

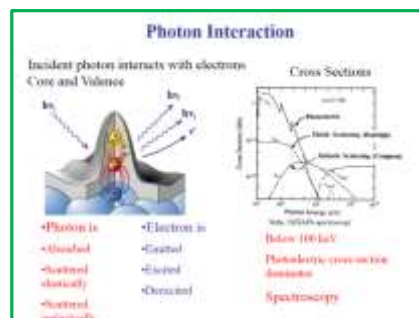
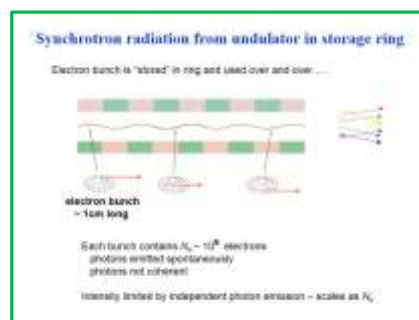
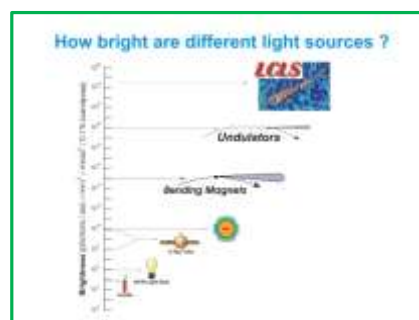
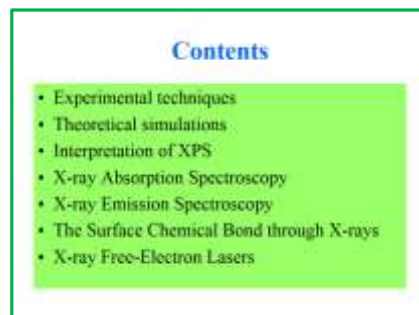


ЕВРОПЕЙСКИ СЪЮЗ
ЕВРОПЕЙСКИ СТРУКТУРНИ И
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ОПЕРАТИВНА ПРОГРАМА
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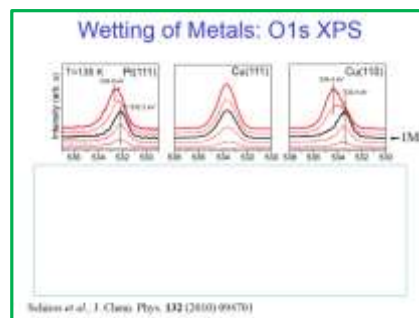
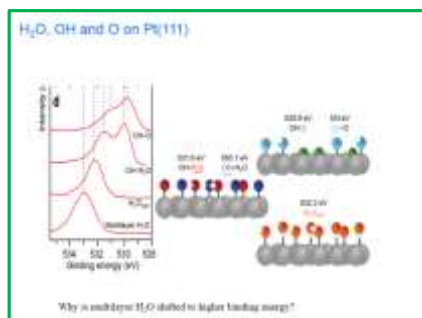
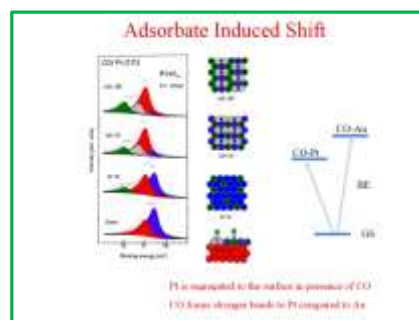
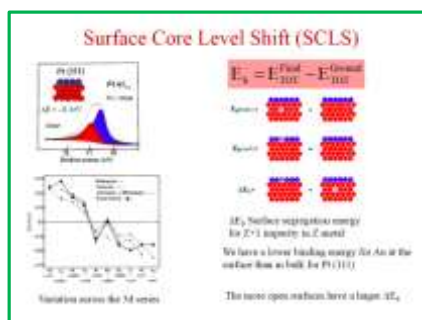
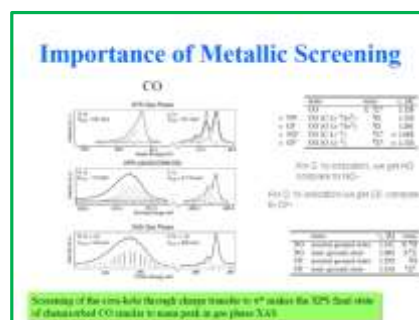
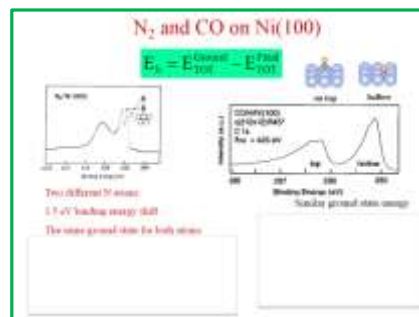
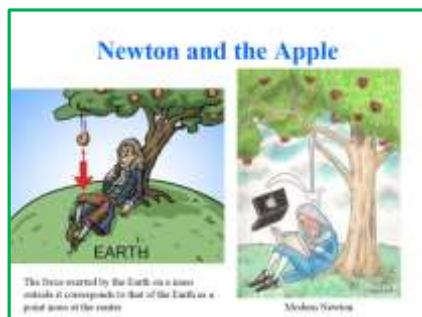


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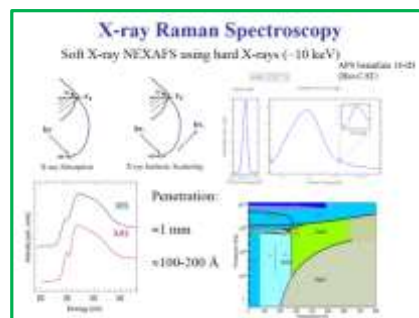
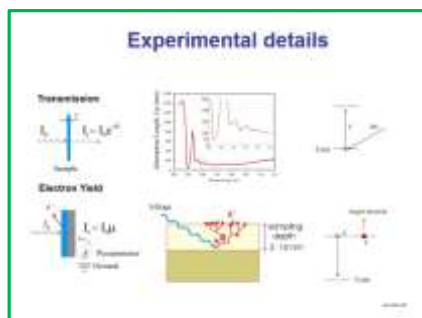
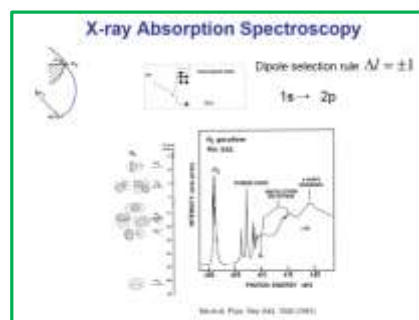
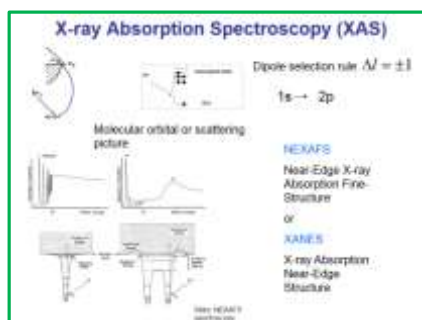
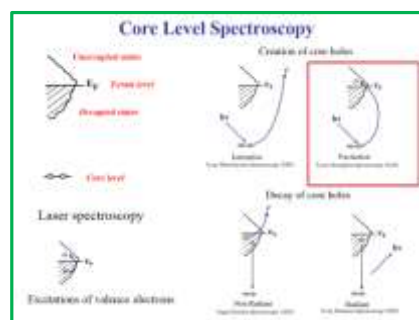
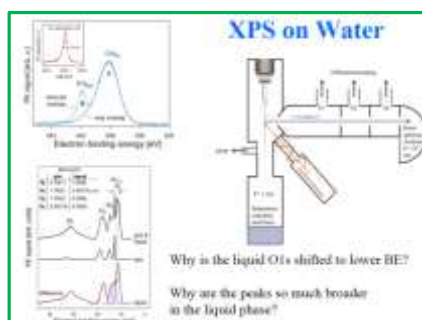
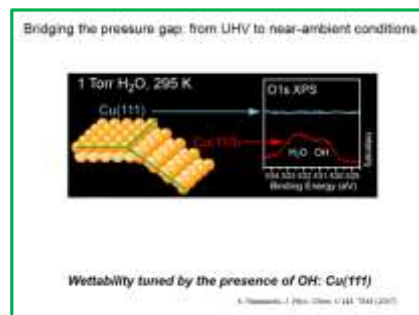
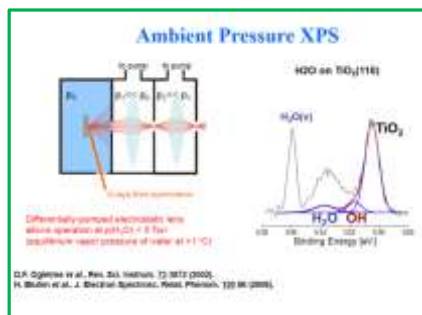


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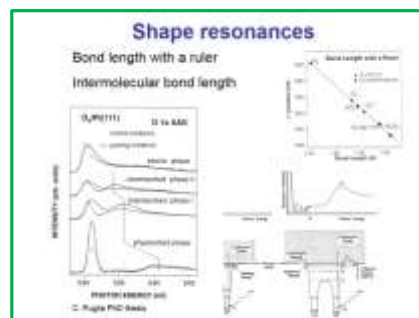
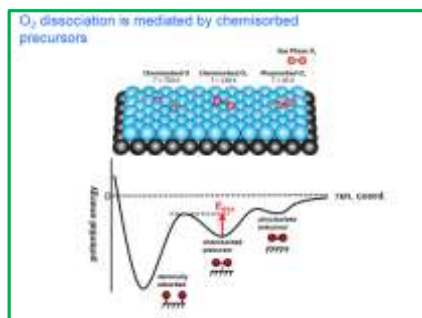
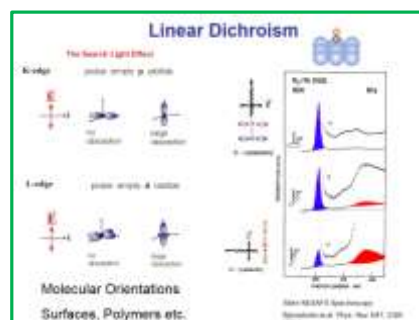
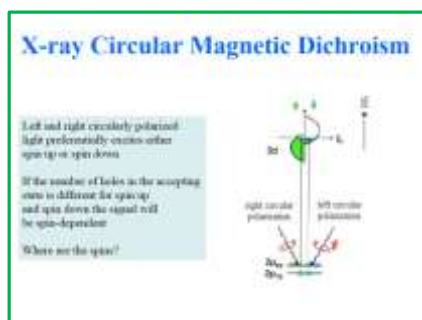
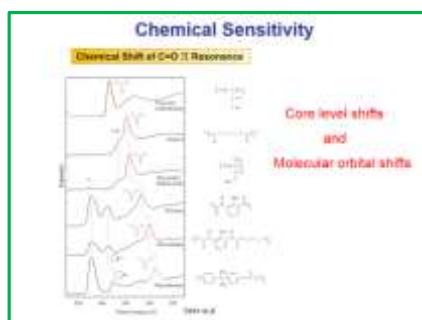
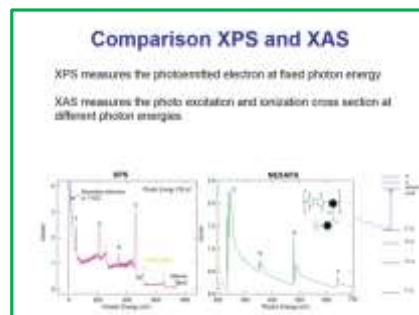
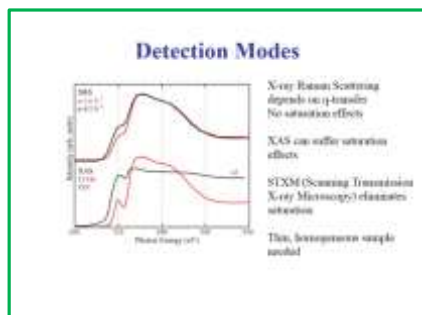


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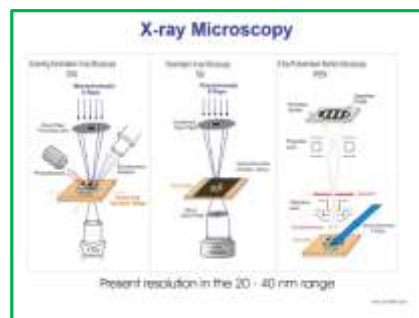
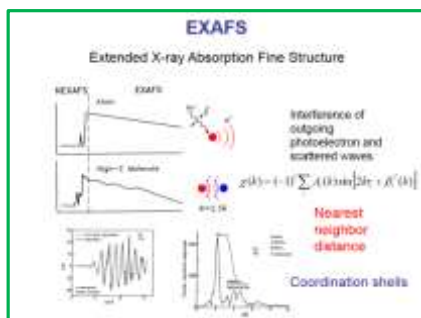
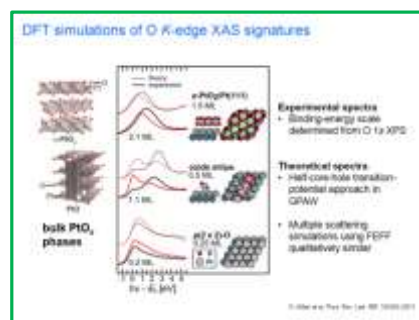
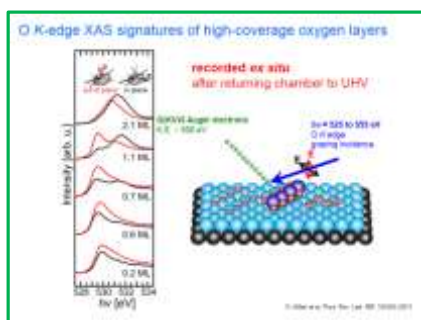
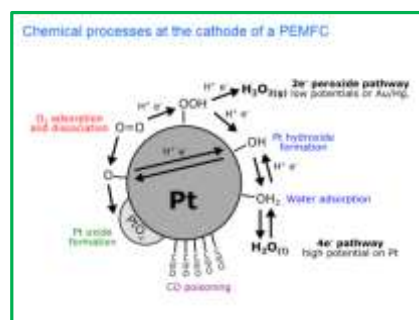
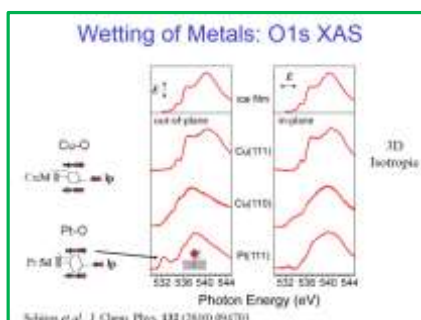
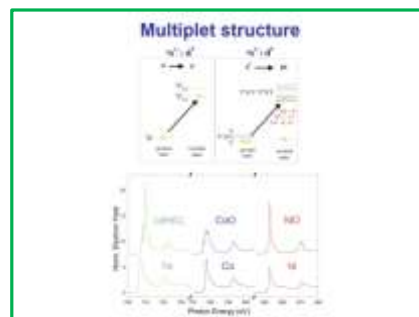
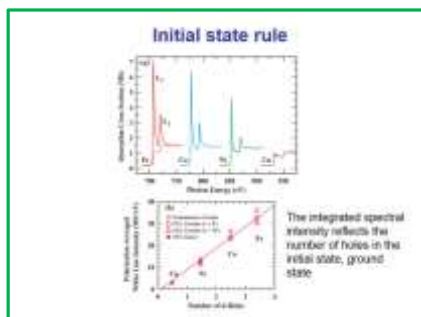


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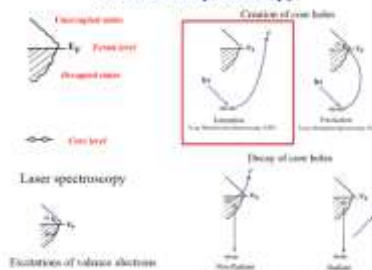


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Theoretical Simulations

- XPS: Δ Kohn-Sham
- XAS: Transition potential, TDDFT, CPP
- XES: TDDFT, Kramers-Heisenberg, SC-KH

Core Level Spectroscopy

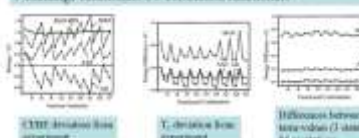


Δ Kohn-Sham

- Compute energy difference between ground and core-ionized state
- Equivalent atoms! Select which core-orbital by removing others using effective core potential or localizing and freezing
- Shifts more reliable

Functional Dependence of XPS and XAS

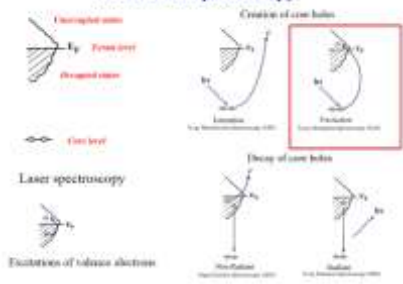
18 molecules with well-established CEBE and term-values (XAS)
9 exchange functionals x 3 correlation functionals



Most of the error due the functionals are associated with the electron dense inner shell. **Caution for excitation energy differences and XPS shifts.** Calibrate against exp. CEBE

Valievskii and Peveretti, JCP 121 (2004) 10109

Core Level Spectroscopy



X-ray Absorption

Unperturbed Hamiltonian $H_0 = \frac{p^2}{2m} + V(r)$

With E-field $p \rightarrow p + e\hbar A$, A is the vector potential

Perturbed Hamiltonian $H = \frac{p^2}{2m} + V(r) + e\hbar A \cdot \frac{p}{m} + \frac{e^2 \hbar^2 A^2}{2m}$

Conductivity tensor $\sigma = \frac{e^2 \hbar^2}{4\pi m^2} \frac{1}{\omega} \frac{\partial^2}{\partial r^2} V(r)$

Linearly polarized monochromatic plane wave $A = \frac{A_0}{\sqrt{2}} \exp[i(k \cdot r - \omega t)] + \text{c.c.}$

Dipole Approximation

Transition rate $\propto \left| \langle f | \frac{\partial V}{\partial r} | i \rangle \right|^2$ (Dipole approximation)

Expand $\exp(i\mathbf{k} \cdot \mathbf{r}) = 1 + i\mathbf{k} \cdot \mathbf{r} + \dots$

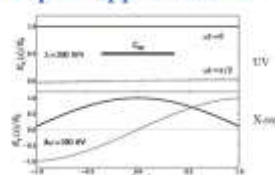
Write $\mathbf{p}$ in the commutator $\mathbf{p} = \frac{m\hbar}{i} \frac{\partial}{\partial \mathbf{r}}$

$\langle f | \frac{\partial V}{\partial r} | i \rangle = \frac{m\hbar}{i} \langle f | \frac{\partial}{\partial \mathbf{r}} V | i \rangle = m\hbar \langle f | \frac{\partial V}{\partial \mathbf{r}} | i \rangle$

$\langle f | \frac{\partial V}{\partial \mathbf{r}} | i \rangle = \frac{e}{m\hbar} \langle f | \mathbf{p} V | i \rangle = \frac{e}{m\hbar} \langle f | \mathbf{p} V | i \rangle$

$\mathbf{p} V = V \mathbf{p} + \hbar \mathbf{k} V$

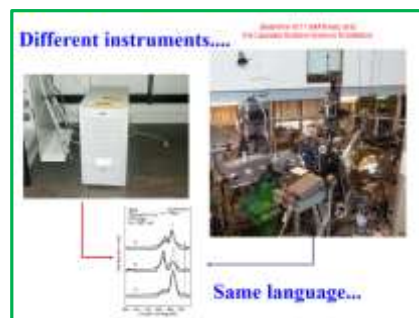
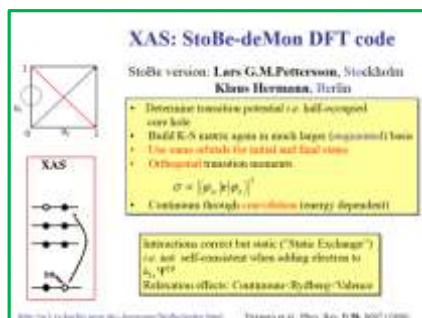
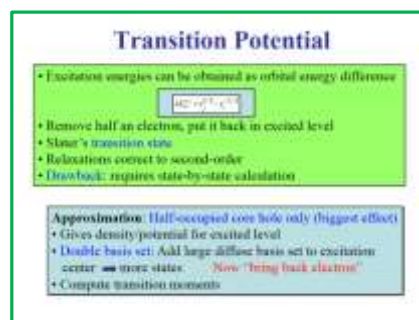
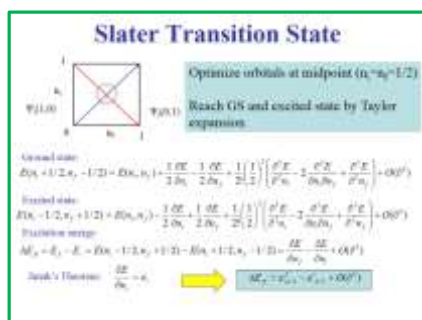
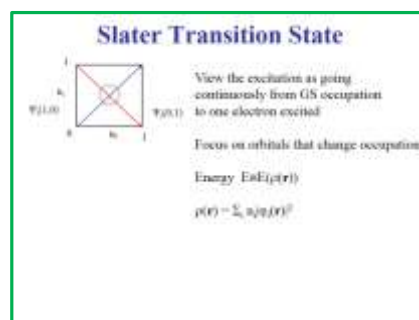
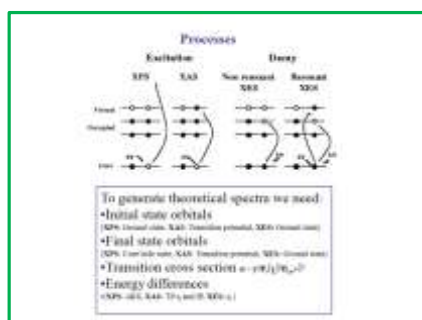
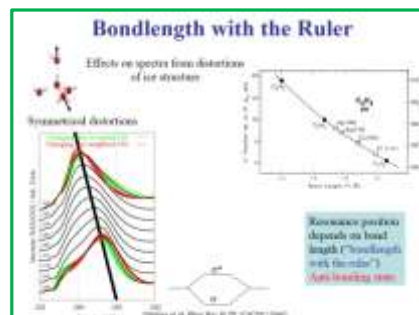
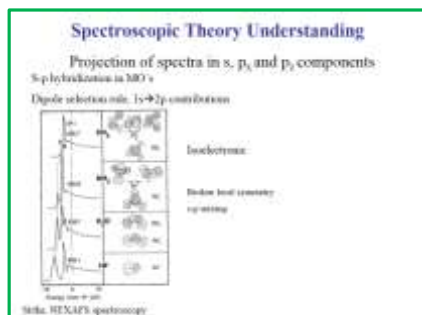
Dipole Approximation



The variation of the electric field over the orbital of interest determines the validity, i.e. for $\omega \ll 1$ where $\omega \equiv \frac{2\pi}{T}$



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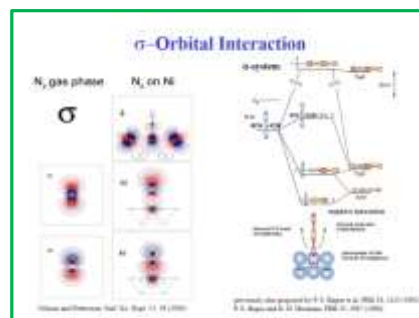
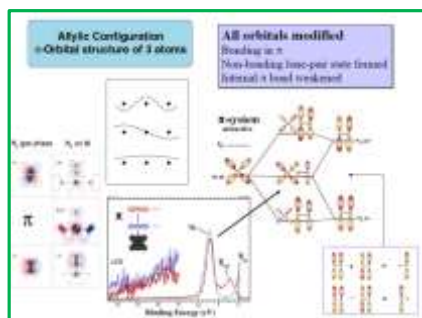
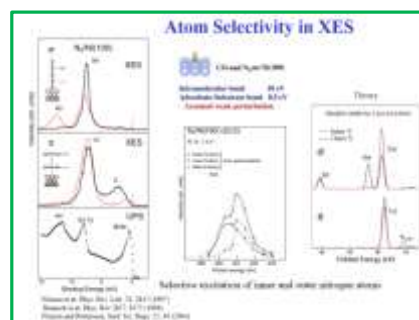
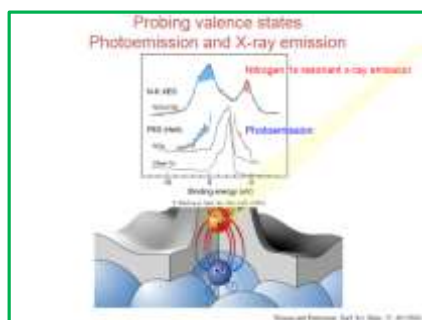
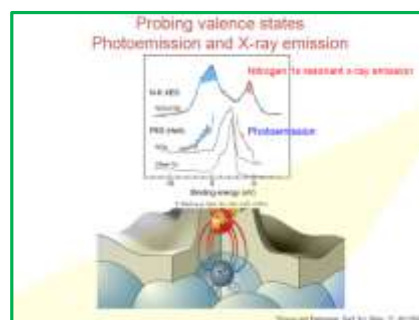
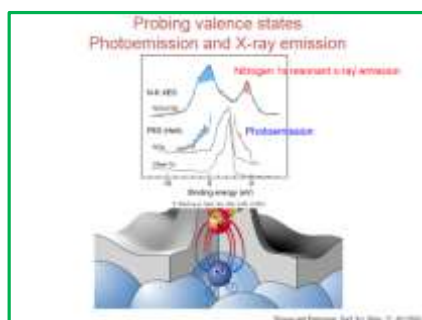
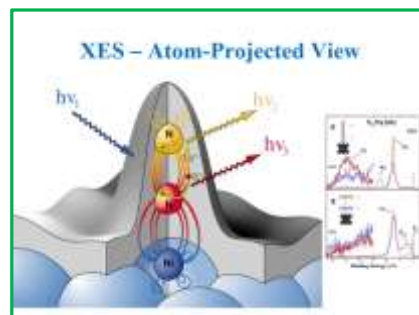
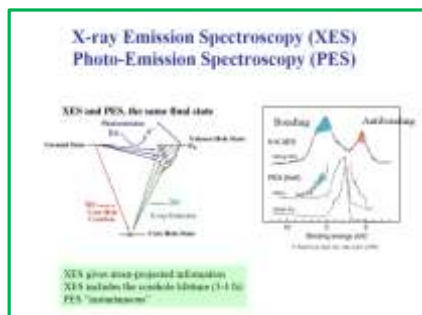


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**Linac Coherent Light Source (LCLS)
X-ray Free-Electron Laser**

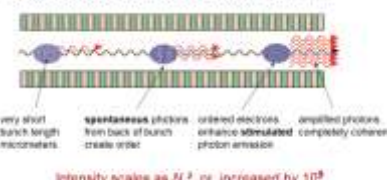
- Electron Energy: 15 GeV
- Photon Energy: 0.5-15 keV
- Pulse length: 5-500 fs
- Flux: 10^{18}
- Frequency: 120 Hz
- E. Bandwidth: 0.1-2%
- Machine Length: 2 km



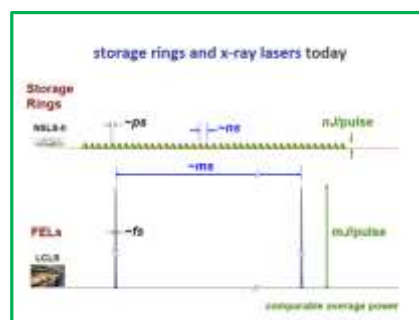
The world's first x-ray laser
Linac Coherent Light Source (LCLS)

Concept of a free electron x-ray laser

- Replace storage ring by a linear accelerator
allows compression of electron bunch – see above, then throw away
- Send electron bunch through a very long undulator



Intensity scales as N_e^2 or increased by 10^8



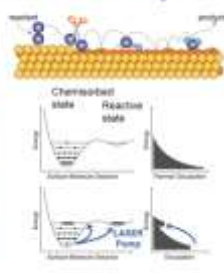
Probing the Reactive State in Catalysis

Most important catalytic reactions are driven by thermal processes

The number of turn-over events at each active site at a given time is extremely low

The Boltzmann energy distribution gives only few molecules to be in a reactive state

Ultrafast laser-induced heating leads to orders of magnitude higher population of the reactive state which can now be probed with ultrafast methods



Femtochemistry through laser excitation

Mechanism: real time scale of energy transfer after optical excitation

