

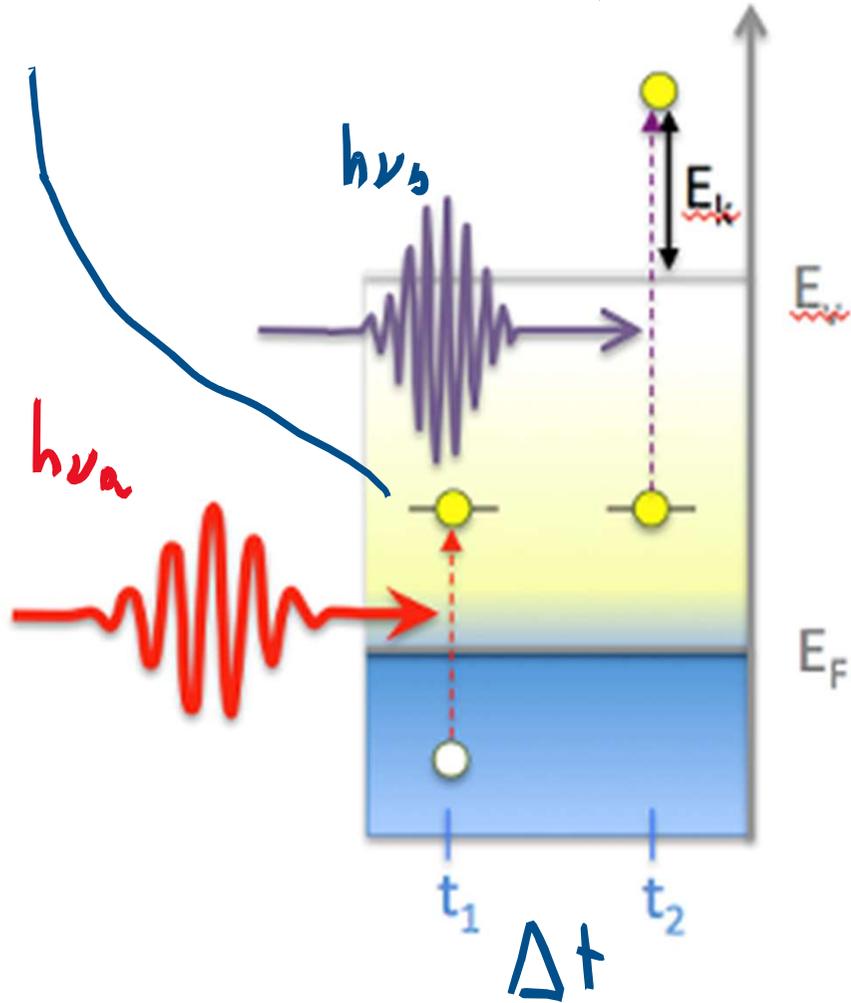
3.2.4

## Two-Photon Photoelectron Spectroscopy

*Thomas Fauster*

state intermediate
{

virtuale  
reale (n.LUMO)

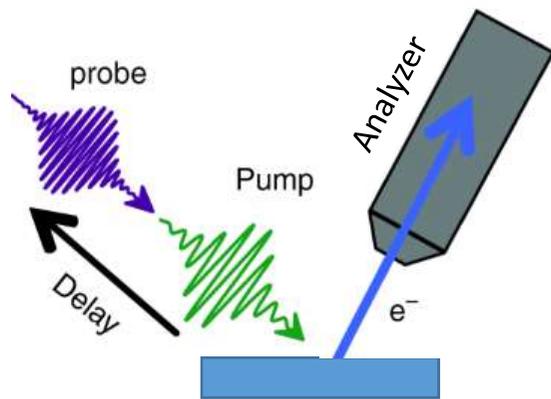


$\Delta t = 0 \rightarrow$  ZPP  
 two photon photoemission

$\Delta t \neq 0 \rightarrow$  time resolved  
 TR-ZPP

$\Delta t = 0, h\nu_a = h\nu_b$

$S_e N_{\text{photons}} \gg \gg (10^{12} \text{ ph/300fs/mm}^2)$

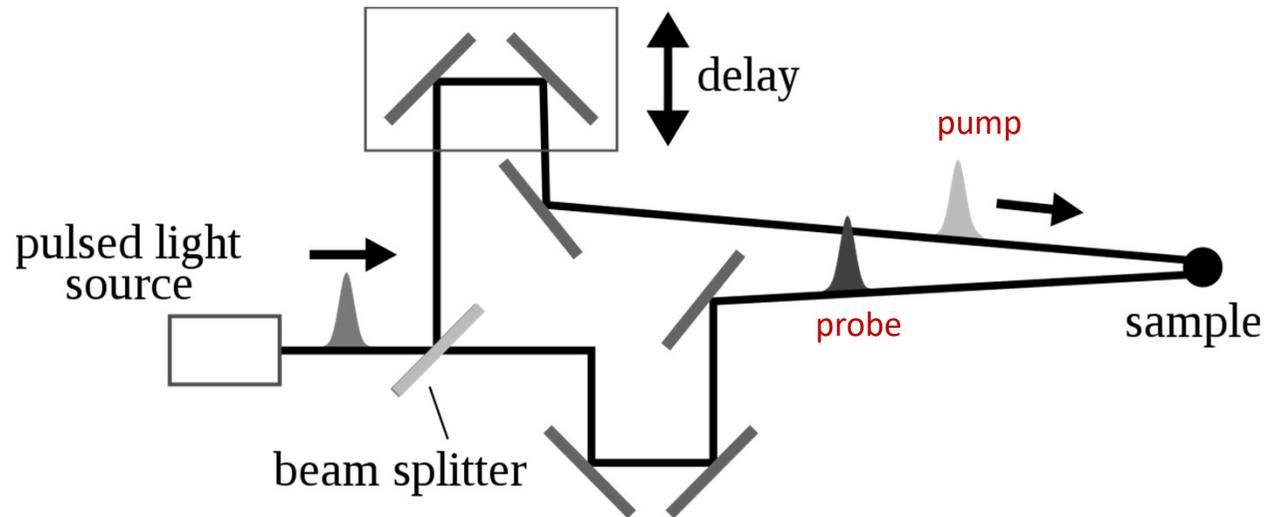


Mi servono due sorgenti di fotoni (pump e probe)

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 regolabile, 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.

## Image potential states

$z \uparrow \bullet e^-$   
⊕ carica immagine metallo

Immaginiamo di portare  $e^-$   
da  $\infty$  alla distanza  $z$

$$F = qE = -eE = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{(2z)^2} \quad \rightarrow \quad F = -\frac{dU}{dz}$$

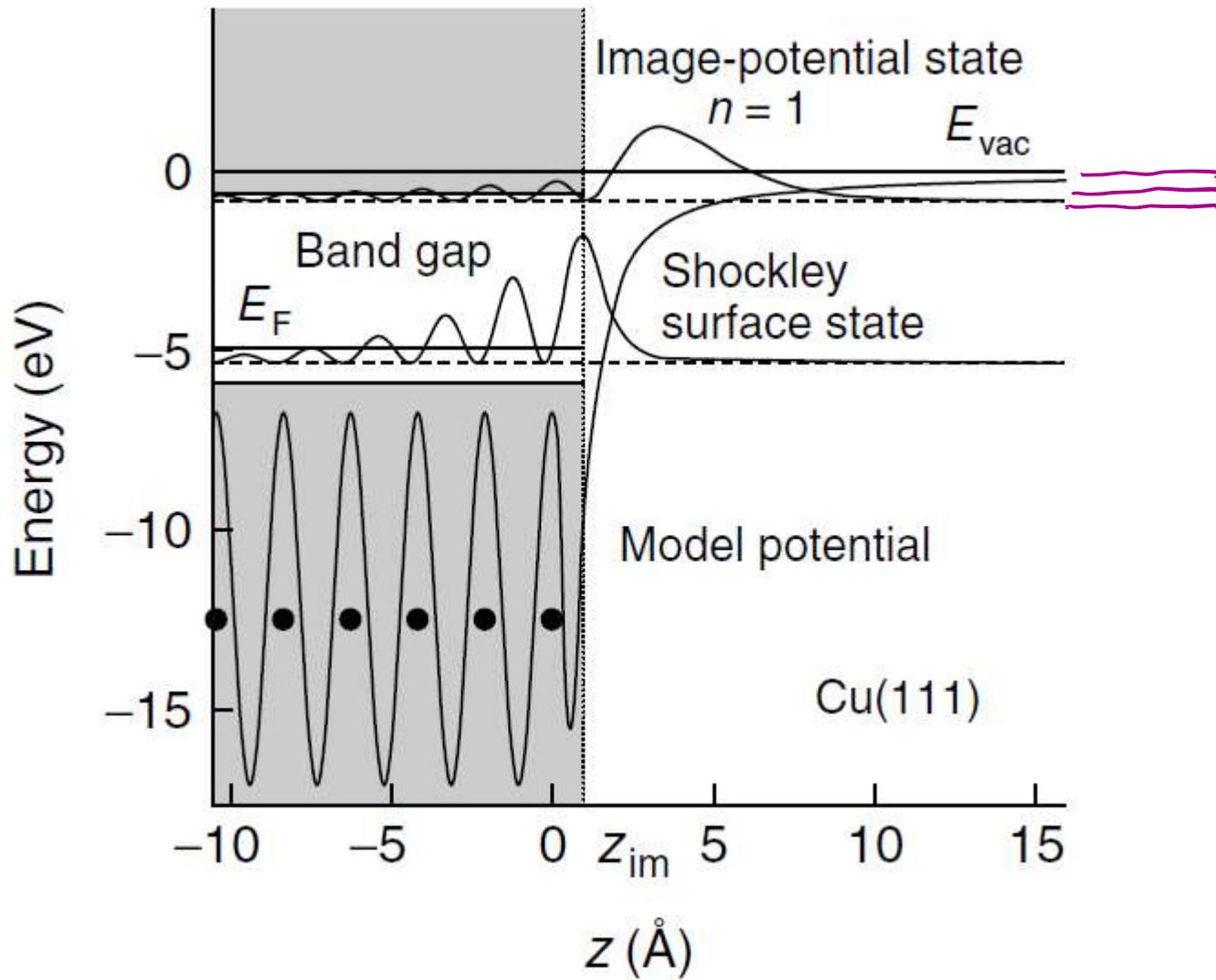
$$U = -\int_{\infty}^z F dz$$

$$= \frac{e^2}{4\pi\epsilon_0} \frac{1}{4} \int_{\infty}^z \frac{1}{z^2} dz = -\left(\frac{1}{4z}\right)$$

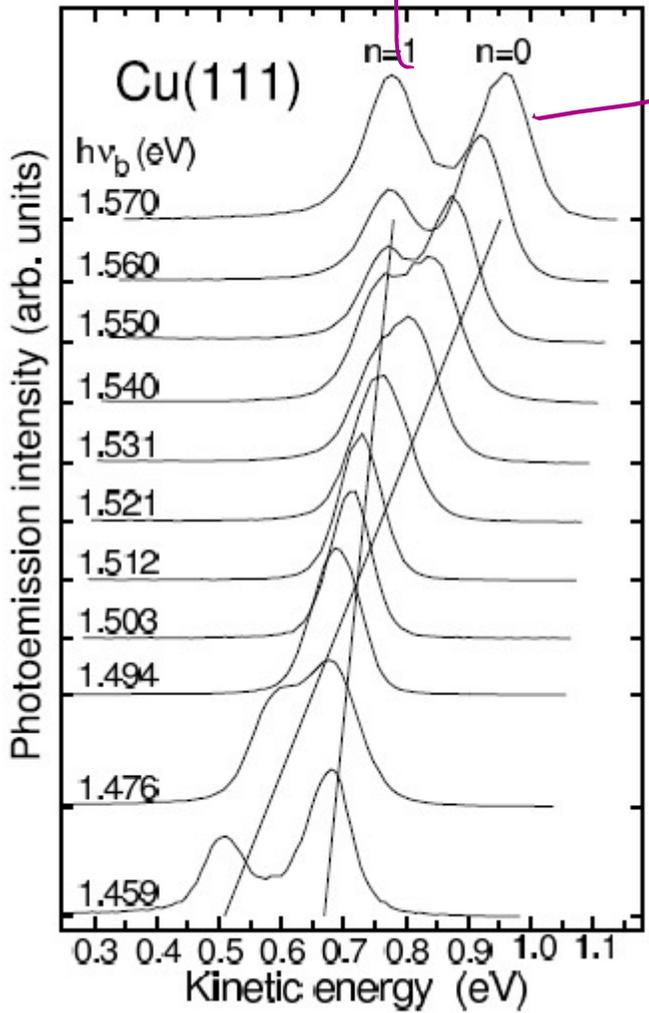
1 in unità atomiche

in u.o.  $U(z) = -\frac{1}{4z}$

# Image potential states



$$E_n = -\frac{0.85}{(n+e)^2} \text{ eV}$$

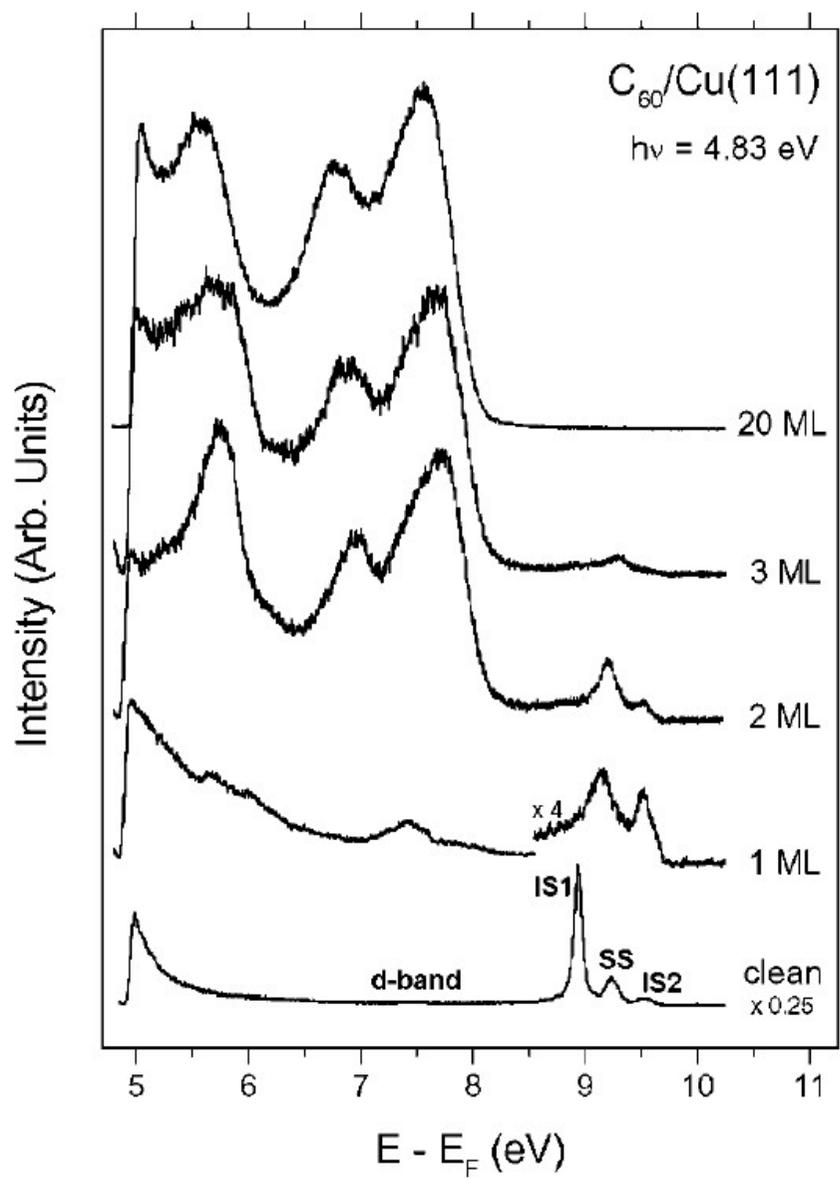
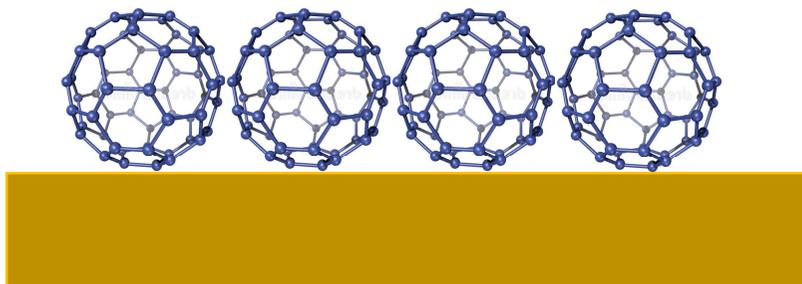


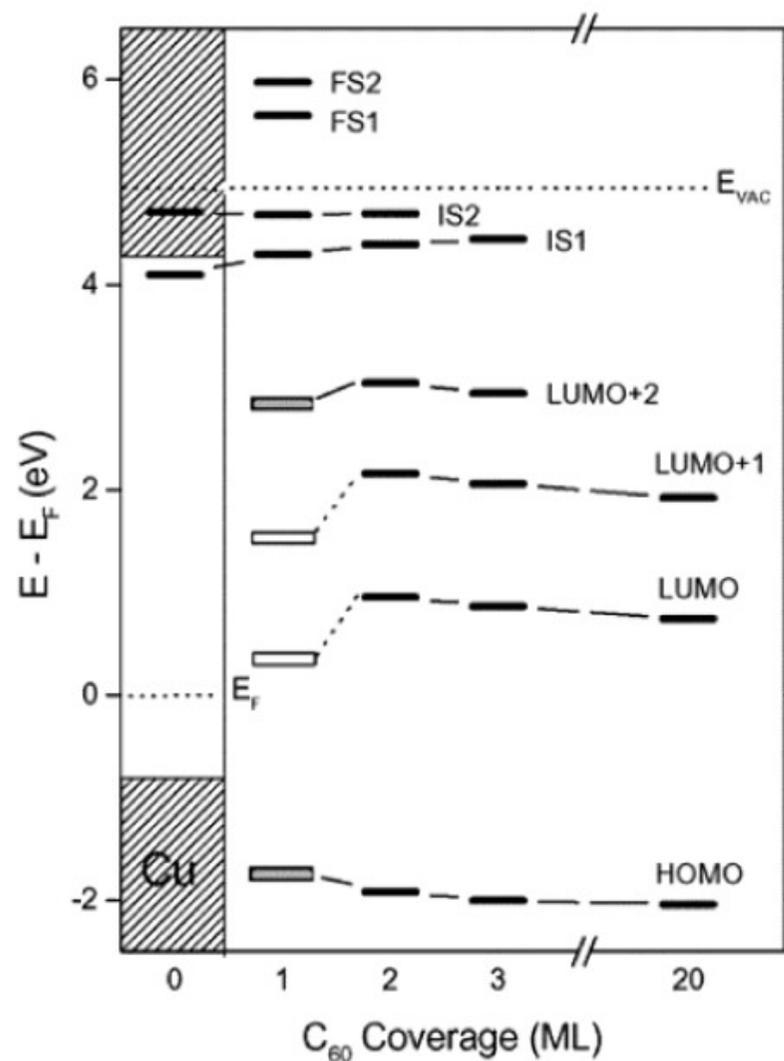
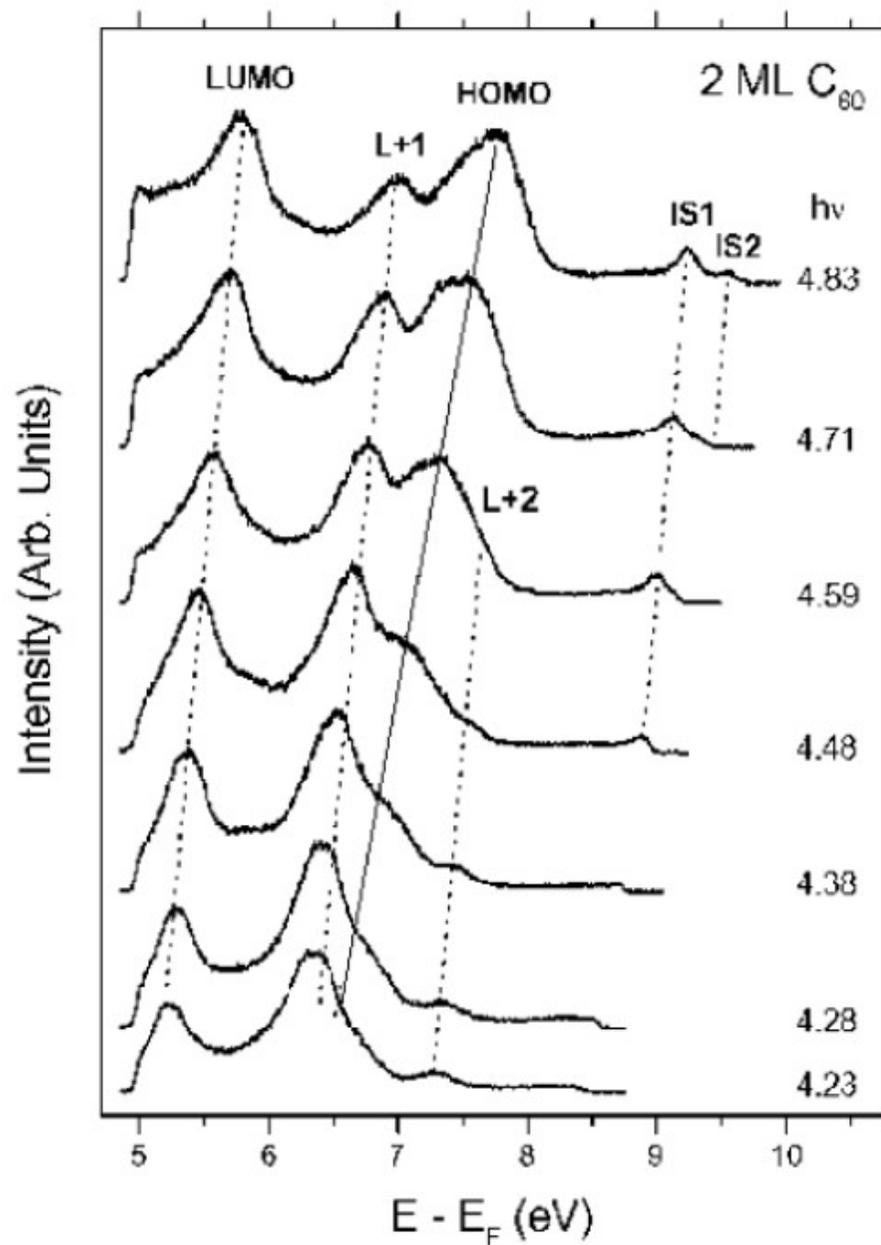
$$\Delta E_{kin} \propto h\nu_b$$

$$h\nu_e = 3 h\nu_b$$

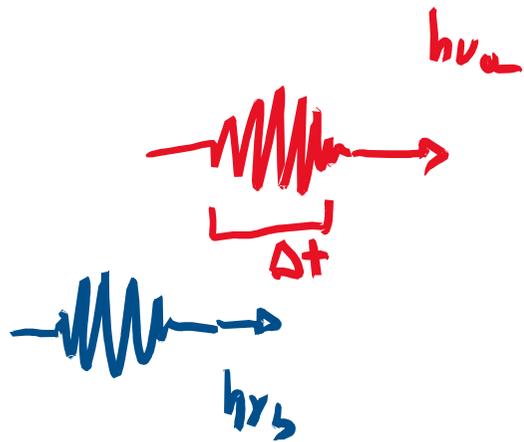
$$\Delta E_{kin} \propto (h\nu_e + h\nu_b)$$

$M=1$  is large Potential State





TR-2PP

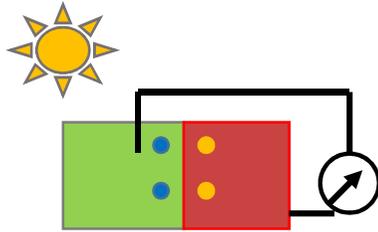


$$\Delta t \approx 40 \text{ fs}$$

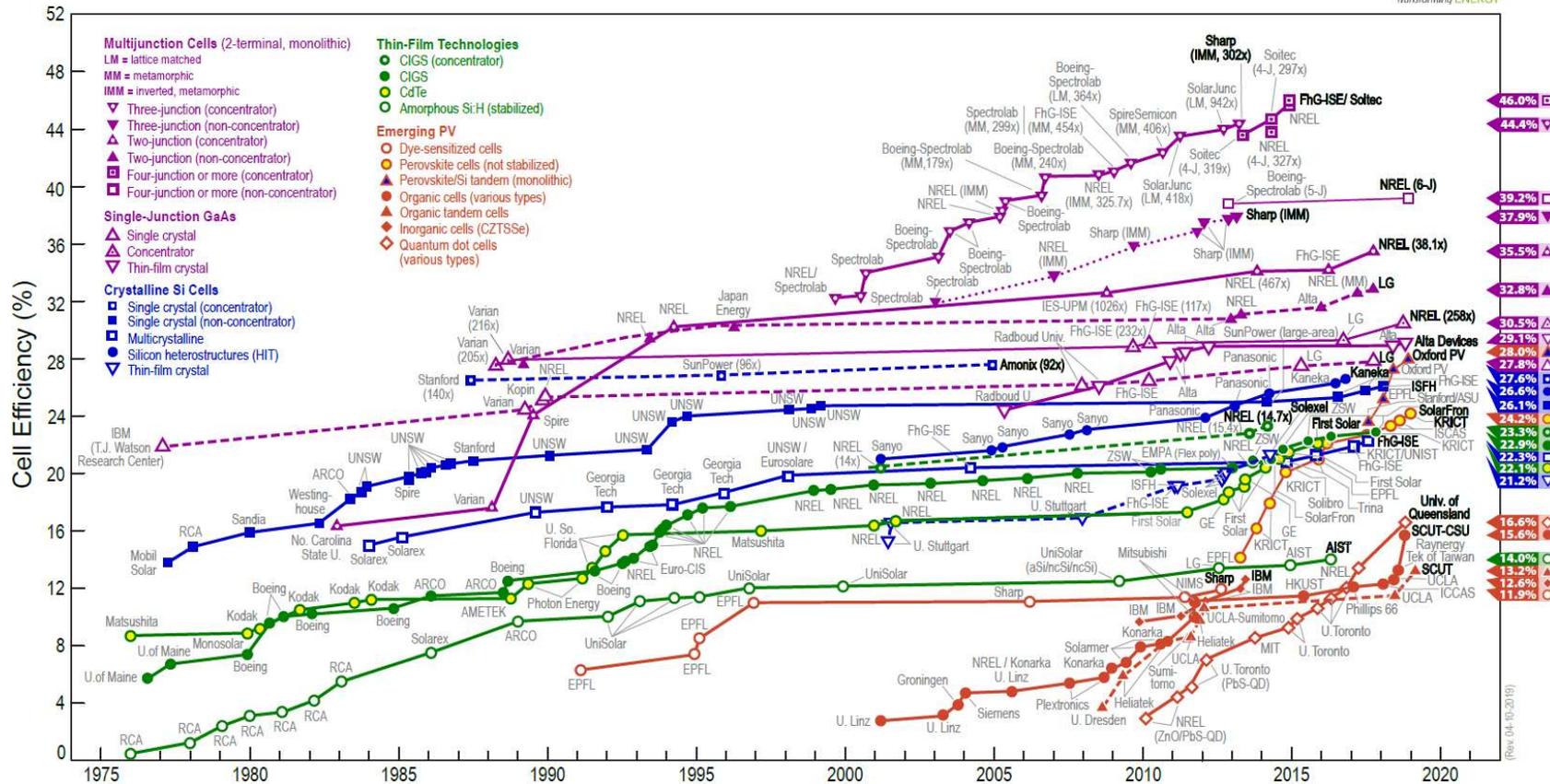
(60-10)

In realtà  $\approx 100 \text{ fs}$  è la risol  
temporale tenendo conto  
di tutto l'apparato strumentale

# Solar Cells

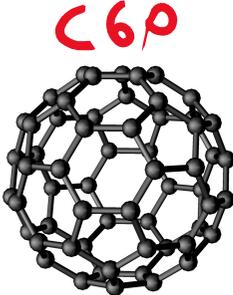
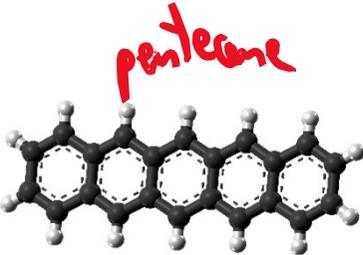
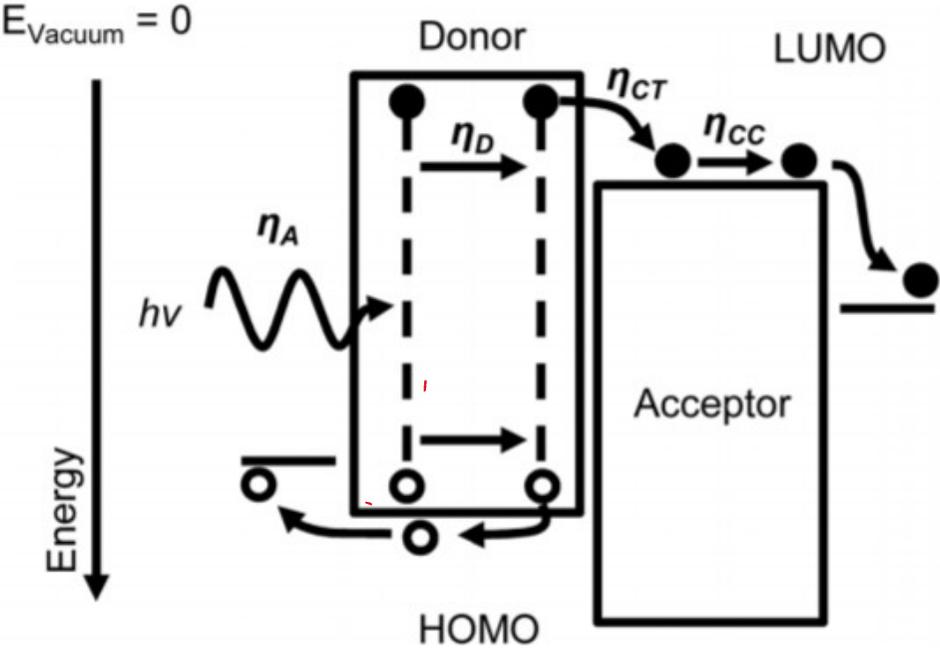


## Best Research-Cell Efficiencies

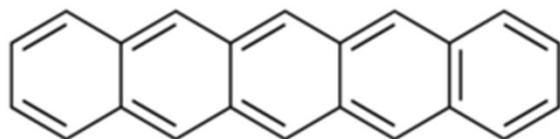




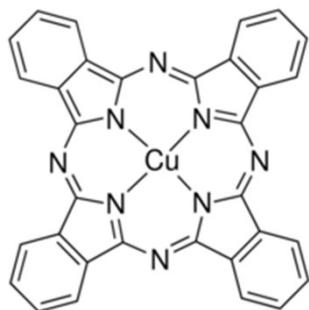
# Giunzione p-n organica



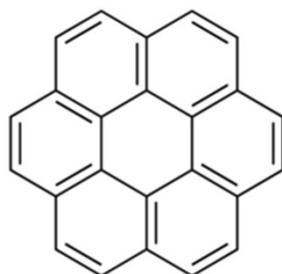
p-type



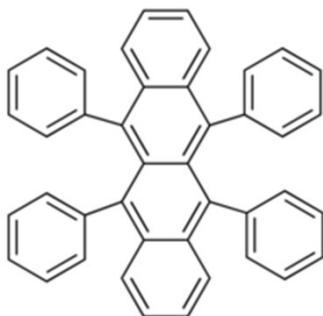
pentacene



CuPc

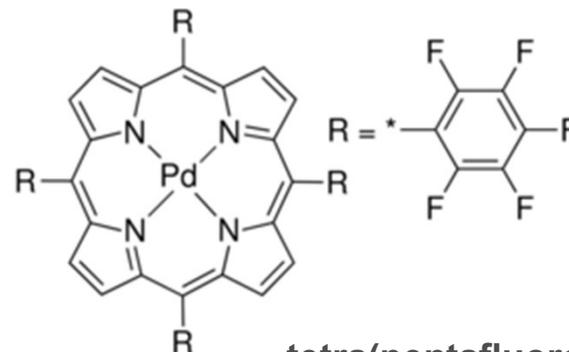


coronene

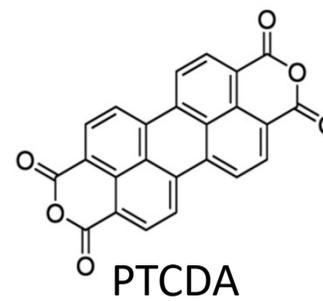
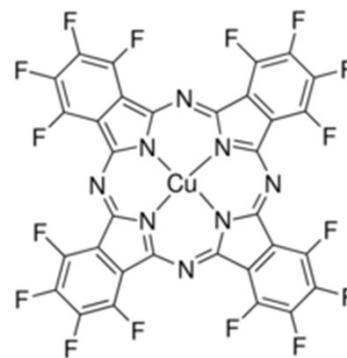


rubrene

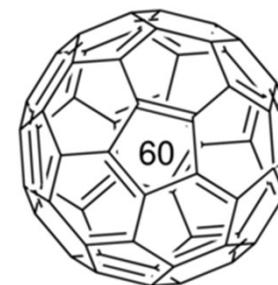
n-type



tetra(pentafluorophenyl)porphin

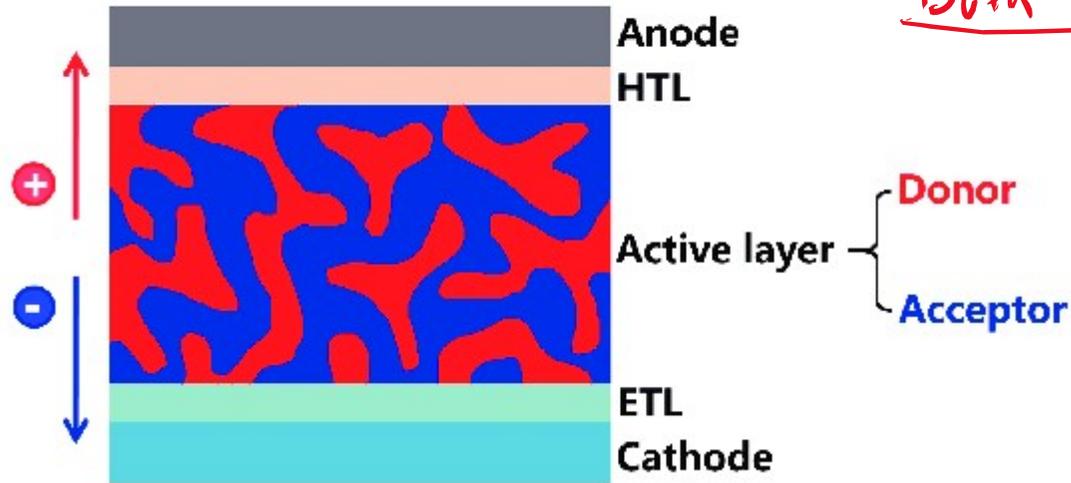


PTCDA

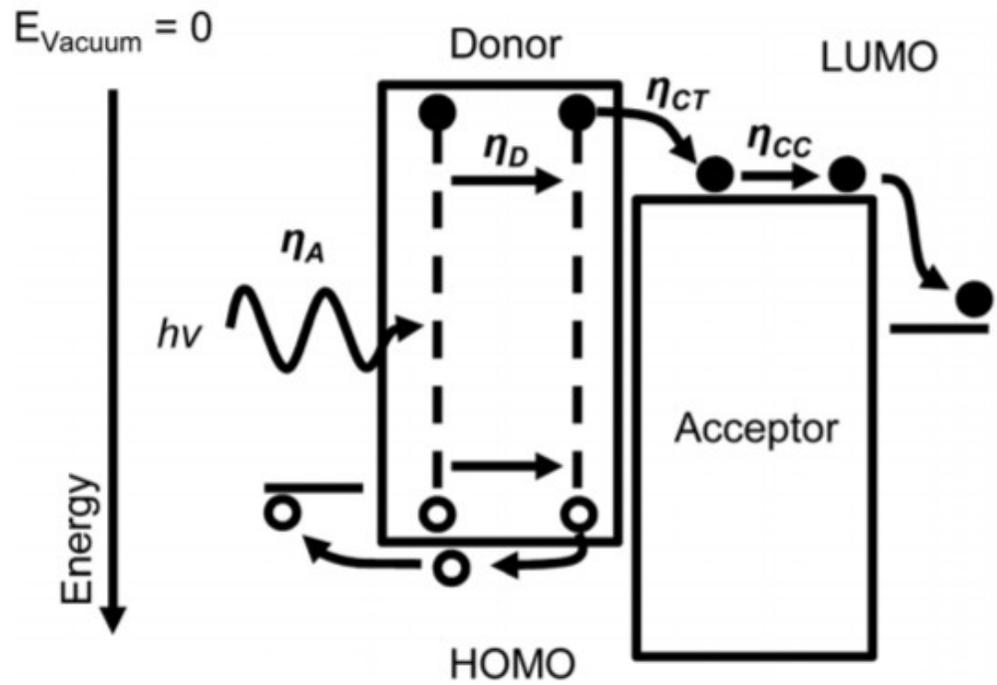
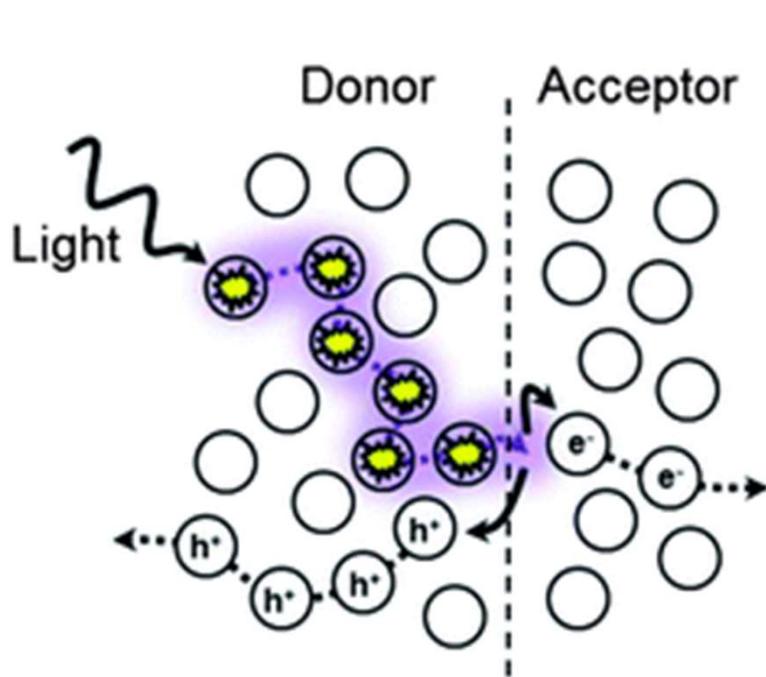


Fullerene

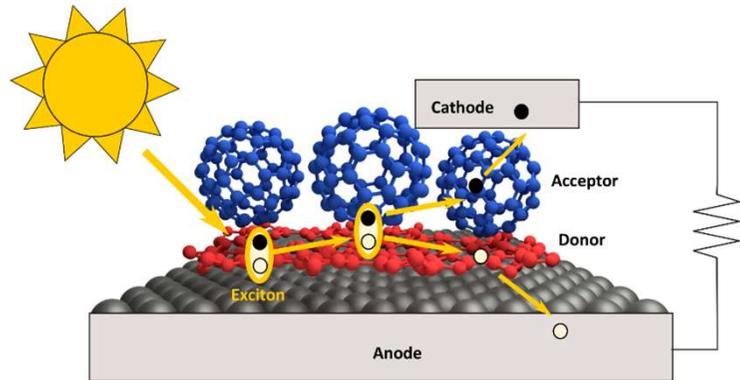
# BHJ Solar Cells



DuPh Heterojunction

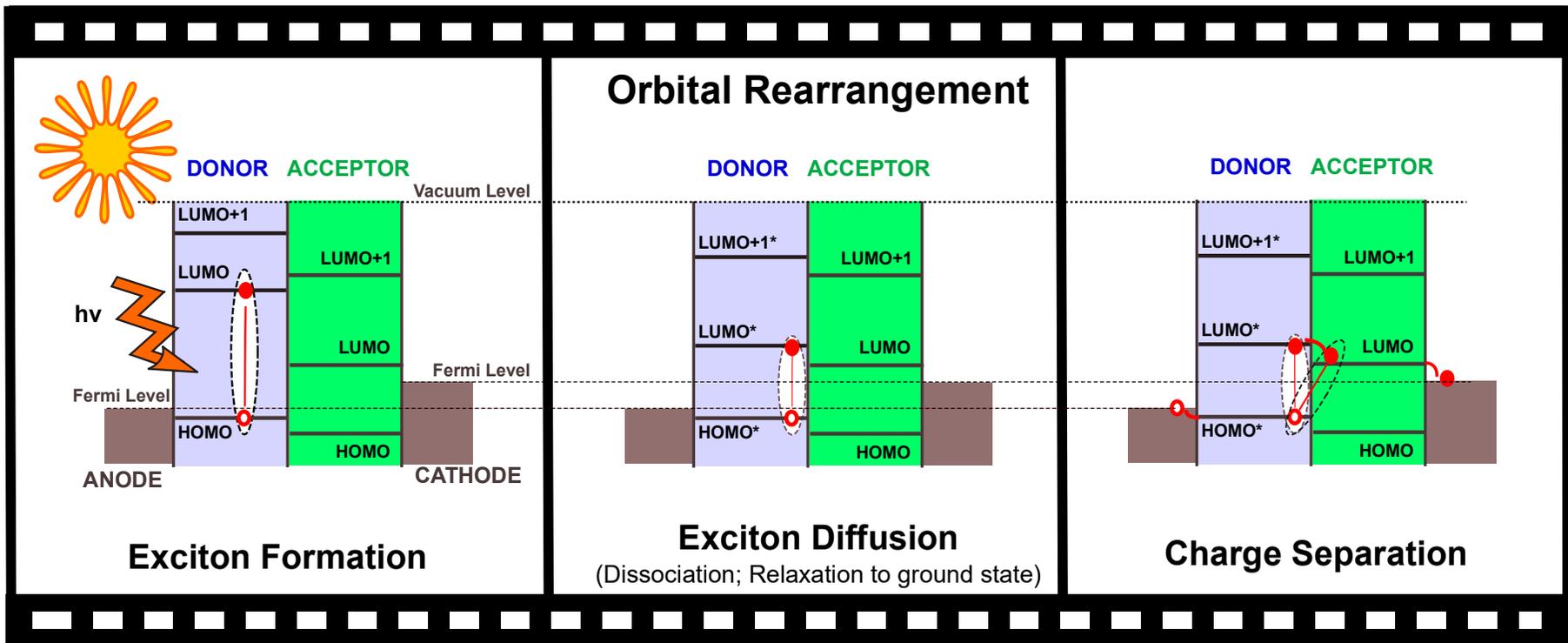


# Organic Solar Cell

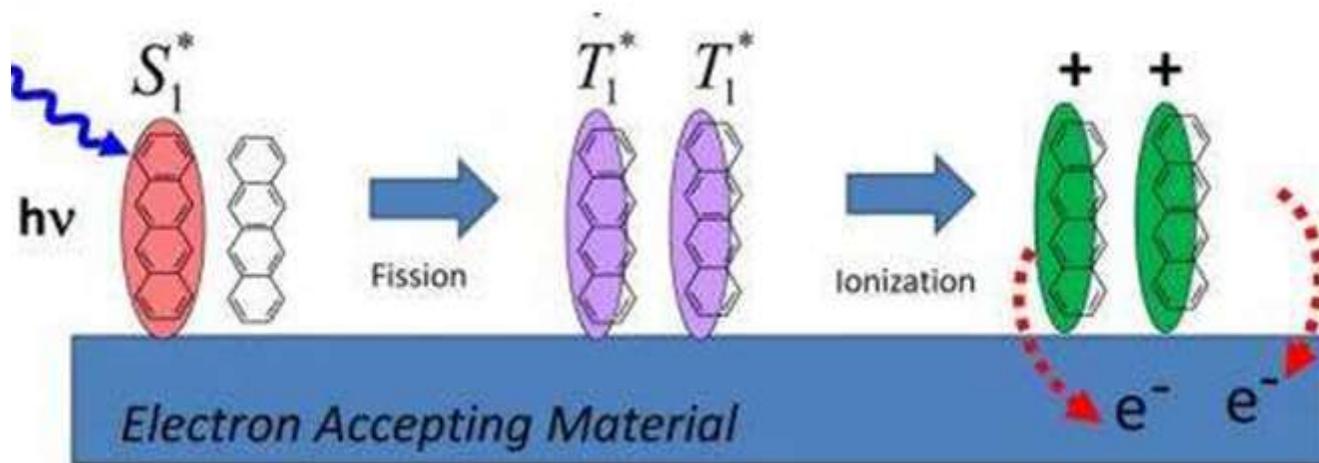
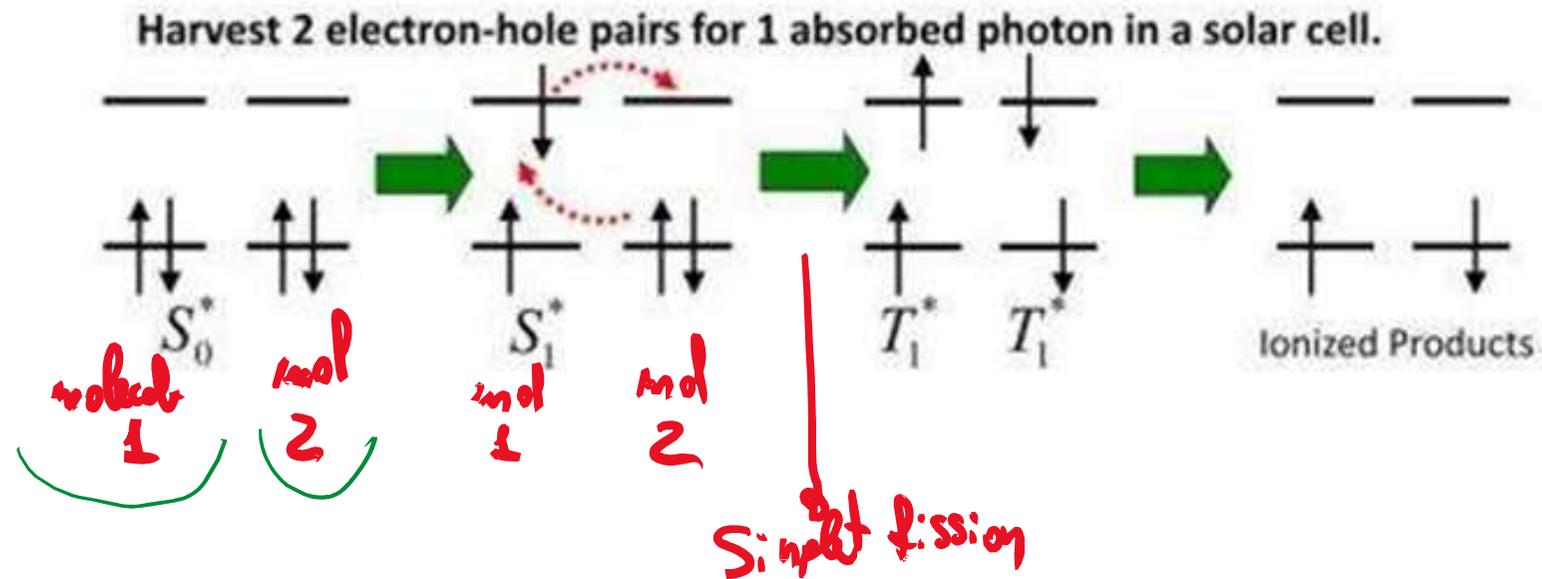


**Challenge:**

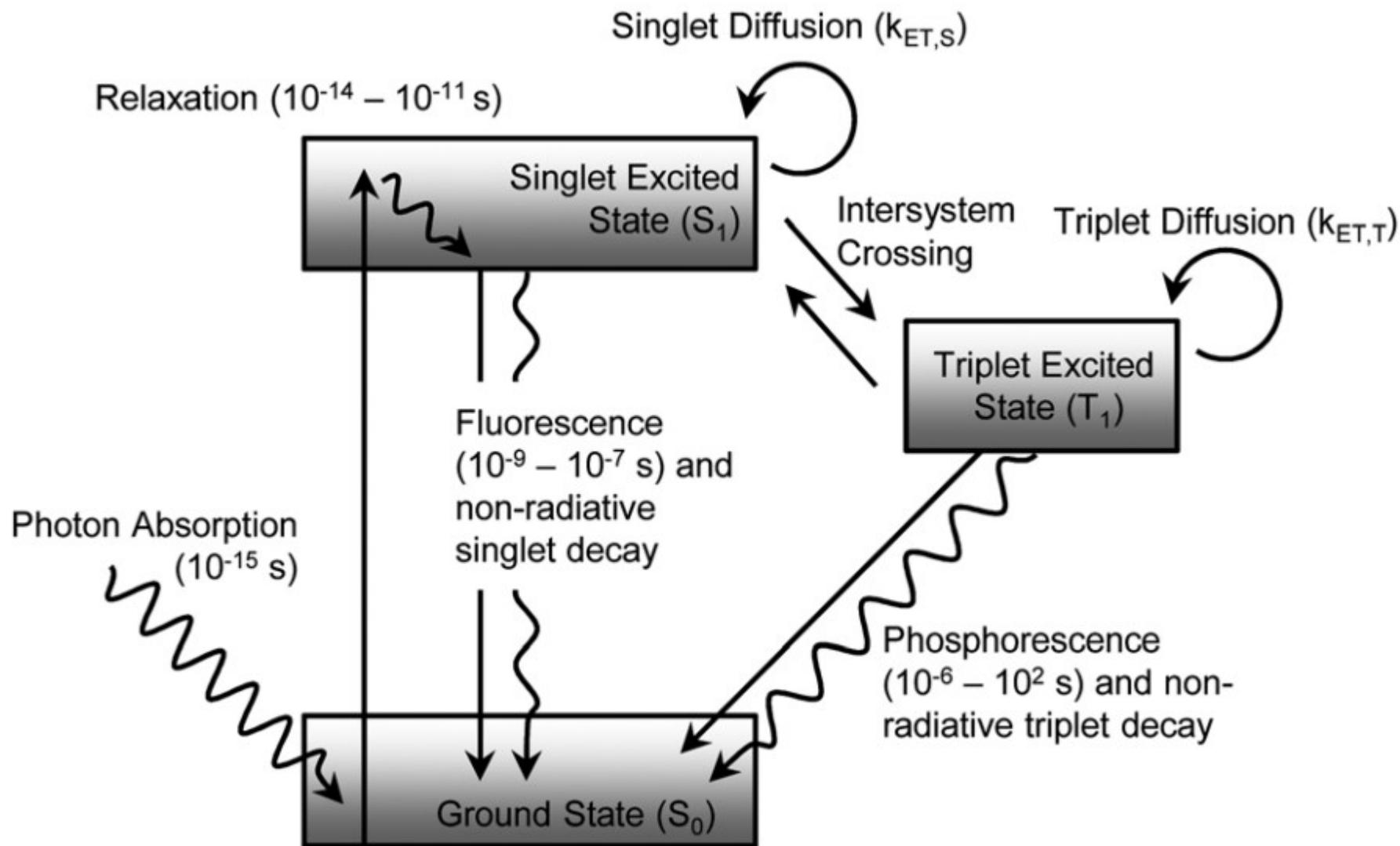
Understanding exciton formation and decay dynamics



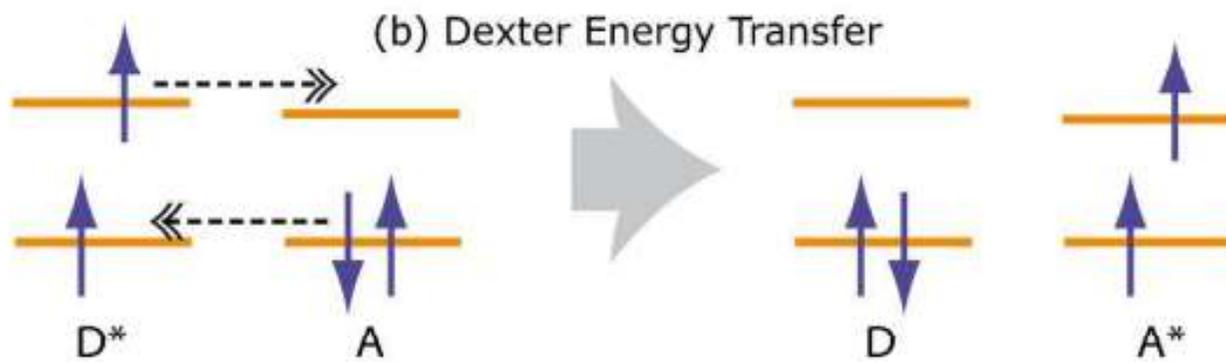
# Singlet Fission



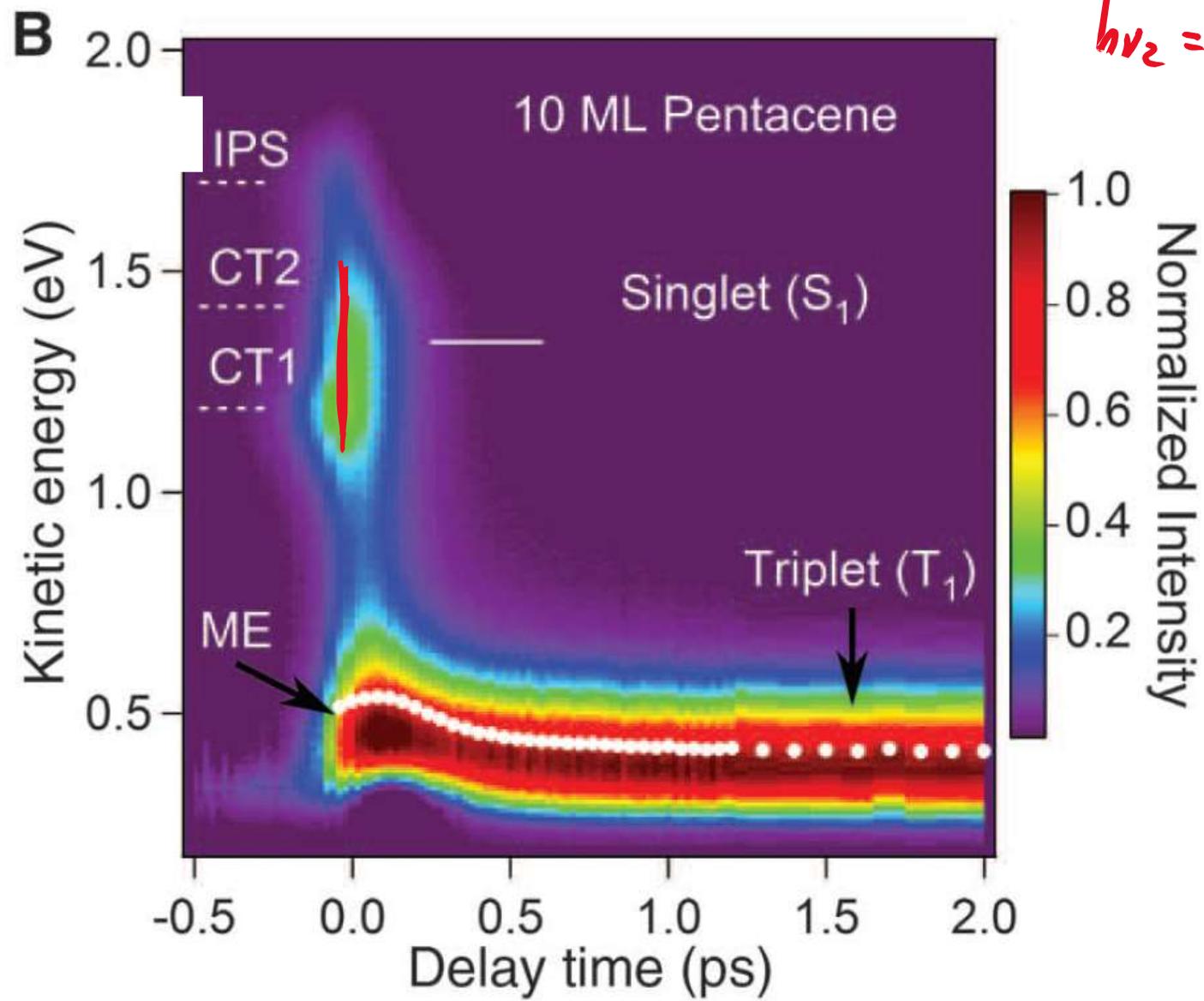
# Jablonski diagram



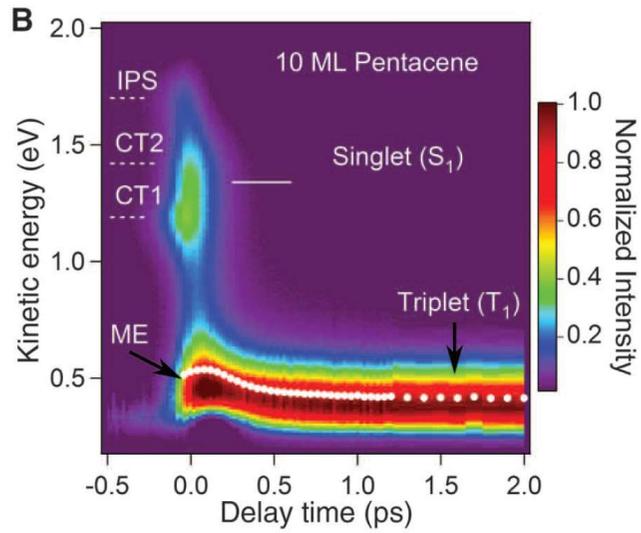
Singletto



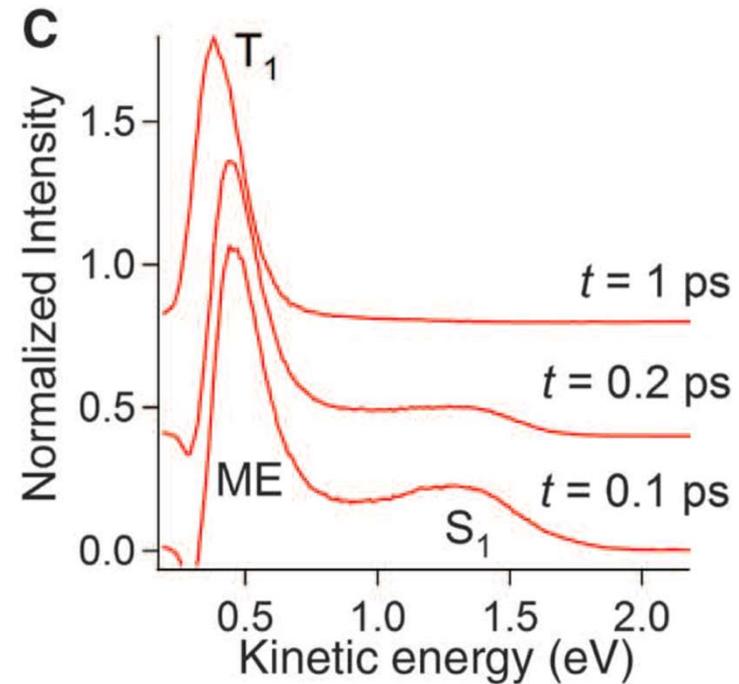
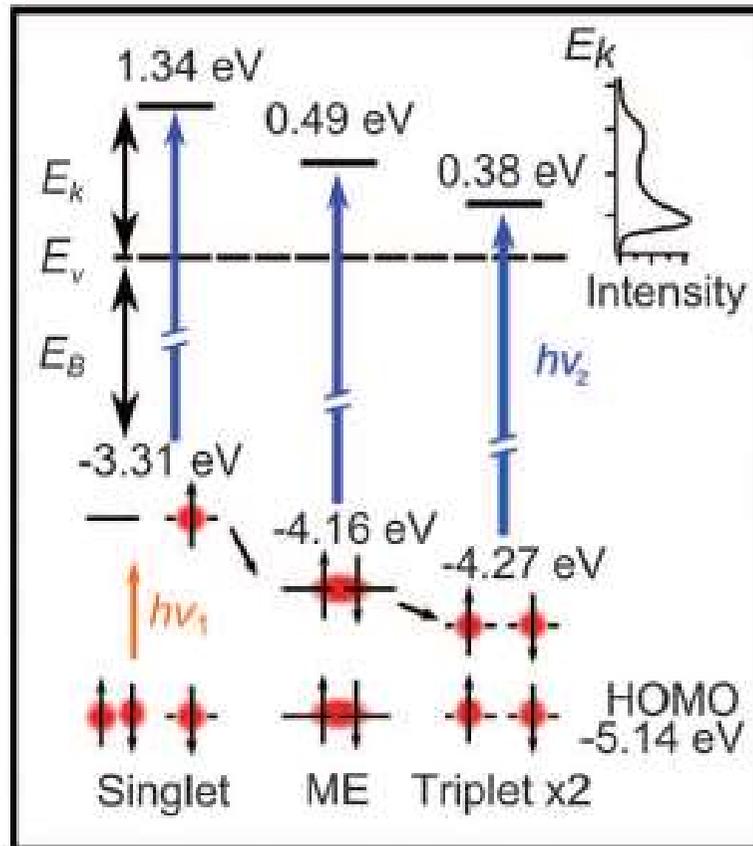
Tripletto

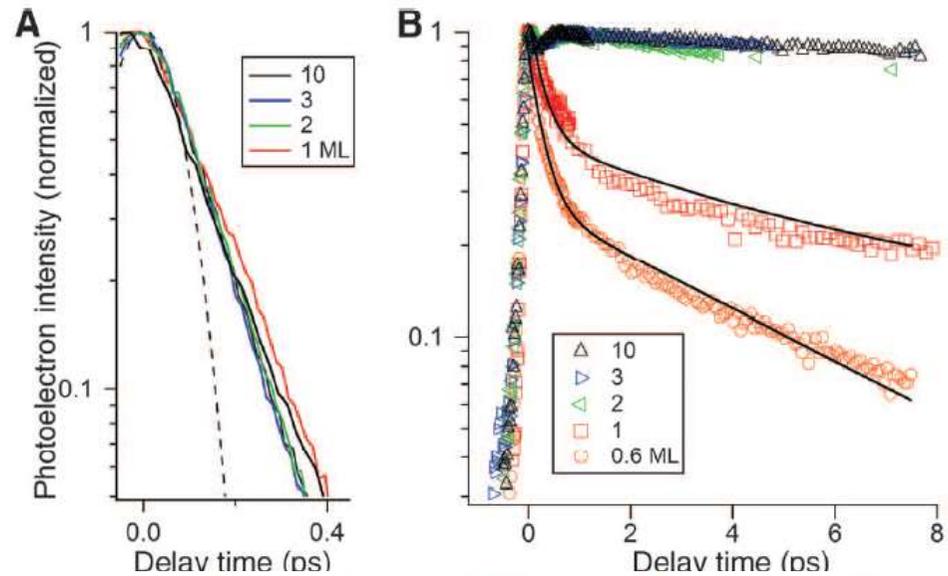
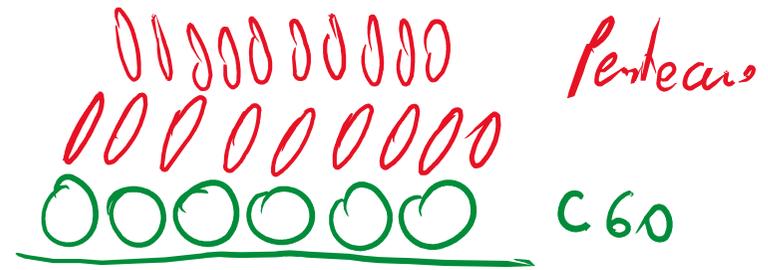
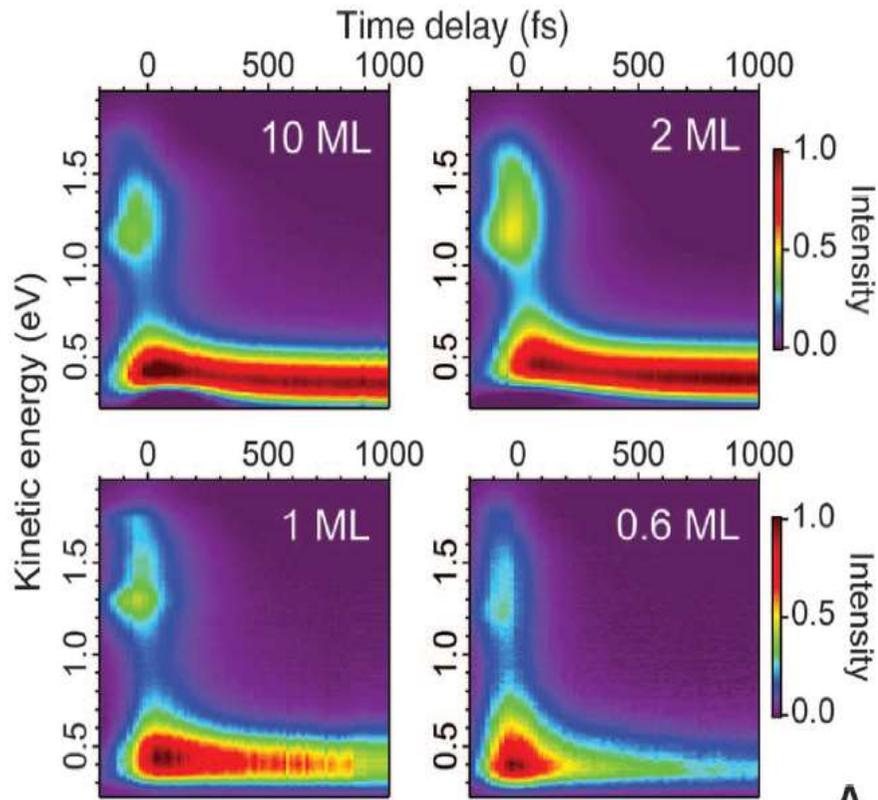


$h\nu_1 = 2.15 \text{ eV}$  (pump)  
 $h\nu_2 = 4.65 \text{ eV}$  (probe)



- ① → risoluzione temporale non permette di stabilire il momento oltre fissare
- ② → Stato correlato  $(S_1 + (T, T_1)^*) = ME$  Multi-excitation

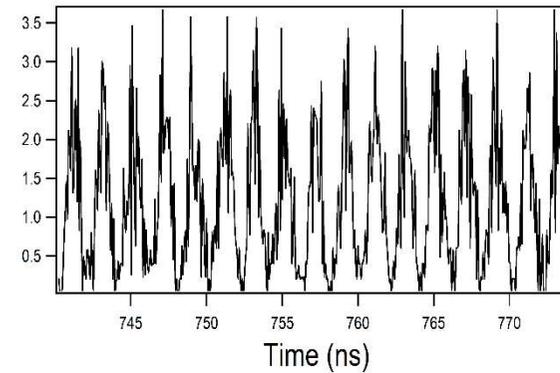
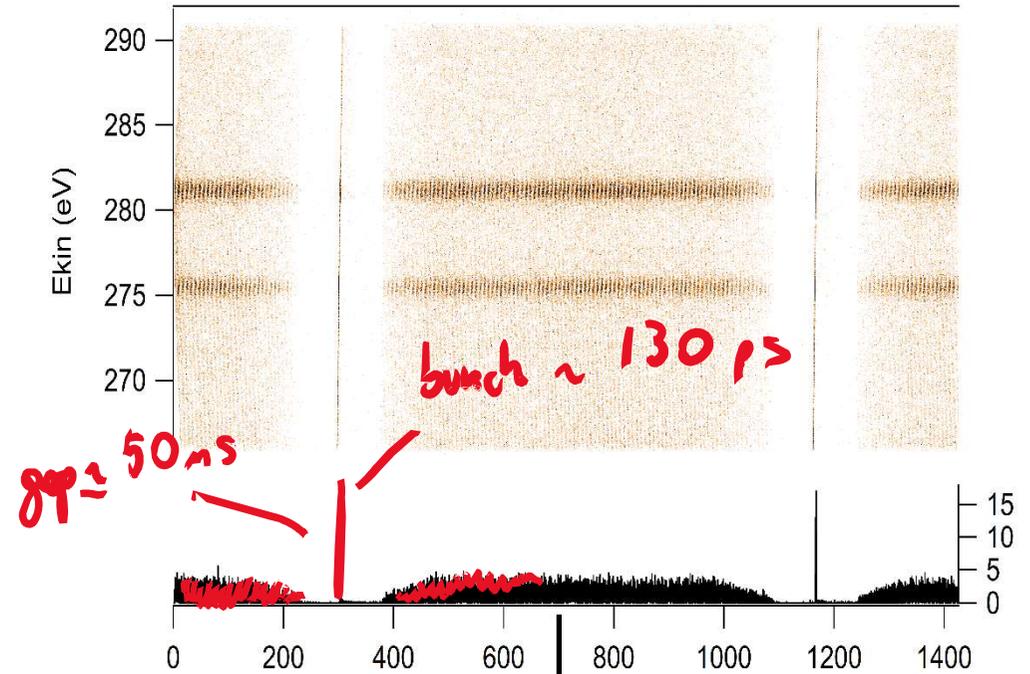
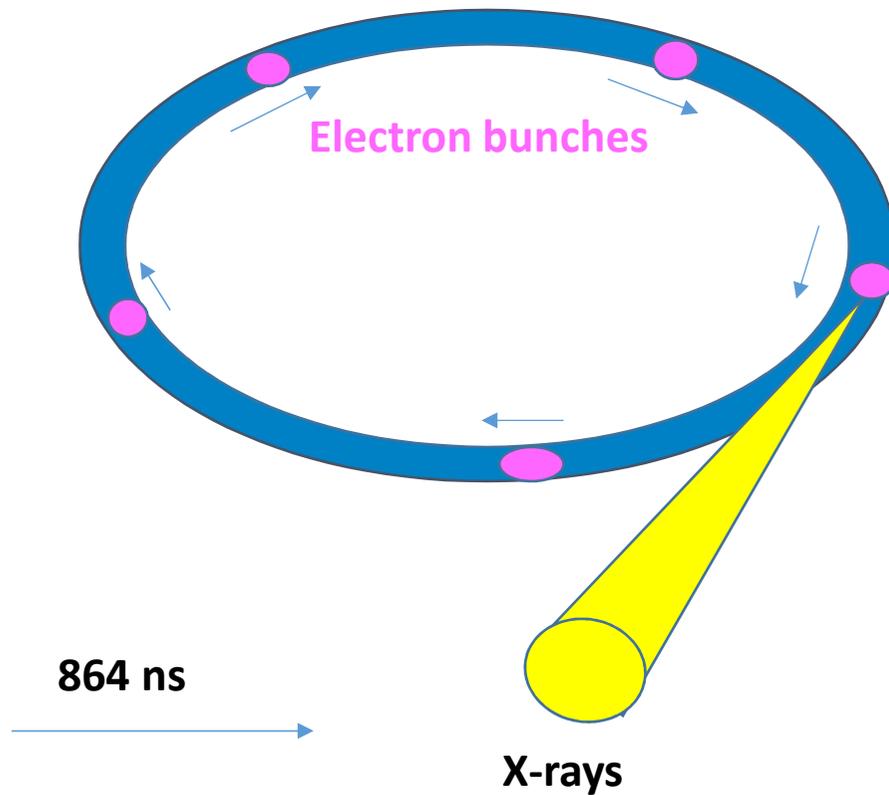




# Synchrotron X-ray pulses

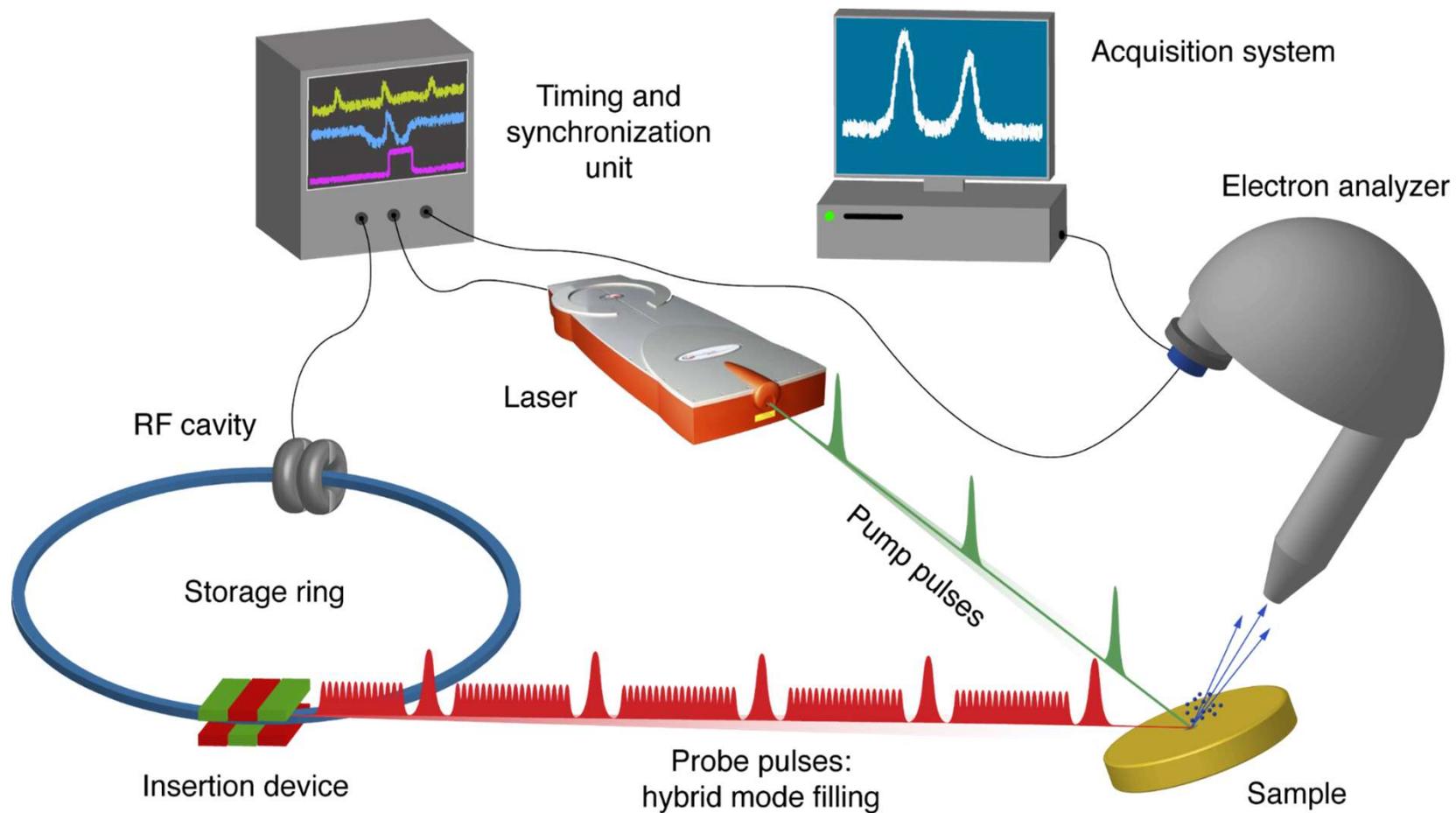
Modello di iniezione ibride

Electron filling pattern



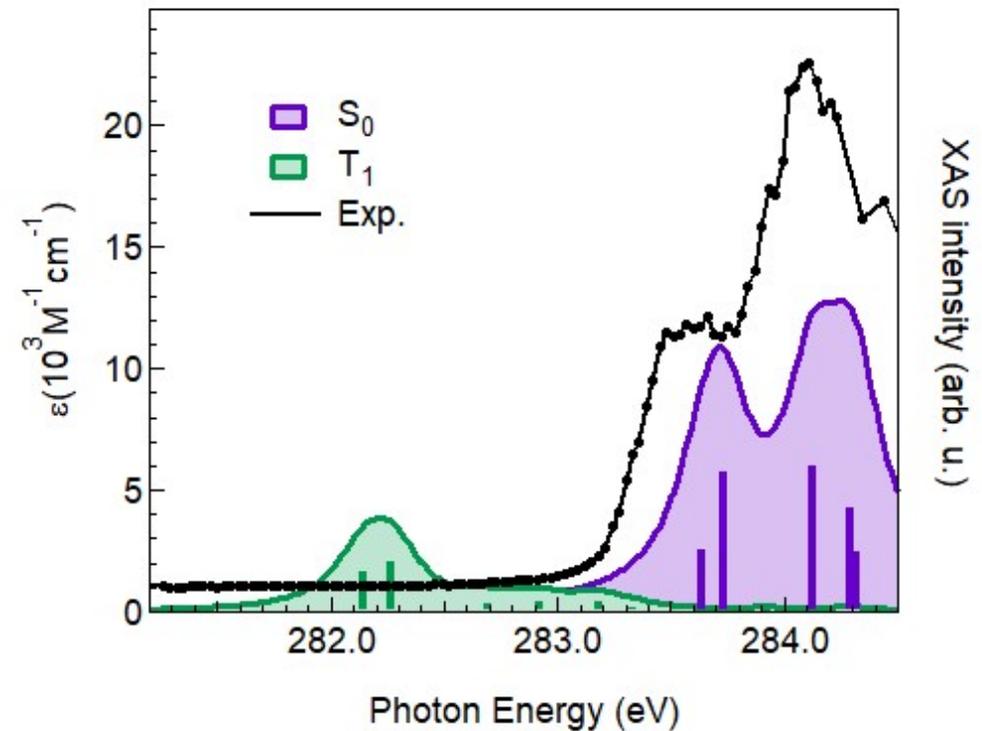
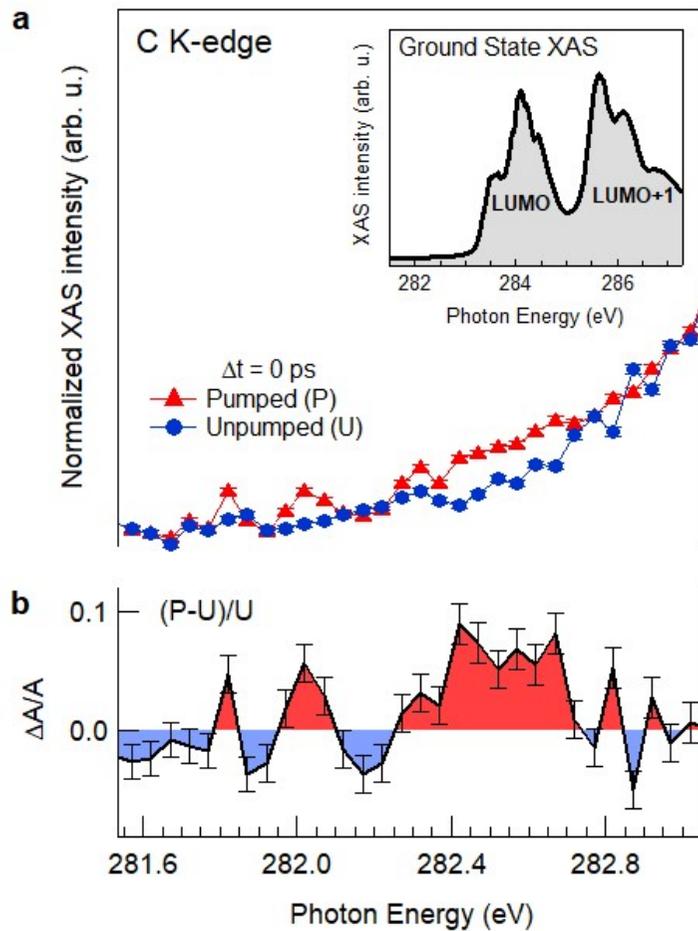
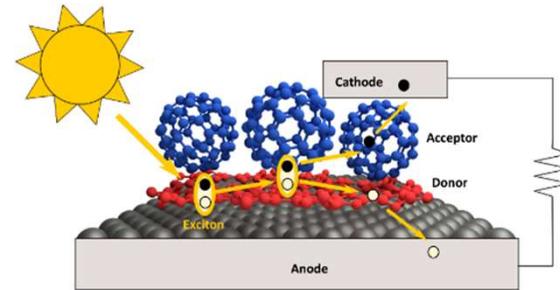
100 ps X-ray pulses

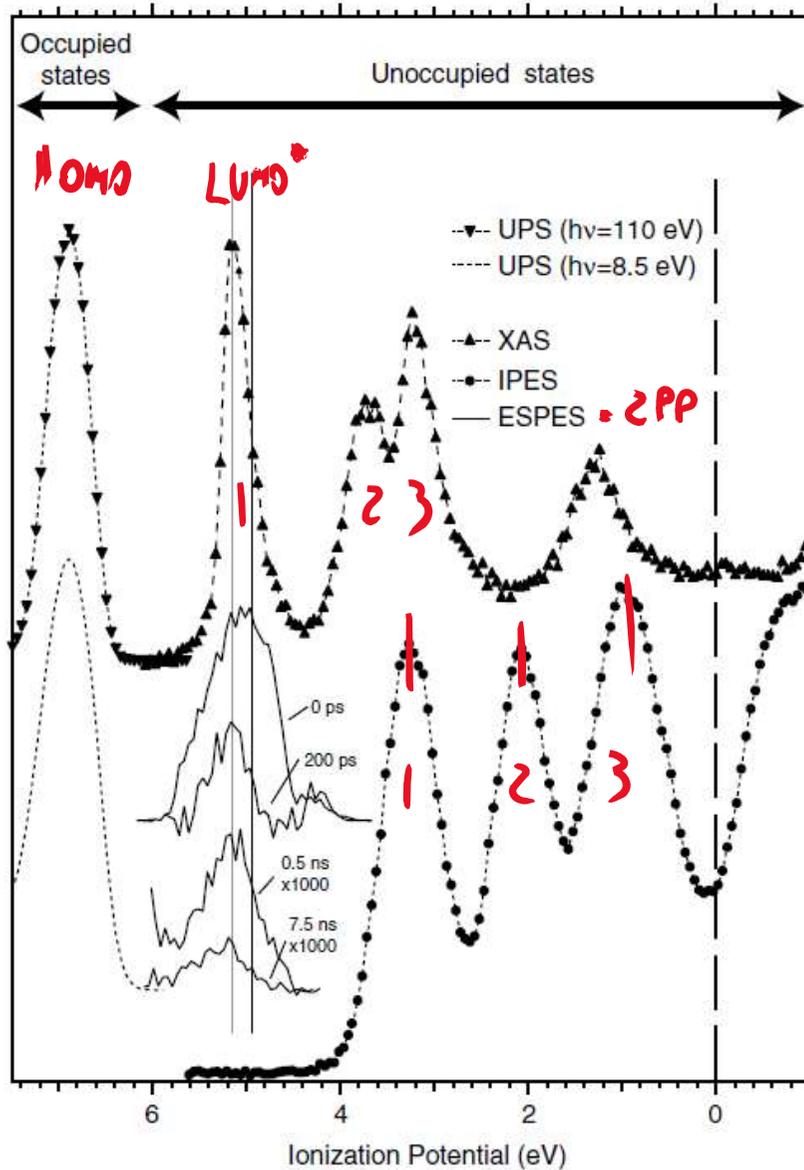
# Experimental Set-Up for Optical Pump-X-ray Probe



# Time resolved XAS

## Triplet picosecond dynamics with chemical sensitivity



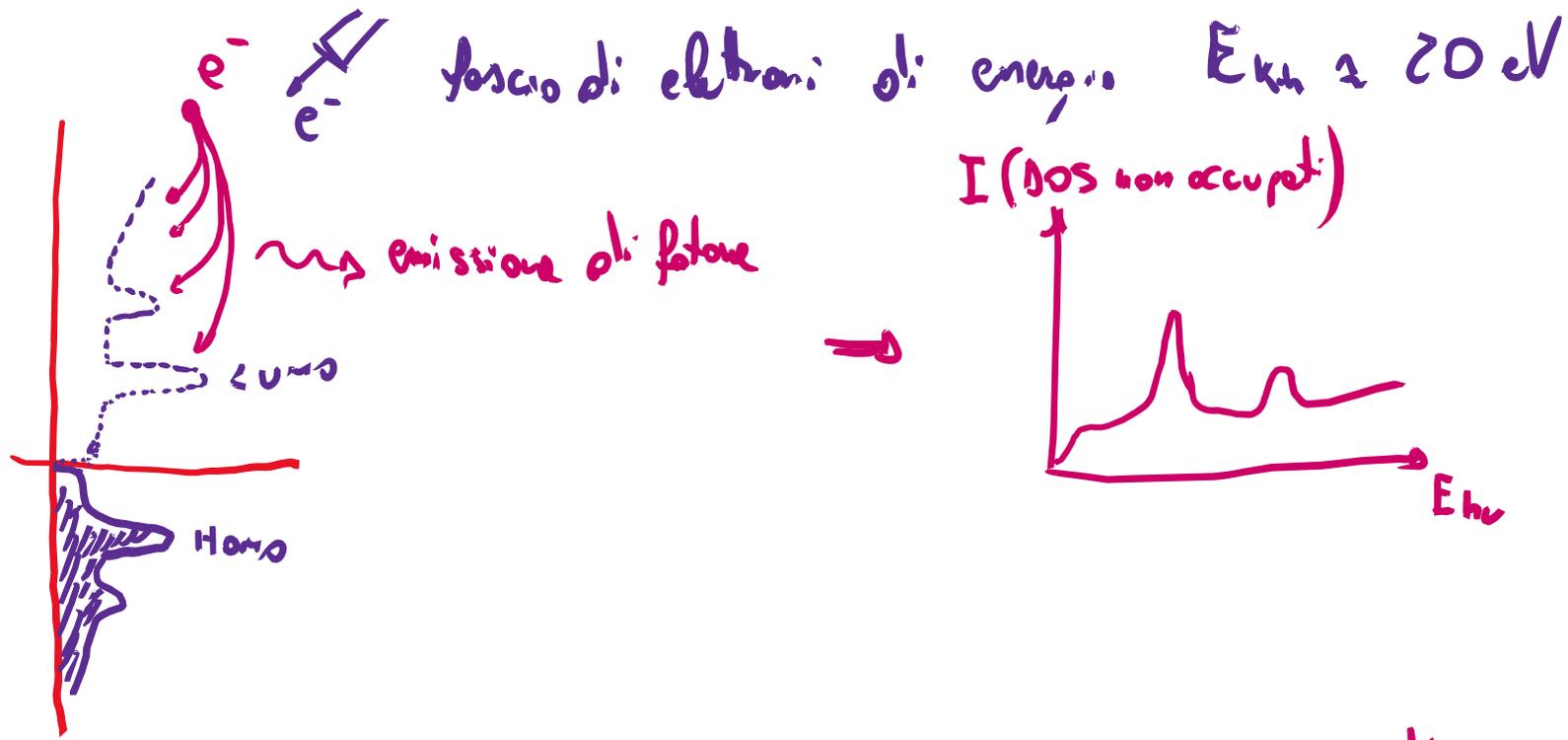


C60: stati occupati/non occupati misurati con diverse tecniche

- NEXAFS e 2PP danno stessa posizione
- IPES indica la posizione di LUMO senza attrazione coulombiana della buca

IPES

Inverse Photo Emission Spectroscopy



DETECTOR di GEIGER-MÜLLER risoluzione  $\approx 0.5 \text{ eV}$

