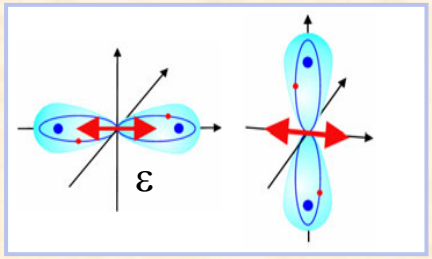
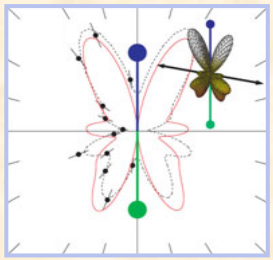
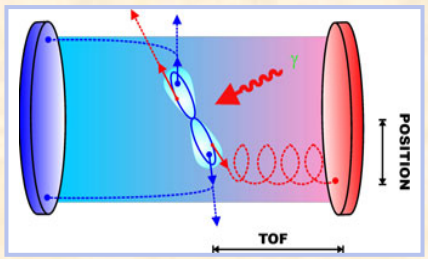
Many Body Problems in Simple Atoms and Molecules

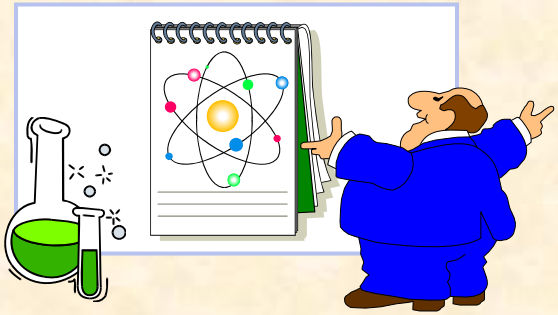
Thorsten Weber

- Chemical Sciences Division -







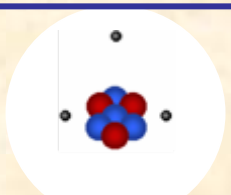


- many particles dynamics: motivation
- photoionization processes: one example
- experimental setup
- projects and ideas

Motivation: Dynamics of Ionization Processes

…correlated motion of electrons in atoms and molecules…

$$|\langle \psi_f | \hat{H} | \phi_i \rangle|^2$$



Motion !?

final state:
- many body problems
- diffraction
- selection rules
- post collision interaction
- symmetries

what?

Mechanism:
- TS1, TS2
- shake-off
- isomerization
- ICD
- recollision, streaking, non-linear effects
- molecular clock
- dichrosim

initial state:
- Hartree Fock
- Multiconfiguration Interaction
- Hylleraas
- Heitler-London
- symmetries, bond length, Compton profile
- correlation/entanglement

Focus: Electrons
- correlated motion = information
- responsible for chemical bond, geometry and atomic properties

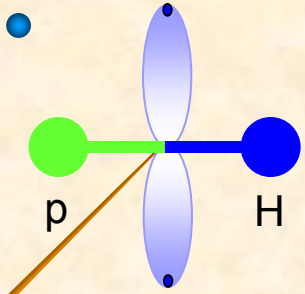
Correlation:
- deviation in ground-state level using independent single particle (Hartree-Fock) approach
- difference between exp. data and theories including many particles interactions (like CCC, 5C…)

Task:
- study the motion of electrons in and in-between atoms and molecules
- learn about mechanisms, selection-rules, symmetry effects, interference, diffraction…
- measure the momentum vectors of electrons and recoil-ions in coincidence

and does that work ?

…one example: Break in symmetry of H_2 molecules…

Born-Oppenheimer



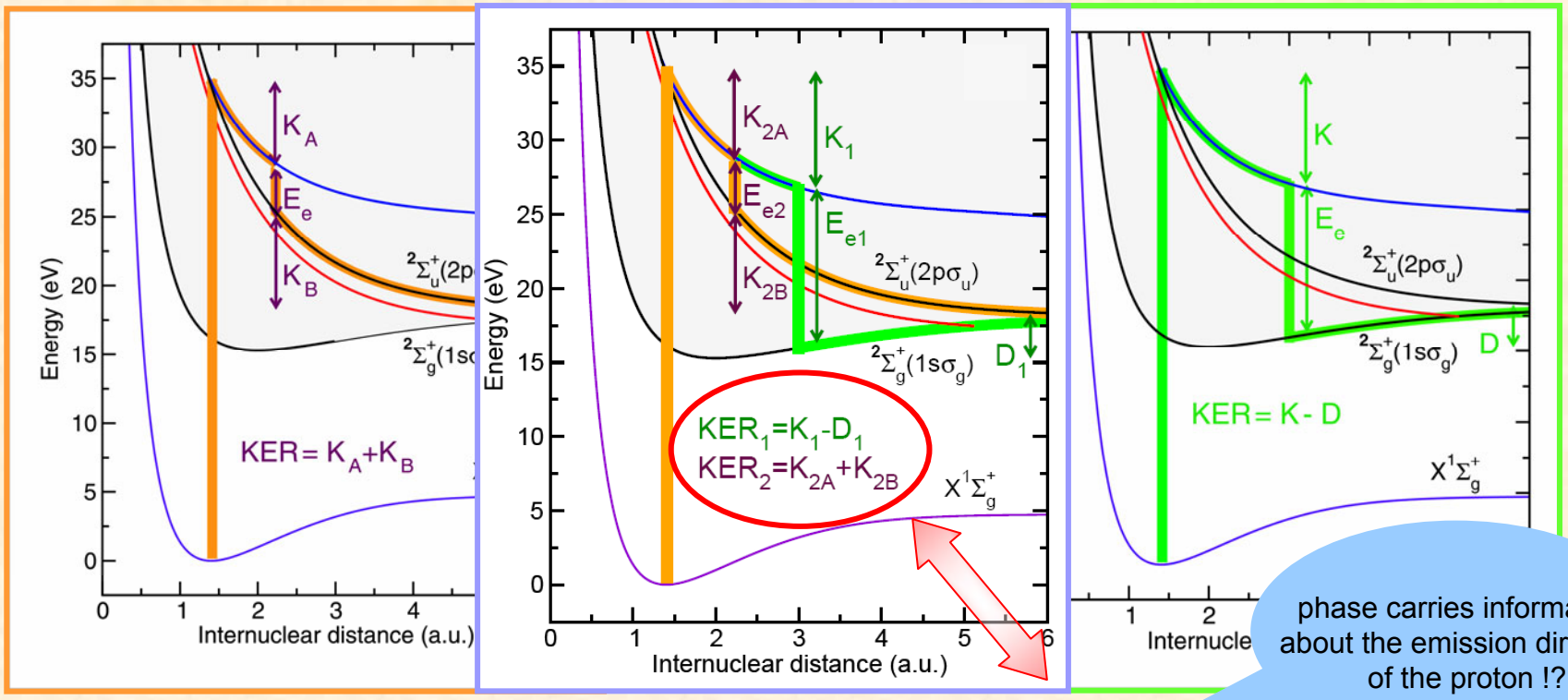
what we expect to see !

Dissociation: $h\nu + H_2 \rightarrow H^+_2 + e^- \rightarrow H + p + e^-$

but

doubly excited states

$h\nu + H_2 \rightarrow H_2(Q_2) \rightarrow H^+_2(2p\sigma_u) + e^-$
$\rightarrow H^+_2(1s\sigma_g) + e^-$

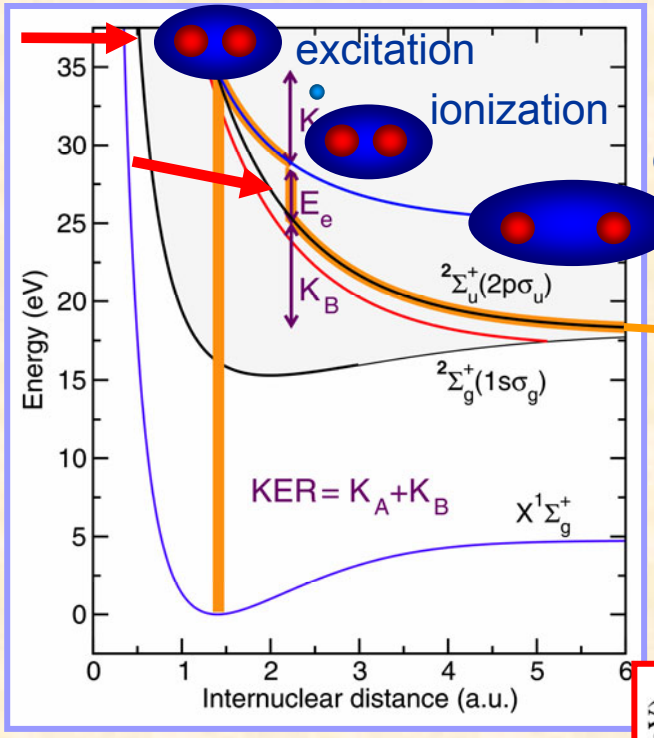


phase carries information about the emission direction of the proton !?

Coherent Sum leads to Interference: $\psi = \Sigma\, a_k \phi_m\, e^{i(\omega t + kx + \delta_m)}$

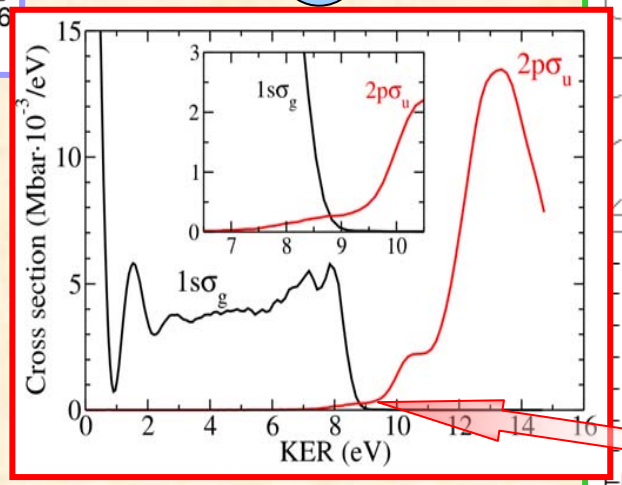
Visualize Molecular Dynamics

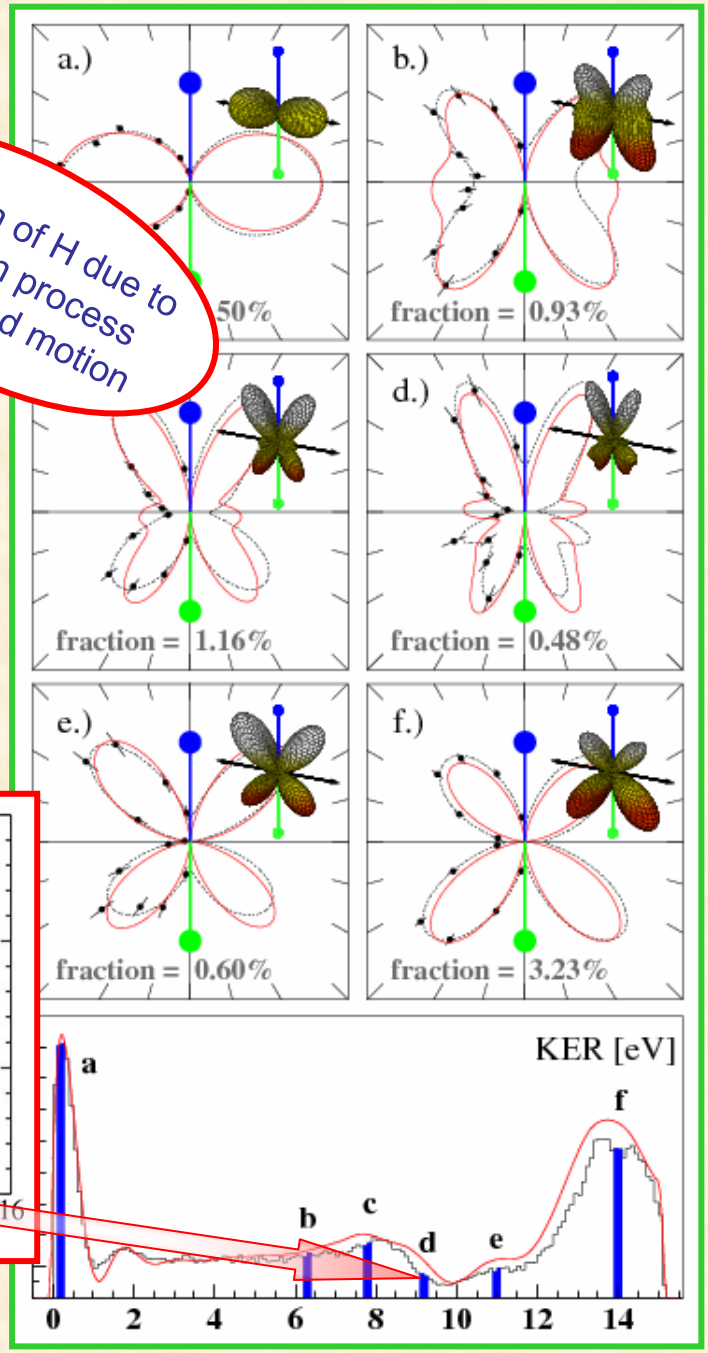
…probing the electron emission angle as a function of the KER…



formation of H due to ionization process = entangled motion

H + p
or
p + H

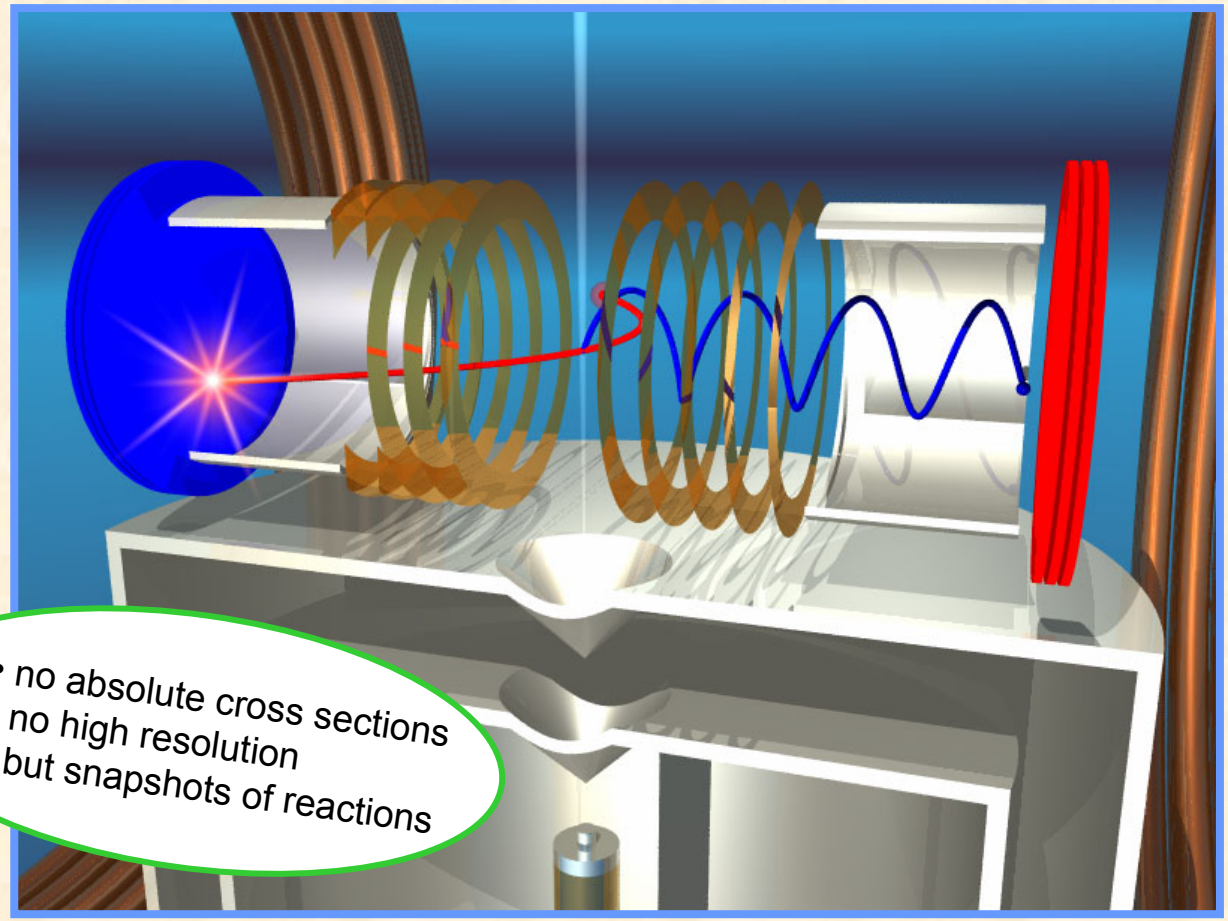




→ nuclei in H^+_2 molecule **<u>are not</u>** indistinguishable anymore

COLTRIMS: A Reaction Microscope for Atoms and Molecules

…measuring the final state momentum vectors…



POSITION

TOF

- no absolute cross sections
- no high resolution
- but snapshots of reactions

features:

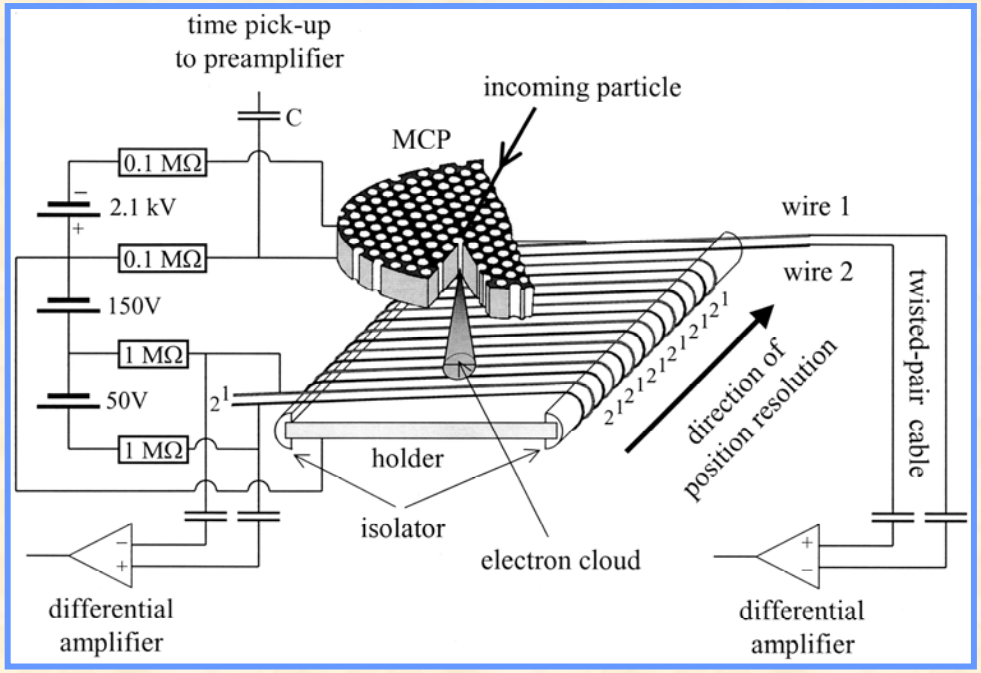
- appropriate resolution (1:10 to 1:20)
- 4π solid angle
- cold target (ground state, n = 0)
- many particle detection (multihit)
- quadruple-coincidence ($2 \cdot e^-$ and $2 \cdot p$)
- e^- : 0 – 300 eV
  ion: 5 meV – 15 eV
- angular distributions in body fixed frames

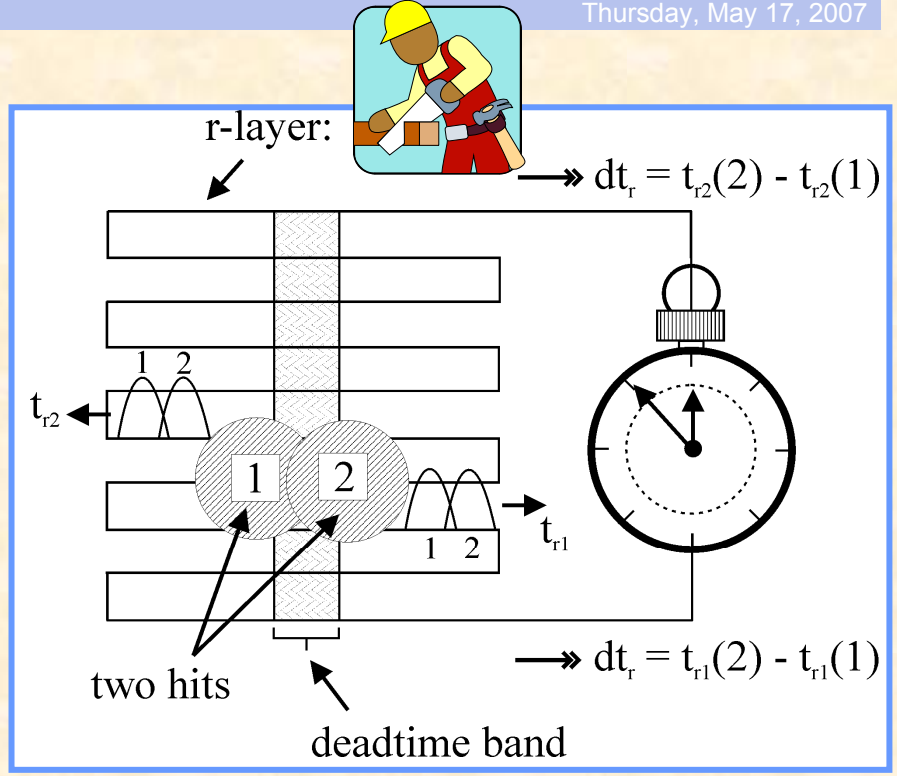
how?

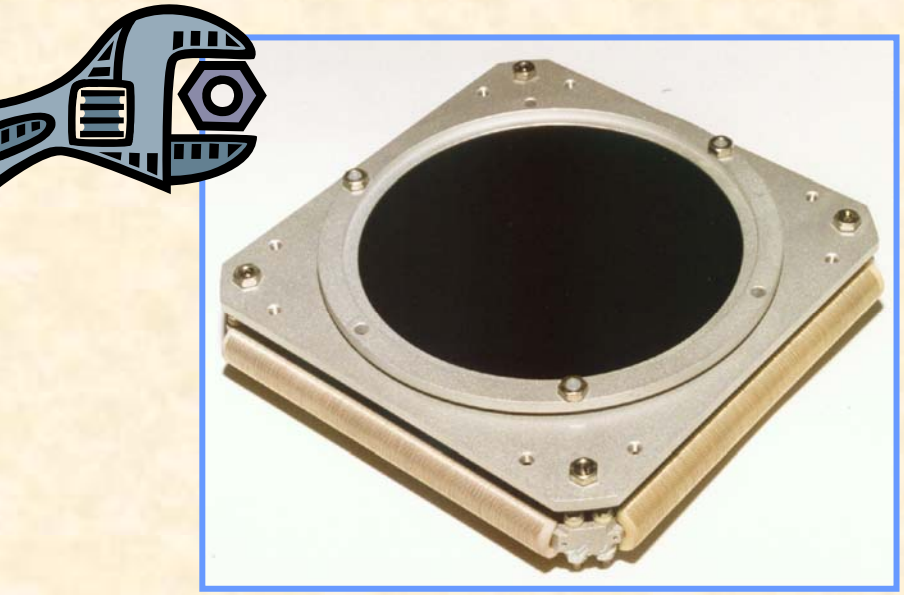
electric field

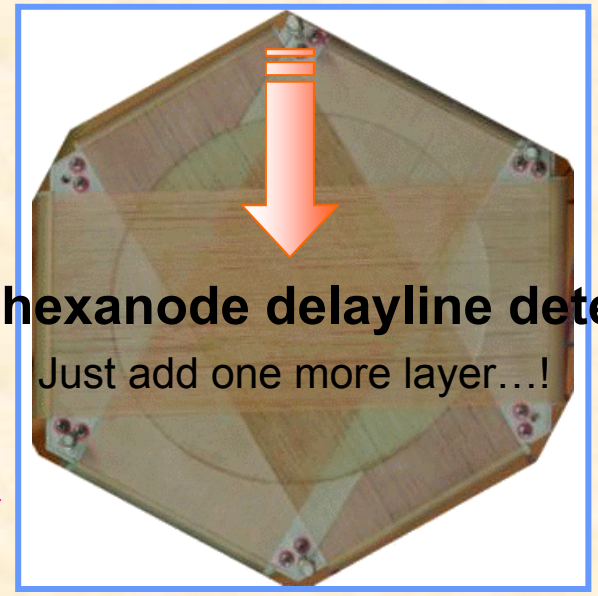
magnetic field

Some more Tools: The detectors…









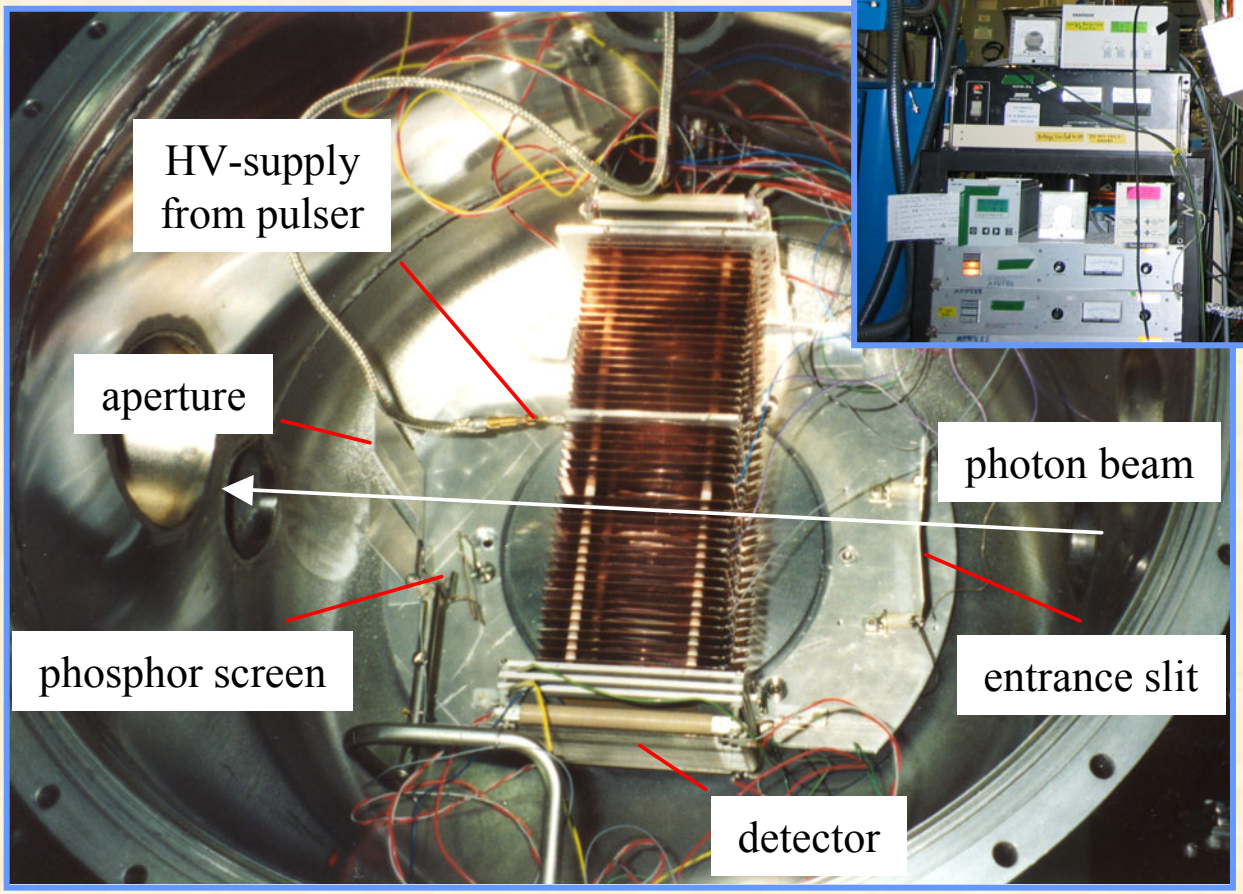
…the hexanode delayline detector:

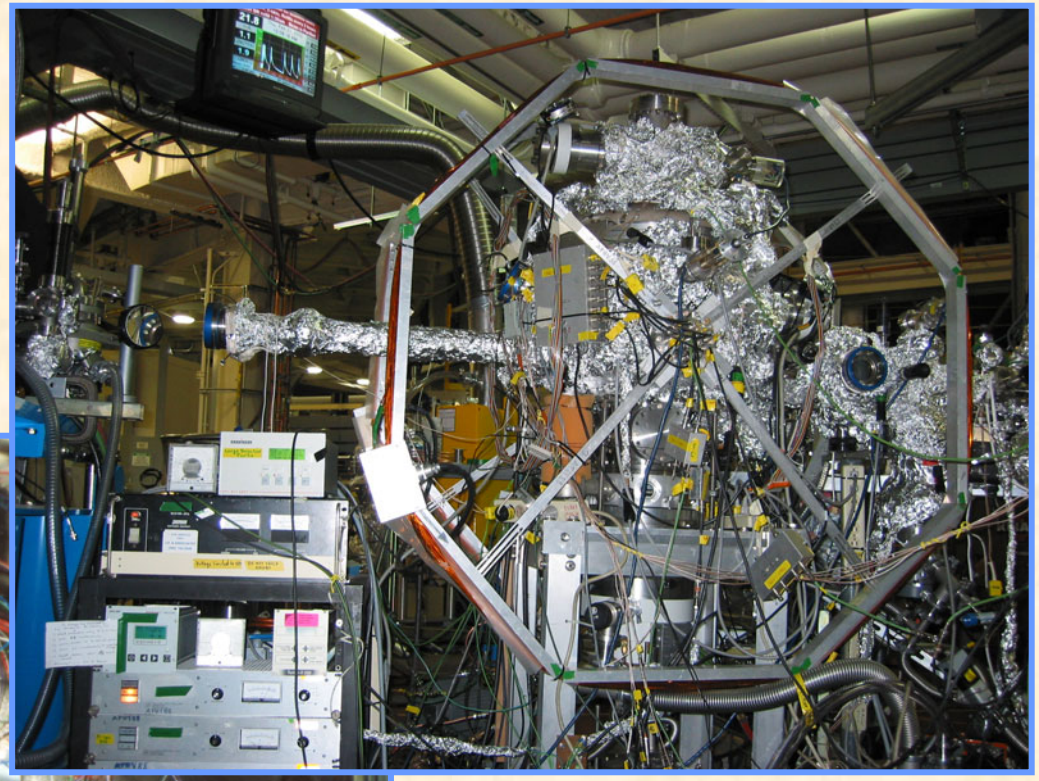
Just add one more layer…!

The Set-Up in Reality

…see some photographs…

inside the vacuum chamber





where?

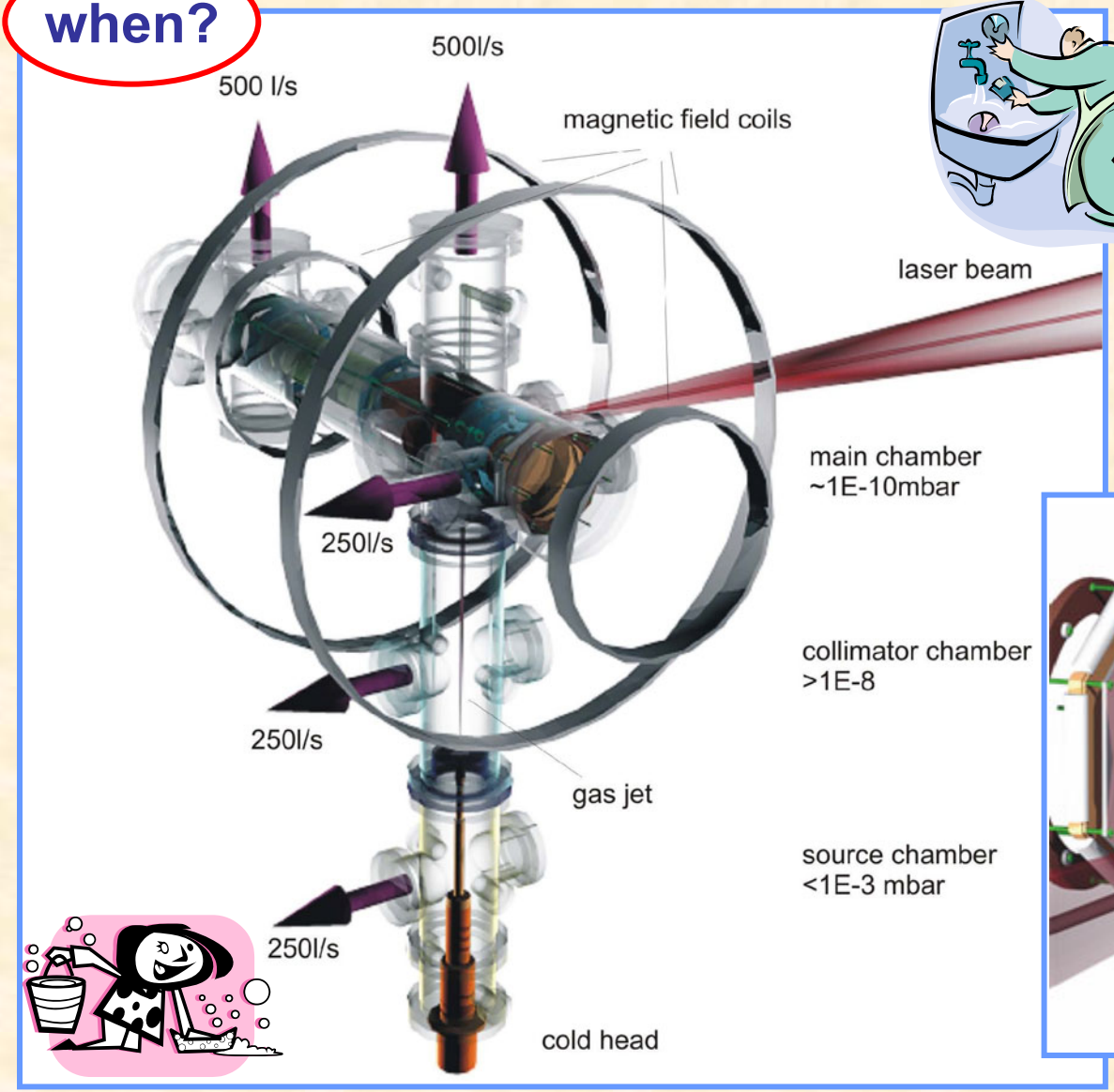
the chamber @ BL 4.0
of the ALS-Berkeley

UHV-COLTRIMS: A new Setup…

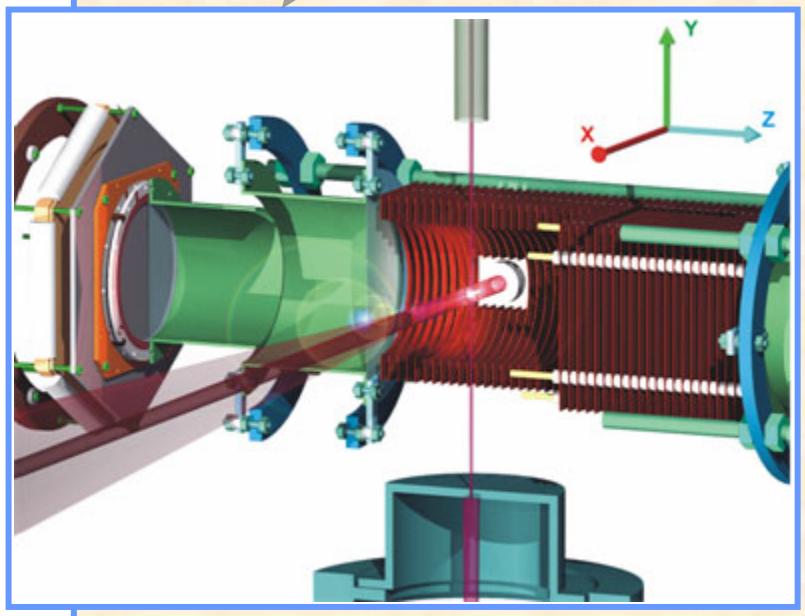
Femto Second Laser pulses, High Harmonics and Sliced Photon Beams

NEW

when?



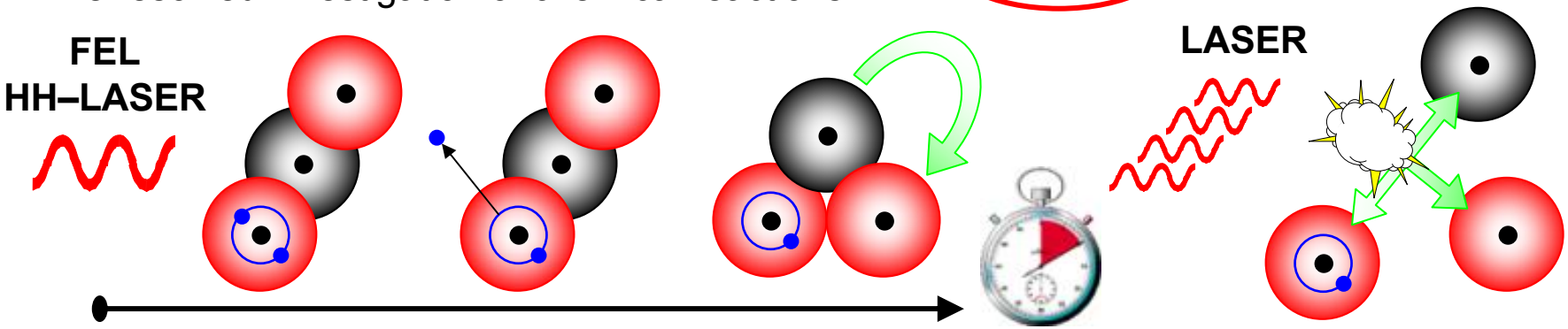
- < 1E-10mbar
- collimated gas jet
- pre-cooled target
- hex detector
- quickly changeable



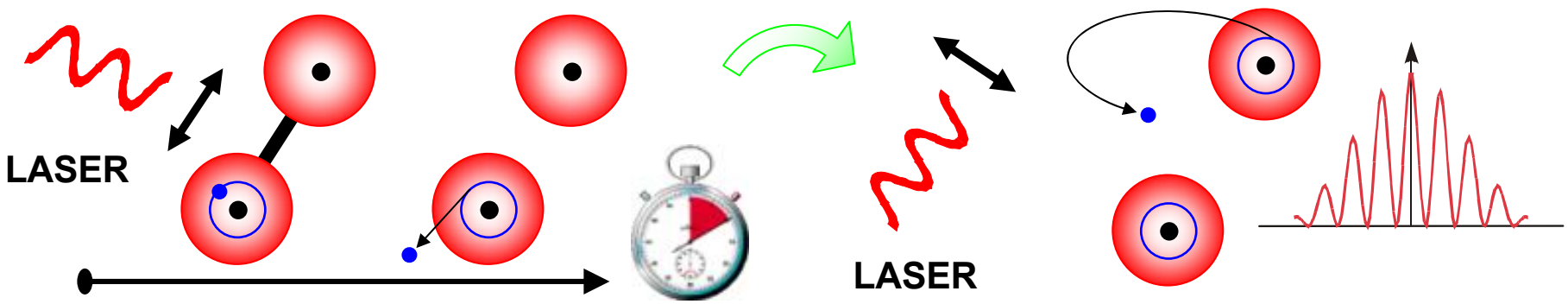
Where is the journey going ?

why?

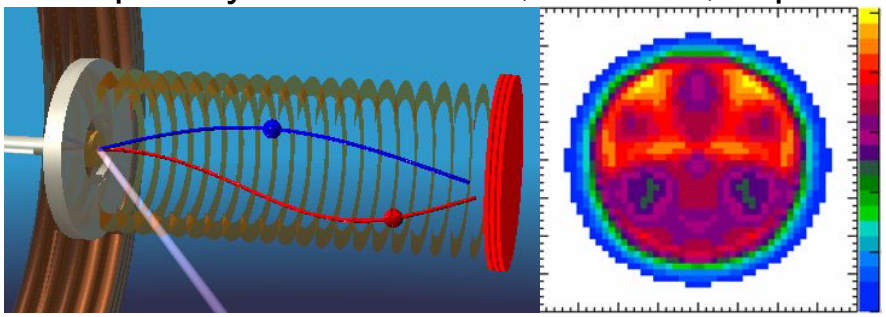
Time resolved investigation of chemical reactions:

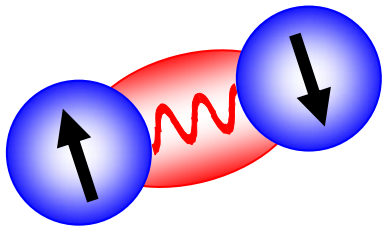


Laser Induced Electron Diffraction of H_2:

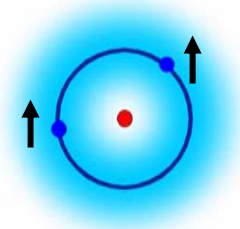


Complex systems: Cluster, surfaces, superconductors, spin polarized He





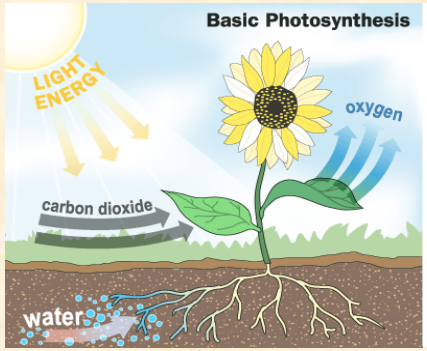
Cooper pairs



He (↑,↑)

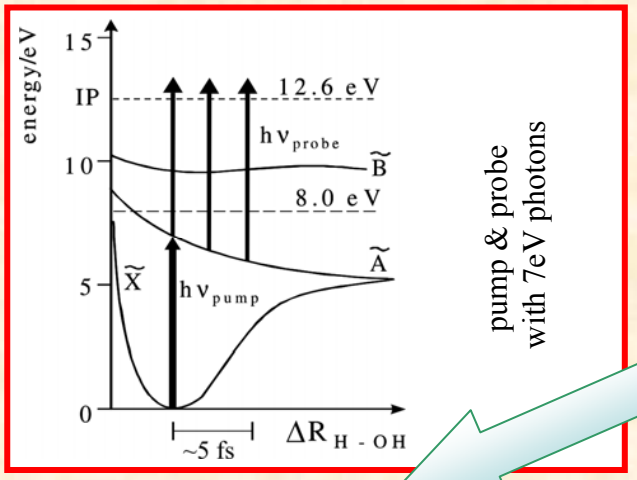
bio molecules

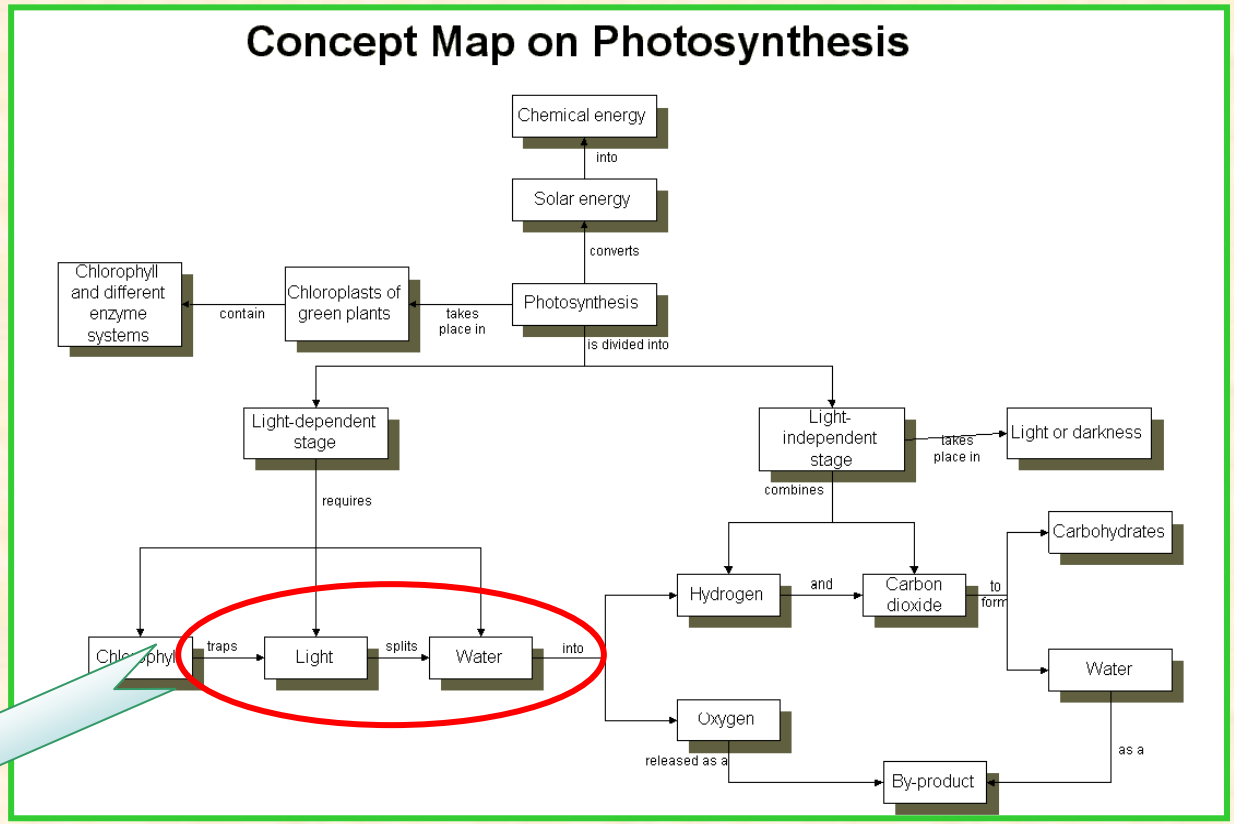
Investigating the Dynamics of single Water Molecules in the Radiolysis



Sunlight drives chemistry

- efficient
- fast
- fundamental process





Radiolysis of Water: Control of Carrier Envelope Phase of the Laser Pulse

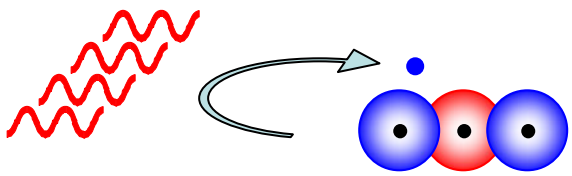
a.) Photoionization $H_20 \rightarrow H_20^+ + e^-$

b.) Protolysis $H_20^+ \rightarrow H^+ + OH'$

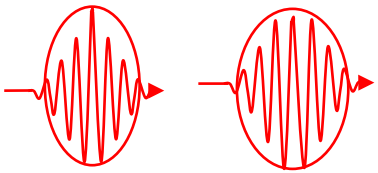
c.) Hydration $2e^-_{aq} + 2H_2O \rightarrow H_2 + 20H^-$

$OH' + OH' \rightarrow H_20_2$

LASER



photosynthesis
radiation damage

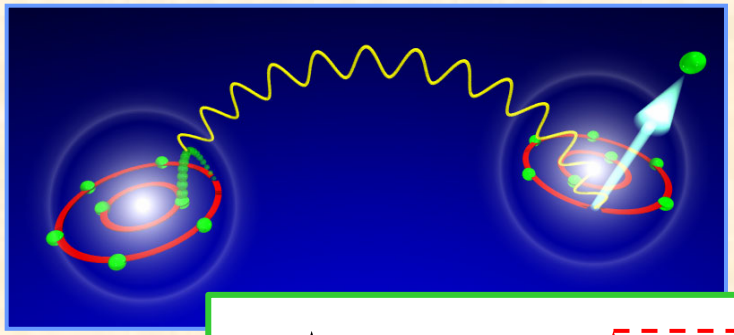


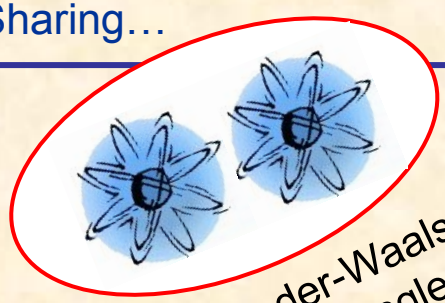
- number of returns
- electron energy
- molecular orientation

Correlation in weakly bound Systems: ICD in Ne-Dimers

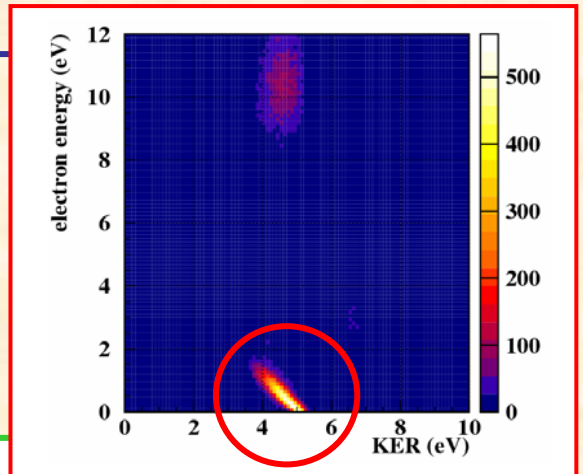
…Potential Curves and Energy Sharing…

Interatomic Coulombic Decay:

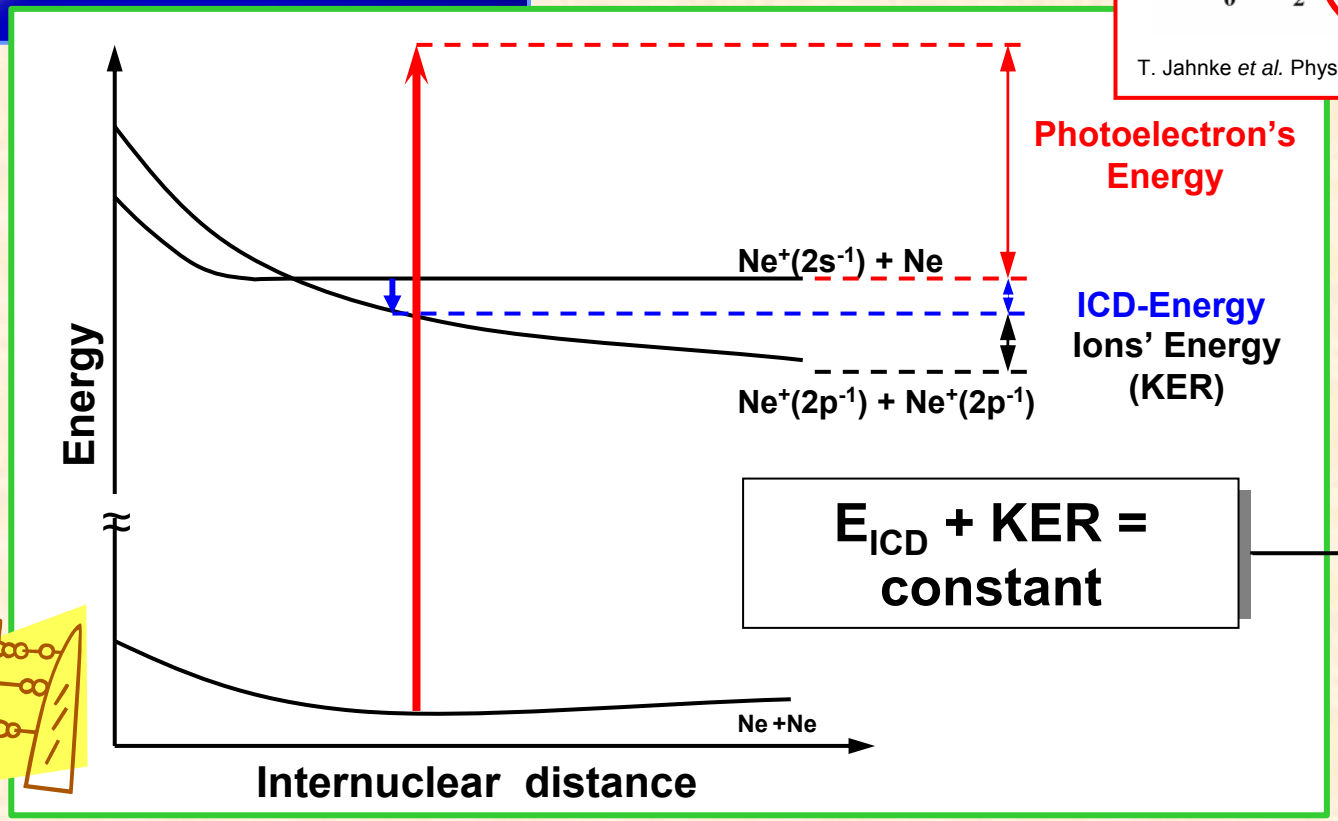




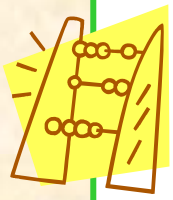
Van-der-Waals bond ↔ entanglement

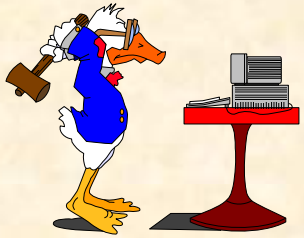


T. Jahnke *et al.* Phys. Rev. Lett., **93**:163401, 2004.



$$E_{ICD} + KER = \text{constant}$$

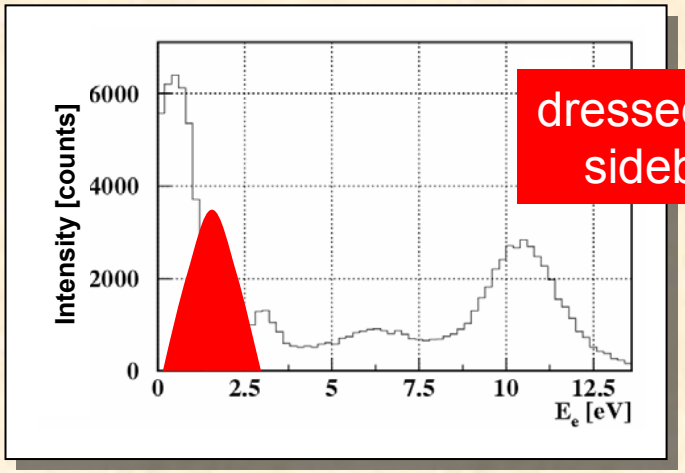




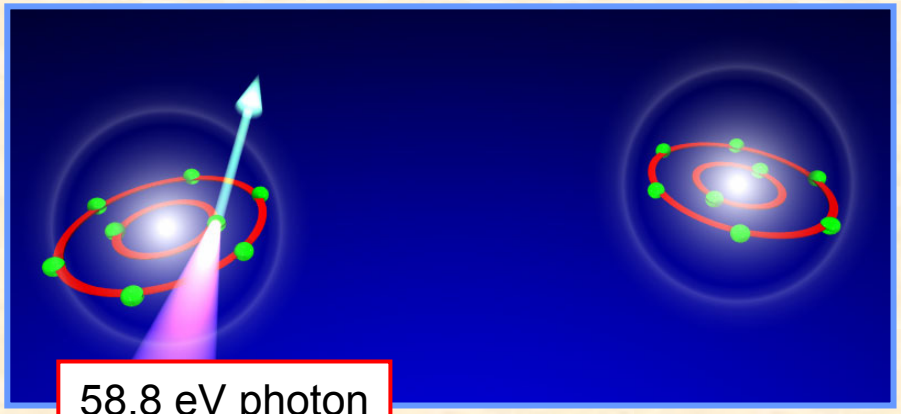
Pump & Probe on fsec Time Scales

time resolved ICD of Ne dimers:

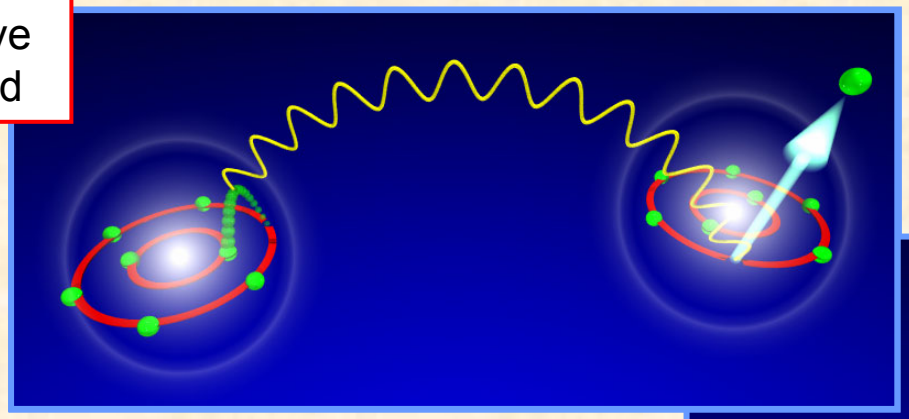
…an ideal test bed…



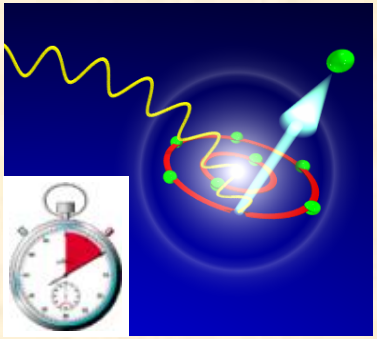
Step 1: 2s-Ionization of the Dimer



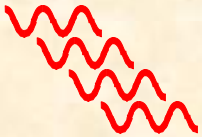
58.8 eV photon
~10 eV above
2s-threshold



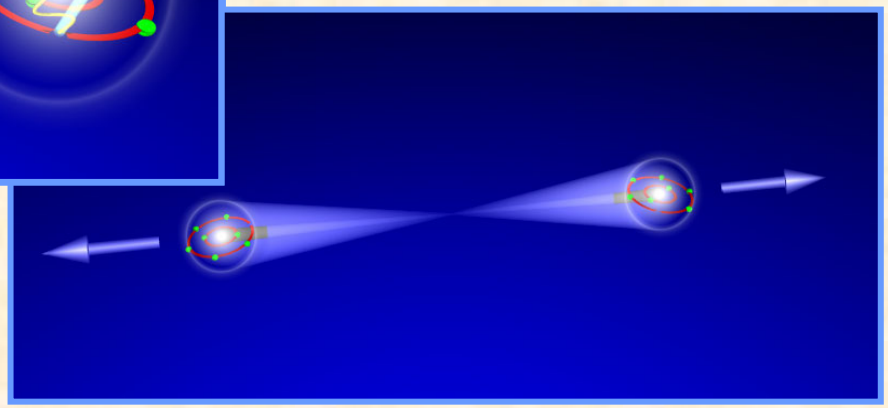
Step 2: Interatomic Coulombic Decay



LASER



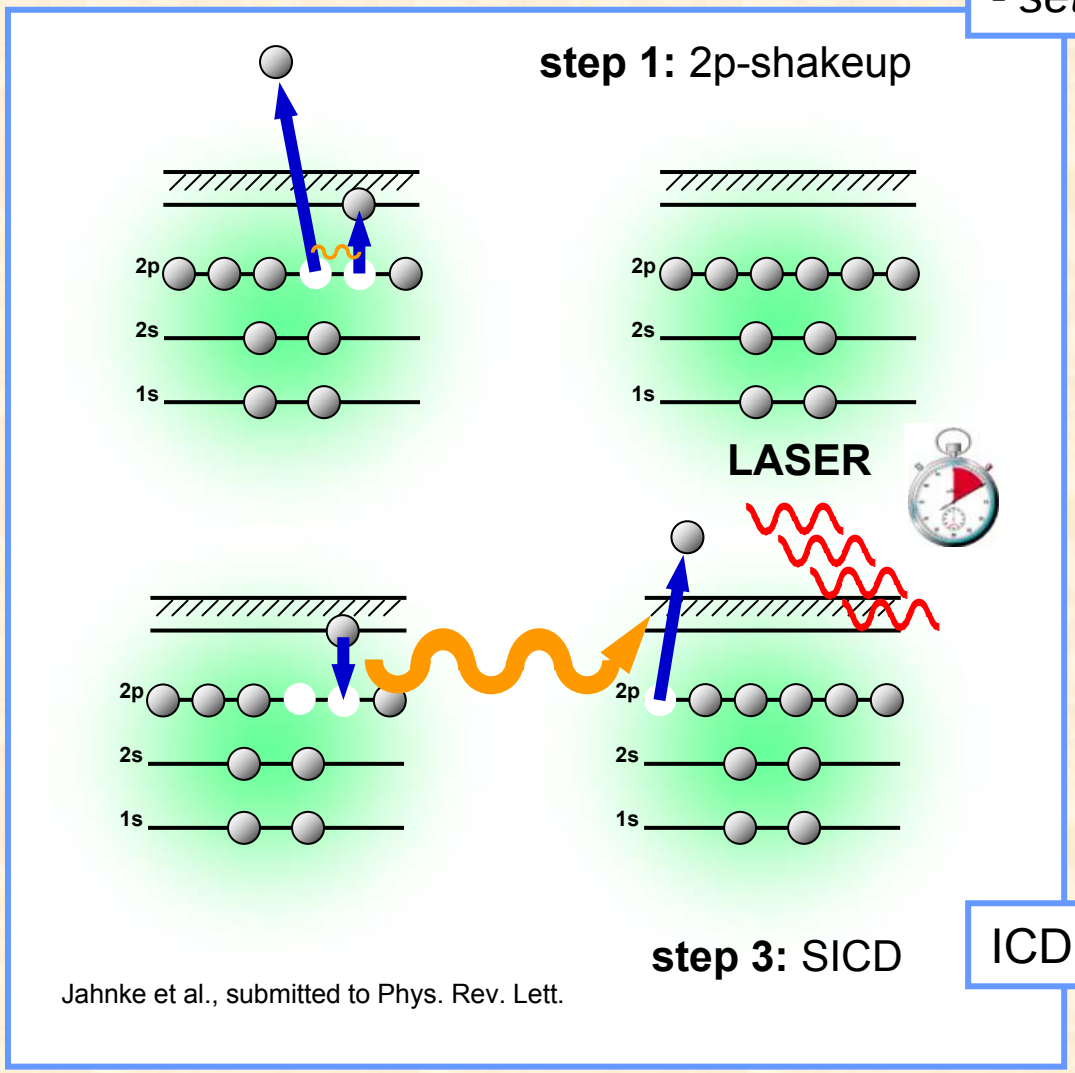
Step 3: Coulomb-Explosion



An even slower Pump & Probe experiment on the fsec time range

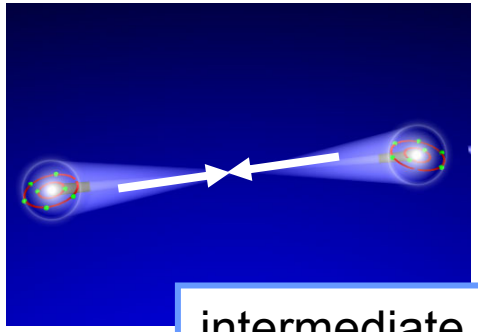
…shake-up induced ICD of Ne dimers…

ionize + excite Ne-atom
- sets time zero for ICD



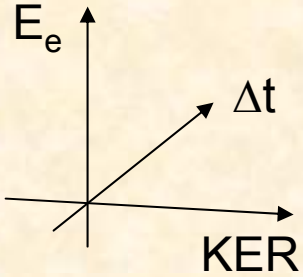
Jahnke et al., submitted to Phys. Rev. Lett.

step 2: distance shortens



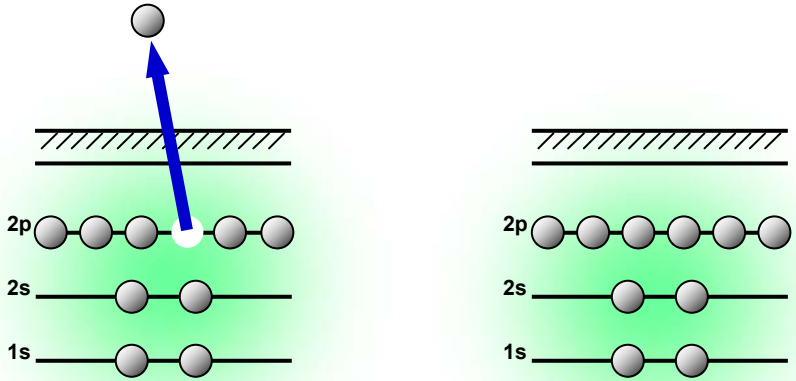
intermediate state
- dynamical process

ICD happens

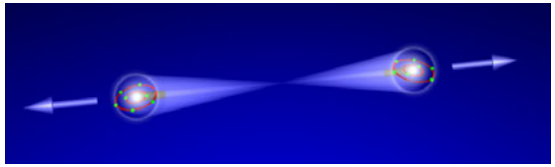


Look for laser dressed states of the electron as a function of time delay Δt

One more on pump and probe of Ne dimers



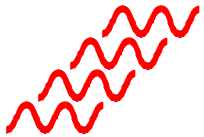
step 1: 2p-ionization with 22 eV

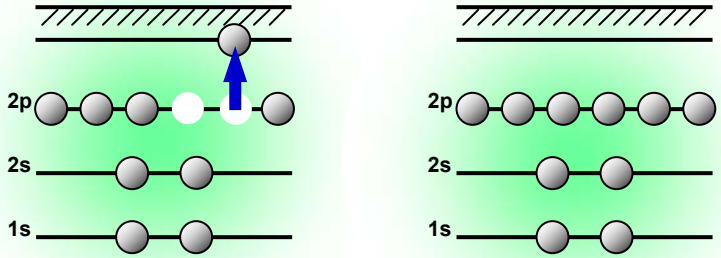


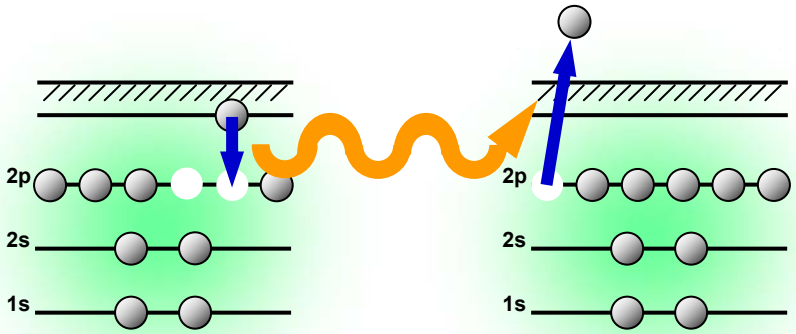
dissociation starts

step 2: excite 2p with ~30 eV

LASER





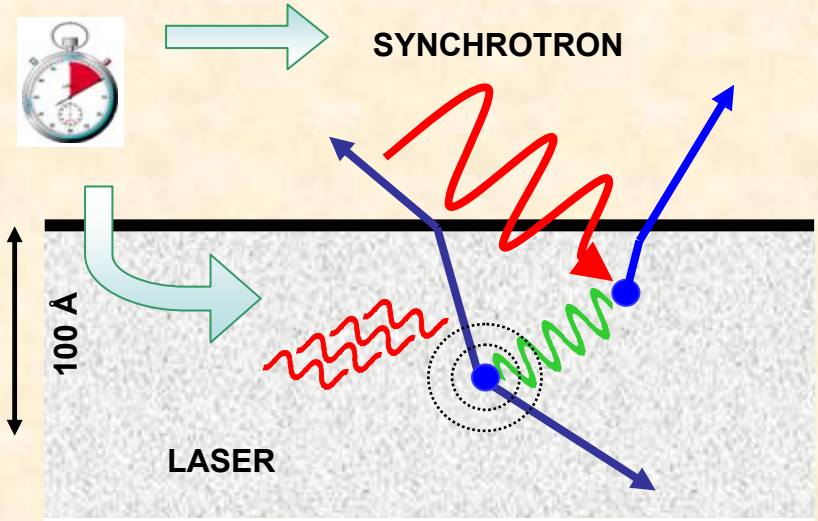


- real pump & probe !
- long time range

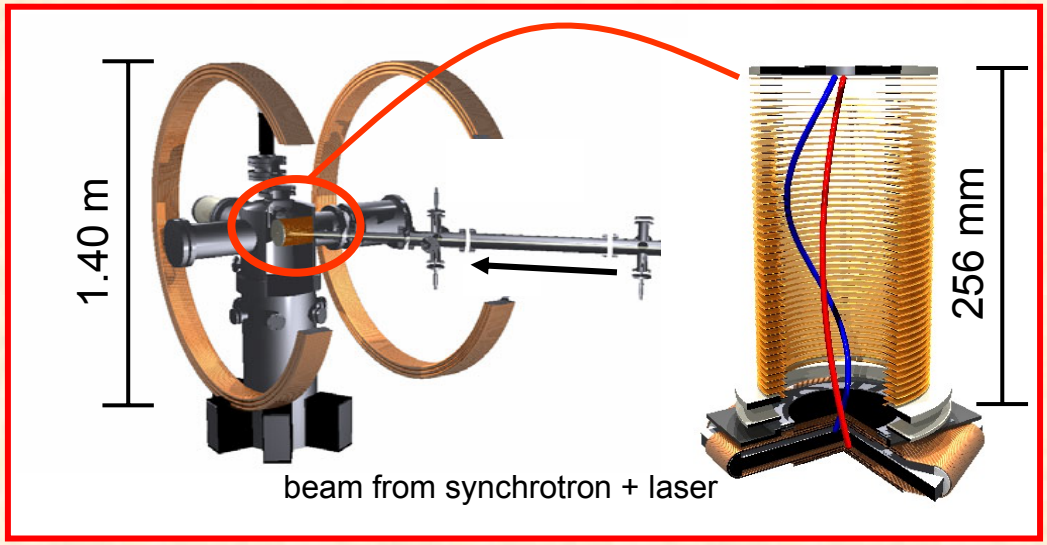
step 3: SICD

Photo Ionization of Solid States at the Ultrafast X-ray Beamline:

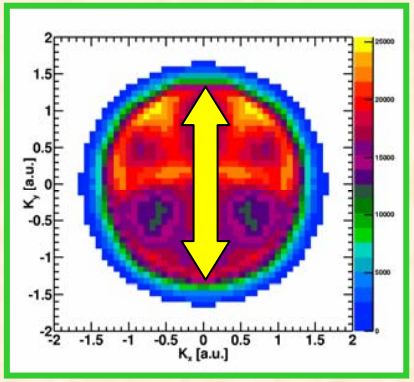
…pump-and-probe experiment



exciting/ionizing & probing delocalized states



polarization vector



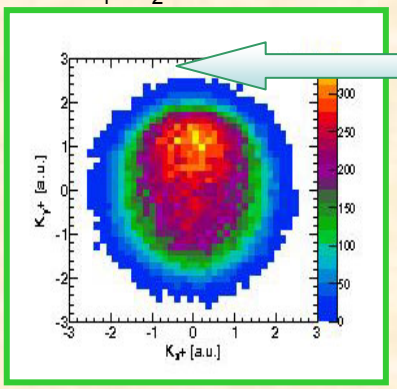
Energy Correlation Diagram

Jacobi Coordinates: Sum-Momentum

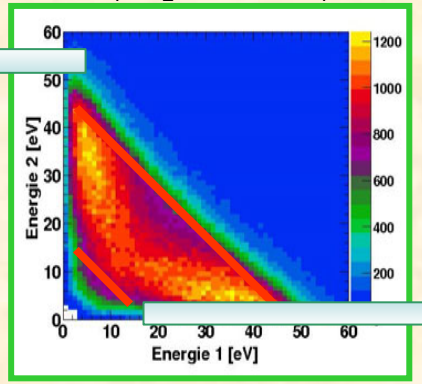
$K_+ = k_1 + k_2$

Electrons carry information about primary process

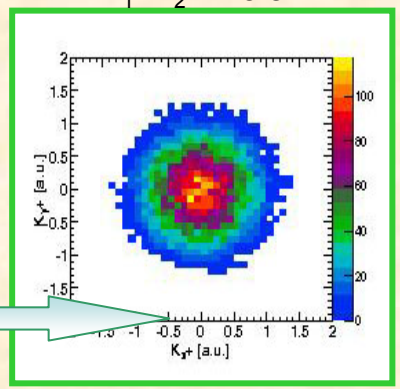
E_1+E_2 = 50 eV



$E_1+E_2 = h\nu - 2W_f$

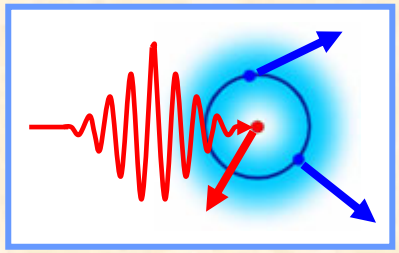


E_1+E_2 = 15 eV



Interaction of many Photons with Atoms:

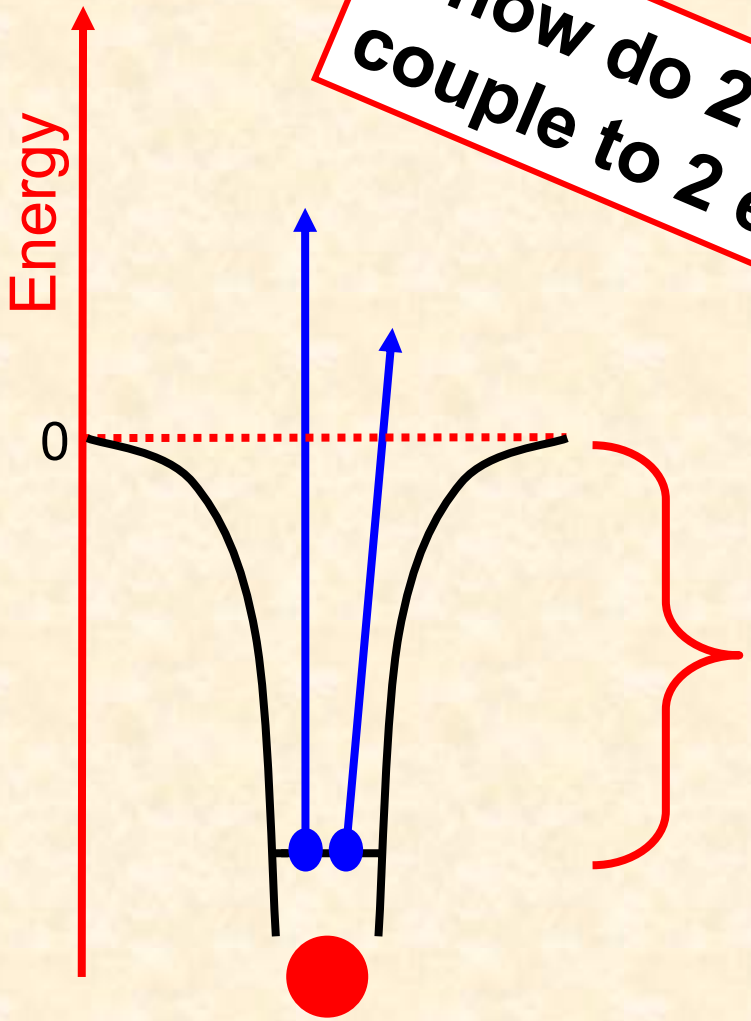
...photo double ionization of Helium with Laser...



10 nJ – 10 μJ

10^{11} - 10^{14} W/cm^2

2 photons @ 30 nm

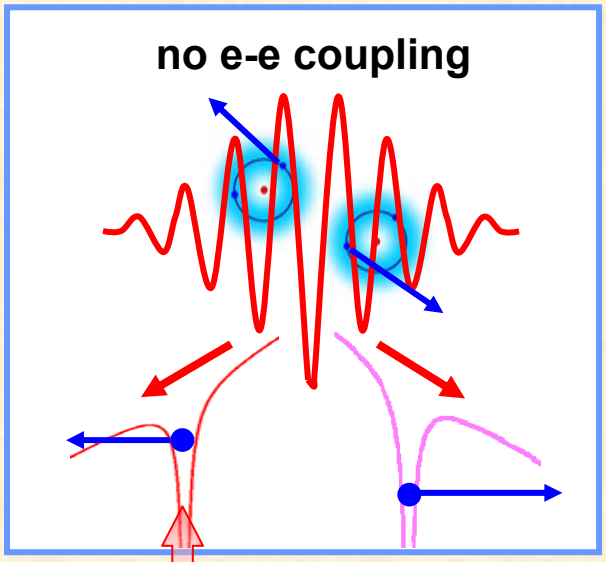


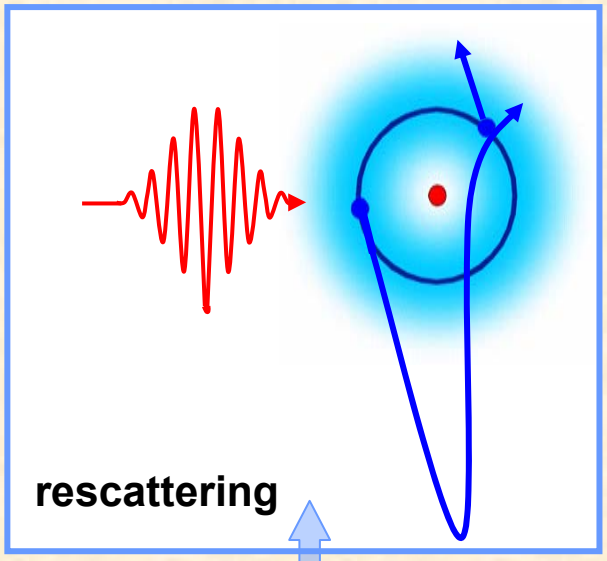
how do 2 photons couple to 2 electrons?

24.6 eV
+ 54.4 eV
79 eV

Photo Double Ionization of Helium with two Photons

…experiments at the High Harmonics Source of the UXSL…

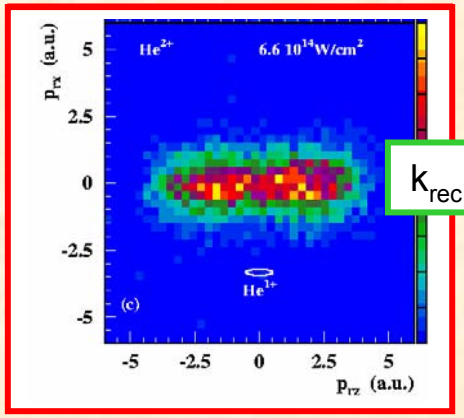




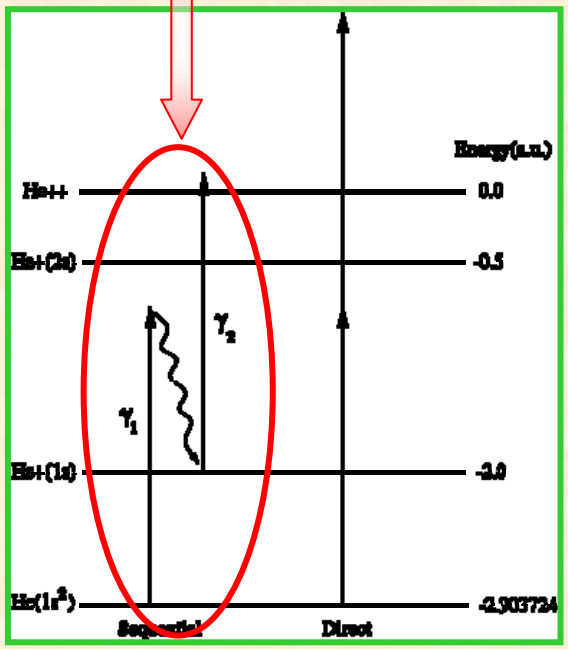
the reaction: $2h\nu + He \rightarrow He^{2+} + 2e-$

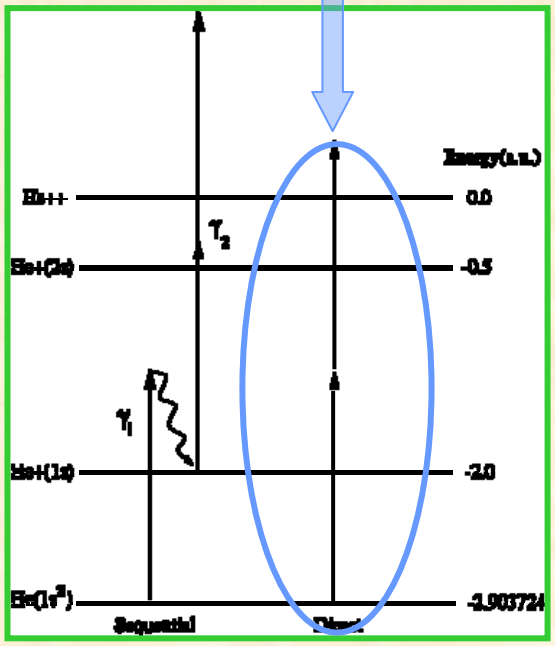
$He^{2+} + e-$

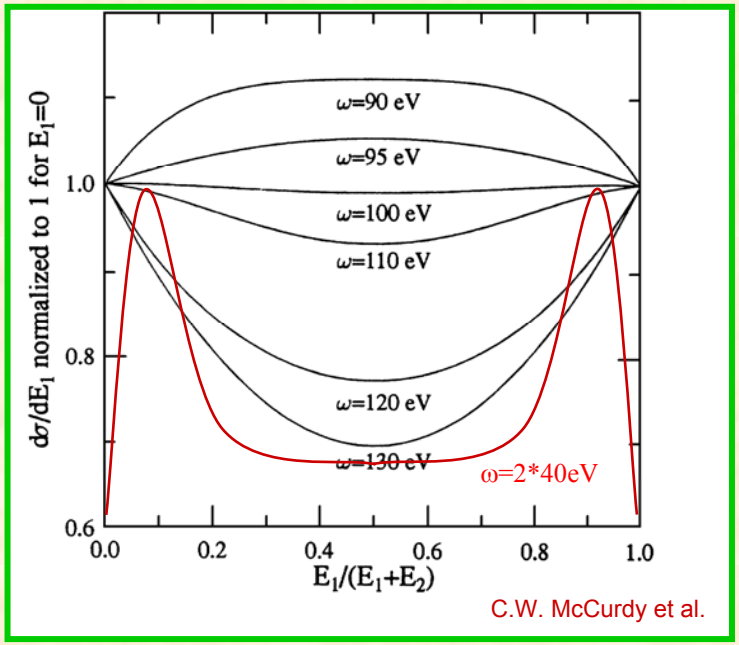
He^{2+}



$k_{rec} = k_{e1} + k_{e2}$





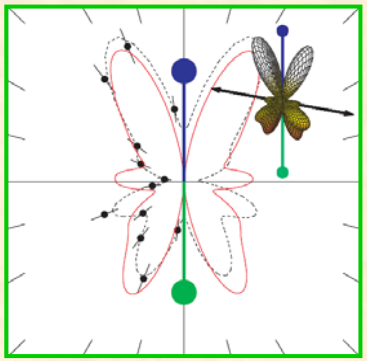


Summary: What should I keep in mind ?

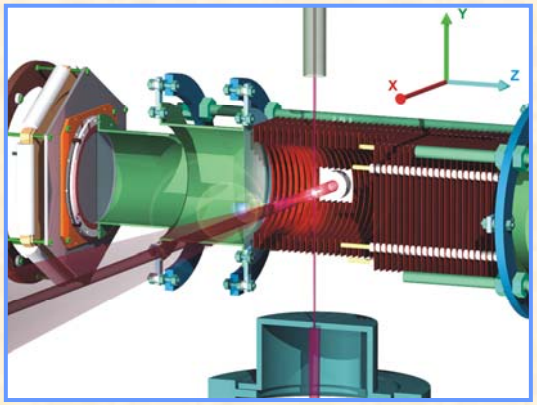
we're close

$|\langle \psi_f | \hat{H} | \phi_i \rangle|^2$

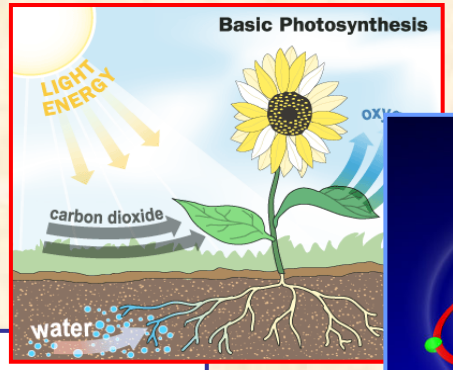
- Electron correlation
- selection rules, ionization processes, symmetries…



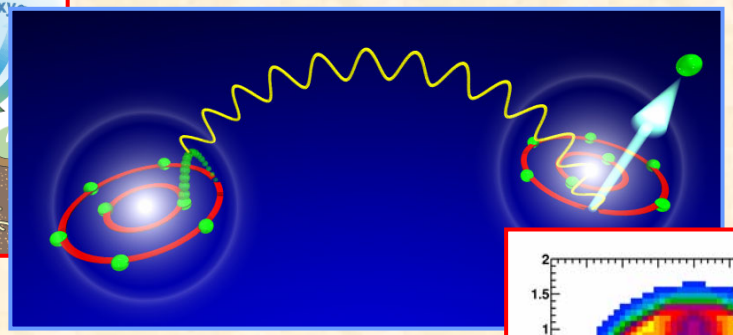
- Example: Break in symmetry of H_2
- F. Martín, *et al., Science* **315**, 629 (2007)



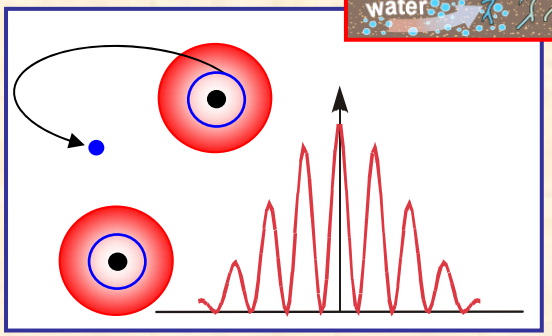
- UHV COLTRIMS
- collimated gas jet, Hex detector, flexible…



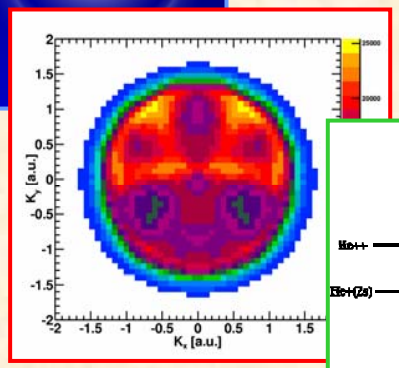
- Radiolysis of Water
- control of the carrier envelope phase



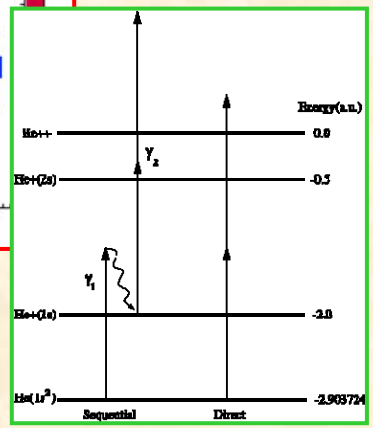
- Pump and Probe in Ne dimers
- dressed states, ICD, SICD



- Laser Induced Electron Diffraction of H_2
- „Pump and Probe" with femto second laser pulses



- emission of electrons from solid states surfaces
- pump and probe of correlated electrons



- photo double ionization of He with 2 photons
- hunt for gradual absorption

…the End:

by the way "who is working on all these crazy ideas" ?

new blood

- Benedikt Rudek
- Markus Schoeffler
- Matthias Weckenbrock
- Thorsten Weber

German Mafia