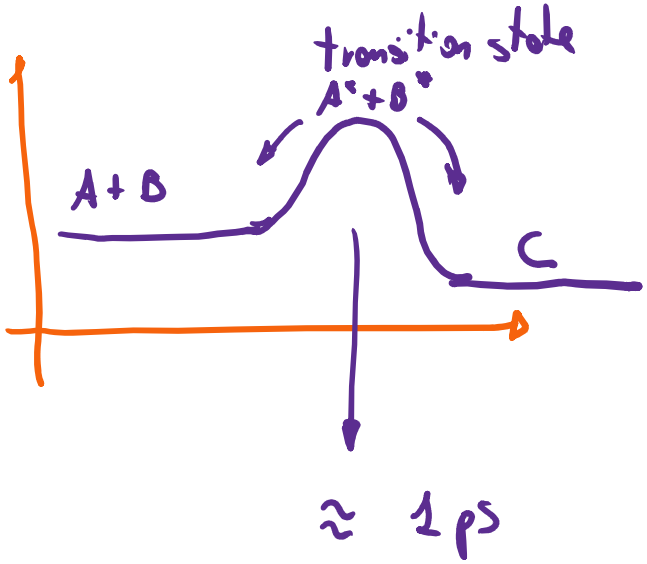
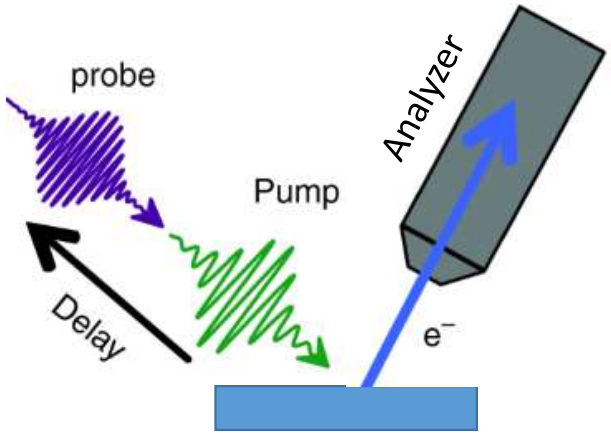
Misure di dinamiche elettroniche

Introduzione a spettroscopie Pump & Probe



Fotoemissione e NEXAFS ci danno informazioni sulla struttura elettronica del sistema quando è in uno stato rilassato.

Posso avere informazioni sulla struttura di un sistema nello stato eccitato o di uno stato metastabile (es. il transition state di una reazione?)

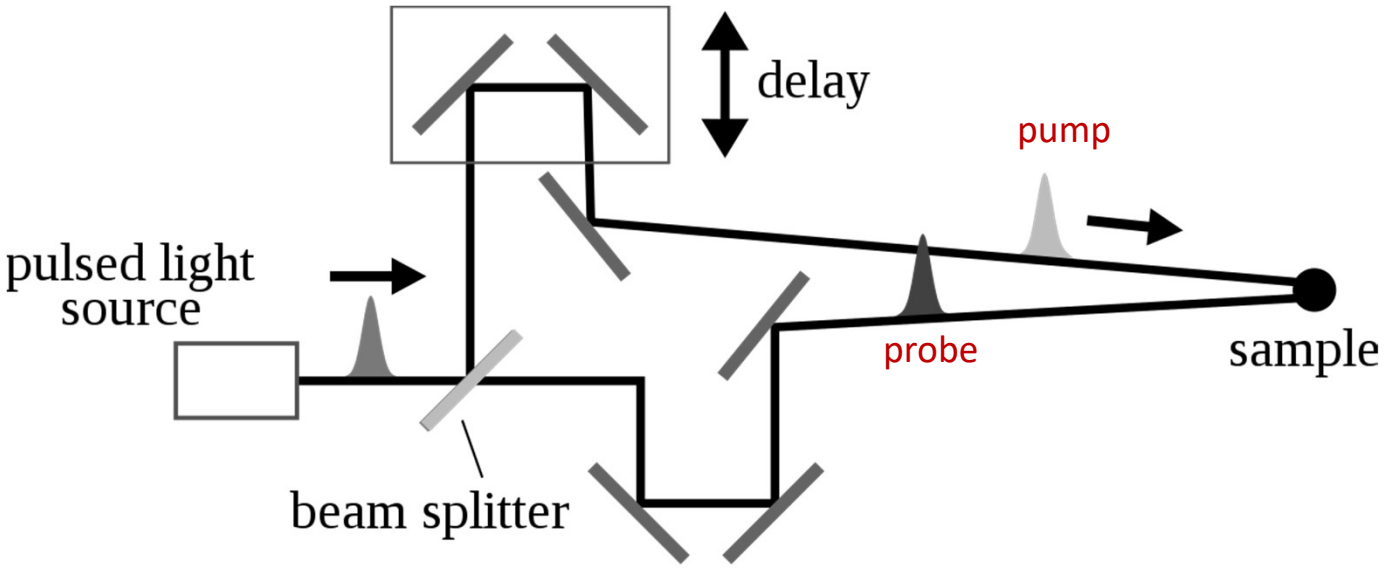


Mi servono due sorgenti di fotoni (pump e probe)

Mando due impulsi ad una certa distanza temporale uno dall'altro (delay)

Misuro al variare del delay come evolve l'eccitazione generata dal pump

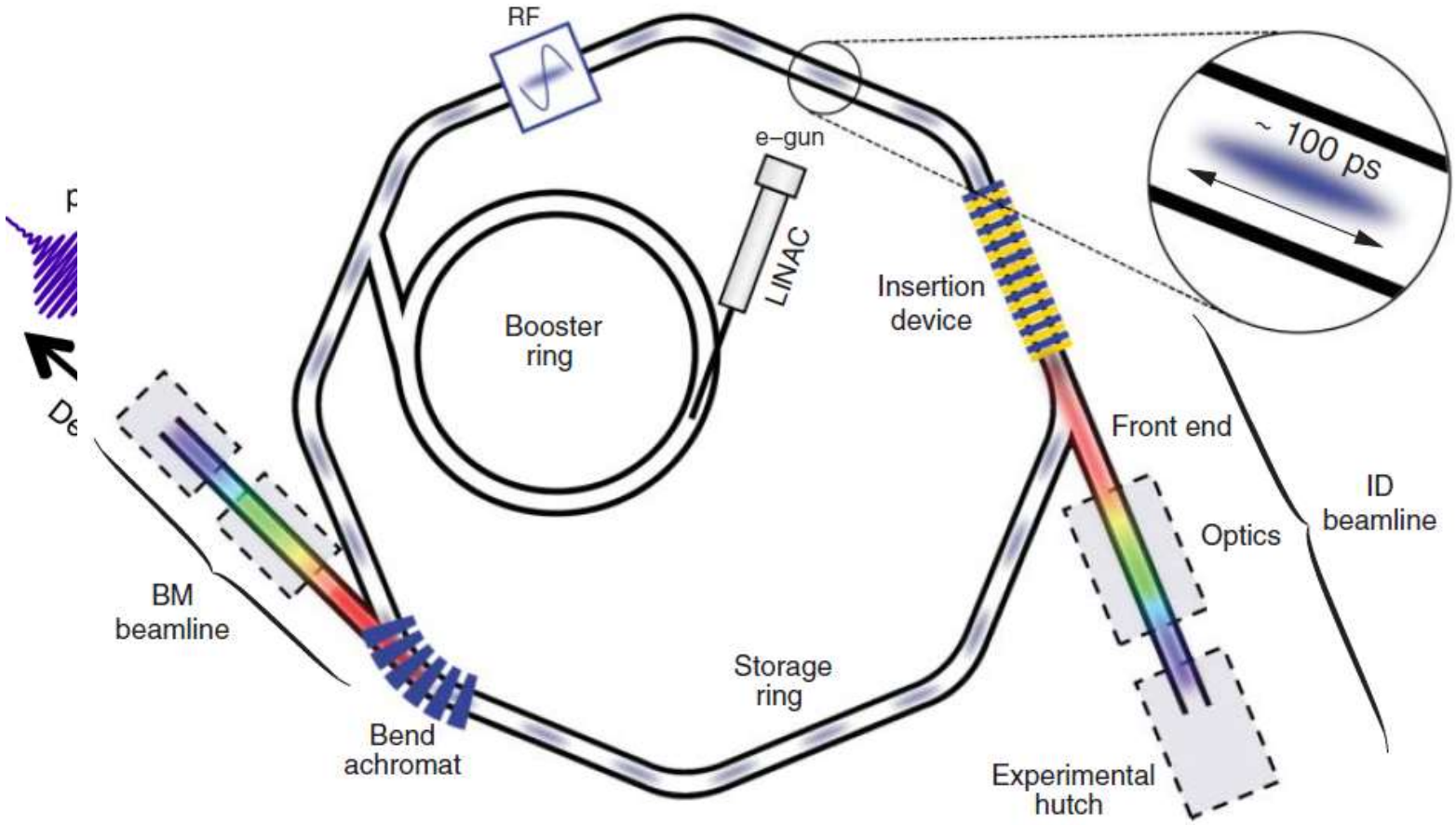
Pump-probe laser-laser: setup sperimentale



Un fascio di laser pulsato viene splittato in due (pump e probe). Il cammino ottico di uno dei due fasci è rergolabile, in modo da poter introdurre un ritardo controllato tra gli impulsi pump e probe che arrivano sul campione.
Per laser commerciali, la larghezza temporale degli impulsi forniti dal laser può essere minore di 100 fs; la distanza tra due impulsi successivi può scendere fino a 1ns.

Lungo uno dei due percorsi (tipicamente il probe) può essere installato un dispositivo HHG (High Harmonic Generation) che permette di ottenere fotoni di energie multiple del fotone di partenza.

Il fotone di pump può essere anche fornito da un sincrotrone…

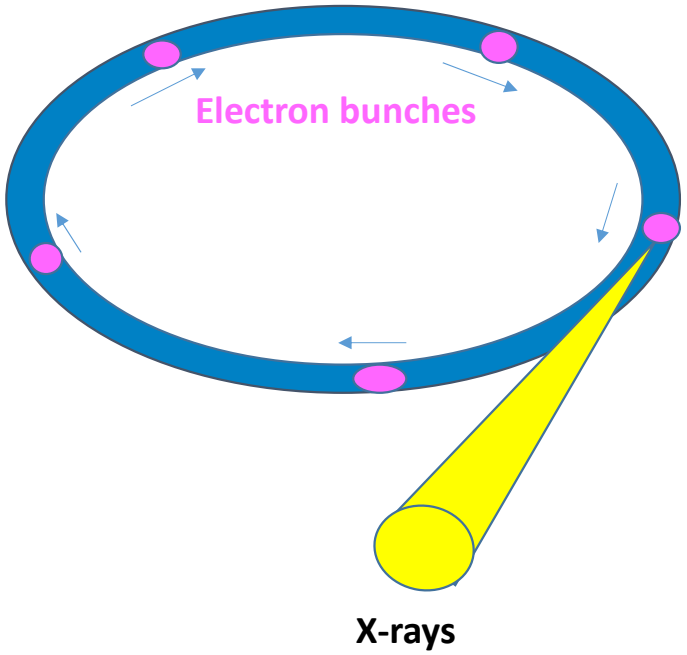


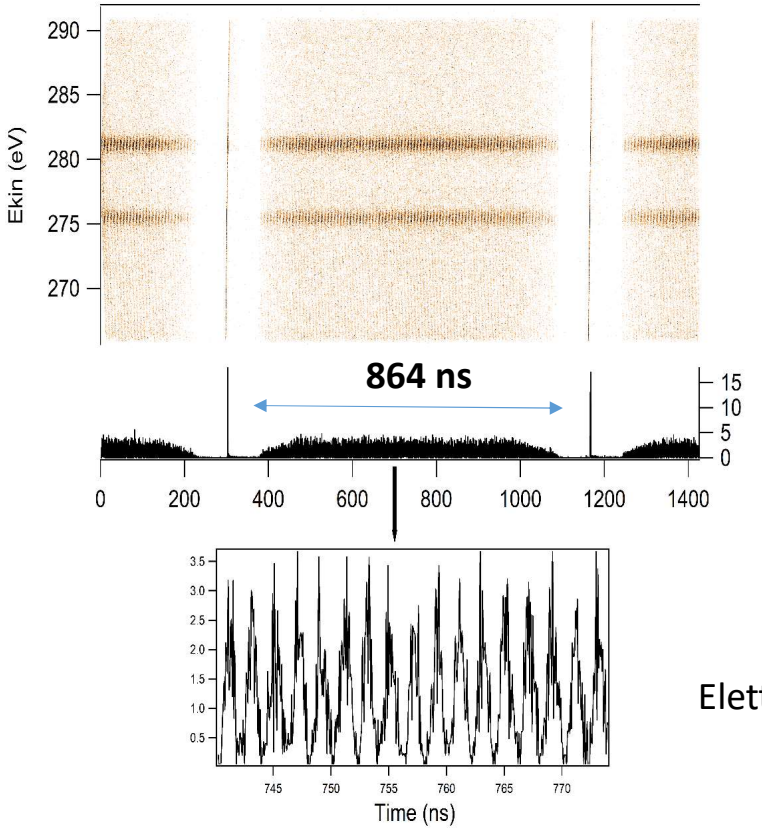
ale uno dall'altro (delay)

ne generata dal pump

Synchrotron X-ray pulses

La luce di sincrotrone è costituita da pacchetti di fotoni, che hanno una frequena di rivoluzione di circa 1 MHz

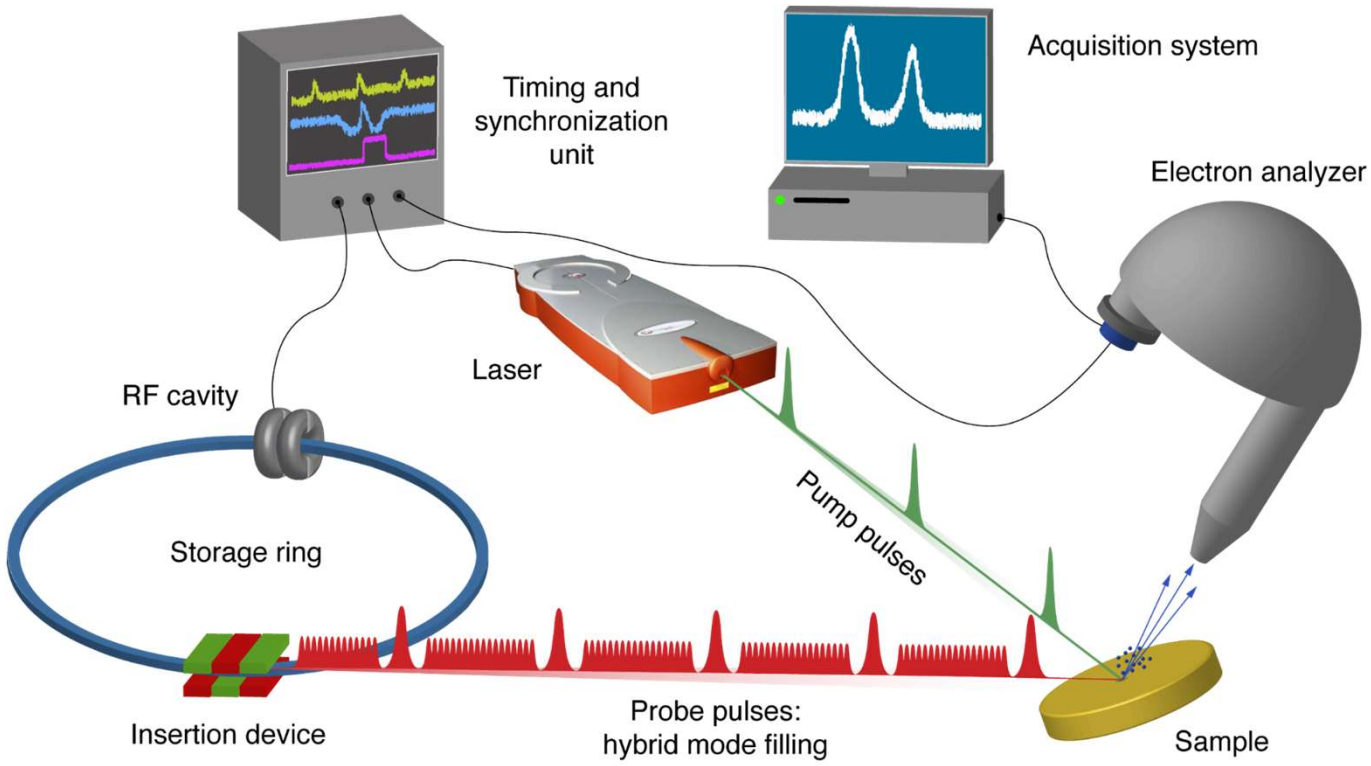




100 ps X-ray pulses

Elettra filling pattern

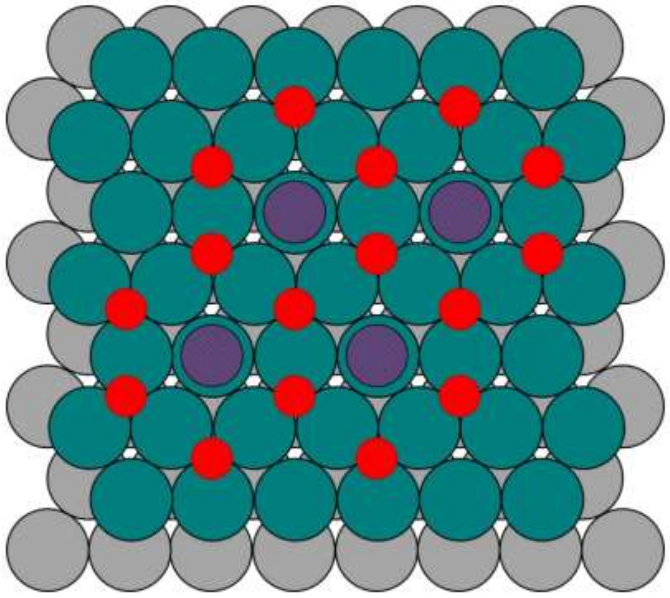
Experimental Set-Up for Optical Pump-X-ray Probe

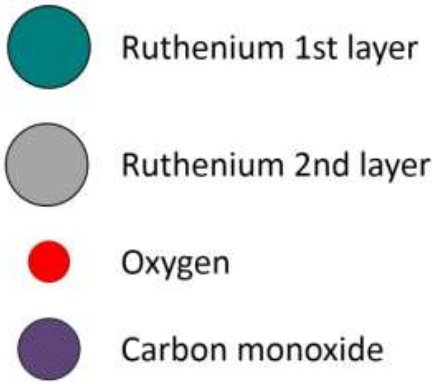


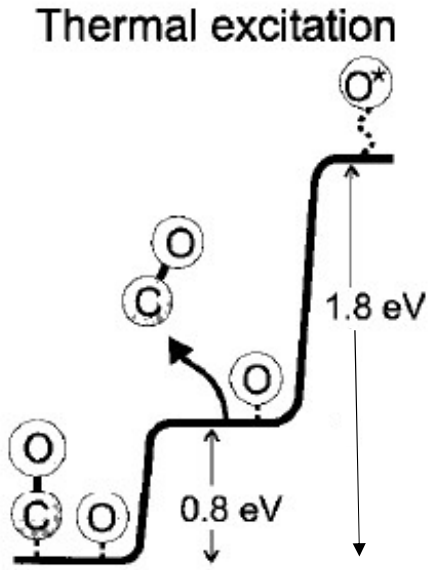
Ossidazione di CO su Ru

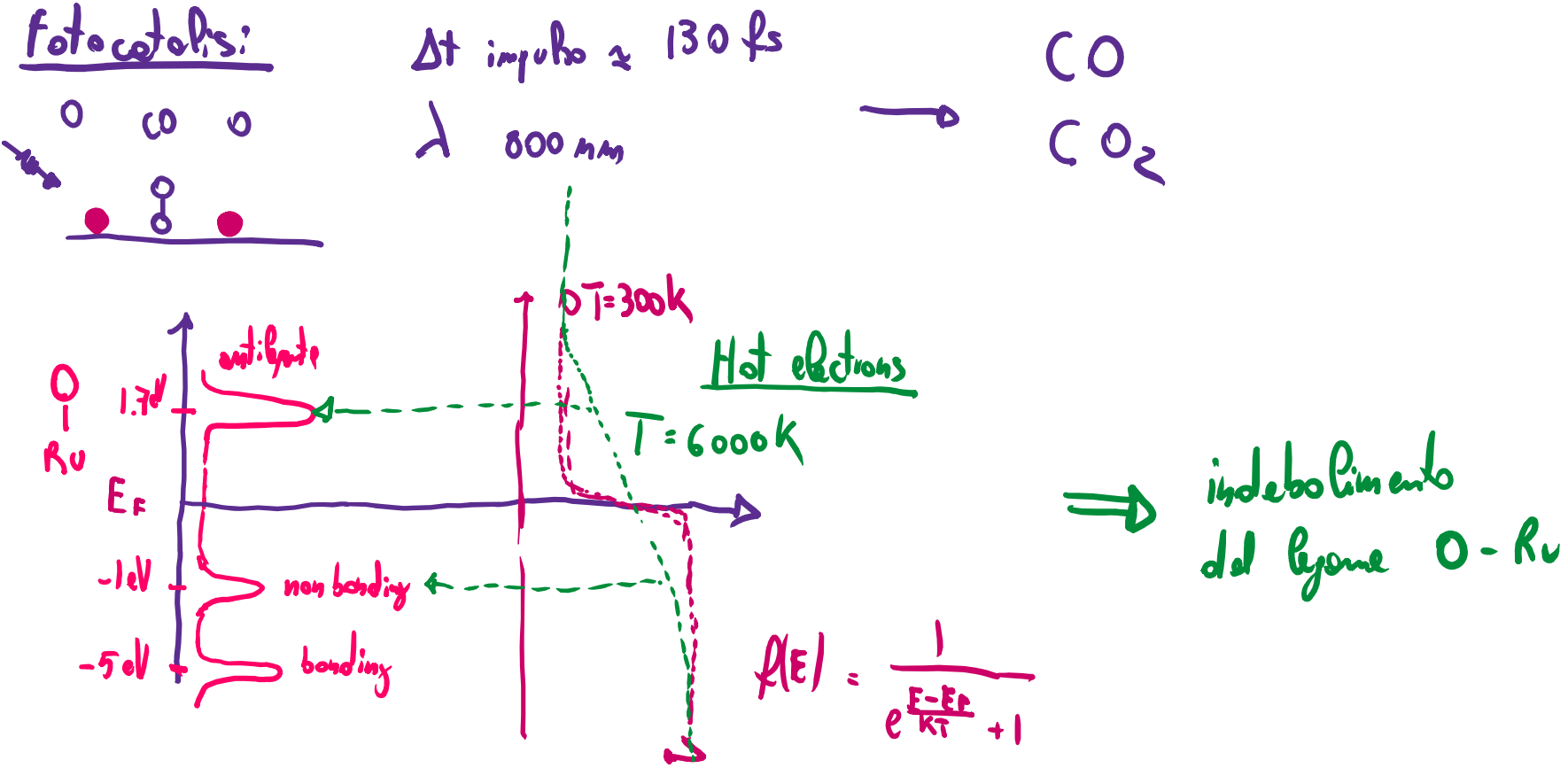
- O_2 dissocia spontaneamente
- CO si lega
- Se scaldo…CO se ne va prima che l'ossidazione avvenga

Ru(100)









Lo stato antilegante viene parzialmente riempito con un impulso di fotoni e la relativa Te=6000K. Lo stesso impulso provoca un parziale svuotamento del primo orbitale occupato, che però ha carattere non legante.
Complessivamente, l'impulso di fotoni indebolisce il legame O-Ru e mette l'ossigeno in uno stato attivo per l'ossidazione di CO che gli sta accanto

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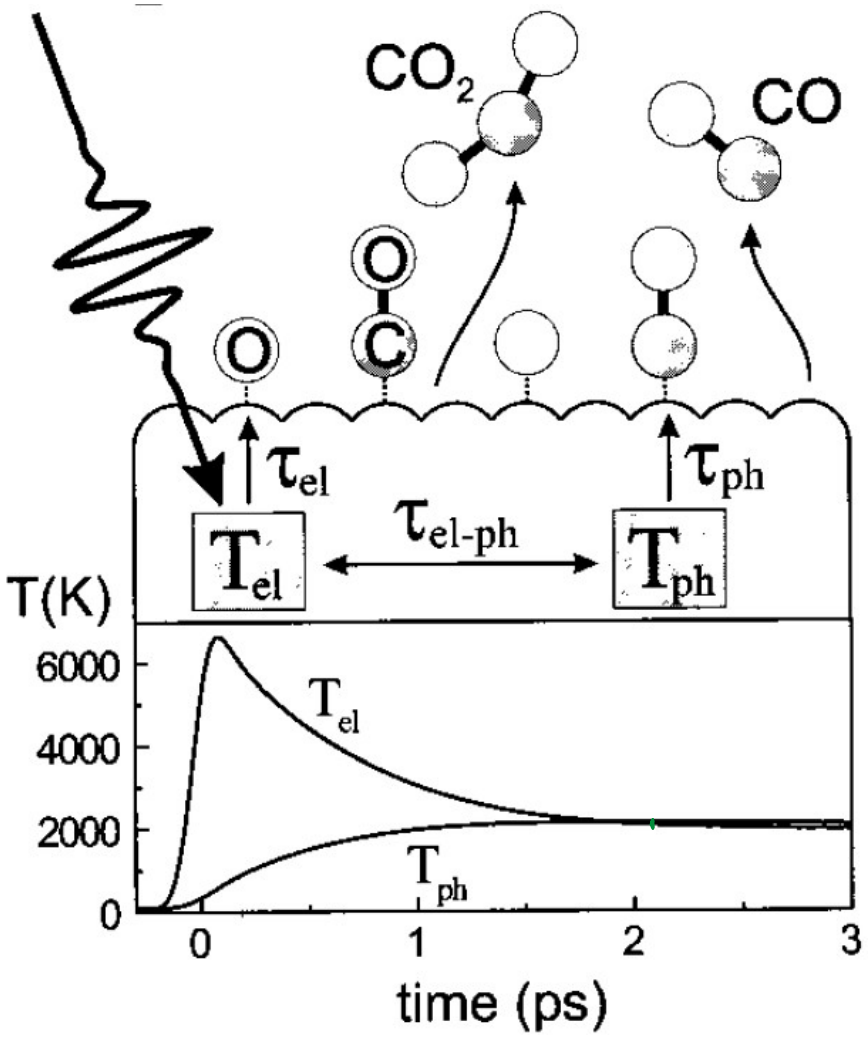
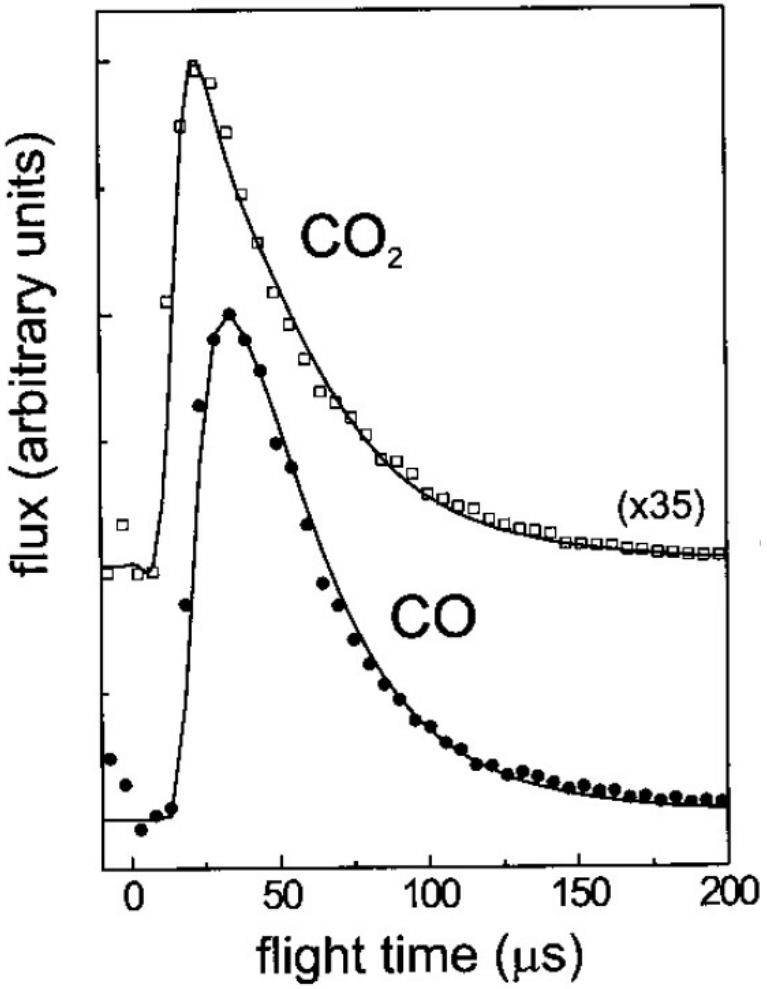
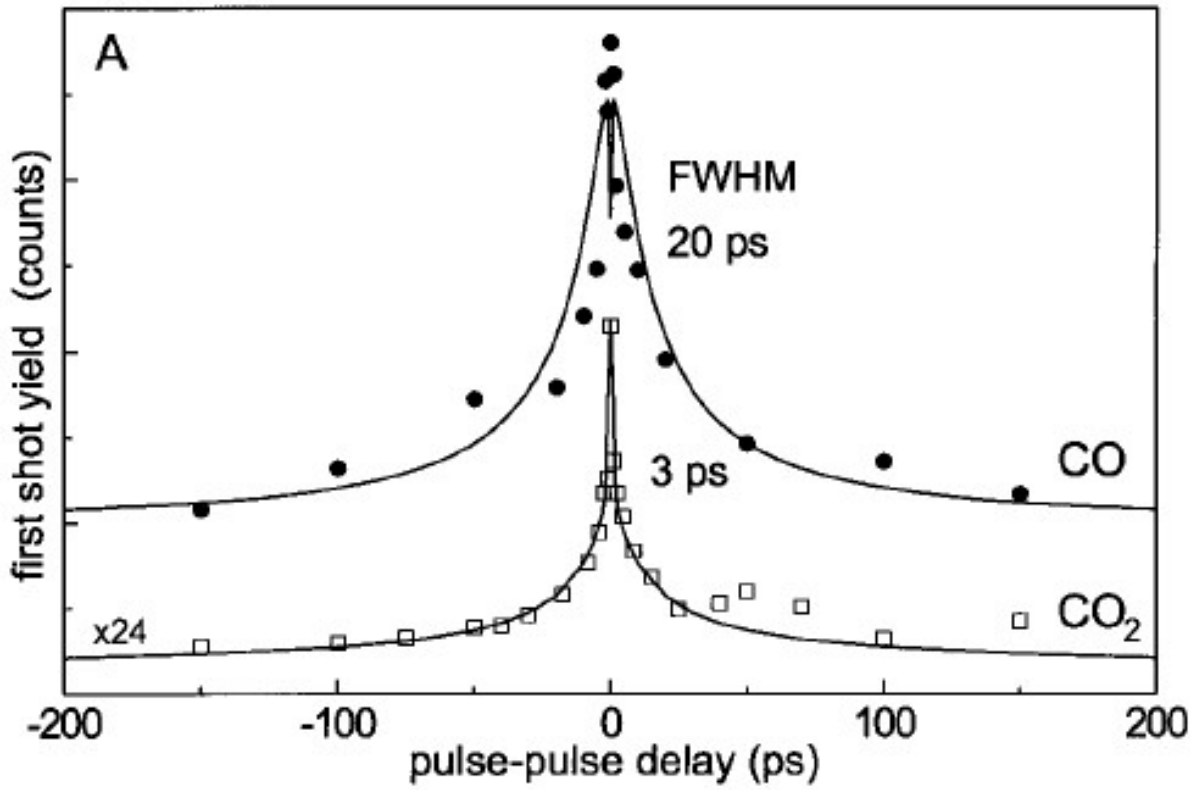

CO2
CO
O
C
O
τel
τph
τel-ph
Tel
Tph
T(K)
6000
4000
2000
0
Tel
Tph
0
1
2
3
time (ps)

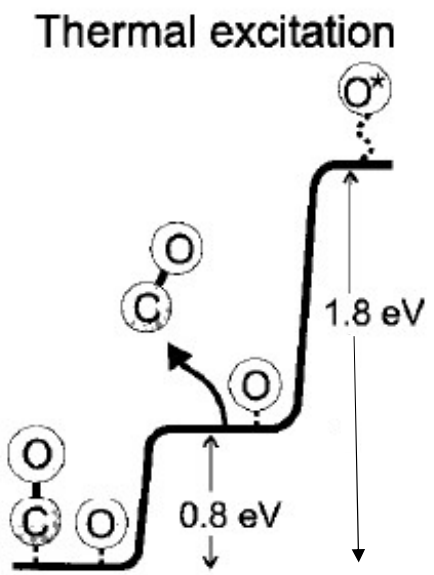

flux (arbitrary units)
CO2
(x35)
CO
0
50
100
150
200
flight time (μs)

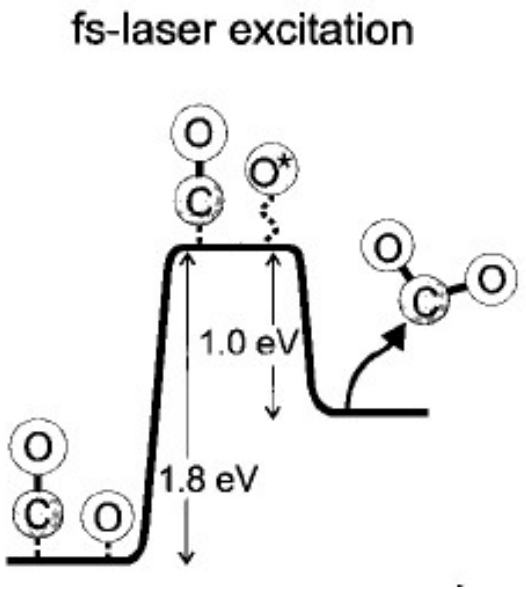
Per verificare se il desorbimento di CO e CO2 è regolato da elettroni o da fononi, mando due impulsi di fotoni al variare dell'intervallo (delay) tra i due. Se ho sovrapposizione tra gli effetti dei due impulsi, mi aspetto un aumento del desorbimento. Questo aumento c'è per entrambe le specie, ma la dipendenza dal delay è molto diversa….



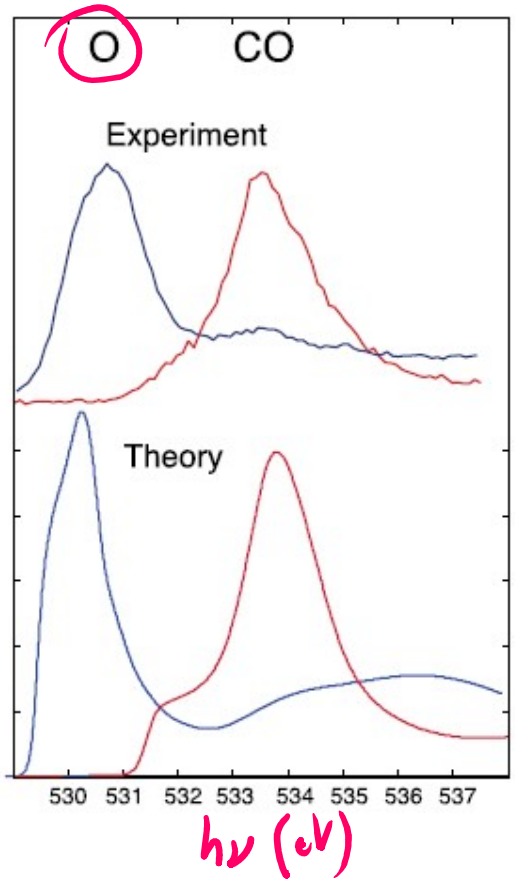
Electron-phonon coupling avviene in 1 ps
I fononi poi rilassano in 50 ps (e la temperatura si media su regioni più ampie del cristallo, scendendo localmente)

Qui perciò è evidente che il desorbimento di CO è legato a fenomeni fononici (temperatura che aumenta); il desorbimento di CO_2 a fenomeni elettronici (*hot electrons*)


Thermal excitation
O*
O
C
O
1.8 eV
O
O
C
O
0.8 eV

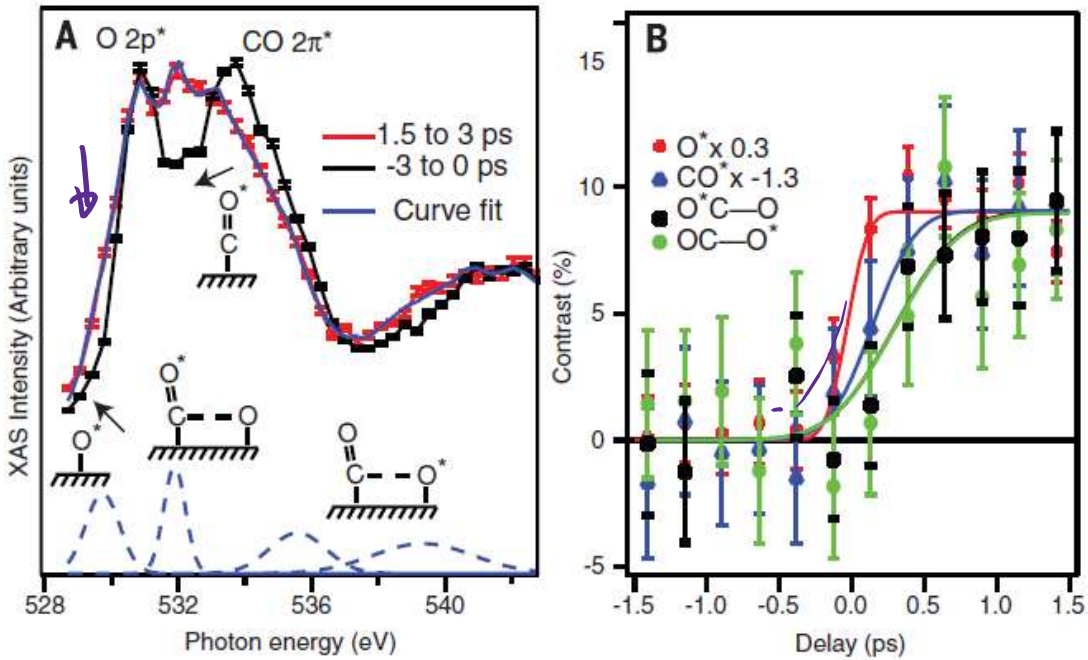

fs-laser excitation
O
C
O*
O
C
O
1.0 eV
O
C
O
1.8 eV

NEXAFS O_{1s}

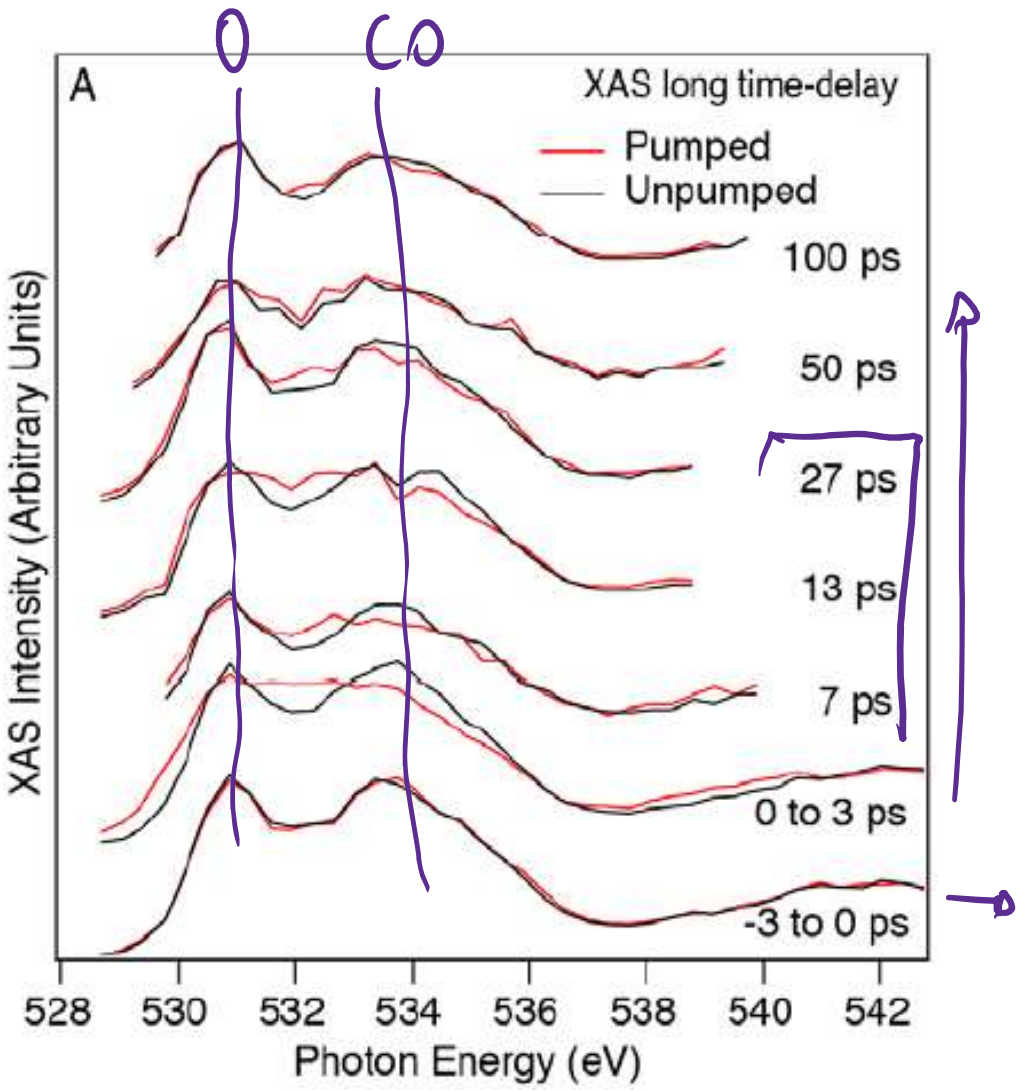


$h\nu_1 \approx 400$ nm

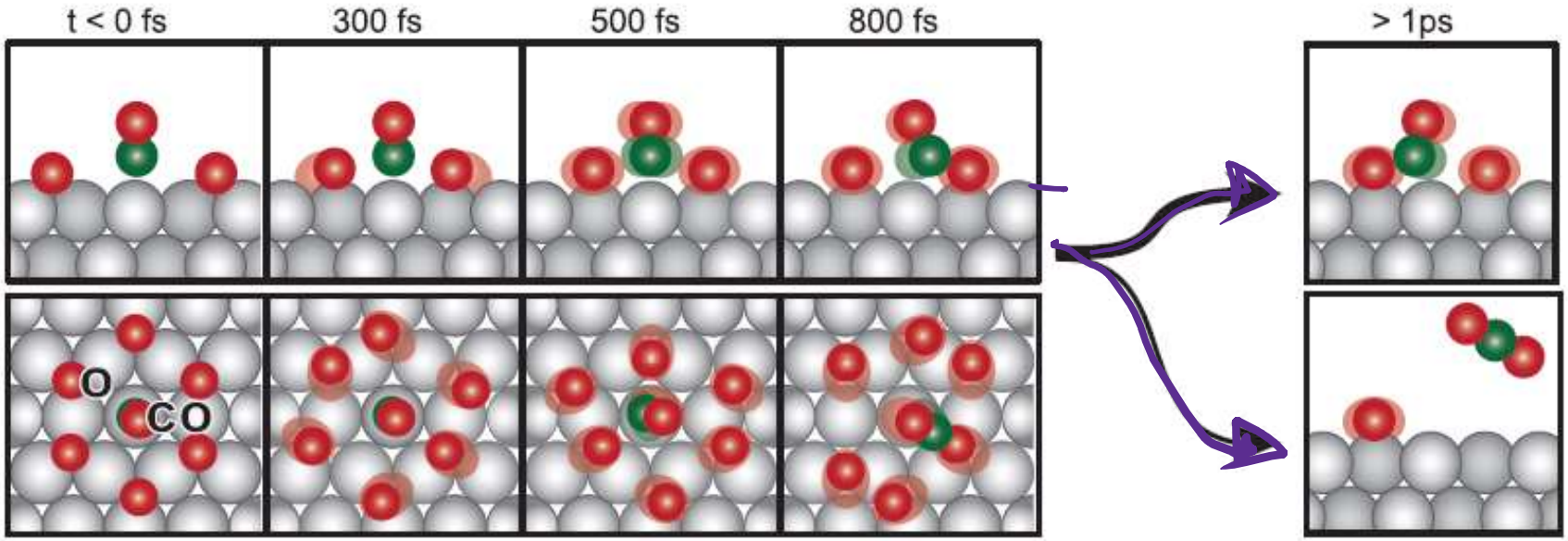
$h\nu_2$



Science, 2015, vol.347



Science, 2015, vol.347



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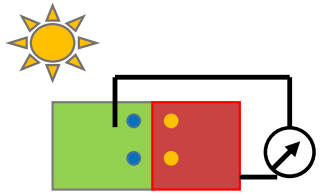
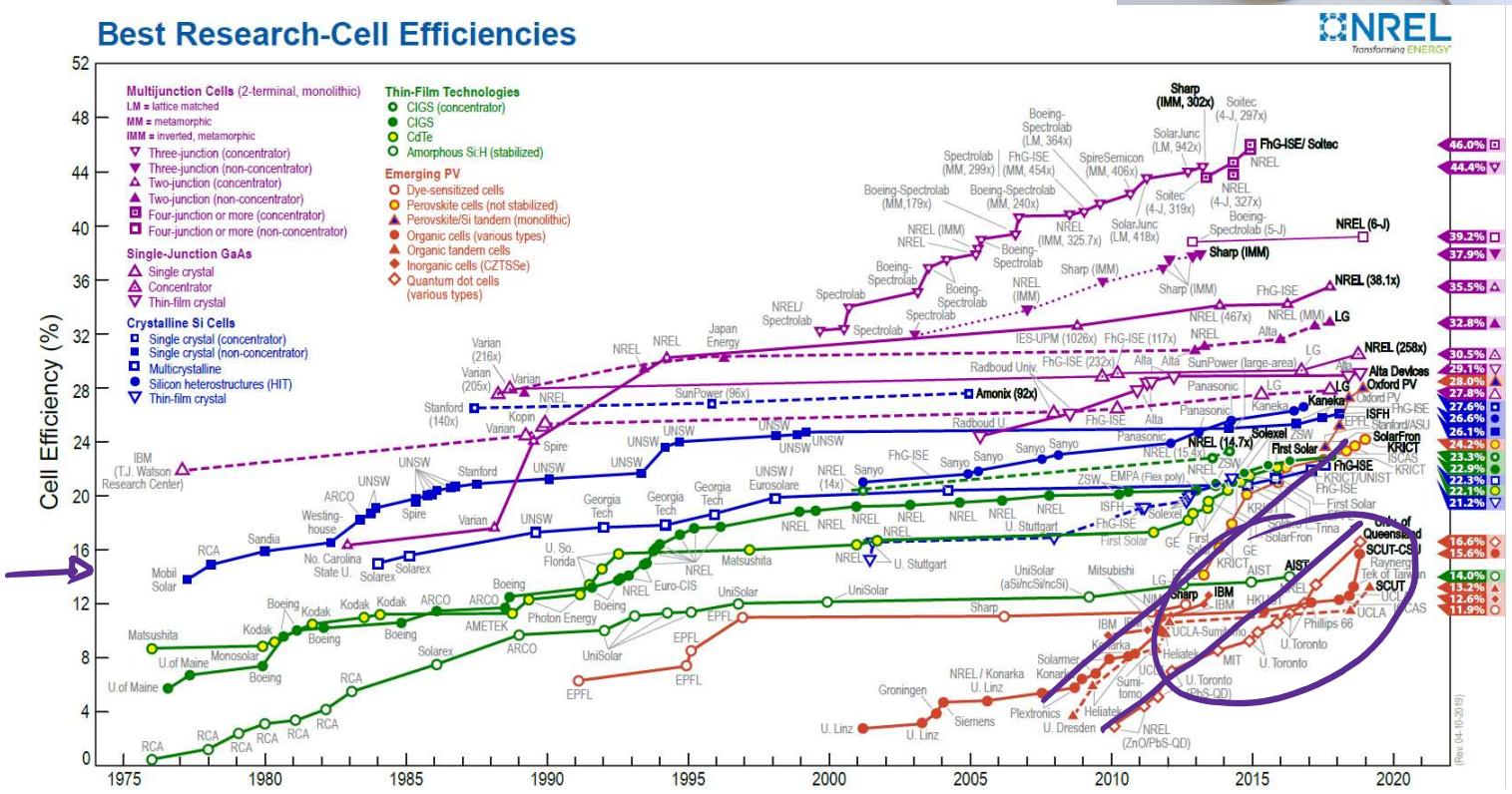
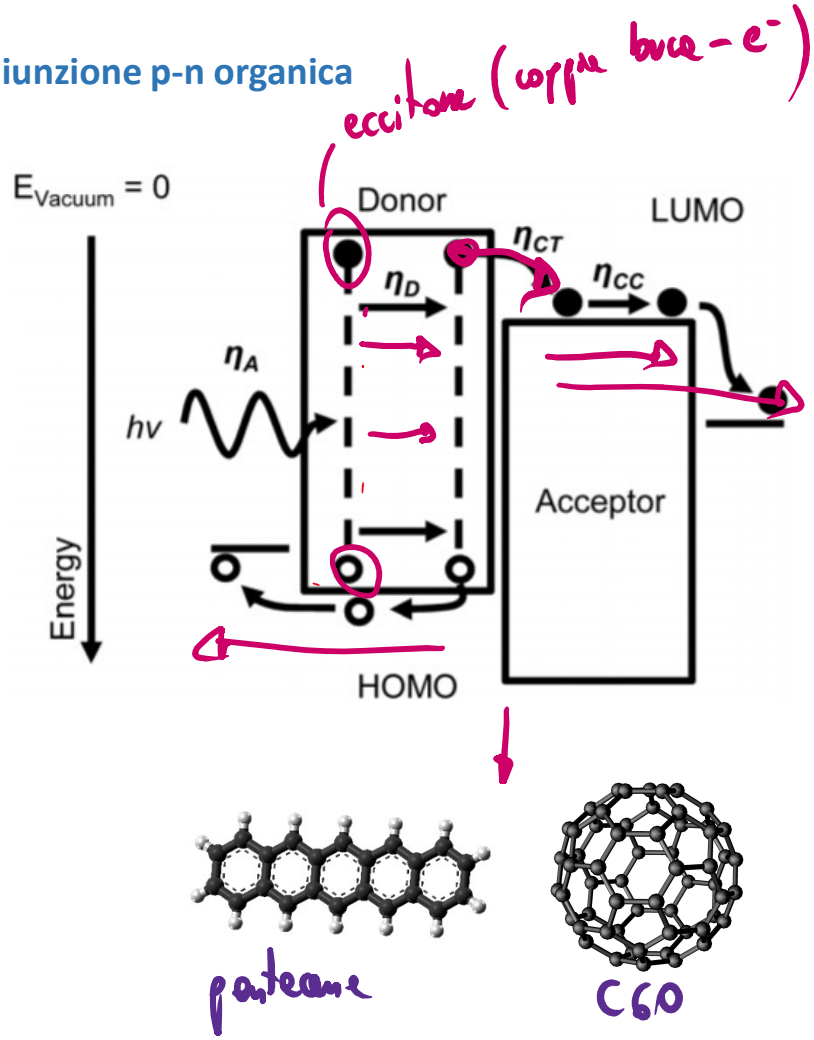
Solar Cells

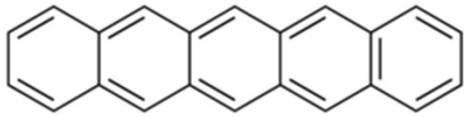



Best Research-Cell Efficiencies
NREL
Transforming ENERGY
Cell Efficiency (%)
Multijunction Cells (2-terminal, monolithic)
LM = lattice matched
MM = metamorphic
IMM = inverted, metamorphic
Three-junction (concentrator)
Three-junction (non-concentrator)
Two-junction (concentrator)
Two-junction (non-concentrator)
Four-junction or more (concentrator)
Four-junction or more (non-concentrator)
Single-Junction GaAs
Single crystal
Concentrator
Thin-film crystal
Crystalline Si Cells
Single crystal (concentrator)
Single crystal (non-concentrator)
Multicrystalline
Silicon heterostructures (HIT)
Thin-film crystal
Thin-Film Technologies
CIGS (concentrator)
CIGS
CdTe
Amorphous Si:H (stabilized)
Emerging PV
Dye-sensitized cells
Perovskite cells (not stabilized)
Perovskite/Si tandem (monolithic)
Organic cells (various types)
Organic tandem cells
Inorganic cells (CZTSSe)
Quantum dot cells (various types)
46.0%
44.4%
39.2%
37.9%
35.5%
32.8%
30.5%
29.1%
28.0%
27.8%
27.6%
26.6%
26.1%
24.2%
23.3%
22.9%
22.3%
22.1%
21.2%
16.6%
15.6%
14.0%
13.2%
12.6%
11.9%
1975
1980
1985
1990
1995
2000
2005
2010
2015
2020

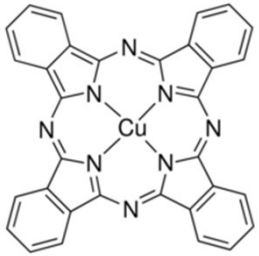
Giunzione p-n organica



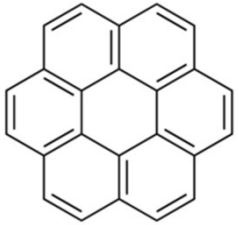
p-type



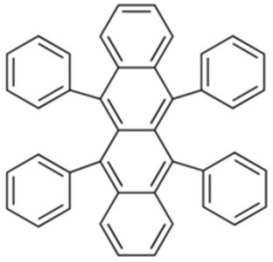
pentacene



CuPc

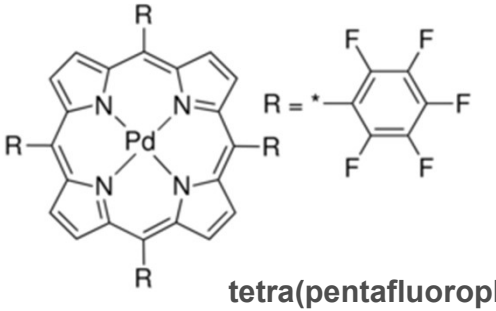


coronene

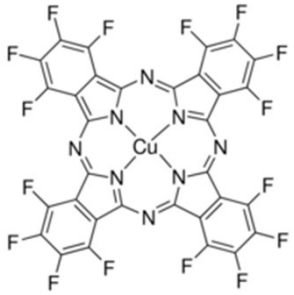


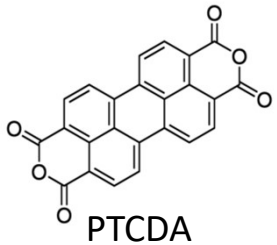
rubrene

n-type

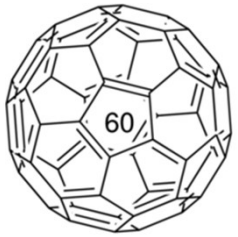


tetra(pentafluorophenyl)porphine

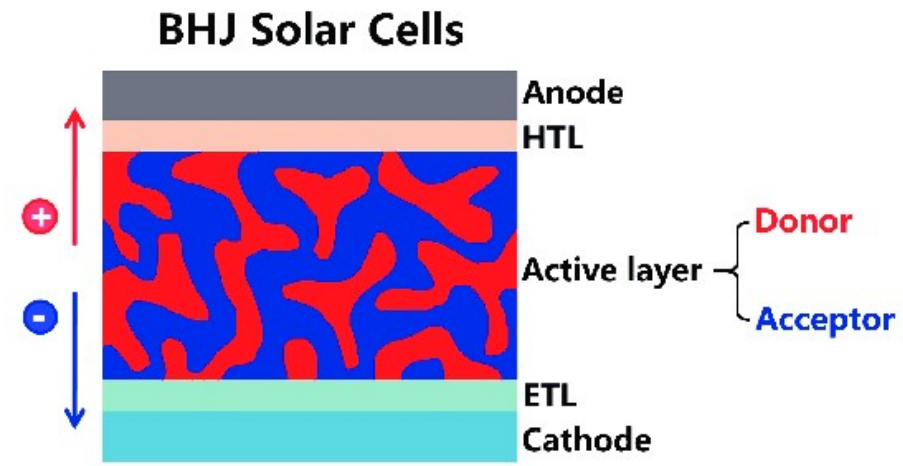


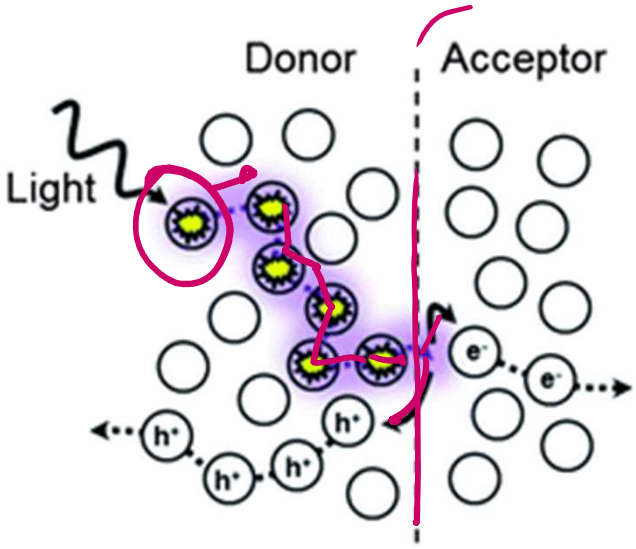


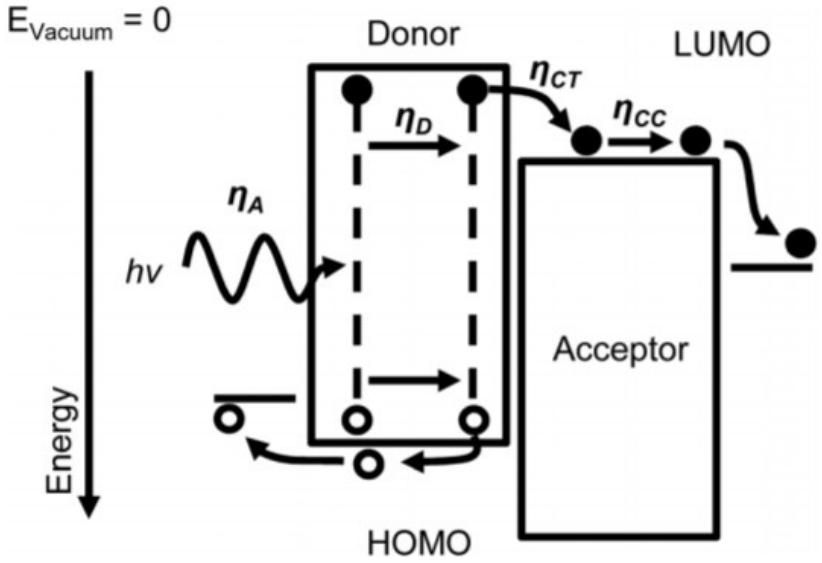
PTCDA



Fullerene

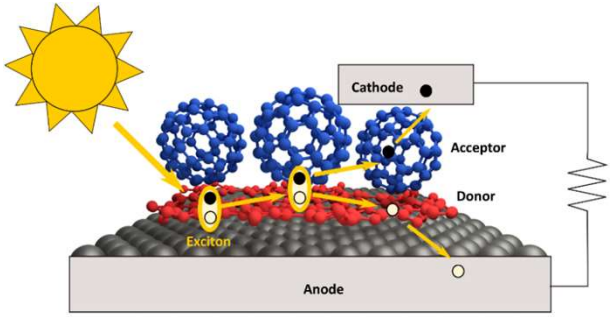






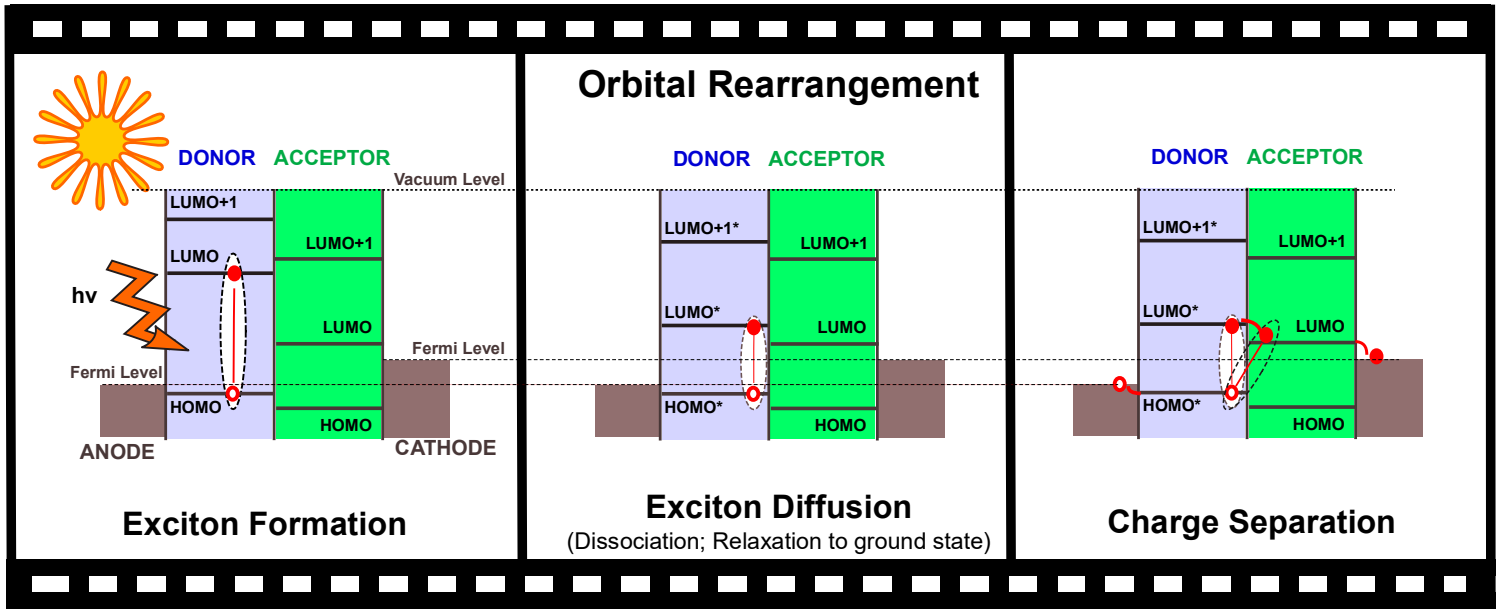
Energy Environ. Sci., 2014,**7**, 499-512

Organic Solar Cell

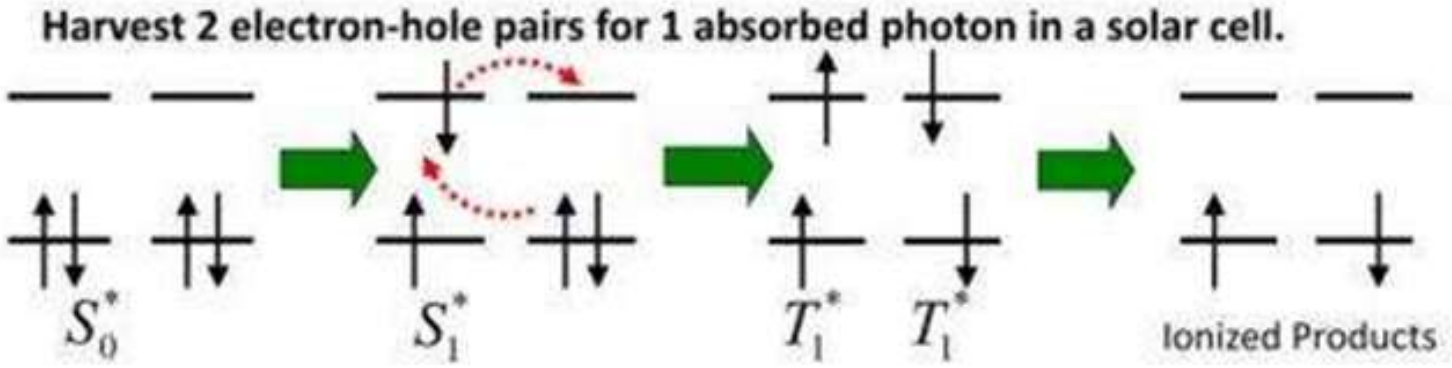


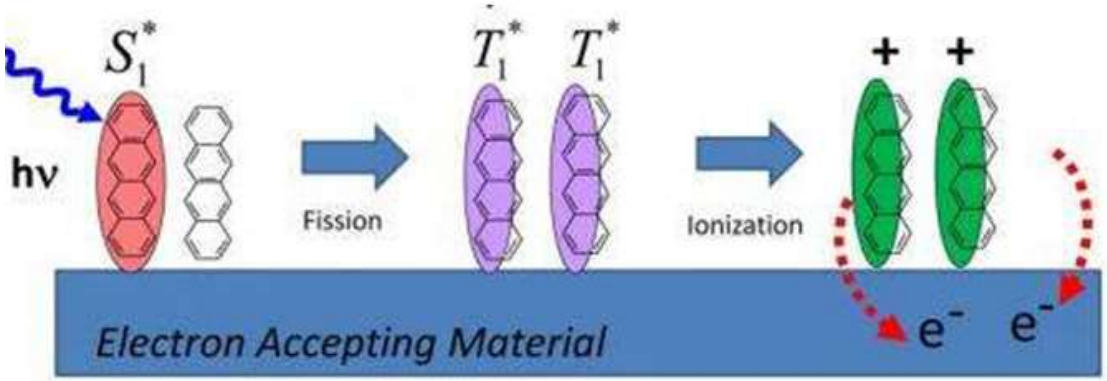
Challenge:

Understanding **exciton formation** and **decay dynamics**

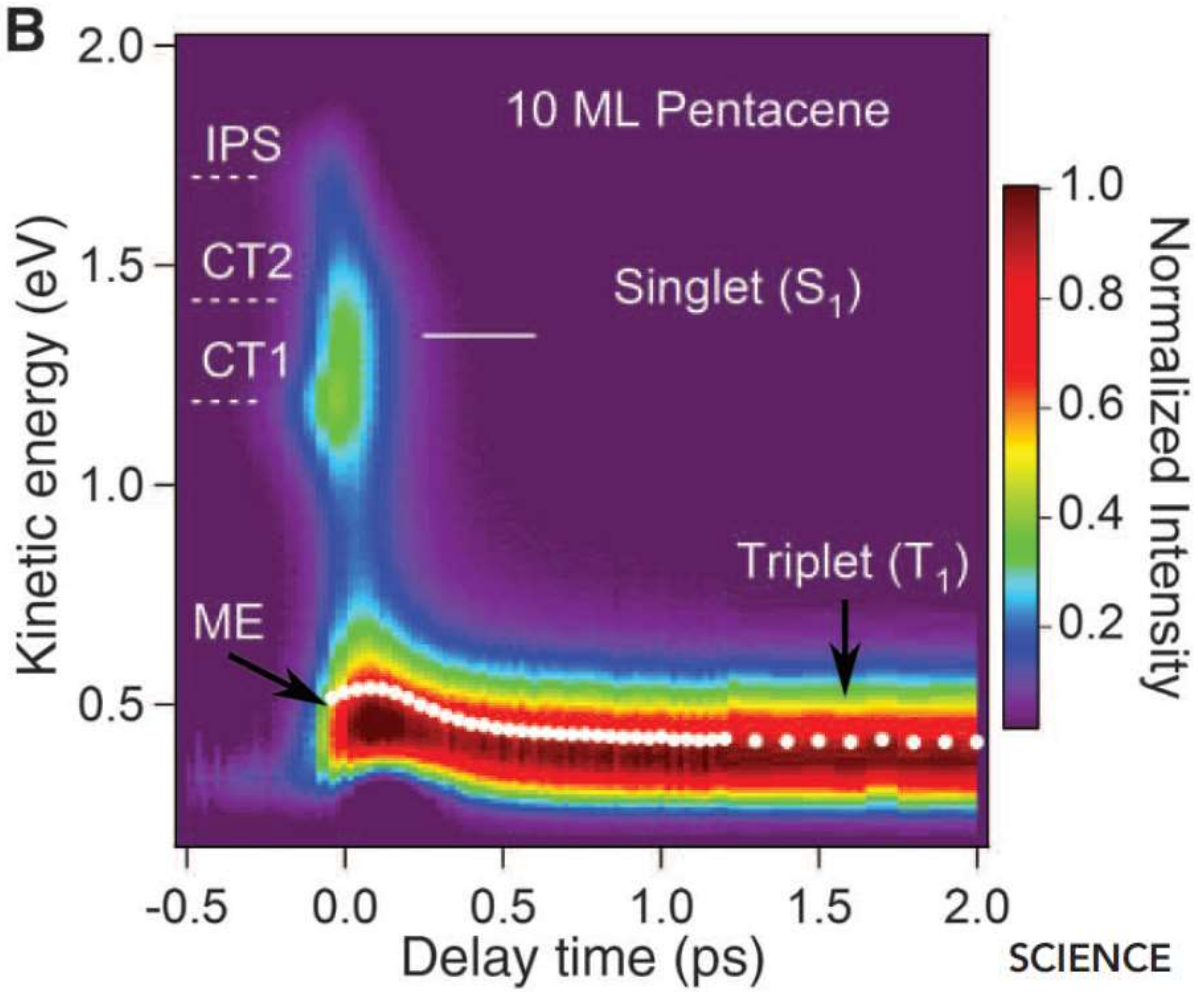


Singlet Fission



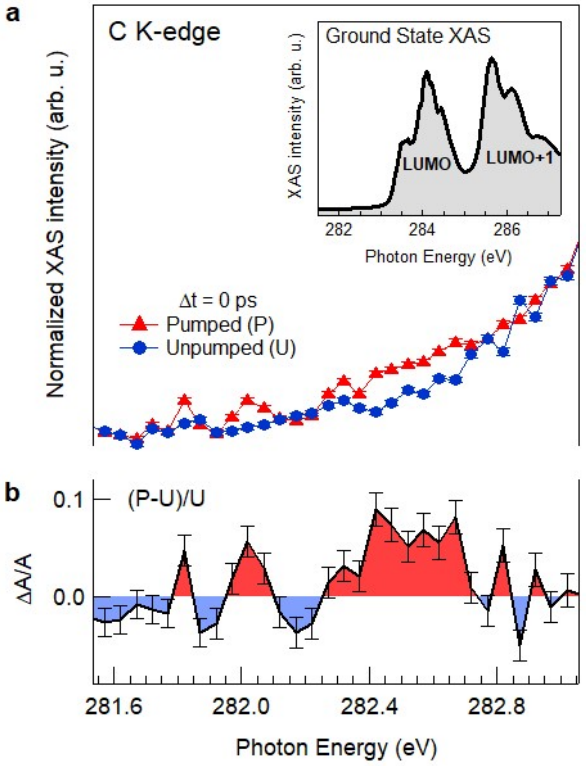


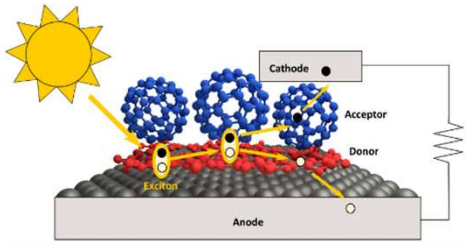
J. Phys. Chem. Lett. 2014, 5, 13, 2312–2319

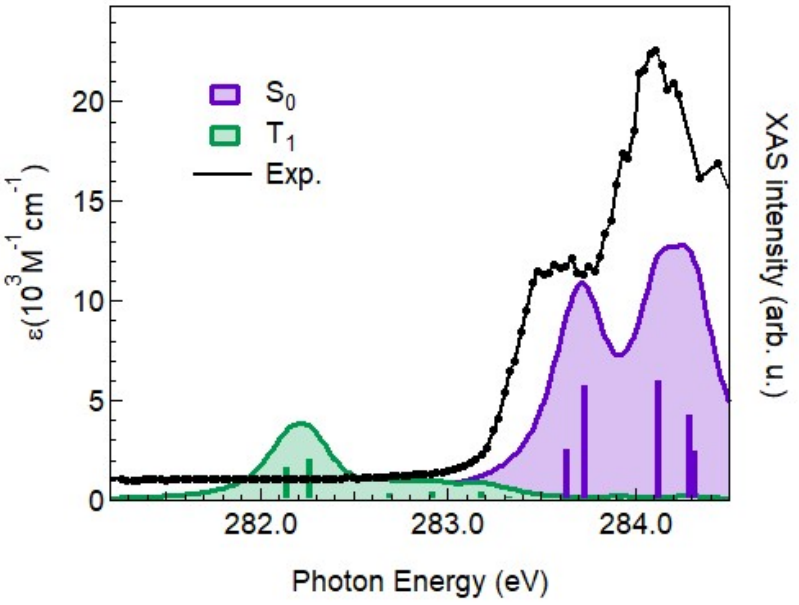

B
10 ML Pentacene
IPS
CT2
CT1
Singlet (S_1)
Triplet (T_1)
ME
Kinetic energy (eV)
2.0
1.5
1.0
0.5
-0.5
0.0
0.5
1.0
1.5
2.0
Delay time (ps)
1.0
0.8
0.6
0.4
0.2
Normalized Intensity

Time resolved XAS

Triplet picosecond dynamics with chemical sensitivity







Commun Phys **2,** 56 (2019)