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

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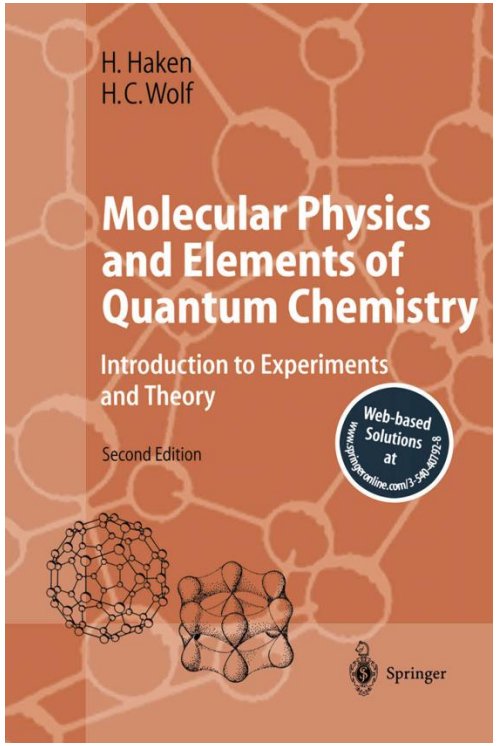
Outline

- A broadly accessible science motivation
- Some basics (throughout)
- One specific example

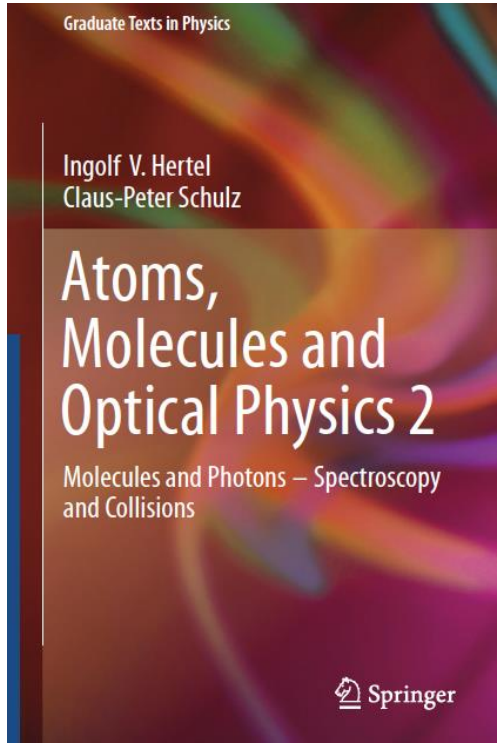
Discussions!

Text book recommendations

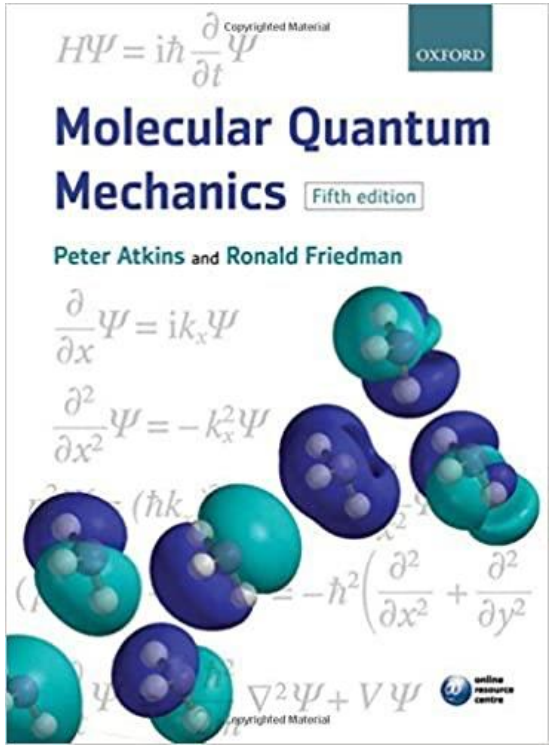
Haken/Wolf



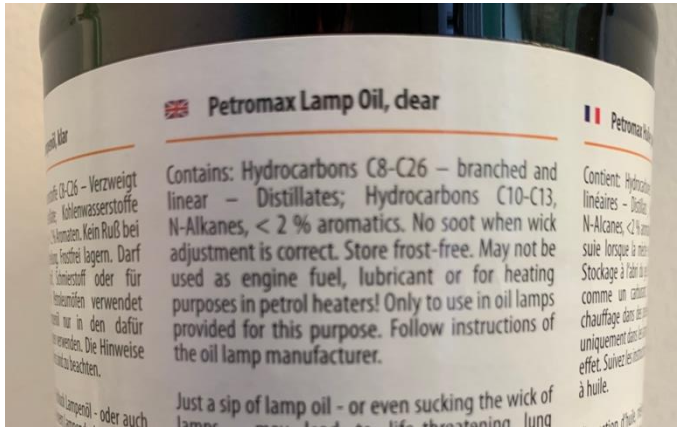
Hertel/Schulz



Atkins/Friedman



Last weekend…

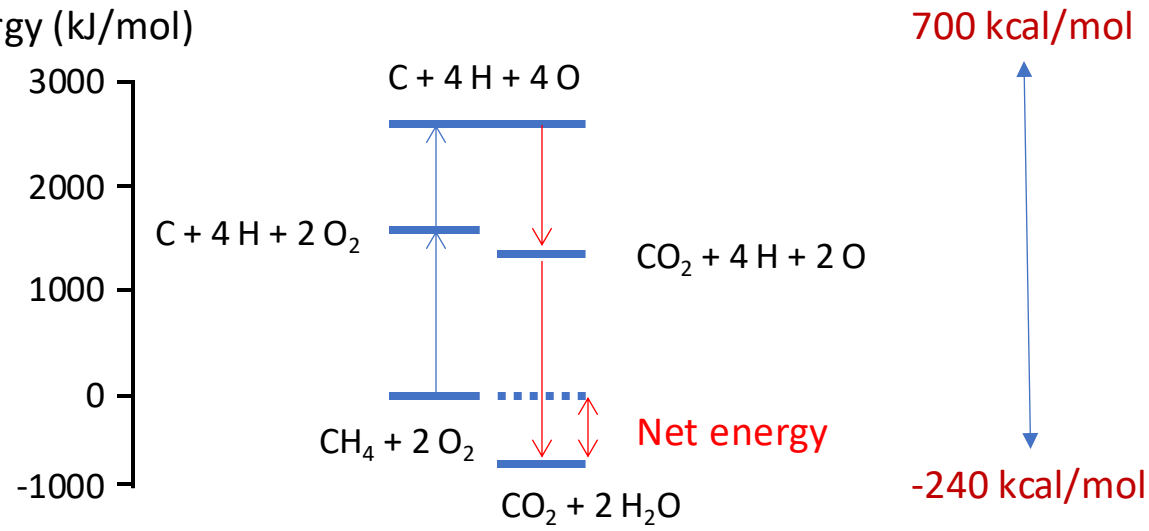


What's in that bottle? What are alkanes? Is it clever to burn alkanes?

Chemical energy

Combustion frees up energy and light stored in chemical bonds, but…

Combustion of methane to CO_2, water, heat and light



What "else" are we doing here?

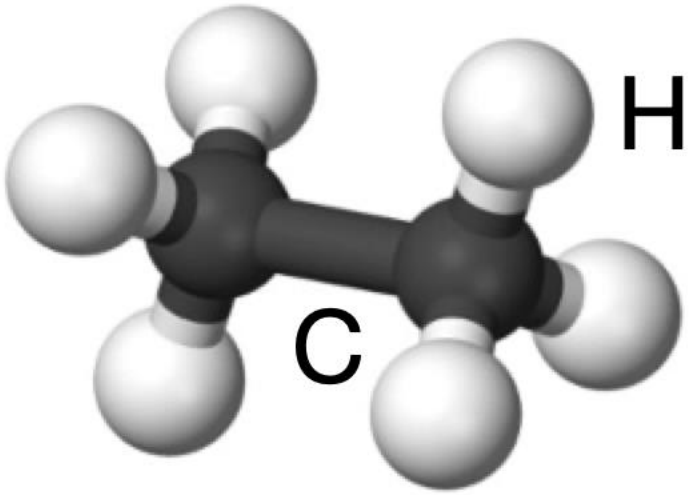
- Making energy (heat, light) by rearranging chemical bonds
- Rearrange chemical bonds
- We are making new molecules!

Catalysis!

Alkanes, a form of hydrocarbons

4.3 eV

100 kcal/mol, 440 kJ/mol



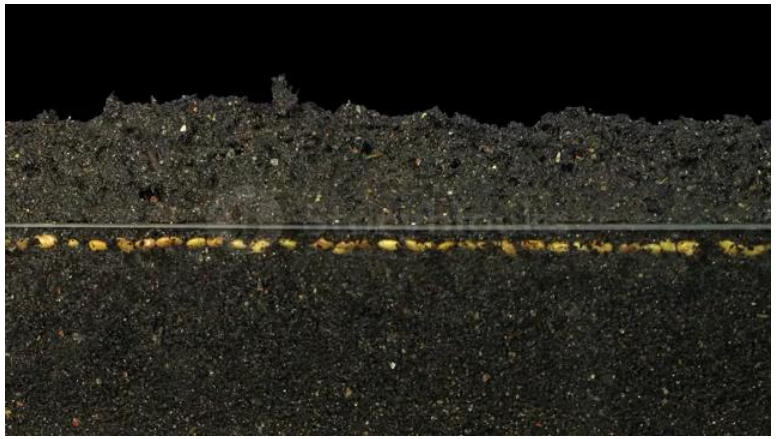
Alkane

Very stable C-H bonds, abundant and stable molecules

(Photo)catalytic C-H activation

Chemical synthesis, transformations, bond engineering

Biology, chemistry and physics at action



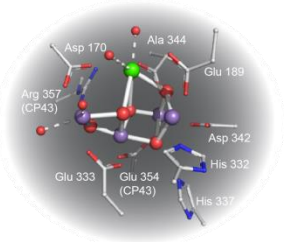
Photosynthesis: Capture, convert, store energy of the sun (with water and CO_2) in the form of chemical bonds, and make organic material.

Curtesy V. Yachandra (LBNL)

Photosynthesis

$$CO_2 + H_2O \xrightarrow{\hbar\omega} (CH_2O)_n + O_2$$

This process generates carbohydrates and the world supply of oxygen



Life Cycle

Photosystem II

How?

Oxygen evolution

$$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$$

The oxygen is derived from water

Cytochrome Oxidase

Aerobic metabolism

$$ATP + CO_2 + H_2O \leftarrow (CH_2O)_n + O_2$$

We consume oxygen to "burn" the energy of carbohydrates to produce ATP, the biological energy currency

Suga et al., Nature **517**, 99 (2015), Young et al., Nature **540**, 453 (2016), Kupitz et al., Nature **513**, 261(2014)

Learn to rearrange bonds

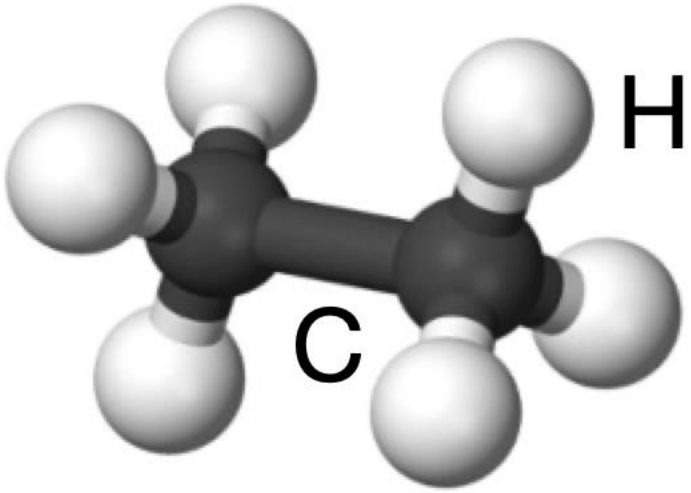
Characterize molecules in weird bonding configurations

Induce and make use of weak interactions

Alkanes, a form of hydrocarbons

4.3 eV

100 kcal/mol, 440 kJ/mol



Alkane

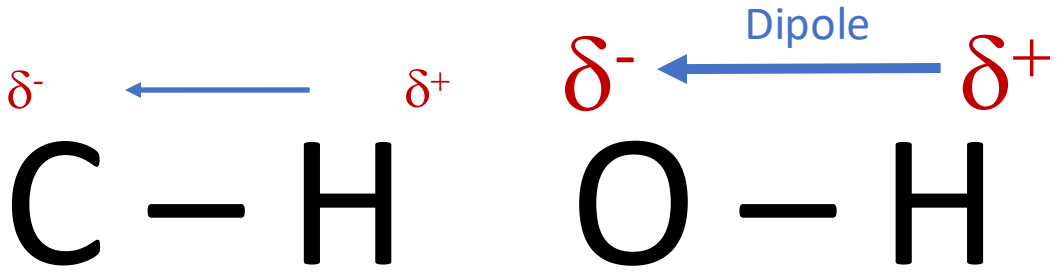
O-H bonds are easier to break

Strength = 110 kcal/mol!?

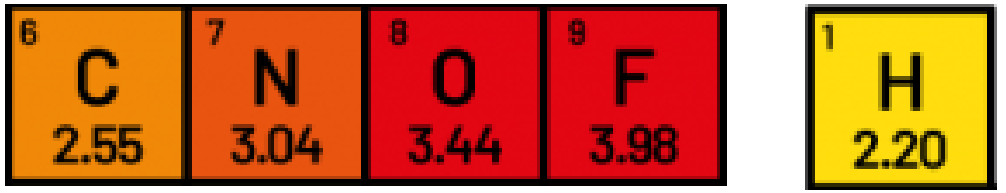
Why are C-H bonds so hard to break?

The C-H bond

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



Electronegativity of the elements



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

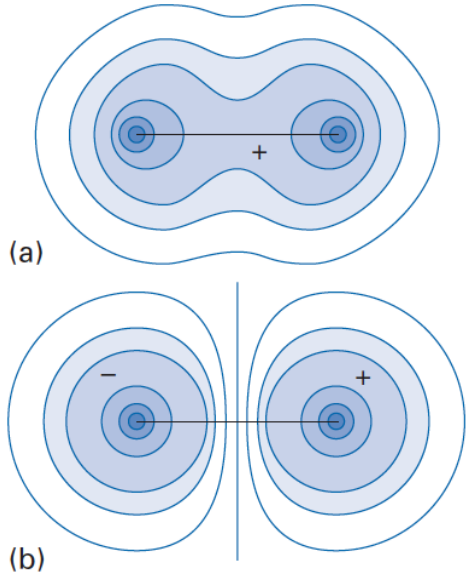


Fig. 8.6 Contour diagrams of the (a) bonding and (b) antibonding orbitals (1σ and 2σ, respectively) of the hydrogen molecule–ion in the LCAO approximation.

Orbital energies

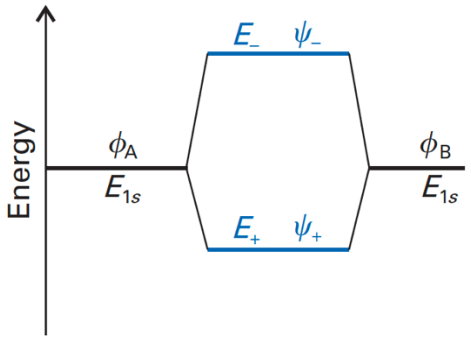


Fig. 8.11 The molecular orbital energy level diagram of the hydrogen molecule–ion in the LCAO approximation. Note that the 2σ-orbital is slightly more antibonding than the 1σ-orbital is bonding.

Atkins/Friedman

Potential energies

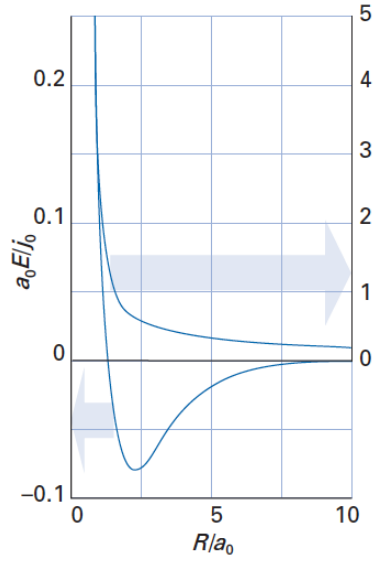
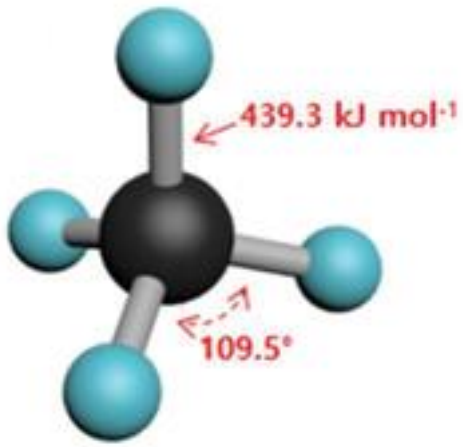
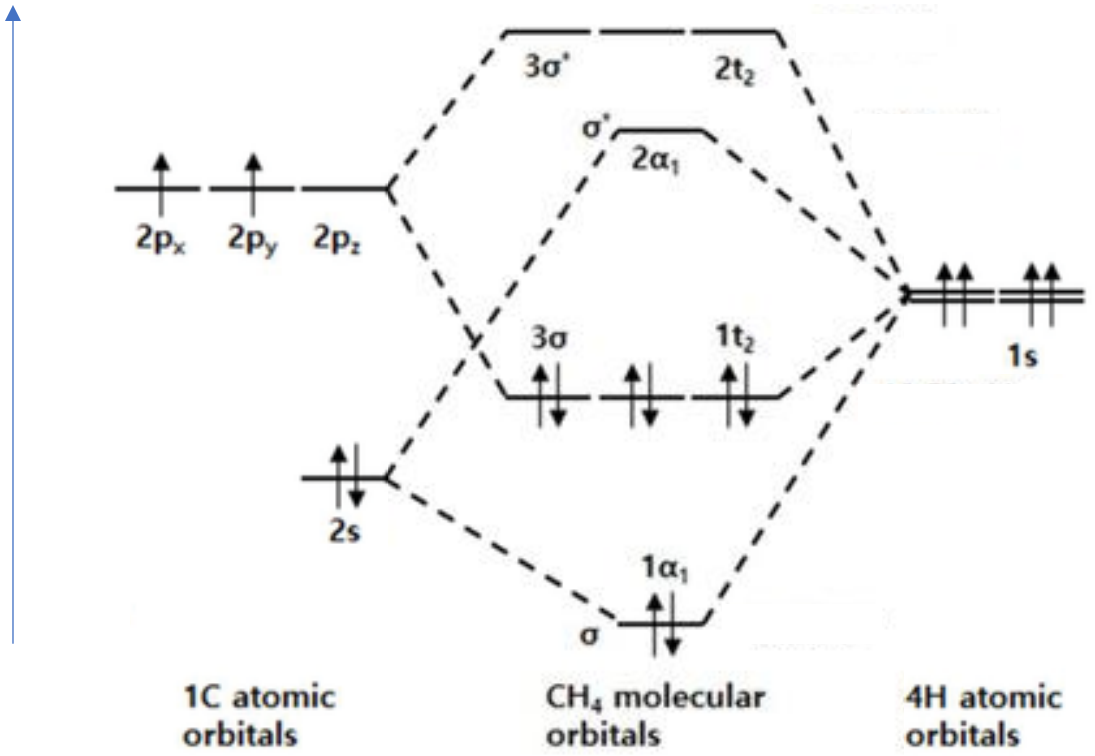


Fig. 8.12 The calculated molecular potential energy curves of the two lowest energy molecular orbitals of the hydrogen molecule–ion within the LCAO approximation. Note the change in scale between the bonding and antibonding curves.

The C-H bond (alkanes, hydrocarbons)

Methane (CH_4)





Anti-bonding

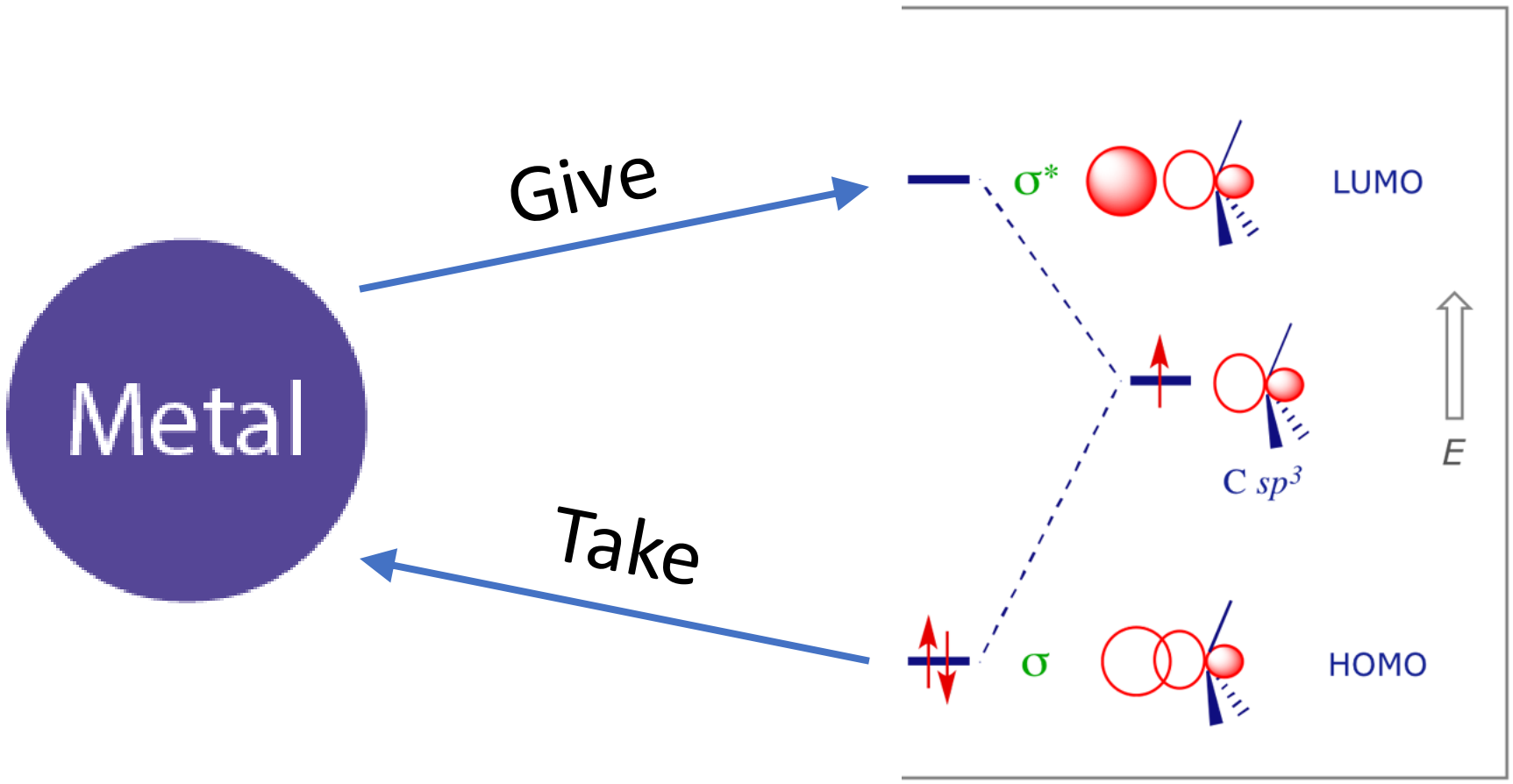
Bonding

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

www.researchgate.net

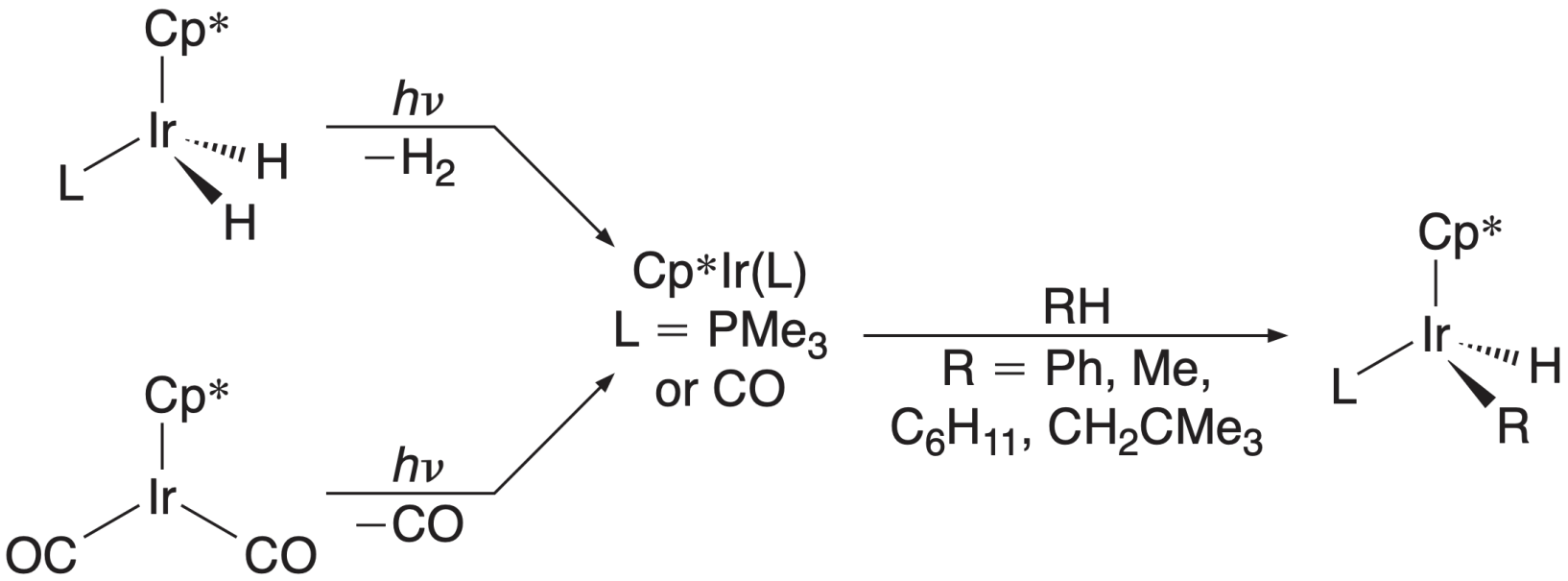
The C-H bond (alkanes, hydrocarbons)

What can we do to destabilize that particular interaction?



https://www.stereoelectronics.org/webPR/PR_01.html

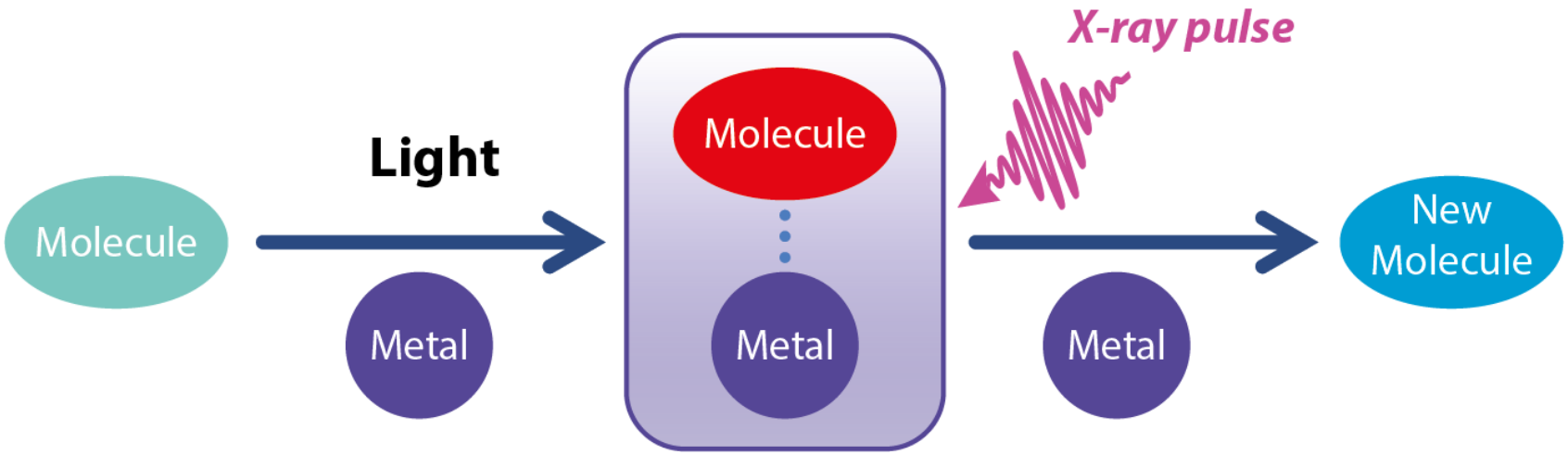
Photochemical C-H bond activation



Discovered by Bergmann, Graham (1982)

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

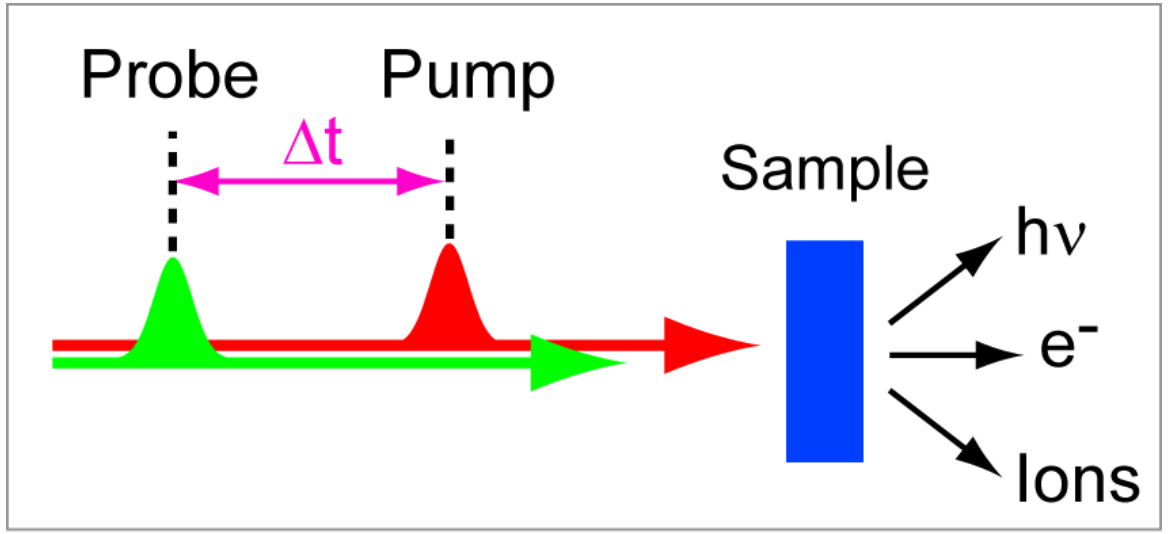
In come metals and X-rays…



- Electronic excitation
- Electron density
- Dynamics – kinetics (fs-ms)

Pump-probe spectroscopy

To catch (characterize) short-lived transient intermediates



Ph. Wernet, *Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions*, Phys. Chem. Chem. Phys. **13**, 16941 (2011).

What time-resolution do I need to resolve molecular motion?

Take the speed of sound

- Resolve corresponding displacements
- “Speed of atoms” several 100-1000 m/s
- This corresponds to resolving $100\text{-}1000 \cdot 10^{10}$ Å/10^{15} fs = 0.1-1 Å/100 fs

What time-resolution do I need to resolve molecular motion?

Take the oscillation period of a molecule

- Resolve the oscillatory motion
- E.g. 3500 cm^{-1} (wavelength of ~3 µm) for the O-H stretch vibration in H_2O
- $T = 1/f$, $c=\lambda \cdot f \rightarrow T = \lambda/c \rightarrow T = 3 \cdot 10^{-6} m/(3 \cdot 10^{8} m/s) = 10^{-14}$ s
- This corresponds to a duration of the vibrational period of ~10 fs

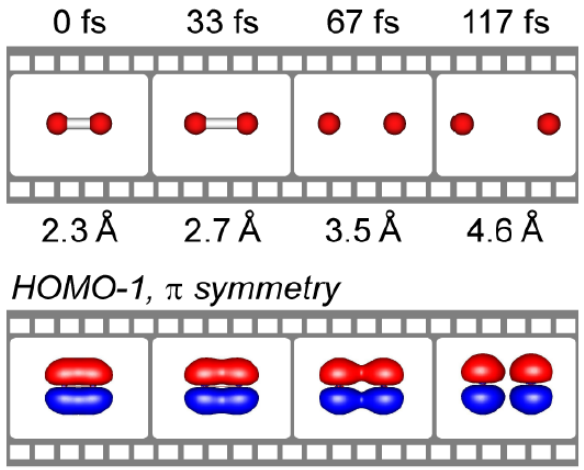
What time-resolution do I need to resolve molecular motion?

Take the Brownian motion

- Resolve the mean square displacement $x^2(t)$ with time t: $x^2(t) = \frac{k_B T}{3\pi R\eta} t$
- With T temperature, R particle radius, η viscosity
- Albert Einstein (1905), Marian Smoluchowski (1906) and Paul Langevin (1908)
- Displacement of 1 Å takes 100 fs (R = 1 Å, $\eta = 20 \cdot 10^{-6}$ kg/(m·s) for O_2, ideal gas)

Imagine what you just did…

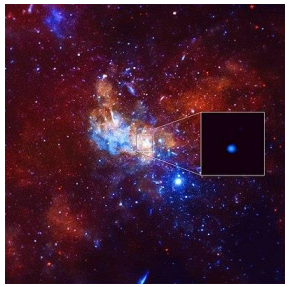
- Size of an atom/orbital 10^{-10} m
- Time scale of atomic motion 100 fs = 100 x 10^{-15} s



You just imagined that

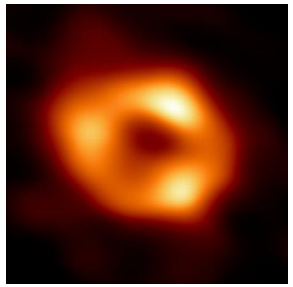
- Size of a supermassive black hole (in our galaxy) 5 x 10^{12} m
- Age of the universe 420 x 10^{15} s

Sagittarius A, supermassive black hole in center of the milky way



Wikipedia

Stars orbiting supermassive black hole in milky way (1 s = 1 year)

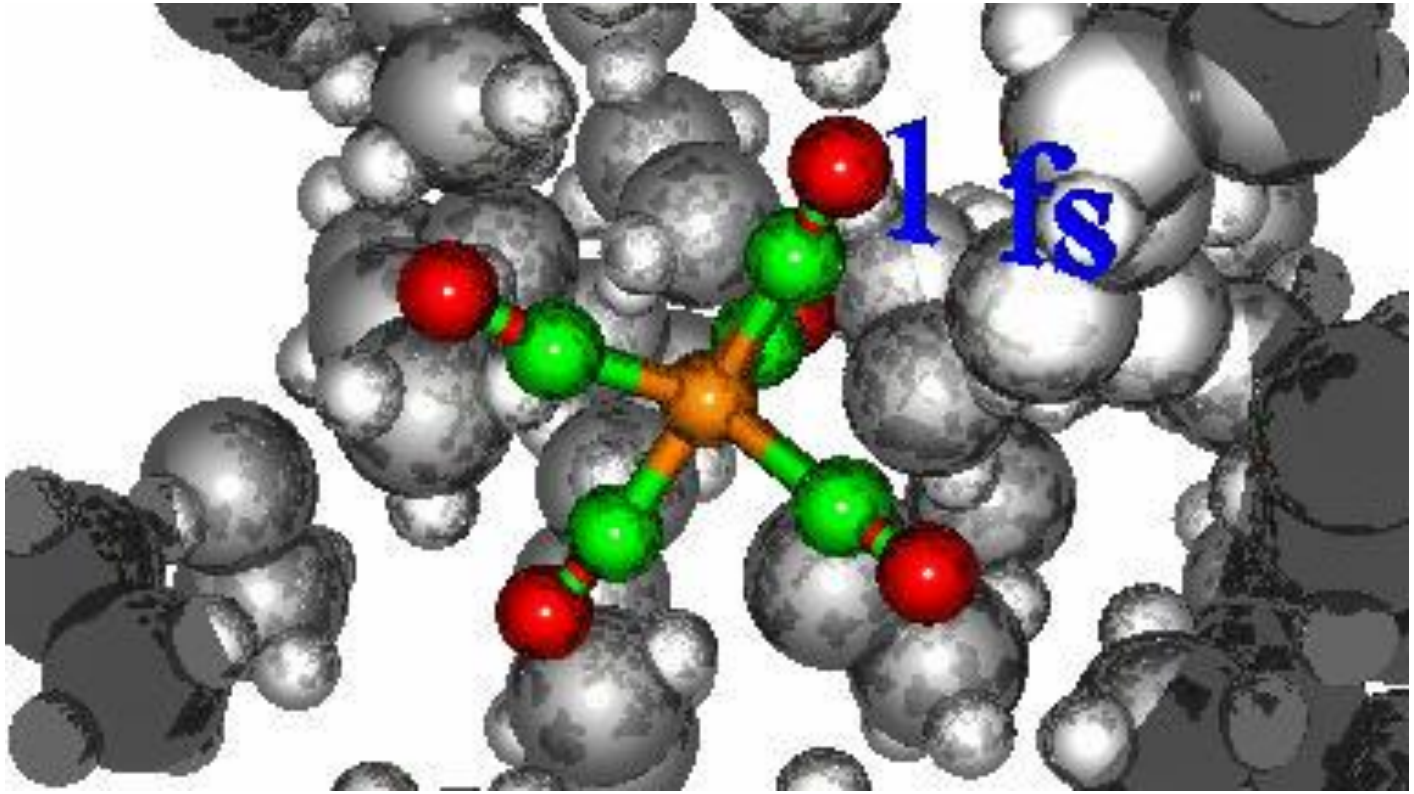


ESO

European Southern Observatory

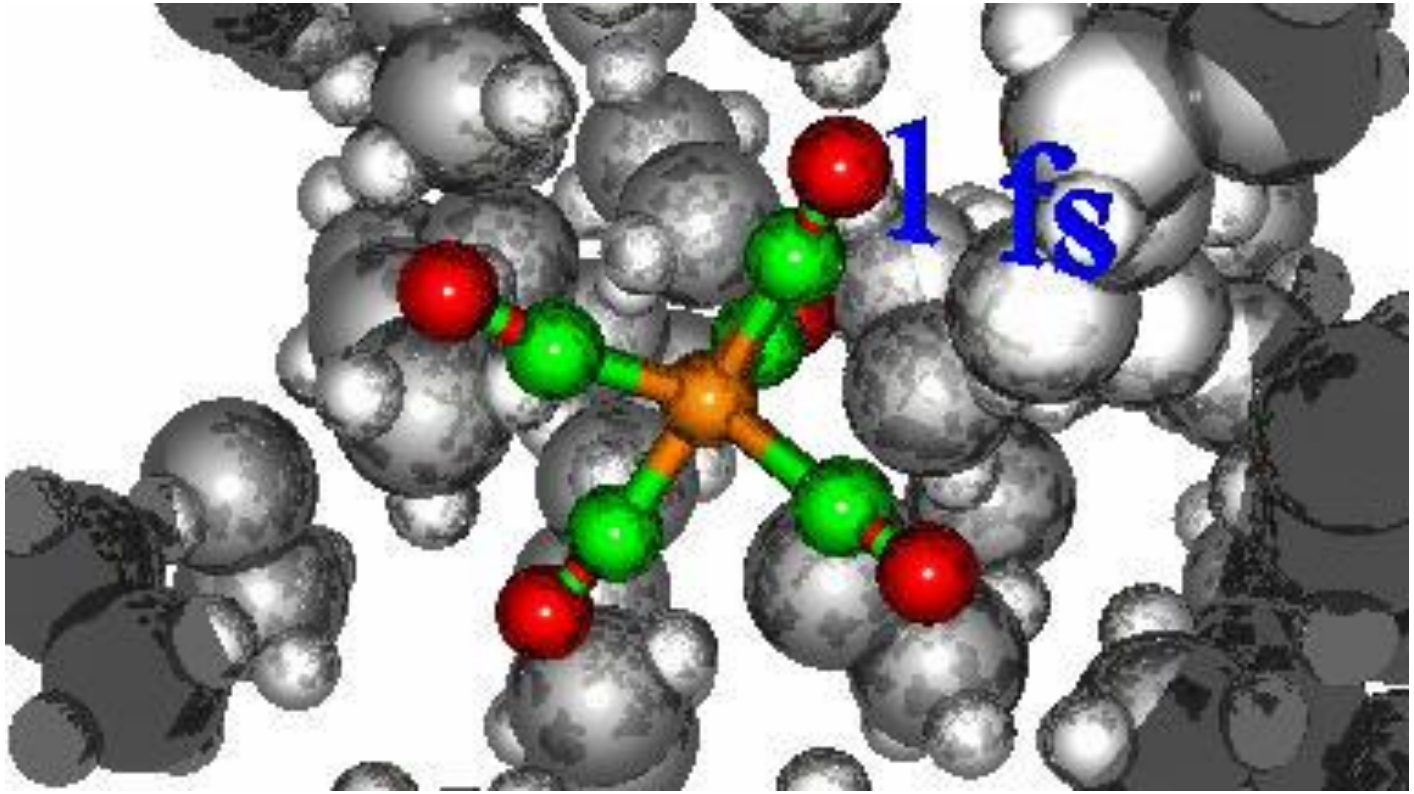
Time slows + stops, things stop existing, information is lost (?)

What do you see?



Where are the electrons?

Molecular dynamics simulation
Michael Odelius (Stockholm University)



$Fe(CO)_5$ dissociation in ethanol

How fast do electrons move?

- Ask yourself: Why do I care?
- Do I want to observe electron motion?
- Do I want to follow the rearrangements of electrons as nuclei are moving?
  - **I need fs time resolution!**

- So, what time resolution do I need to observe electron motion?

How fast do electrons move?

Take the most basic atom and look at the electron in the ground state of the atom

- Classically the electron takes 150 as to circulate the proton
- I need as temporal resolution

How fast do electrons move?

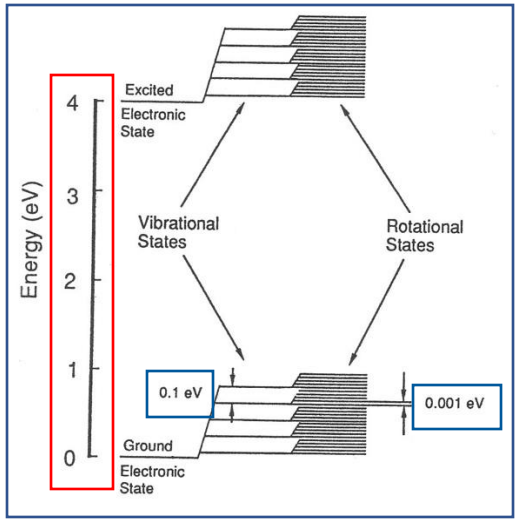
Adopt the same approach as for speed of atoms (O-H stretch vibration and IR probing)

- Now: Speed of electrons
- Probing: With UV/Vis or X-ray wavelengths (*electronic* transitions = motions of e)

- Case A: Valence electronic excitation (take 4 eV)
- At least one cycle of 4 eV radiation (310 nm) to effectuate this transition
- $T = 1/f$, $c=\lambda \cdot f \rightarrow T = \lambda/c \rightarrow T = 310 \cdot 10^{-9}m/(3 \cdot 10^{8}m/s) = 1 \cdot 10^{-15}$ s = 1 fs = 1000 as

- Case B: Knock off an electron (photo-ionize the atom, take 1s ionization of the O atom
- At least one cycle of 550 eV (2.25 nm) to knock off 1s electron
- $T = 1/f$, $c=\lambda \cdot f \rightarrow T = \lambda/c \rightarrow T = 2.25 \cdot 10^{-9}m/(3 \cdot 10^{8}m/s) = 7.5 \cdot 10^{-18}$ s = 7.5 as

Svanberg
Atomic and Molecular Spectroscopy



Will different kinds of electronic transitions occur on different time scales? Can we measure that?

How fast do electrons move?

Take a scattering approach and the Heisenberg uncertainty principle

- $\Delta t \cdot \Delta E = h$
- Time it takes to excite an atom = the scattering time Δt
- Associated with the transition of the atom from its initial to its final state
- Where ΔE is the energy transferred from to the atom
- May be given by $\Delta t = h/\Delta E$
- For photo-excitation, specifically electronic excitation
- With an energy ΔE on the order of 5 eV transferred from the photon to the atom
- This corresponds to $\Delta t = 3 \cdot 10^{-17}$ s = 30 as (electronic excitation of 5 eV)

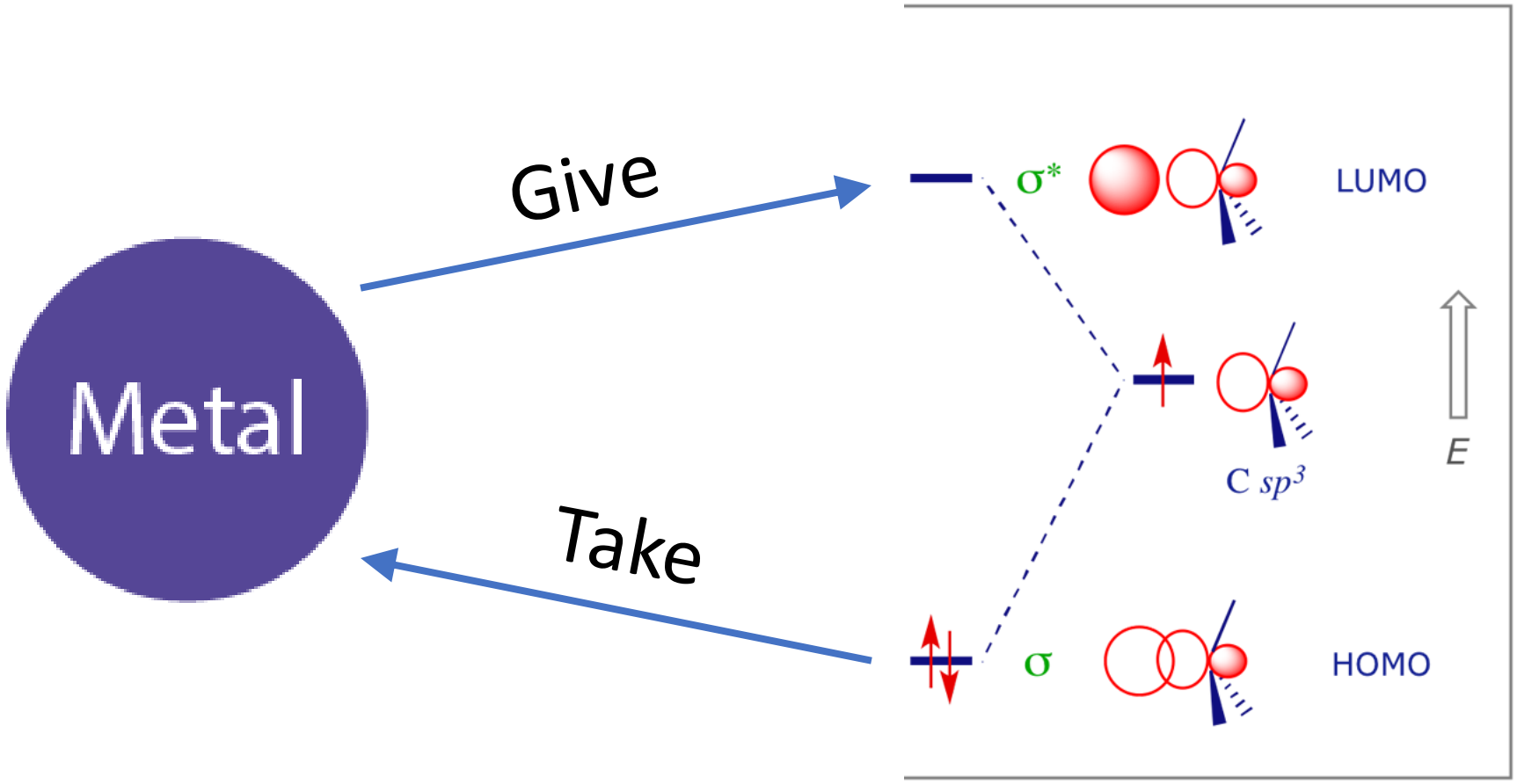
How fast do electrons move?

Take the Sommerfeld model of metals (Drude model + quantum theory)

- For simplicity consider T = 0 K (doesn‘t limit the generality)
- Electrons are particles with momentum $p = \hbar k$ and velocity $v = \hbar k / m$
- Electrons are waves with wave vector k and de Broglie wavelength $\lambda = 2\pi/k$ (e.g. plane wave exp(i k r))
- Fermi-Dirac distribution of velocities
- Occupied region in (quantized) k space containing all occupied one-electron levels is a sphere (Fermi sphere with Fermi surface) with radius k_F (largest possible wave vector)
- Fermi momentum $\hbar k_F$ = Momentum of the occupied one-electron levels of highest energy (Energy E_F)
- Fermi velocity $v_F = \hbar k_F/m$ = Velocity of the occupied one-electron levels of highest energy
- Fermi velocity is the velocity of Fermions (electrons) with kinetic energy = Fermi energy
- For most metals $v_F \approx 10^6$ m/s (e.g. Fe metal $2 \cdot 10^6$ m/s)
- Now it’s very simple: 10^6 m/s = 10^6 10^{10} Å/10^{-18} as = 1 Å/100 as (even at T = 0 K and 1% of speed of light…)

Photochemical C-H activation with TM complexes

What can we do to destabilize that particular interaction?



https://www.stereoelectronics.org/webPR/PR_01.html

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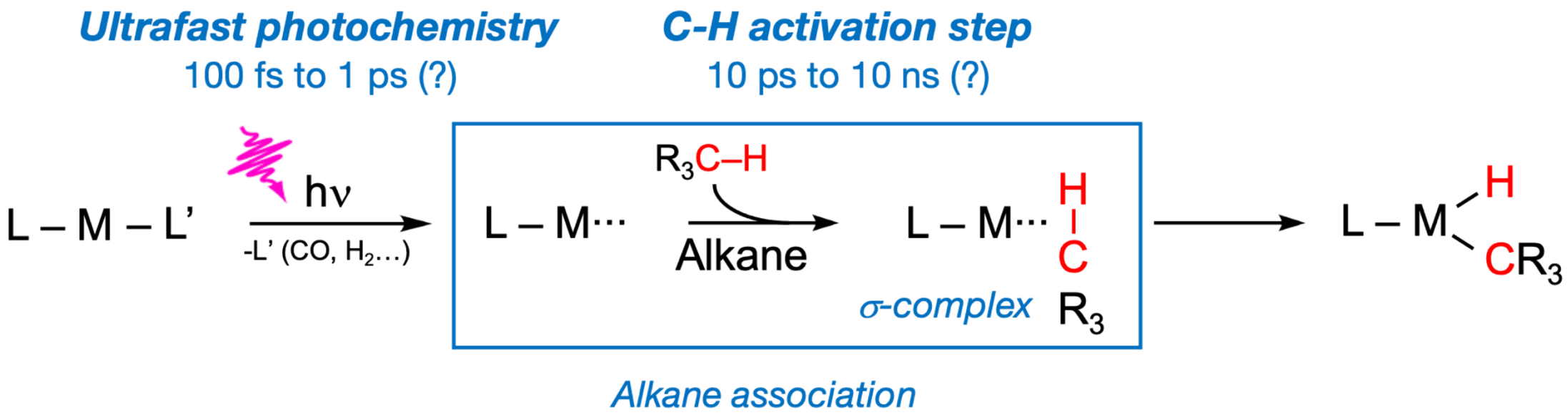

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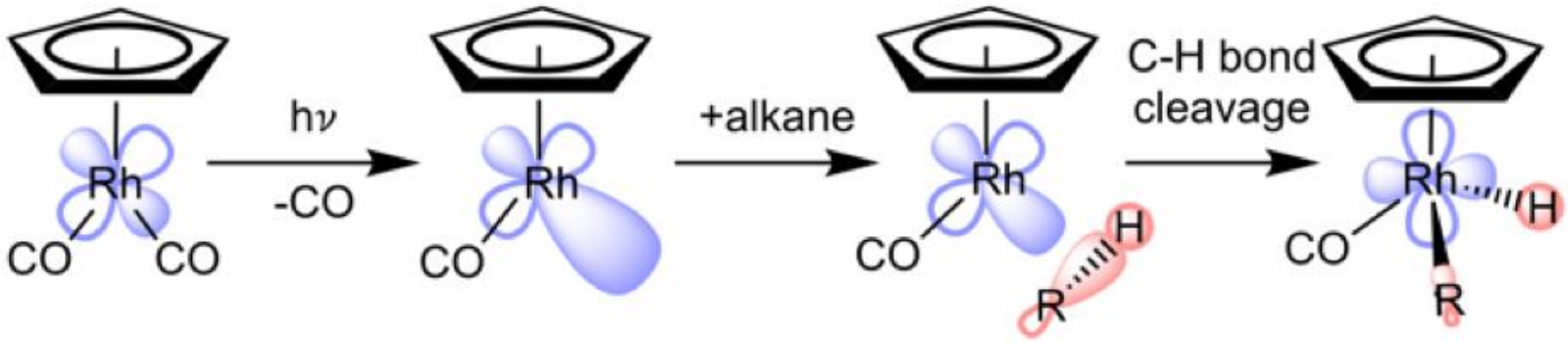

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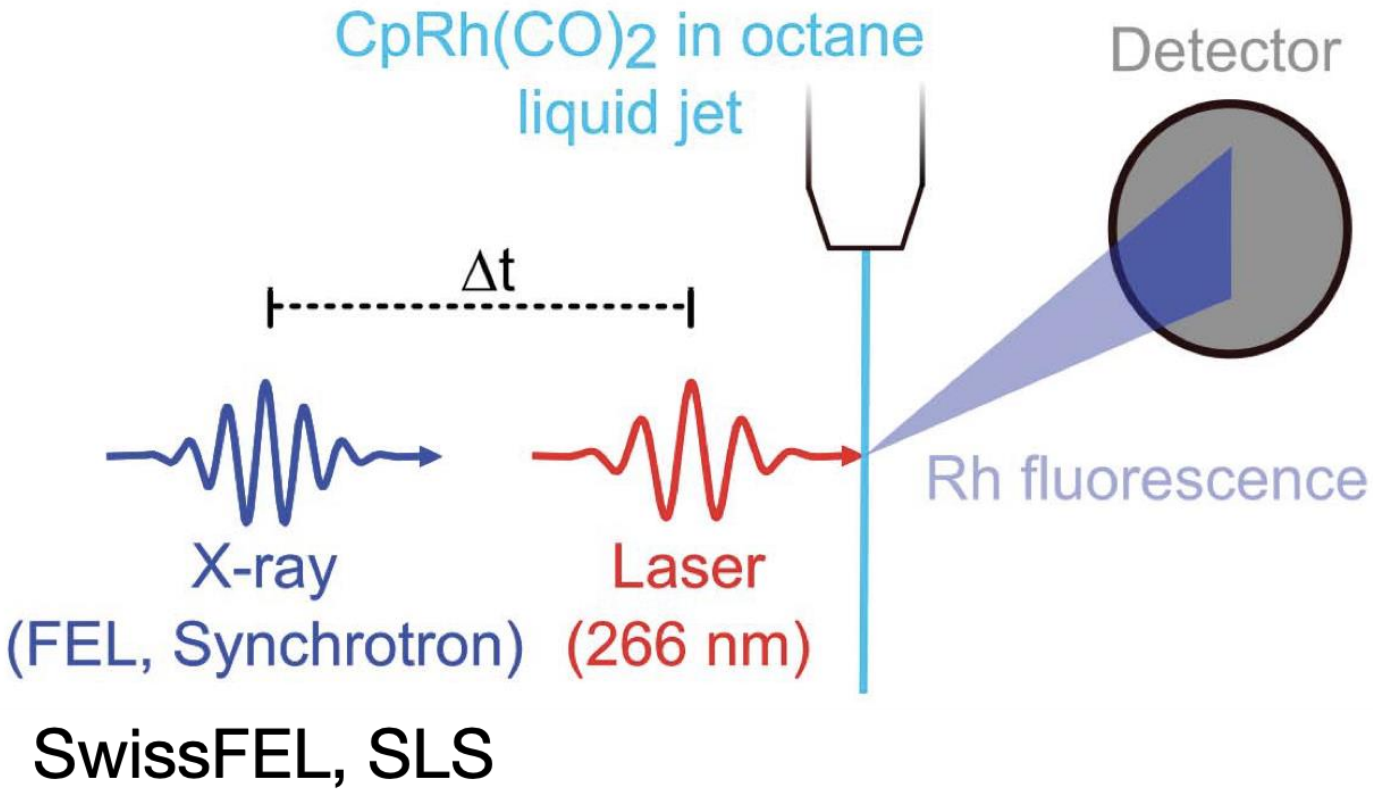
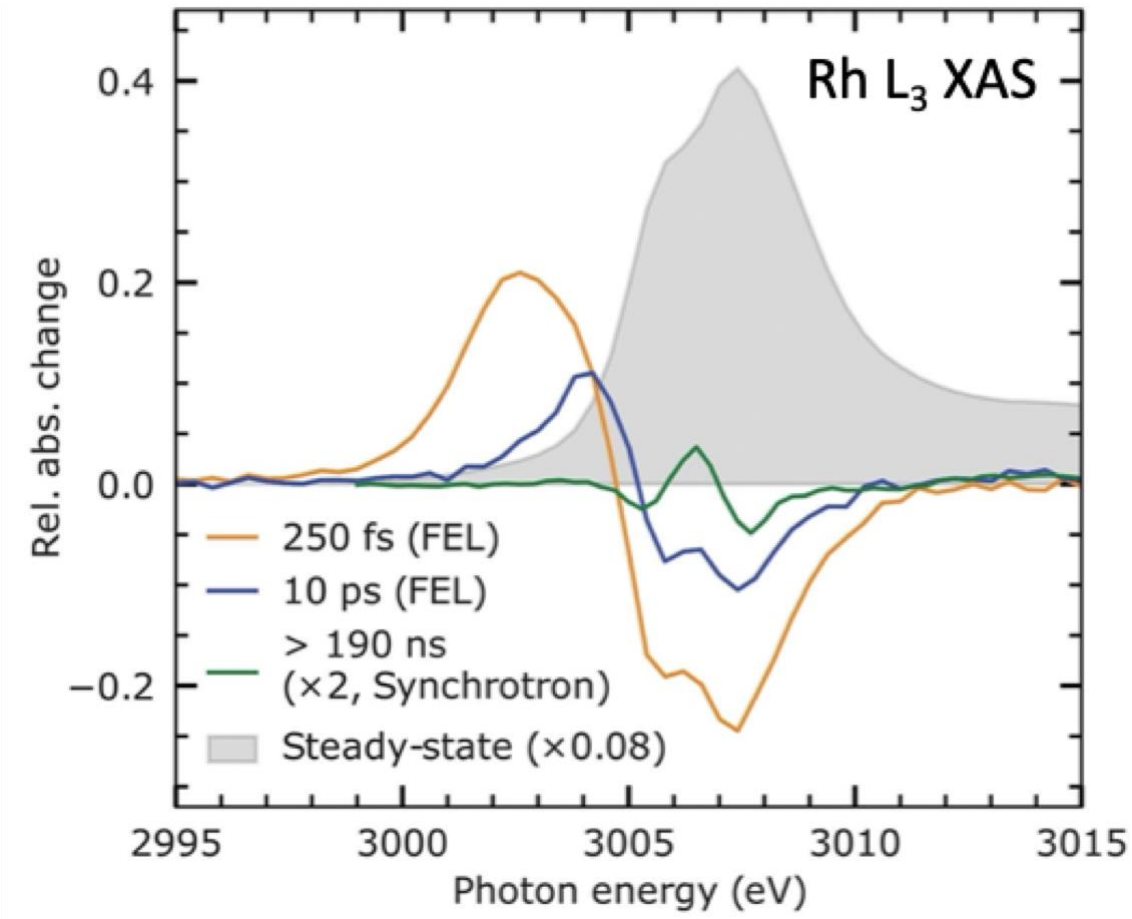


Jay, Banerjee, et al., Science 380, 955-960 (2023)

Tracking C-H activation with orbital resolution



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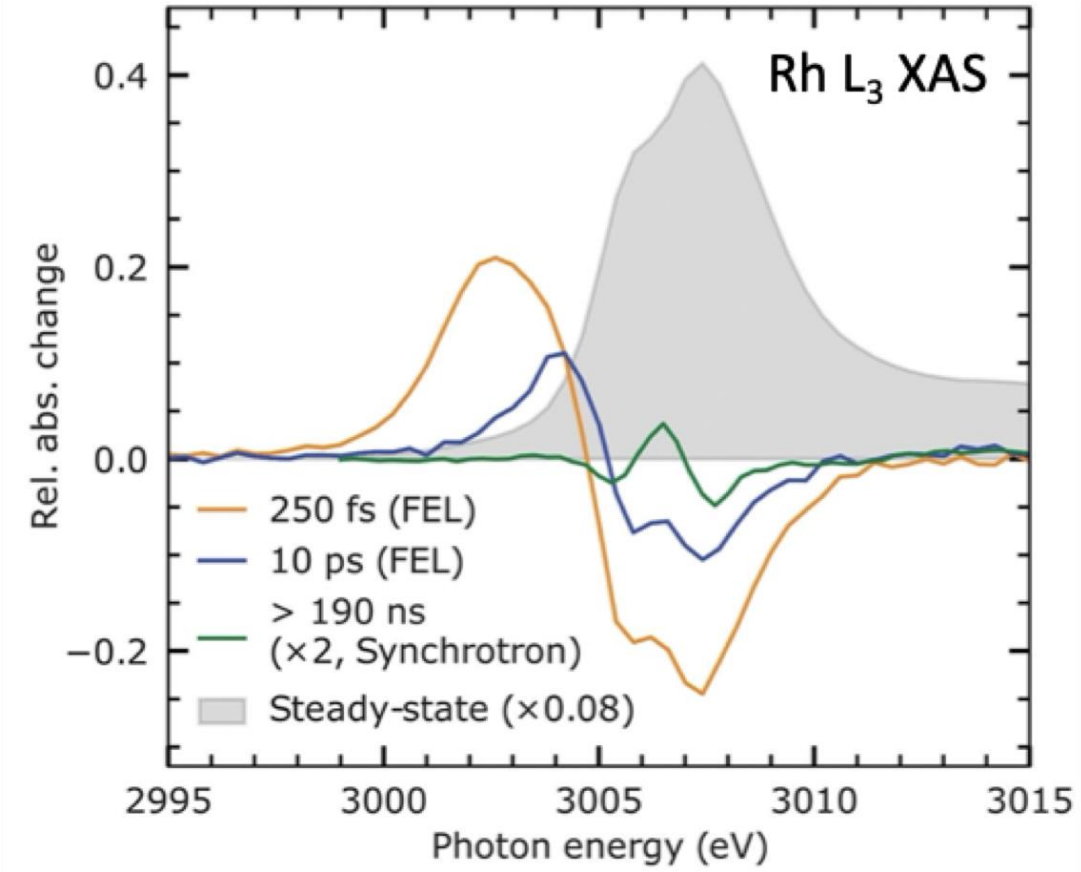

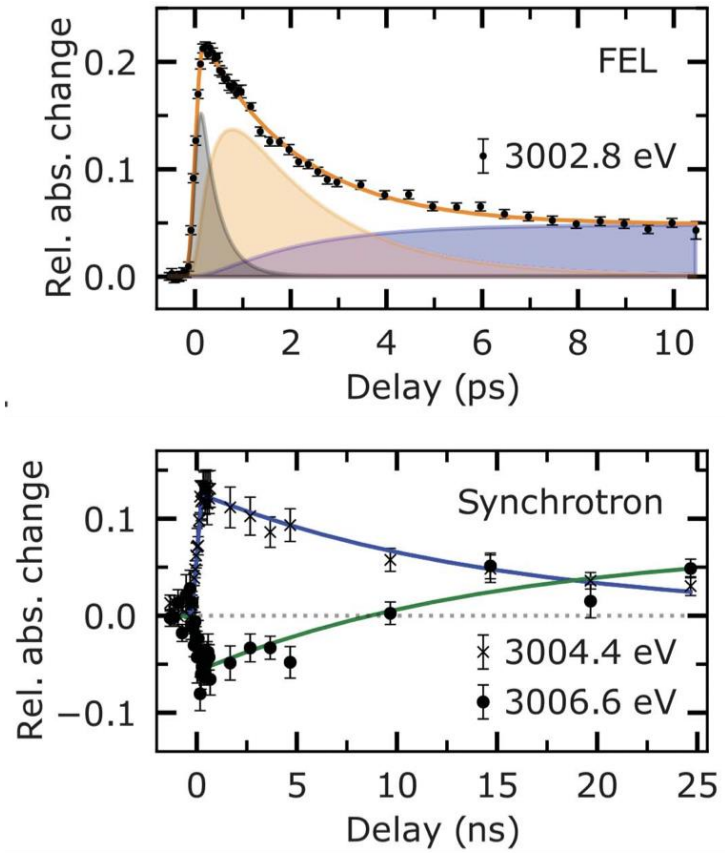

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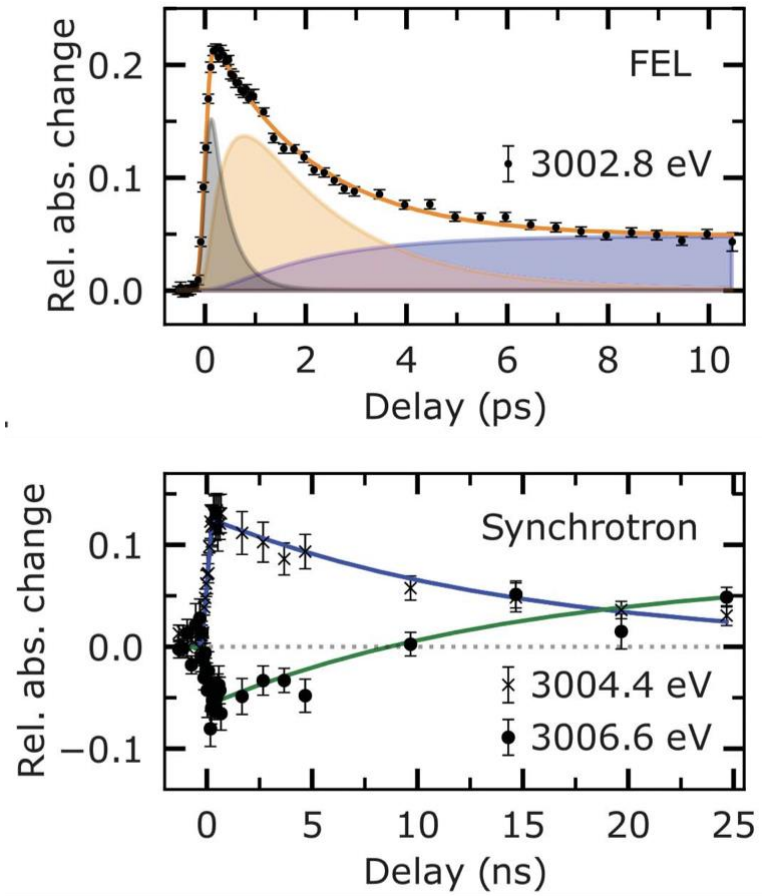
Tracking C-H activation with orbital resolution



- τ_1 = 370 fs Dissociation
- τ_2 = 2 ps Octane association
- τ_3 = 14 ns C-H activation

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

Testing fundamental notions of orbital interactions

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

By Roald Hoffmann*

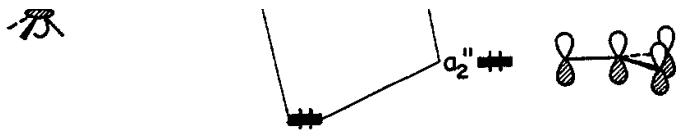
Robert B. Woodward, a supreme patterner of chaos, was one of my teachers. I dedicate this lecture to him, for it is our collaboration on orbital symmetry conservation, the electronic factors which govern the course of chemical reactions, which is recognized by half of the 1981 Nobel Prize in Chemistry. From Woodward I learned much: the significance of the experimental

Fragments

Chains, rings, substituents—those are the building blocks of the marvelous edifice of modern organic chemistry. Any hydrocarbon may be constructed on paper from

fragment is not merel
er: it transforms ess
lationships in the mc
Structures **4—6** co
ligand (Cp), two of tl

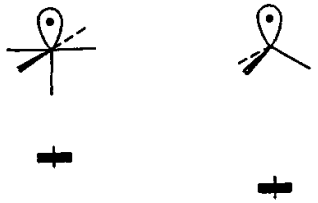
Nobel Prize in Chemistry 1981 awarded jointly to Kenichi Fukui and Roald Hoffmann "for their theories, developed independently, concerning the course of chemical reactions"



27

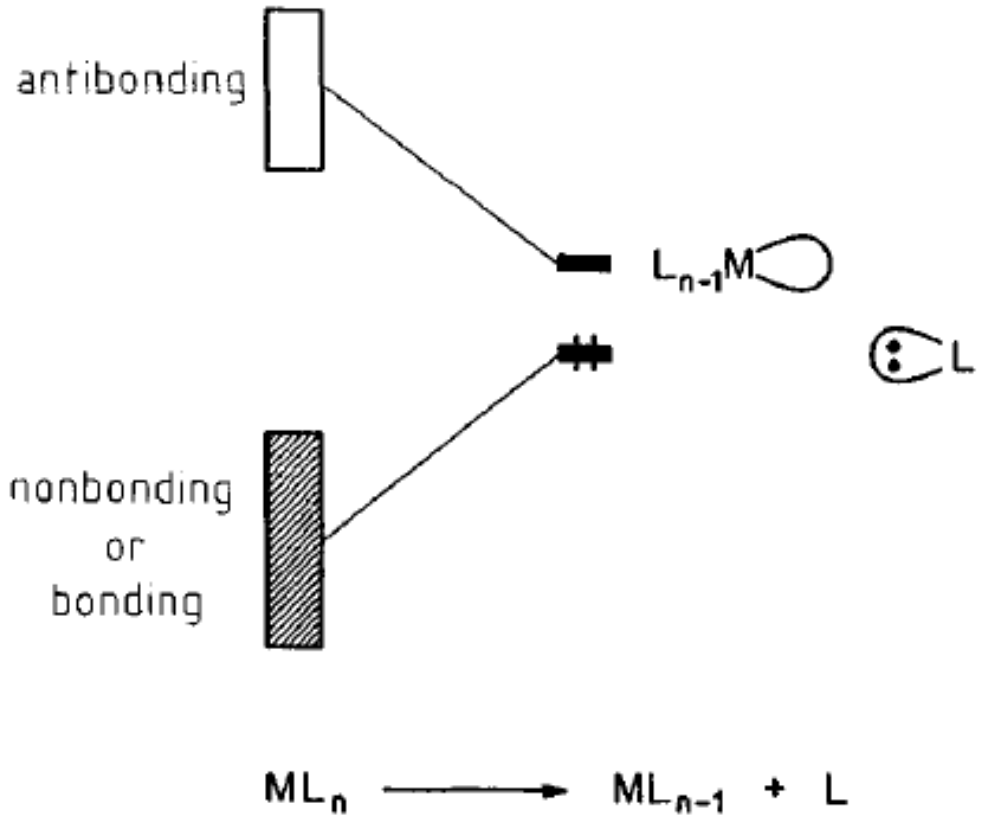
The Isolobal Analogy

Consider the d^7-fragment, $Mn(CO)_5$ (or $Co(CN)_5^{3-}$). Above the three lone pairs in the t_{2g} set this doublet molecule has a single electron in a hybrid pointing away from the ML_5. The similarity to CH_3, the methyl radical, is obvious (cf. **28**).



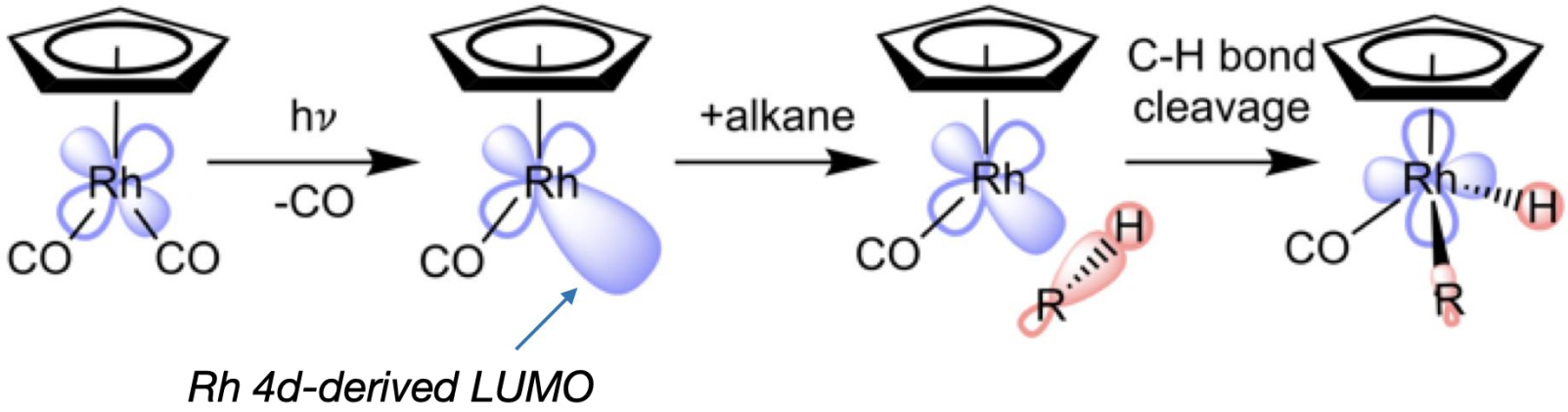
R. Hoffmann, Angew. Chem. Int. Ed. Engl. **21**, 711-724 (1982).

Testing fundamental notions of orbital interactions



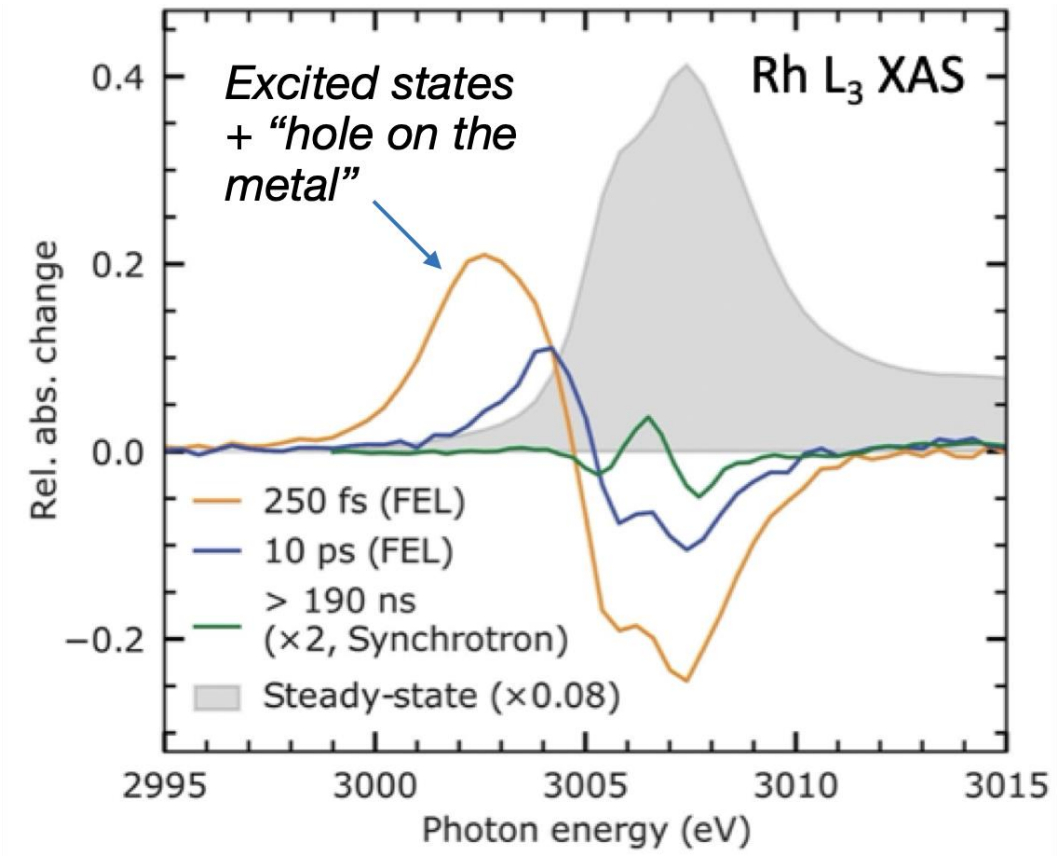
R. Hoffmann, Angew. Chem. Int. Ed. Engl. **21**, 711-724 (1982): "A localized hole on the metal, a directional hybrid, is created."

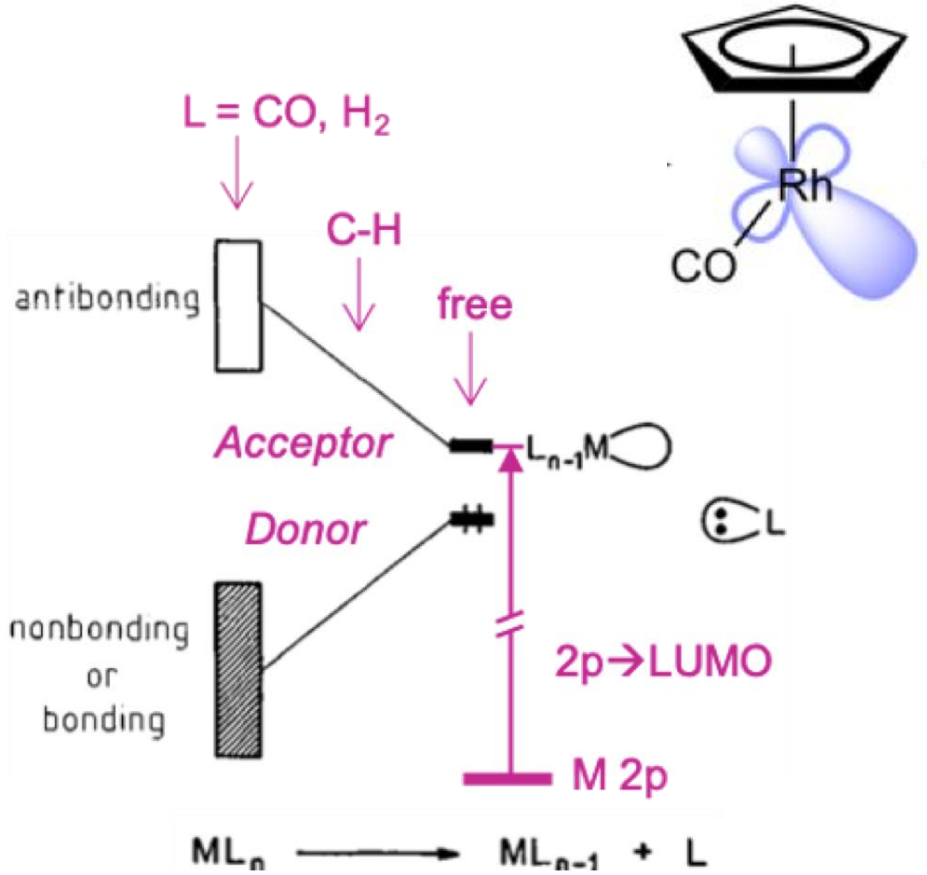
Tracking C-H activation with orbital resolution



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

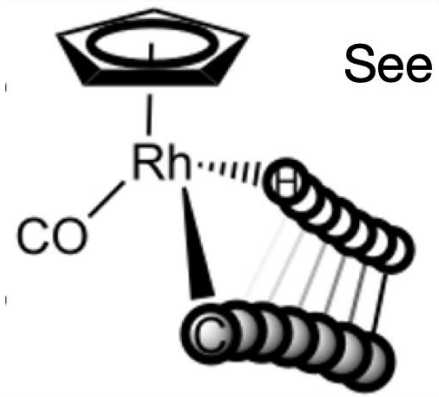
Tracking C-H activation with orbital resolution



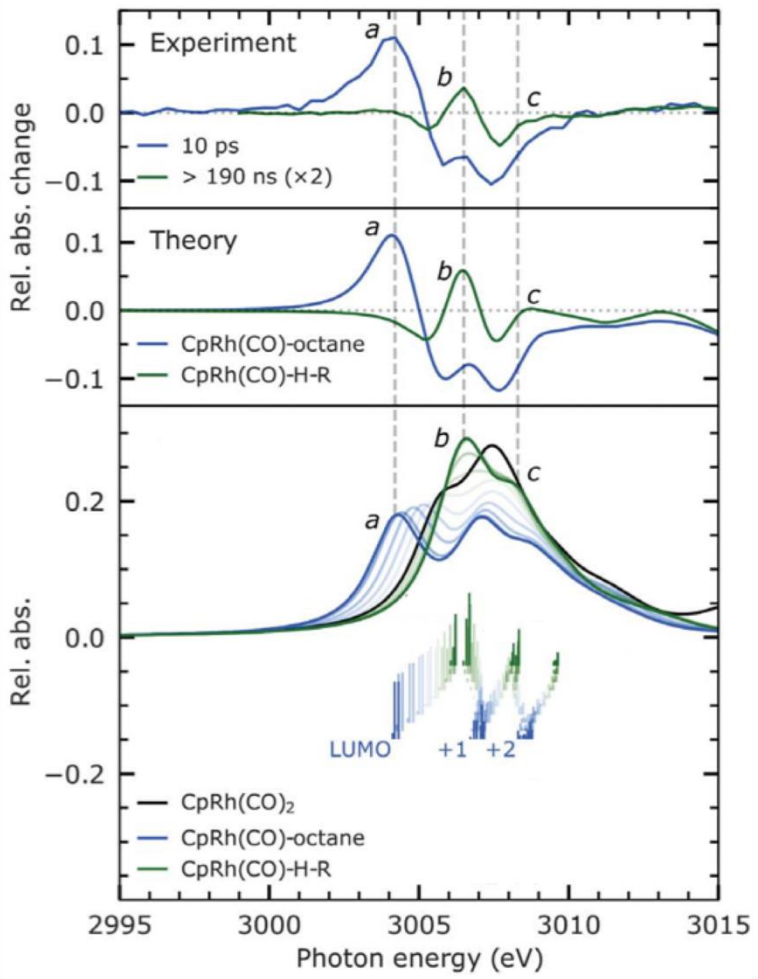


R. Hoffmann, Angew. Chem. Int. Ed. Engl. 21, 711-724 (1982)
Jay, Banerjee, et al., Science 380, 955-960 (2023)

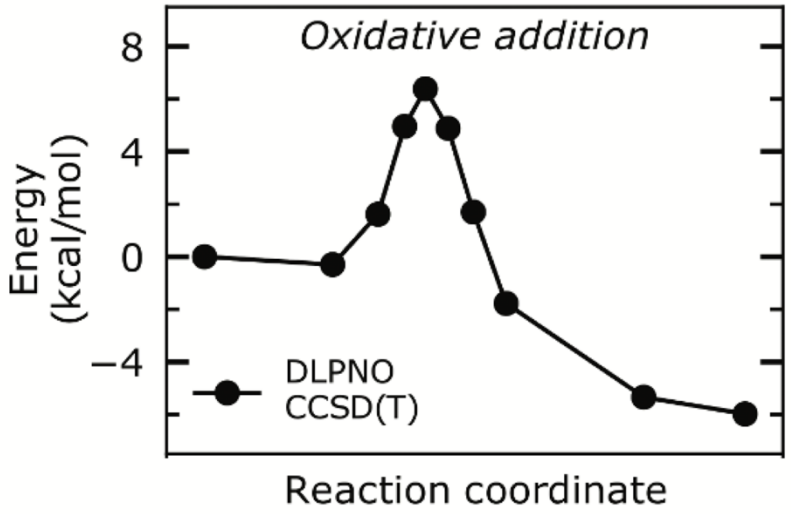
Tracking C-H activation with orbital resolution



See Crabtree



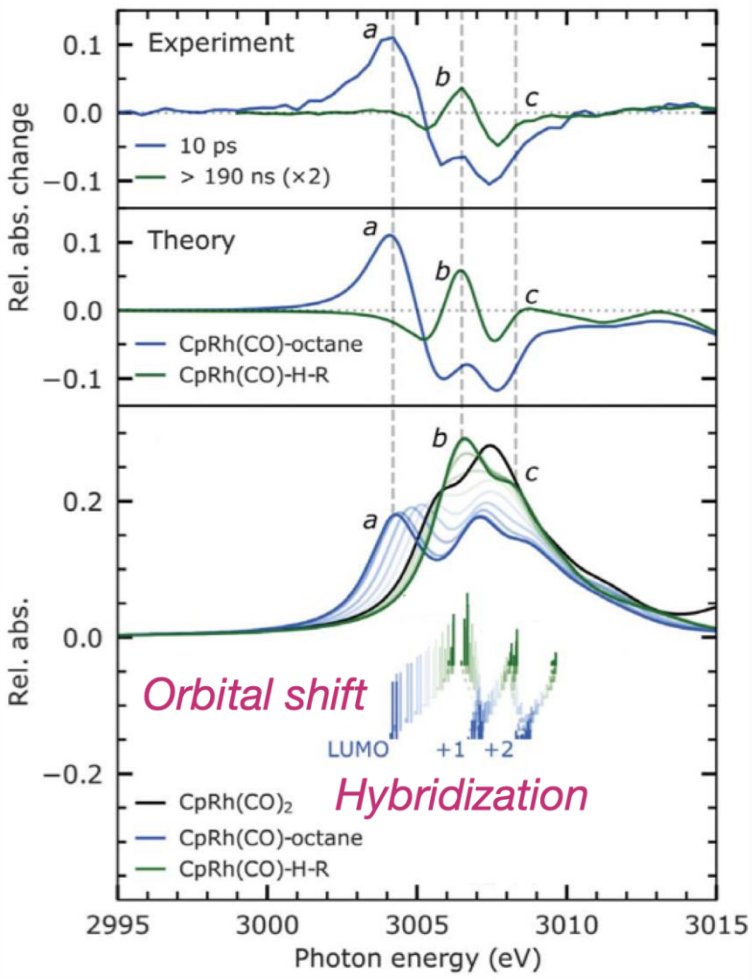
4.6 eV/molecule
100 kcal/mol, 440 kJ/mol



DFT-based modelling (B3LYP)

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

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

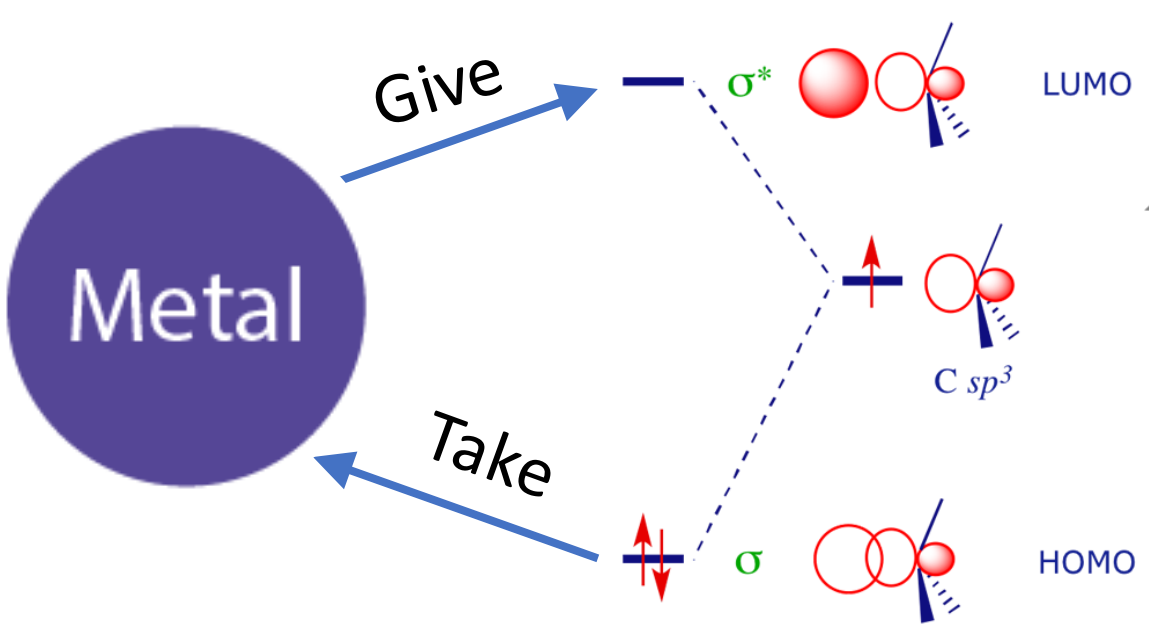
Rh 2p→LUMO+1 int. increases

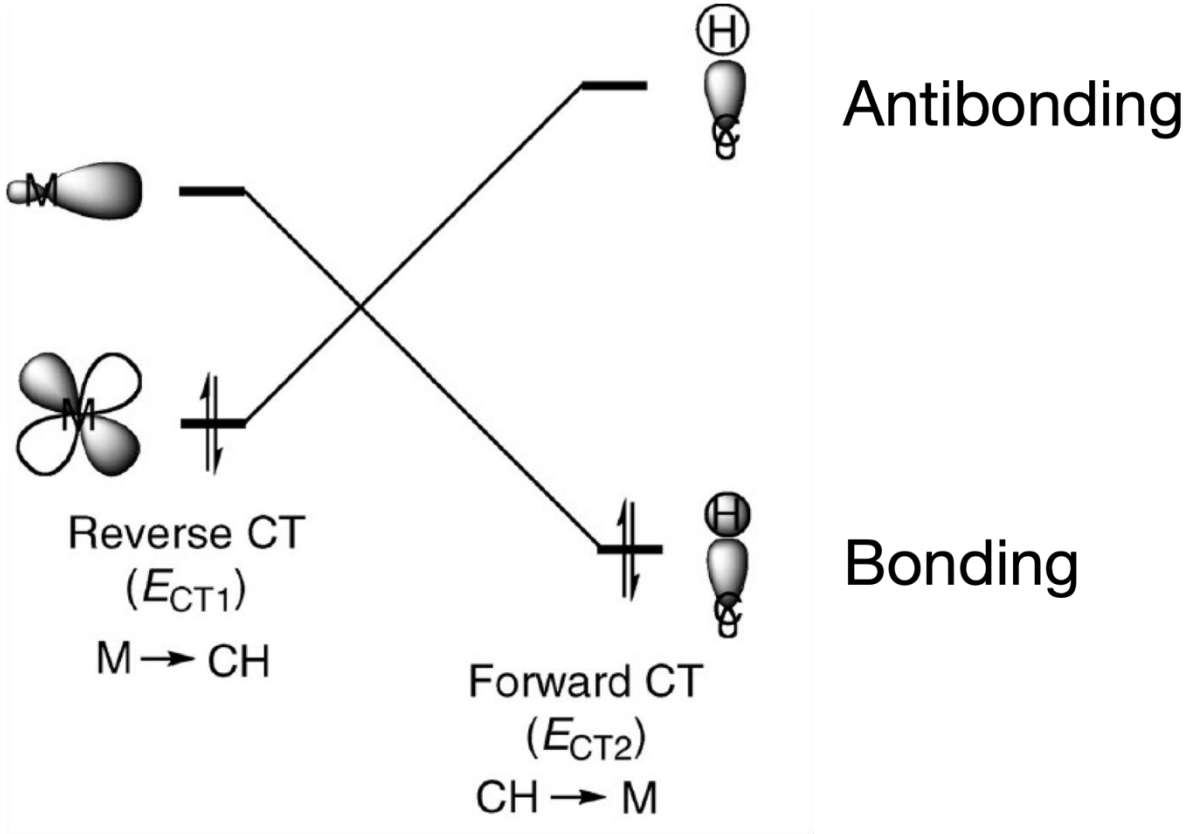
Oxidative addition = LUMO+1 rehybridization

"Oxidation" Rh(I) d^8 to Rh(III) d^6

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

Tracking C-H activation with orbital resolution



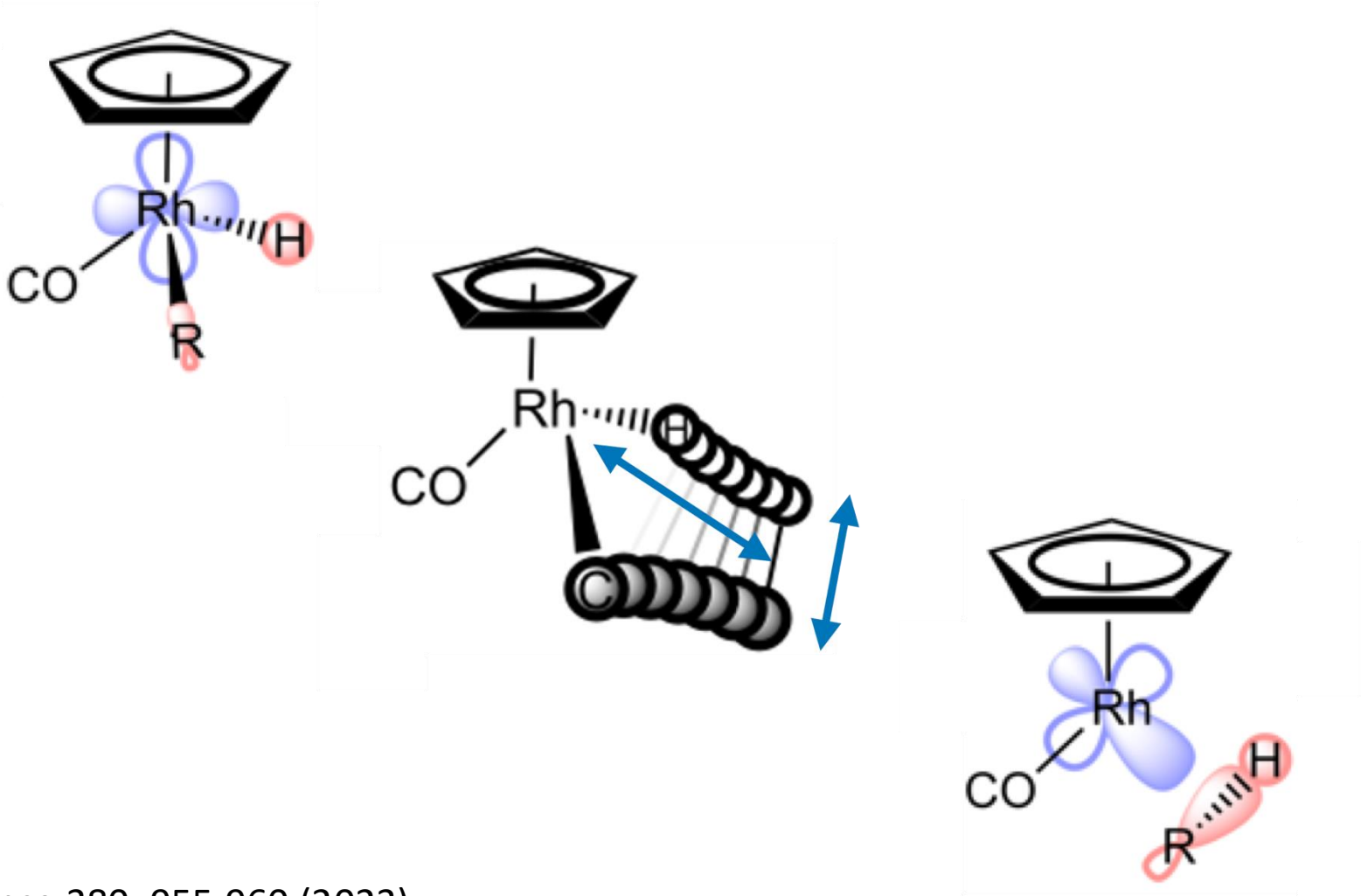


R. Hoffmann 1960s-1980s
P. Siegbahn JACS 116, 10124 (1994)
M. Head-Gordon PNAS 104, 6963 (2007)

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

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

Tracking C-H activation with orbital resolution



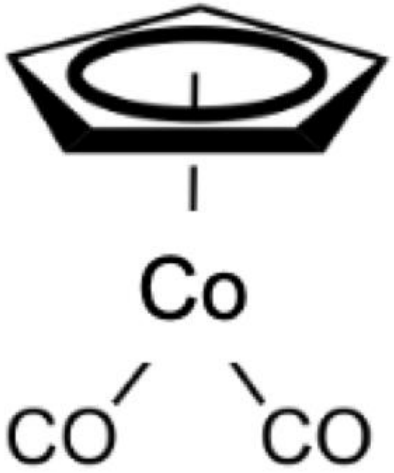
Jay, Banerjee, et al., Science 380, 955-960 (2023)

Tracking C-H activation with orbital resolution

3d

4d

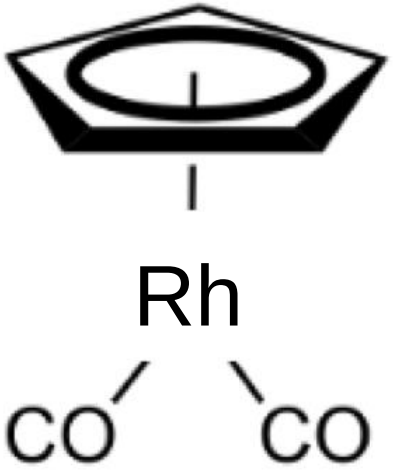
5d



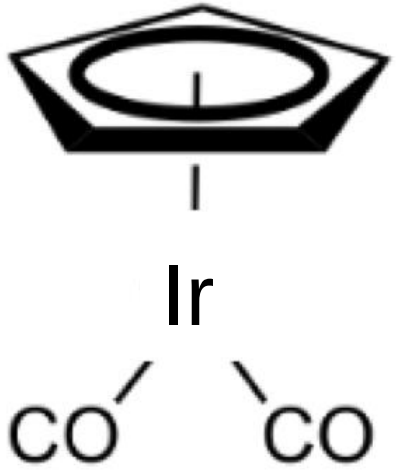
3d soft X-rays
European XFEL

DOES NOT ACTIVATE
C-H BONDS!

Metal L-edge spectroscopy (2p→LUMO)



4d tender X-rays
SwissFEL



5d tender X-rays
LCLS

Why is that so?

Tracking C-H activation with orbital resolution

3d

4d

5d

What's the size of an atom?

Tracking C-H activation with orbital resolution

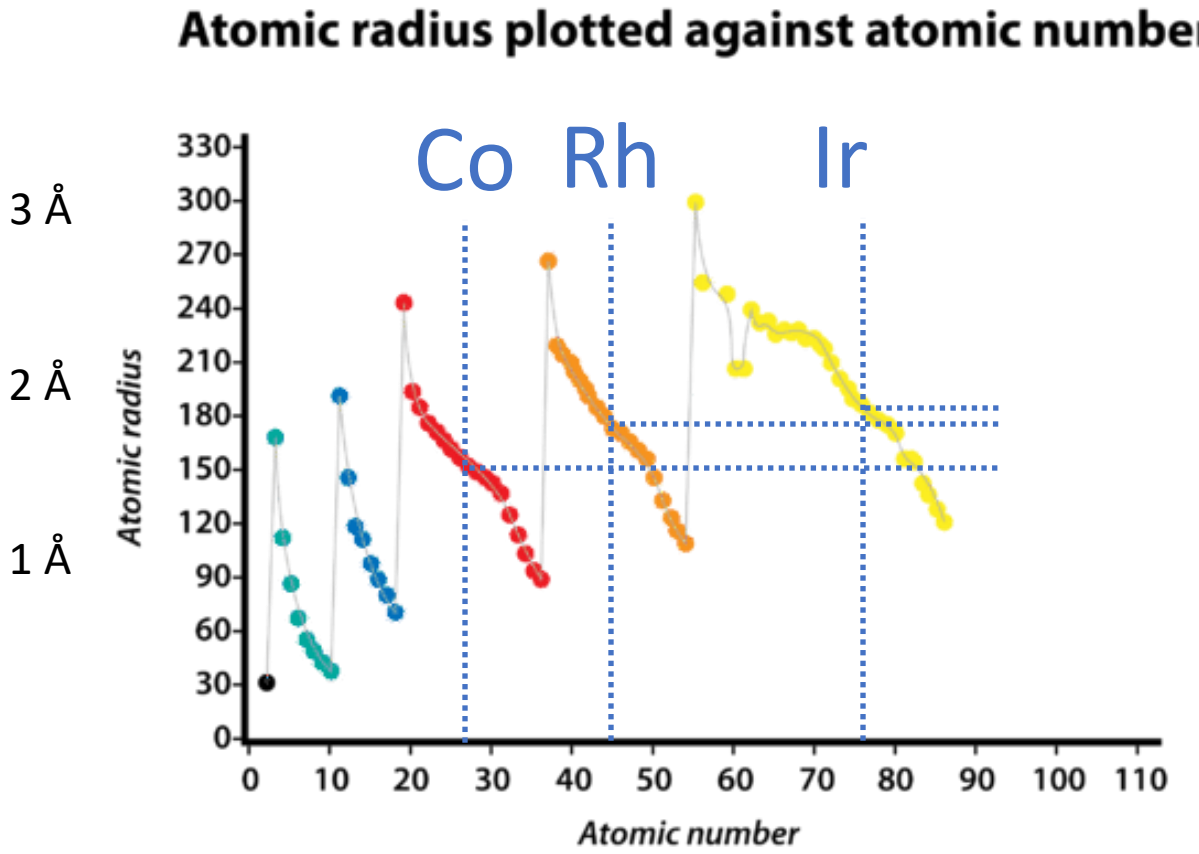
What's the size of an atom?

3d

4d

5d

27 Co 1.88	45 Rh 2.28	77 Ir 2.2



$Ar\ 4s^2\ 3d^7$

$Kr\ 5s^2\ 4d^7$

$Xe\ 6s^2\ 5d^7$

Size ≈ Extent of d orbital

https://flexbooks.ck12.org, similar in Hertel/Schulz

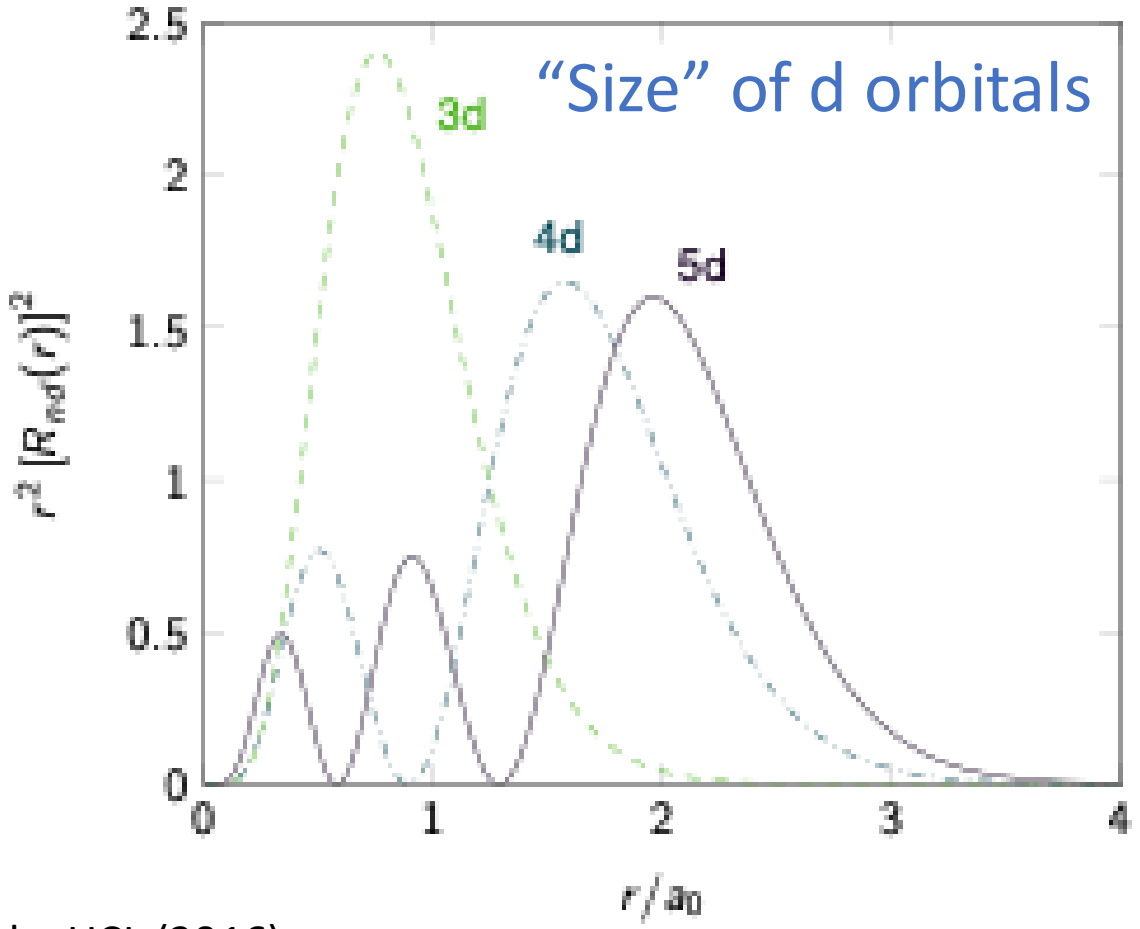
Tracking C-H activation with orbital resolution

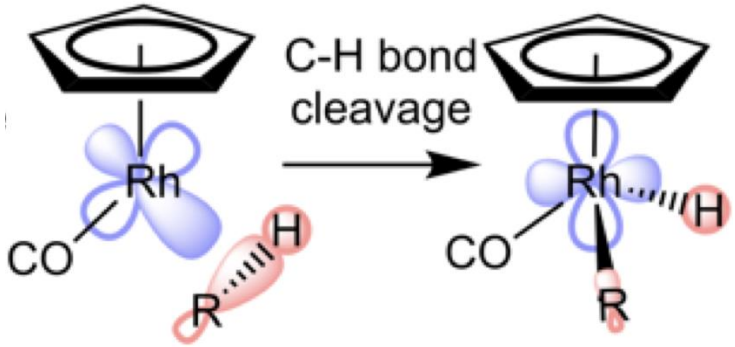
3d

4d

5d

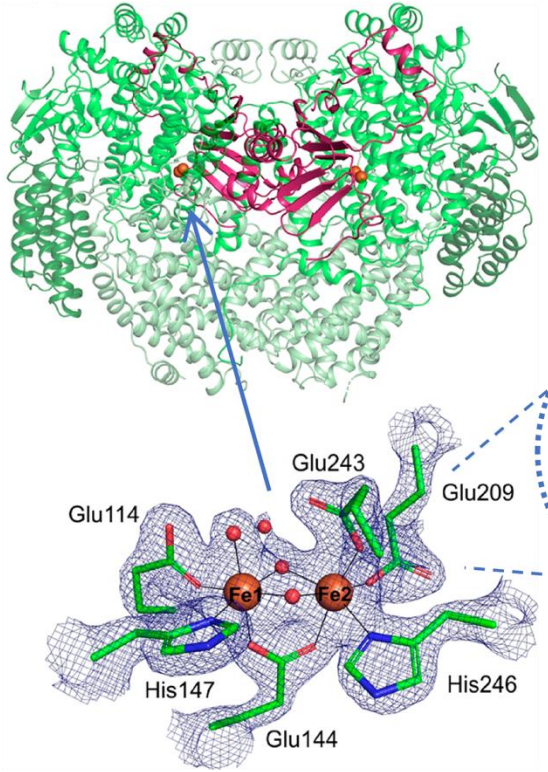
Size ≈ Extent of d orbital





PhD thesis James George Vale, UCL (2016)

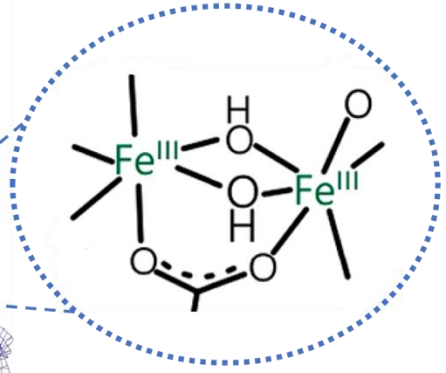
Chemical and biological hydrocarbon activation

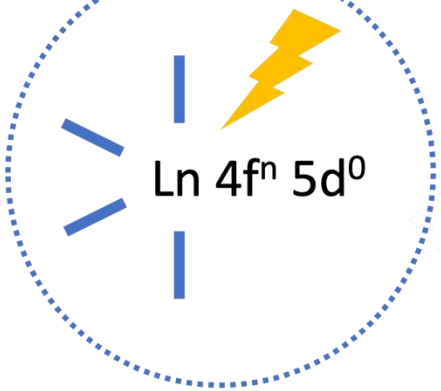


Soluble methane mono-oxygenase with di-Fe cluster

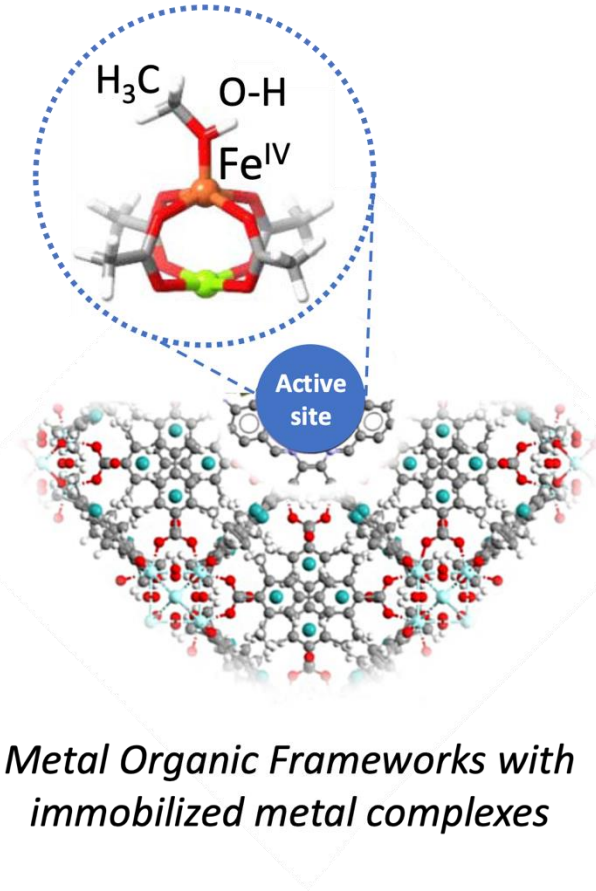
$H_3C–H + ½\ O_2 \xrightarrow{\textit{Metal catalyst}} H_3C–O–H$

Methane *Methanol*



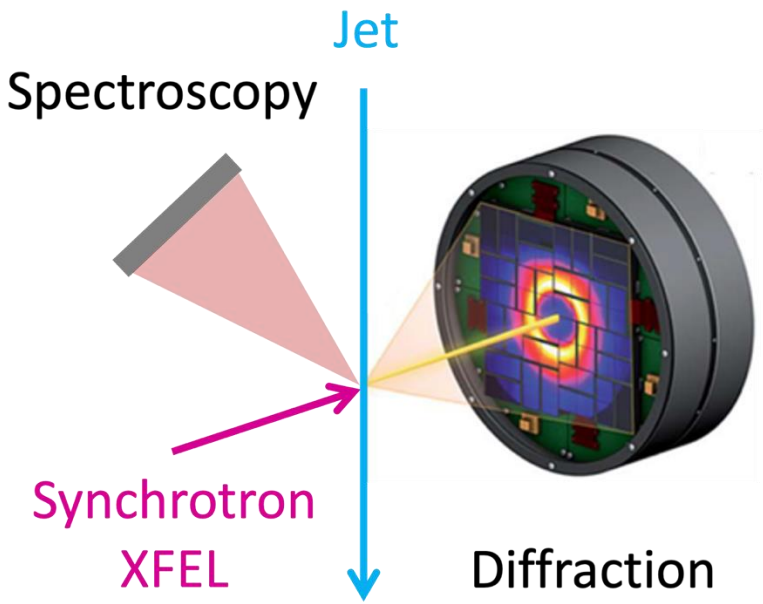


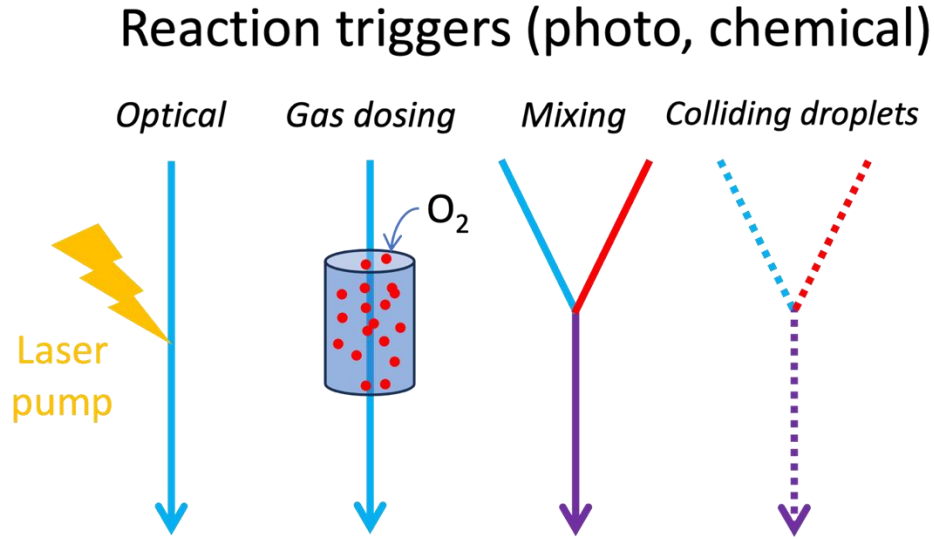
Lanthanide complexes



Metal Organic Frameworks with immobilized metal complexes

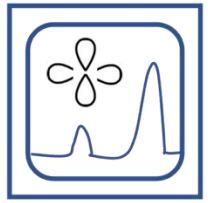
Chemical and biological hydrocarbon activation





Quantum chemical

predictions + explanations



$$\psi_{HOMO} = \alpha_M d_M + \alpha_L p_L$$
$$\psi_{LUMO} = \beta_M d_M + \beta_L p_L$$

What we are after

Learning how to rearrange electrons (bonds)

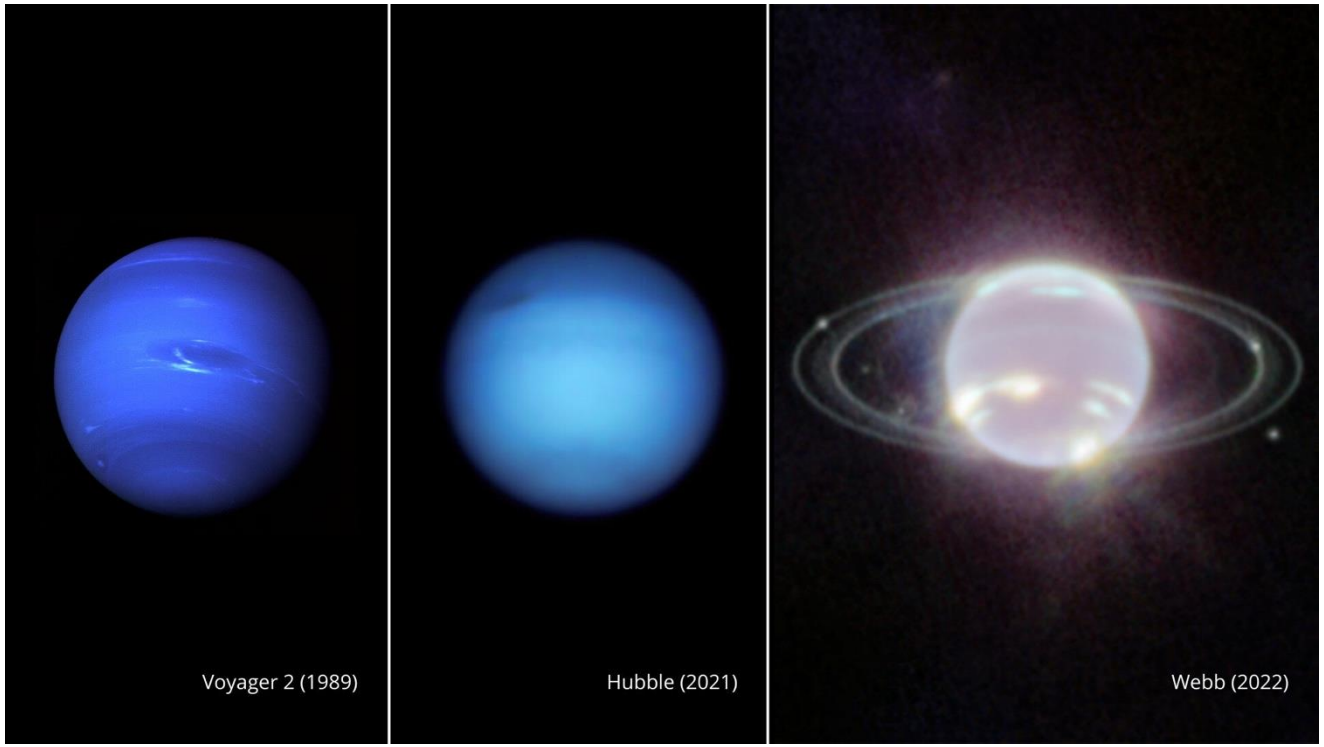
To control molecular transformations

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

Under "mild conditions"

Why X-rays, why pulsed X-rays?

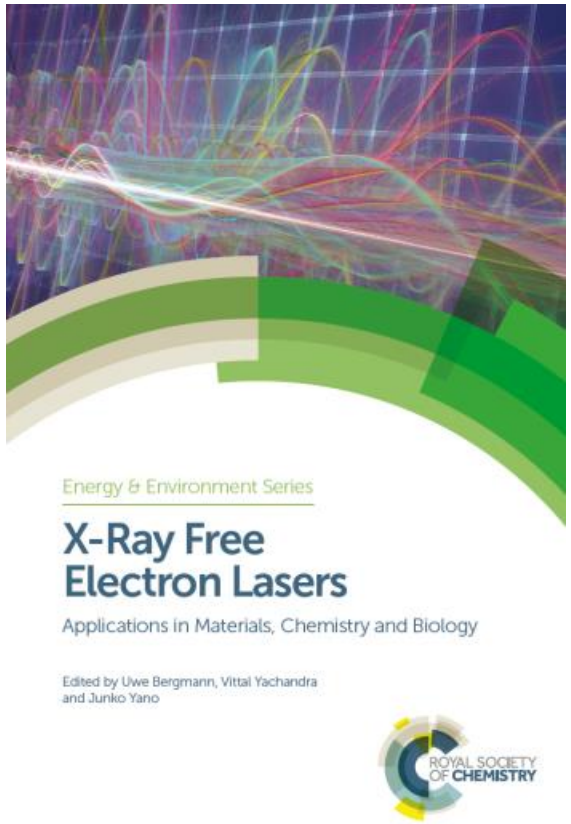
Neptune



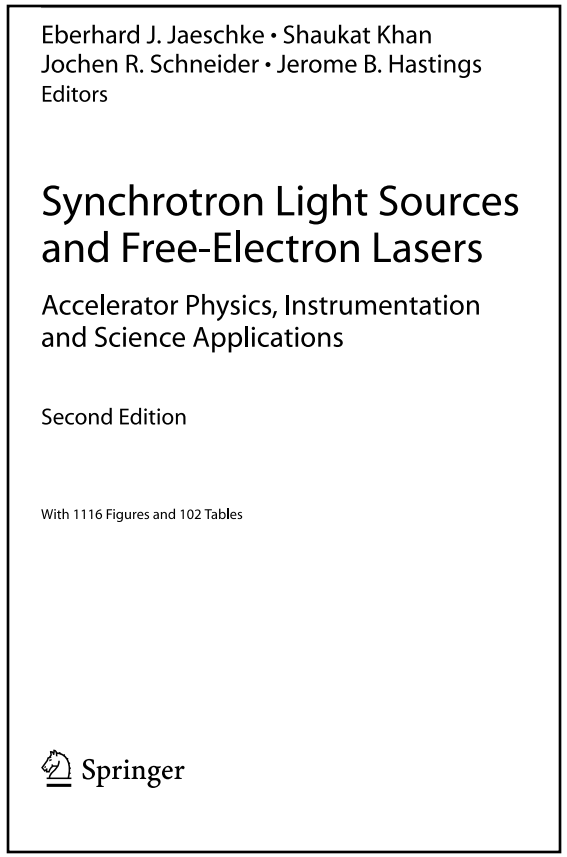
NASA, ESA, CSA, STScI via AP

- Discover new things
- Look at things in a new way

Further reading recommendations



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).



- 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

Thank you