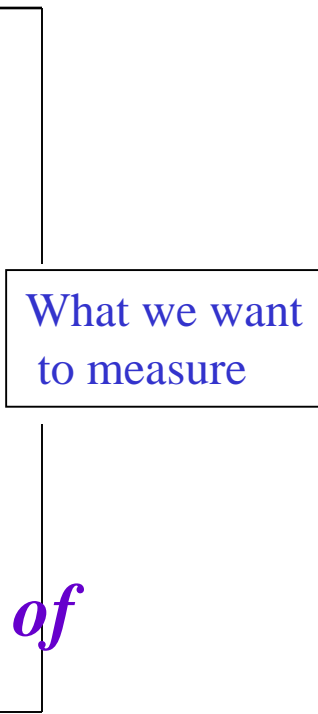


Absorption-based spectroscopy

- Absorption spectroscopy (*modulation of μ*)
 - **NEXAFS** spectroscopy of low Z elements (C, N, O, F, etc K-edge, Si, P, S, L-edges)
 - **XAFS** (**XANES** and **EXAFS**) spectroscopy or **XAS** of intermediate Z and high Z elements
 - Photoemission spectroscopy or photoelectron spectroscopy (*binding energy and distribution of electrons*) XPS, UPS ESCA etc.
 - gas phase (relative to vacuum level)
 - solids (relative to Fermi level of the spectrometer)
- 
- What we want to measure

NEXAFS, XANES and EXAFS

- **NEXAFS** (Near Edge X-ray Absorption Fine Structures) is used to describe the absorption features in the vicinity of an absorption edge up to ~ 50 eV above the edge (for low Z elements for historical reasons).
- It is exactly the same as **XANES** (X-ray Absorption Near Edge Structures), which is often used together with **EXAFS** (Extended X-ray Absorption Fine Structures) to describe the modulation of the absorption coefficient of an element in a chemical environment from ~ 50 eV to as much as 1000 eV above the threshold

NEXAFS, XANES and EXAFS

- XAFS (X-ray Absorption Fine Structure) (XAS for short, XAS is sometimes used to represent XANES or NEXAFS)

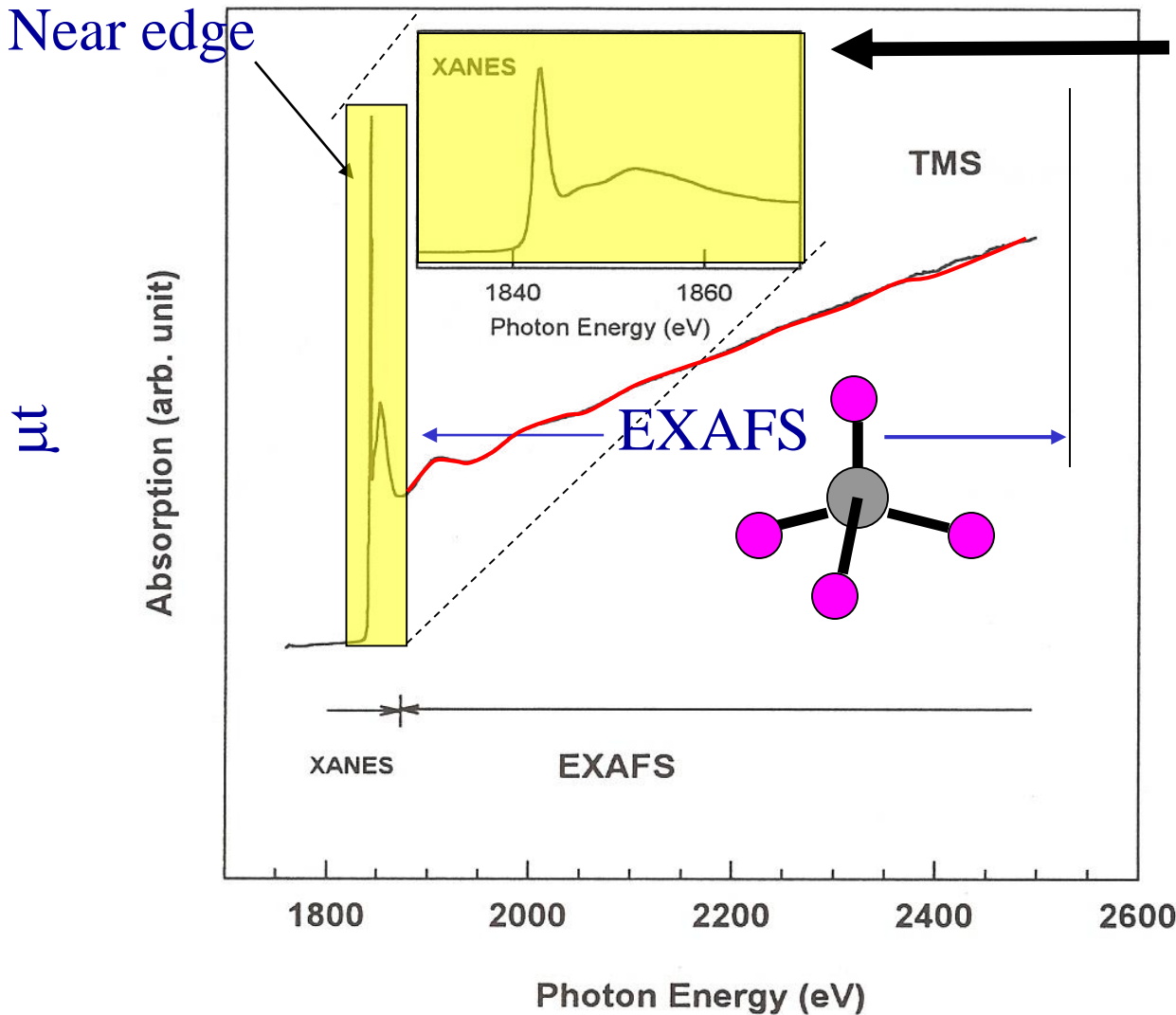
more contemporary term:

$$\text{XAFS} = \text{XANES} + \text{EXAFS}$$

- NEXAFS and XANES are used interchangeably

What is XAFS?

Near edge



XANES

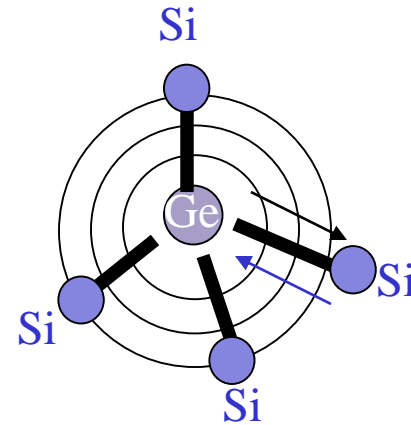
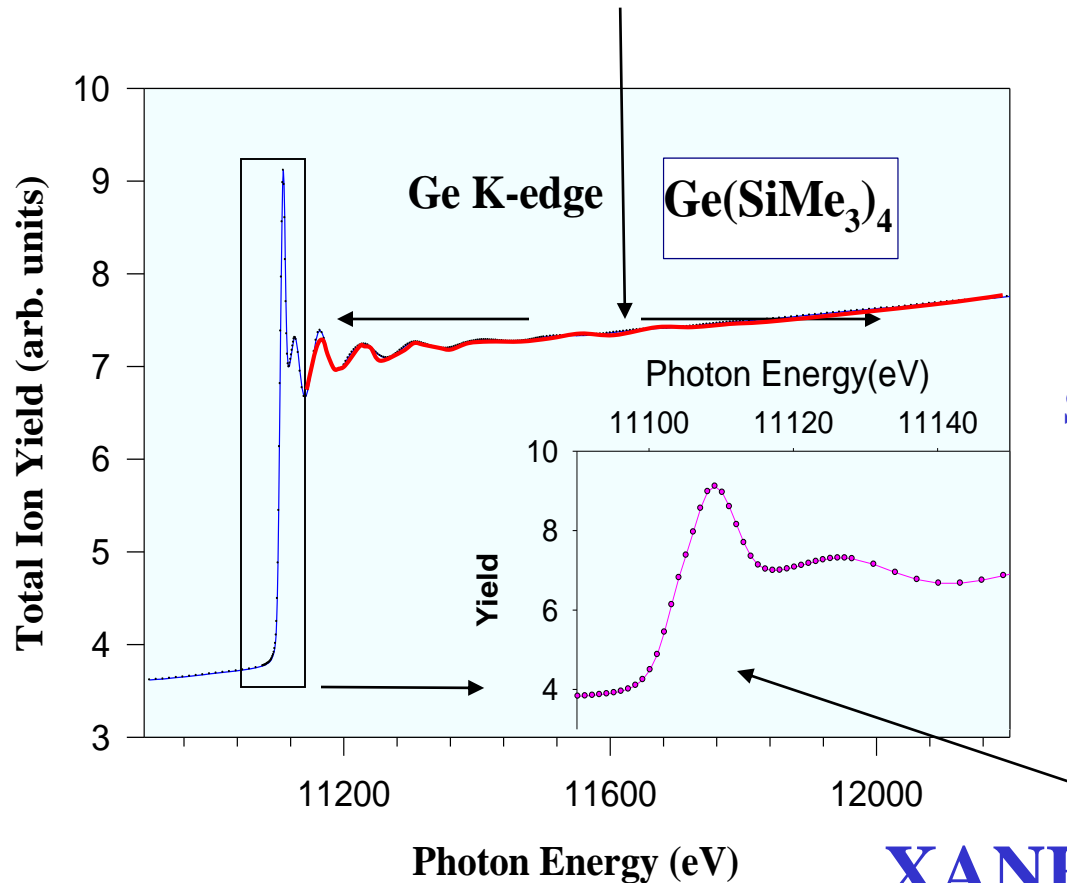
NEXAFS

Si 1s to LUMO

$(t_3), a_1$

$\text{Si}(\text{CH}_3)_4$

EXAFS (the interference of outgoing and backscattered electron waves) 1s - continuum

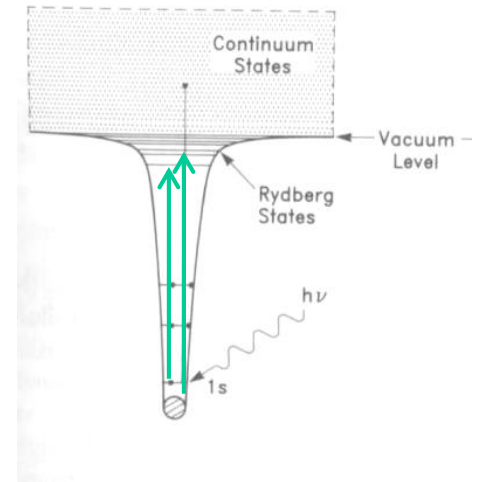
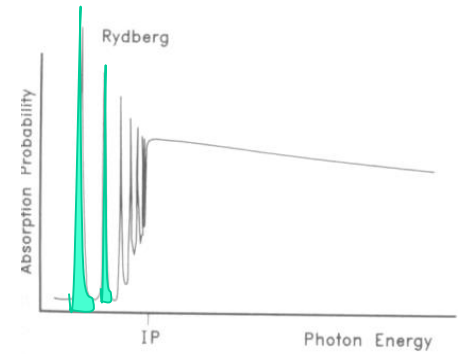


XANES (1s – LUMO, etc.)
1s – bound, quasi bound

**Region of interest for
XEOL, XES, Auger**

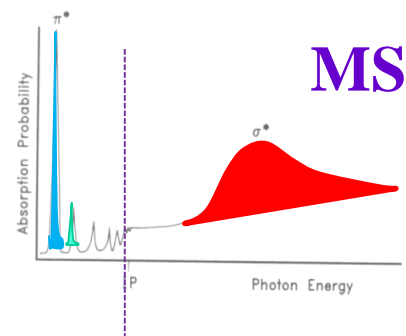
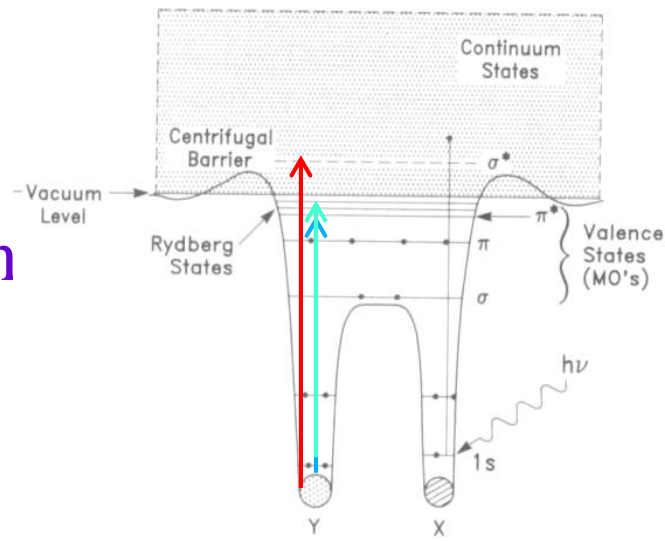
XAFS of free atom and small molecules

- In rare gases, the pre-edge region exhibits a series of sharp peaks arising from bound to bound transitions (dipole) called Rydberg transitions
- Spectra can be interpreted in terms of Term Values (TV) defined as the difference between ionization limit A and the Rydberg energy E_n (often dealt with the quantum defect theory, a defect parameter modifies the hydrogen-like E_n expression)



XAFS of free atom and small molecules

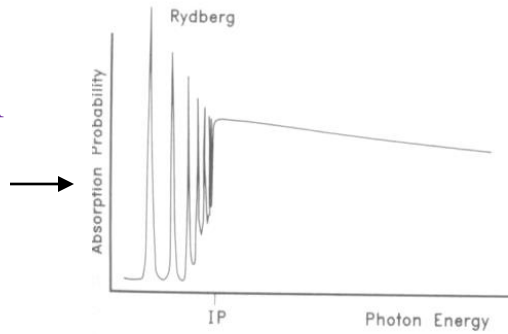
- Small molecules exhibit transitions to LUMO, LUMO + 1 etc and **virtual orbital, MO** in the continuum trapped but a potential barrier (centrifugal potential barrier set up by high angular momentum states and the presence of neighboring atoms), or sometimes known as **multiple scattering (MS) states**



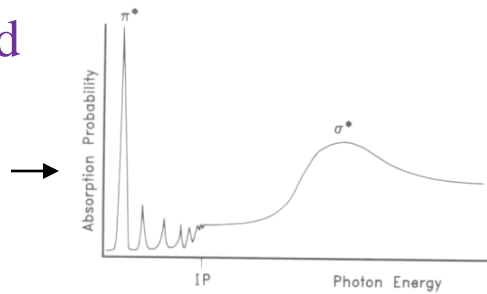
vacuum level

States trapped in the potential barrier are virtual MO's
Or multiple scattering states (quasi bound states)

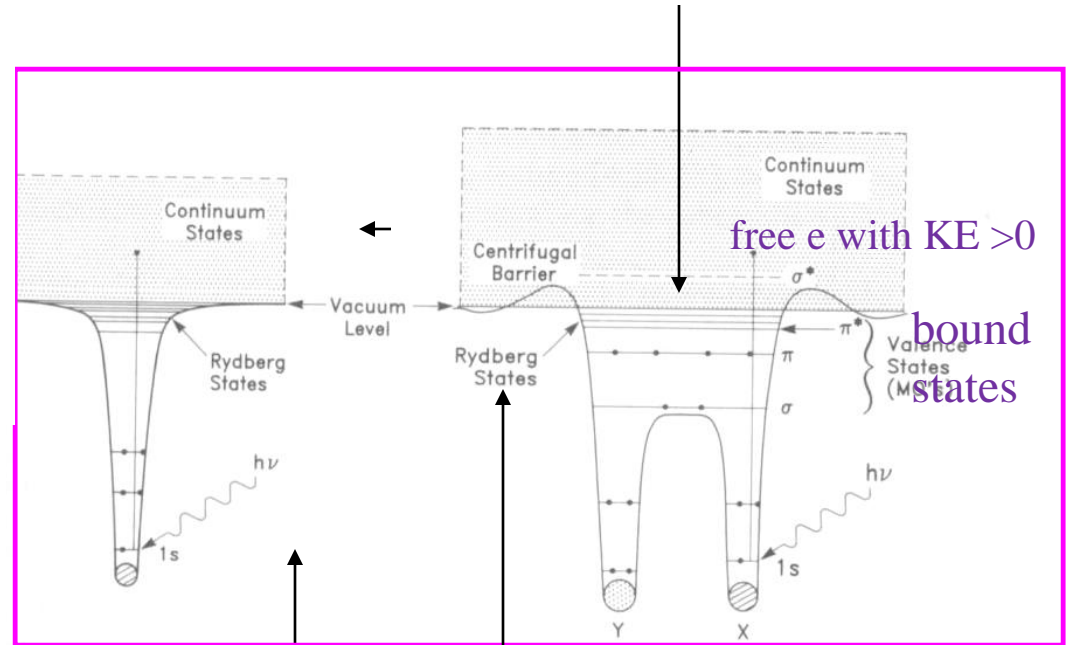
Free atom



diatomic with unsaturated Bonding
 N_2 , NO , CO etc.



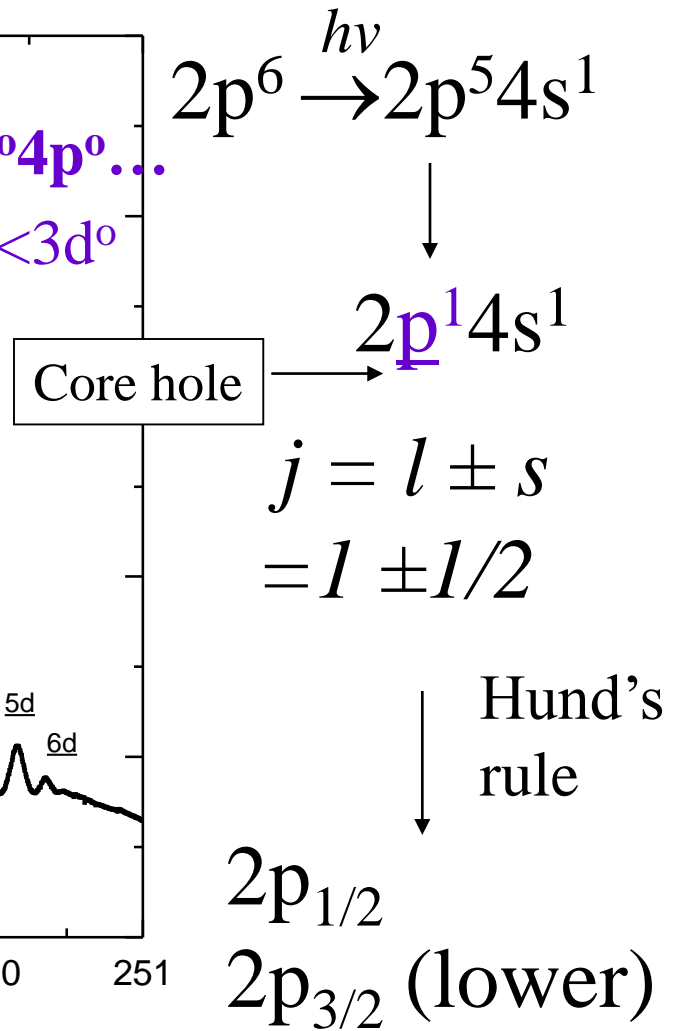
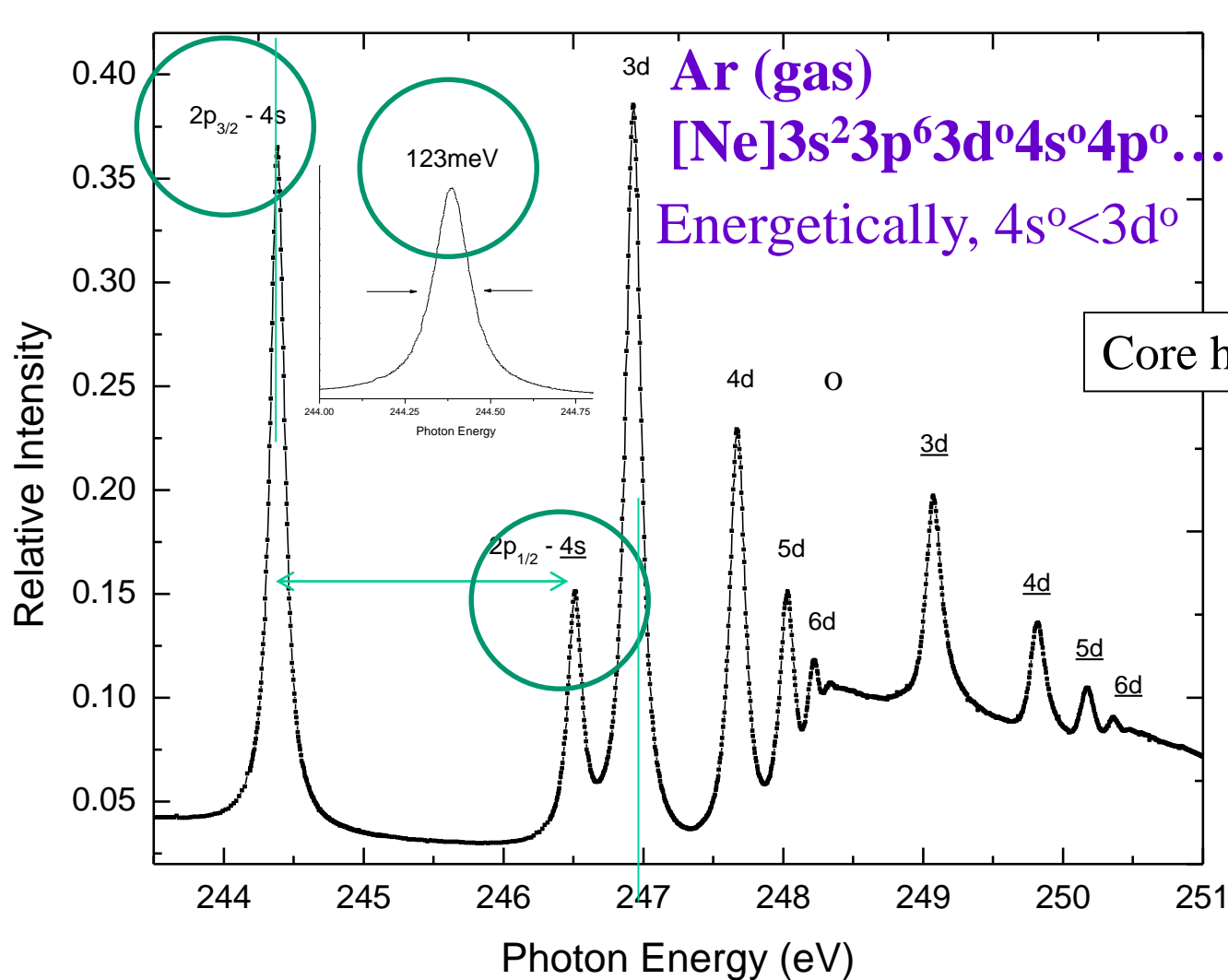
Low Z molecules with unsaturation (bond order >1, double, triple bonds, aromatic etc.)



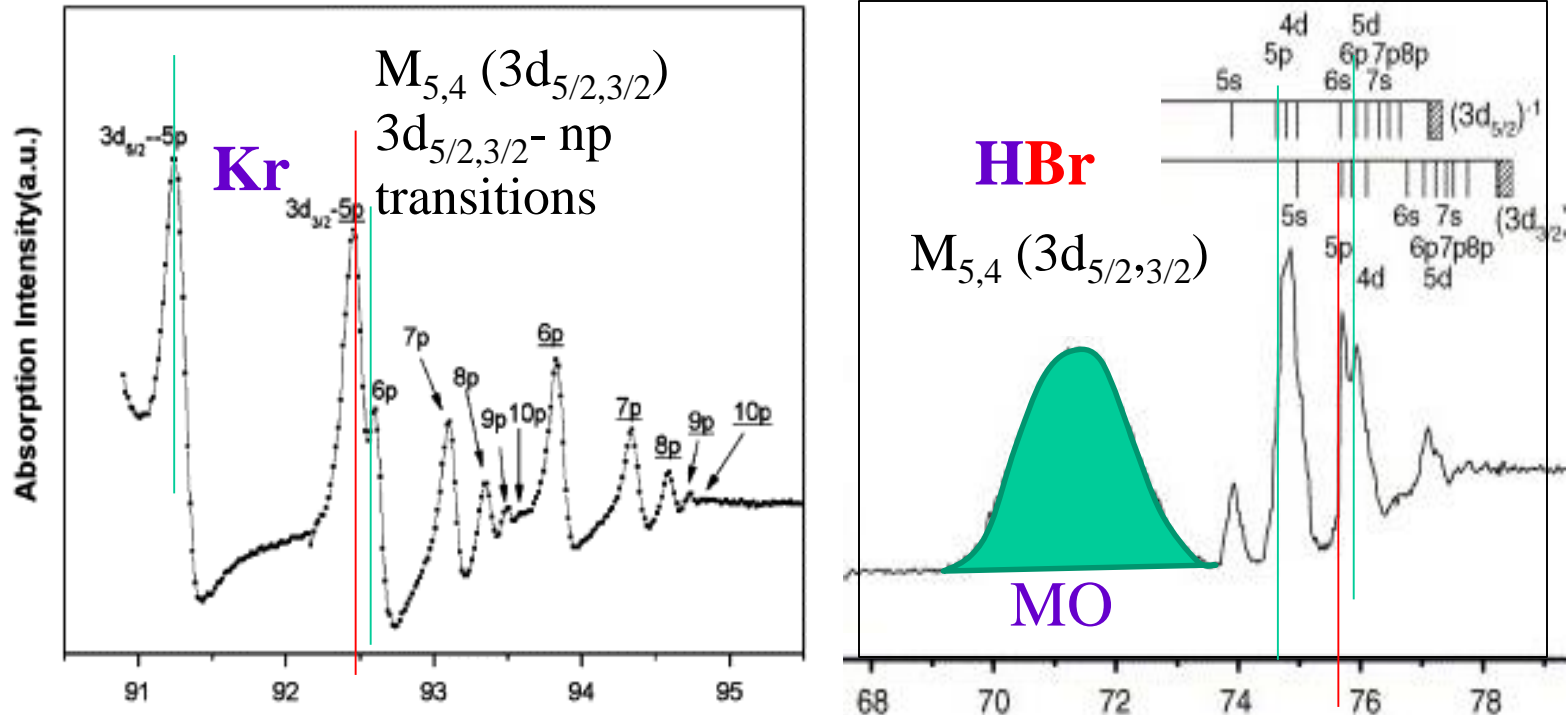
Asymptotic wing of the coulomb potential supports the Rydberg states

Ar L_{3,2} edge XANES: (Ar 2p → ns,d transitions)

Data: PGM High Energy Grating (CLS)



NEXAFS of atom and small molecules



Rydberg transitions in **HBr**, which is **isoelectronic with Kr** remain strong and a broad transition to molecular orbital emerges

What is in a resonance (peak) ?

Energy position (E): one electron energy (core level)

Peak width (Γ): convolution of the core hole lifetime broadening, instrument resolution and densities of states

$$\Delta x \cdot \Delta p = \tau \cdot \Delta E_{\tau} \geq \frac{\hbar}{2}$$

$$\Gamma = \sqrt{E_I^2 + E_{\tau}^2}$$

Peak Intensity (I): area under the curve, transition matrix element and occupancy of the final state

$$\left| \langle \psi_i | r | \psi_f \rangle \right|^2 \rho(E)$$

Physics of X-ray absorption spectroscopy (XANES XAFS etc.)

Dipole transition between quantum states

- **core to bound states** (Rydberg, MO below vacuum level, -ve energy, the excited electron remains in the vicinity of the atom)- long life time-sharp peaks
- **core to quasi-bound state** (+ve energy, virtual MO, multiple scattering states, shape resonance, etc. these are the states trapped in a potential barrier, and the electron will eventually tunnel out of the barrier into the continuum-short lifetime, broad peaks
- **core to continuum** (electron with sufficient kinetic energy to escape into the continuum) -photoelectric effect.

Physics of X-ray absorption spectroscopy (XANES, XAFS etc.) cont'

Scattering of photoelectron by the molecular potential
– how the electron is scattered depends on its **kinetic energy**

- **Low kinetic energy** - Multiple scattering of electron by the molecular potential of the neighboring atoms (typically up to ~ 50 eV above the threshold, the region where bound to quasi-bound transitions take place); e is scattered primarily by valence and inner shell electrons of the neighboring atoms - XANES region
- **High kinetic energy** (50 -1000 eV) are scattered primarily by the core electrons of the neighboring atoms, single scattering pathway dominates - EXAFS region

Electron scattering - general considerations

- Free electron (plane wave) scattered by an atom (spherical potential) travels away as a spherical wave
- Electrons with kinetic energy > 0 in a molecular environment is scattered by the surrounding atoms
- Low KE e^- is scattered by valence electrons, undergoes multiple scattering in a molecular environment
- High KE e^- is scattered by core electrons, favors single scattering

k space

It is often convenient to look at e⁻ with + ve KE in k space

In a free atom, the KE of a photoelectron excited by photon energy E above the threshold E₀ is, $\Delta E = E - E_0$ (eV)

$k = 2\pi / \lambda$ (wave vector, $\lambda =$ de Broglie wavelength)

$$= \sqrt{2m \Delta E / \hbar^2}$$

$$= \sqrt{0.263 \Delta E} \text{ (\AA}^{-1}\text{)} = 0.513 (\Delta E)^{1/2} \text{ (\AA}^{-1}\text{)}$$

← Conversion from energy to k space

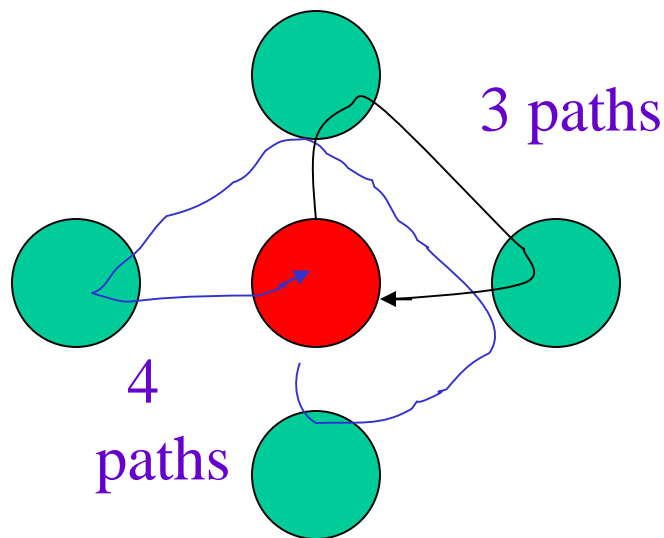
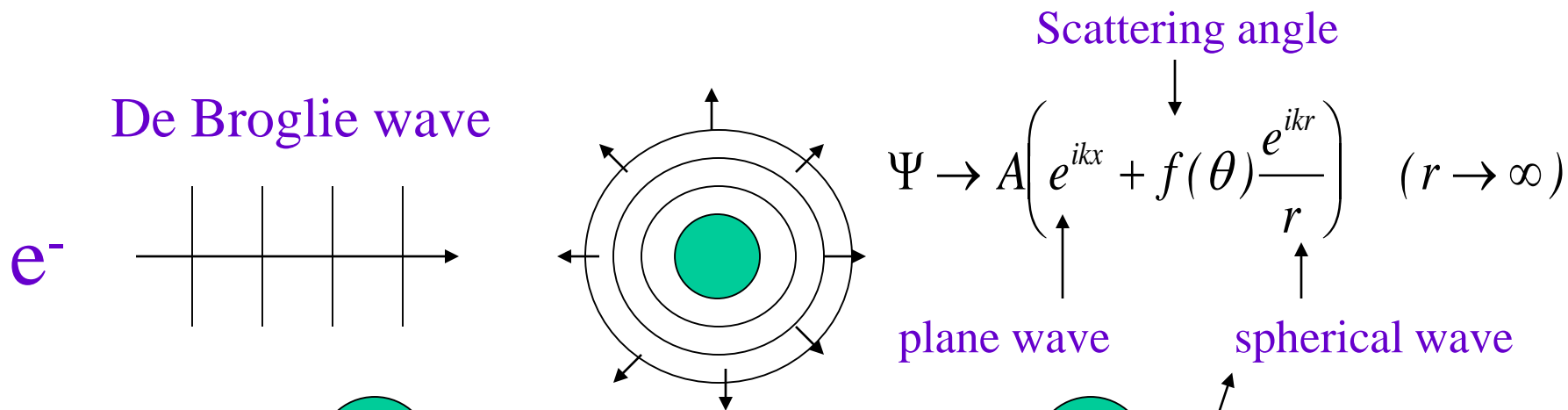
$$\text{KE} = \Delta E = 1/2 (mv^2) = 1/2(p^2/m) = \hbar^2 / 2\lambda^2 m$$

$$\lambda = 1/2(\hbar^2/m\Delta E)^{1/2}$$

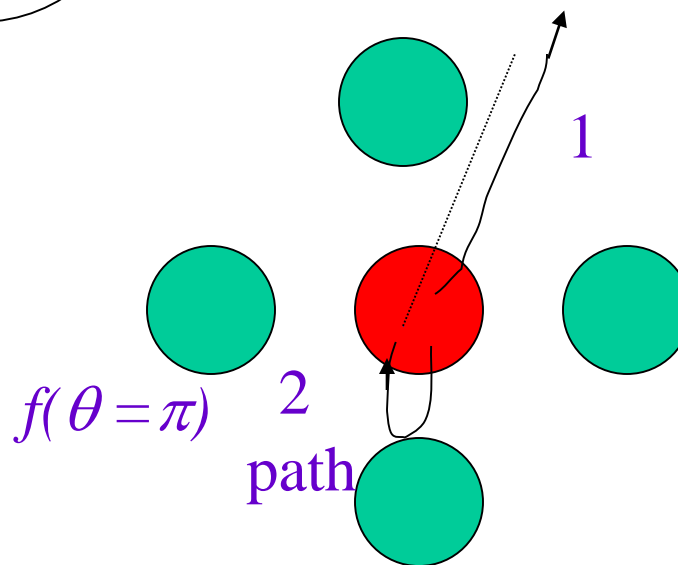
$$k = 2\pi / \lambda = 2\pi / \hbar(1/m\Delta E)^{1/2} = \sqrt{2m \Delta E / \hbar^2} \quad \hbar = \hbar/2\pi$$

$$\text{At 50 eV, } k = 0.13 \times \sqrt{50} = 3.63 \text{ (\AA}^{-1}\text{)}$$

Electron scattering - physical picture

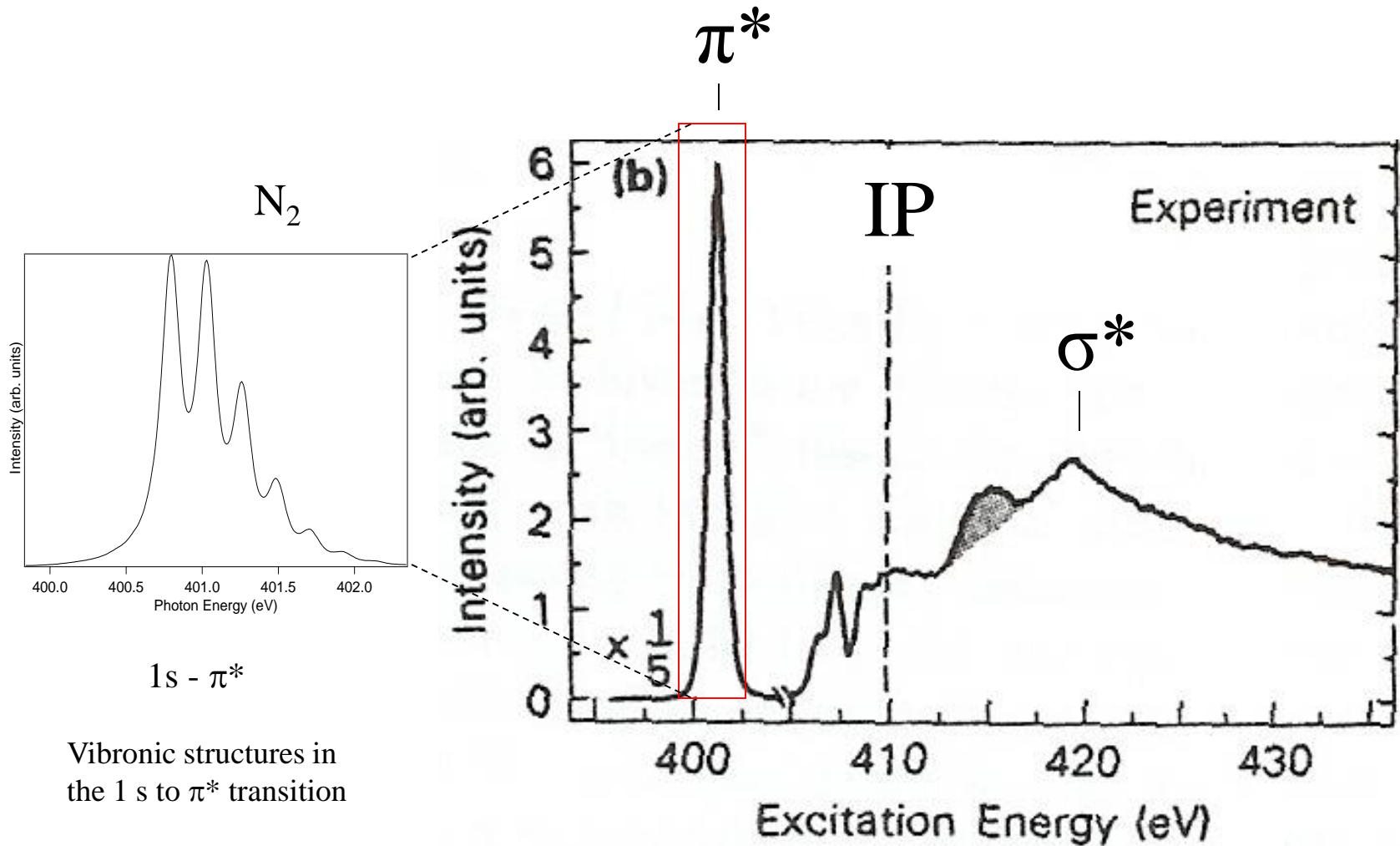


Low KE e, multiple scattering
(XANES)

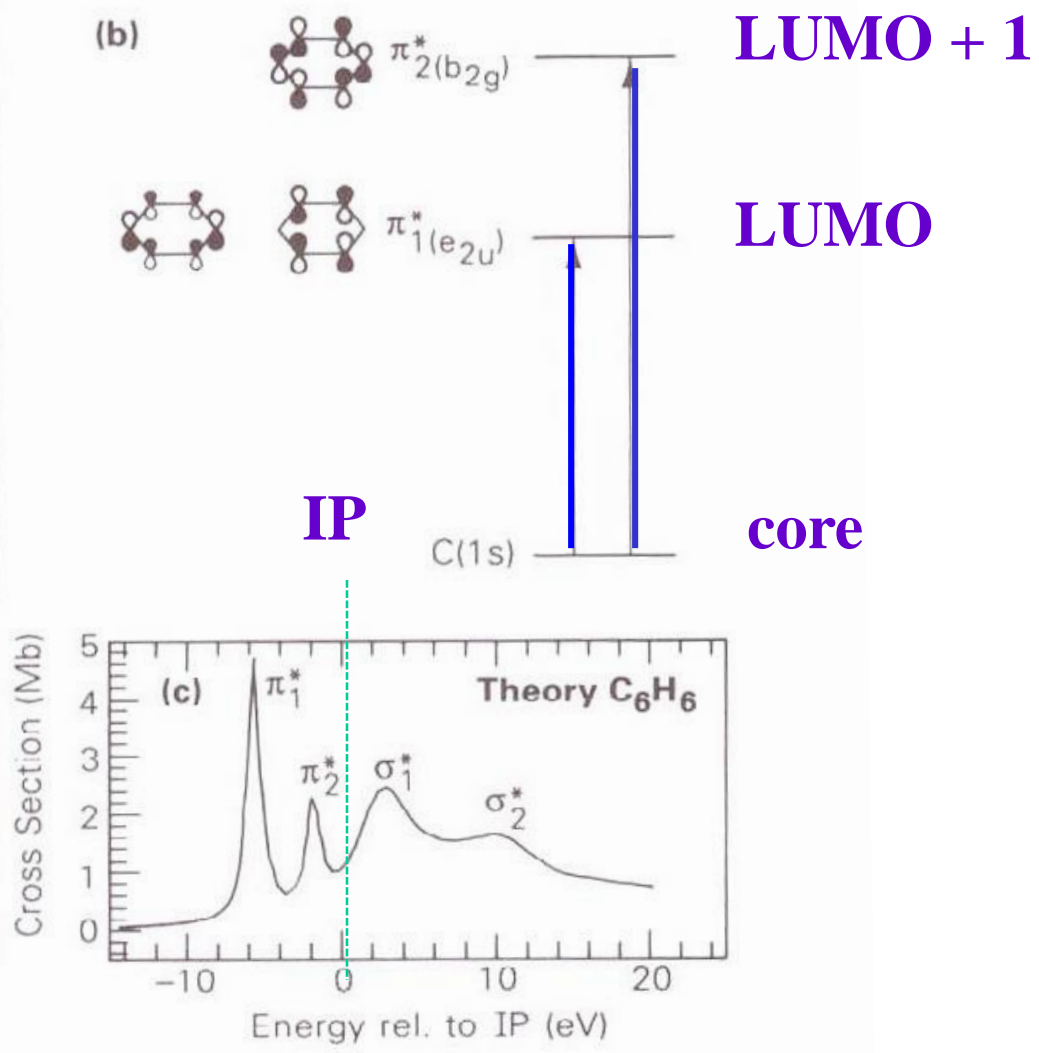
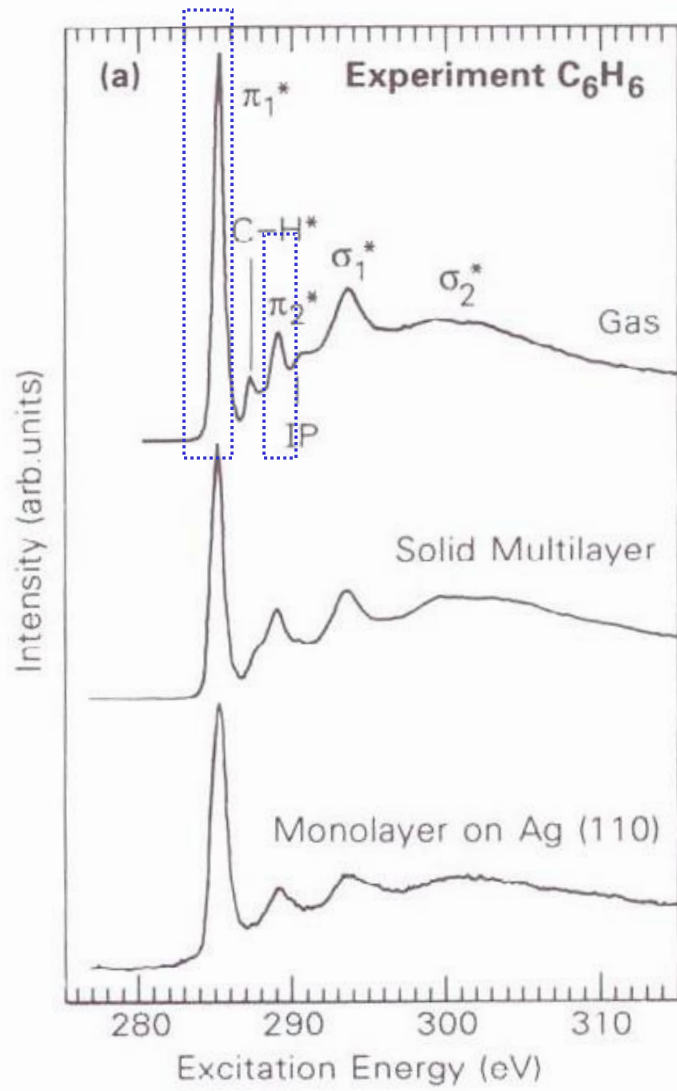


High KE e, single scattering along
the bond (EXAFS)

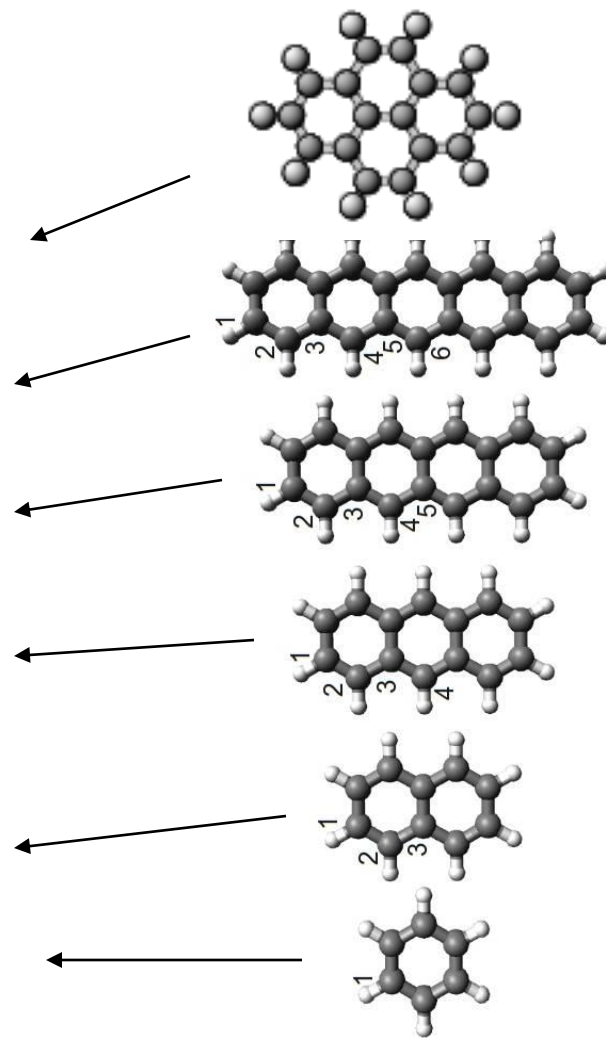
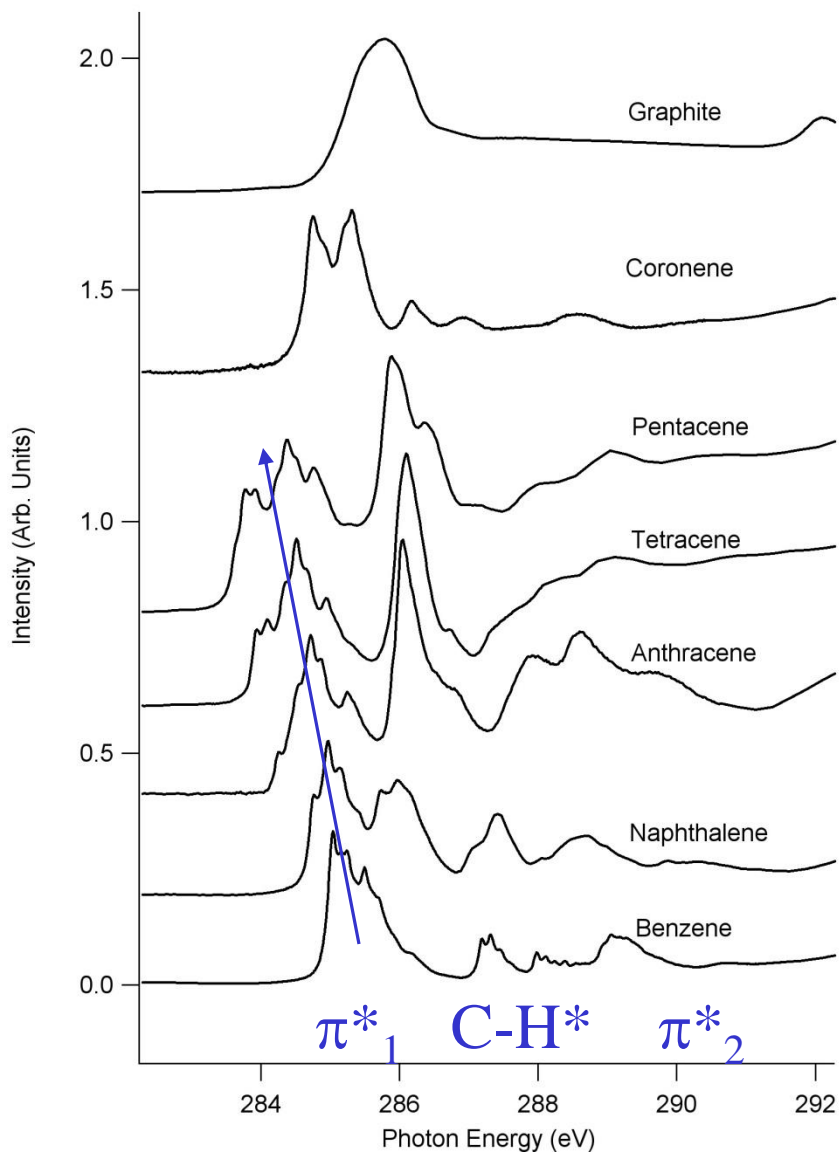
N K-edge NEXAFS (XANES)



XANES of Benzene



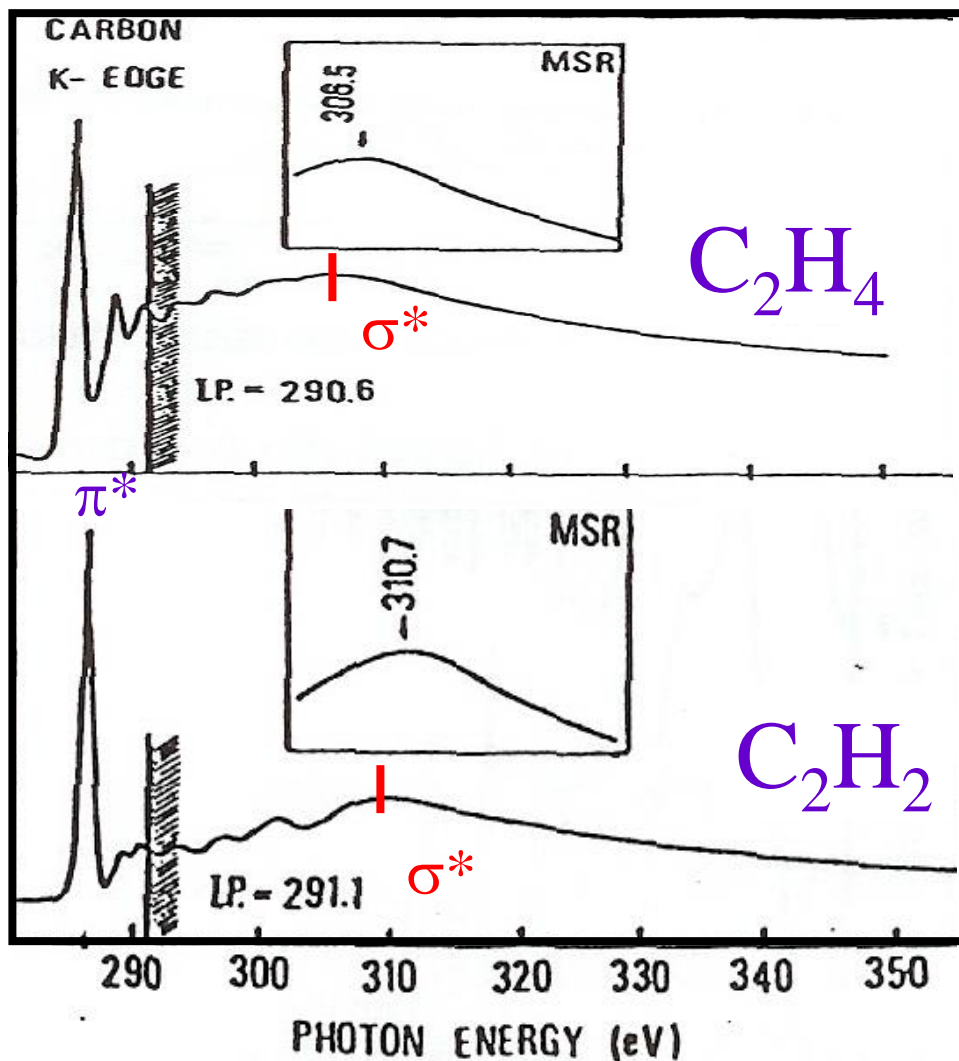
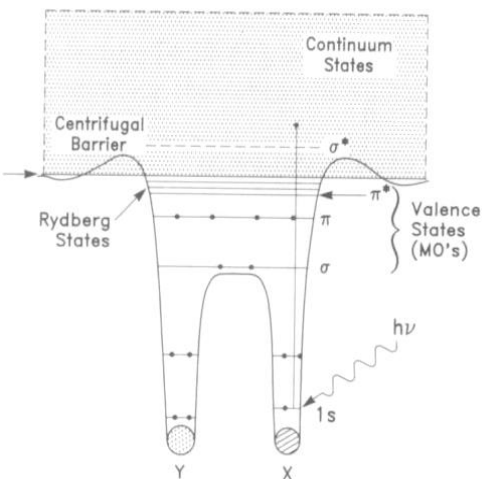
XANES chemical systematic



Increasing no. of benzene rings

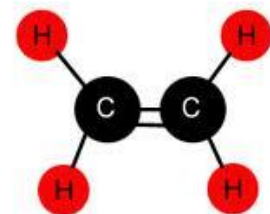
Correlation of σ^* resonance with bond length in low z molecules

$$(E_{\sigma^*} - E_0) \propto 1/r$$



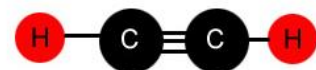
$$\Delta E = 16.5 \text{ eV}$$

$$R = 1.33 \text{ \AA}$$



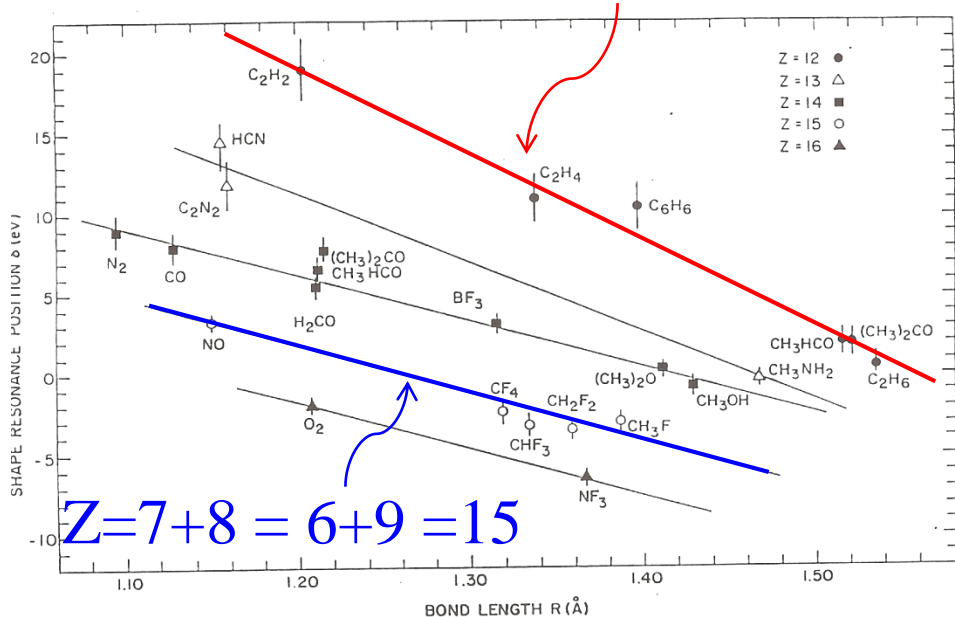
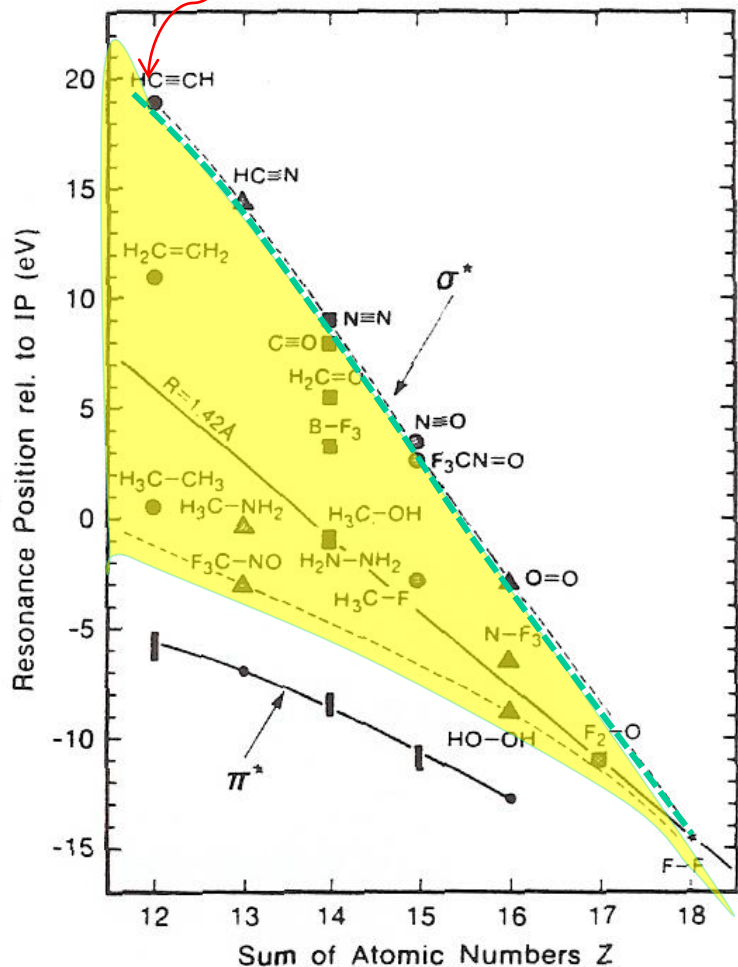
$$\Delta E = 19.6 \text{ eV}$$

$$R = 1.20 \text{ \AA}$$



$$Z=6(\text{C})+6(\text{C})=12 \quad \Delta E = (E_{\sigma^*} - E_0) \propto 1/r$$

$$Z=6(\text{C})+6(\text{C})=12$$

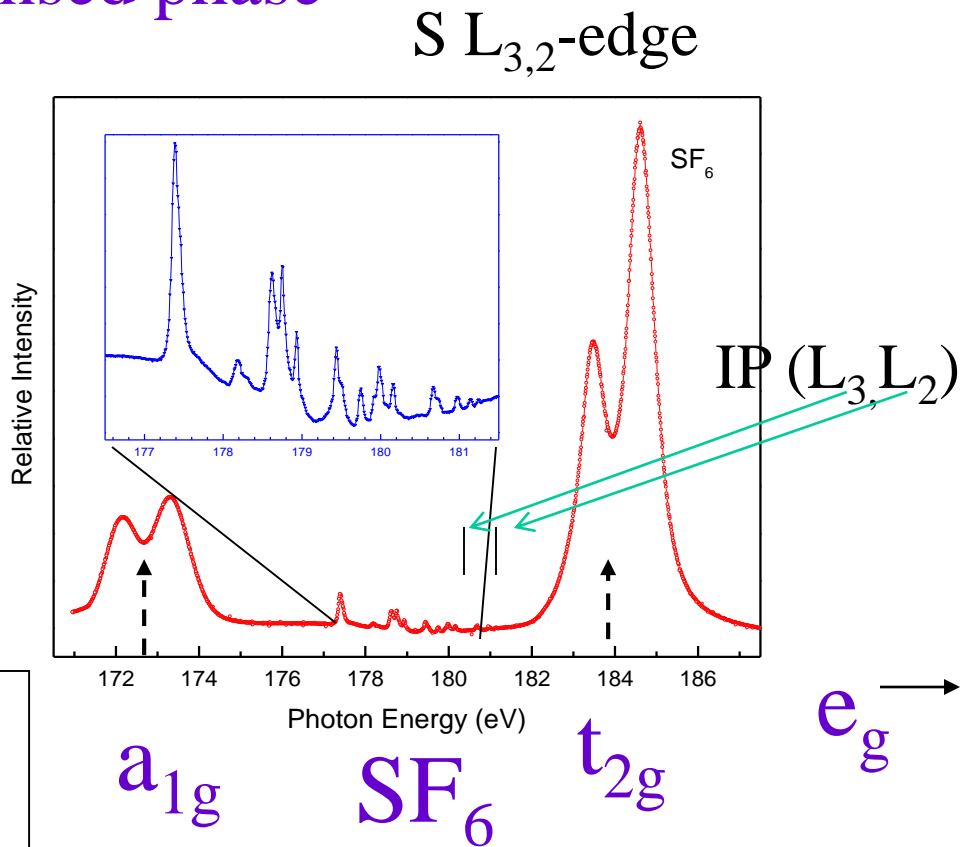
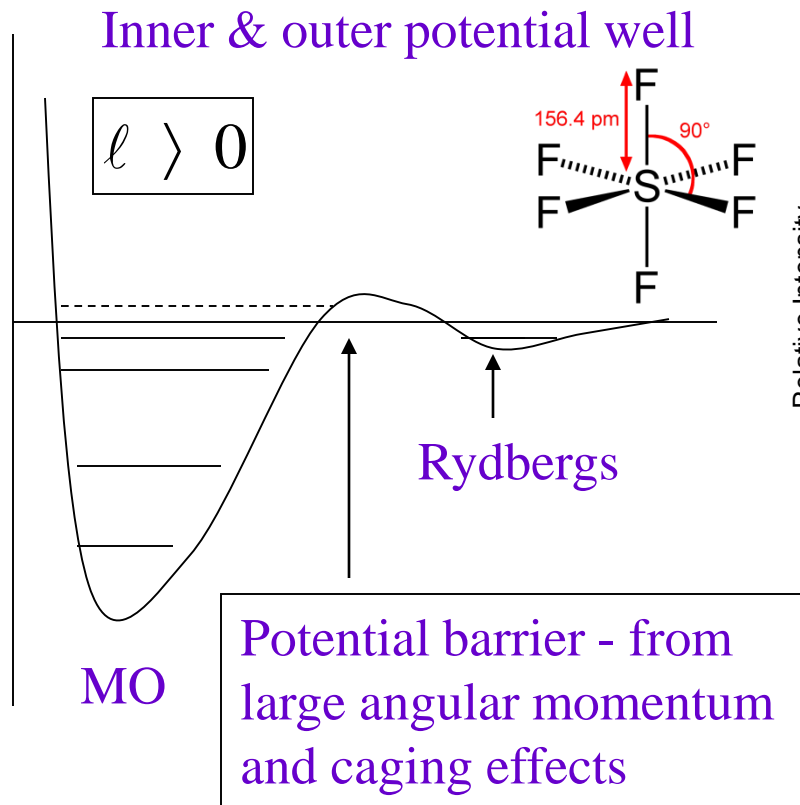


Why would this correlation exist?

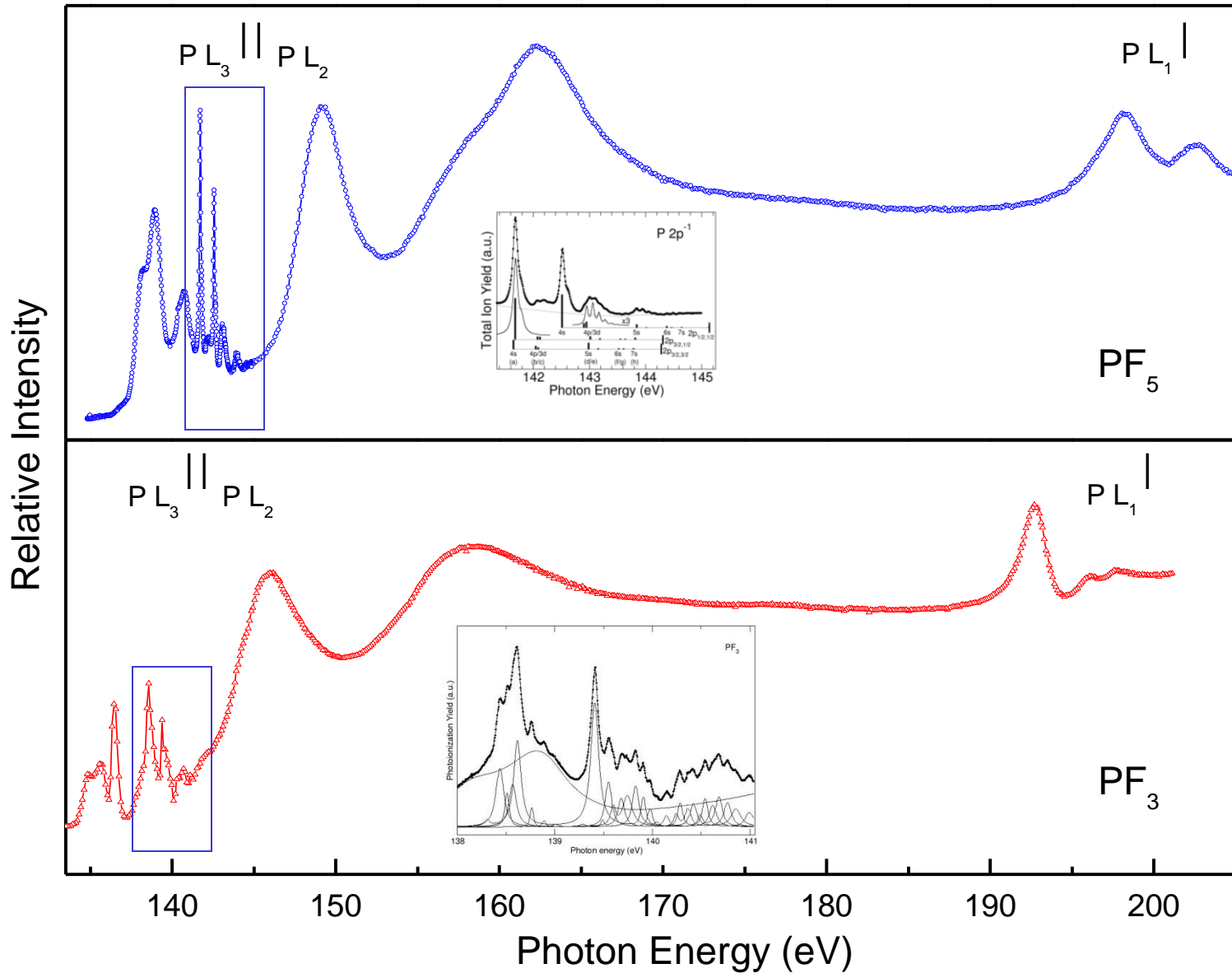
- i) Multiple scattering theory
- ii) Simple picture- particle in a box- the shorter the bond the farther the energy separation

NEXAFS of polyatomic molecules

As the molecule gets bigger, Rydberg gets weaker; molecular transitions become dominant. Rydbergs are quenched in the condensed phase



PF₅ and PF₃



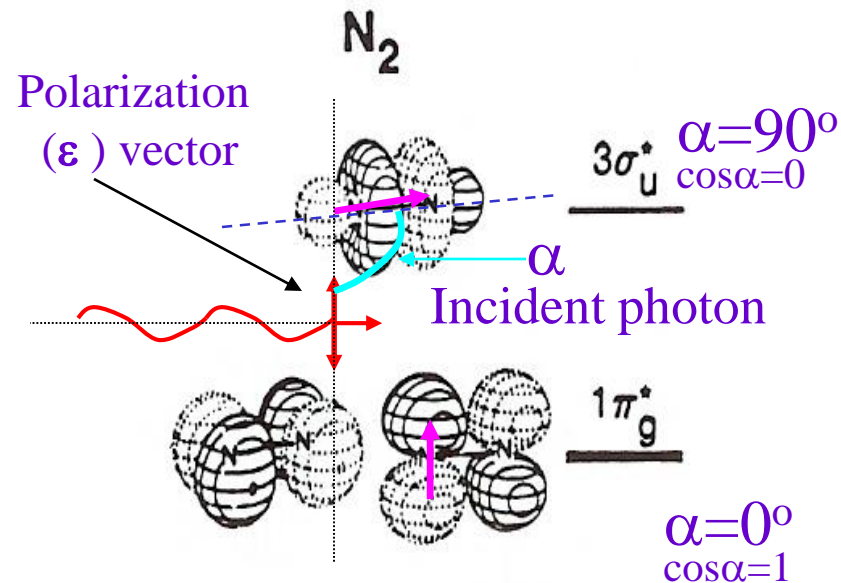
NEXAFS and polarization

We recall $\sigma \propto \left| \langle f_i | \boldsymbol{\varepsilon} \cdot \mathbf{r} | f_f \rangle \right|^2 \rho(E_f)$

Can have values
between 0 and 1

Thus, the intensity, $I \propto \sigma \propto |\boldsymbol{\varepsilon}|^2 |\mathbf{r}|^2 \cos^2 \alpha$
where α is the angle between the $\boldsymbol{\varepsilon}$ (polarization) vector
of the light and the vector of the molecular orbital (MO
axis)

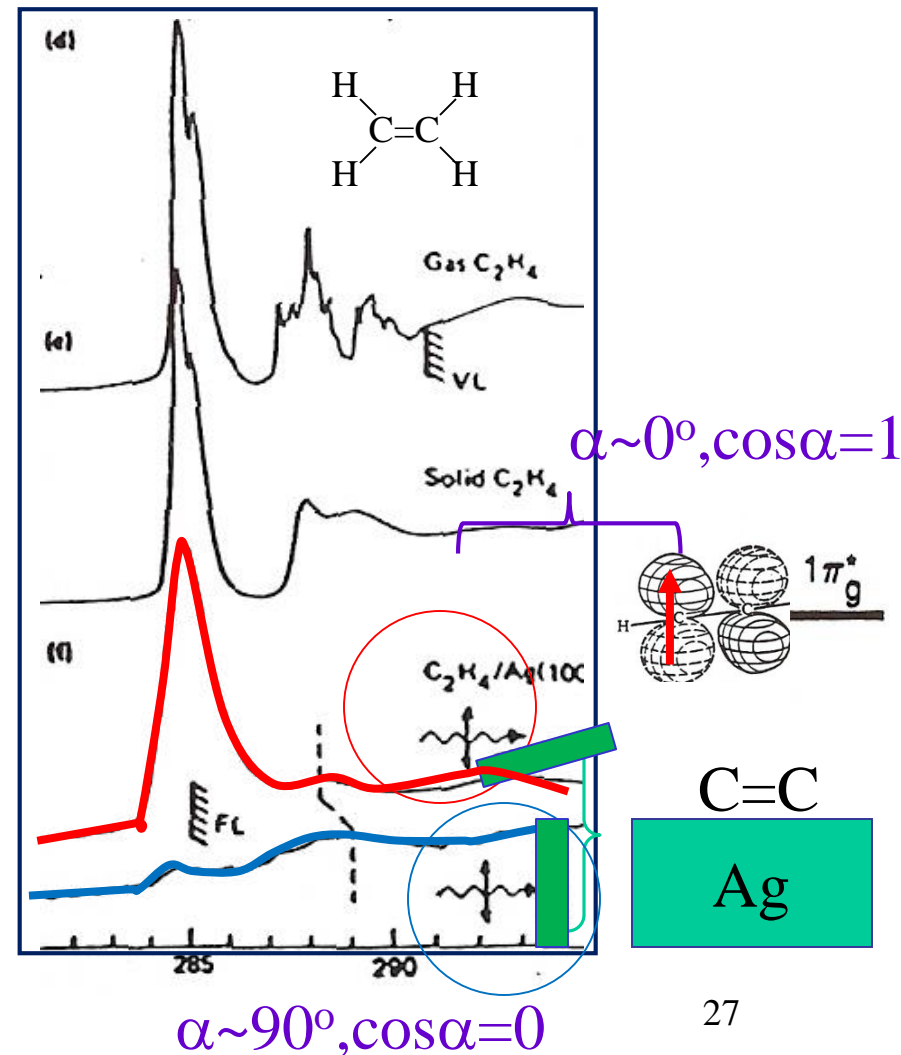
E.g. for N_2 , the MO axes are shown
for the π^* and σ^* ; if the *photon
polarization* is parallel to the MO
axis (\mathbf{r}) of the $1\pi_g^*$ in N_2 , the $1s - \pi^*$
transition intensity is a maximum
($\cos^2 \alpha = 1$) and $1s - \sigma^*$ is minimum
($\cos^2 \alpha = 0$)



NEXAFS of molecules oriented on a surface (angular dependence of resonance intensity)

When molecule adsorbs on a surface, the molecular axis is defined

A series of XAS made by rotating the substrate with respect to the polarization reveals the orientation of the molecule.



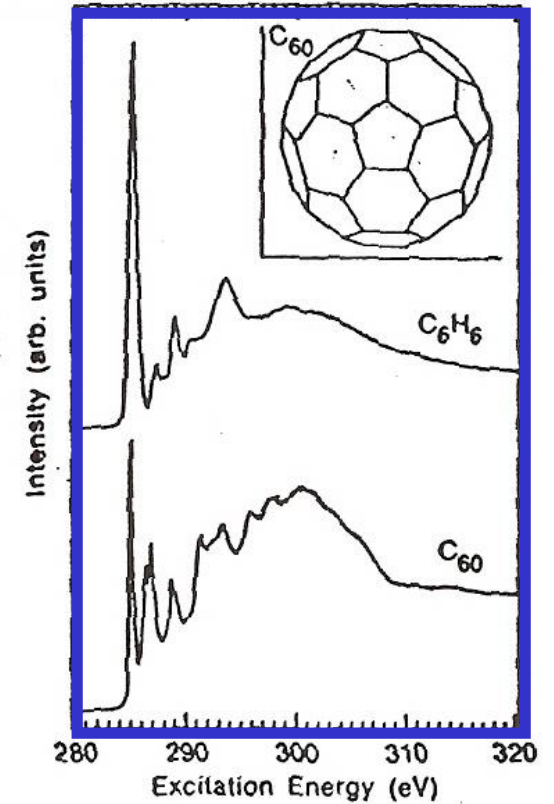
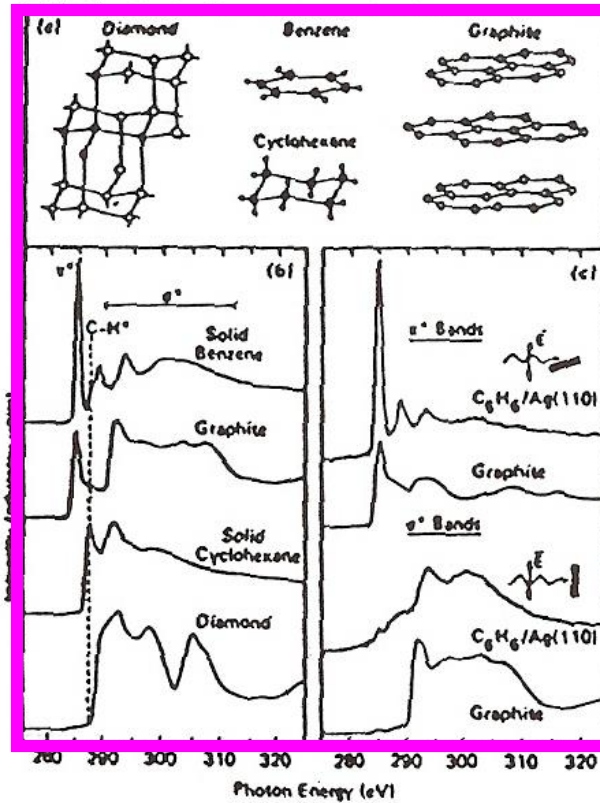
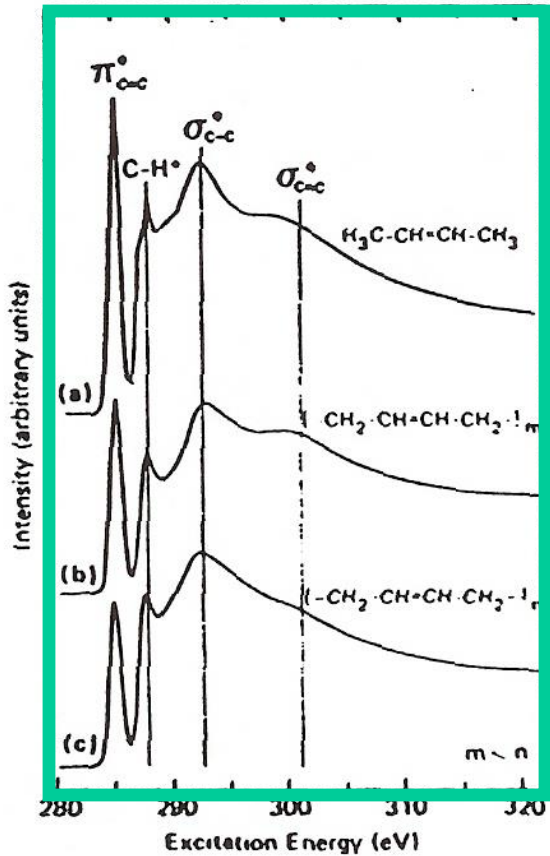
Chemical systematic

Polymer

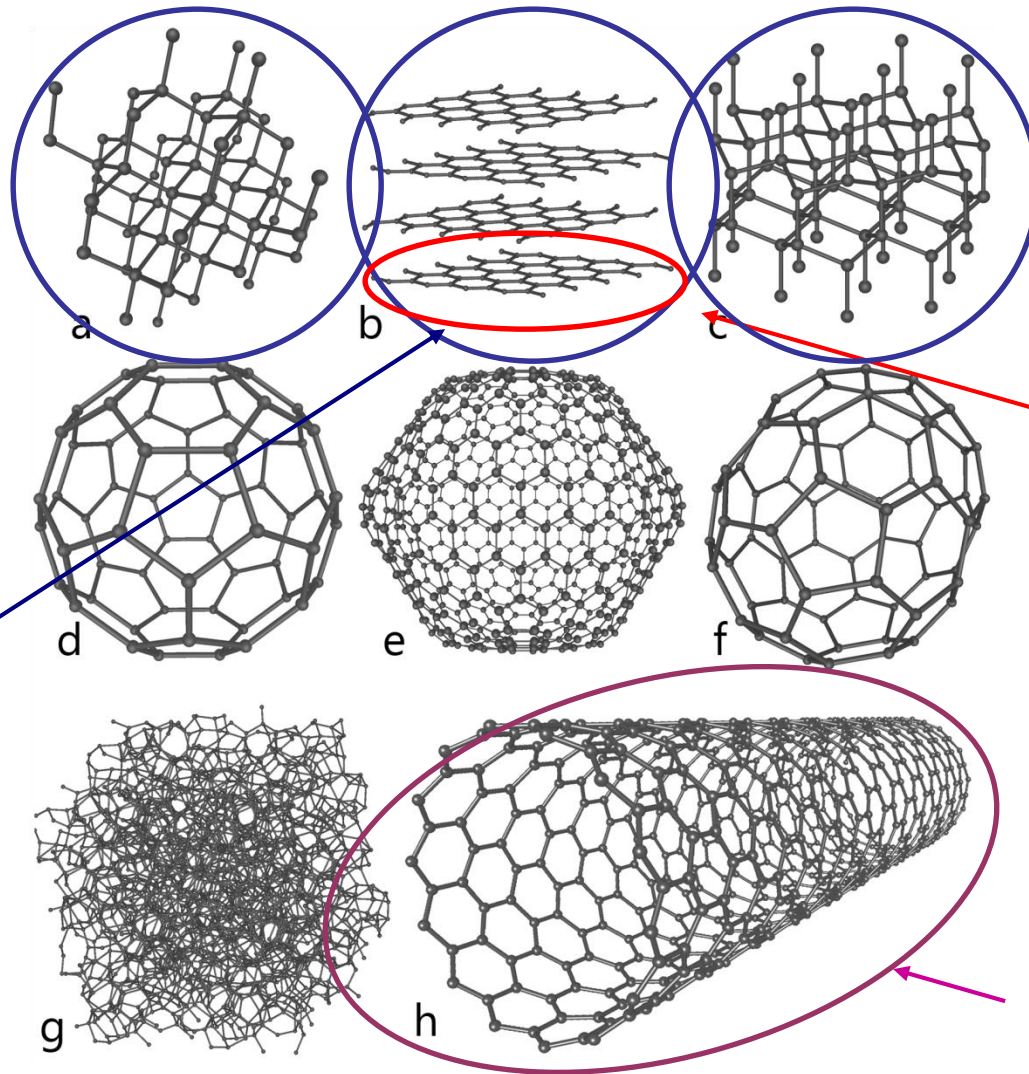
Allotropes

C₆₀

Butene and Polymers



Carbon Allotropes



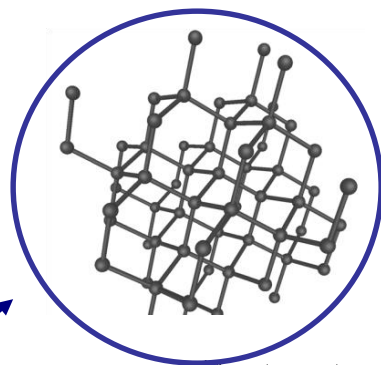
Hexagonal
Diamond
(Lonsdaleite)

Graphene

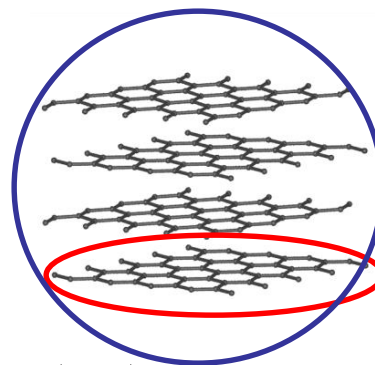
Nanotube

Carbon Allotropes: C K-edge XAS

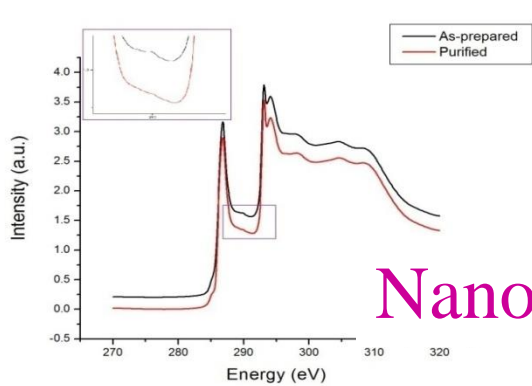
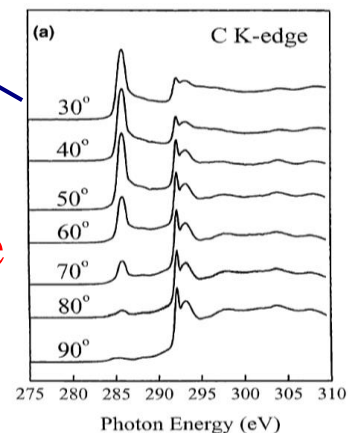
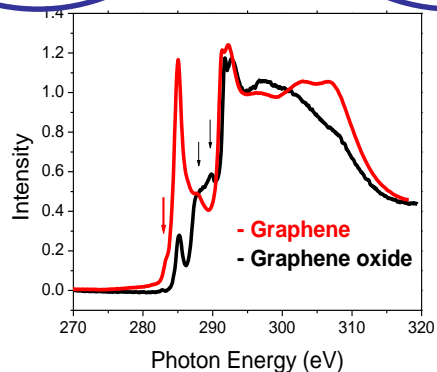
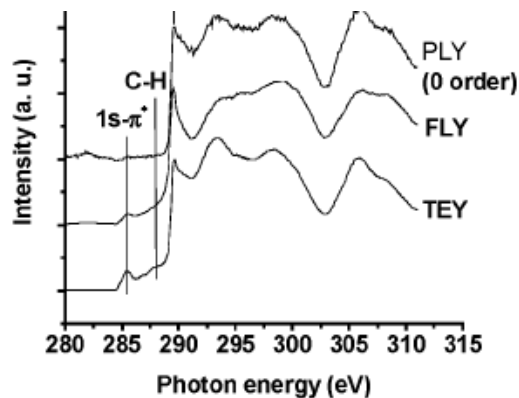
Diamond



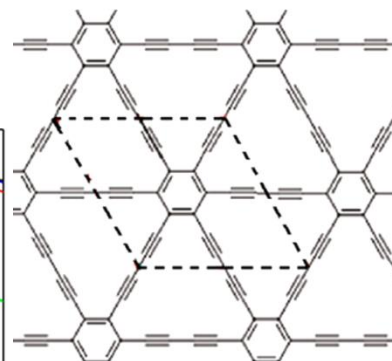
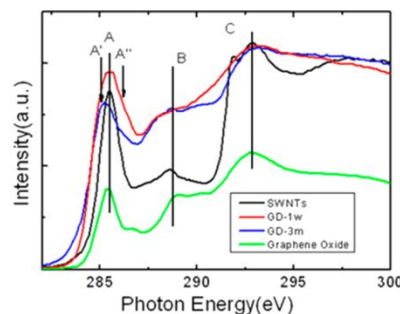
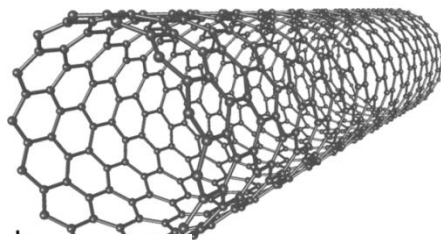
Graphite



Graphene



Nanotube



Graphidyne