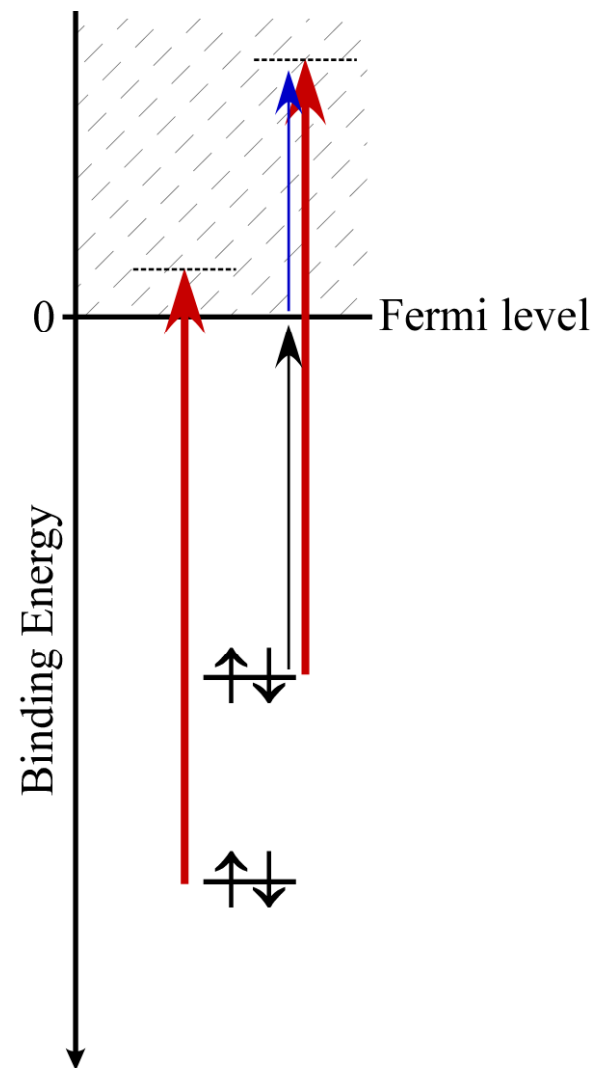


The Photoelectric effect and Photoelectron Spectroscopy

- photoelectron spectroscopy is based on *photoelectric effect*
- binding energy of ejected photoelectrons is obtained from *kinetic energy* after ionisation

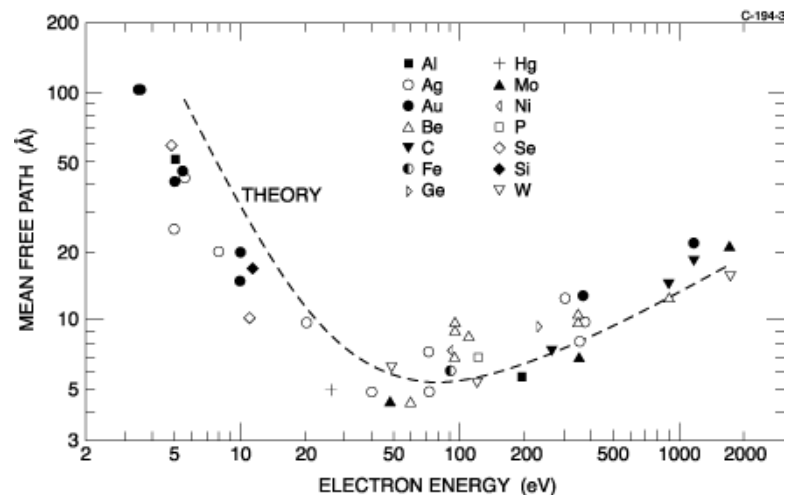
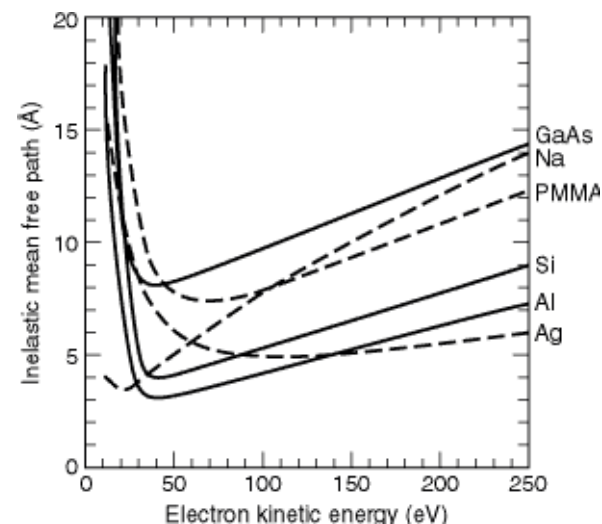
$$E_k = h\nu - E_b$$
- requires that e^- are not perturbed by collisions or other interactions
- assumes that electronic structure doesn't change upon ionisation (*Koopmans' theorem*)
- need to detect *primary* photoelectrons
- *secondary* photoelectrons are useless
- PES is therefore usable for
 - surfaces (very surface sensitive – *vide infra*)
 - gas phase samples (low concentration)



Mean Free Path of Electrons

- avg distance travelled by primary photoelectron
- depends on e^- kinetic energy \rightarrow *Universal Curve*
- PES is *very* surface sensitive
 - important technique for surface science
 - must be careful for bulk properties
 - worry about effects due to surface
 - defects, contamination, & charging

(not an issue for gas phase experiments)
- important – sensitivity changes with photoelectron kinetic energy
 - intensities are affected by this
 - from 20-250 eV: \sim constant (5-10Å only)



Experimental Considerations for Electron Detection

- electrons can't get very far
- need to know kinetic energy of primary electrons
- must do experiments in Ultra High Vacuum (UHV... $<10^{-9}$ torr)
 - gas phase and/or clean surfaces
 - no solutions, no dirty surfaces, no interfaces
 - cannot withstand UHV
- electron analysers – electric/magnetic fields as deflect
 - hemispherical analyzer (HSA)
 - cylindrical mirror analyzer (CMA)
- electron detectors – “channeltrons”
 - *a.k.a.* electron channel multiplier
 - create secondary electron avalanche (signal enhancement)
 - signal gain $\sim 10^9$!

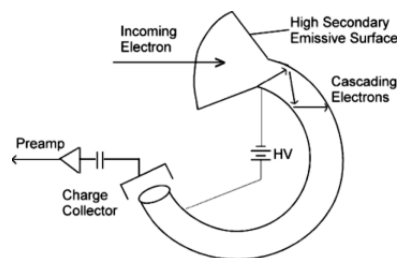
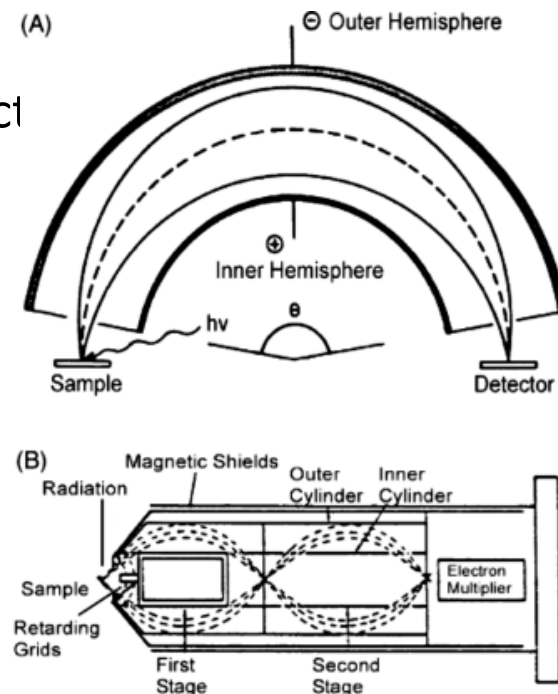


Fig. 5. Schematic of channeltron.



3.1.4 Valence Photoelectron Spectroscopy

Sources of high-energy radiation

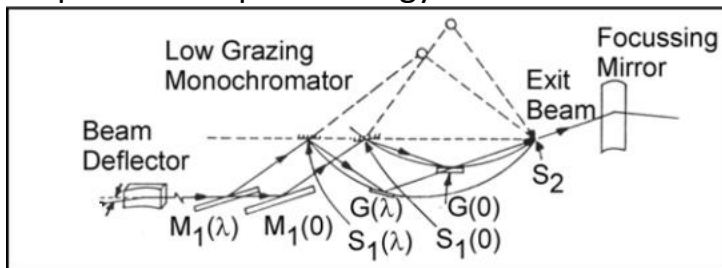
- Gas Arc Lamps → e.g. Helium, Neon
 - gas 'anode' is excited by electrical discharge
 - photon emission brings gas atoms back to ground state
- X-ray arc lamps → e.g. Mg, Al
 - higher energy (X-ray) emission
 - same principle...
- Synchrotron Radiation Source
 - acceleration of relativistic electrons → broadband light emission
 - collect photons – optical energy selection

$$He(I) = 21.2eV$$

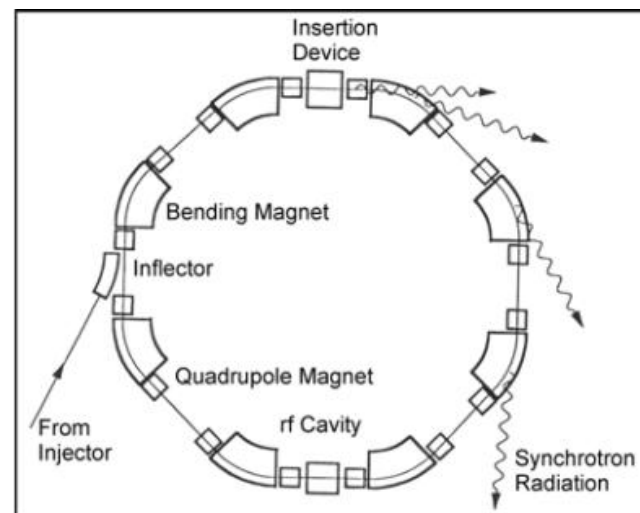
$$He(II) = 40.8eV$$

$$Mg K_{\alpha} = 1254eV$$

$$Al K_{\alpha} = 1487eV$$



- completely tunable photon energy source
- significantly brighter source (10^2 - 10^8 more intense)



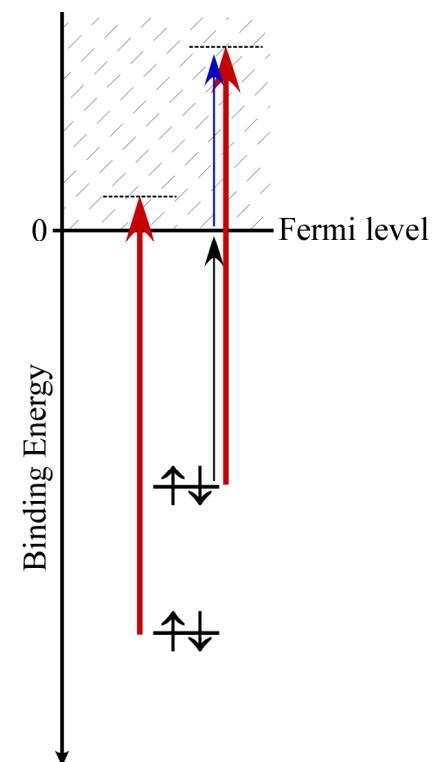
Basic considerations of the PES experiment

- spectrum is “snapshot” of a series of one-electron *ionised* states
 - correlate with initial state of *unionised* molecule
 - *Franck-Condon Principle* → *i.e.*, Born-Oppenheimer - nuclei don't have a chance to move
 - *Koopmans' theorem* → electronic structure of molecule doesn't change upon ionisation



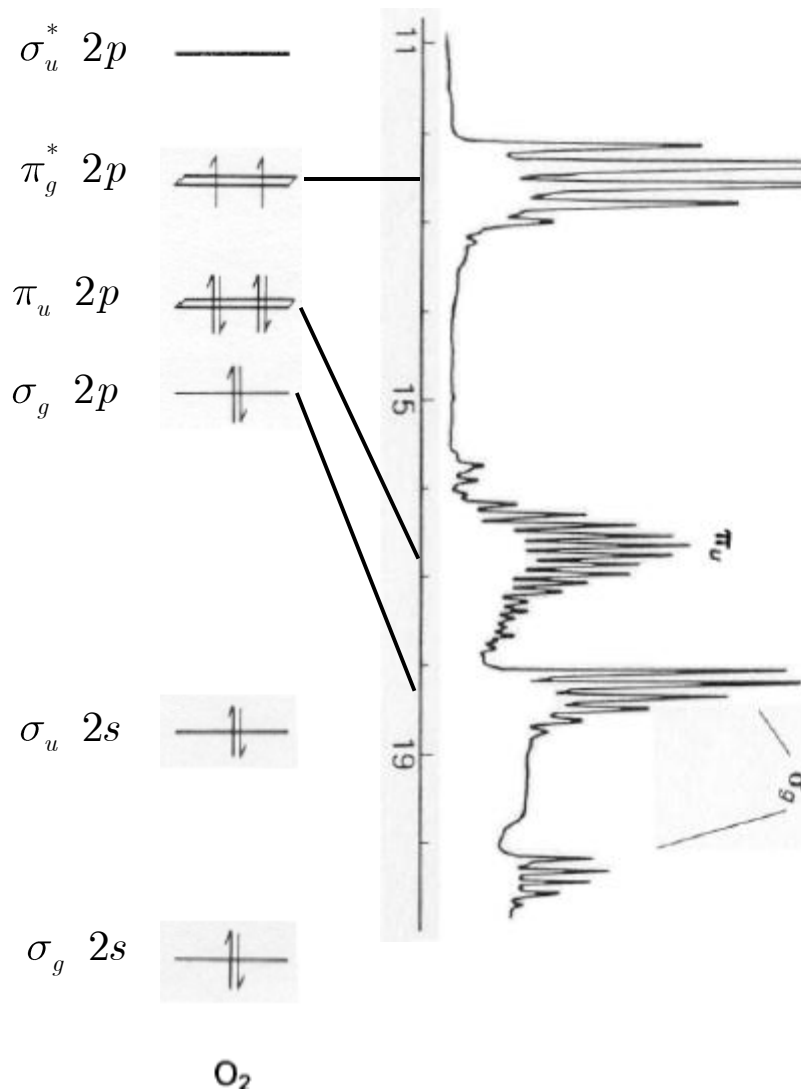
$$\left. \begin{aligned} \psi_1^{GS} &\rightarrow a|\phi_A\rangle + b|\phi_B\rangle \\ \psi_1^+ &\rightarrow c|\phi_A\rangle + d|\phi_B\rangle \end{aligned} \right| a = c, b = d$$

- Gives an ‘energy map’ of valence molecular orbitals (energies)
 - including vibrational information (in gas phase)
- can also be used to get composition of MOs (intensities)
 - atomic photoionisation cross-sections
 - *e.g.*, the gas phase spectrum of O₂
 - very high resolution
 - provides information about *electronic and vibrational* final states



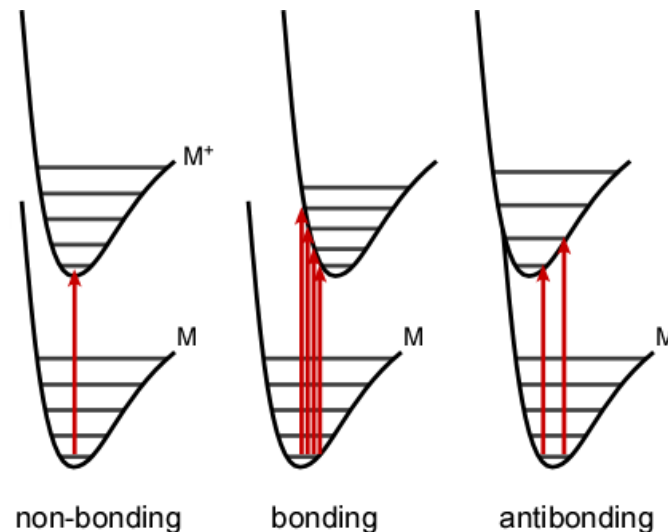
3.1.4 Valence Photoelectron Spectroscopy

Gas Phase Valence Photoelectron Spectroscopy of O₂



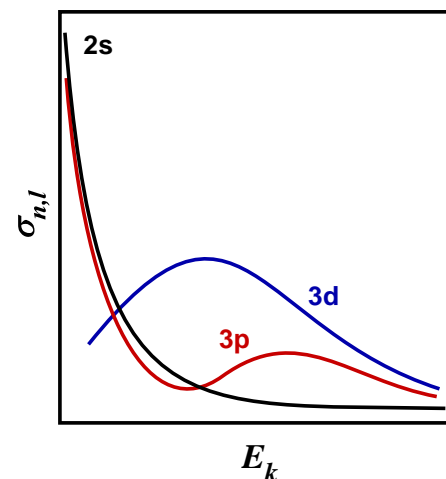
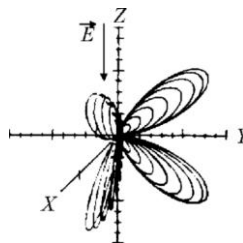
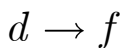
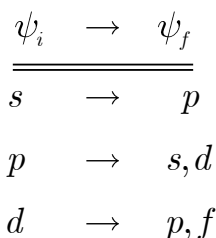
assignment is aided by vibrational structure
(luxury of gas phase spectroscopy)

$\Delta r = 0$	$\Delta r > 0$	$\Delta r < 0$
$\nu_{M^+} = \nu_M$	$\nu_{M^+} < \nu_M$	$\nu_{M^+} > \nu_M$



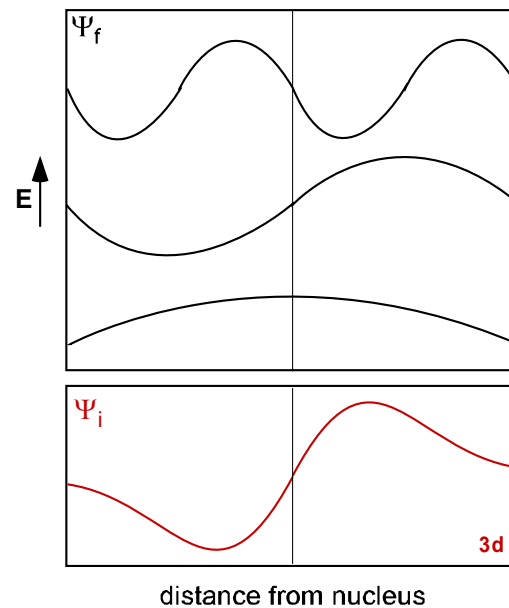
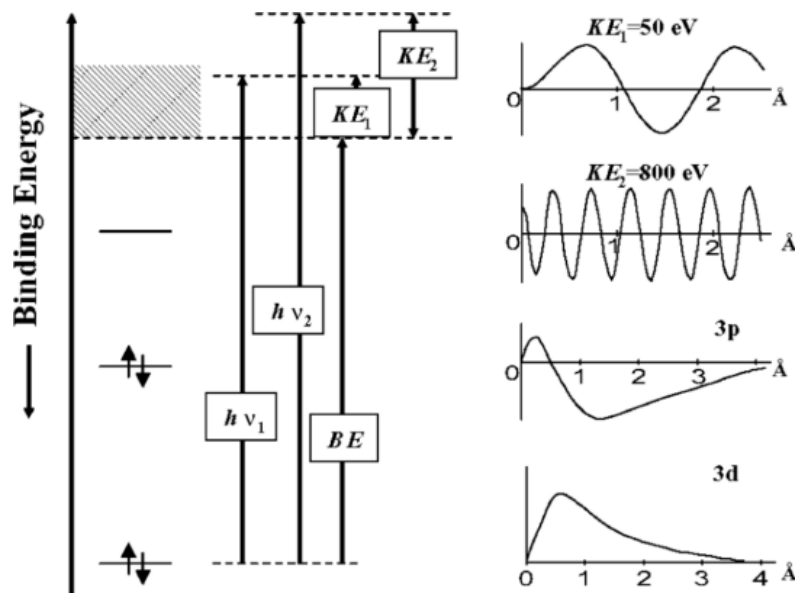
Atomic Photoionisation Cross-Sections

- equation that defines photoionization probability $\rightarrow \sigma_{n,l} = \frac{4\pi^2 a_0^2 \alpha}{3g} h\nu |M_{if}|^2$
 - similar to bound-state transitions, *i.e.*, $f \propto \langle \Psi_i | \vec{\mu} | \Psi_f \rangle^2$
 - biggest difference is nature of final state
 - wavefunction of emitted photoelectron *depends on its kinetic energy*
- symmetry of final state wavefunction
 - must include both oxidized molecule + photoelectron
 - Koopmans' theorem allows us to simplify and only worry about behaviour of photoelectron
 - depends on initial state wavefunction (completely flexible – always dipole allowed)



3.1.4 Valence Photoelectron Spectroscopy

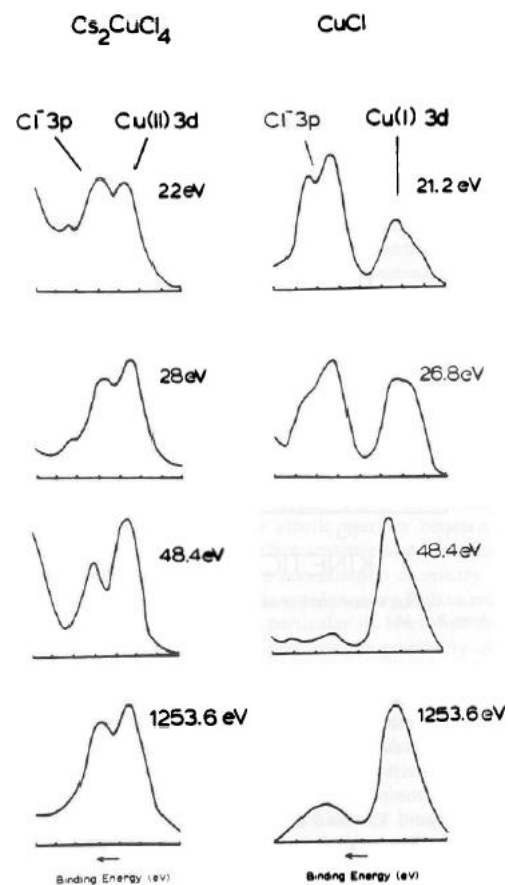
- symmetry of photoelectron wave defined by initial AO
- λ of final state gets shorter at higher kinetic energies
 - best overlap when “matching” *photoelectron* radial distribution with orbital wavefunction \rightarrow delayed maxima (e.g. 3d orbital)
 - presence of radial nodes in orbital wavefunction generally leads to destructive interference at certain photoelectron energies \rightarrow Cooper minima (e.g. 3p orbital)



Molecular Photoionisation Cross-Sections

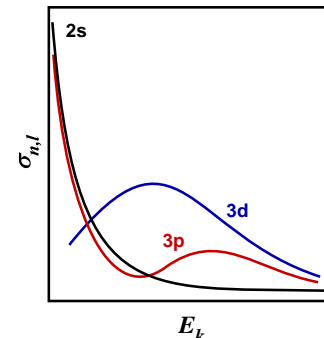
- describe molecular orbital wavefunctions as LCAO $\rightarrow \psi_{MO} = \sum_i c_i \phi_i$
- consider σ_{MO} as sum of atomic contributions $\rightarrow \sigma_{MO} = \sum_i c_i^2 \sigma_i$

- the cross-section of a molecular orbital is directly related to the c_i^2 from each contributing AO
 - look at changes in the PES peak intensities as a function of photon energy
 - direct probe of *initial state* molecular orbital description
 - final state wavefunction is dominated by photoelectron
 - coupling to initial state is key component to intensity
- e.g., valence PES spectra of $[\text{Cu(II)Cl}_4]^{2-}$ and Cu(I)Cl
 - comparison of Cu(II) and Cu(I)
 - which is more covalent?
 - does this make sense?



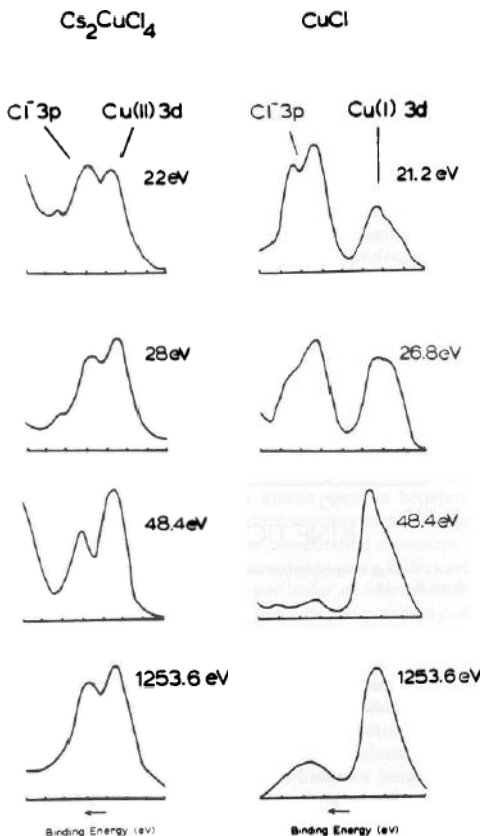
3.1.4 Valence Photoelectron Spectroscopy

• Electronic Structure of Copper Chlorides



Experimental values: $65 \pm 7\%$ Cu 3d
X α theoretical values: 50% (avg) Cu 3d

$D_{2d} \text{Cu(II)Cl}_4^{2-}$					
	Binding energy (eV)	Percent Cu 3d	Percent Cl 3p	Percent other	
3d	5b ₂	-4.6	45.9	51.9	2.1 Cu p
	6e	-5.3	46.7	50.9	2.3 Cu p
	2b ₁	-5.8	56.7	43.3	
	4a ₁	-5.8	46.1	53.9	
	1a ₂	-6.0	0.0	100.0	
3p	5e	-6.1	1.0	99.0	
	4b ₂	-6.8	1.8	95.2	3.0 Cu p
	4e	-7.1	7.4	88.8	3.8 Cu p
	3a ₁	-7.2	57.5	40.3	2.0 Cu s
	1b ₁	-7.7	54.4	45.6	
	3e	-7.9	51.7	46.3	2.0 Cu p
	3b ₂	-8.2	56.6	42.4	1.0 Cu p
2a ₁	-8.5	7.1	73.8	18.6 Cu s	

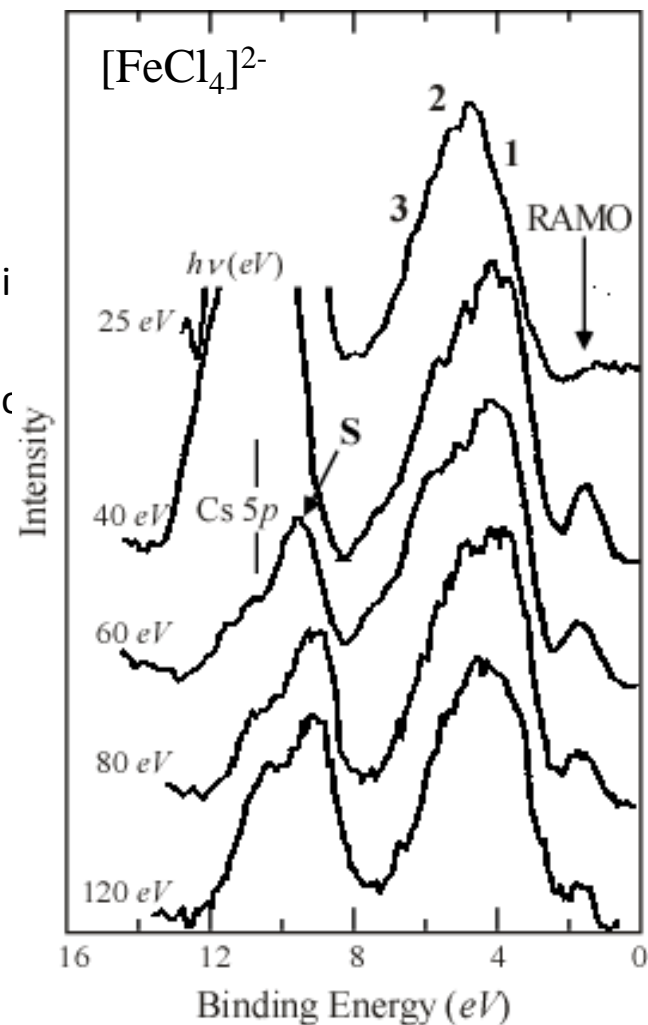
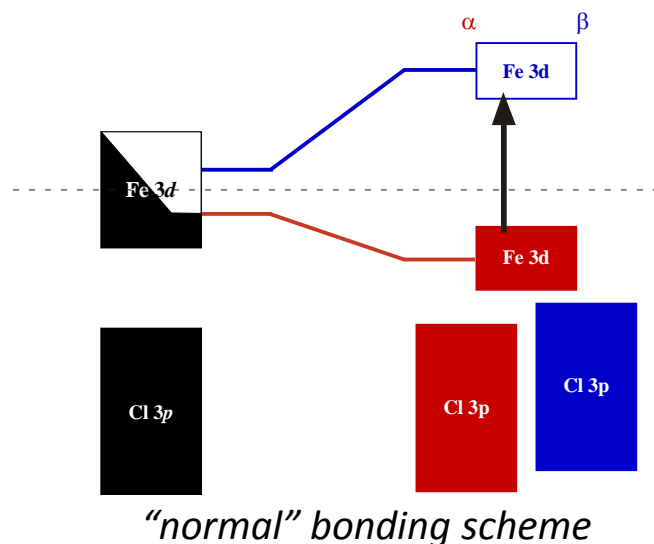


Cu(I)
85 ± 7% Cu 3d
84% (avg) Cu 3d

$D_{2d} \text{Cu(I)Cl}_4^{1-}$					
	Binding energy (eV)	Percent Cu 3d	Percent Cl 3p	Percent other	
3d	5b ₂	-3.2	73.1	25.5	1.4 Cu p
	6e	-3.7	81.6	17.2	1.2 Cu p
	2b ₁	-4.0	89.5	10.5	
	4a ₁	-4.1	90.4	9.6	
	1a ₂	-6.0	0.0	100.0	
3p	5e	-6.1	1.3	98.7	
	3a ₁	-6.7	10.9	89.1	
	4b ₂	-6.8	5.3	93.3	1.4 Cu p
	4e	-6.9	15.4	84.6	
	1b ₁	-7.1	13.7	86.3	
	3b ₂	-7.2	26.2	70.2	3.6 Cu p
	3e	-7.2	8.0	85.4	6.6 Cu p
2a ₁	-8.2	2.2	79.7	18.0 Cu s	

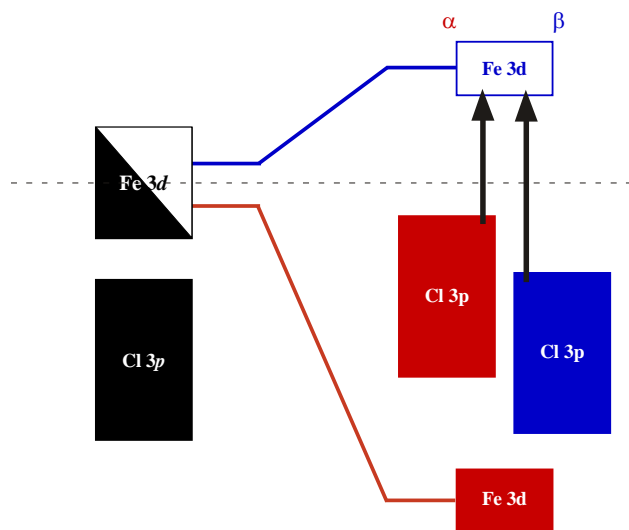
3.1.4 Valence Photoelectron Spectroscopy

- *e.g.*, variable photon energy PES (VEPES) of iron chlorides
 - $[\text{FeCl}_4]^{2-}$ (near T_d HS $3d^6$ complex)
 - delayed maxima observed in 1 and RAMO
 - Fe 3d-character is in highest occupied MOs
 - compare with theoretical calculations
 - use *spin unrestricted* molecular orbital representati
 - splits into α and β orbitals
 - includes “spin pairing energy” into orbital descriptio



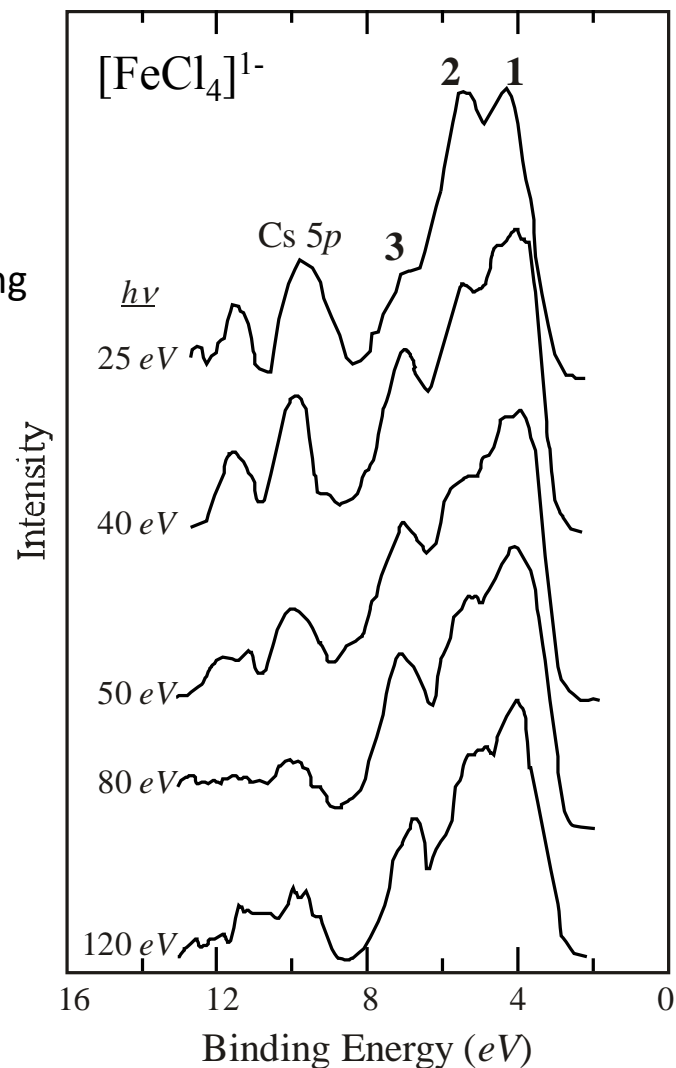
3.1.4 Valence Photoelectron Spectroscopy

- $[\text{FeCl}_4]^{1-}$ (oxidized to HS $3d^5$ complex)
 - delayed maxima observed in peak 3
 - ligand orbitals above the metal orbitals?
 - not “normal” for TM complexes
 - normally think of metal orbitals being antibonding
 - look at theoretical description
 - spin polarization is huge \rightarrow symmetric $S = 5/2$
 - splitting of Fe $3d_{\alpha/\beta}$ orbitals is very large
 - filled Fe $3d_{\alpha}$ drop below Cl $3p$ orbitals



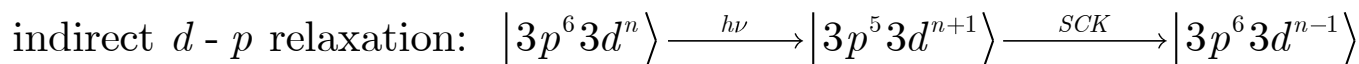
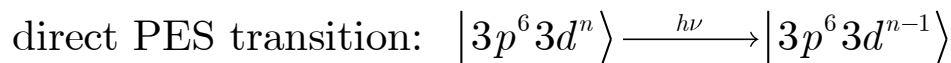
Lowest energy electronic transitions are LMCT transitions, and not LF transitions!

“inverted” bonding scheme



Resonance Effects in VEPES

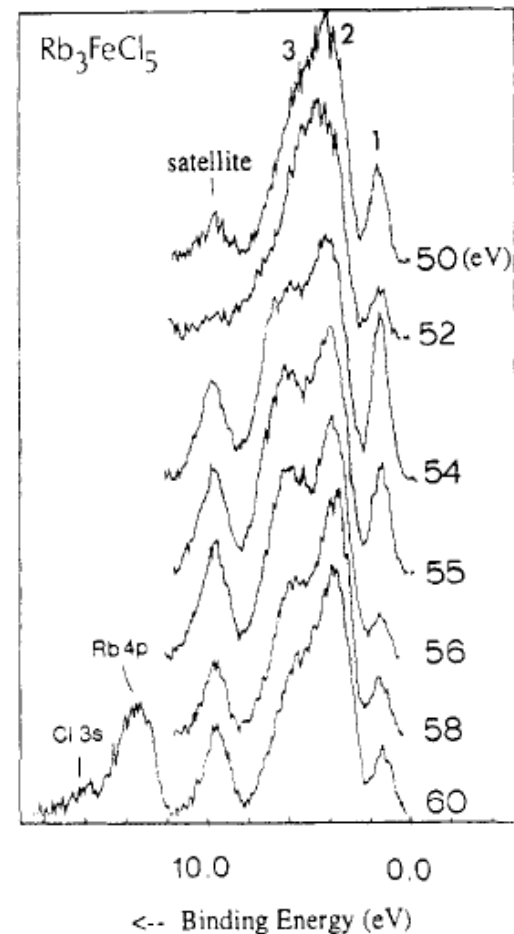
- what happens when PES spectrum is taken using $h\nu$ which correspond to other transitions?
- provides new pathways to reach the same ionized *final states*
 - more pathways = more intensity = enhancement of peaks
 - gives information about final states (not initial states)
- *e.g.*, looking for metal character in Fe complexes
 - look at behaviour across Fe 3*p* ionisation threshold (~54eV)
 - what happens?



additional pathway to same final state
through *super-Coster-Kronig* (SCK) decay

3.1.4 Valence Photoelectron Spectroscopy

- Resonance Effects in $[\text{FeCl}_4]^{2-}$
 - we know that going from $3d^6 \rightarrow 3d^5$ causes huge electronic relaxation
 - can we see this in the *ionized final state* of the ferrous complex?
 - resonance enhancement occurs in peak 3
 - big change from $i \rightarrow f$
 - energy of Fe orbitals drops significantly
 - confirms “initial state” description of ferric species
 - resonance effects are direct indication of ionisation process and its effect on electronic structure...
 - can be very useful in understanding redox processes



Overall information content for Valence PES

- *binding energies* dominated by interactions with other orbitals
- photoionisation *cross-sections* give MO compositions (from initial state)
- *resonance effects* give final state compositions
- still have to worry about atomic multiplets and CT states

core electronic spectroscopies