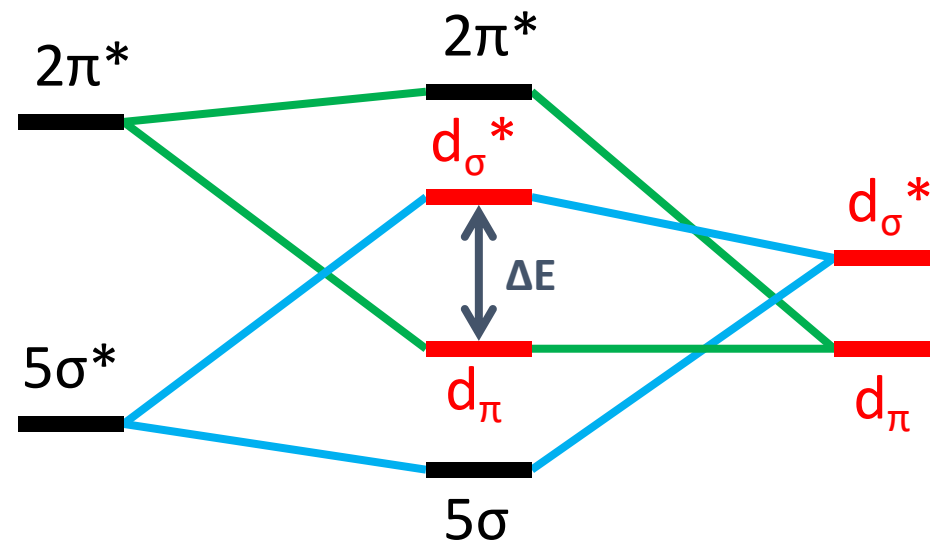
Fe(CO)₄



CO

$\text{Fe}(\text{CO})_5$

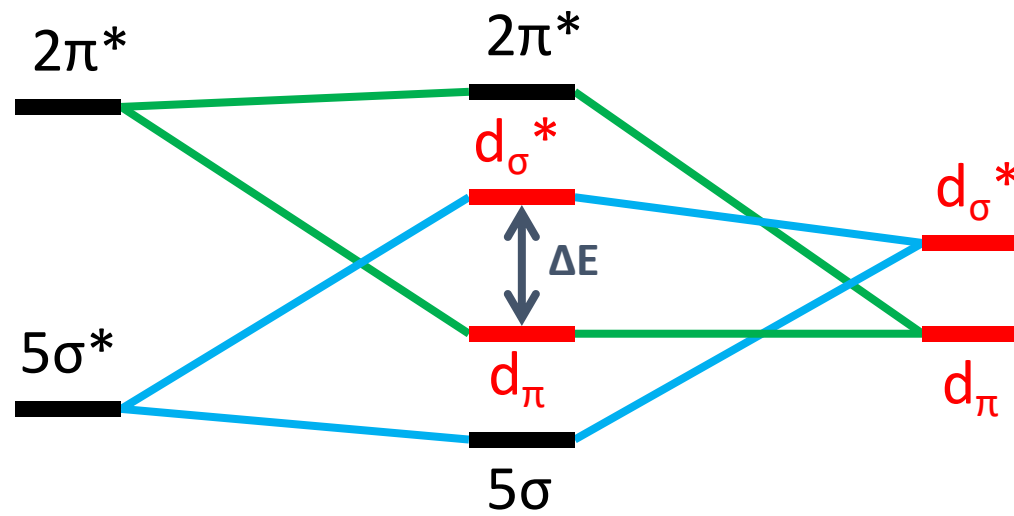
$\text{Fe}(\text{CO})_4$

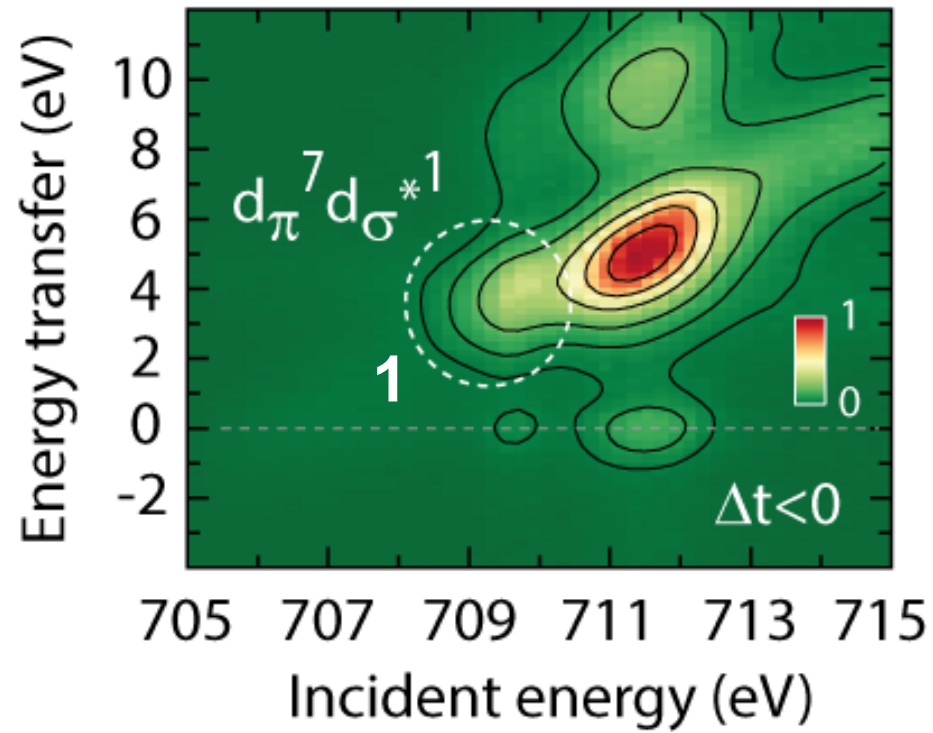
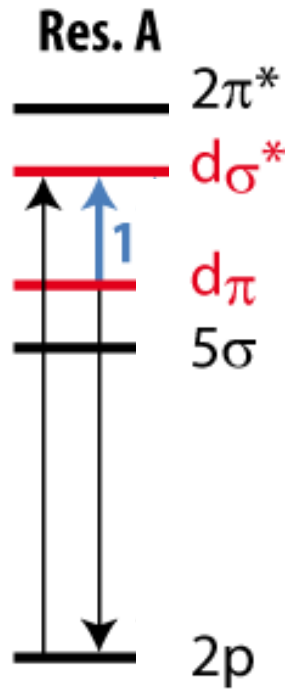


CO

$\text{Fe}(\text{CO})_5$

$\text{Fe}(\text{CO})_4$



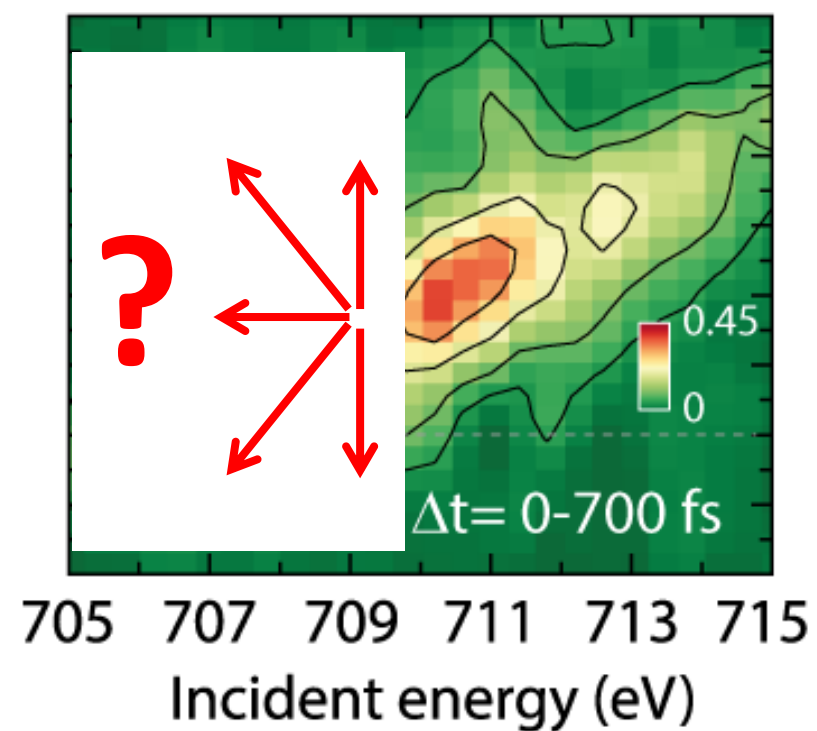
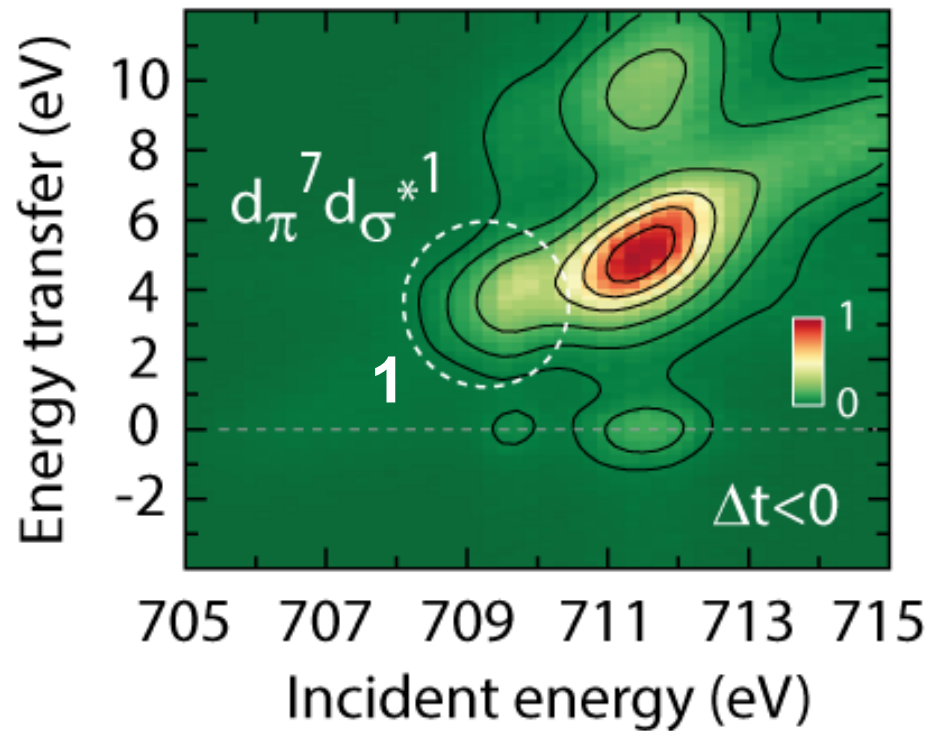
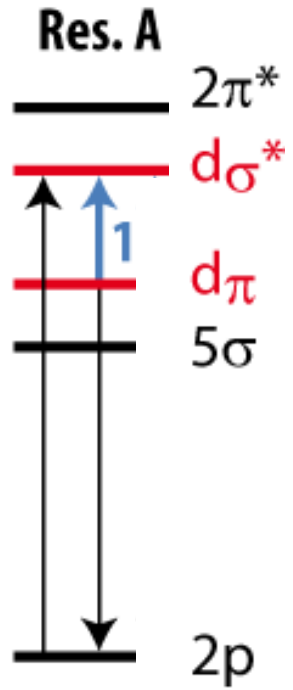


Fe L_3 -absorption edge

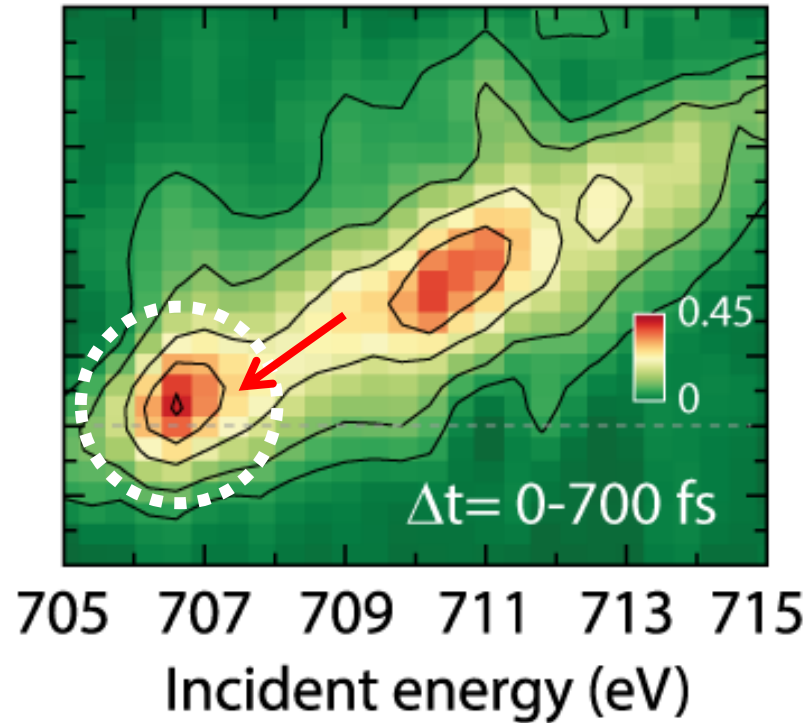
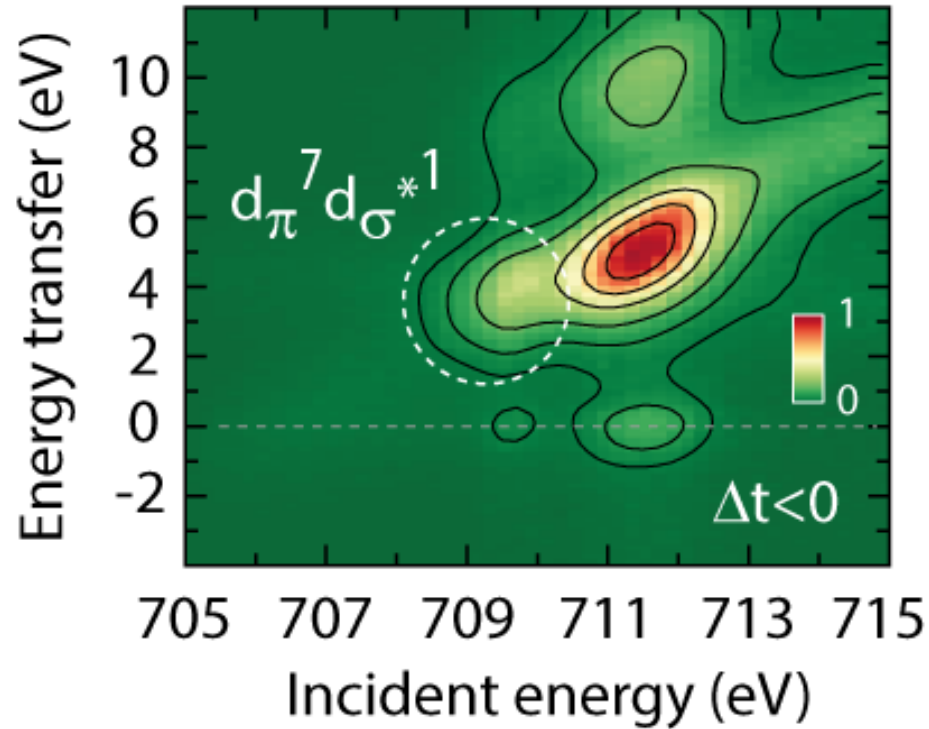
Predict the experimental outcome!

$\text{Fe}(\text{CO})_5$

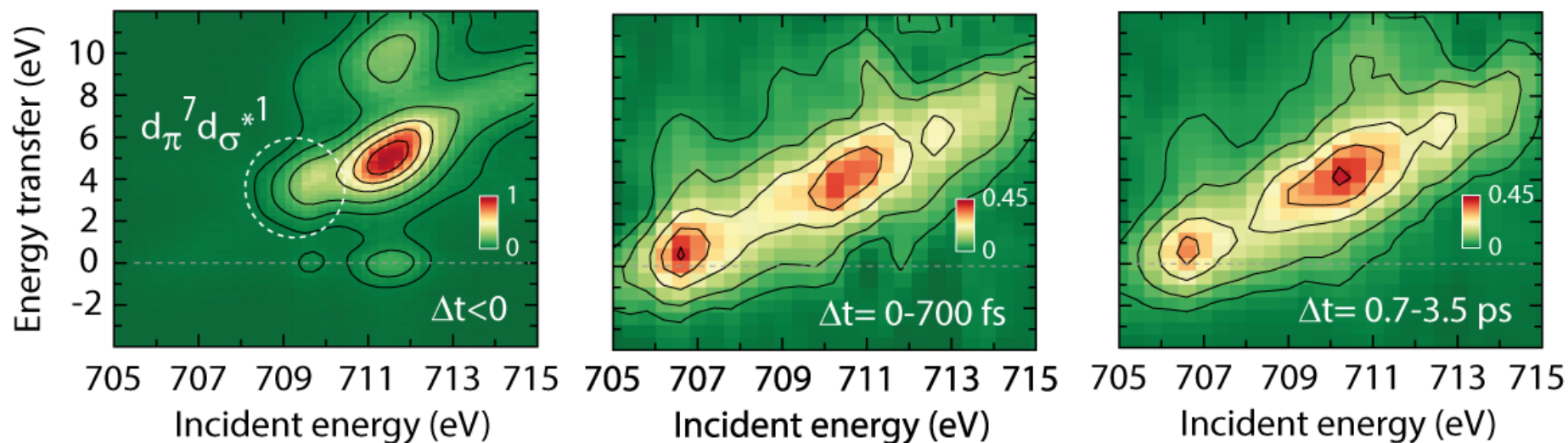
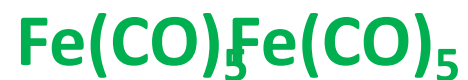
$\text{Fe}(\text{CO})_4$ fragments



$\text{Fe} L_3$ -absorption edge

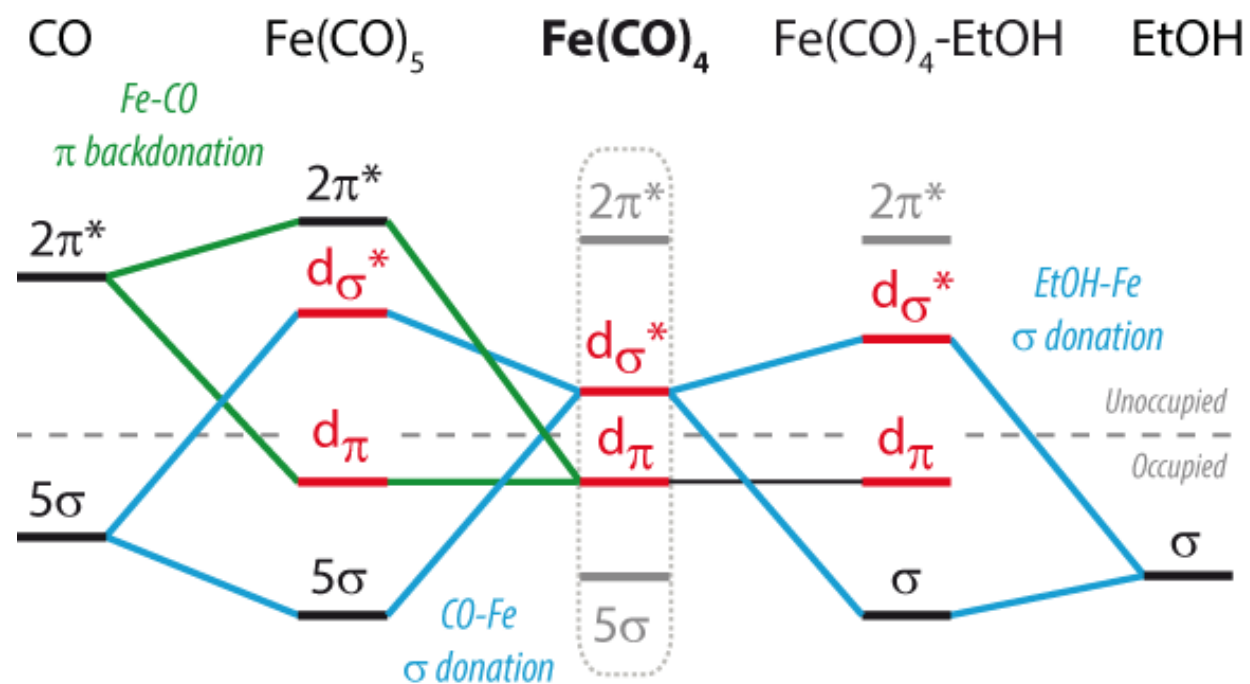


*Delays between 0 and 700 fs
mashed together for the moment!*



Ph. Wernet, K. Kunnus, I. Josefsson, I. Rajkovic, W. Quevedo, M. Beye, S. Schreck, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. W. Hartsock, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, F. M. F. de Groot, K. J. Gaffney, S. Techert, M. Odelius, A. Föhlisch, *Nature* **520**, 78-81 (2015).

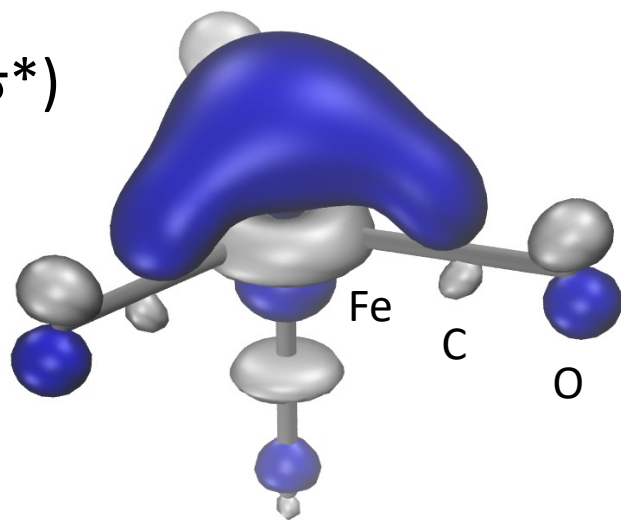
Solvent ligation (ethanol association)



Solvent ligation (ethanol association)

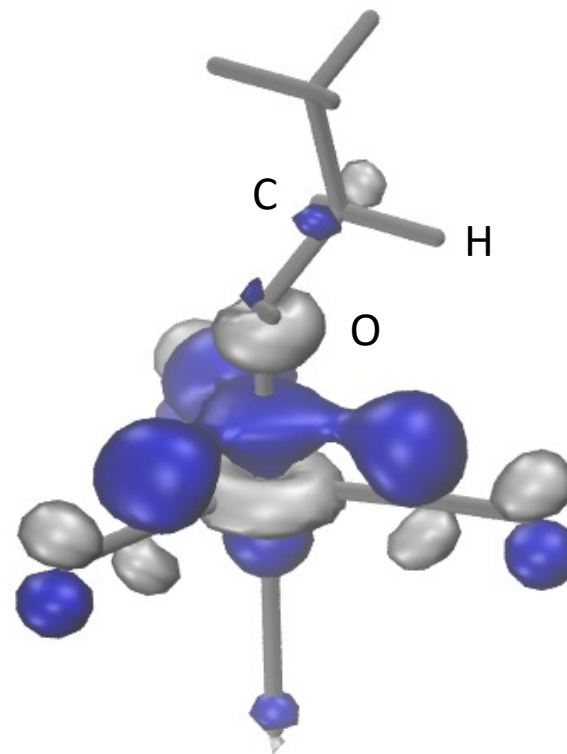
$\text{Fe}(\text{CO})_4$

LUMO ($d\sigma^*$)



$^1\text{Fe}(\text{CO})_4$ (Ax)

$\text{Fe}(\text{CO})_4$ -Ethanol solvent complex ($\text{C}_2\text{H}_5\text{OH}$)

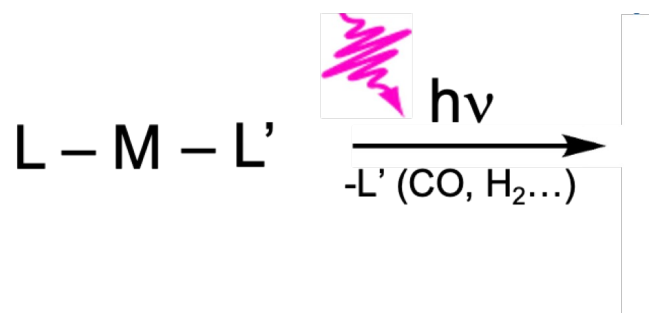


$^1\text{Fe}(\text{CO})_4\text{-OH-R}$ (Ax)

Photochemical C-H bond activation with metal complexes

Ultrafast photochemistry

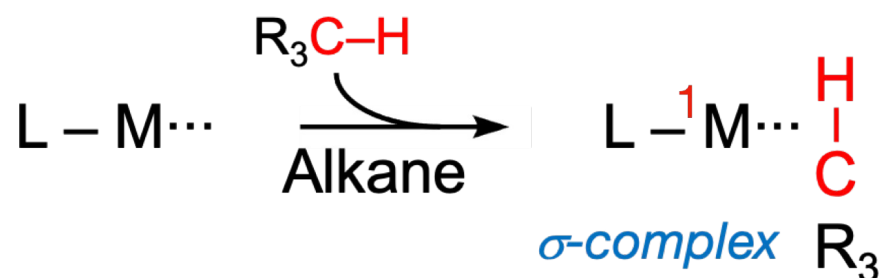
< 1 ps



*Excited-state and
dissociation dynamics*

Alkane association

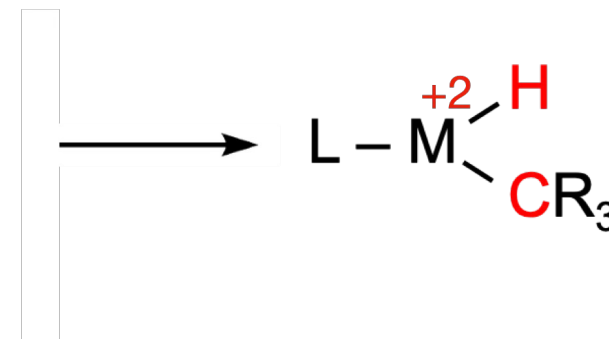
1-10 ps



*Triggered ground-state reactions
Ligand substitution*

C-H activation

1-10 ns



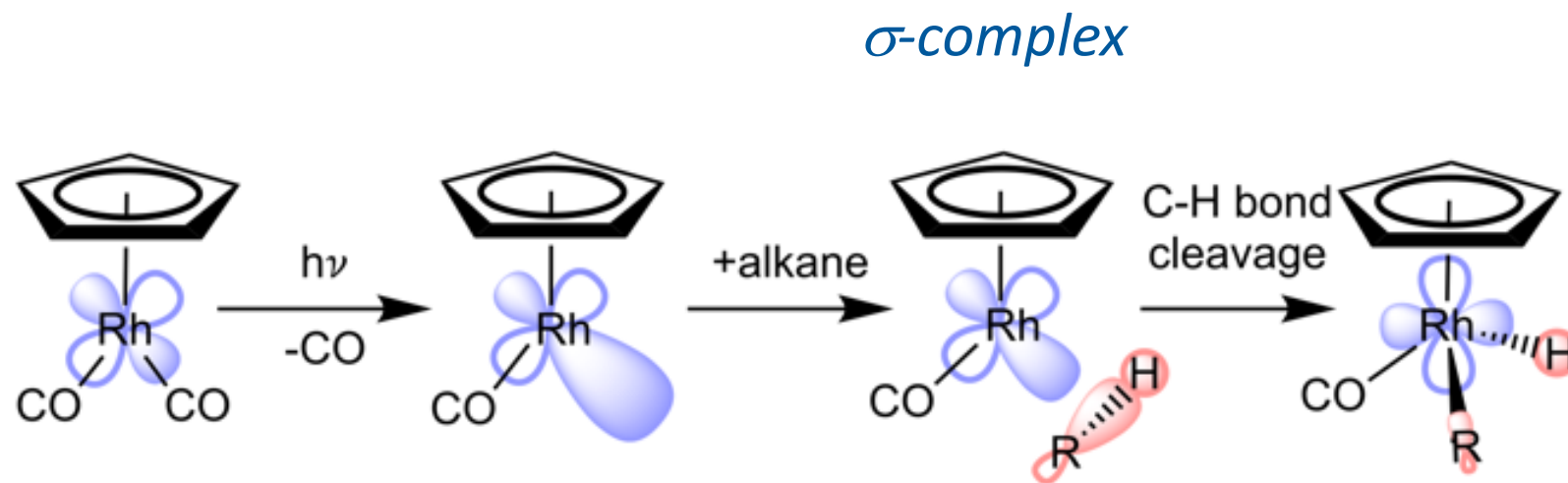
*Oxidative addition
reactions*

Discovered by Bergmann and Graham (1982)

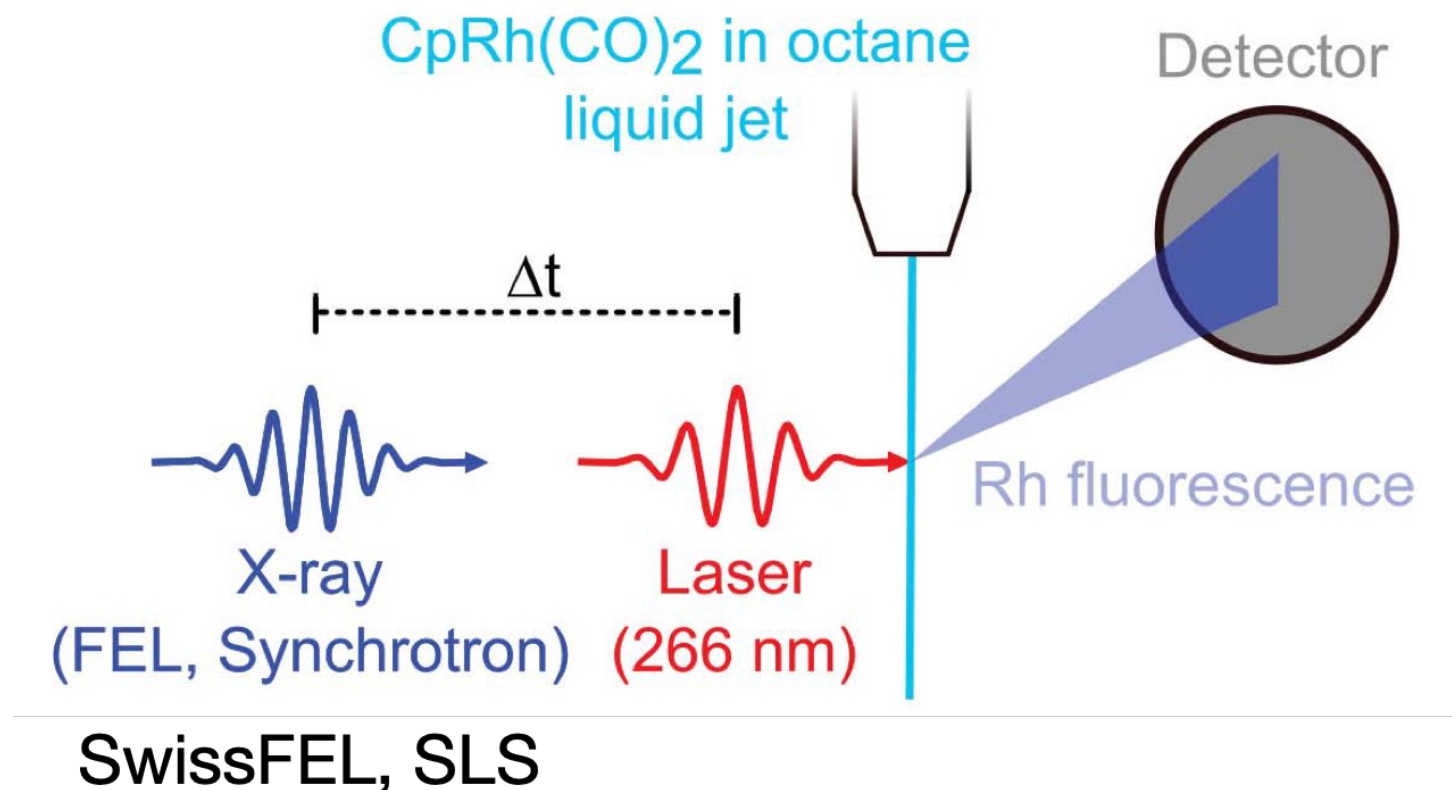
Janowicz, Bergman, *J. Am. Chem. Soc.* **104**, 352 (1982), Hoyano, Graham, *J. Am. Chem. Soc.* **104**, 3723 (1982)

John F. Hartwig, *Organotransition Metal Chemistry: From Bonding to Catalysis* (2010)

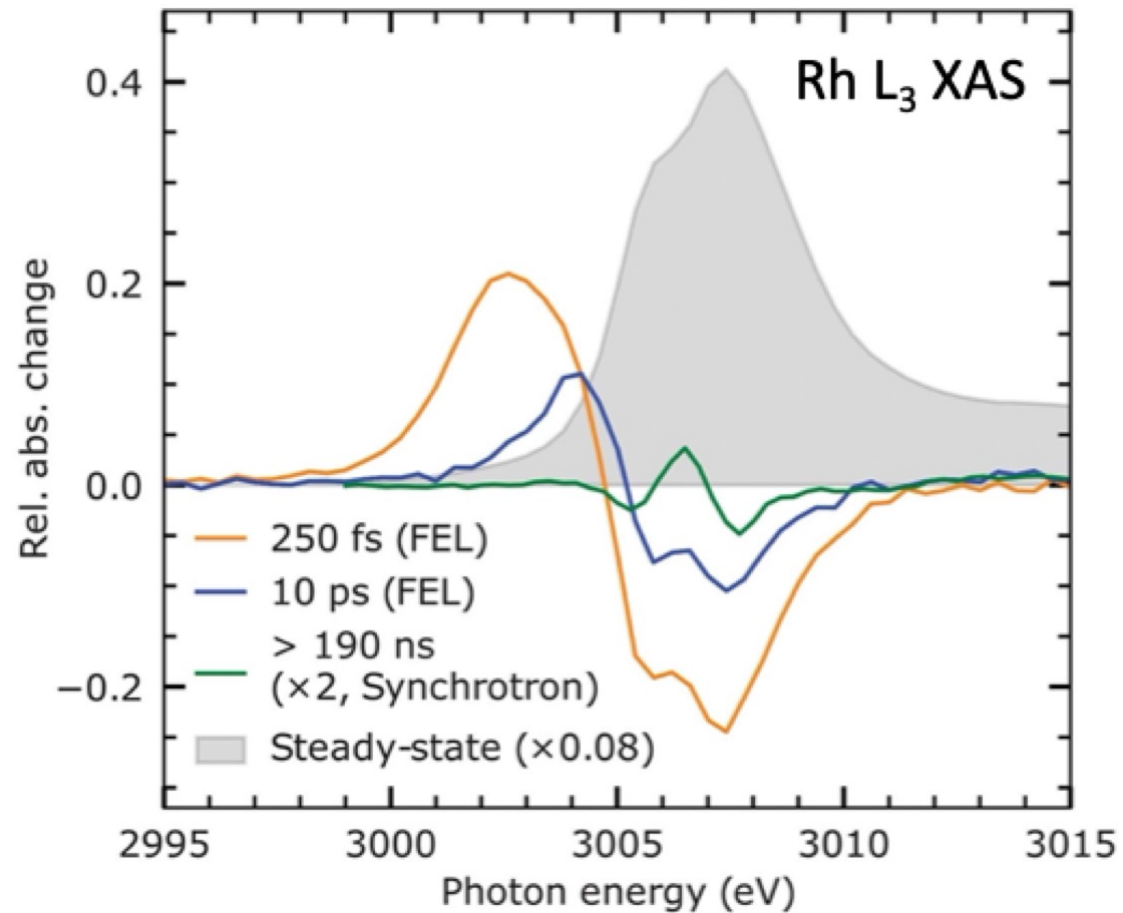
Photochemical C-H activation with TM complexes



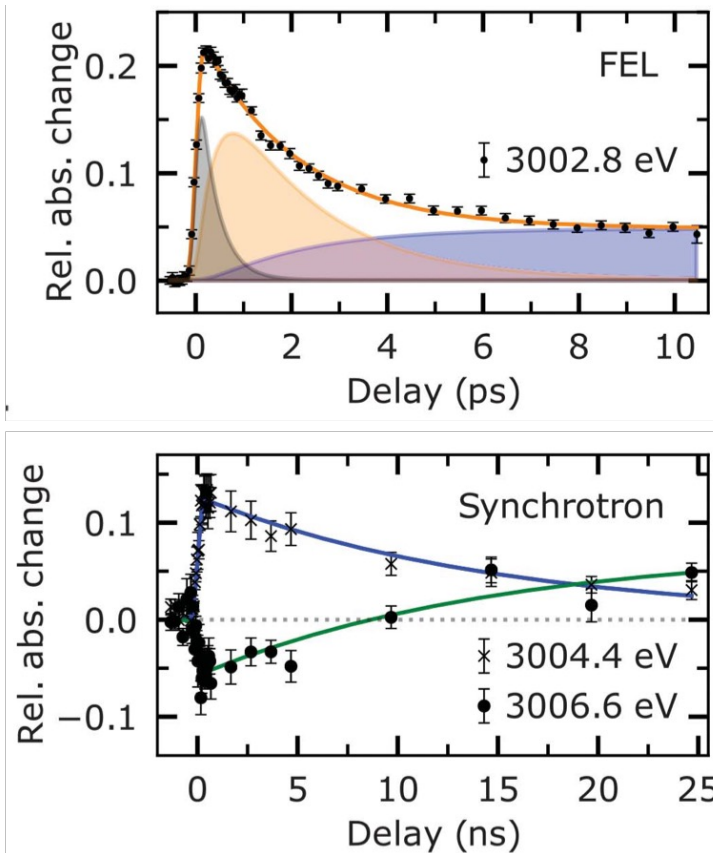
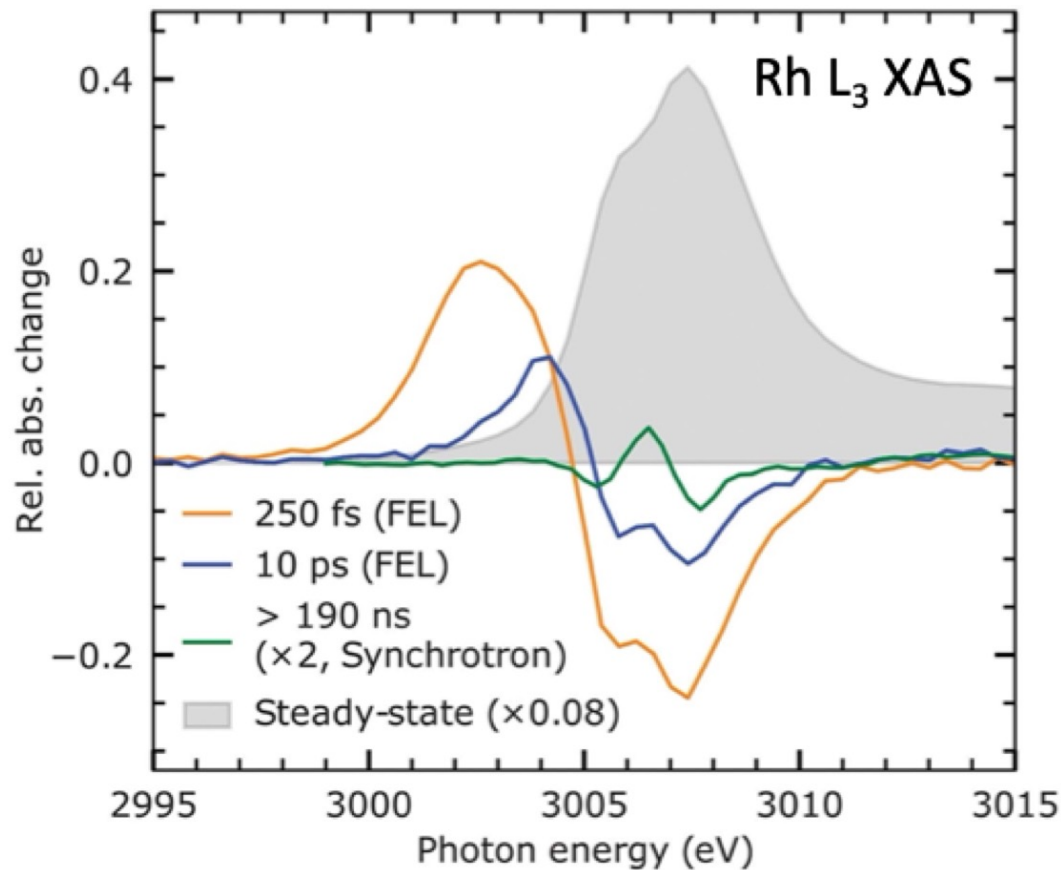
Photochemical C-H activation with TM complexes



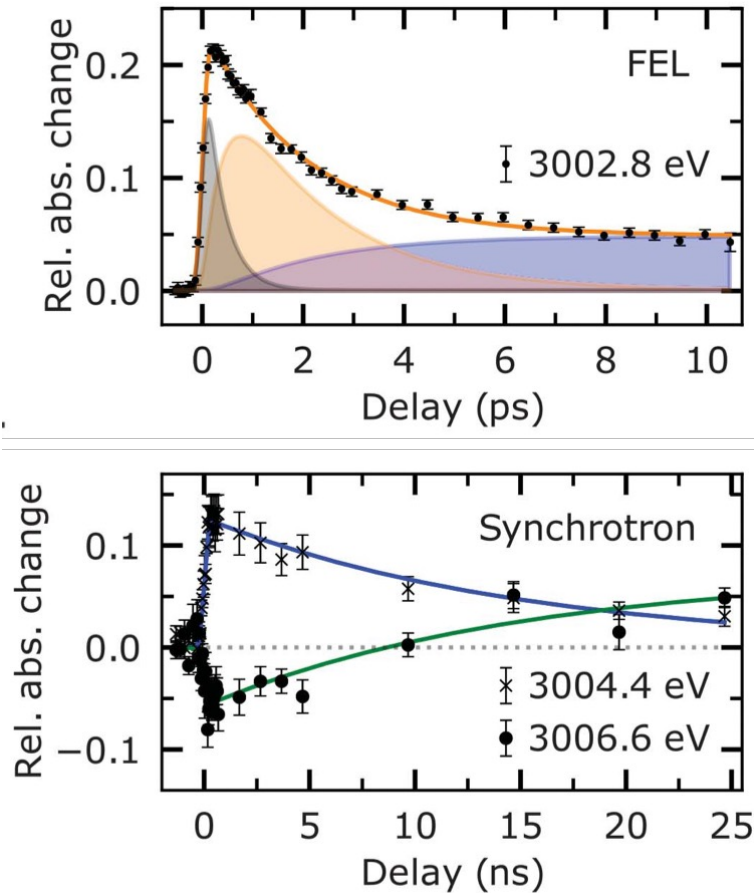
Tracking C-H activation with orbital resolution



Tracking C-H activation with orbital resolution



Tracking C-H activation with orbital resolution



- $\tau_1 = 370$ fs Dissociation
- $\tau_2 = 2$ ps Octane association
- $\tau_3 = 14$ ns C-H activation

Testing fundamental notions of orbital interactions

ANGEWANDTE CHEMIE

Volume 21 · Number 10

October 1982

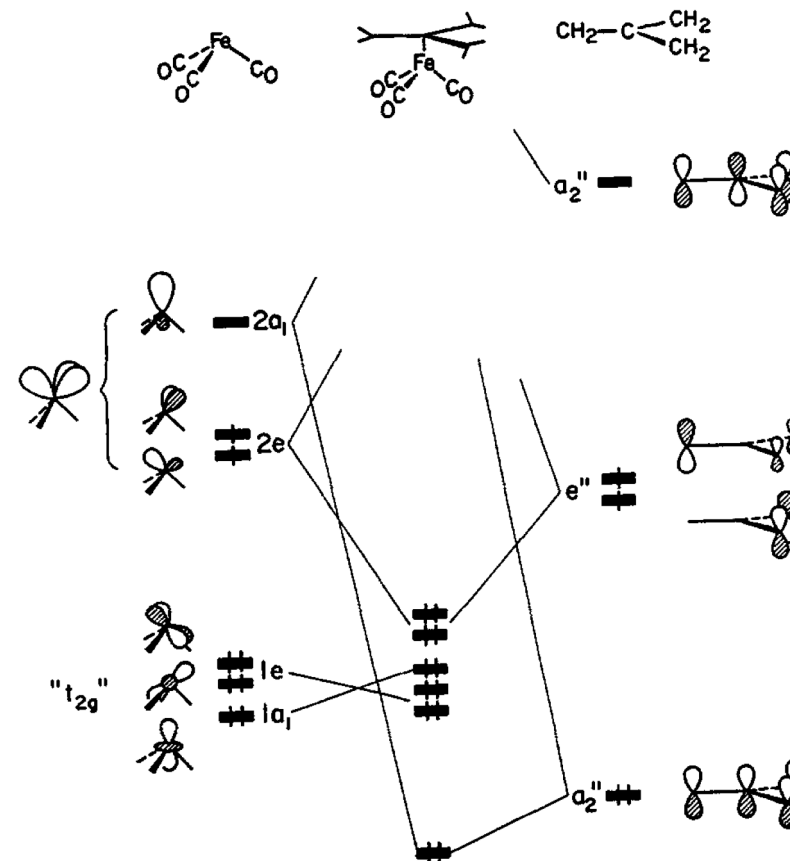
Pages 711–800

International Edition in English

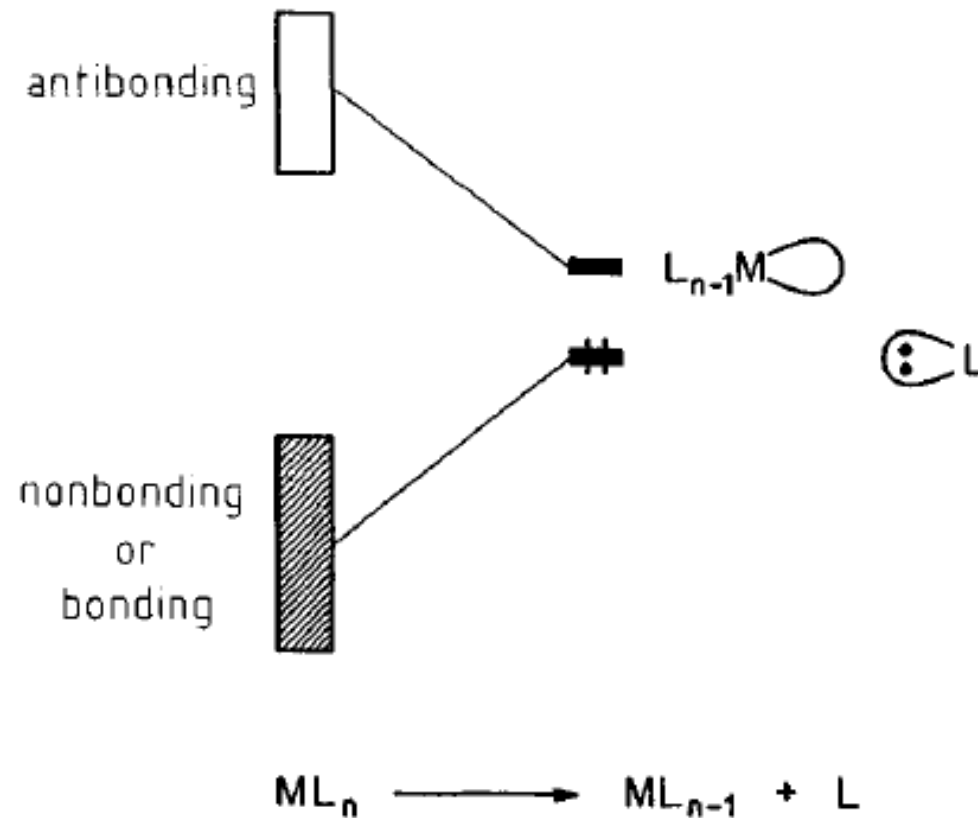
Building Bridges Between Inorganic and Organic Chemistry
(Nobel Lecture)**

By Roald Hoffmann*

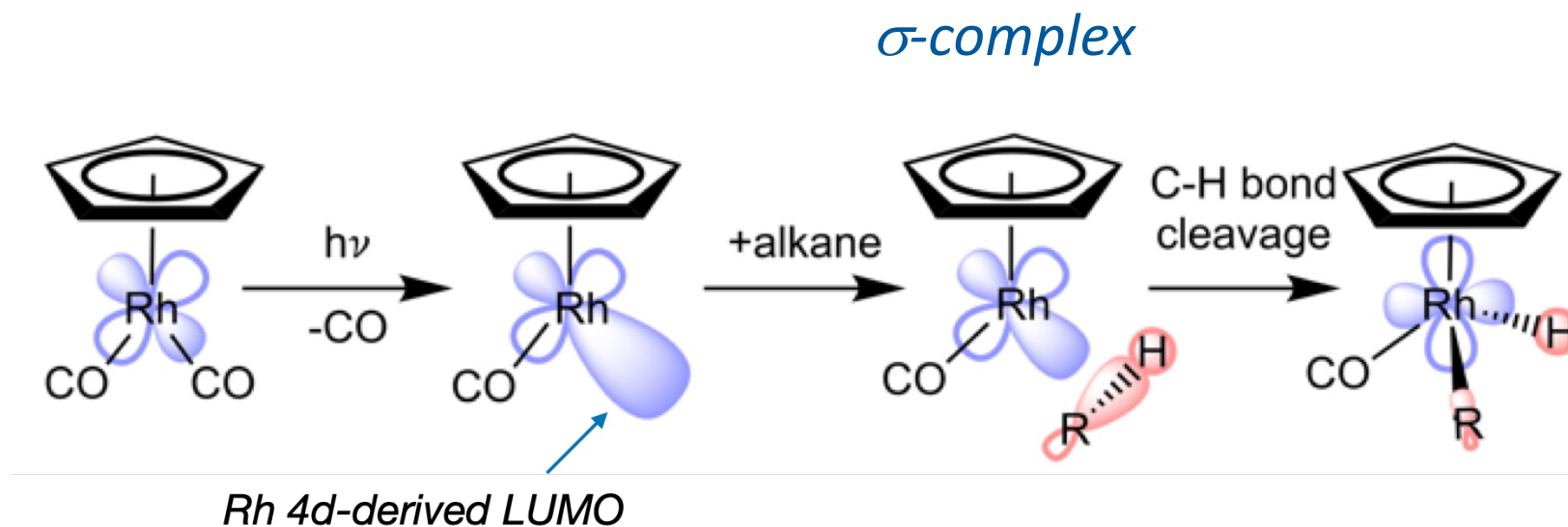
Nobel Prize in Chemistry 1981 awarded jointly to Kenichi Fukui and Roald Hoffmann "for their theories, developed independently, concerning the course of chemical reactions"



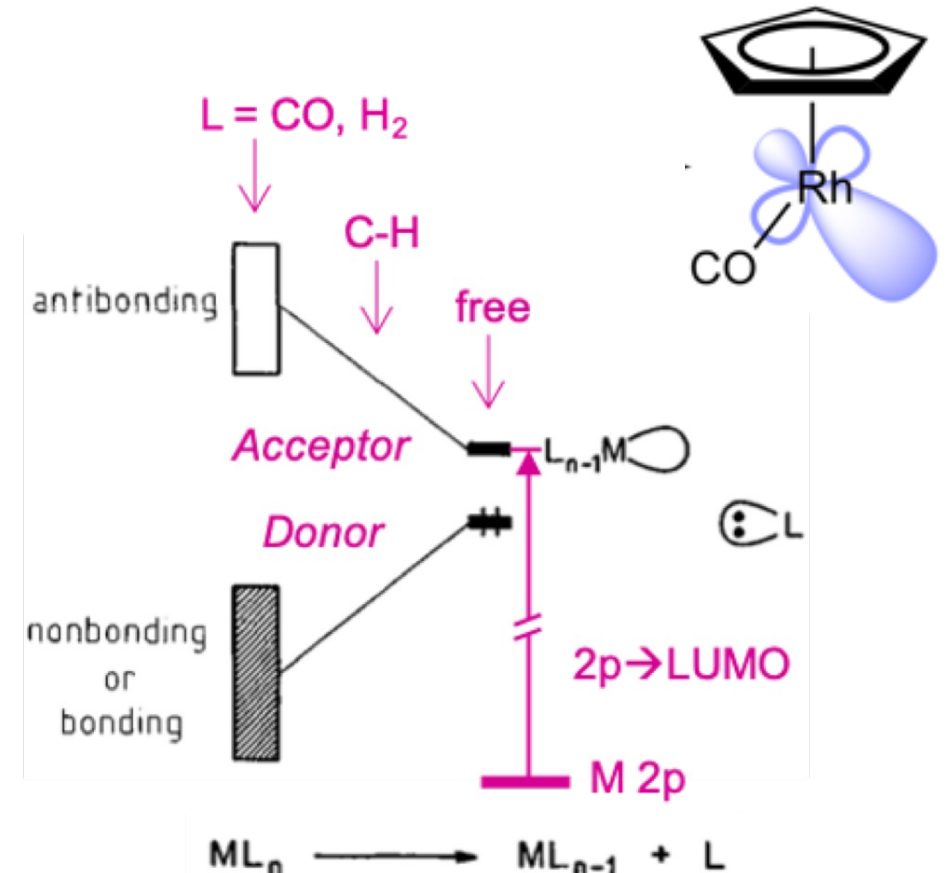
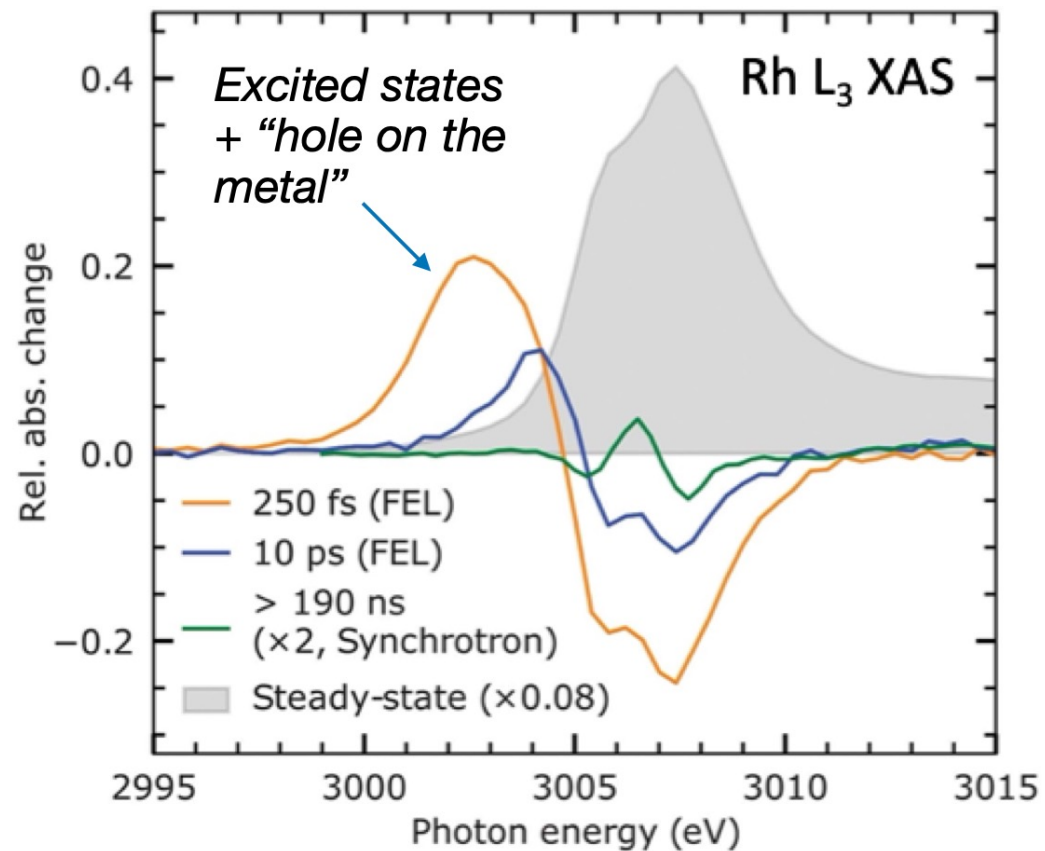
Testing fundamental notions of orbital interactions



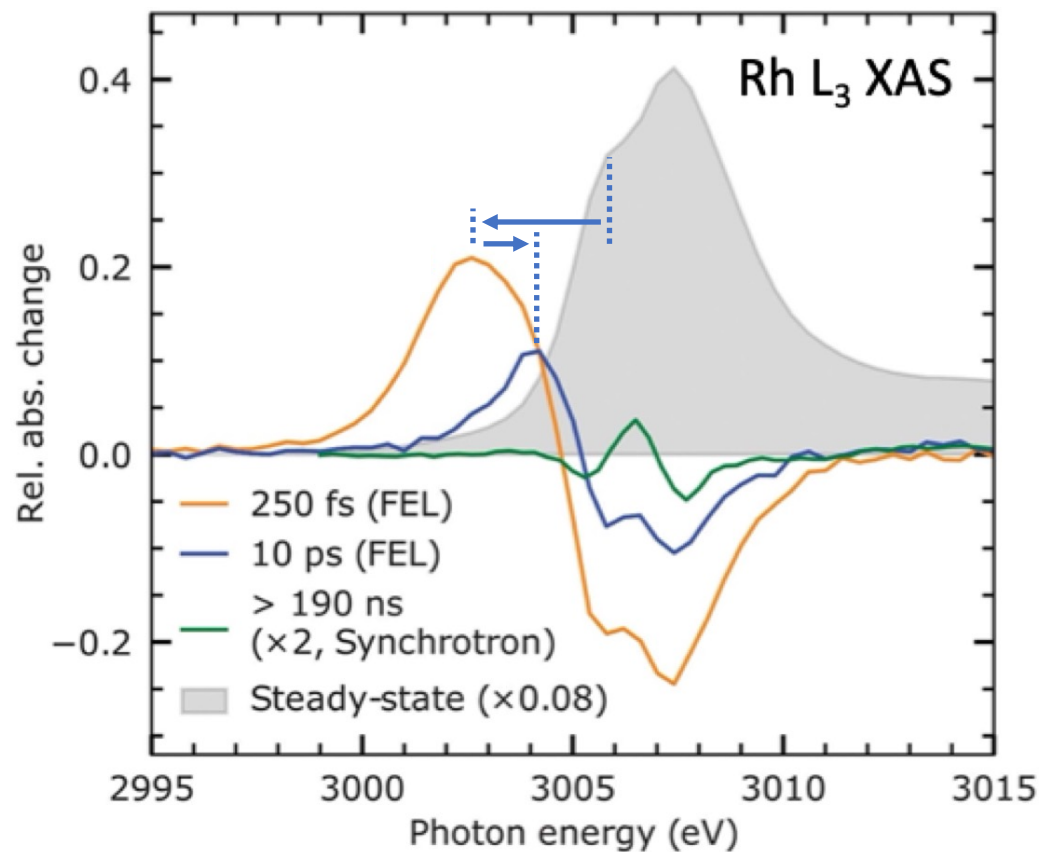
Tracking C-H activation with orbital resolution



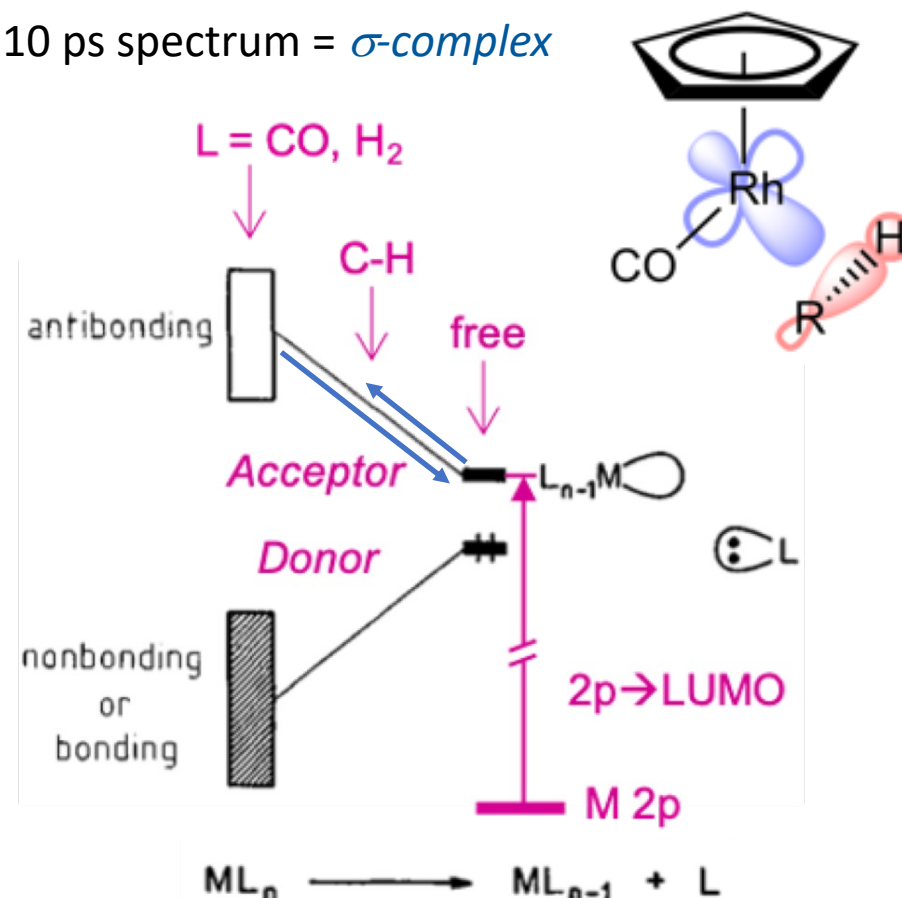
Tracking the hole on the metal (dissociation)



Tracking solvent association (alkane association)



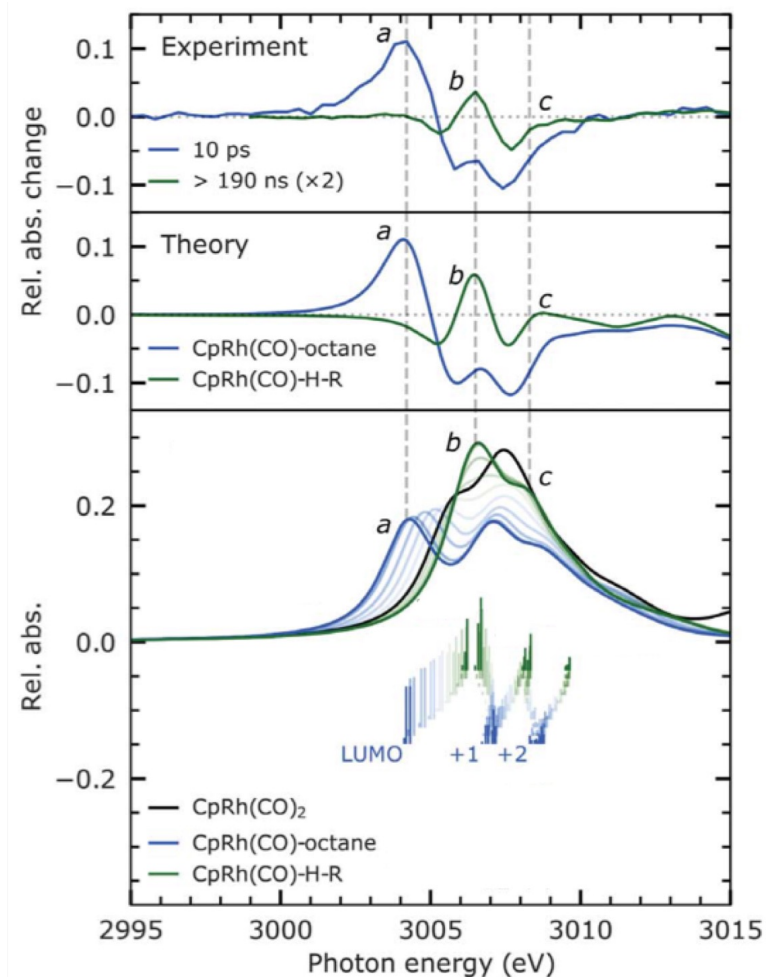
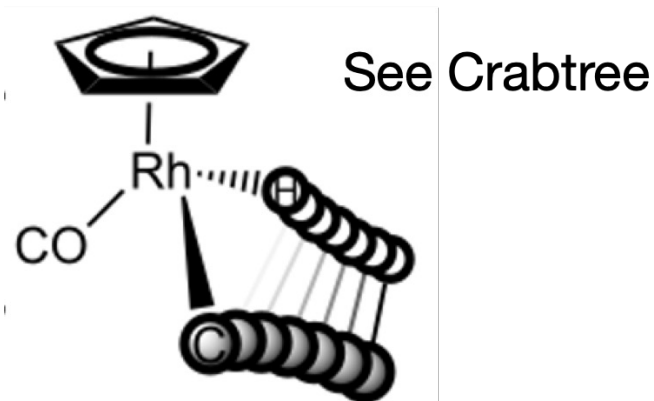
10 ps spectrum = σ -complex



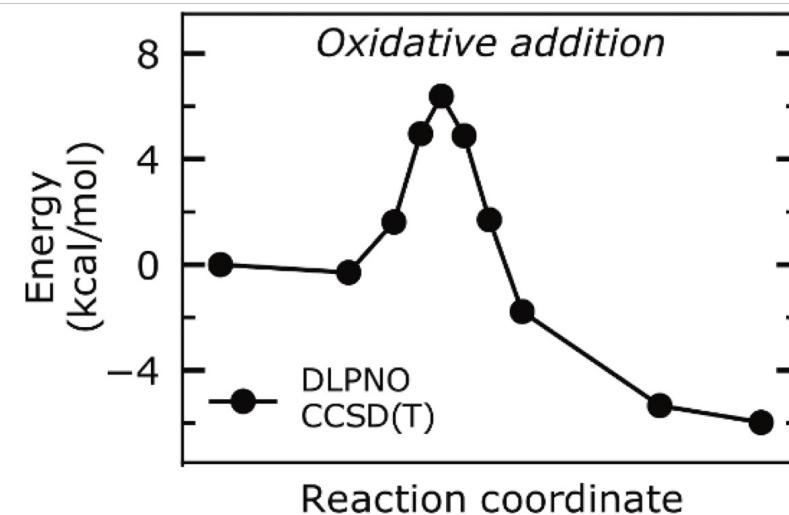
R. Hoffmann, Angew. Chem. Int. Ed. Engl. 21, 711-724 (1982)

Jay, Banerjee, et al., Science 380, 955-960 (2023)

Tracking C-H activation with orbital resolution

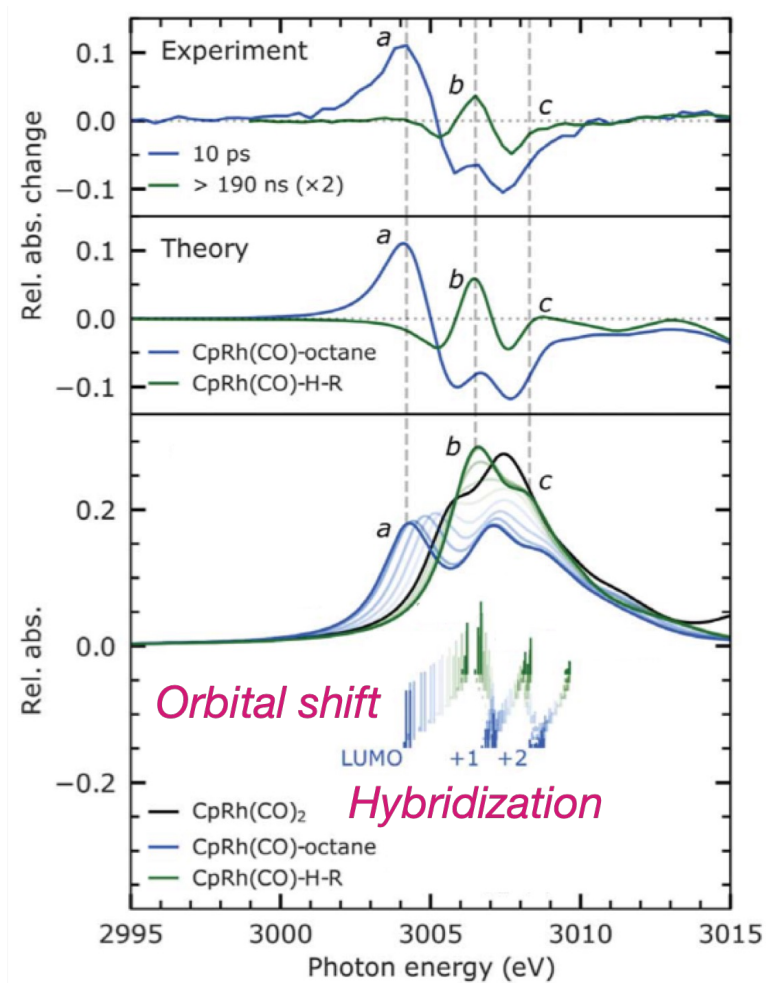


4.6 eV/molecule
100 kcal/mol, 440 kJ/mol



DFT-based modelling (B3LYP)

Tracking C-H activation with orbital resolution



LUMO increases overlap with C-H bond until C-H cleaves

Rh 2p → LUMO blue-shifts

C-H bond cleavage = LUMO destabilization

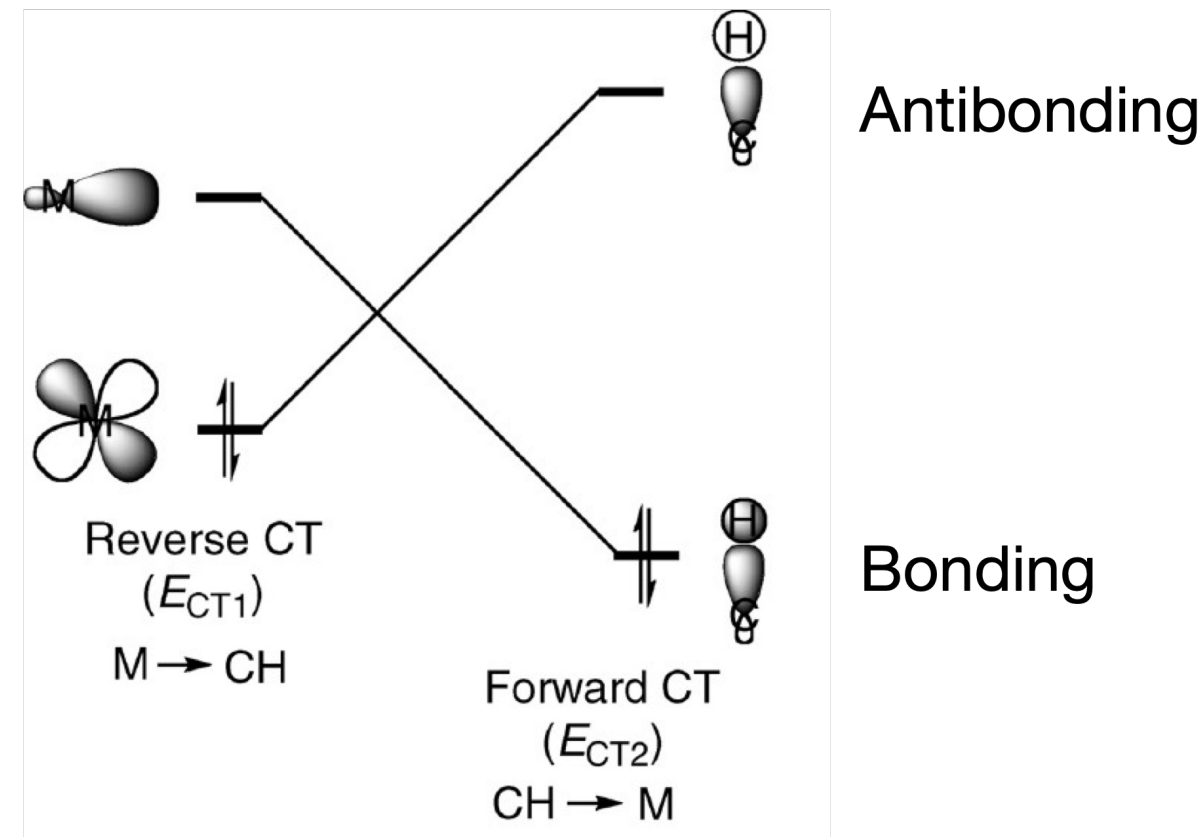
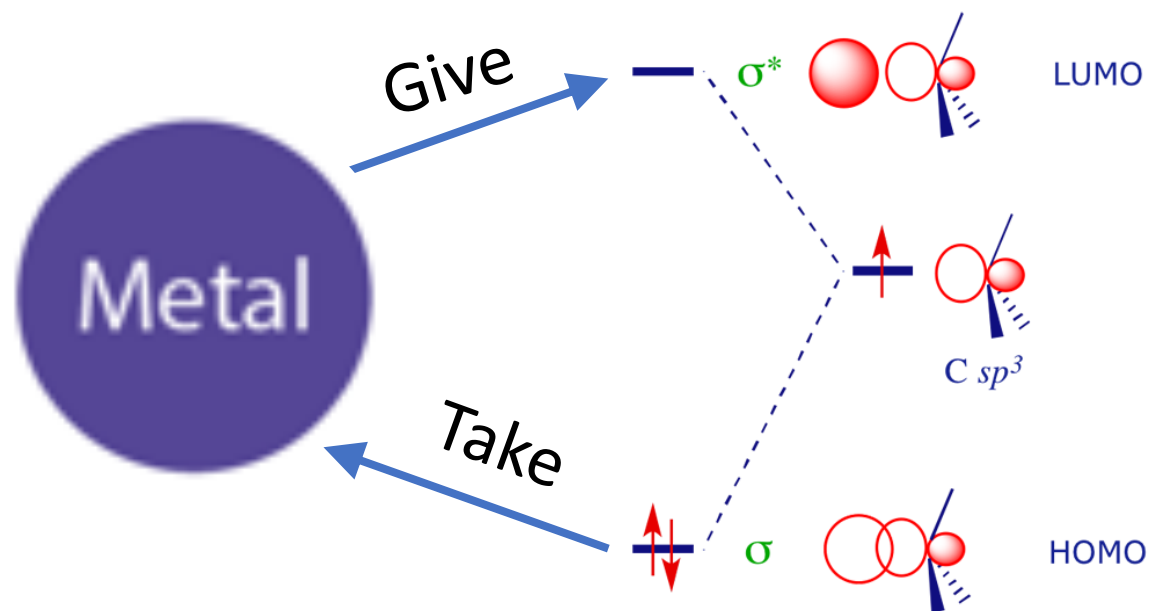
LUMO+1 CO π^* gains Rh 4d becomes 2nd unocc. 4d orbital

Rh 2p → LUMO+1 int. increases

Oxidative addition = LUMO+1 rehybridization

“Oxidation” Rh(I) d⁸ to Rh(III) d⁶

Tracking C-H activation with orbital resolution

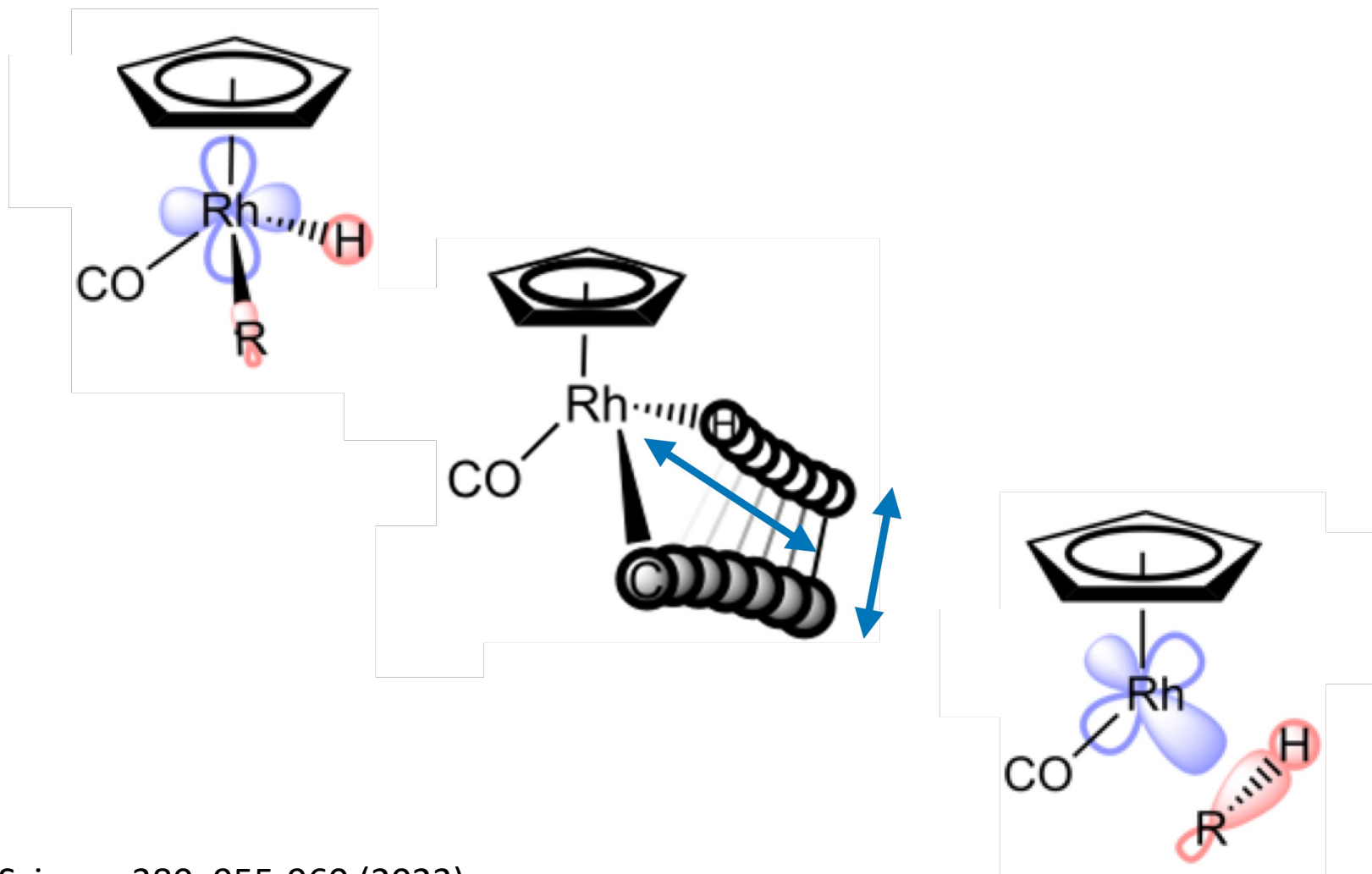


R. Hoffmann 1960s-1980s
 P. Siegbahn JACS 116, 10124 (1994)
 M. Head-Gordon PNAS 104, 6963 (2007)

Jay, Banerjee, et al., Science 380, 955-960 (2023)

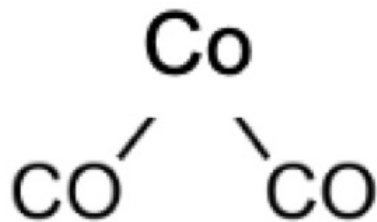
Ess et al., Organometallics **23**, 6459 (2010)

Tracking C-H activation with orbital resolution



Tracking C-H activation with orbital resolution

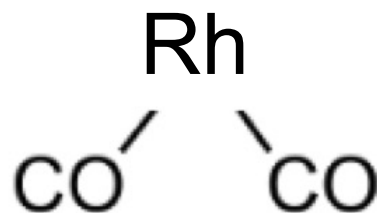
3d	27 Co 1.88
4d	45 Rh 2.28
5d	77 Ir 2.2



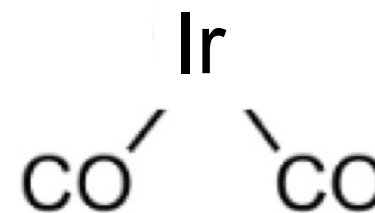
3d soft X-rays
European XFEL

DOES NOT ACTIVATE
C-H BONDS!

Metal L-edge spectroscopy ($2p \rightarrow \text{LUMO}$)



4d tender X-rays
SwissFEL



5d tender X-rays
LCLS

Why is that so?

What we are after

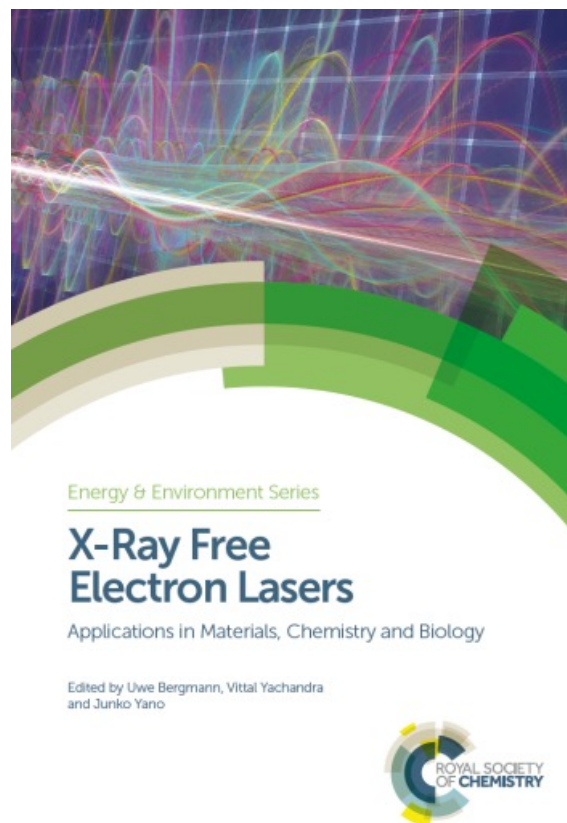
Learning how to rearrange electrons (bonds)

To control molecular transformations

- Make available energy stored in chemical bonds
- Make new, more valuable molecules from abundant resources

Under “mild conditions”

Further reading recommendations



Eberhard J. Jaeschke • Shaukat Khan
Jochen R. Schneider • Jerome B. Hastings
Editors

Synchrotron Light Sources and Free-Electron Lasers

Accelerator Physics, Instrumentation
and Science Applications

Second Edition

With 1116 Figures and 102 Tables

 Springer

- Wernet, Phil. Trans. R. Soc. A **377**, 20170464 (2019) Chemical interactions and dynamics with femtosecond x-ray spectroscopy and the role of x-ray free-electron lasers
- Bergmann, Kern, Schoenlein, Wernet, Yachandra, Yano, Nature Reviews Physics **3**, 264 (2021) Using x-ray free-electron lasers for spectroscopy of molecular catalysts and metalloenzymes
- Jay, Kunnus, Wernet, Gaffney, Annu. Rev. Phys. Chem. **73**, 187 (2022) Electronic structural dynamics of transition-metal complexes with ultrafast soft X-ray spectroscopy

X-Ray Free Electron Lasers – Applications in Materials, Chemistry and Biology Royal Society of Chemistry Energy and Environment Series)
J. Yano, V. Yachandra, U. Bergmann (Eds.) (2016).

Thank you