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High Resolution Soft X-Ray Emission and Resonant Inelastic X-Ray Scattering: New Probes of Electronic Structure in Complex Materials.

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Outline

- Limitations of Photoemission Spectroscopy
- Soft X-Ray Emission Spectroscopy
  - *Example: Thin Film Nitride Alloys*
- Resonant Inelastic X-Ray Scattering
  - *Example: Cr-doped V2O3*
- Resonant Soft X-Ray Emission
  - *Example: CuPc thin films*
- Future Directions

The Bottom Line:

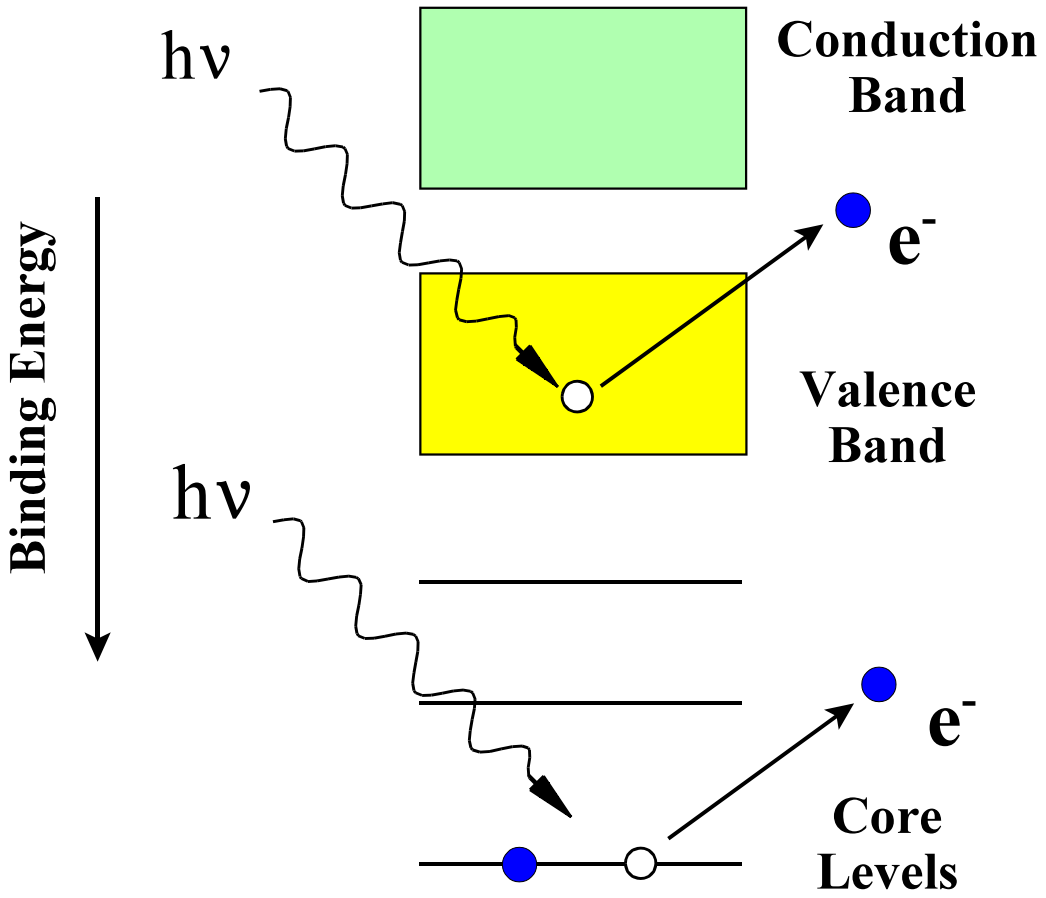
SXE/RIXS can measure

1) the local, chemically and site resolved, partial density of states,
2) shallow core level hybridization, and
3) electronic excitations across a gap or E_F,

for materials that are:

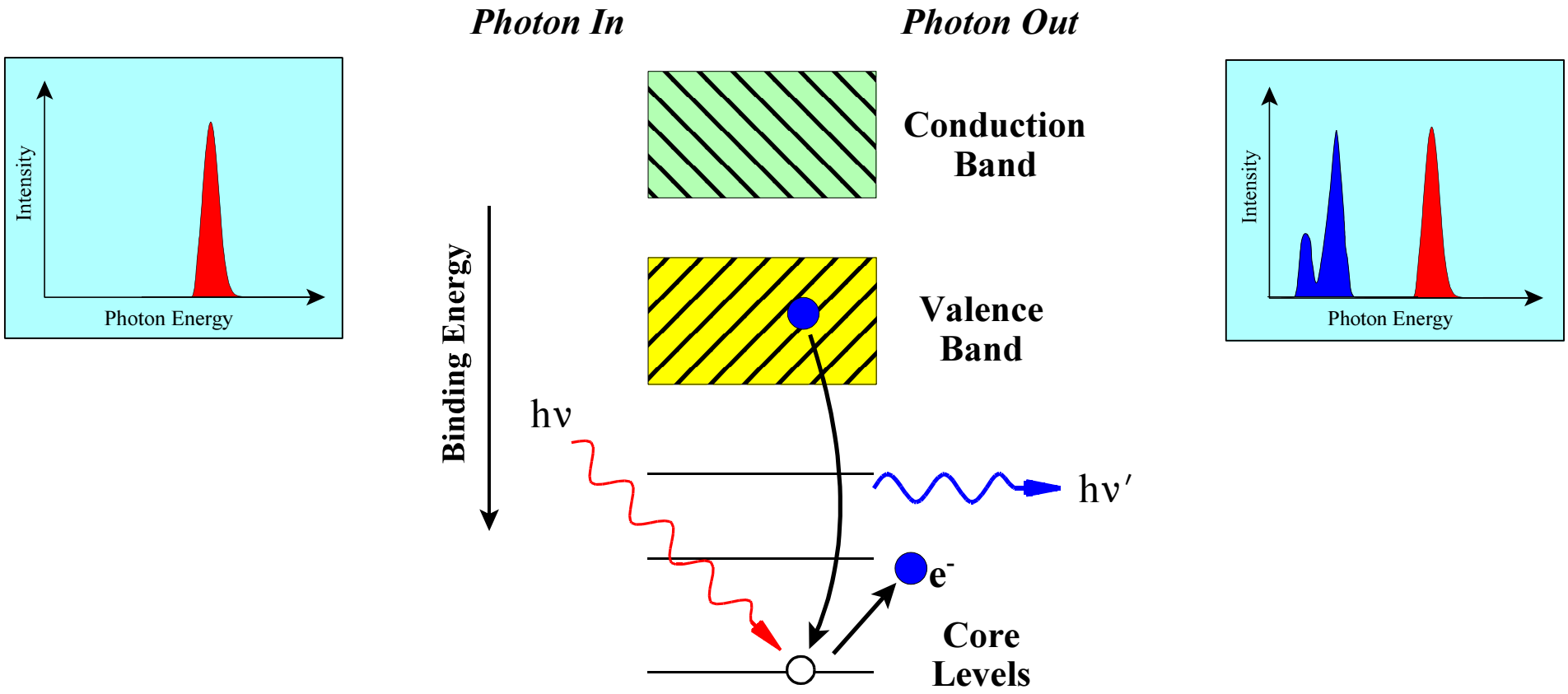
1) non-crystalline
2) insulating
3) in applied electric or magnetic fields
4) in non-vacuum environments
5) have ill-defined surfaces.

Photoemission Spectroscopy



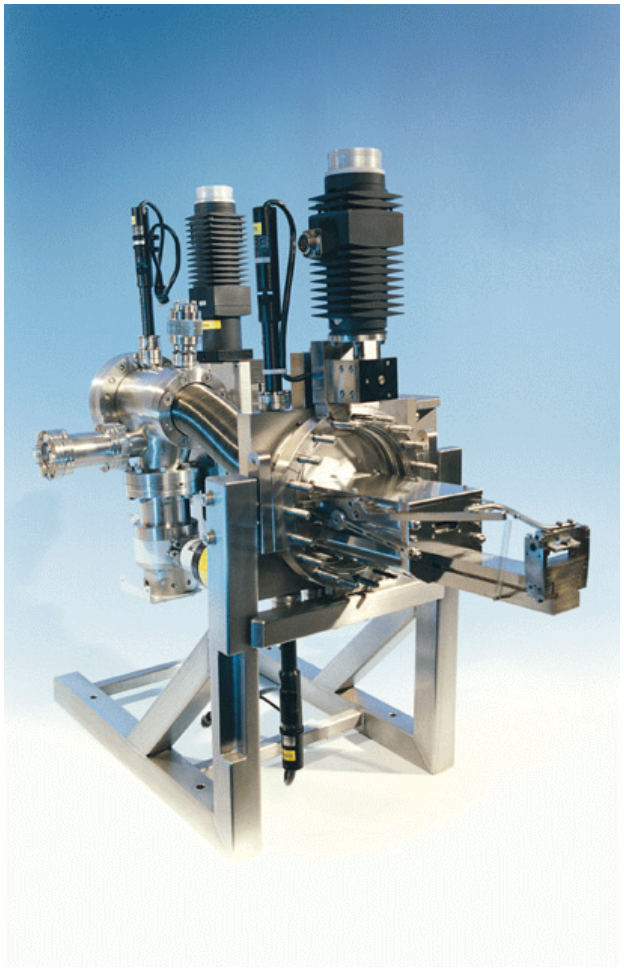
- Measure the kinetic energy of emitted electrons - get binding energy
- Angle resolved photoemission (**ARP**) measures momentum of emitted electrons -get band dispersion
- Angle integrated photoemission (**AIP**) integrates momentum of emitted electrons -get joint density of states
- X-ray photoemission spectroscopy (**XPS**) -get core level binding energies
- **Highly surface sensitive** (~ 5 → 50 Å) - need single crystals, and atomically clean surfaces
- **UHV required**
- **Inapplicable to insulating samples**
- **Inapplicable in applied electric or magnetic fields**

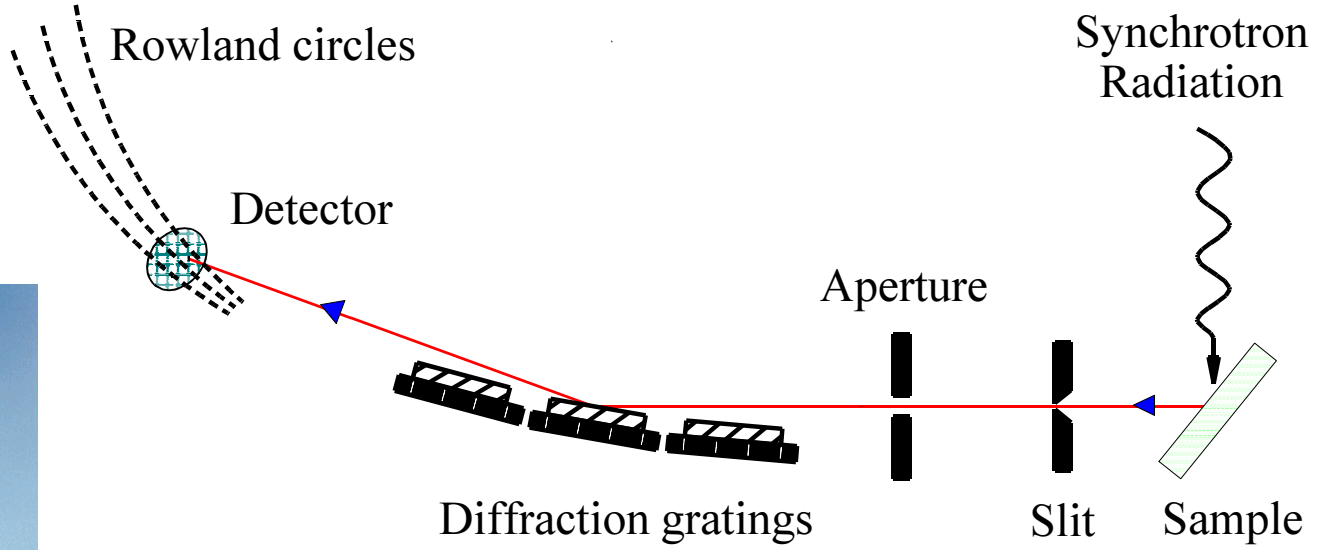
Soft X-Ray Emission Spectroscopy



- hν = 50 → 1000 eV
- Bulk sensitive (~ 1000 Å) ⇒ no need for large crystals, clean ordered surfaces
- Atomic and chemical specific
- Dipole selection rules ⇒ measure occupied PDOS; hybridization
- Operational in external fields and (windowed) liquid environments

Soft X-Ray Emission Spectrometer





- Rowland circle instrument
- Detector = 5 stacked microchannel plates + resistive anode encoder
- Gratings cover energy range 50 eV - 1000 eV
- high resolution (100's of meV @ hν = 500 eV)
- Compact and “portable”
- UHV compatible

The Boston University
High Resolution Photoemission and
Soft X-Ray Emission Spectrometer System

Funded by the U.S. Army Research Office, the Fritz Haber Institute, and Boston University.

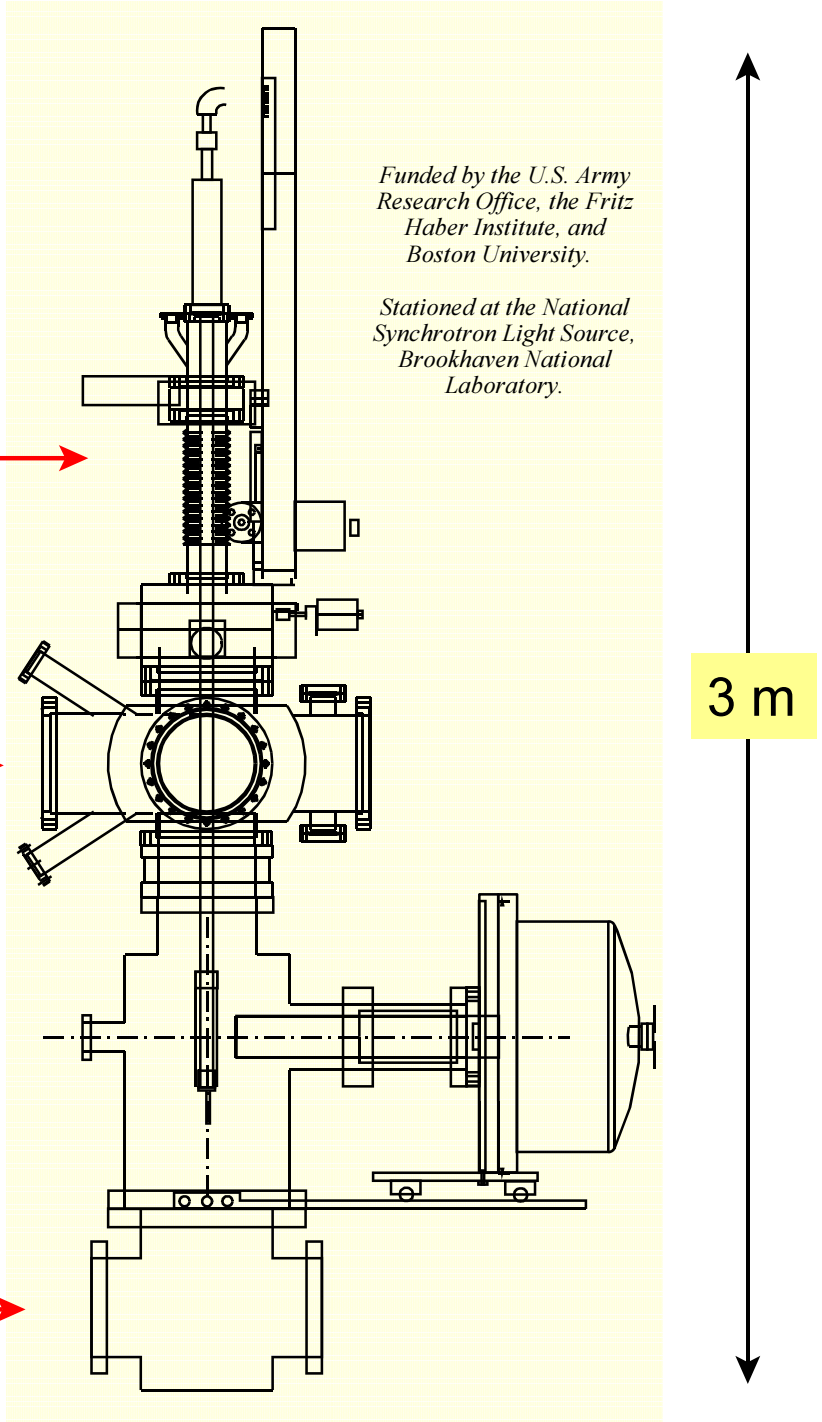
Stationed at the National Synchrotron Light Source, Brookhaven National Laboratory.

Sample manipulator, with liquid helium cooling, electron beam heating, 5 degrees of freedom for sample motion, sample transfer and load lock.

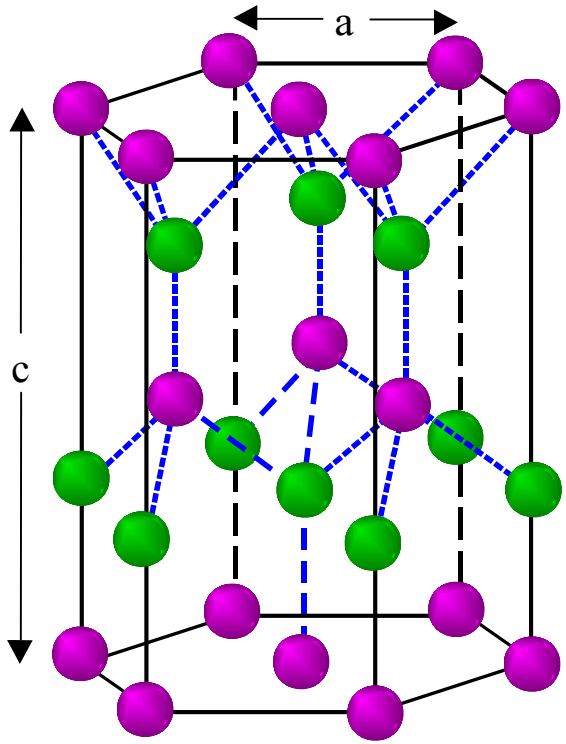
Sample preparation chamber: pumped with a 360 l/s turbo pump, titanium sublimation pump, and cryoshield. Features a Low Energy Electron Diffraction optics, CMA Auger spectrometer, multiple metal evaporators and gas dosing system.

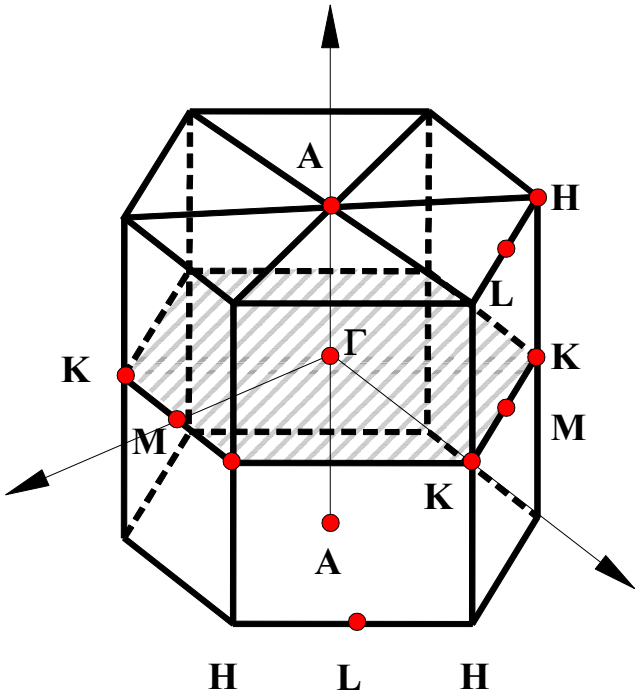
Spectrometer Level: double μ metal lined chamber, housing 100 mm Scienta electron analyzer, and soft x-ray emission spectrometer

Pumping level for Spectrometer Chamber: 400 l/s ion pump, titanium sublimation pump, cryoshield



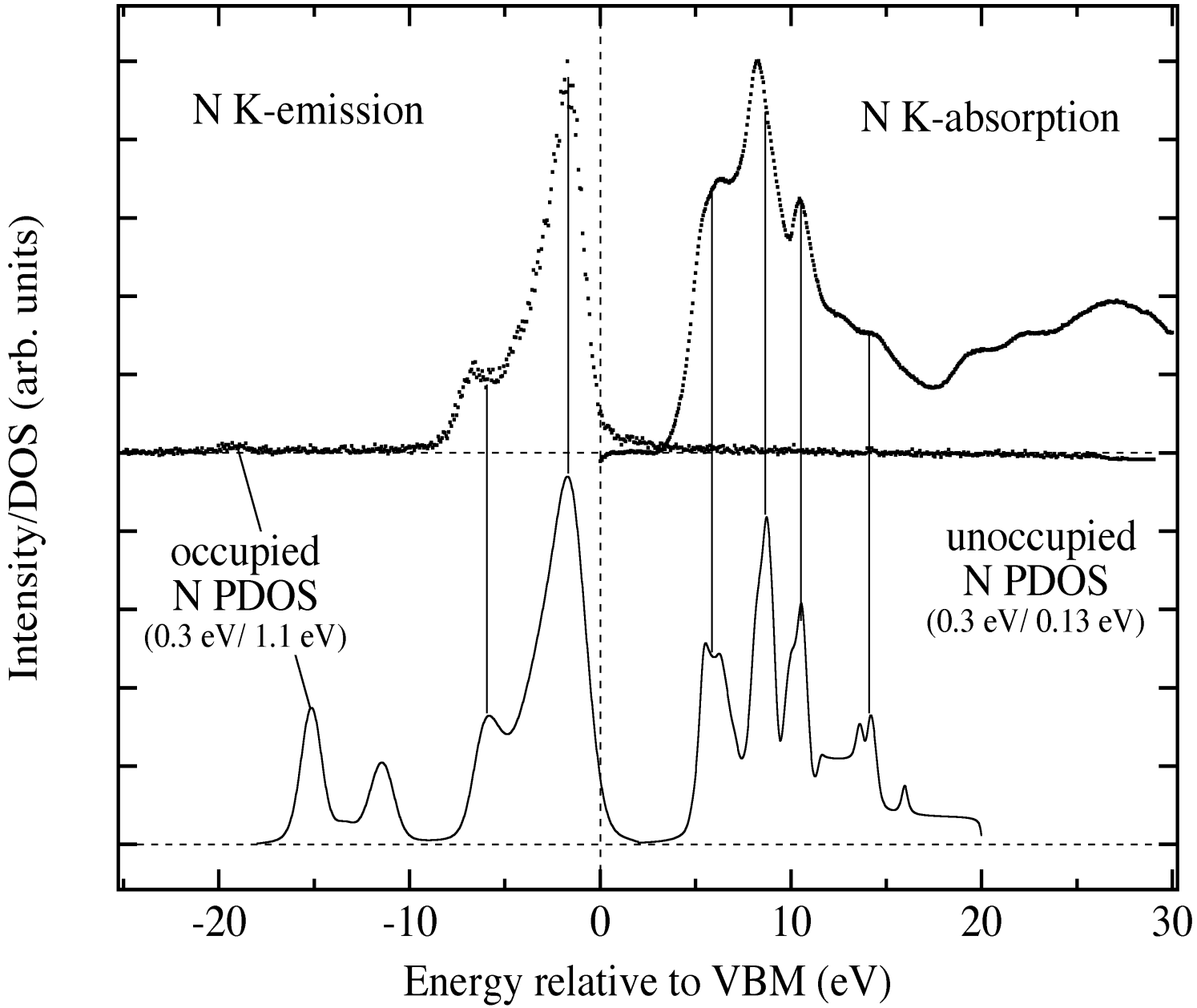
Wurtzite GaN: Crystal Stucture and Bulk Brillouin Zone



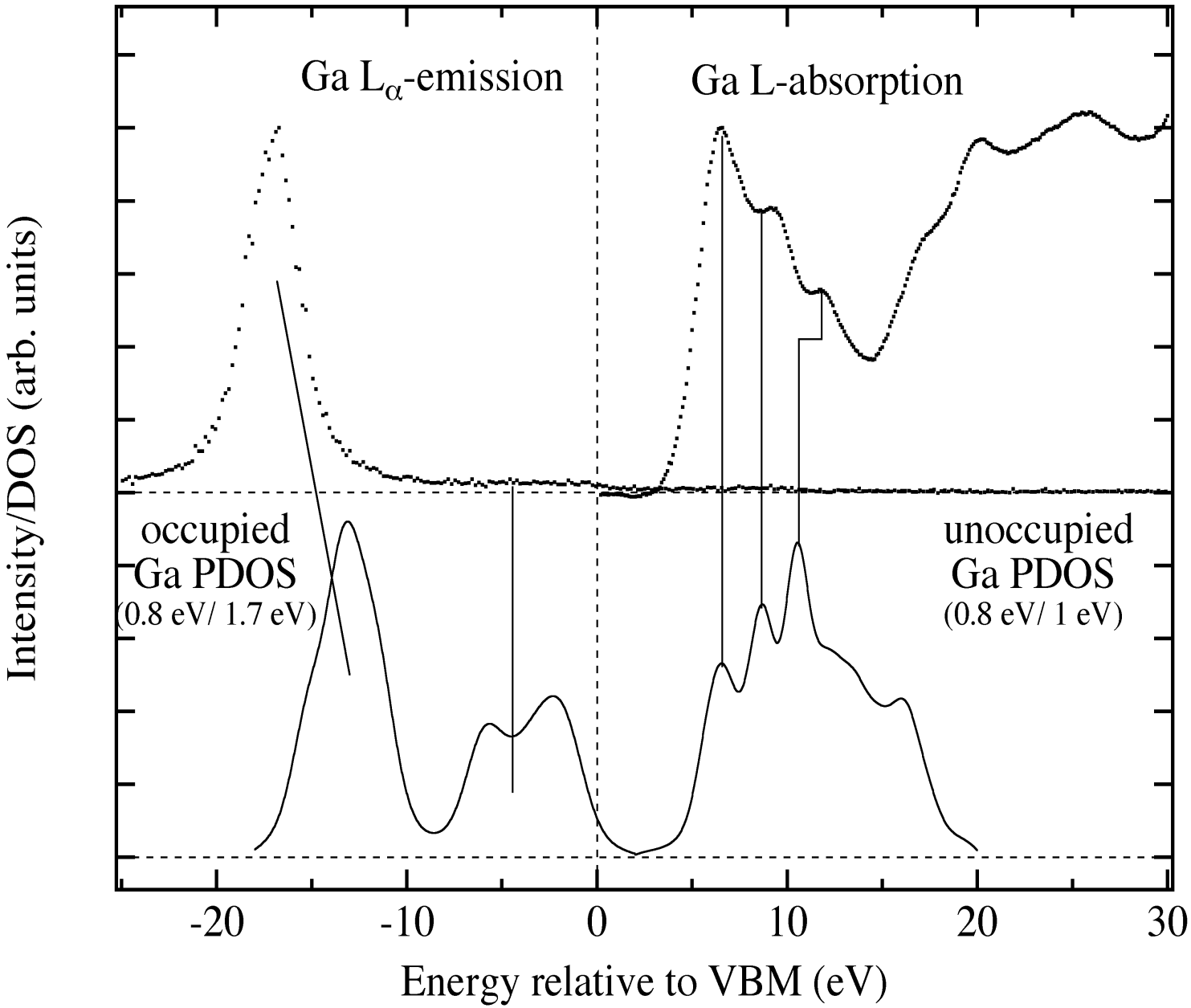


- Wurtzite GaN has a hexagonal crystal structure
- Lattice parameters: a = 3.18 Å, c = 5.185 Å
- Band gaps
  - GaN: 3.4 eV;
  - AlN: 6.2 eV
  - InN: 1.8 eV,
- Bulk and surface Brillouin zones are hexagonal

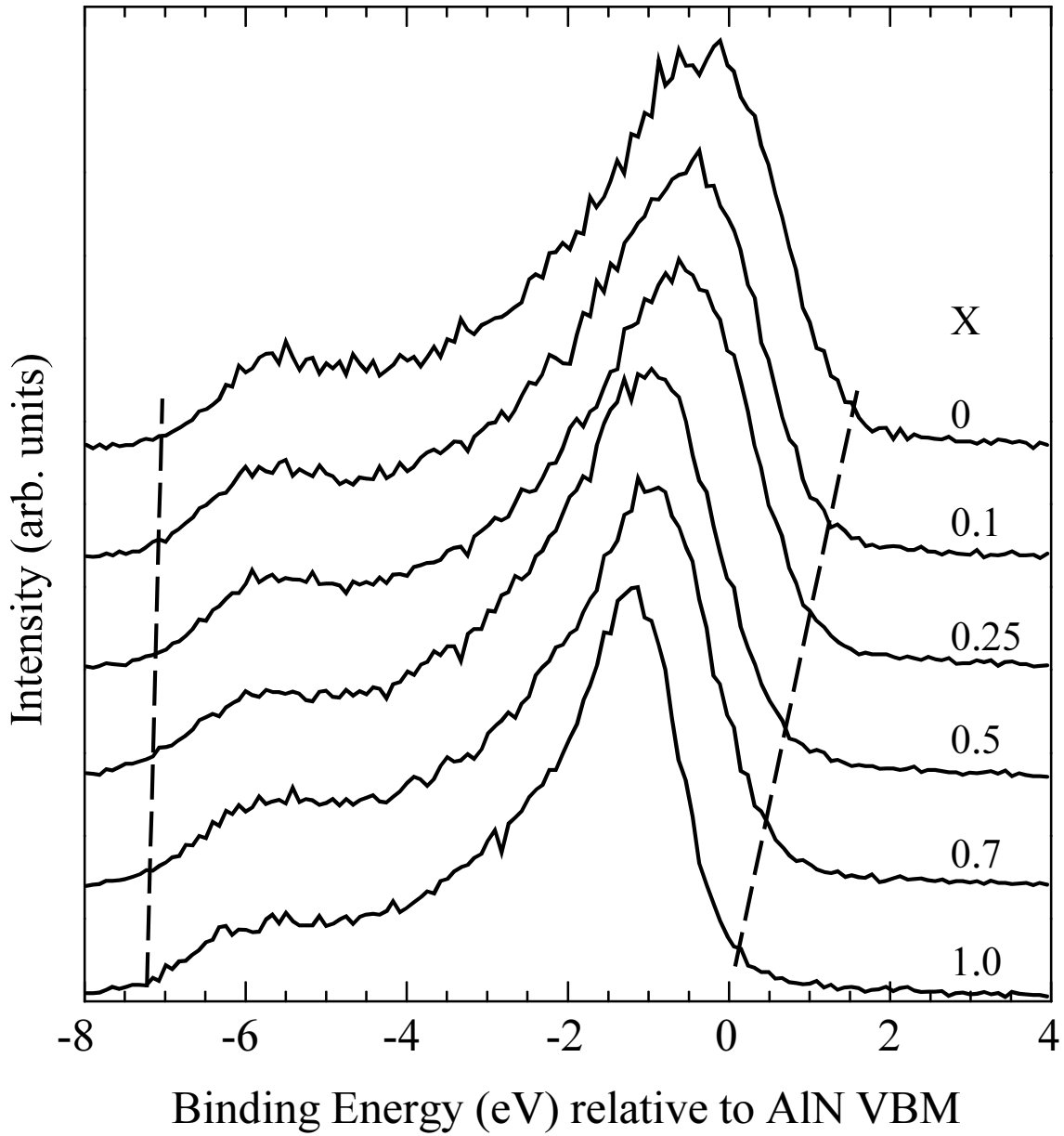
N *2p* PDOS in GaN



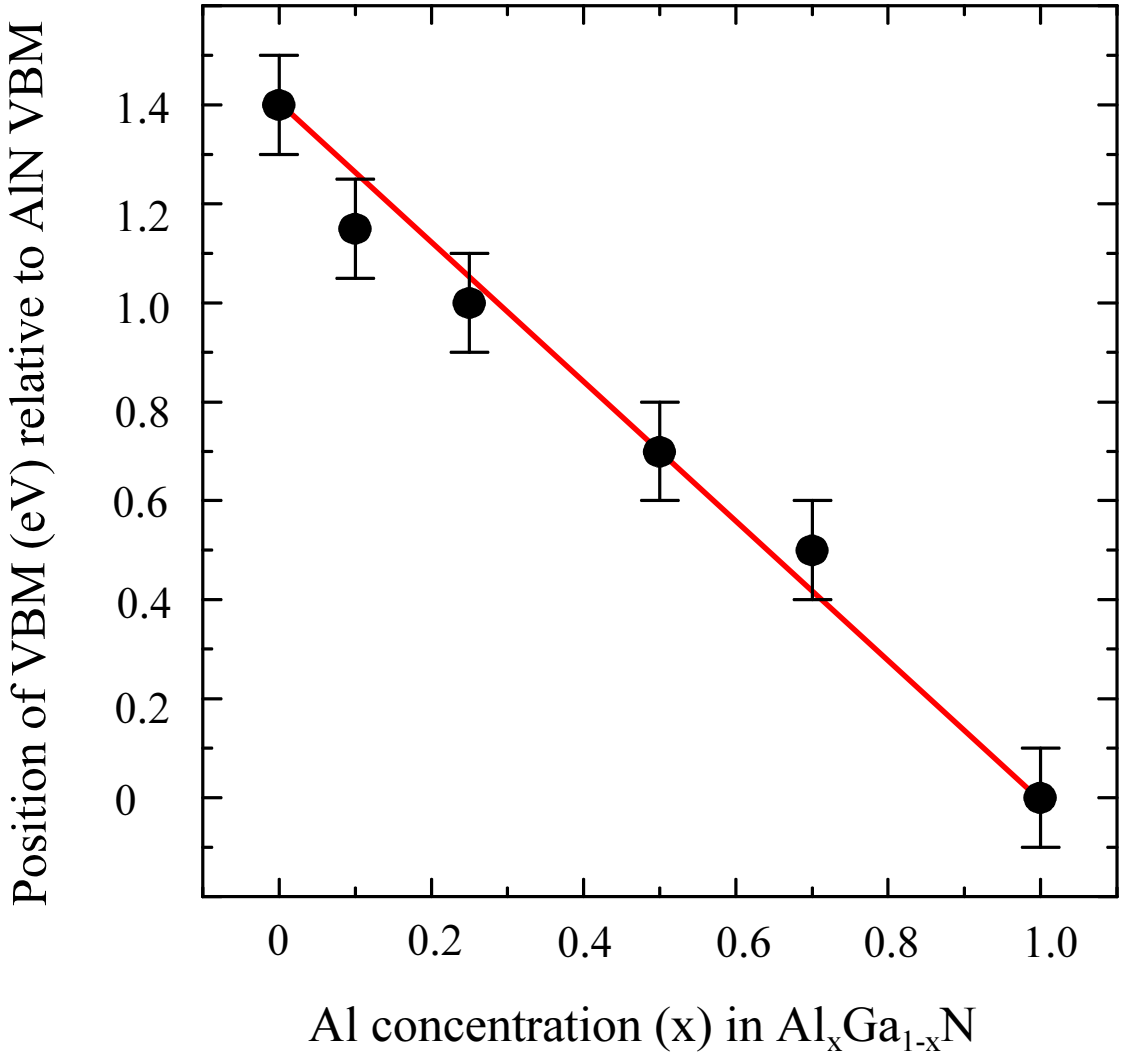
Ga PDOS in GaN



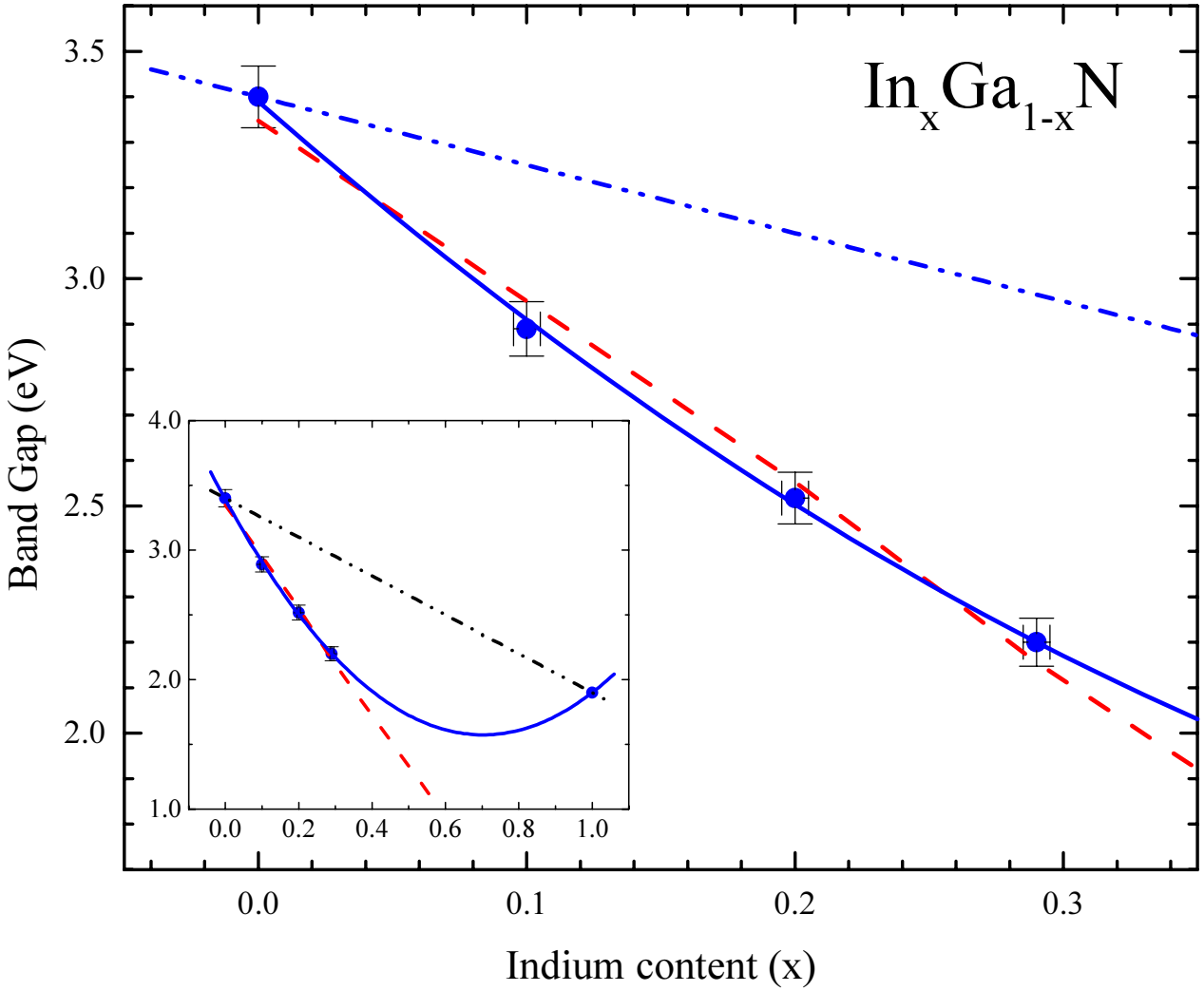
N *2p* PDOS for $Al_xGa_{1-x}N$



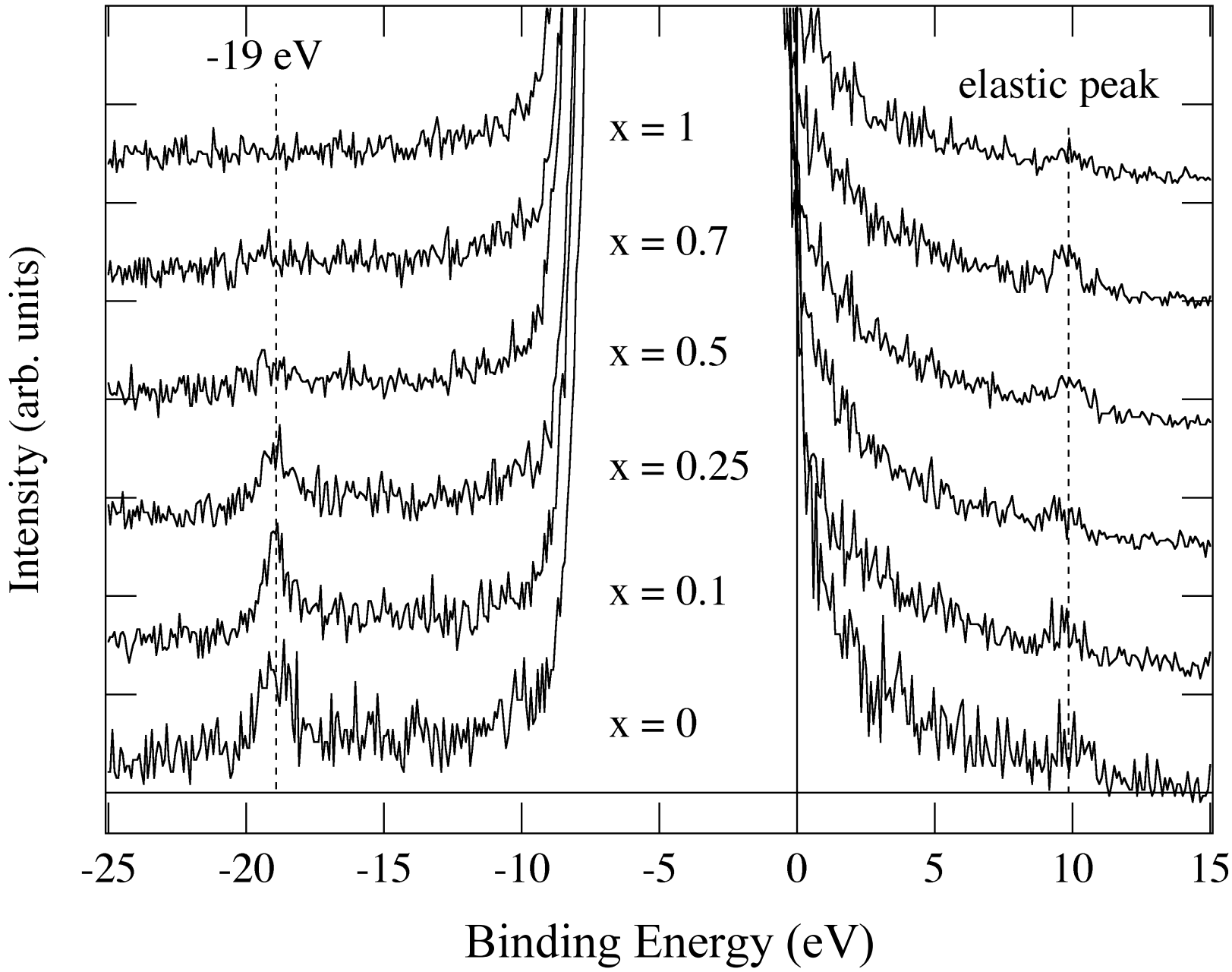
Elementally resolved motion of the valence band maximum in $Al_xGa_{1-x}N$



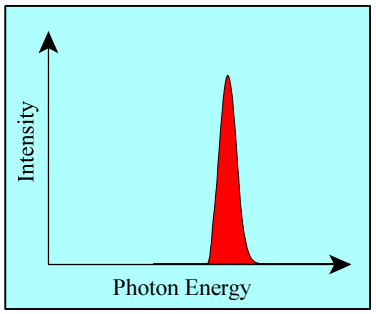
Elementally resolved band gap evolution in $In_xGa_{1-x}N$

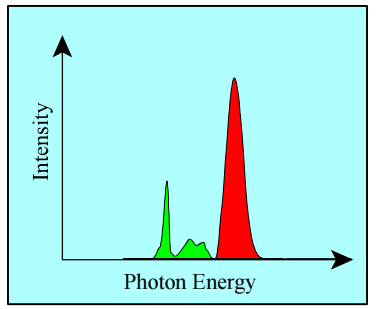


N *2p* - Ga *3d* hybridization in $Al_xGa_{1-x}N$



Resonant Inelastic X-Ray Scattering





Conduction Band

Valence Band

Binding Energy

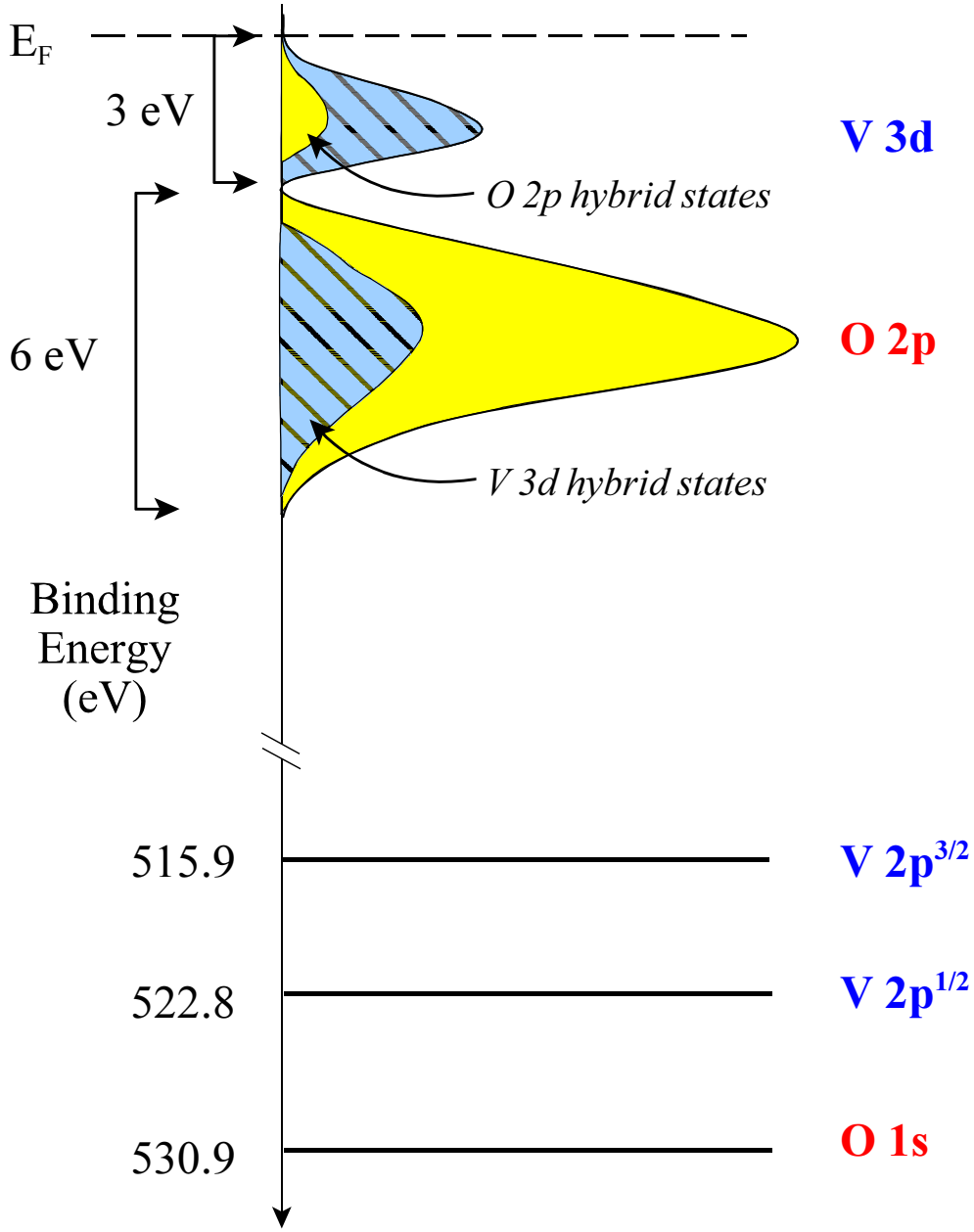
$E_{ex} = h\nu - h\nu'$

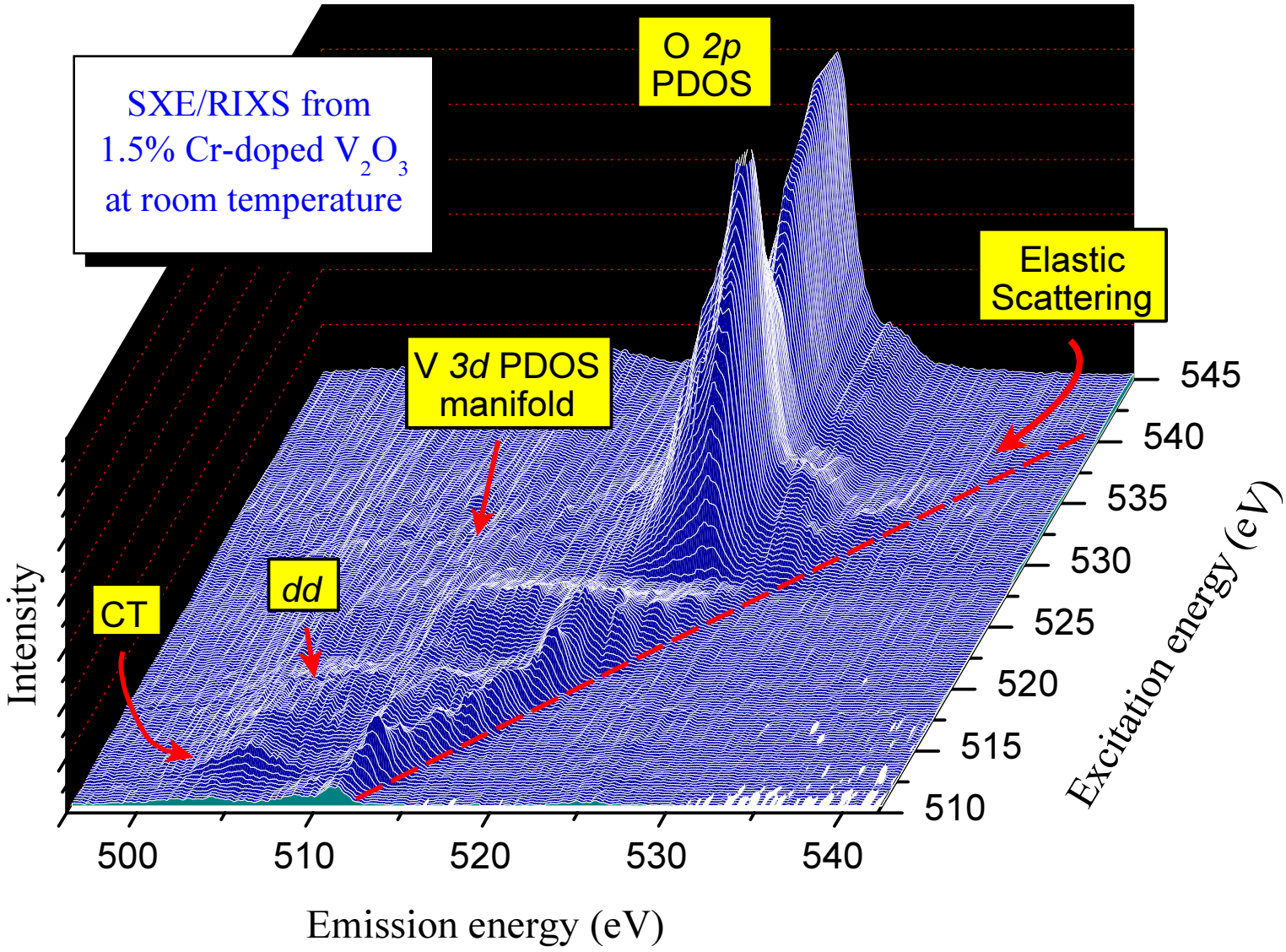
$h\nu$

$h\nu'$

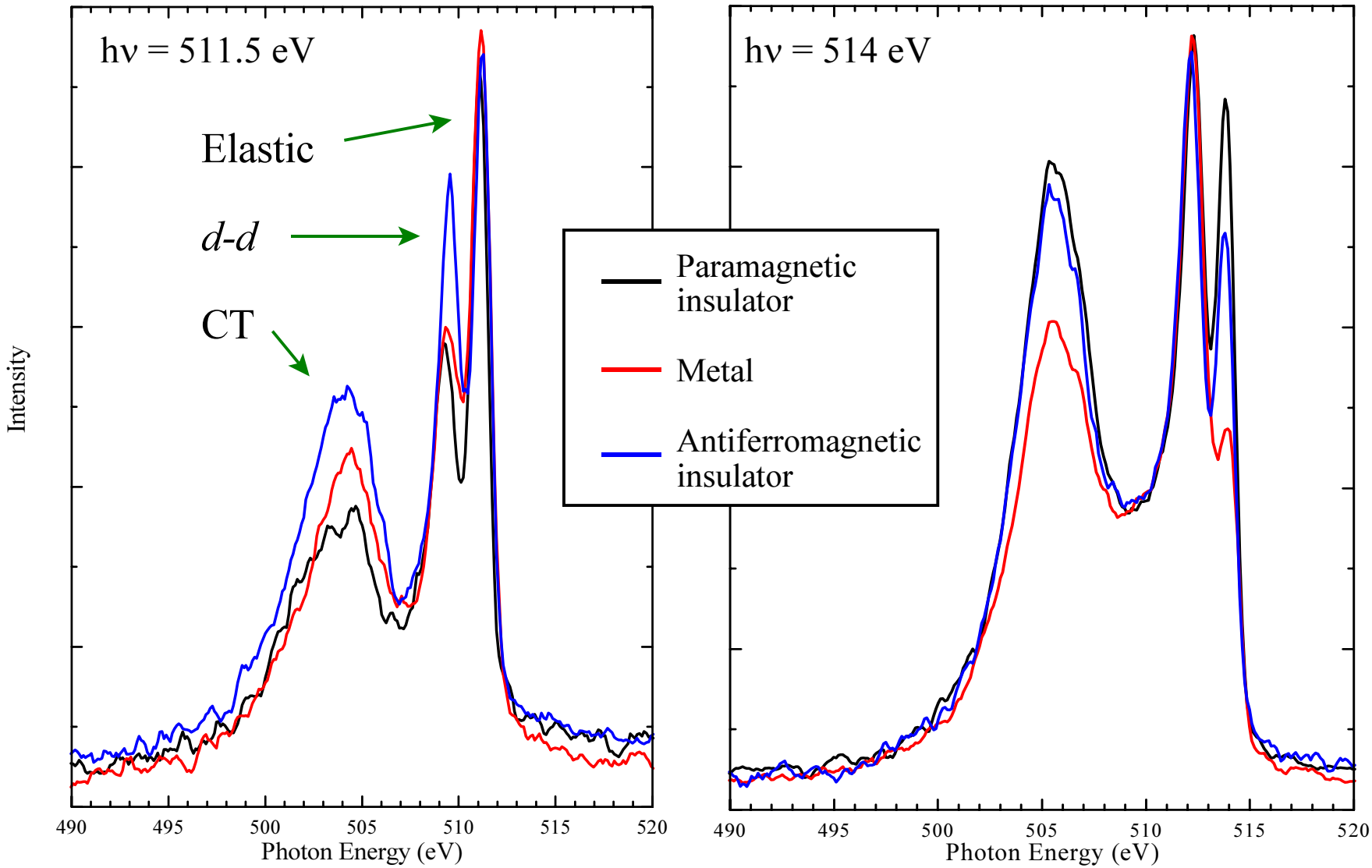
Core Level

Schematic Electronic Structure for V_2O_3

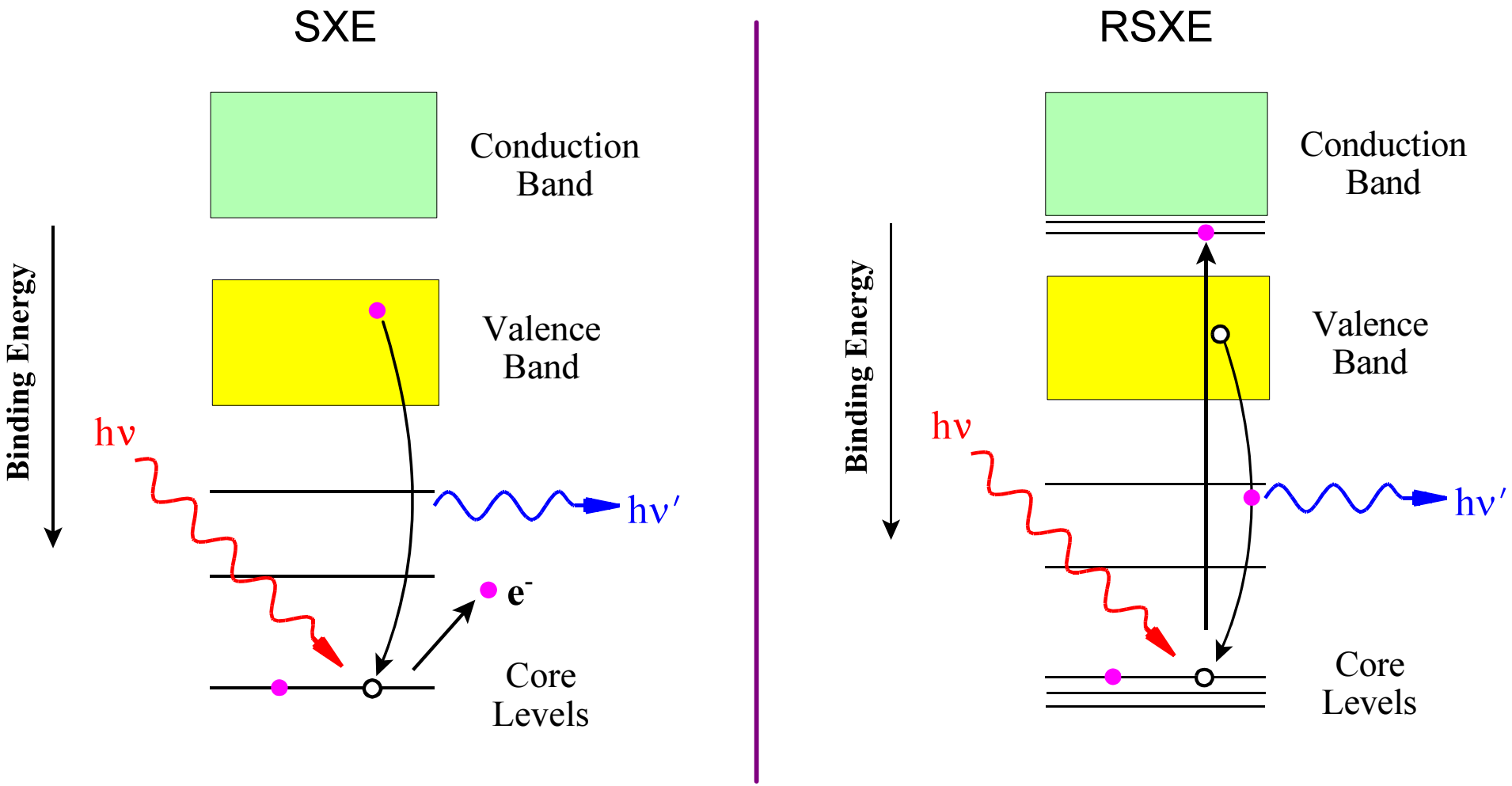



SXE/RIXS from
1.5% Cr-doped V_2O_3
at room temperature
O 2p
PDOS
Elastic
Scattering
V 3d PDOS
manifold
dd
CT
Intensity
500
510
520
530
540
Emission energy (eV)
545
540
535
530
525
520
515
510
Excitation energy (eV)

RIXS from 1.5% Cr-doped V_2O_3

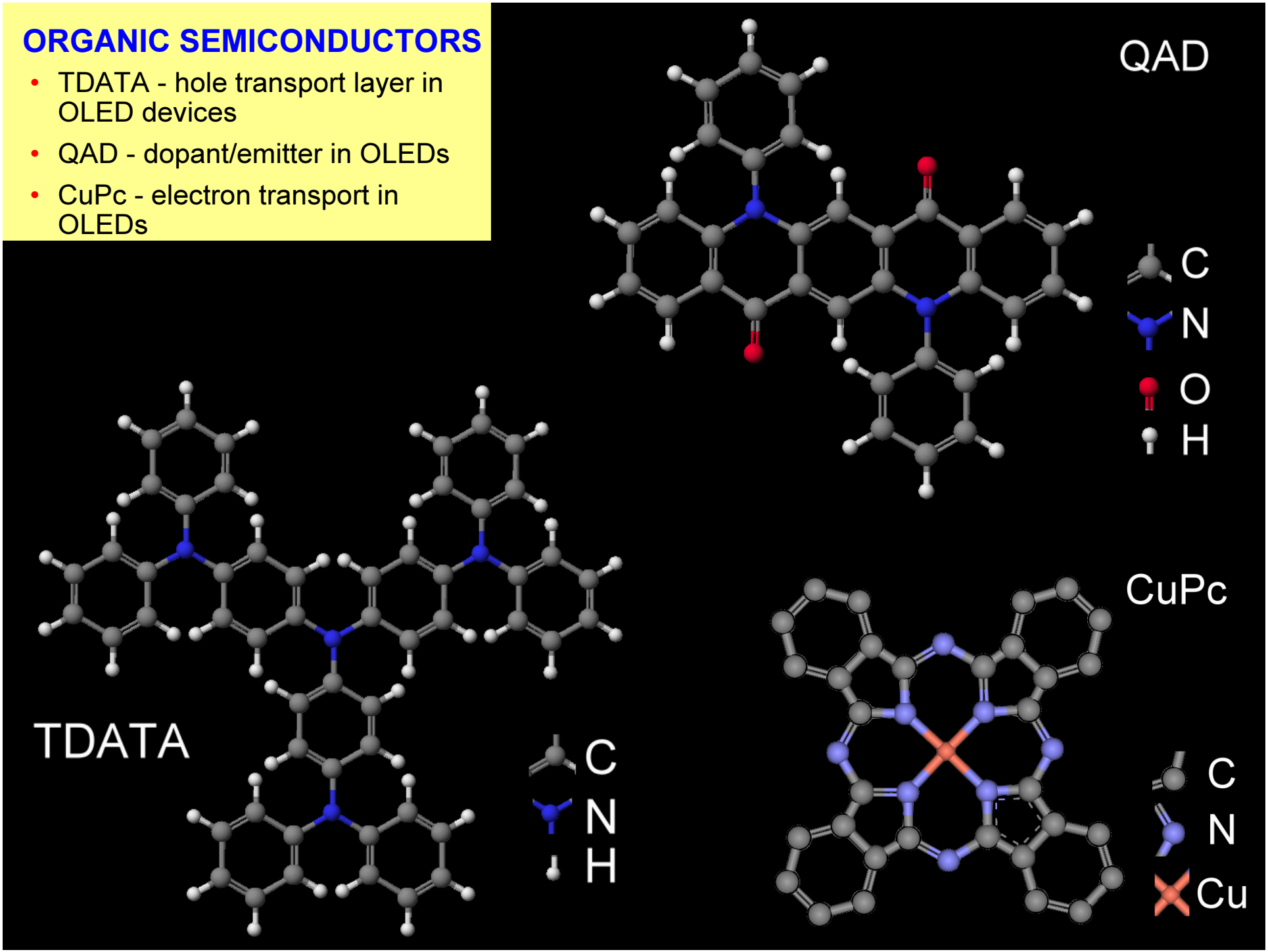


Resonant and Non-Resonant Soft X-Ray Emission

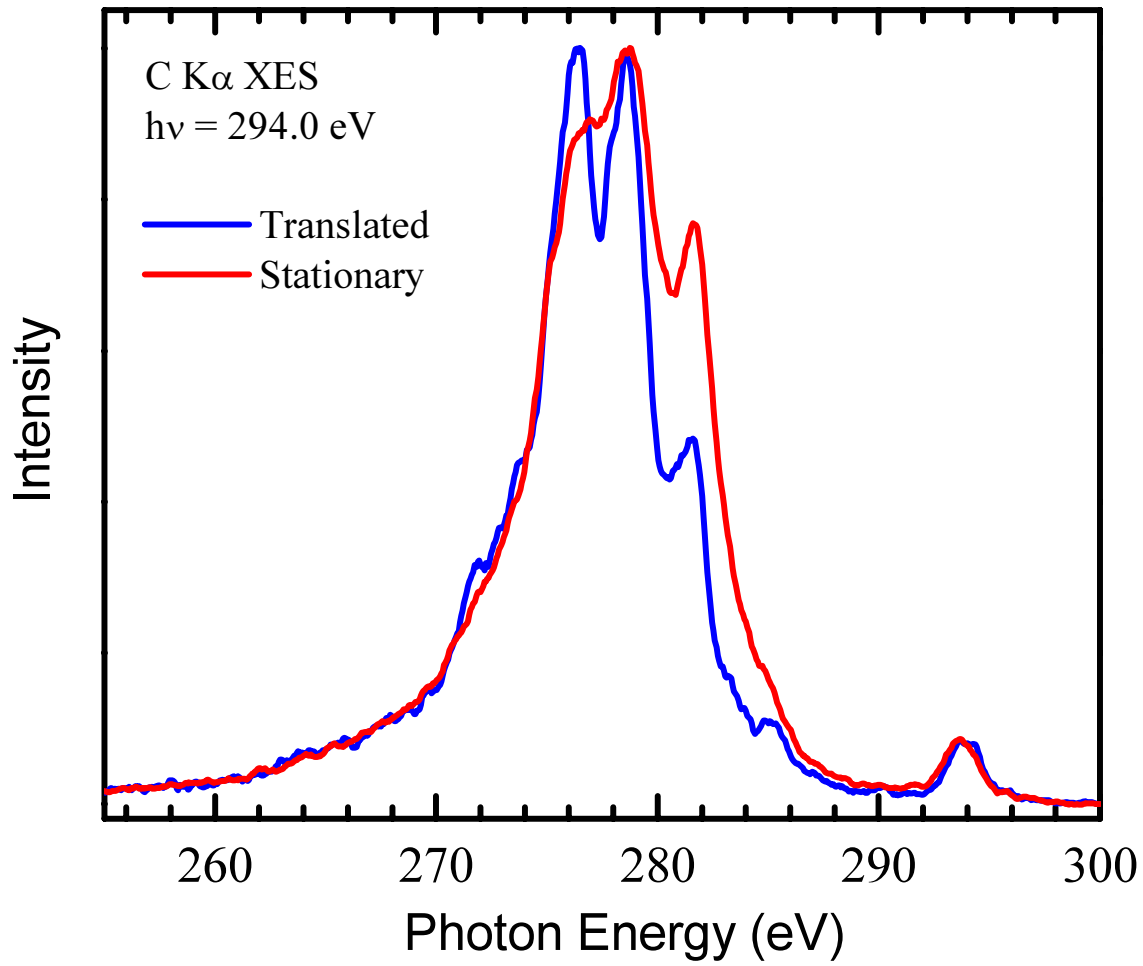


ORGANIC SEMICONDUCTORS

- TDATA - hole transport layer in OLED devices
- QAD - dopant/emitter in OLEDs
- CuPc - electron transport in OLEDs

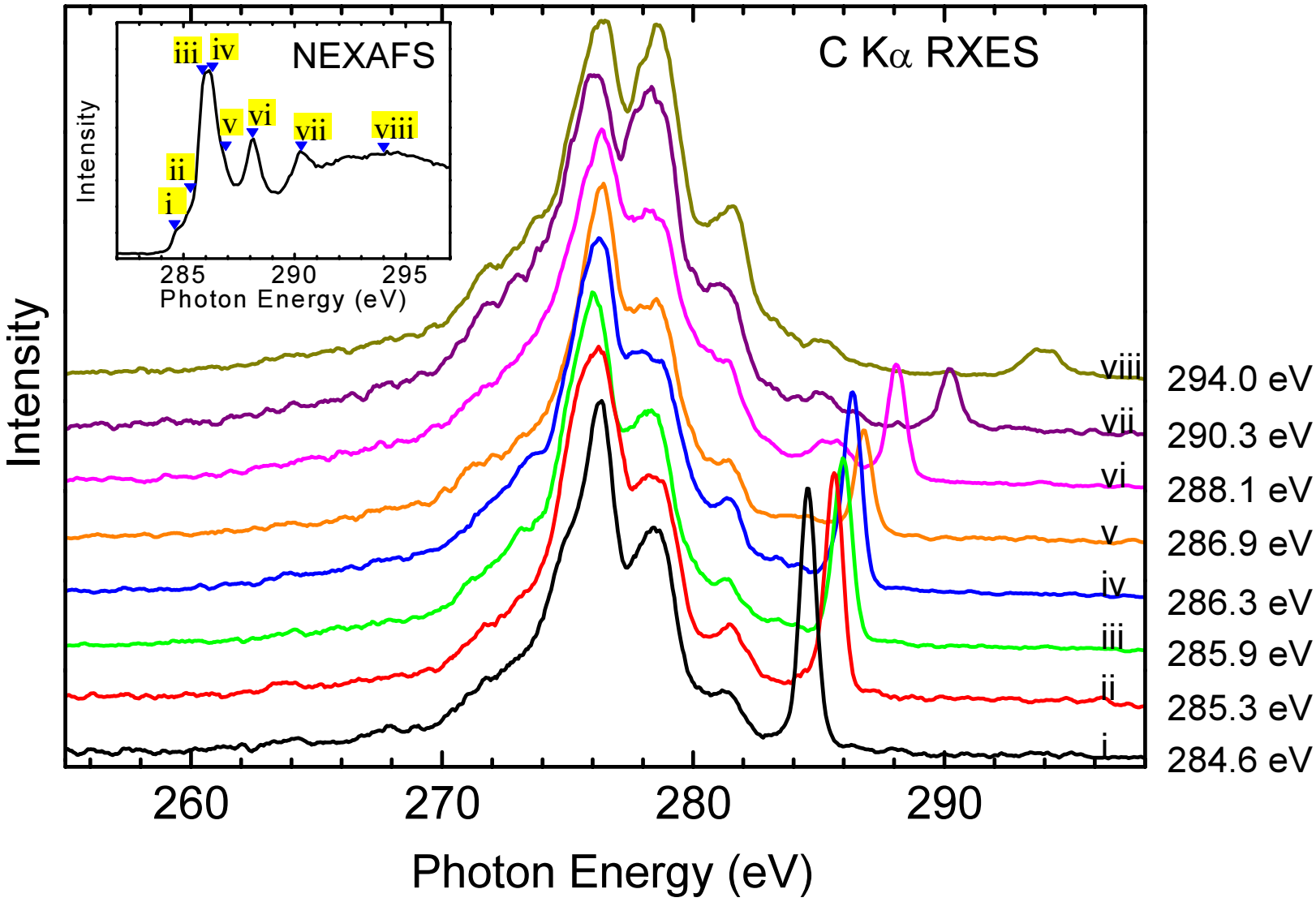


SXE from CuPc - Translated vs. Stationary samples

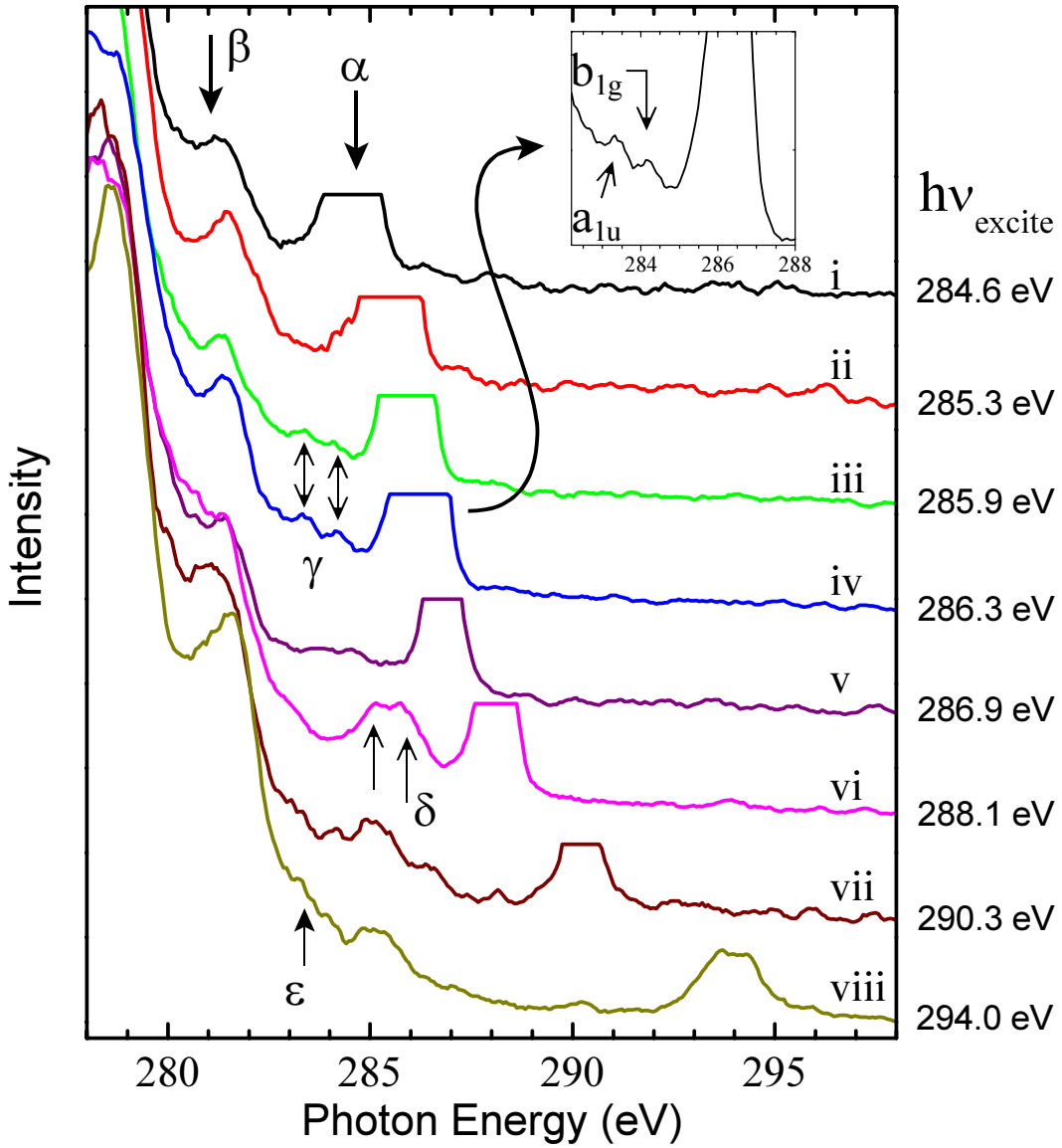


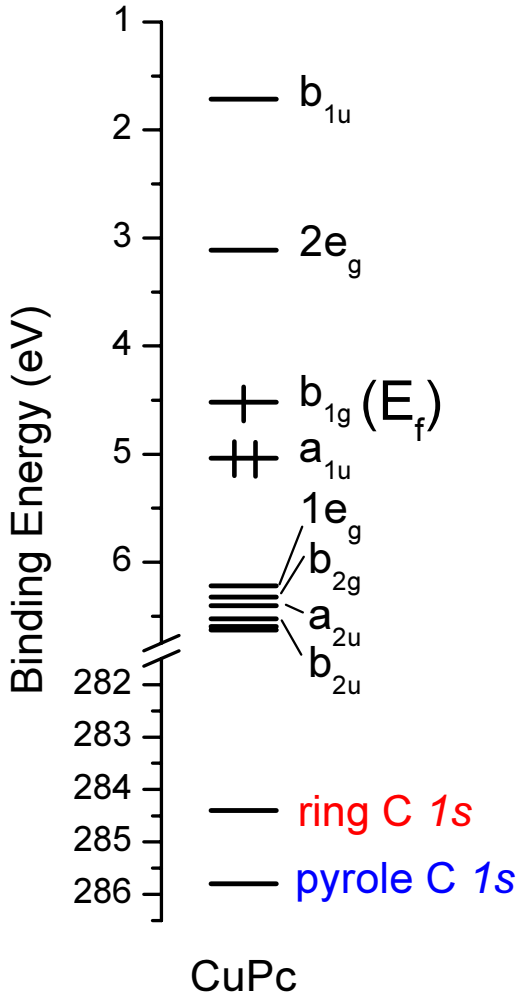
Copper phthalocyanine RXES

- Presence of two C *1s* levels is masked in NEXAFS, but visible in RXES



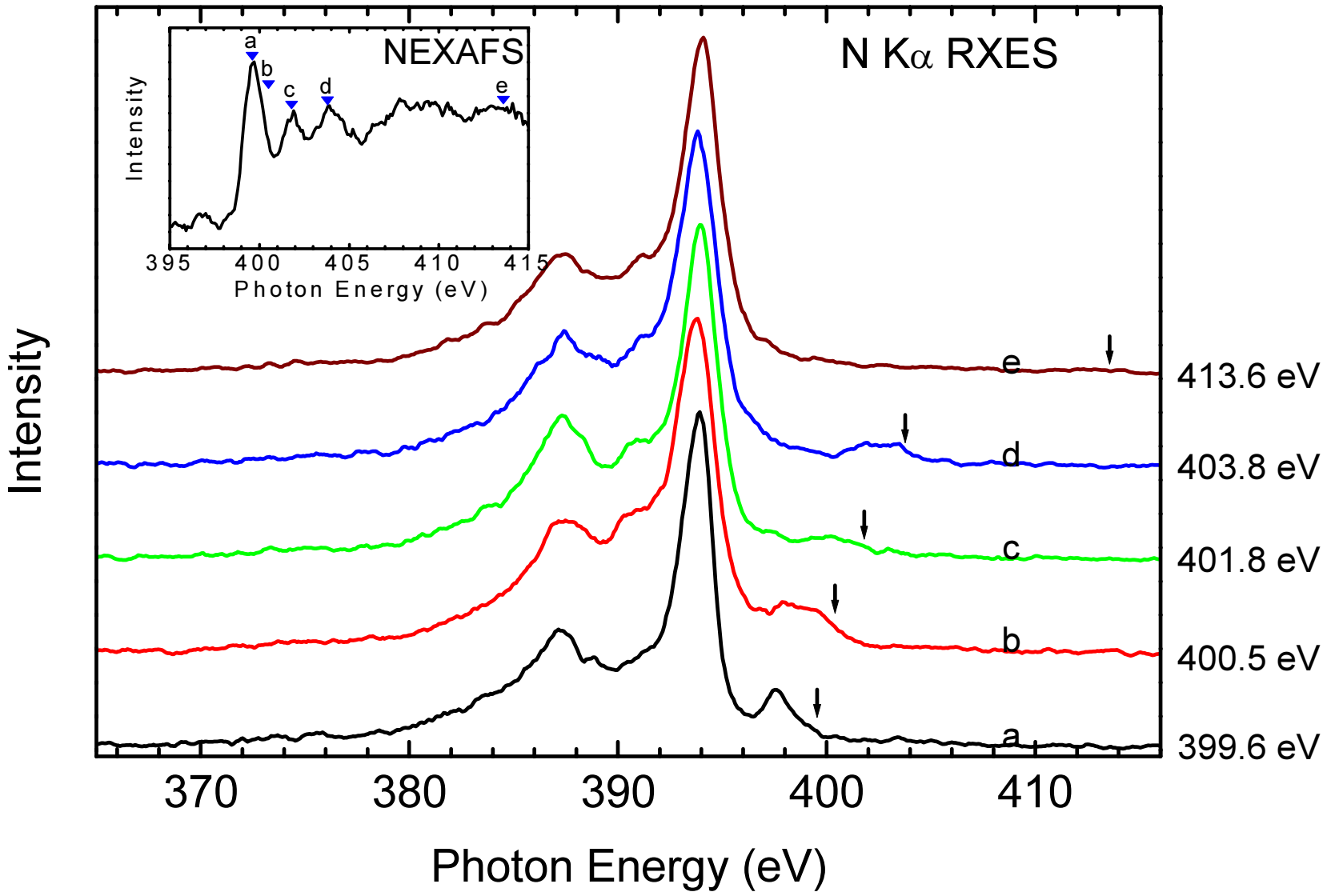
CuPc - RXES detail





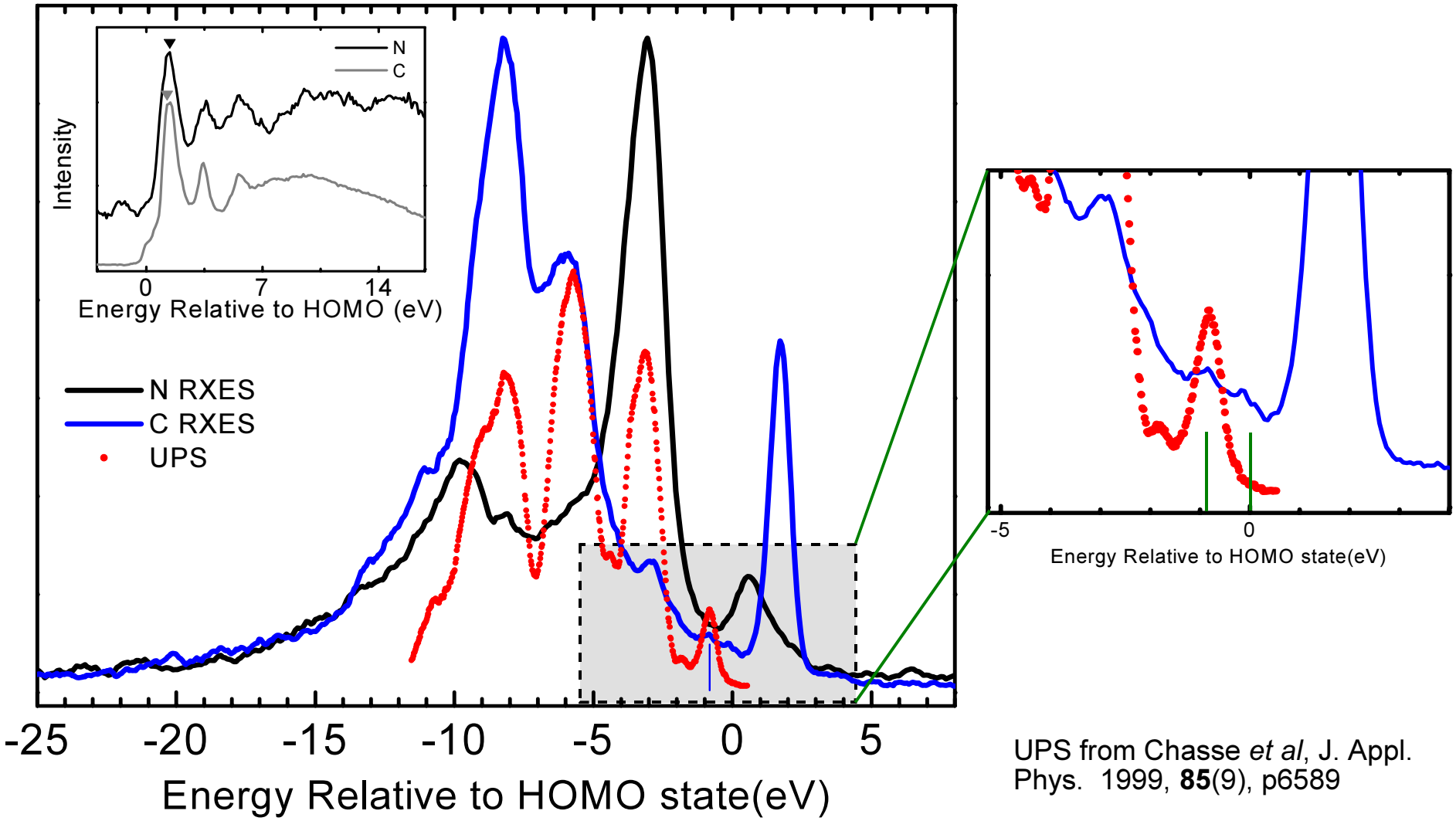
DFT calculation Liao *et al*, J. Chem Phys. 2001, 114(22), p 9780

Copper phthalocyanine RXES



CuPc RXES / UPS comparison

- RXES represents *2p* character of C and N states of the valence band
- UPS represents joint or total density of states of the valence band

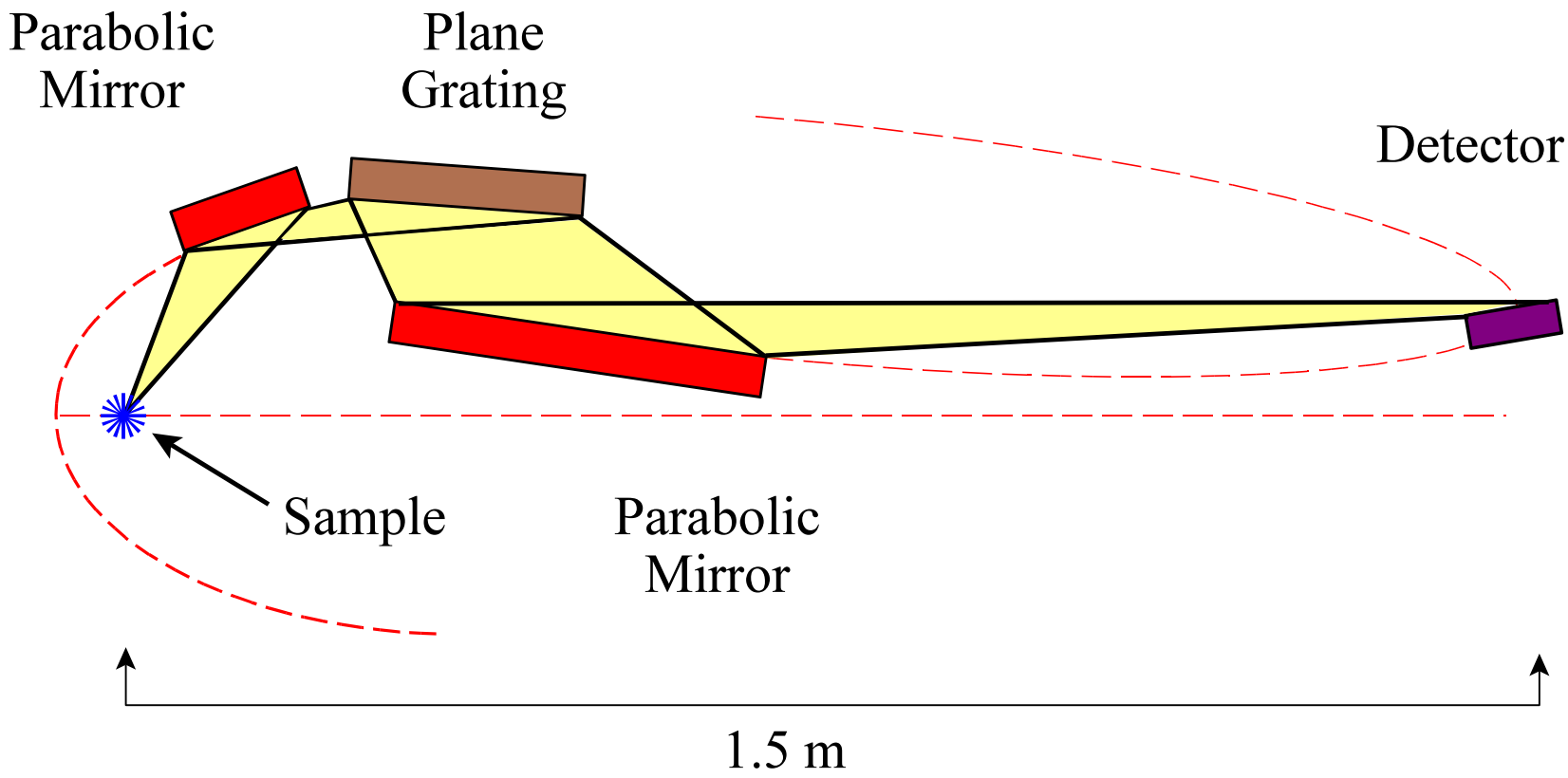


UPS from Chasse *et al*, J. Appl. Phys. 1999, **85**(9), p6589

Conclusions

- Synchrotron-radiation excited soft x-ray emission (SXE) is a new, versatile probe of electronic structure in complex materials where photoemission is inapplicable.
  - *Organic solids*
  - *Insulating or poorly conducting materials*
  - *Powdered or nanostructured samples*
  - *Materials in liquid suspension*
  - *Samples in applied electrical or magnetic fields.*
- Resonant inelastic x-ray scattering (RIXS) allows direct measurement of low energy excitations under the same circumstances as SXE
- Signal strength for RIXS experiments is a significant limitation, indicating a need for new spectrometer designs.....

Next Generation RIXS Spectrometer



- High transmission
- Fixed detector
- Design resolution <10 meV @ 100 eV photon energy