Intro to SR & FEL spectroscopy; interaction between radiation & matter (1)

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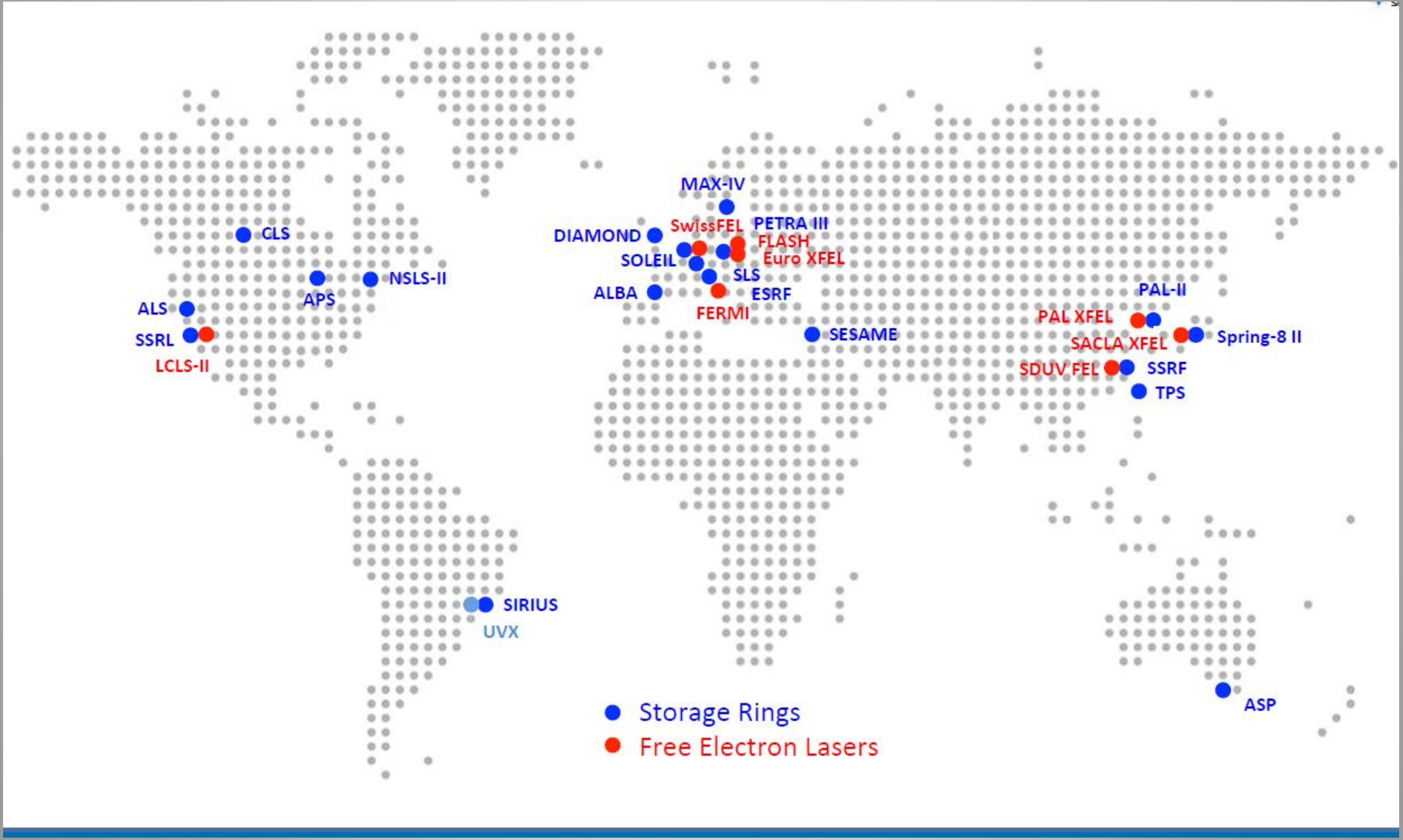
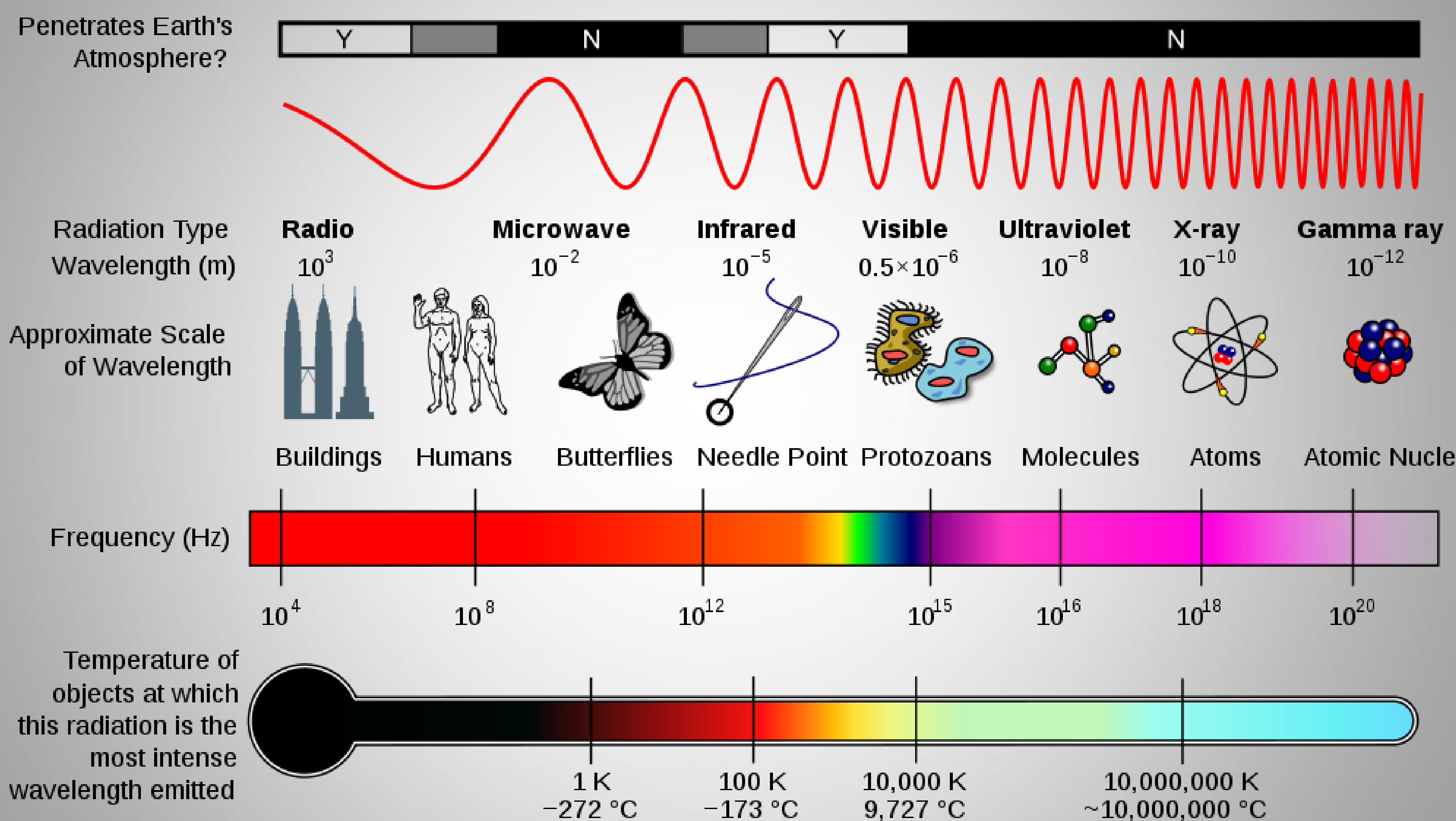
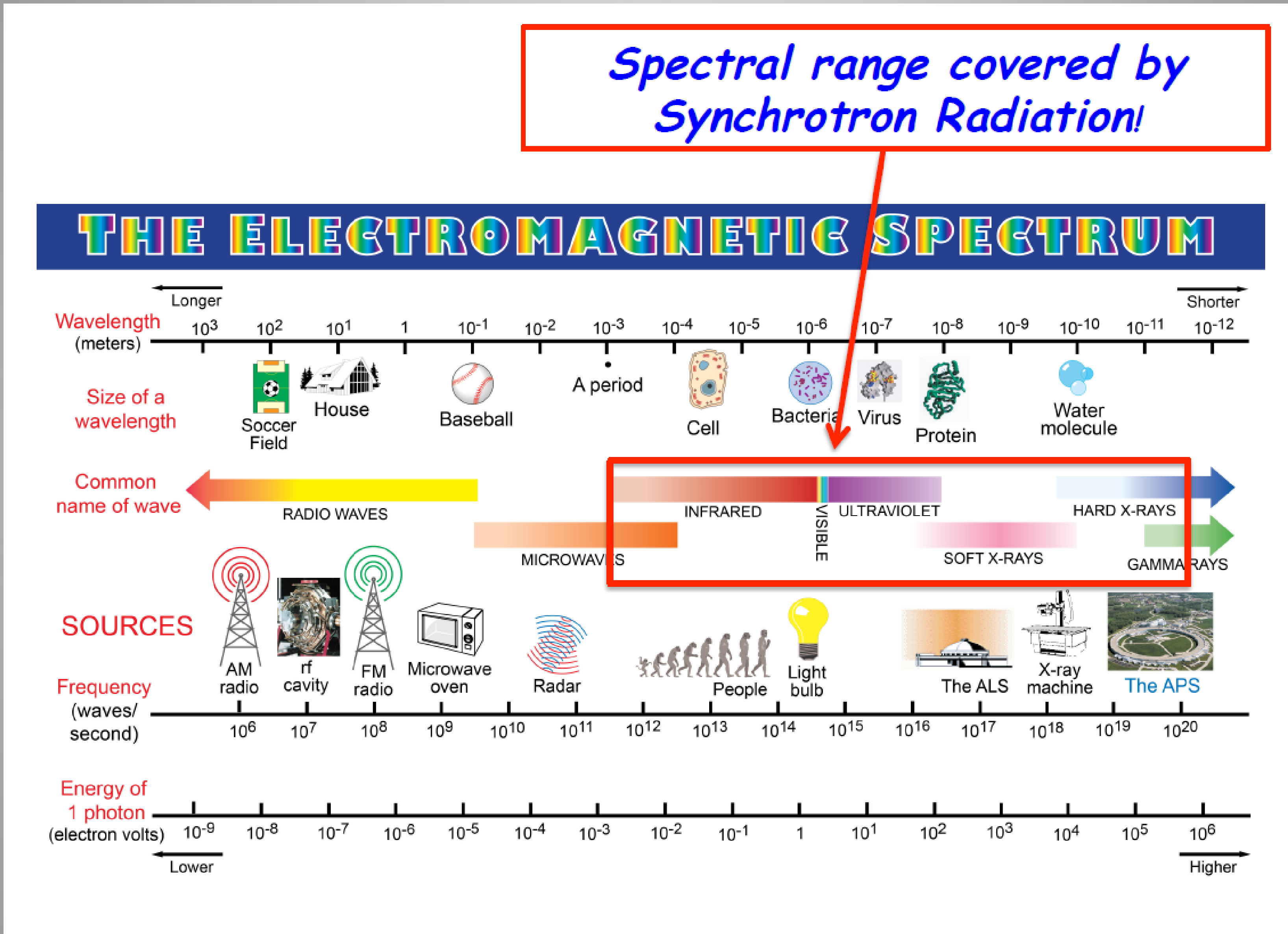
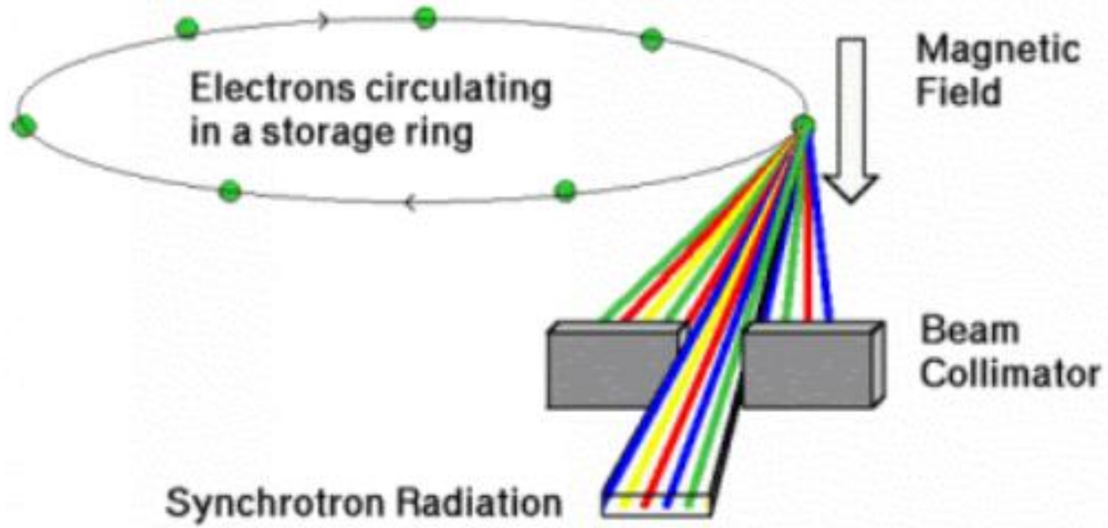
SR and FEL sources




Penetrates Earth's Atmosphere?
Y
N
Y
N
Radiation Type
Wavelength (m)
Radio
10^{3}
Microwave
10^{-2}
Infrared
10^{-5}
Visible
0.5×10^{-6}
Ultraviolet
10^{-8}
X-ray
10^{-10}
Gamma ray
10^{-12}
Approximate Scale of Wavelength
Buildings
Humans
Butterflies
Needle Point
Protozoans
Molecules
Atoms
Atomic Nuclei
Frequency (Hz)
10^{4}
10^{8}
10^{12}
10^{15}
10^{16}
10^{18}
10^{20}
Temperature of objects at which this radiation is the most intense wavelength emitted
1 K
−272 °C
100 K
−173 °C
10,000 K
9,727 °C
10,000,000 K
~10,000,000 °C

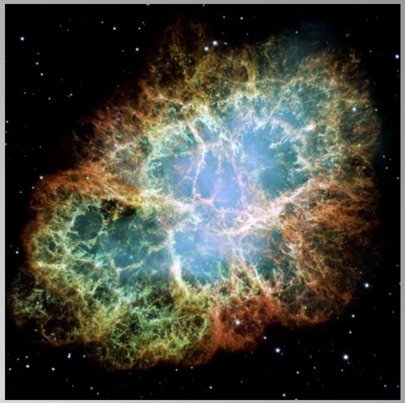

Spectral range covered by Synchrotron Radiation!
THE ELECTROMAGNETIC SPECTRUM
Longer
Shorter
Wavelength (meters)
10^{3} 10^{2} 10^{1} 1 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9} 10^{-10} 10^{-11} 10^{-12}
Size of a wavelength
Soccer Field
House
Baseball
A period
Cell
Bacteria
Virus
Protein
Water molecule
Common name of wave
RADIO WAVES
MICROWAVES
INFRARED
VISIBLE
ULTRAVIOLET
SOFT X-RAYS
HARD X-RAYS
GAMMA RAYS
SOURCES
AM radio
rf cavity
FM radio
Microwave oven
Radar
People
Light bulb
The ALS
X-ray machine
The APS
Frequency (waves/ second)
10^{6} 10^{7} 10^{8} 10^{9} 10^{10} 10^{11} 10^{12} 10^{13} 10^{14} 10^{15} 10^{16} 10^{17} 10^{18} 10^{19} 10^{20}
Energy of 1 photon (electron volts)
10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1 10^{1} 10^{2} 10^{3} 10^{4} 10^{5} 10^{6}
Lower
Higher

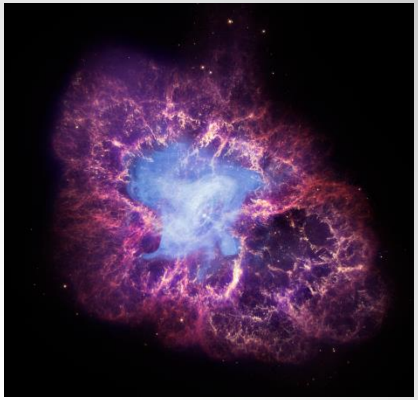
- **Synchrotron radiation is electromagnetic radiation emitted when charged particles are radially accelerated (moved on a circular path).**



HOW OLD IS SYNCHROTRON RADIATION?

Natural synchrotron radiation from charged particles spiraling around magnetic-field lines in space is as old as the stars, for example the light we see from the Crab Nebula.





HOW OLD IS <u>USABLE</u> SYNCHROTRON RADIATION?

Short-wavelength synchrotron radiation generated by relativistic electrons in circular accelerators is only a half-century old.

The first observation, literally since it was visible light that was seen, came at the General Electric Research Laboratory in Schenectady, New York, on April 24, 1947. In the 60 years since, synchrotron radiation has become a premier research tool for the study of matter in all its varied manifestations, as facilities around the world constantly evolved to provide this light in ever more useful forms.

X-RAY BACKGROUND

From the time of their discovery in 1895, both scientists and society have recognized the exceptional importance of x rays, beginning with the awarding of the very first Nobel Prize in Physics in 1901 to Röntgen. By the time synchrotron radiation was observed almost a half-century later, the scientific use of x rays was well established.

- X-rays were discovered (accidentally) in 1895 by Wilhelm Konrad Roentgen.
- Roentgen won the first Nobel Prize in 1901 “for the discovery with which his name is linked for all time: the... so-called Roentgen rays, as he himself called them, X-rays...”

Picture by Röntgen (1895)

Some milestones in X-ray research:

→1909: Barkla and Sadler discover characteristic x-ray radiation (1917 Nobel Prize to Barkla)

→1912: von Laue, Friedrich, and Knipping observe x-ray diffraction (1914 Nobel Prize to von Laue)

→1913: Bragg, father and son, build an x-ray spectrometer (1915 Nobel Prize)

→1916: Siegbahn and Stenstrom observe emission satellites (1924 Nobel Prize to Siegbahn)

→1922: Meitner discovers Auger electrons

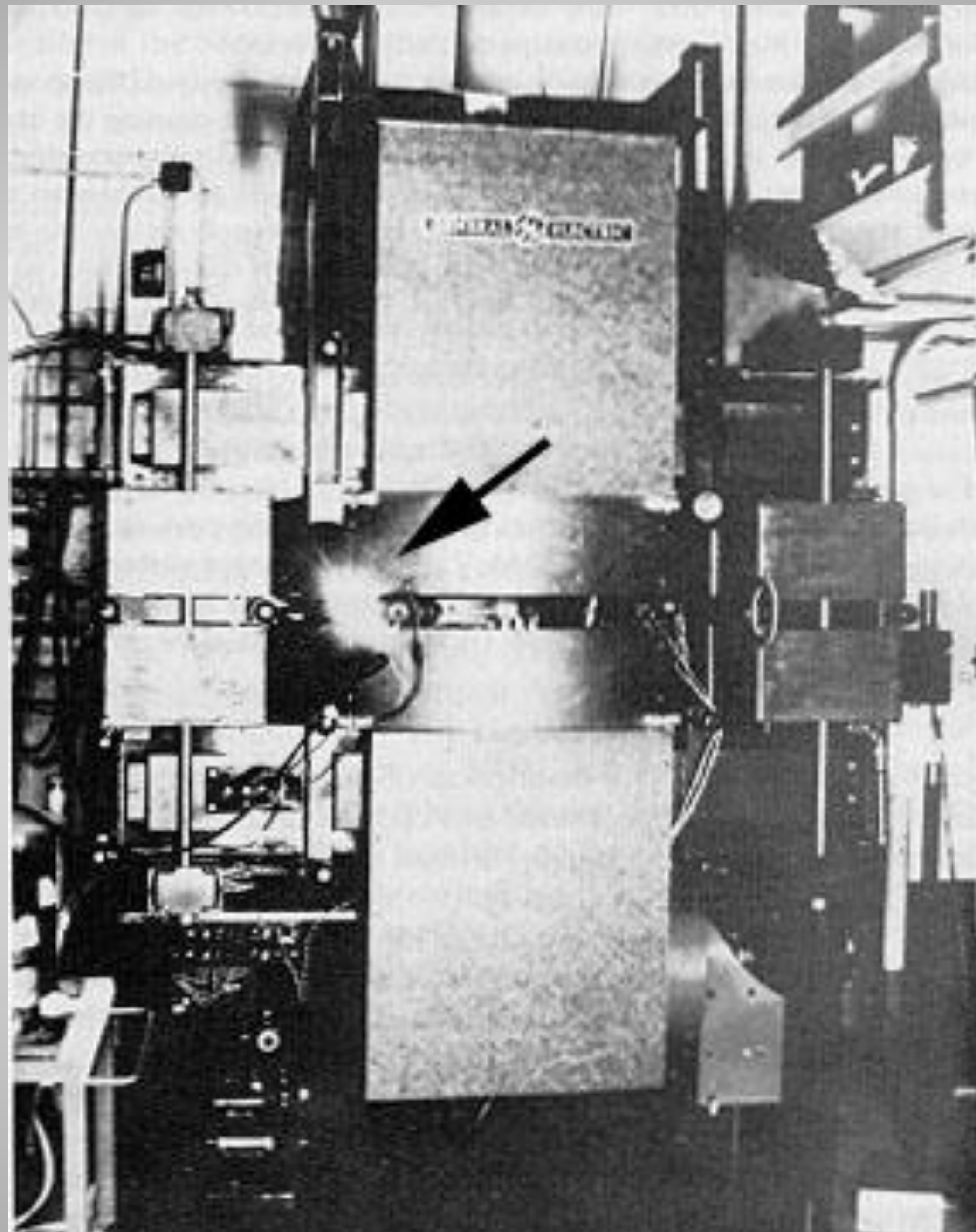
→1924: Lindh and Lundquist resolve chemical shifts

DISCOVERY OF SYNCHROTRON RADIATION

In 1945, the *synchrotron* was proposed as the latest accelerator for high-energy physics, designed to push particles, in this case electrons, to higher energies than could a *cyclotron*, the particle accelerator of the day. An accelerator takes stationary charged particles, such as electrons, and drives them to velocities near the speed of light.

The General Electric (GE) Laboratory in Schenectady built the world's second synchrotron, and it was with this machine in 1947 that synchrotron radiation was first observed. Radiation by orbiting electrons in synchrotrons was predicted by, among others, John Blewett, then a physicist for GE who went on to become one of Brookhaven's most influential accelerator physicists.

For high-energy physicists performing experiments at an electron accelerator, synchrotron radiation **is a nuisance** which causes a loss of particle energy. But condensed-matter physicists realized that this was exactly what was needed to investigate electrons surrounding the atomic nucleus and the position of atoms in molecules.

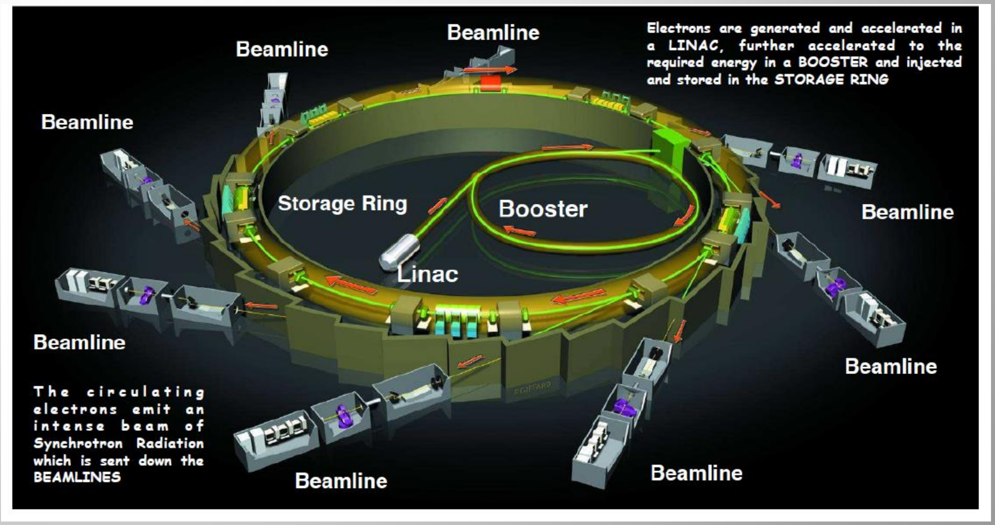


A synchrotron (sometimes called a synchro-cyclotron) is a circular accelerator which has an electromagnetic resonant cavity (or perhaps a few placed at regular intervals around the ring) to accelerate the particles.

As the particles increase in energy, the strength of the magnetic field that is used to steer them must be changed with each turn to keep the particles moving in the same ring. The change in magnetic field must be carefully synchronized to the change in energy or the beam will be lost. Hence the name "synchrotron".

Storage Ring

A storage ring is the same thing as a synchrotron, except that it is designed just to keep the particles circulating at a constant energy for as long as possible, not to increase their energy any further. However, the particles must still pass through at least one accelerating cavity each time they circle the ring, just to compensate for the energy they lose to synchrotron radiation.

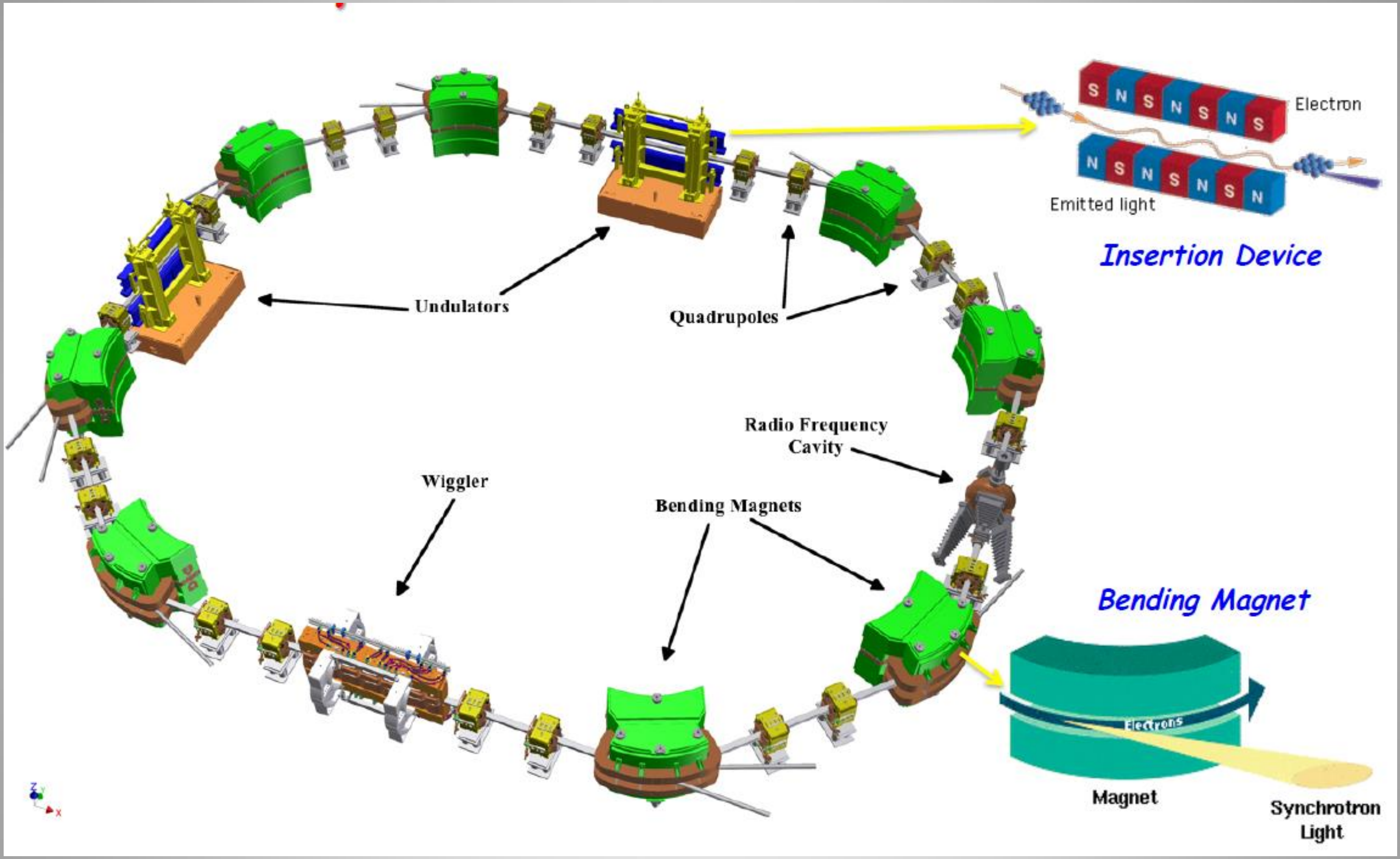


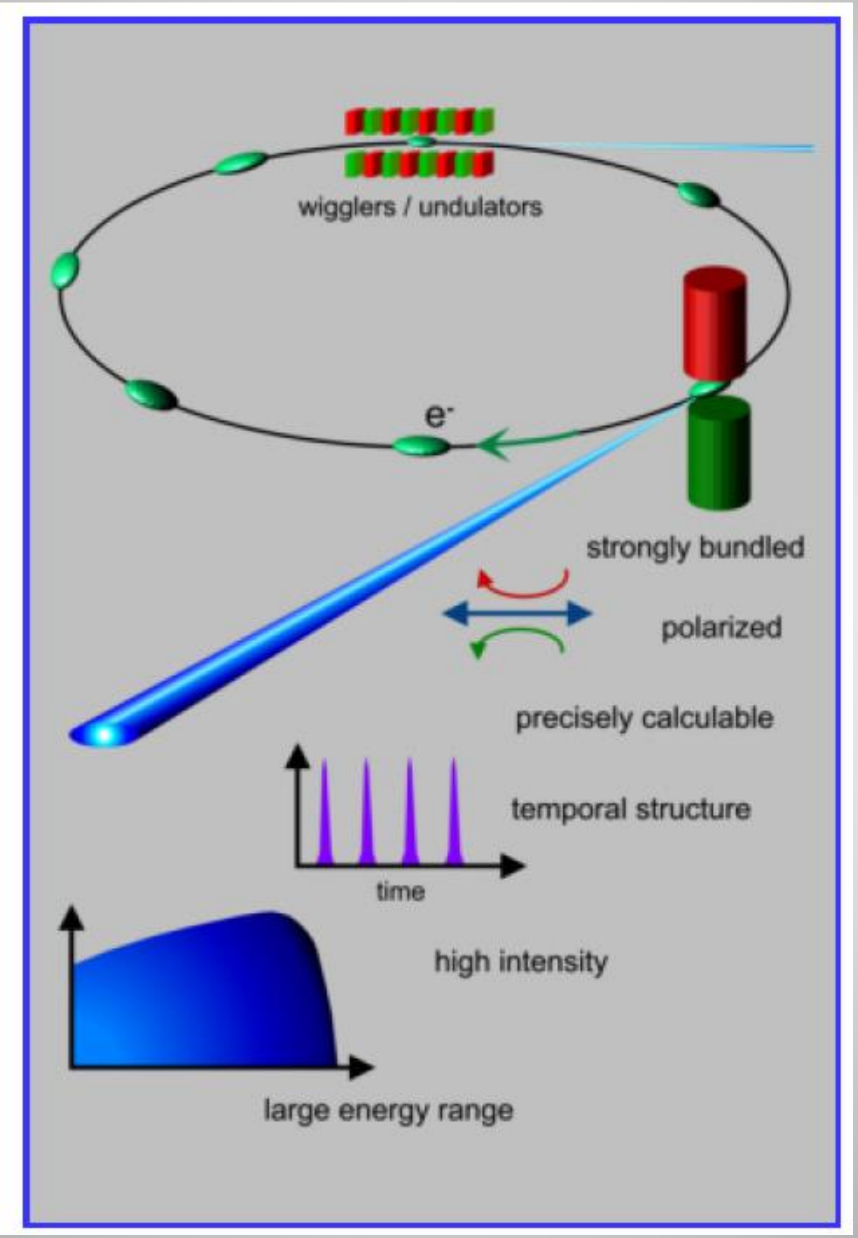
Storage Rings

First generation: parasitic operation

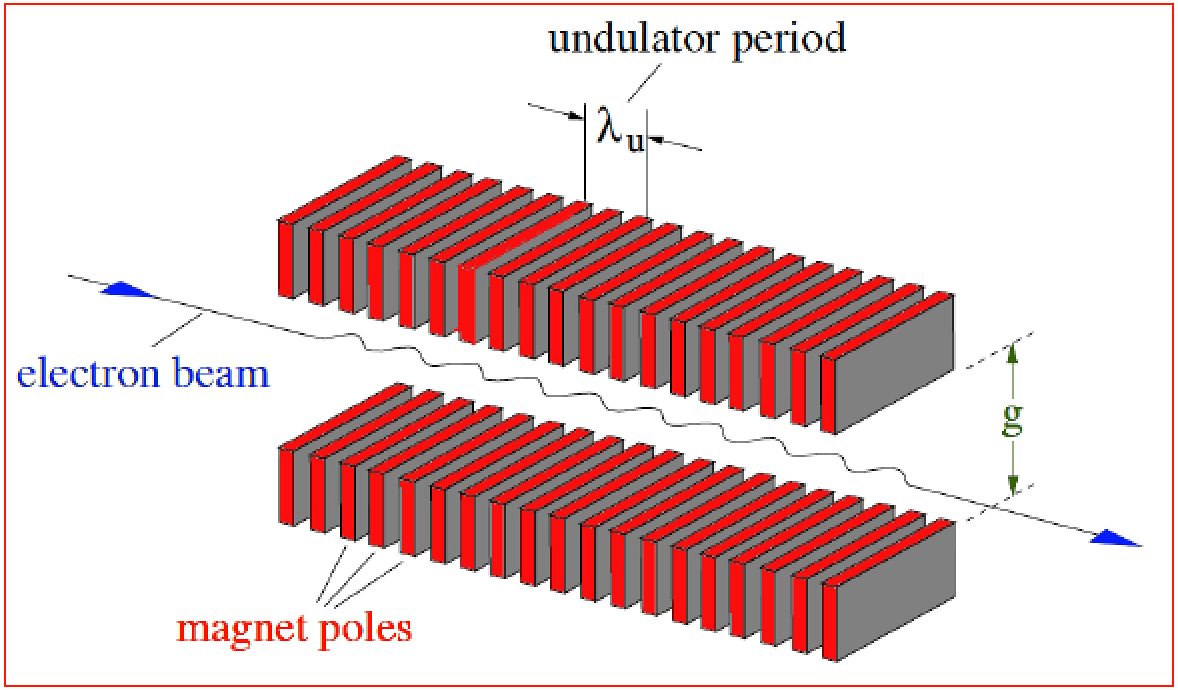
Second generation: dedicated operation

Third generation: undulators and wigglers


Undulators
Quadrupoles
Radio Frequency Cavity
Wiggler
Bending Magnets
Electron
Emitted light
Insertion Device
Bending Magnet
Electrons
Magnet
Synchrotron Light


wigglers / undulators
e-
strongly bundled
polarized
precisely calculable
temporal structure
time
high intensity
large energy range

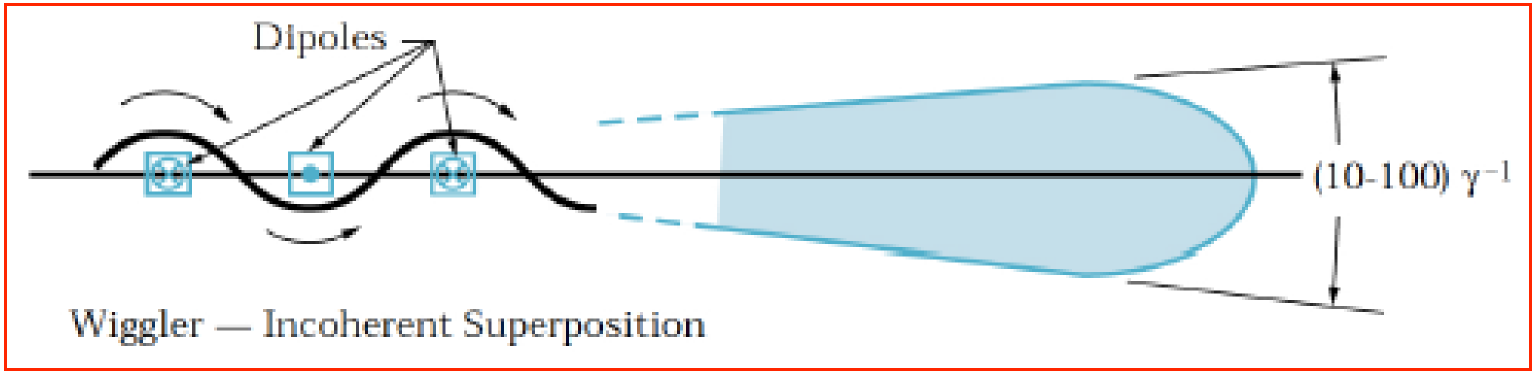
Insertion Devices



Insertion devices (ID) are ***periodic arrays of magnetic poles*** with alternating field directions installed, in the straight sections of storage rings that force the particles to oscillate passing through the device.

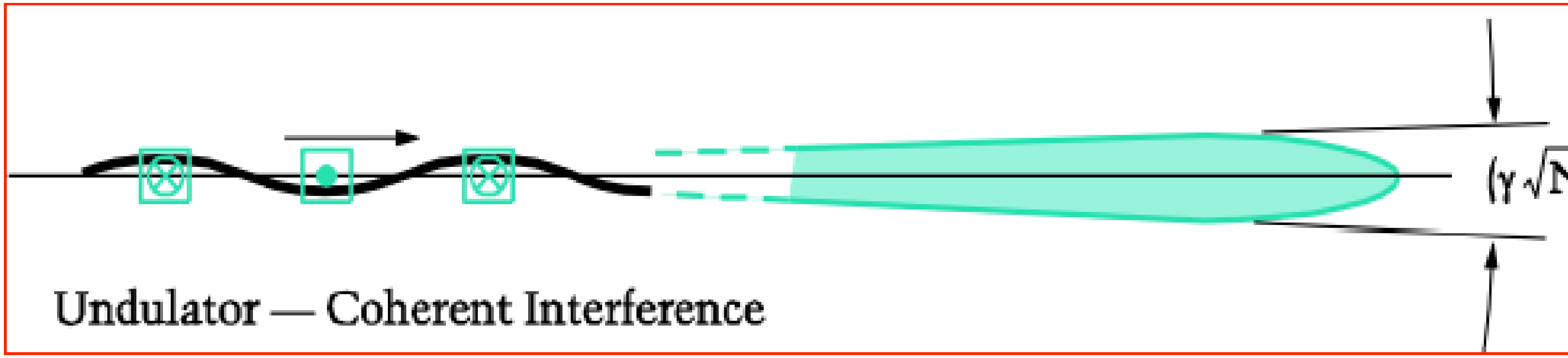
Wigglers

A ***wiggler*** is a ***multipole magnet (MPW)*** made up of a periodic series of magnets. ***Electrons are forced to follow a sinusoidal trajectory*** with a ***smaller local radius of curvature*** with respect to the one of the dipole-bending magnet, because in a wiggler, a ***magnetic field higher than in a bending magnet can be used.***

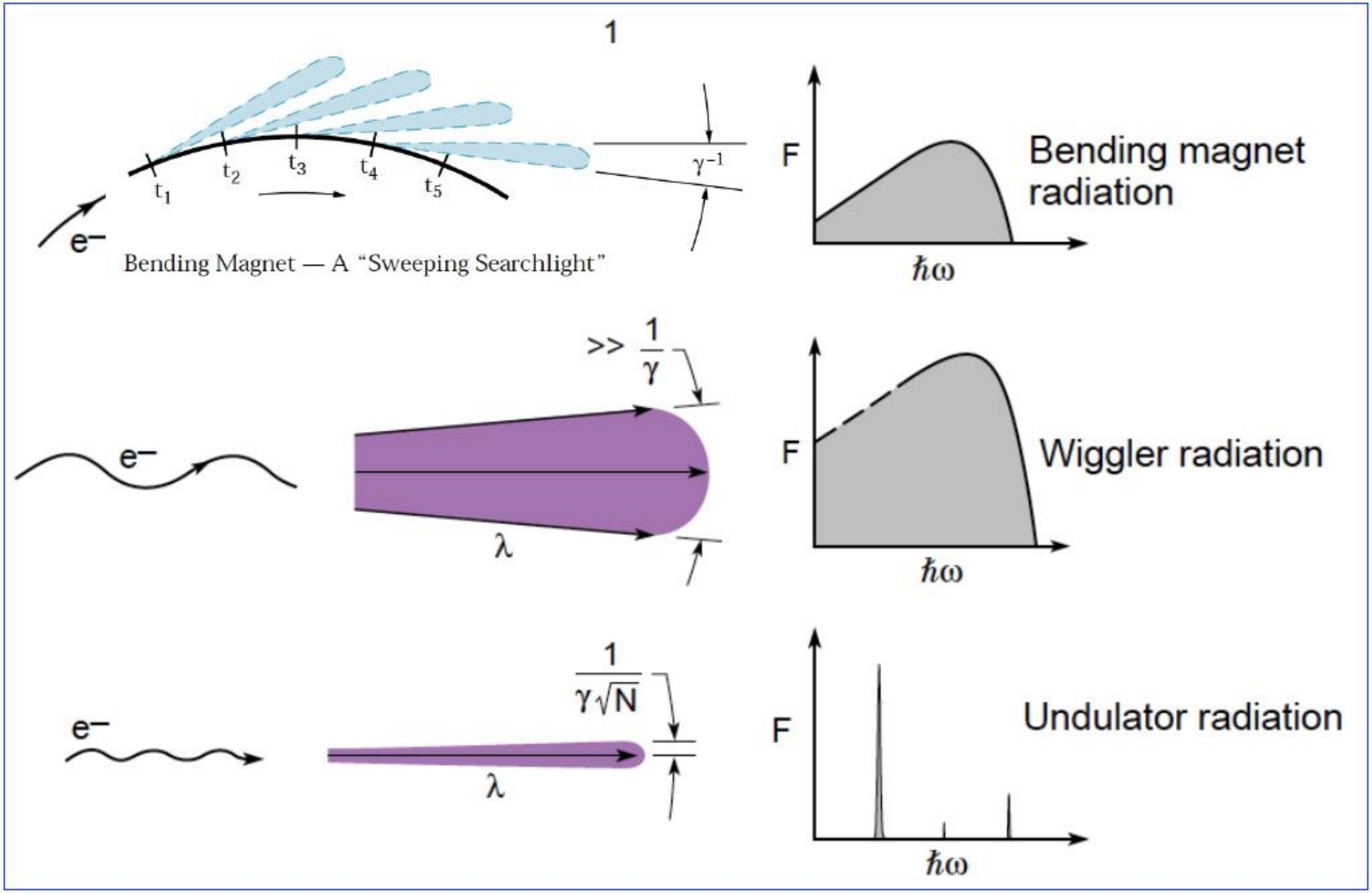


Undulators

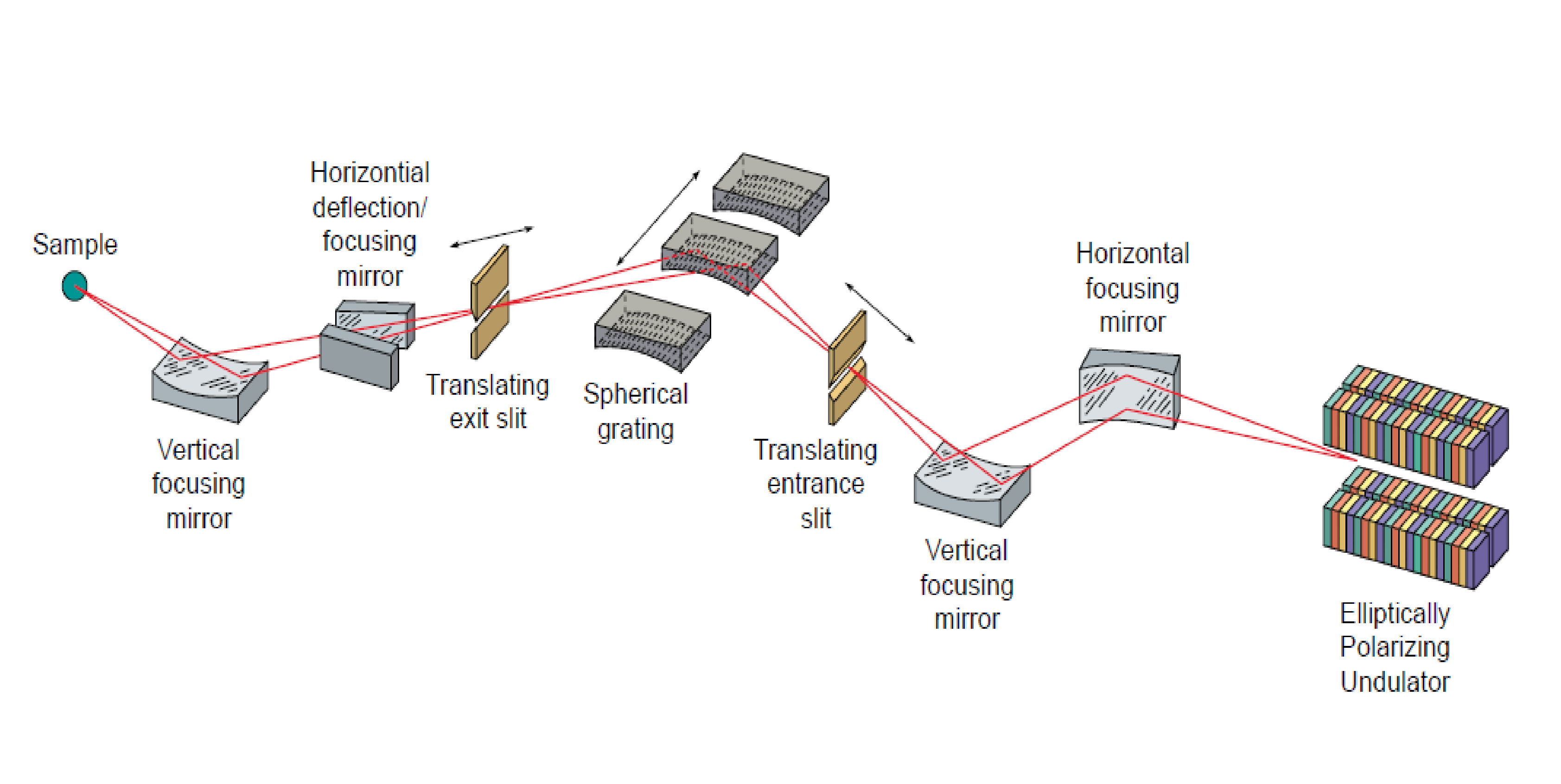
In an ***undulator K ≈ 1***, so the ***wiggling angle*** α ***is smaller than, or close to, the photon natural emission angle*** $1/\gamma$ and in this case ***constructive interference***, at ***specific wavelengths*** *occurs between* ***the radiation emitted by electrons at different poles along the trajectory***.



Undulator — Coherent Interference


1
t1
t2
t3
t4
t5
γ-1
e−
Bending Magnet — A "Sweeping Searchlight"
F
ħω
Bending magnet radiation
>> 1/γ
e−
λ
F
ħω
Wiggler radiation
1/γ√N
e−
λ
F
ħω
Undulator radiation

Beam lines



Sample
Horizontial deflection/ focusing mirror
Translating exit slit
Spherical grating
Translating entrance slit
Horizontal focusing mirror
Vertical focusing mirror
Vertical focusing mirror
Elliptically Polarizing Undulator

- *Continuum source from IR to X-rays* **(tunability)** which covers from **microwaves to hard X-rays**: the user can select the wavelength required for experiment- **continuous** *(Bending Magnet/Wiggler)* - **quasi-monochromatic** *(Undulator)*

- *Source in a clean UHV environment*

- *Very high flux and brightness (**with undulators**)* highly **collimated photon beams** generated by a ***small divergence*** and **small size sources** .

- *Highly Polarized*

- *Pulsed time structure* - pulsed length down to tens of picoseconds allows the resolution of processes on the same time scale

- *High stability* (**submicron source stability**)

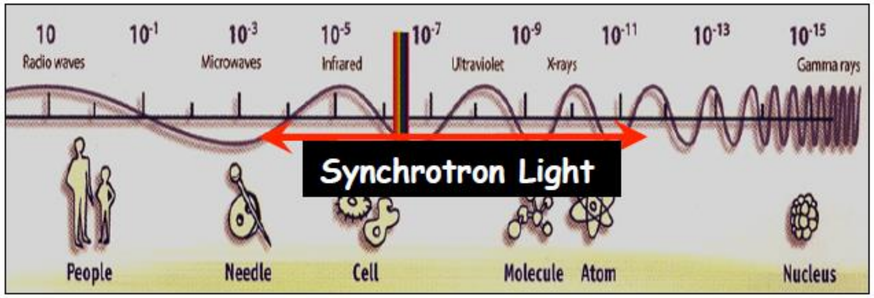
The Physics of Synchrotron Radiation
By *Albert Hofmann*
Cambridge University Press, 2004

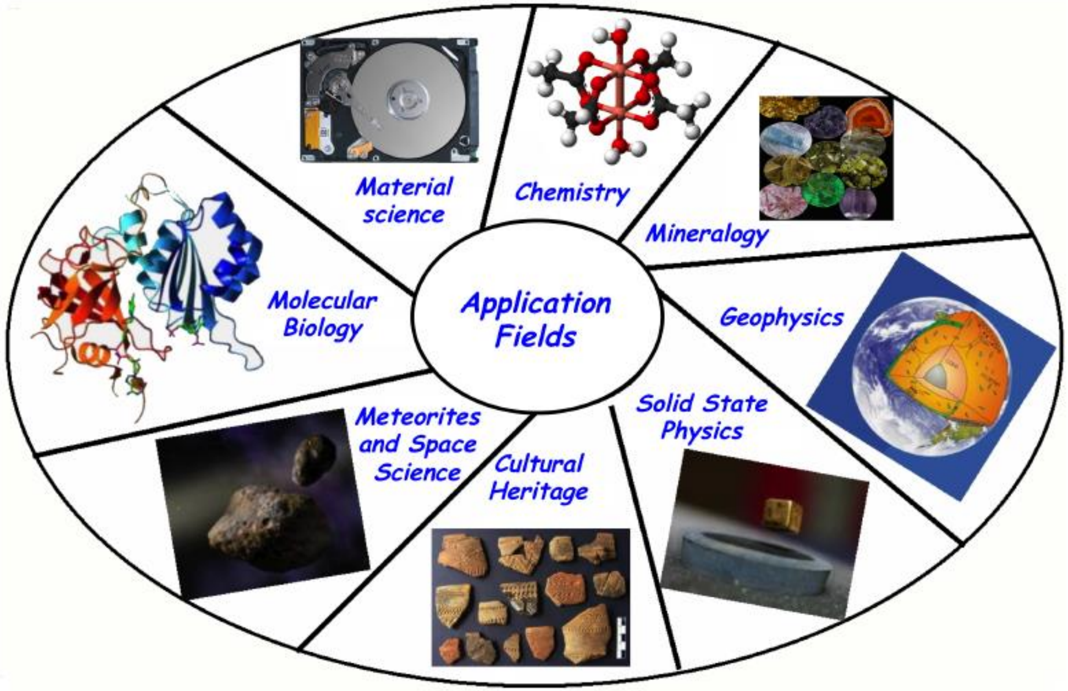
An Introduction to Synchrotron Radiation: Techniques and Applications
By *Philip Willmott*
J. Wiley, 2011

Soft X-Rays and Extreme Ultraviolet Radiation: Principles and Applications
By *David Attwood*
Cambridge University Press, 2007

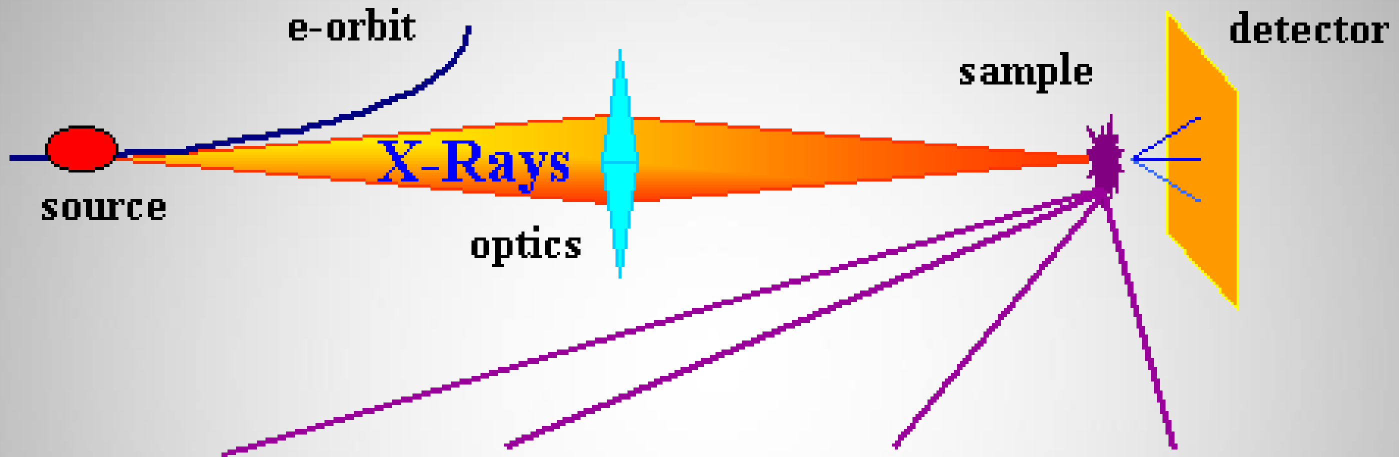
Synchrotron Radiation
Basics, Methods and Applications
Eds *Settimio Mobilio, Federico Boscherini, Carlo Meneghini*
Springer, 2015

Synchrotron radiation applications





Scientific Topics



Energy

Spectroscopy

EXAFS
XANES
Fluorescence
Spectromicro-
scopy

Momentum

Scattering

MAD
SAD
SAXS
XMS
Interferometry

Position

Imaging

Microscopy
Tomography
Topography
Phasing
Litography

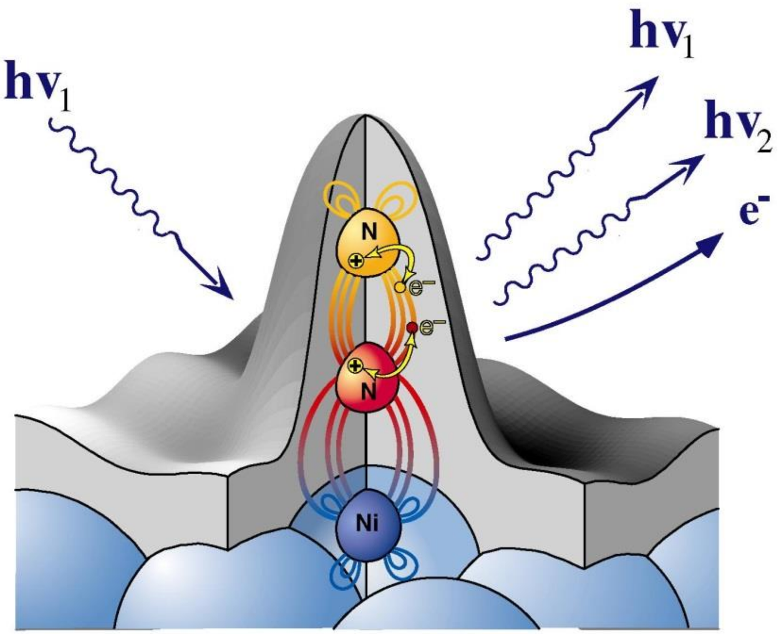
Dynamics

Time-resolving

Diffraction
Luminescence
Spectroscopy
Scattering
Imaging

Photon Interaction

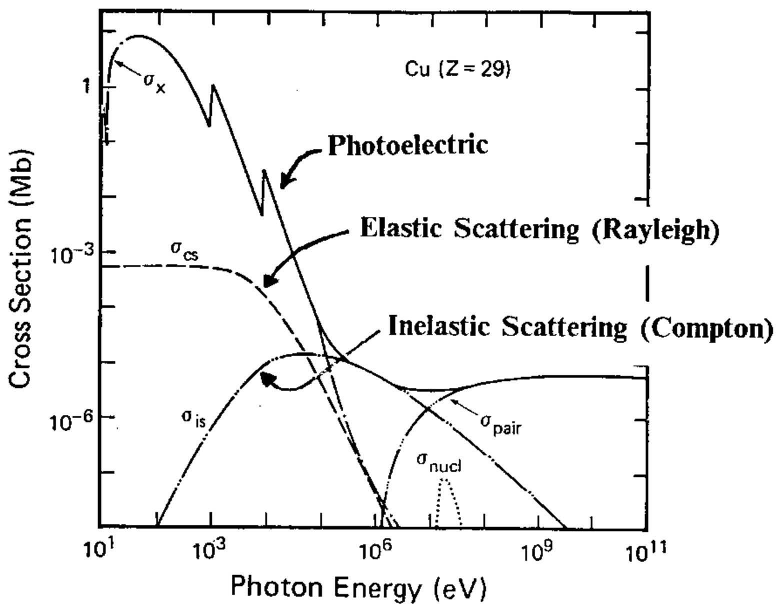
Incident photon interacts with electrons
Core and Valence



- Photon is
- Adsorbed
- Elastic Scattered
- Inelastic Scattered

- Electron is
- Emitted
- Excitated
- Dexcitated

Cross Sections

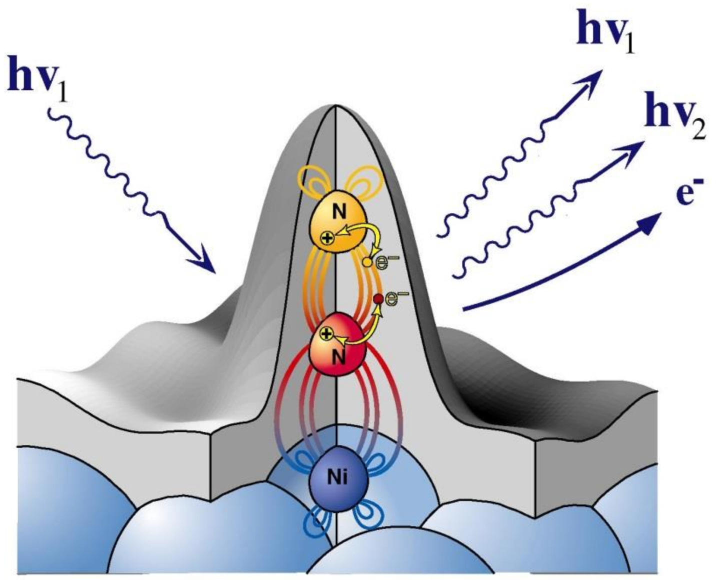


Below 100 keV

Photoelectric and elastic cross section dominates

Spectroscopy-Scattering

Detected Particles



EMITTED PARTICLE

- *Elastic Scattering* X-Diffraction, Speckle
- *Inelastic Scattering* X-ray Emission Spectroscopy
- *Electron Emission* Photoelectron Spectroscopy

NO EMITTED PARTICLE

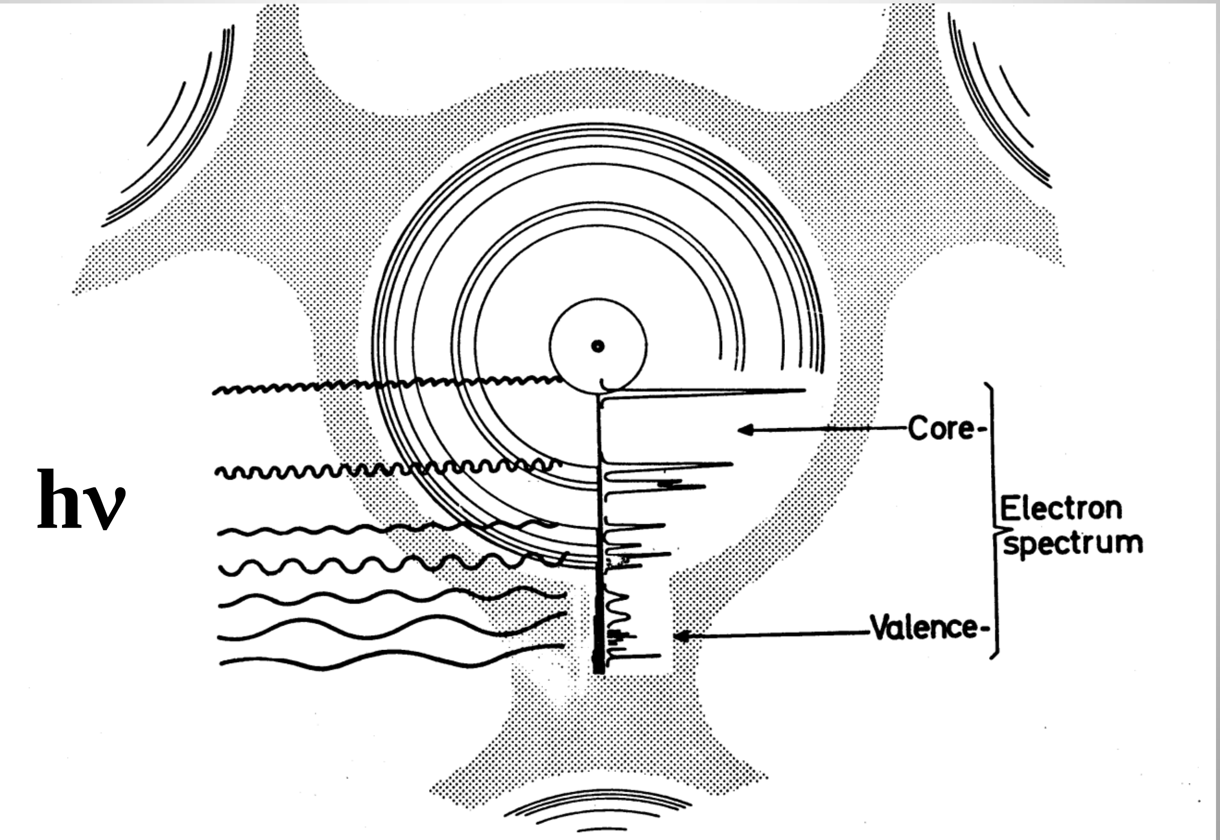
- *Photon Adsorbed* X-ray Absorption Spectroscopy

Spectroscopy

Valence electrons → Chemical Bonding

Core electrons → Non interacting

Ionization → Photoelectron Spectroscopy



Methods

- X-ray Diffraction
- Photoelectron Spectroscopy (PES)

Core level electron spectroscopy

Valence band photoemission

Resonant photoemission

Photoelectron Diffraction

- X-ray Absorption Spectroscopy (XAS)

Near Edge X-ray Absorption Spectroscopy (NEXAFS)

Extended X-ray Absorption Fine Structure (EXAFS)

X-ray Magnetic Circular Dichroism (XMCD)

- X-ray Emission Spectroscopy (XES)

Resonant Inelastic X-ray Scattering (RIXS)

Selected examples:

NEXAFS

Core-level spectroscopy

Resonant photoemission

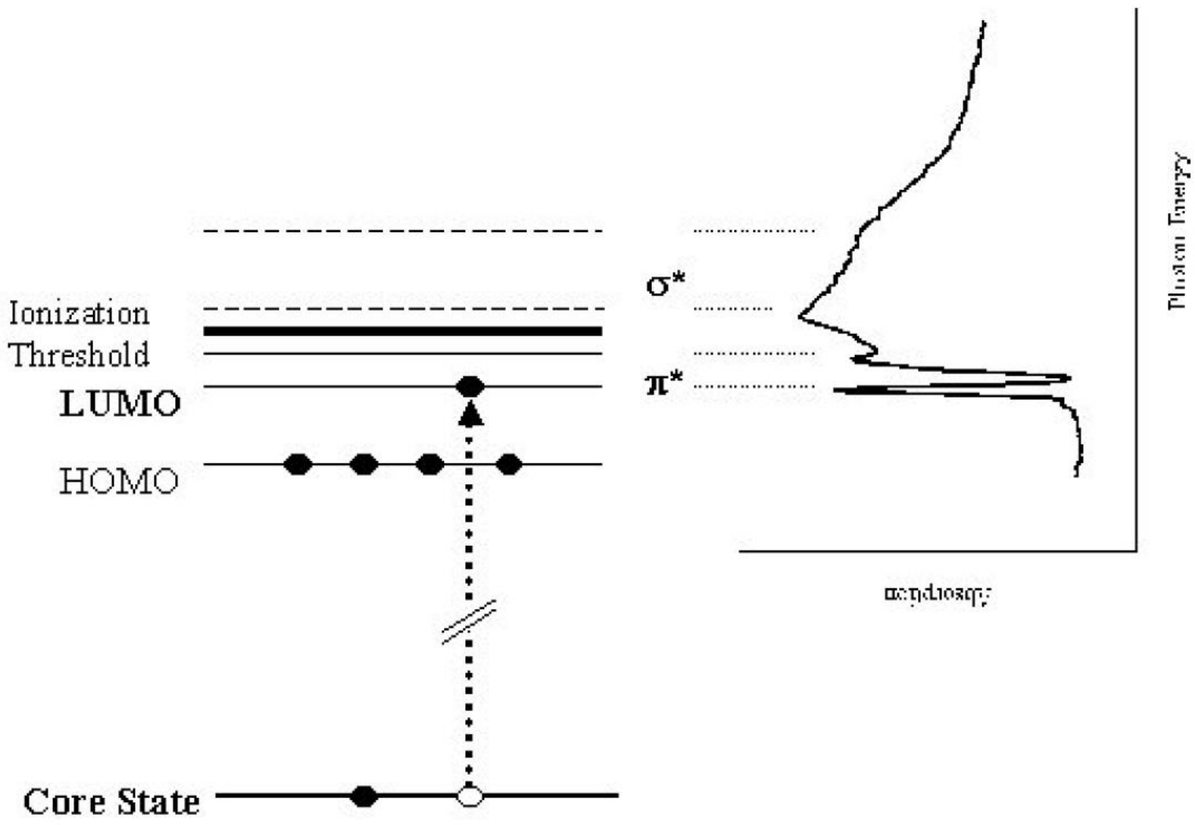
Ultrafast dynamics

NEXAFS (Near-Edge X-ray Absorption Fine Structure)

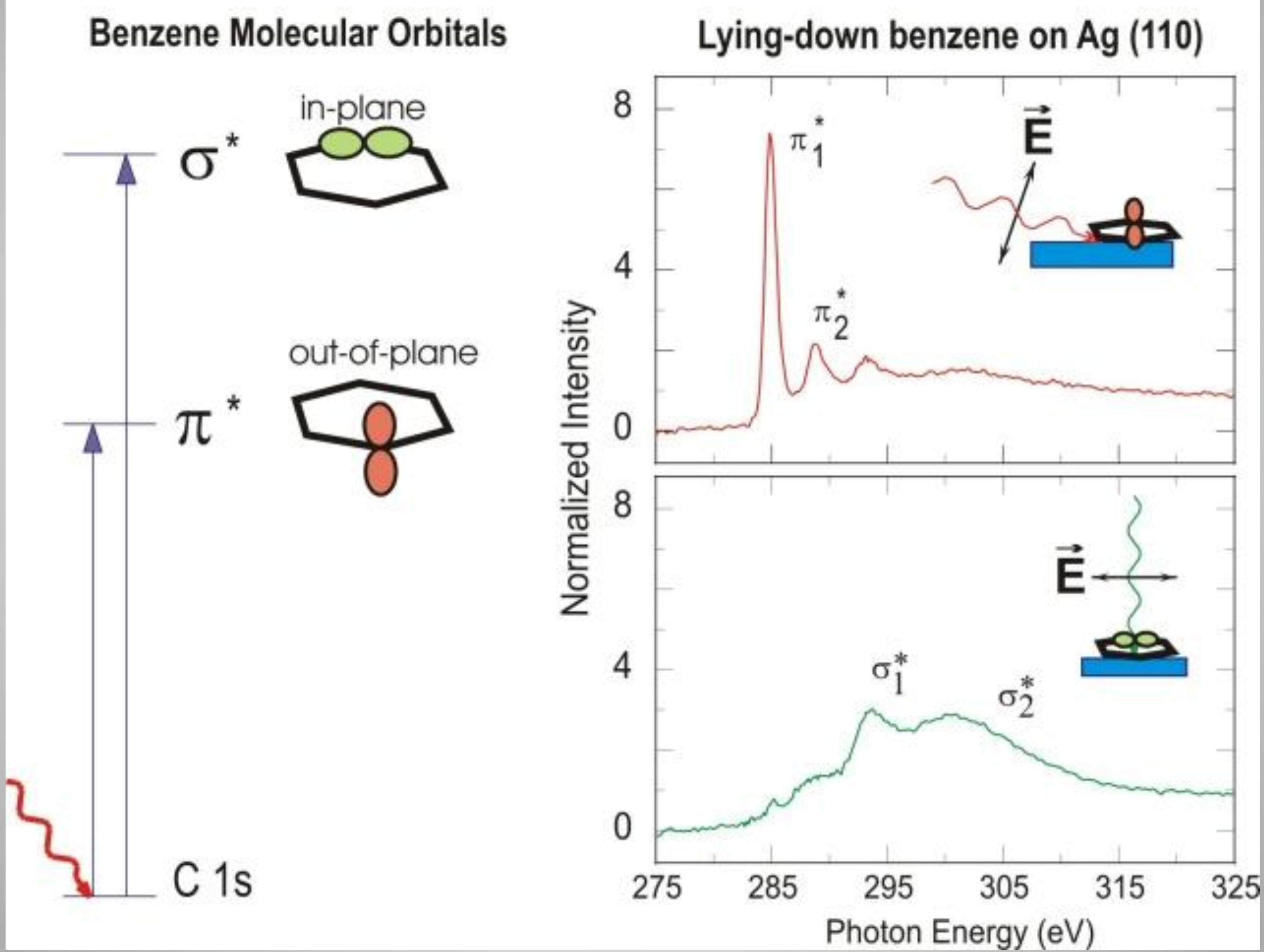
Near Edge X-Ray Absorption Fine Structure, NEXAFS, spectroscopy refers to the absorption fine structure close to an absorption edge, about 30 eV around the actual edge.

This region usually shows the largest variations in the x-ray absorption coefficient and is often dominated by intense, narrow resonances.

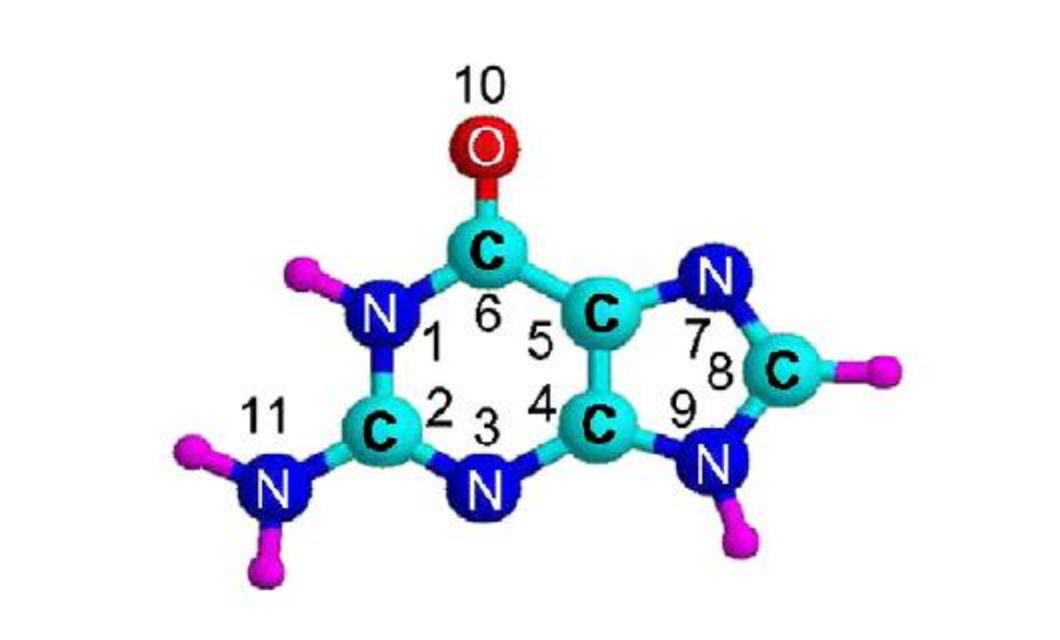
NEXAFS is also called X-ray Absorption Near Edge Structure, XANES. Today, the term NEXAFS is typically used for soft x-ray absorption spectra and XANES for hard x-ray spectra.


Ionization
Threshold
LUMO
HOMO
Core State
σ*
π*

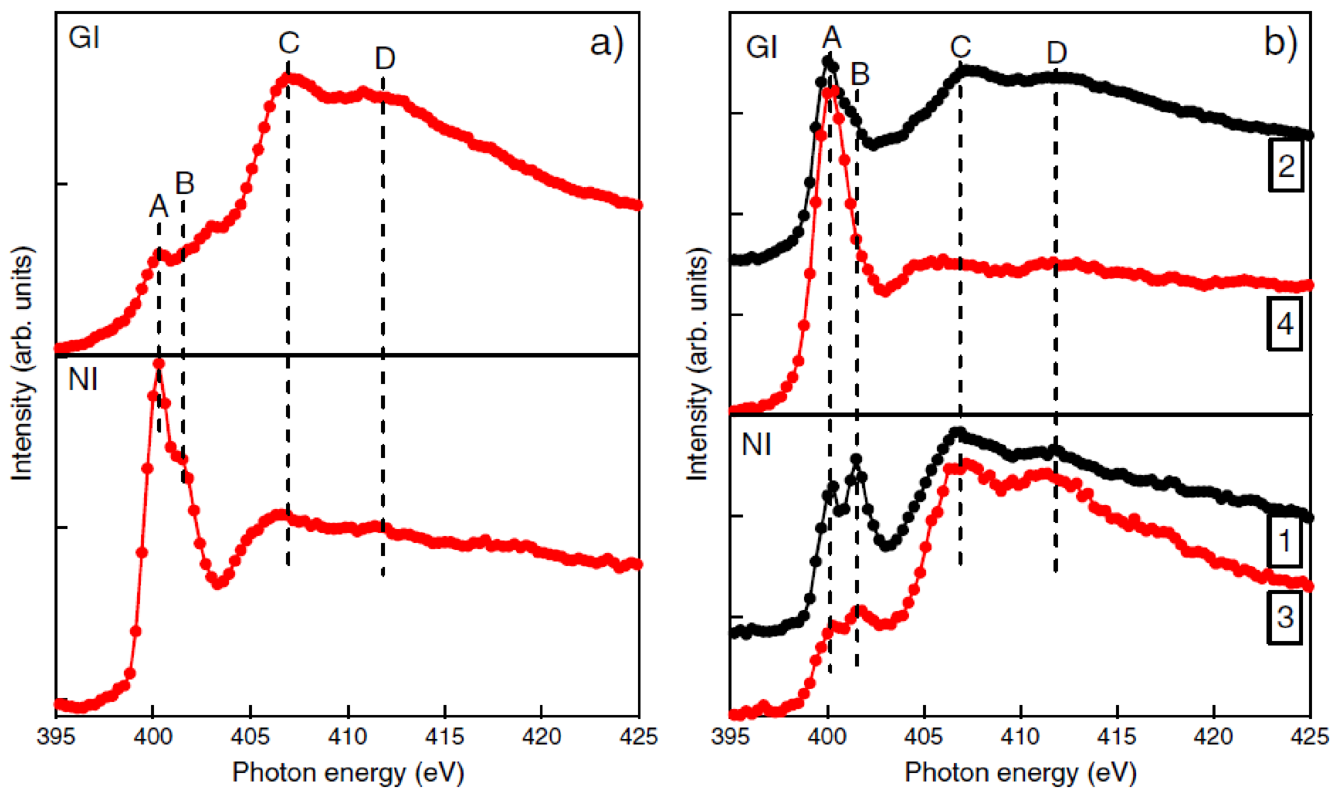
The Search Light Effect

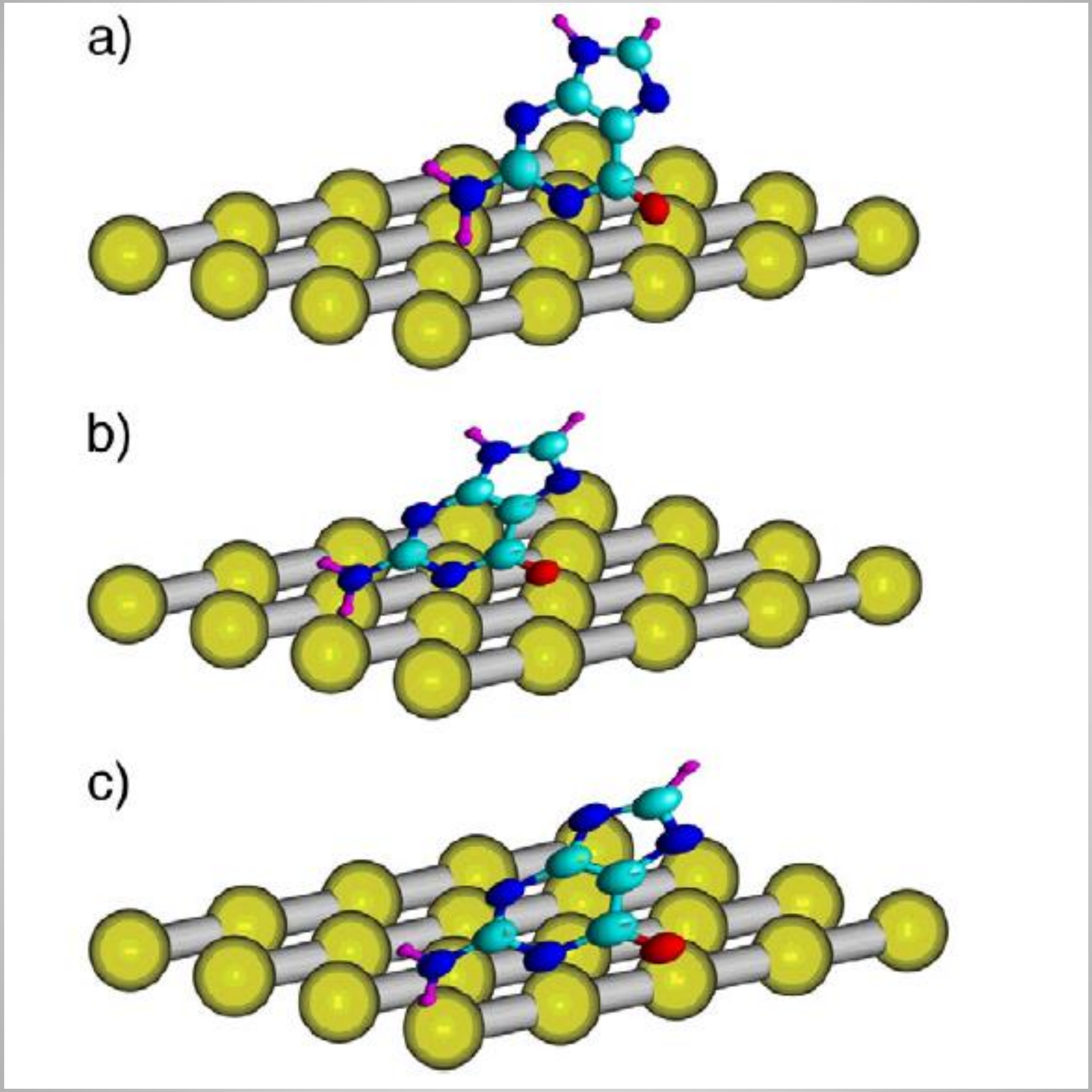


GUANINE



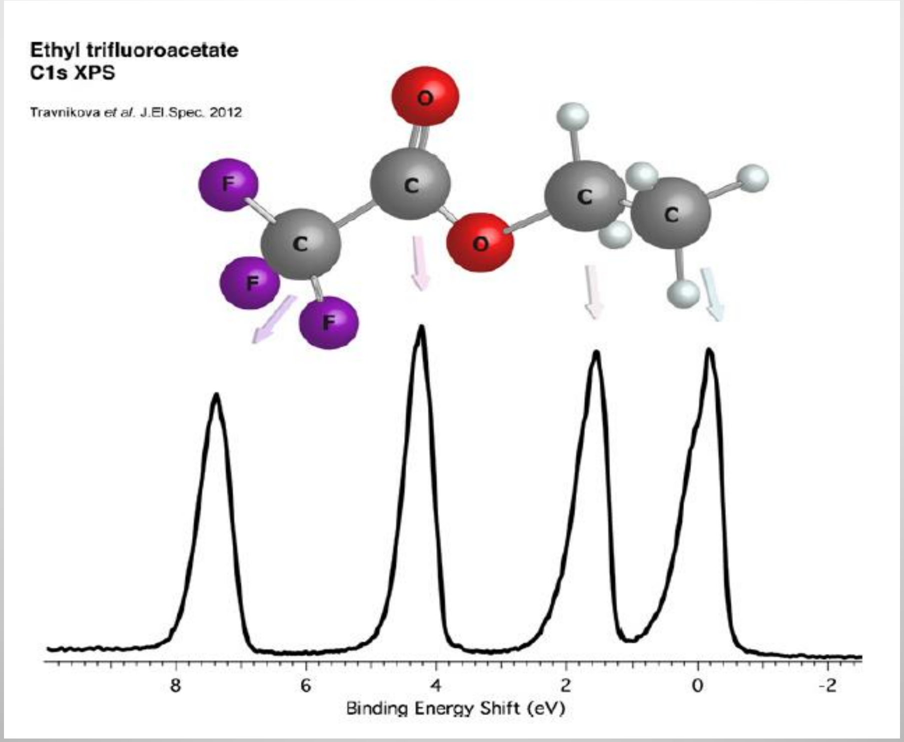
V. Feyer, O. Plekan, F. Šutara , V. Cháb , V. Matolín and K.C. Prince,
Surf.Sci. 605,(2011) 361

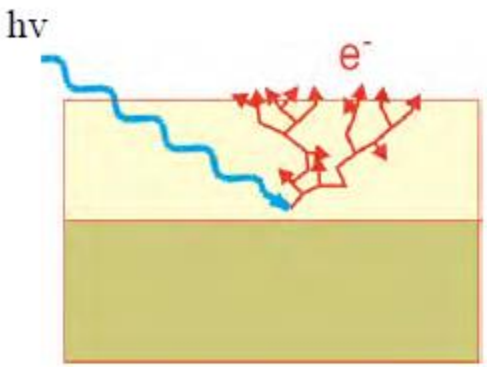

GI
a)
A
B
C
D
NI
Intensity (arb. units)
395
400
405
410
415
420
425
Photon energy (eV)
GI
b)
A
B
C
D
2
4
NI
1
3
Intensity (arb. units)
395
400
405
410
415
420
425
Photon energy (eV)


a)
b)
c)

Core-level spectroscopy

Si surfaces and chemical shift

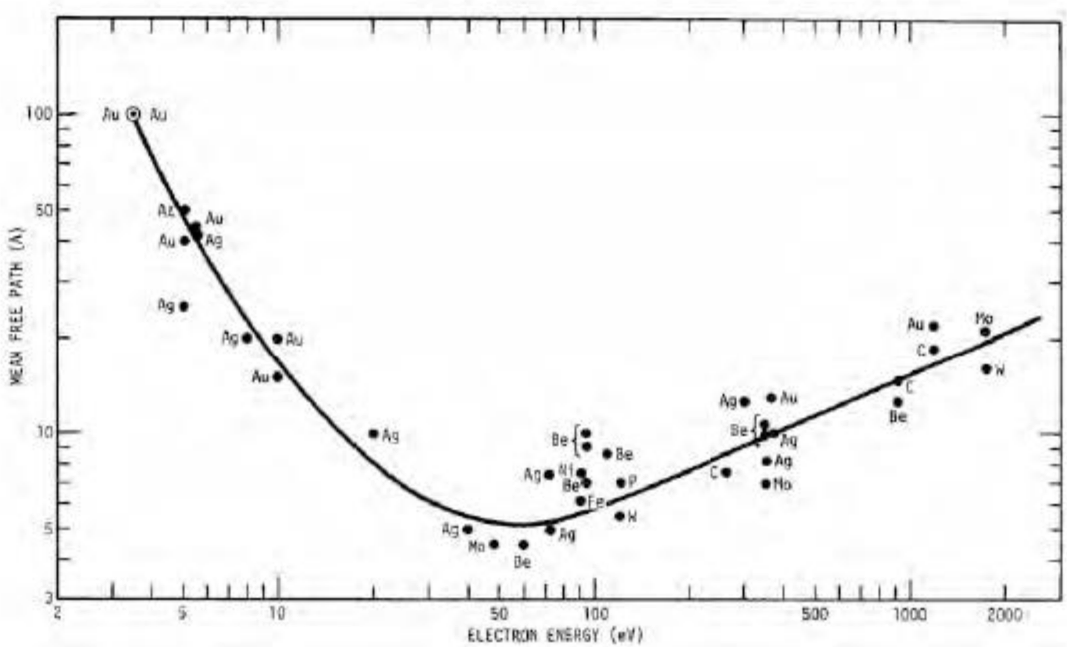




Electrons interact strongly

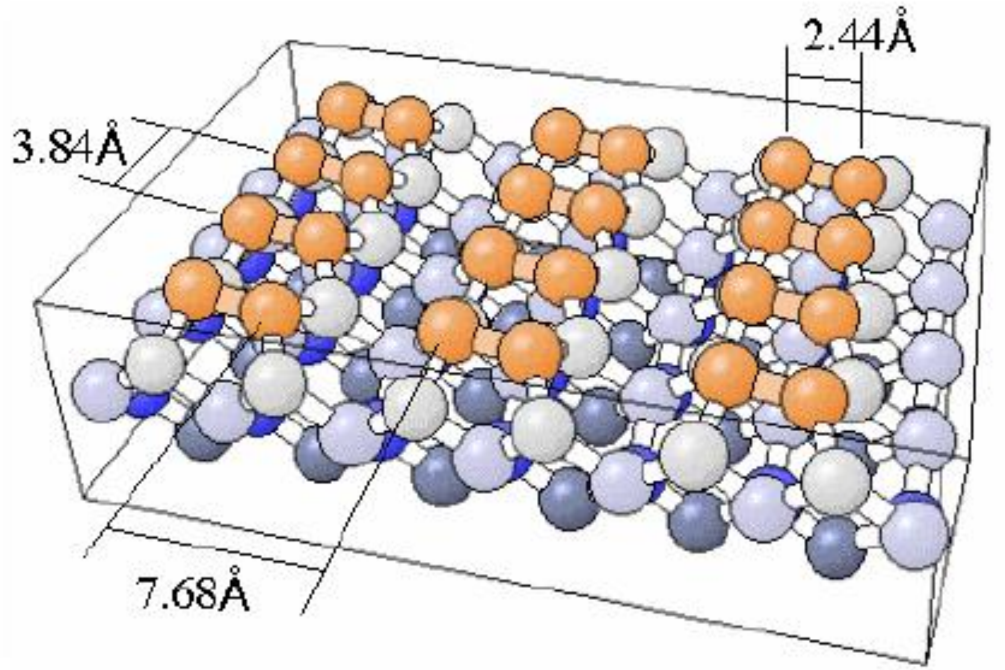
Surface Sensitivity

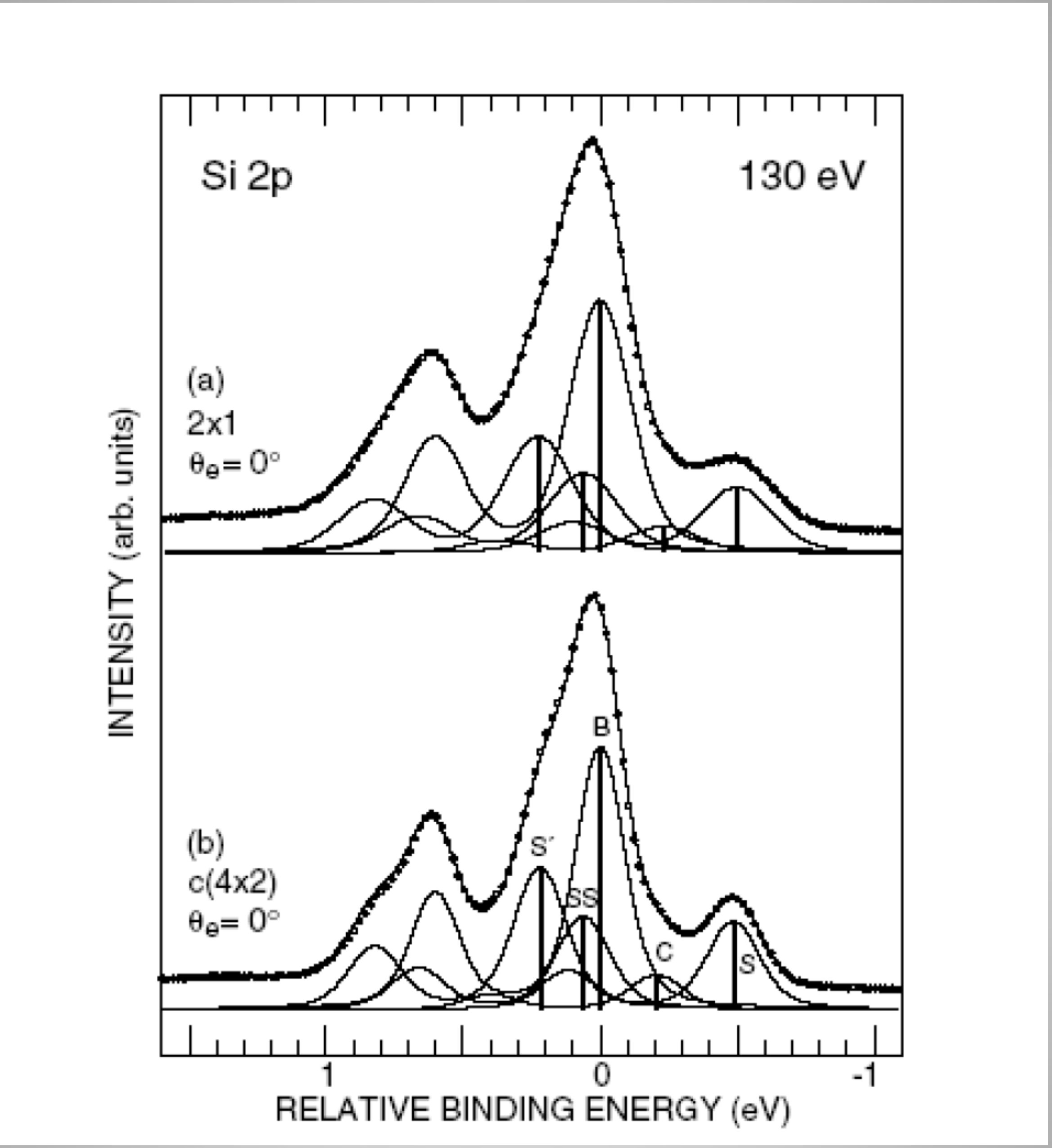
5-20 Å



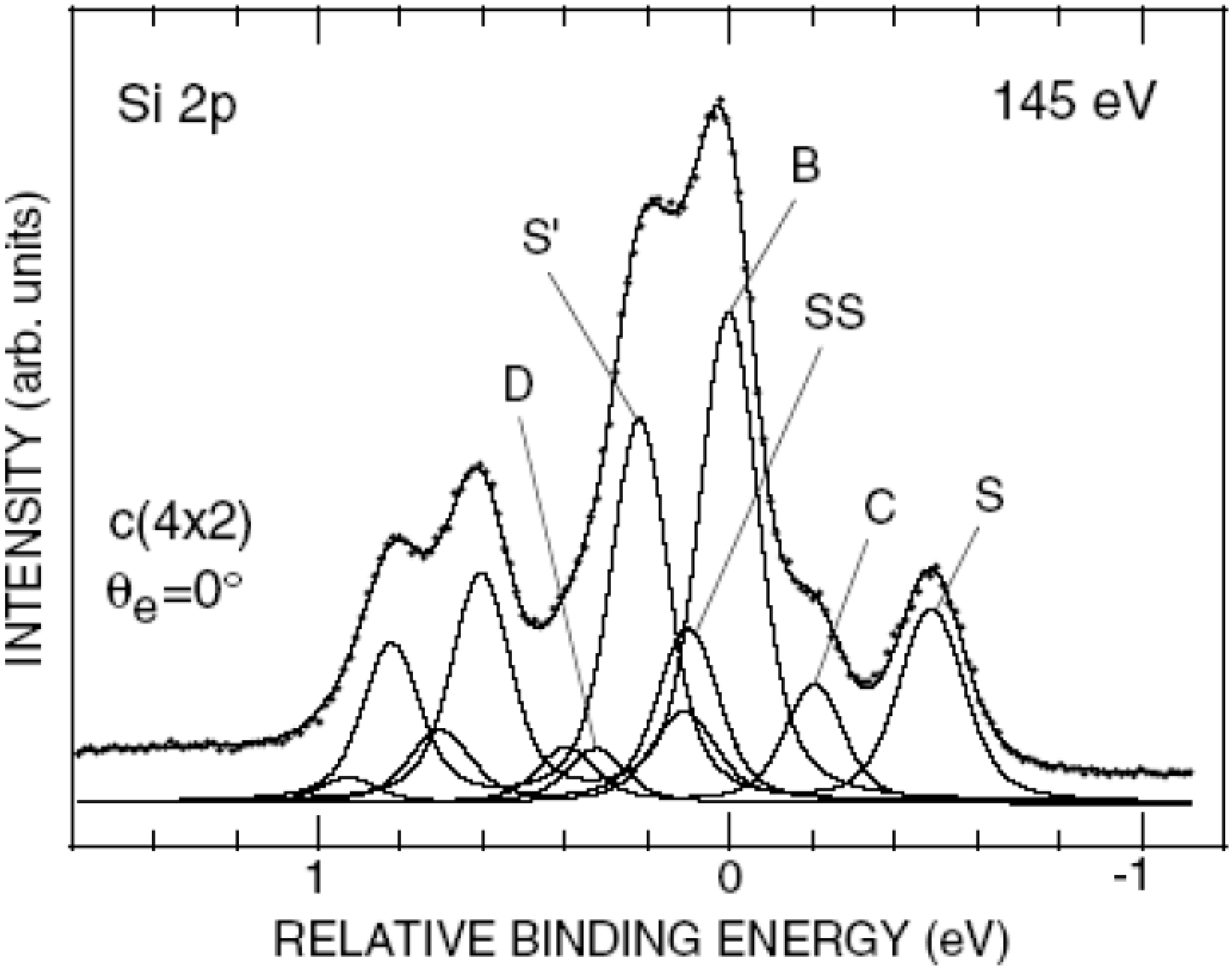
Dependent on electron kinetic energy

Si(100)-2x1



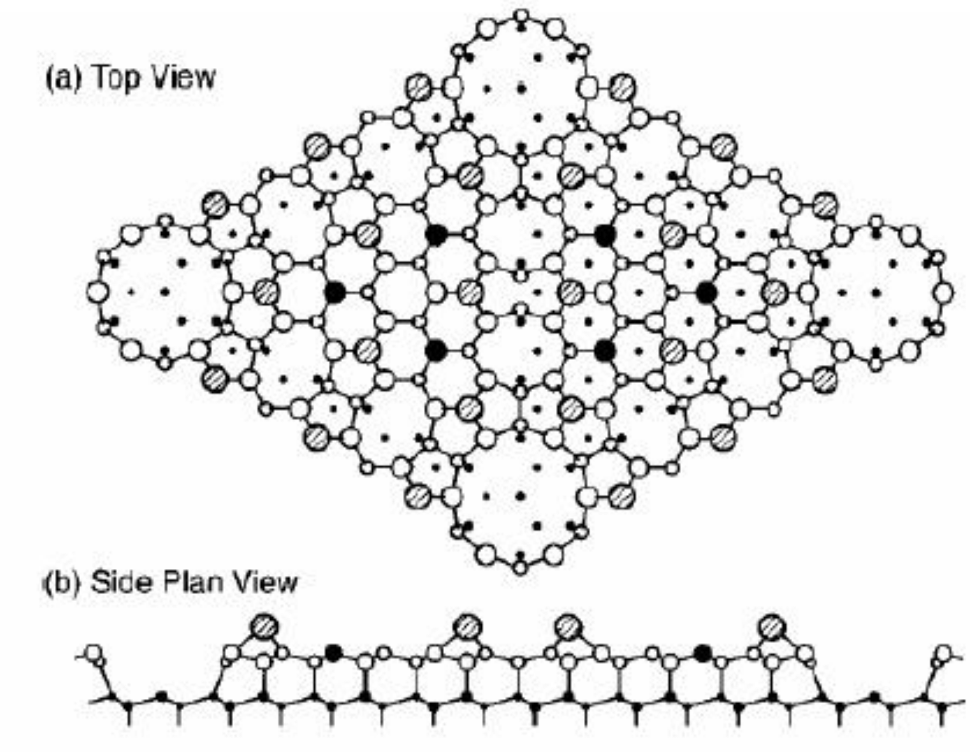


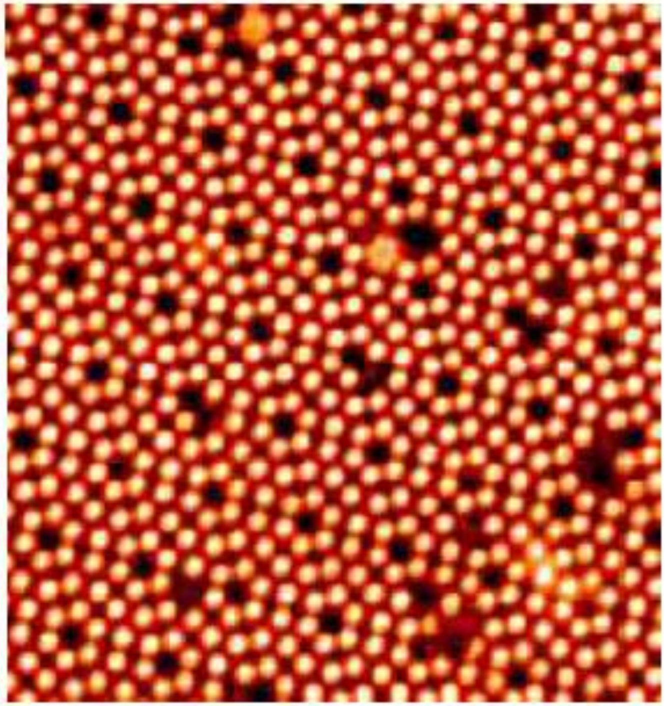
R. I. G. Uhrberg, J. Phys.: Condens. Matter 13 (2001) 11181

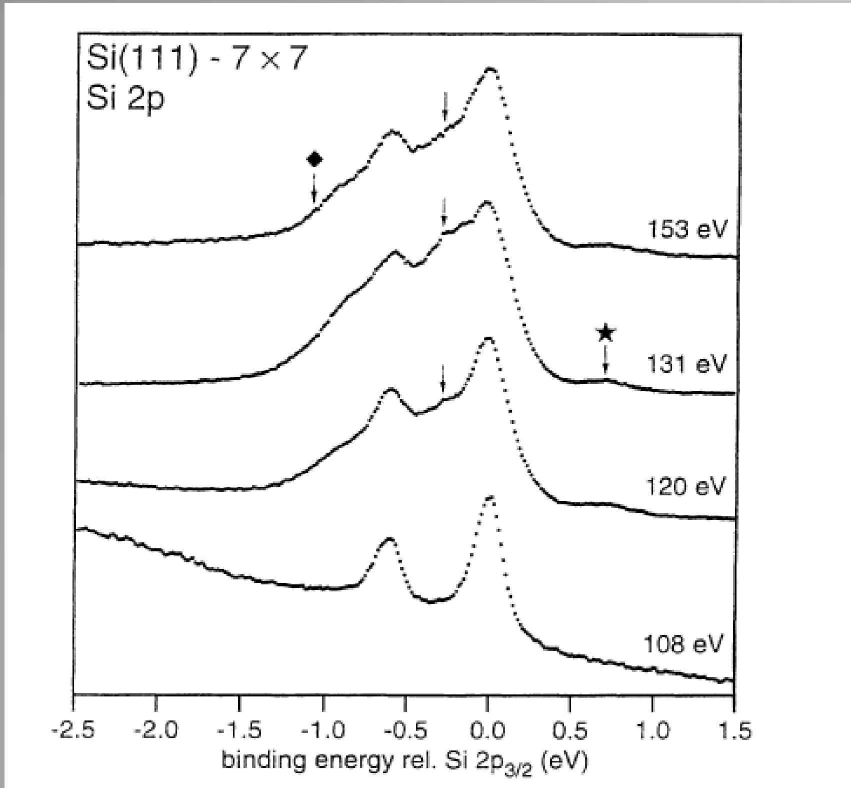


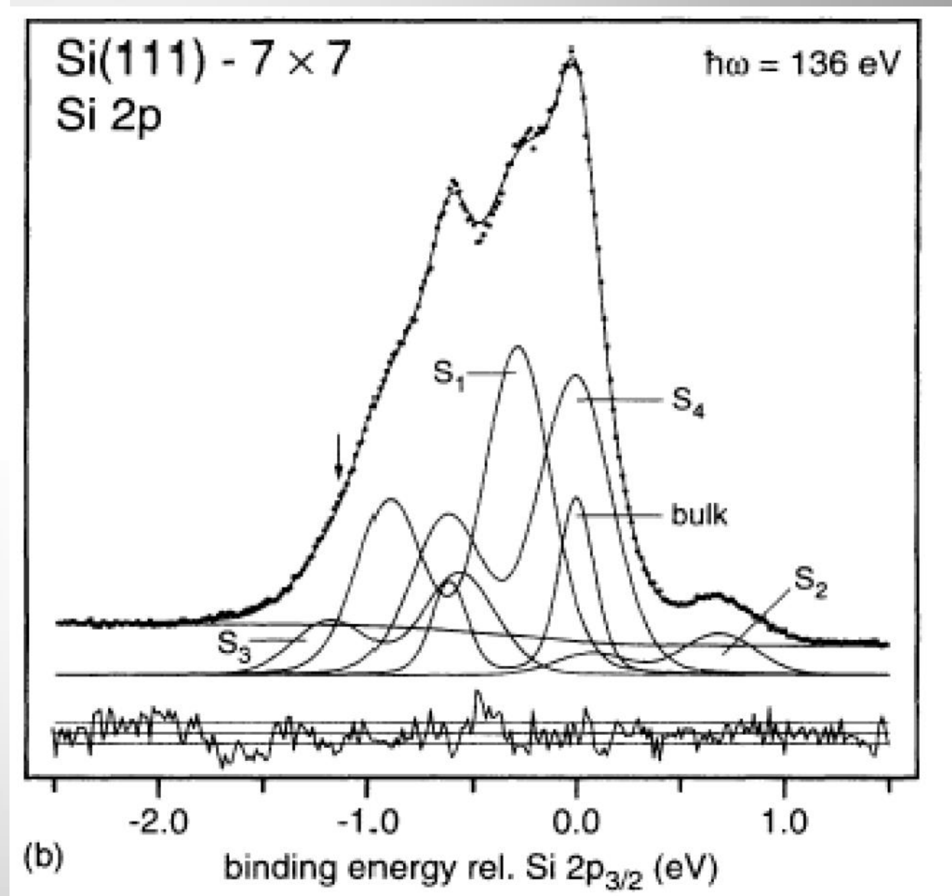
Si 2p
145 eV
B
S'
SS
D
C
S
c(4x2)
$\theta_e=0°$
INTENSITY (arb. units)
1
0
-1
RELATIVE BINDING ENERGY (eV)

STM image of Si(111)-7x7



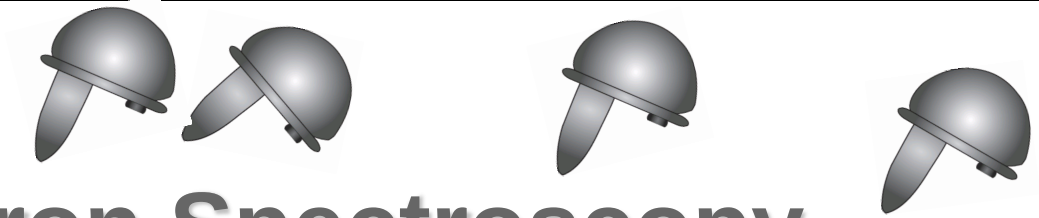




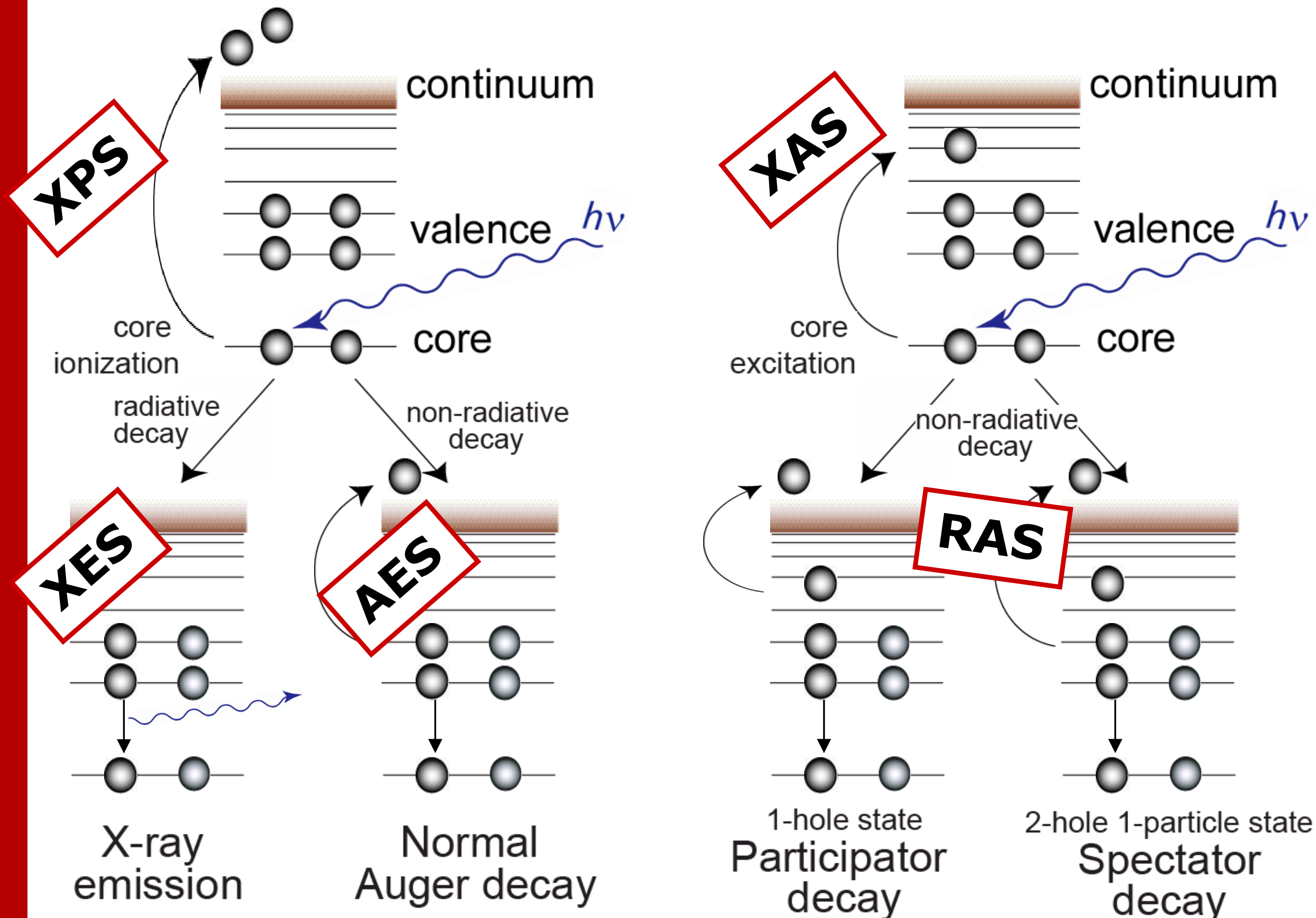


J.J.Paggel, W.Theis. K.Horn, Ch.Jung, C.Hellwing and H.Petersen
Phys.Rev.B 50, (1994) 18686

UPPSALA UNIVERSITET



Electron Spectroscopy



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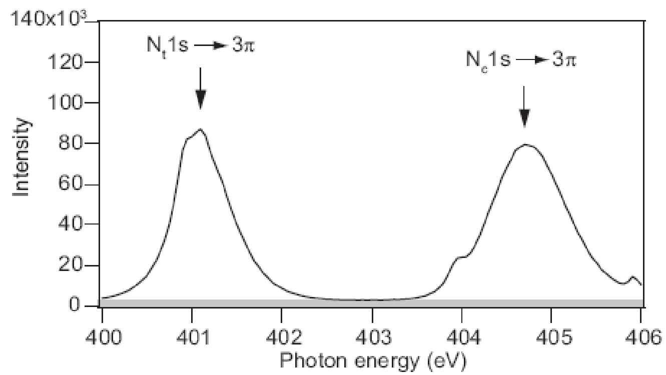
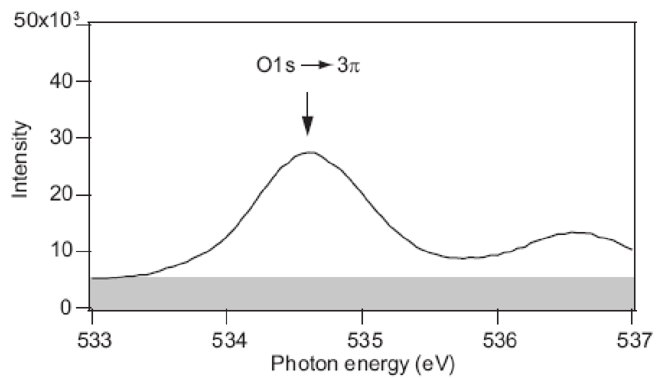
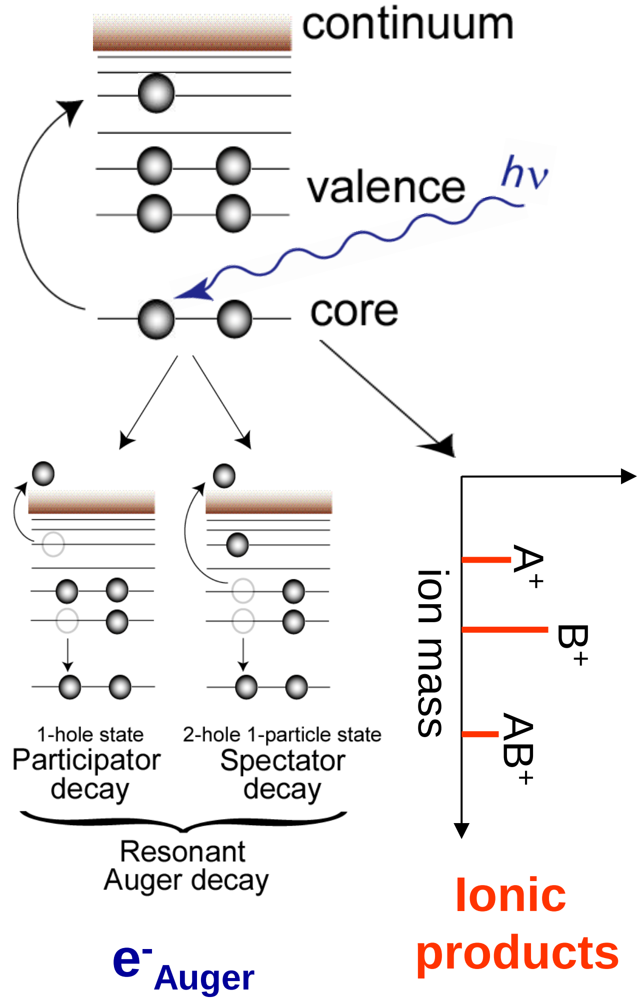
X-ray Absorption Spectroscopy of N_20

N≡N=O

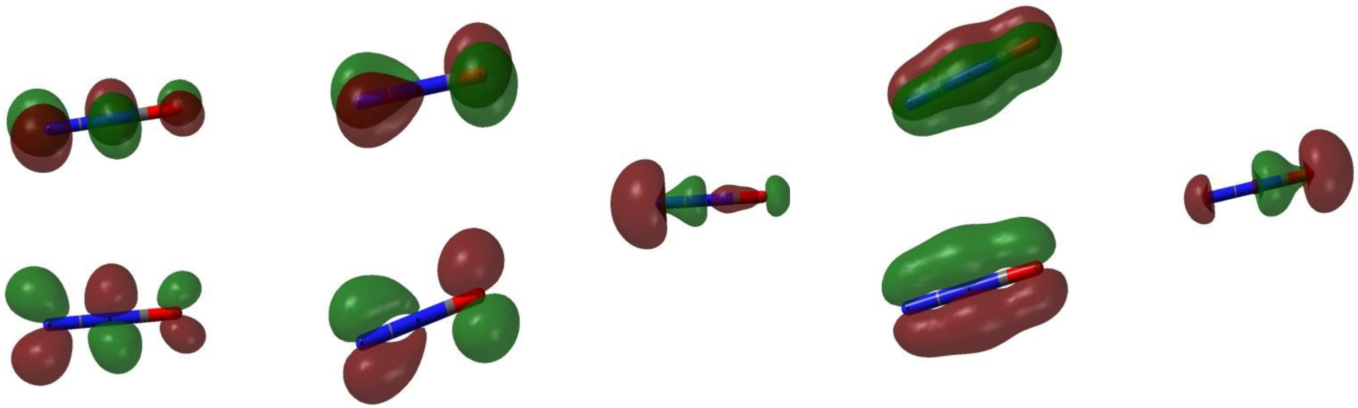






Decay Processes in Core-Excited N2O

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4 7\sigma^2 2\pi^4 3\pi \quad {}^1\Sigma^+$$



M N Piancastelli et al., J.Phys.B: At.Mol.Opt.Phys. 40, 3357(2007)

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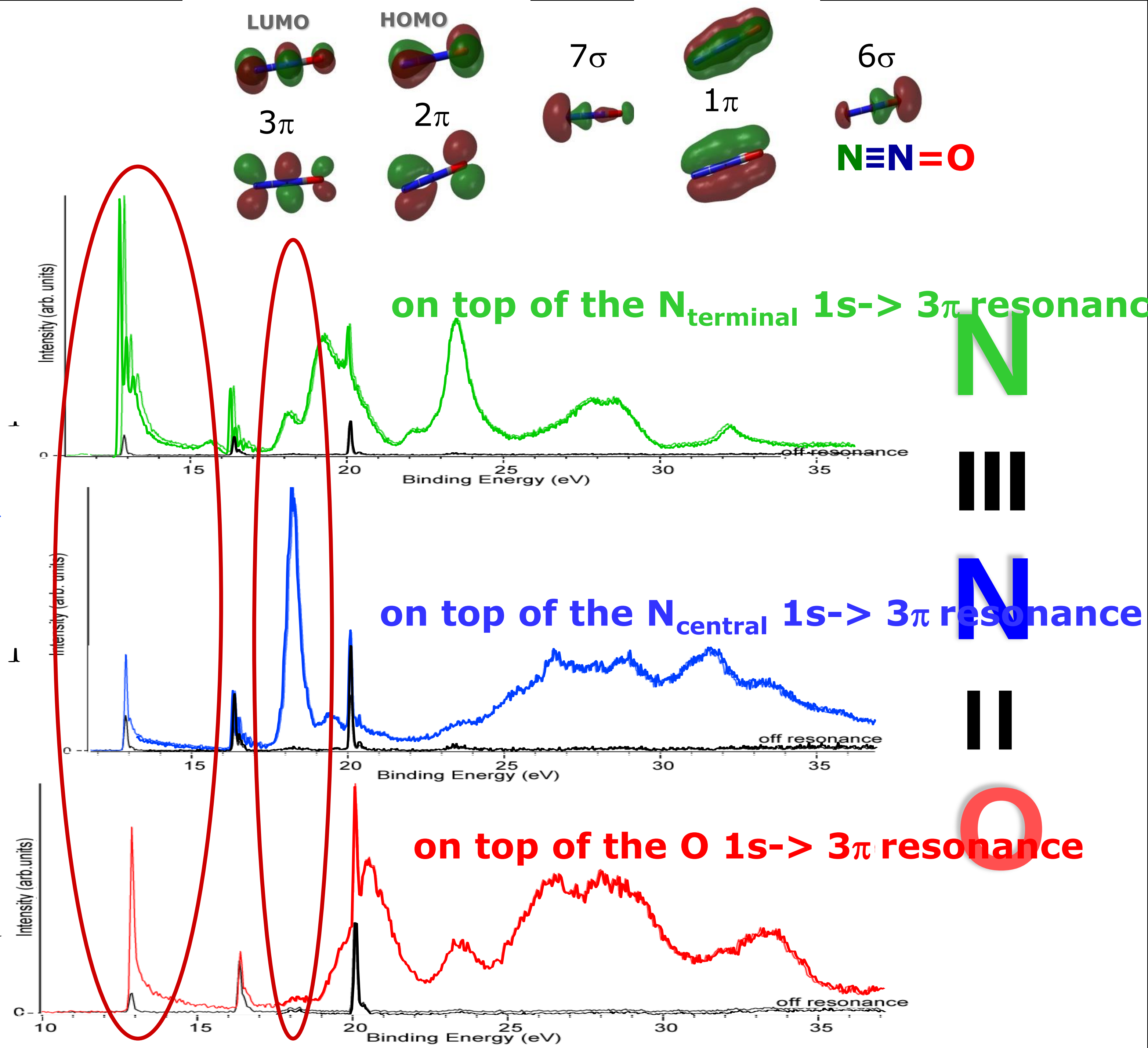
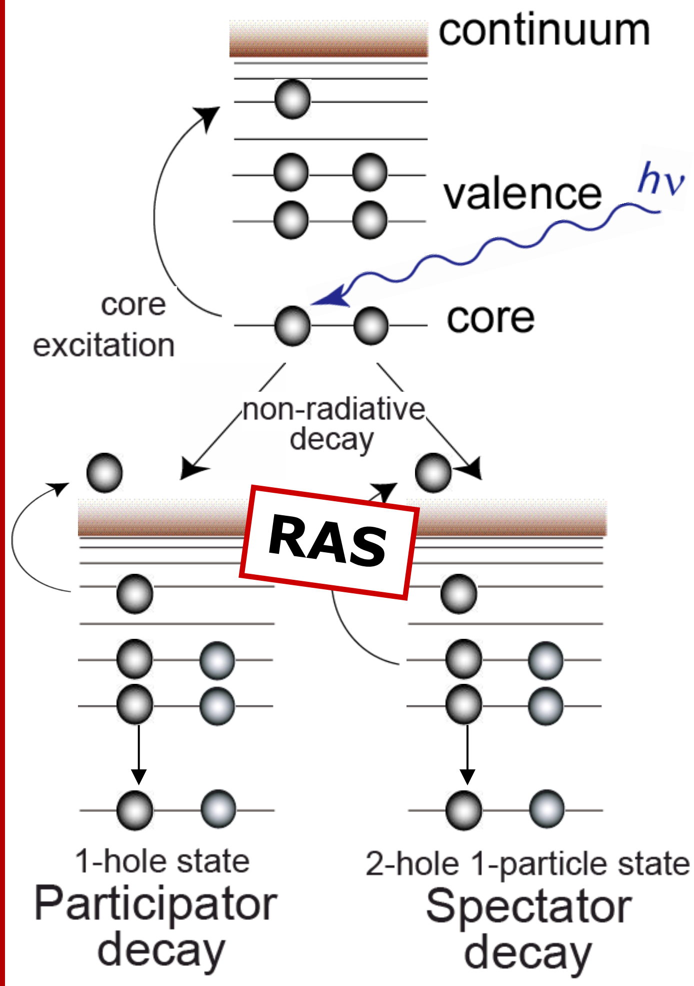
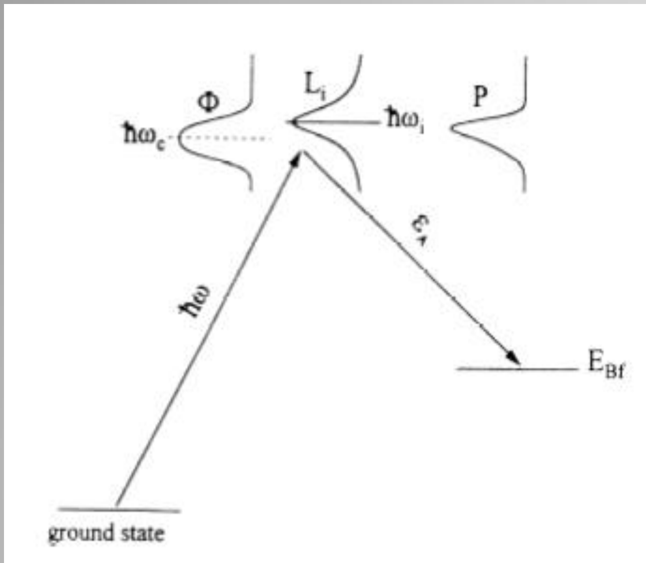


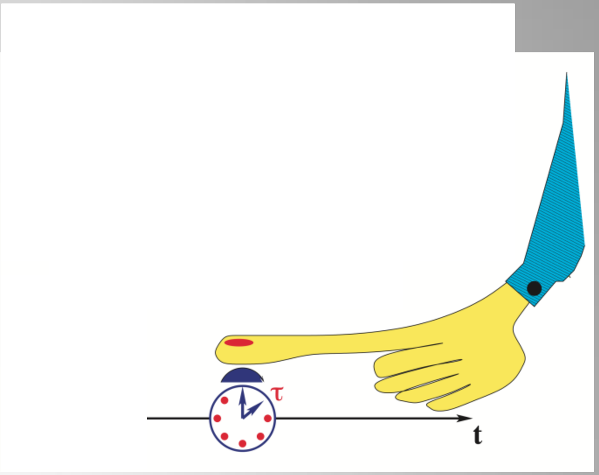
Nuclear dynamics of core-excited systems



Possible mechanisms of nuclear dynamics:

- ultrafast dissociation
- geometry change
  - e.g. bending, twisting
- conformational changes



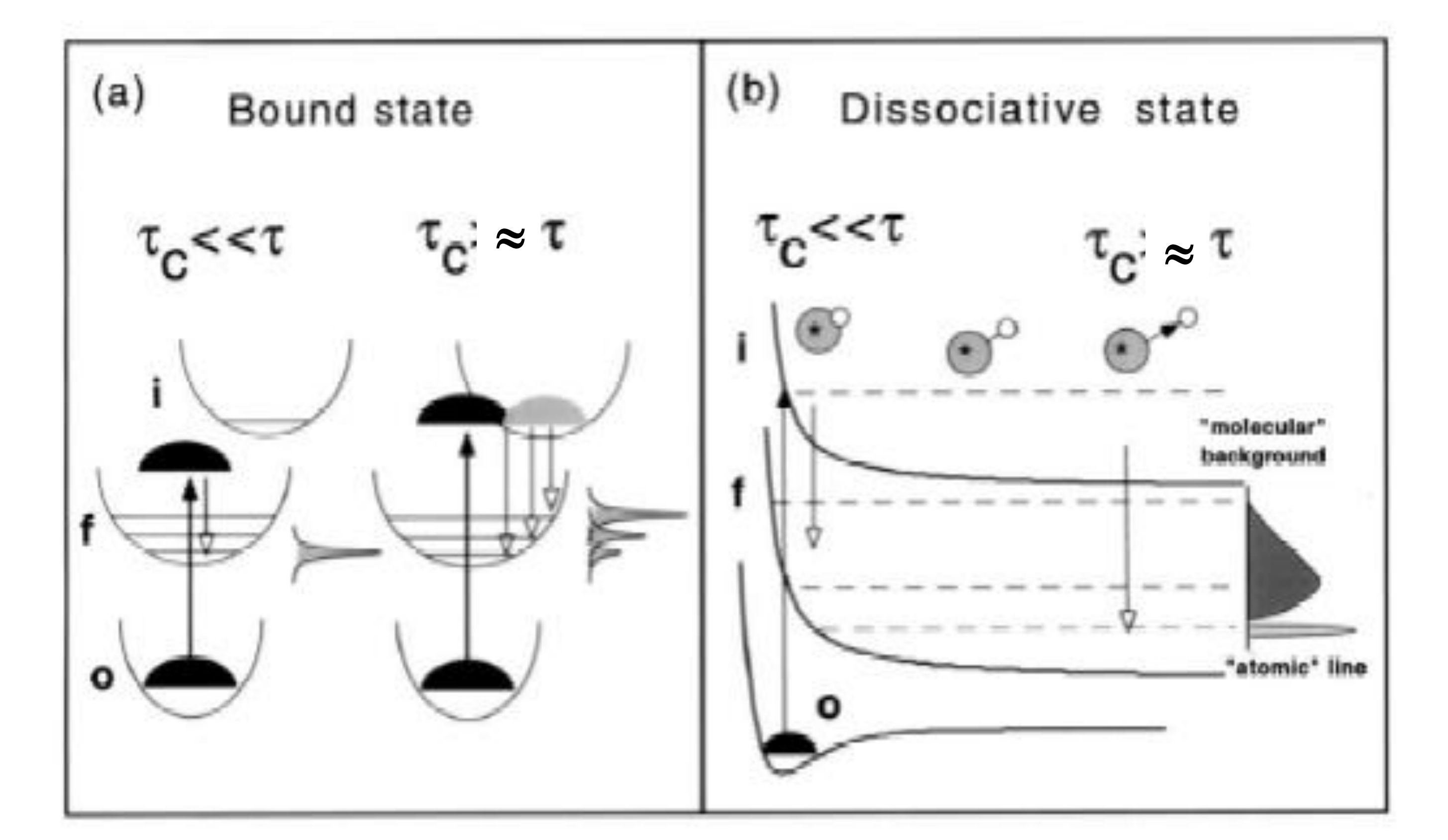


Auger resonant Raman conditions:

Photon bandwidth much narrower than the natural lifetime width of the intermediate state

Core-hole clock

$$(\Delta T)\ (\Delta E) \geq \hbar/2$$



duration time

$$\tau_c = \frac{1}{\sqrt{\Gamma^2 + \Omega^2}}$$

Nuclear Dynamics of core-excited systems

Ultrafast dissociation

VOLUME 56, NUMBER 18 PHYSICAL REVIEW LETTERS 5 MAY 1986

Atomic Autoionization Following Very Fast Dissociation of Core-Excited HBr

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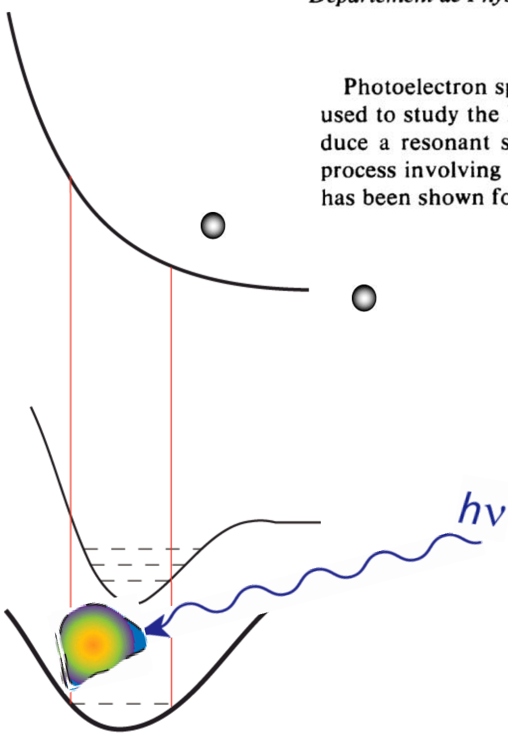
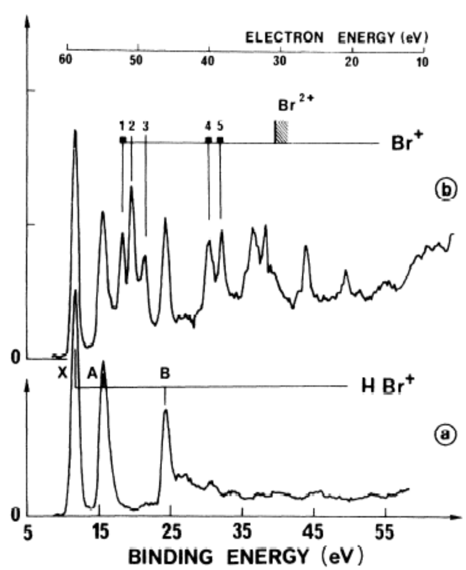
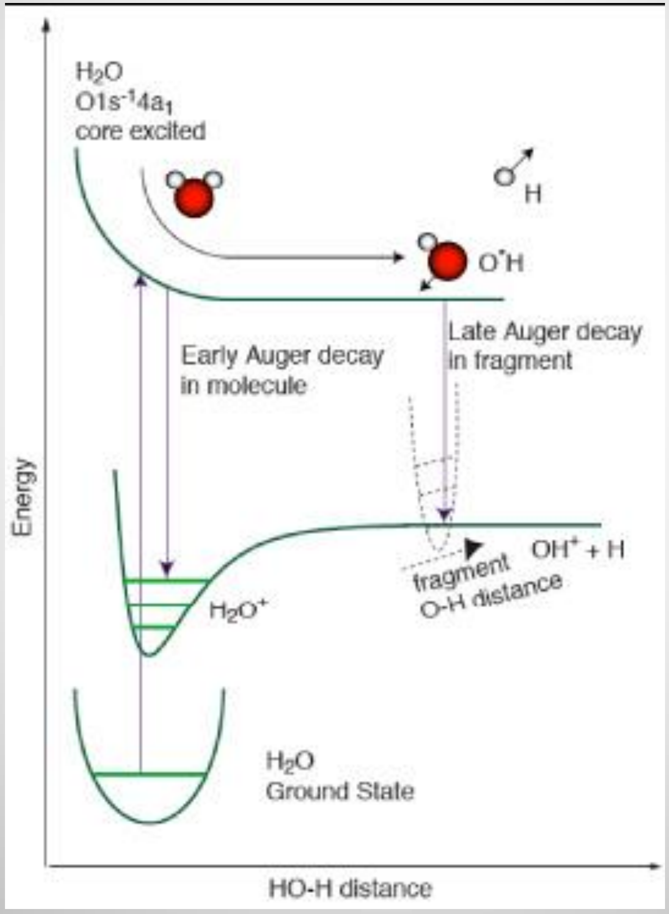
(Received 28 February 1986)

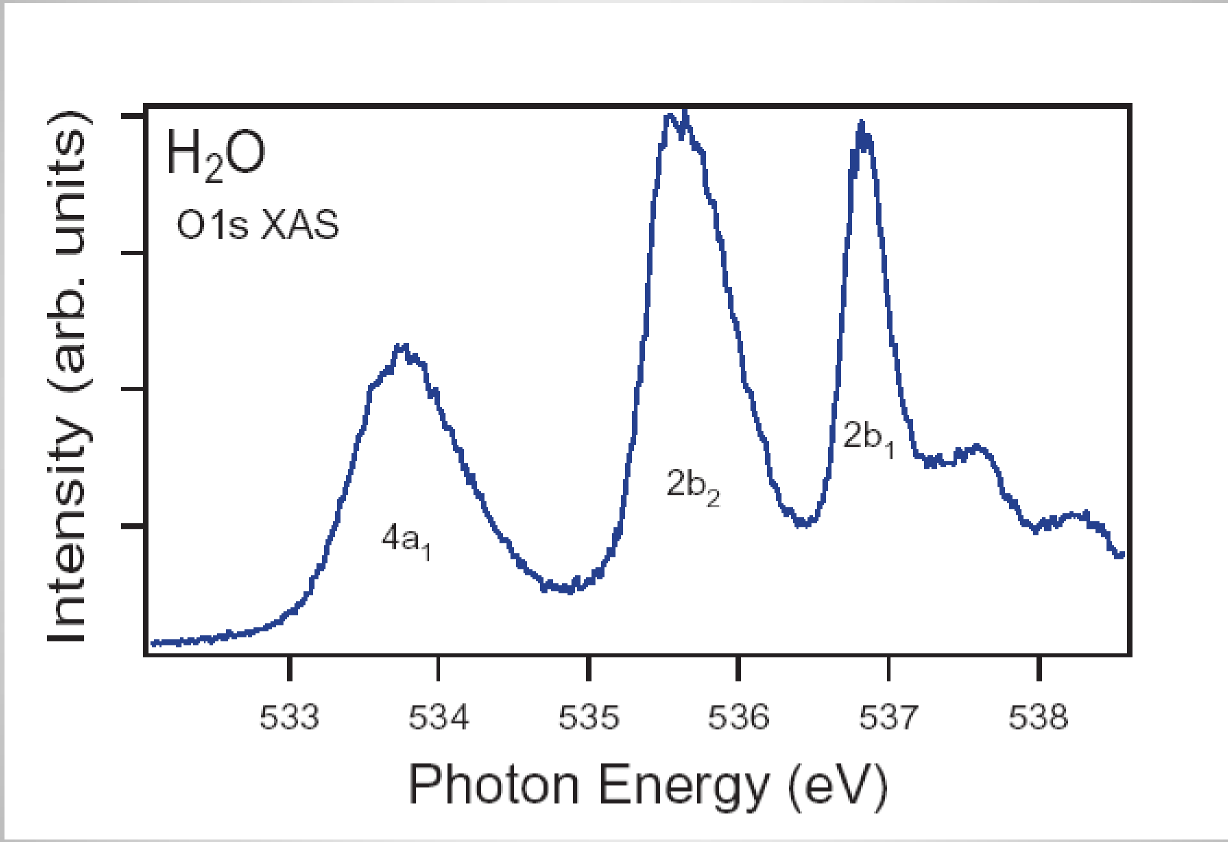
Photoelectron spectroscopy excited by monochromatic synchrotron radiation (68–80 eV range) is used to study the Br 3*d* excitation in HBr. The transition to an antibonding orbital is shown to produce a resonant state whose repulsive nature has been observed directly. A two-step relaxation process involving a fast neutral dissociation followed by the autoionization of the excited fragment has been shown for the first time.



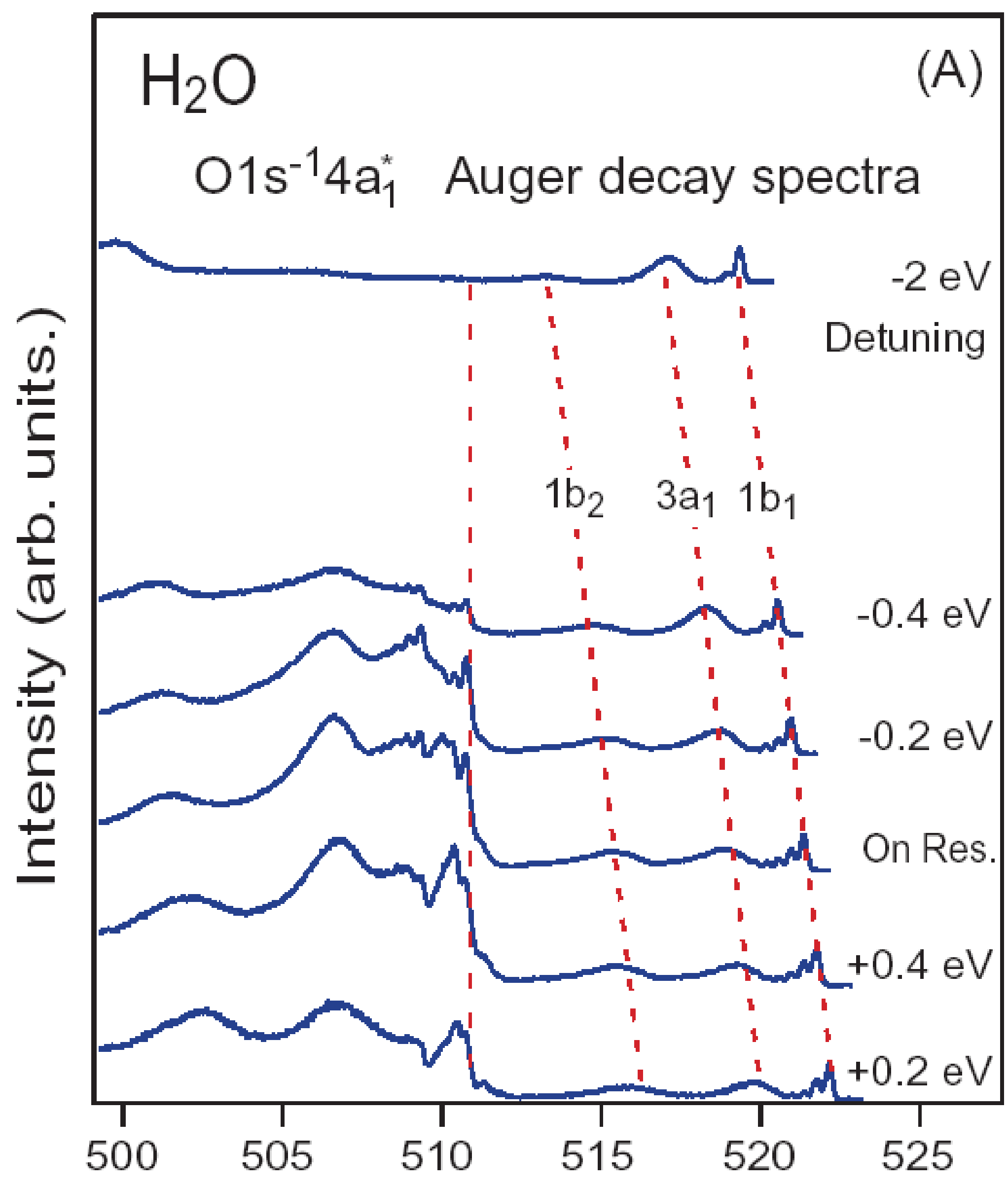


I.Hjelte, M.N.Piancastelli, R.F.Fink, O.Björneholm, M.Bässler, R.Feifel, A.Giertz, H.Wang, K.Wiesner, A.Ausmees, C.Miron, S.L.Sorensen and S.Svensson, Chem.Phys.Lett. 334, (2001) 151

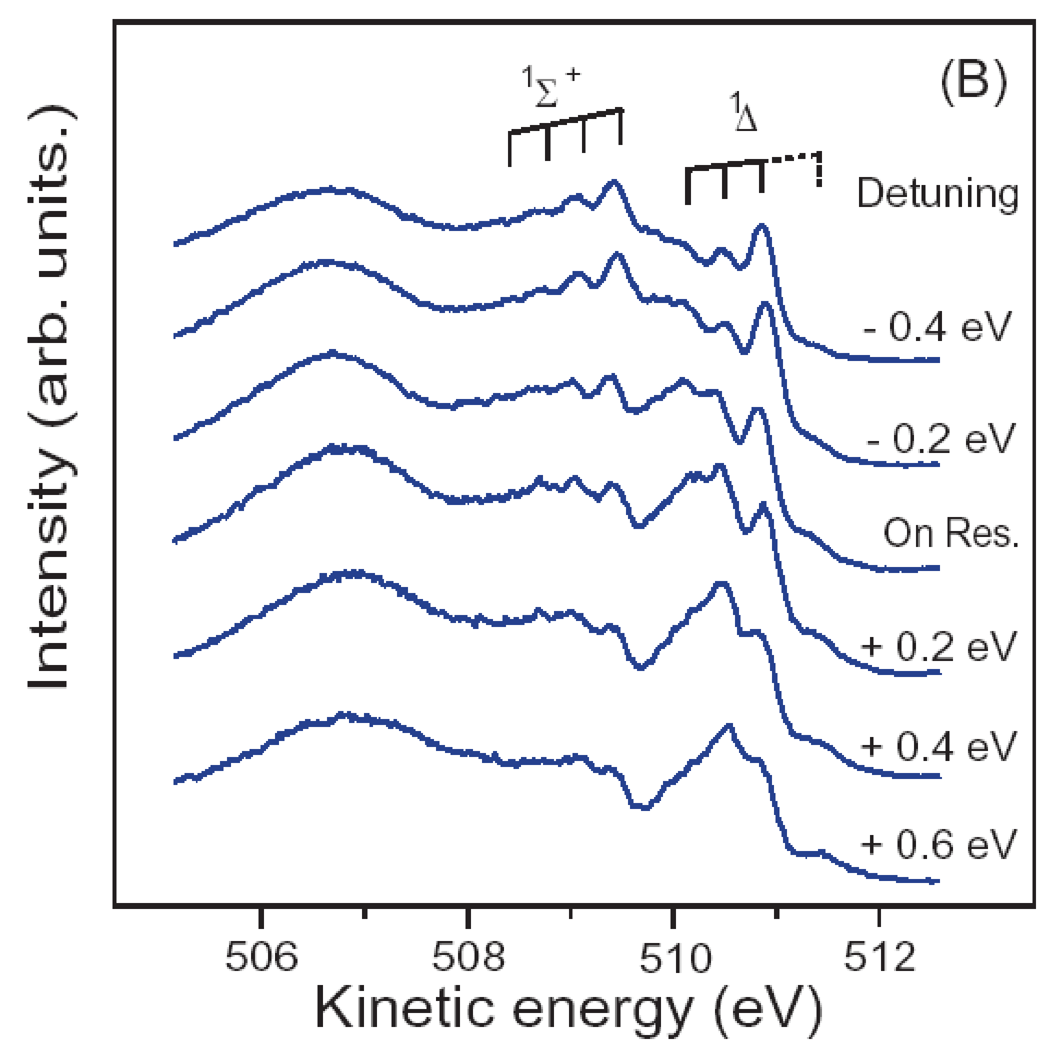




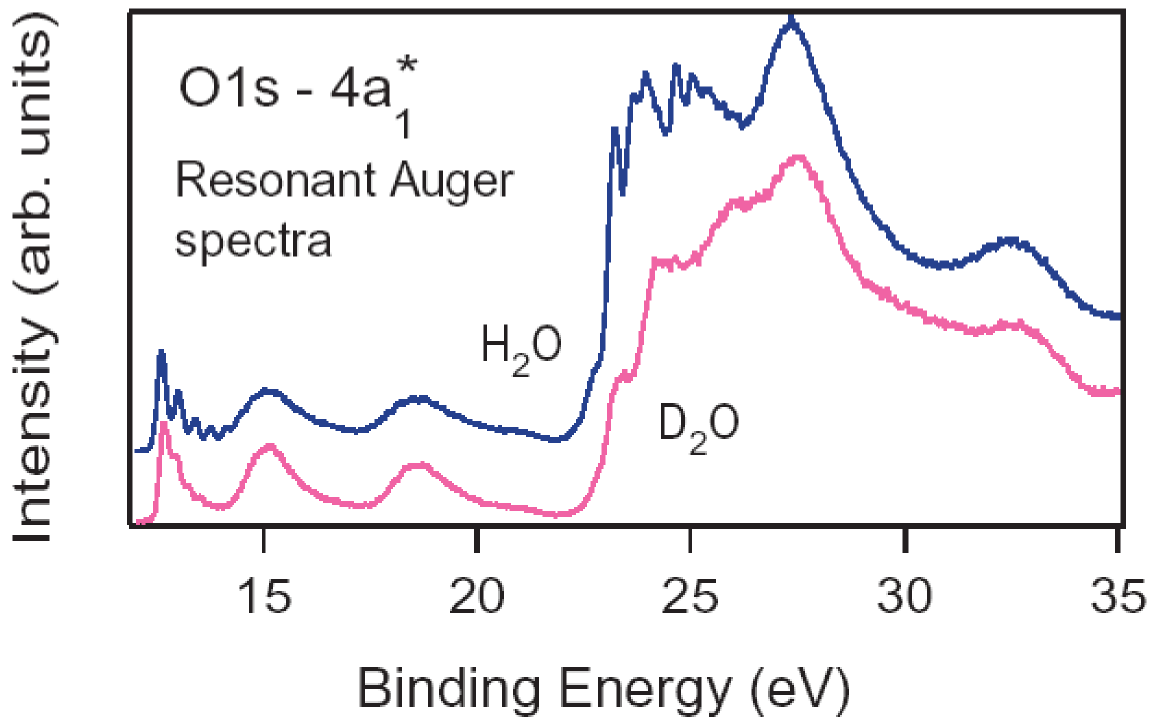
H2O
O1s XAS
4a1
2b2
2b1
Intensity (arb. units)
533
534
535
536
537
538
Photon Energy (eV)



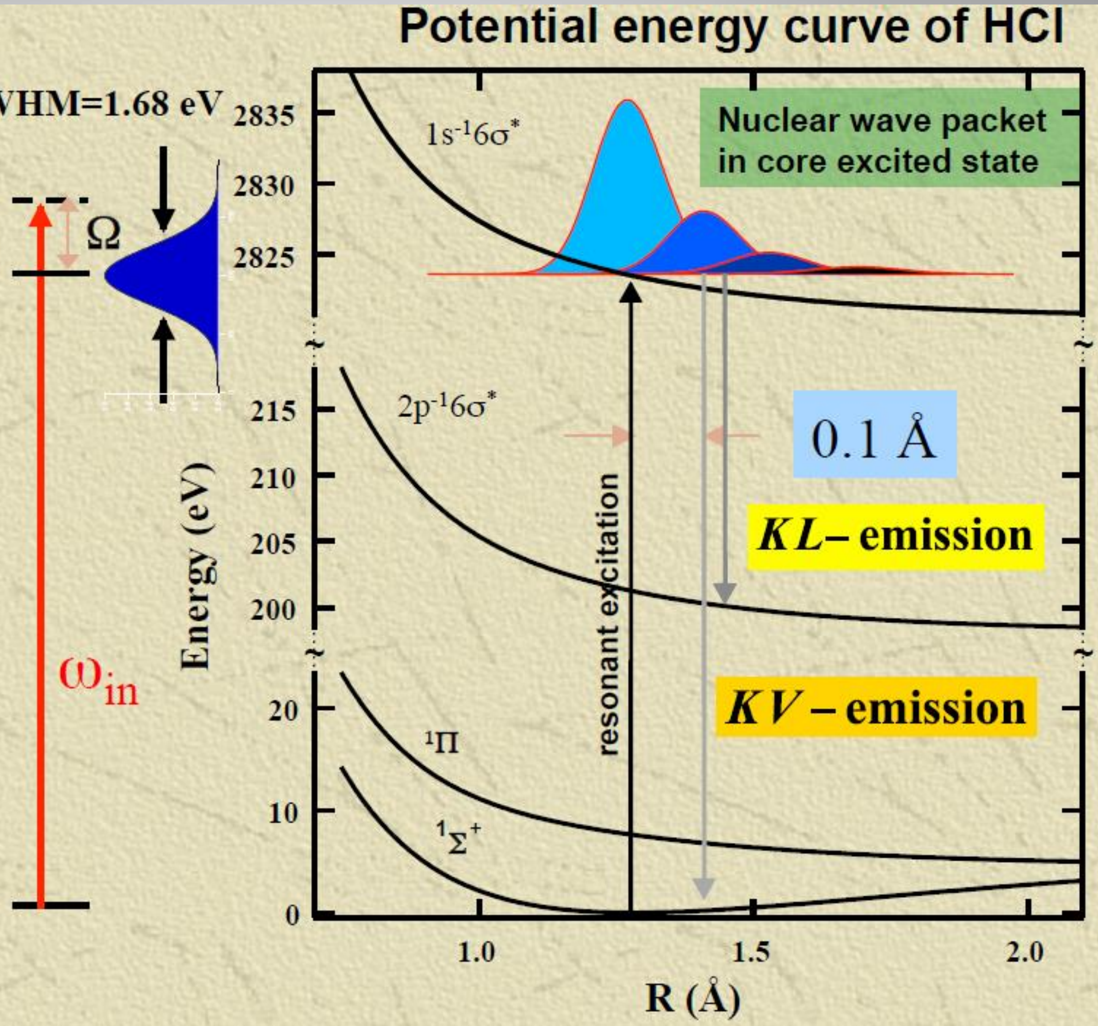
H_2O
(A)
$O1s^{-1}4a_1^*$ Auger decay spectra
-2 eV
Detuning
$1b_2$
$3a_1$
$1b_1$
-0.4 eV
-0.2 eV
On Res.
+0.4 eV
+0.2 eV
Intensity (arb. units.)
500
505
510
515
520
525



(B)
$^1\Sigma^+$
$^1\Delta$
Detuning
- 0.4 eV
- 0.2 eV
On Res.
+ 0.2 eV
+ 0.4 eV
+ 0.6 eV
Intensity (arb. units.)
506
508
510
512
Kinetic energy (eV)


O1s - 4a$_1^*$
Resonant Auger
spectra
H_2O
D_2O
Intensity (arb. units)
15
20
25
30
35
Binding Energy (eV)

- lifetime(~1 fs)
- Fluorescence yield
- Cl K edge HCl, CH_3Cl, CF_3Cl….
- "Core-hole clock experiment" using RIXS
- Nuclear dynamics



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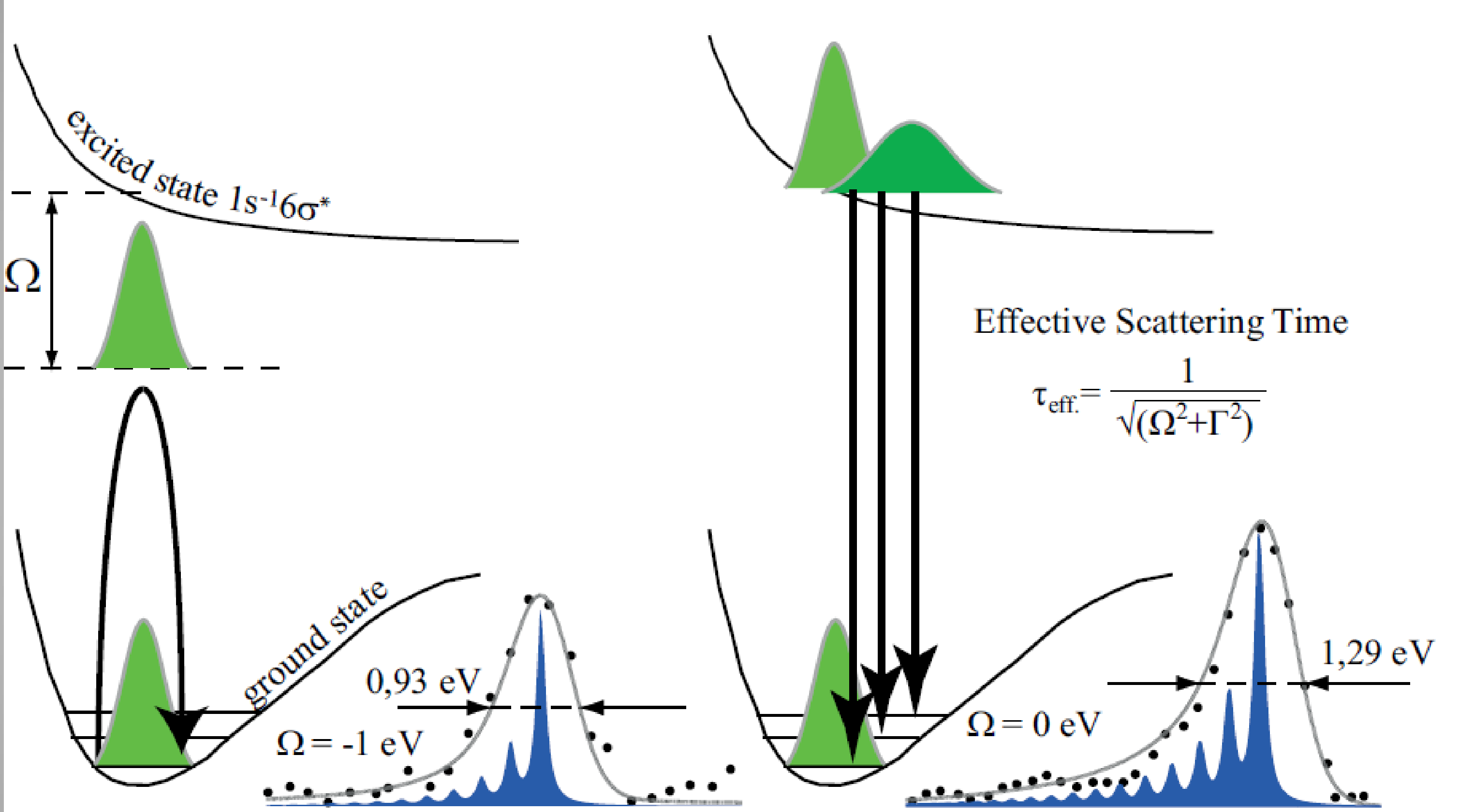
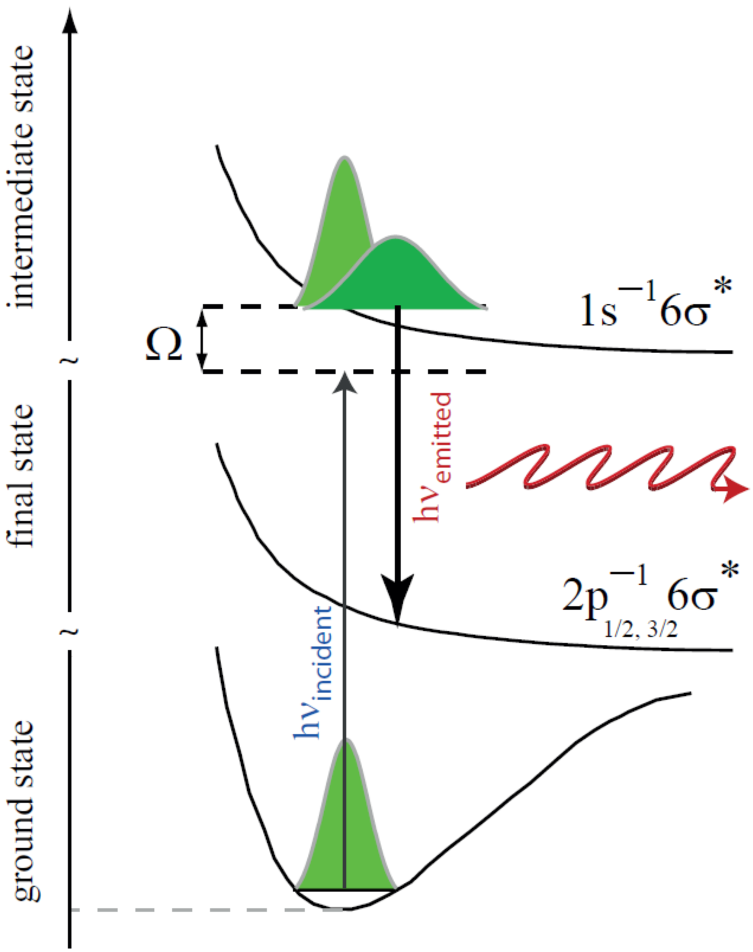
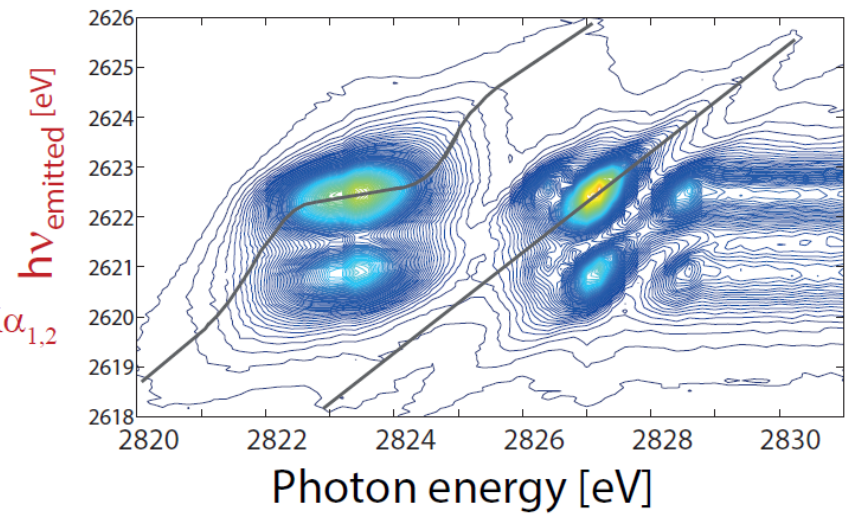

excited state $1s^{-1}6\sigma^*$
Ω
ground state
0,93 eV
Ω = -1 eV
Effective Scattering Time
$\tau_{eff.} = \frac{1}{\sqrt{(\Omega^2+\Gamma^2)}}$
1,29 eV
Ω = 0 eV


intermediate state
final state
ground state
Ω
$1s^{-1}6\sigma^*$
$2p^{-1}_{1/2,\,3/2}\,6\sigma^*$
$h\nu_{incident}$
$h\nu_{emitted}$
$K\alpha_{1,2}$


$h\nu_{emitted}$ [eV]
2626
2625
2624
2623
2622
2621
2620
2619
2618
2820
2822
2824
2826
2828
2830
Photon energy [eV]

https://www.elettra.trieste.it/XIIISILS/index.php?n=Main.Lessons

http://talkminer.com/viewtalk.jsp?videoid=YDlYHw09QrI&q=#.VqnnWeZG8QM

http://www-ssrl.slac.stanford.edu/nexafs.html