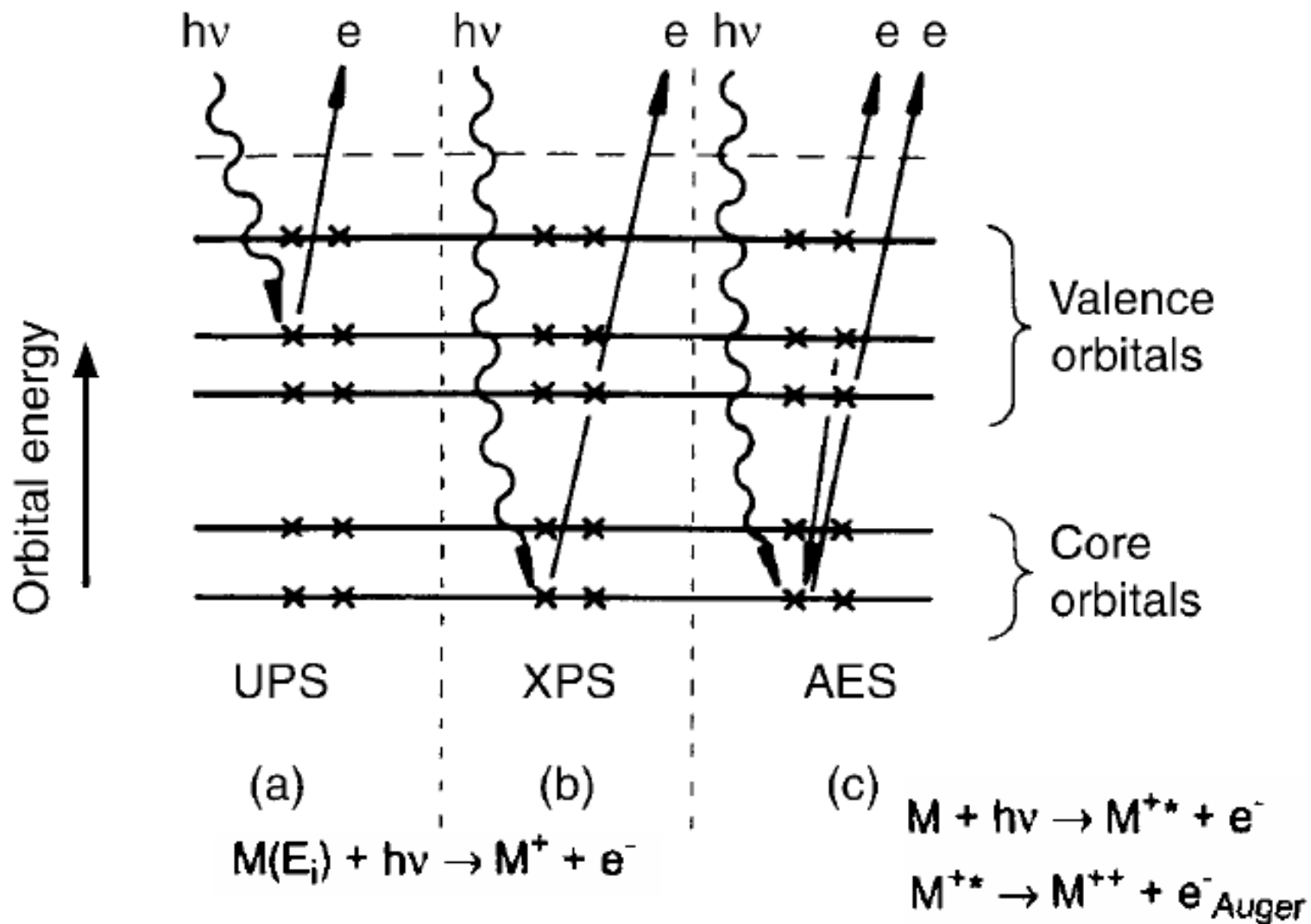
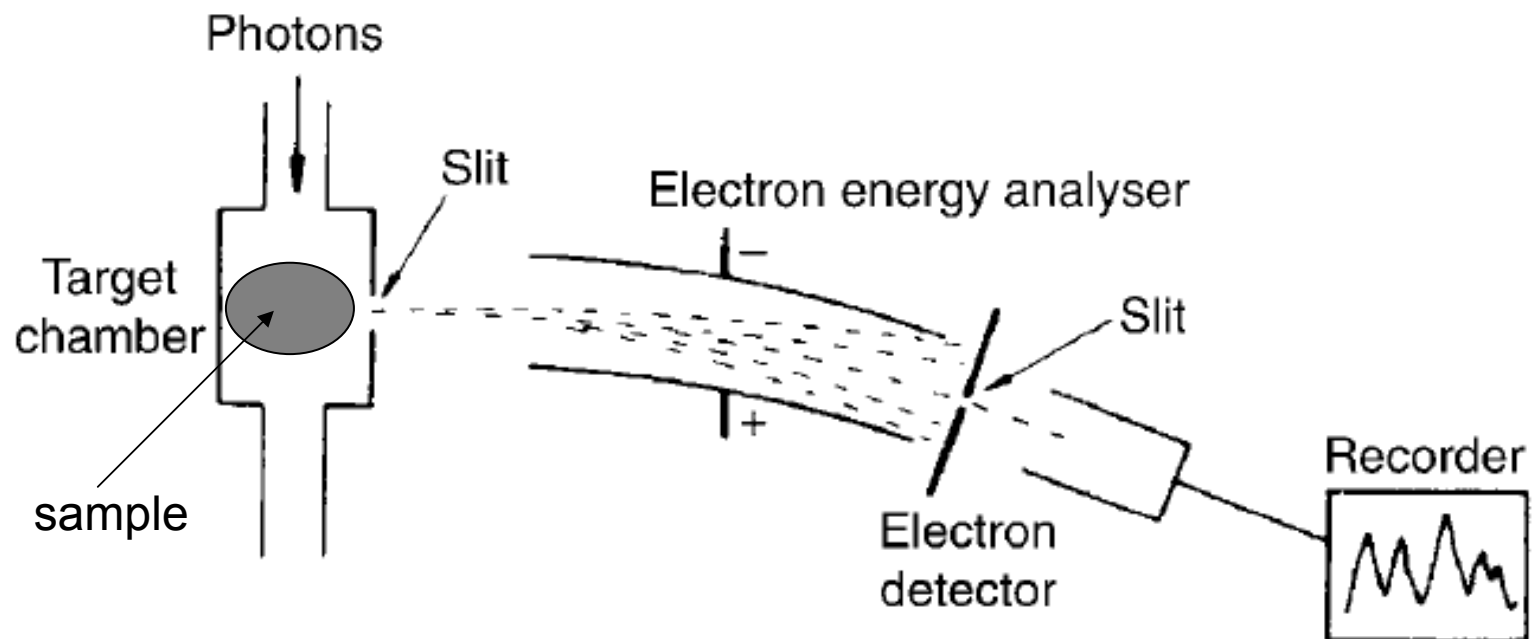


Photoelectron spectroscopy

$$h\nu = I + \frac{1}{2}m_e v^2$$

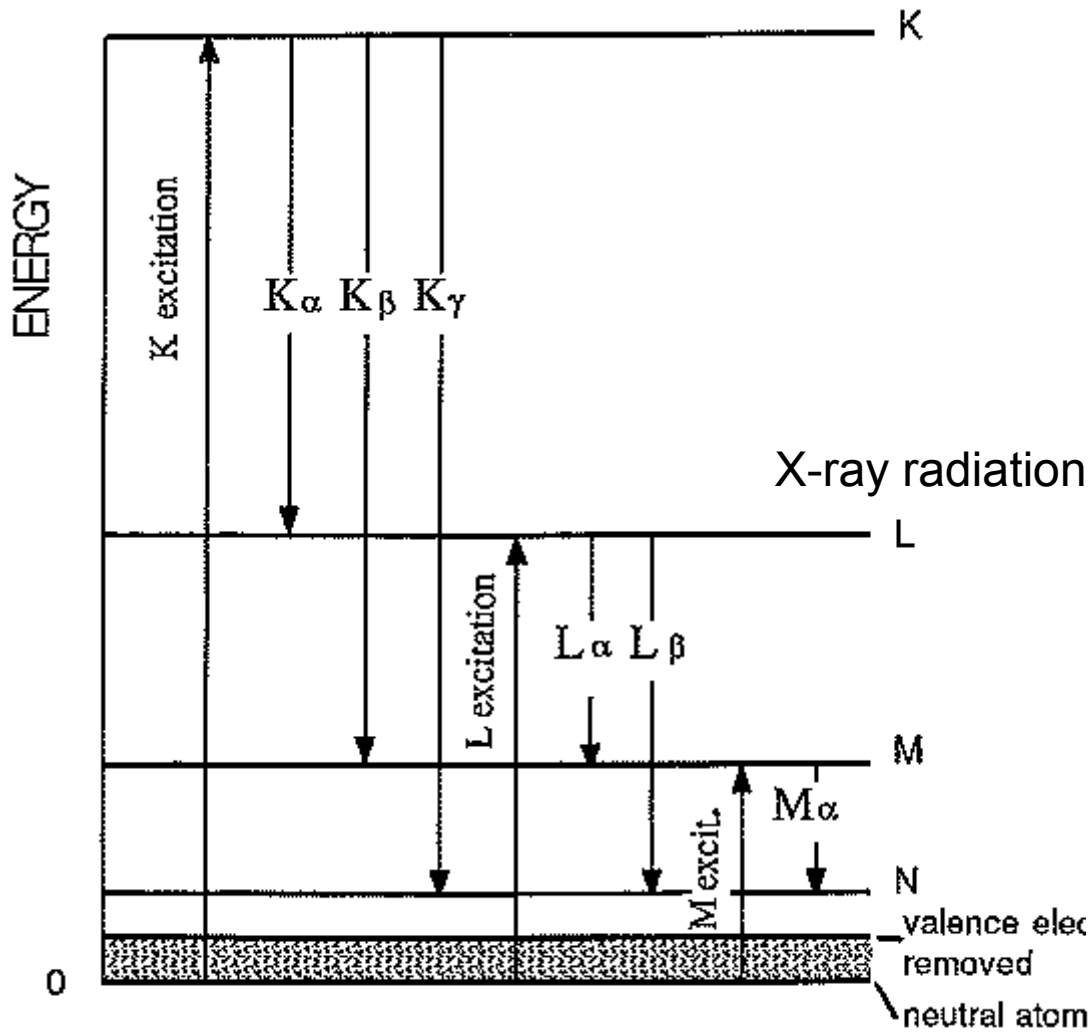


Experimental setup

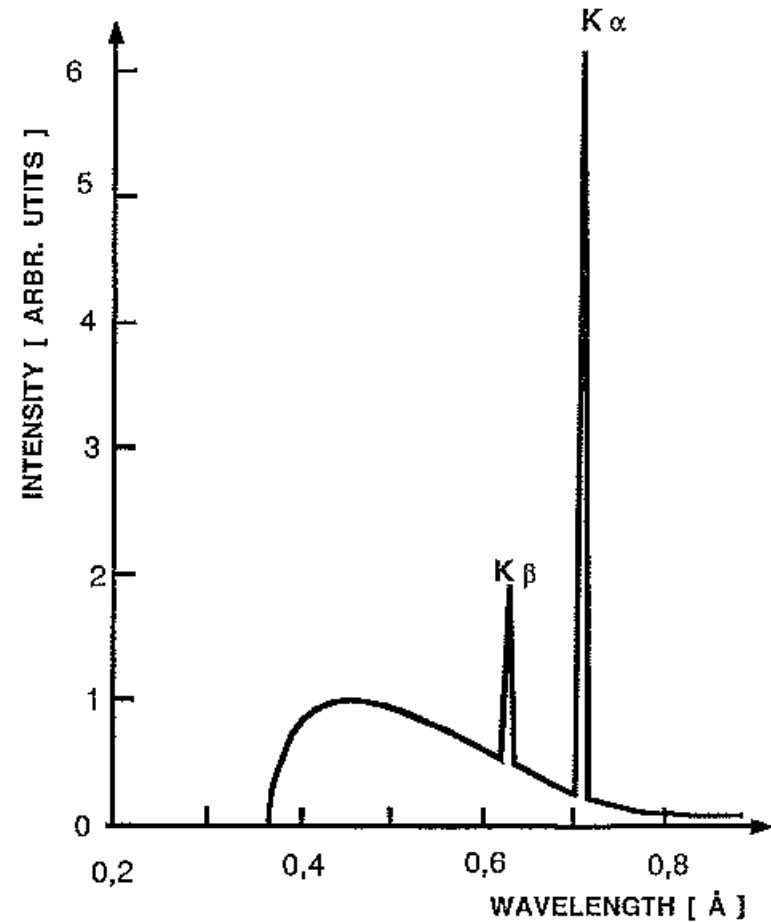


UPS sources: He I radiation 21.22 eV $2^1P_1 (1s^12p^1) - 1^1S_0 (1s^2)$

X-ray radiation: $MgK\alpha$ and $AlK\alpha$ 1253.7 eV / 1253.4 eV and 1486.7 eV / 1486.3 eV



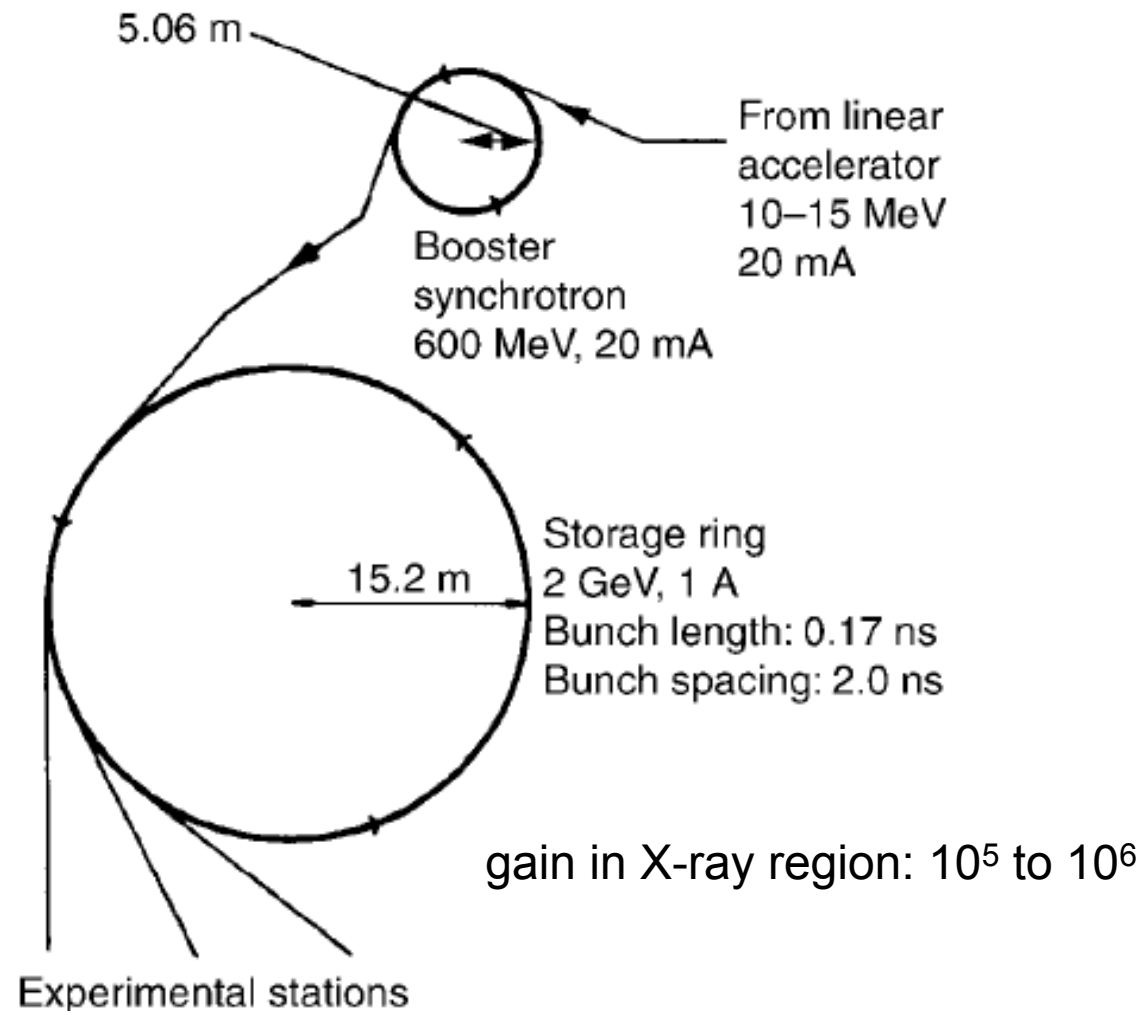
Inner electron energy levels and corresponding X-ray transitions



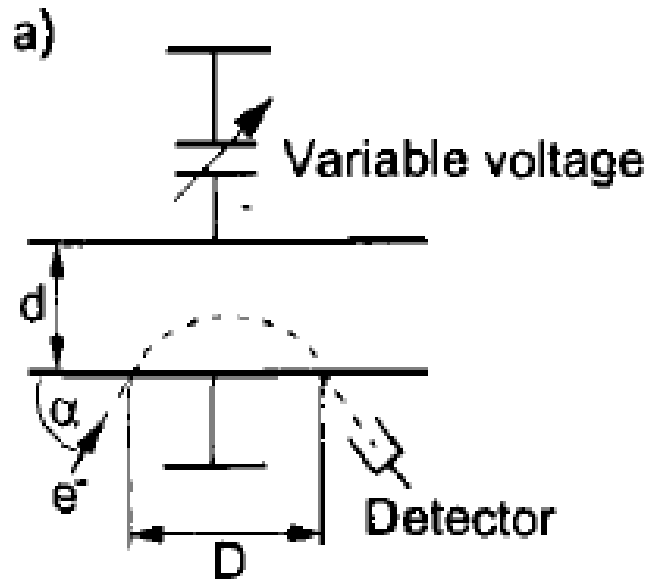
$$1/\sqrt{\lambda} = C(Z - \sigma)$$

Moseley's law

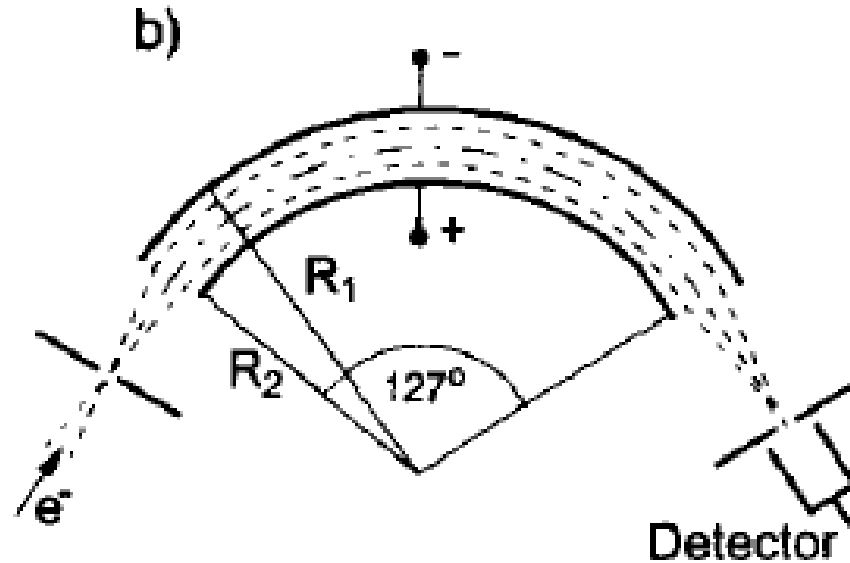
Synchrotron:



Electron velocity analysers



$$E_{\text{el}} = \frac{DeU}{2d \sin 2\alpha}$$



$$E_{\text{el}} = \frac{eU}{2 \ln(R_2/R_1)}$$

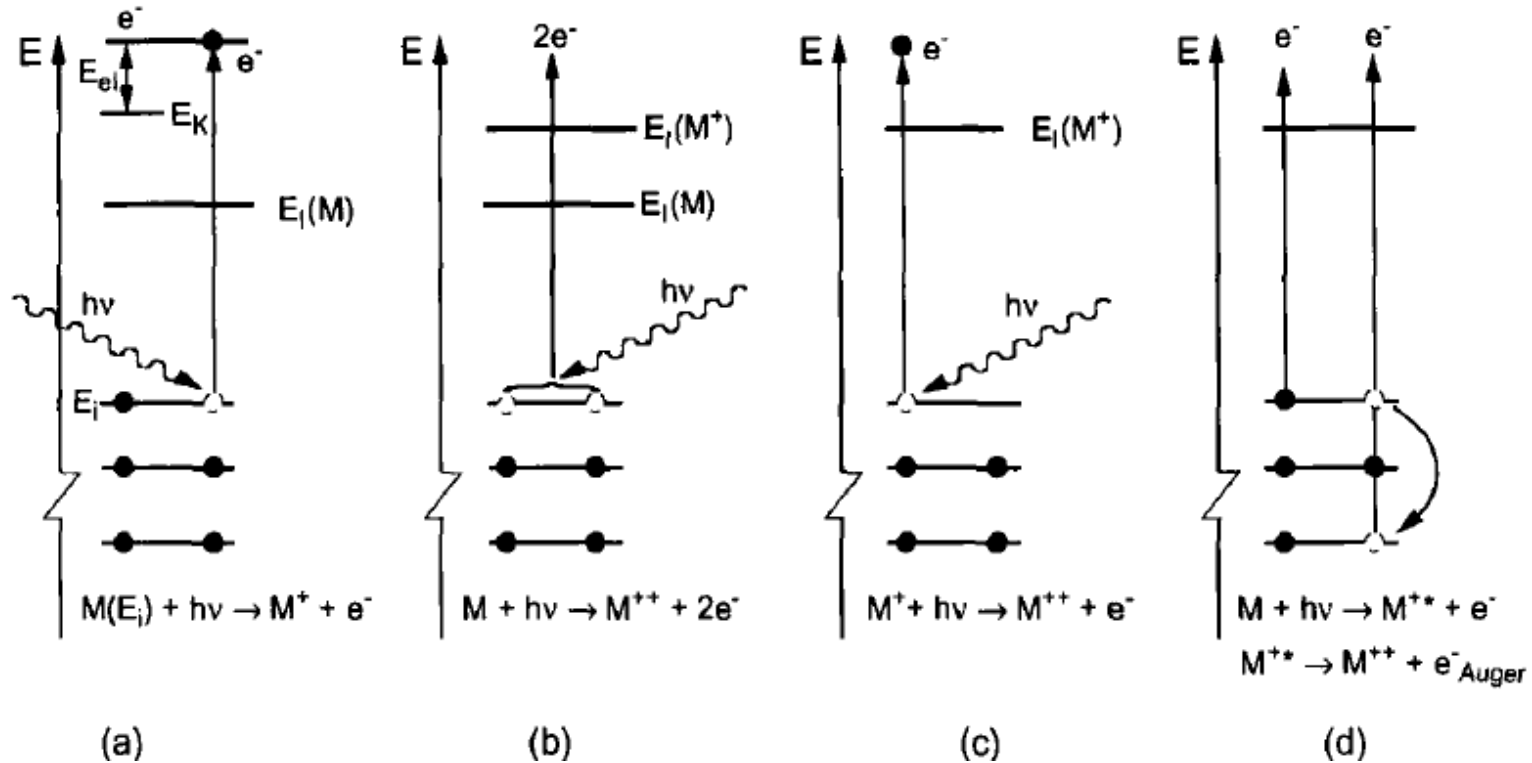
Energy resolution: spectral width of source, energy resolution of the energy analyser, kinetic energy of the molecules

Energy resolution (UPS): 4 meV (32 cm⁻¹)

Energy resolution (XPS): 0.2 eV (1600 cm⁻¹)

Ionization processes

$$h\nu = I + \frac{1}{2}m_e v^2$$



M is an **atom**: $\Delta\ell = \pm 1$

d orbital ($\ell = 2$) the ejected electron has *p* and *f* character

M is a **molecule**: no restriction on the removal of an electron

The ejected electron is described by a more complex mixture of *s*, *p*, *d*, *f*, . . . character

Koopmans' theorem



Koopmans' theorem: for orbital i

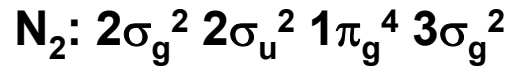
$$I_i \simeq -\varepsilon_i^{\text{SCF}}$$

SCF = self-consistent field: Hartree-Fock

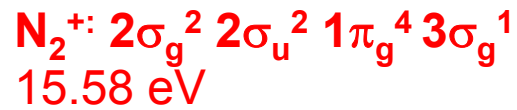
Main deficiencies in SCF calculations:

- Electron reorganization: the orbitals of M^+ and M are slightly different
- Electron correlation: electron movements are correlated
- Relativistic effects: are large for core electrons

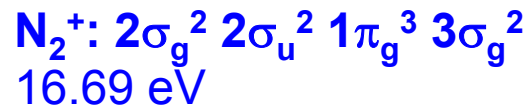
Ultraviolet photoelectron spectra of molecules



re: 1.097 69 Å



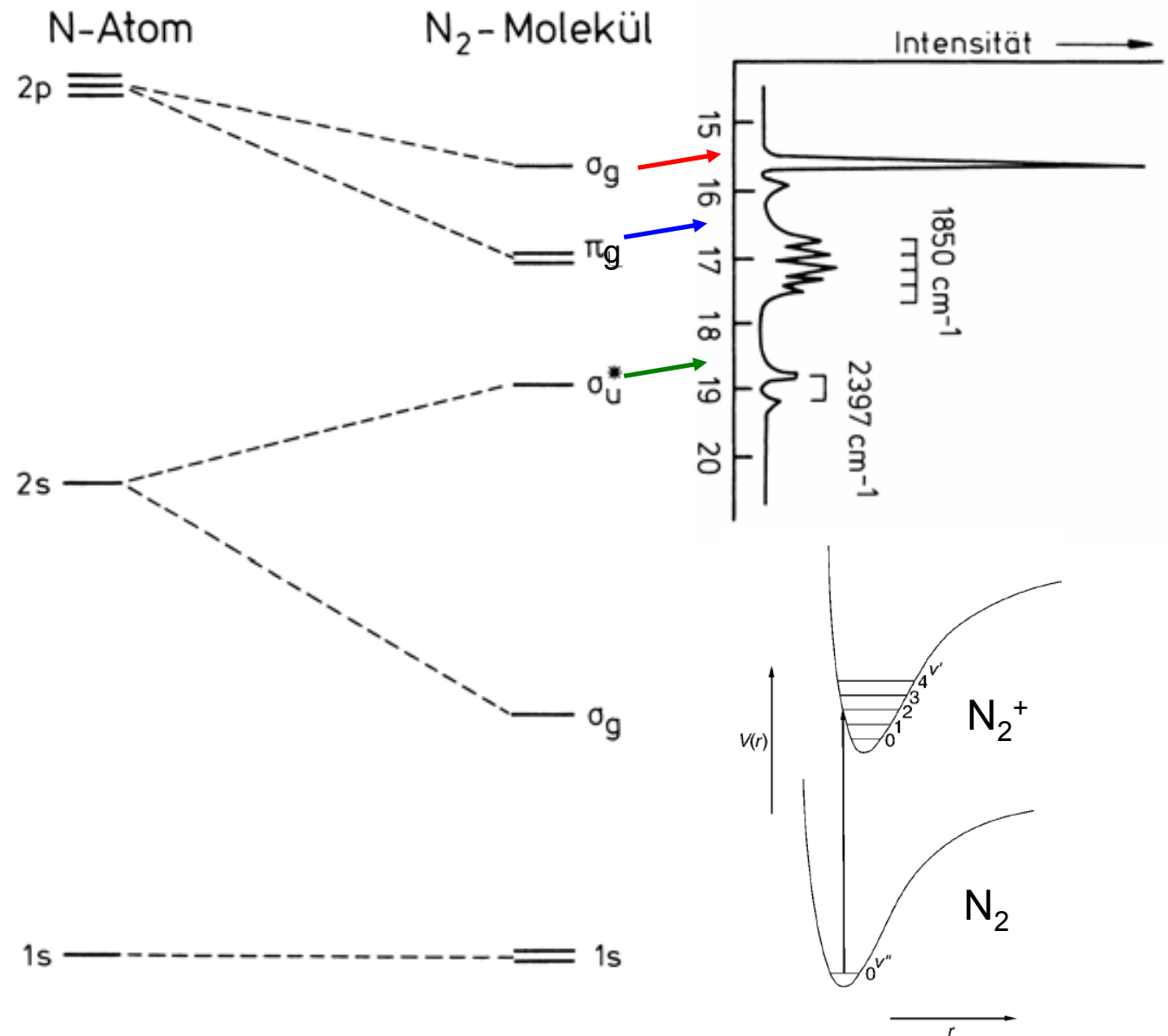
1.116 42 Å



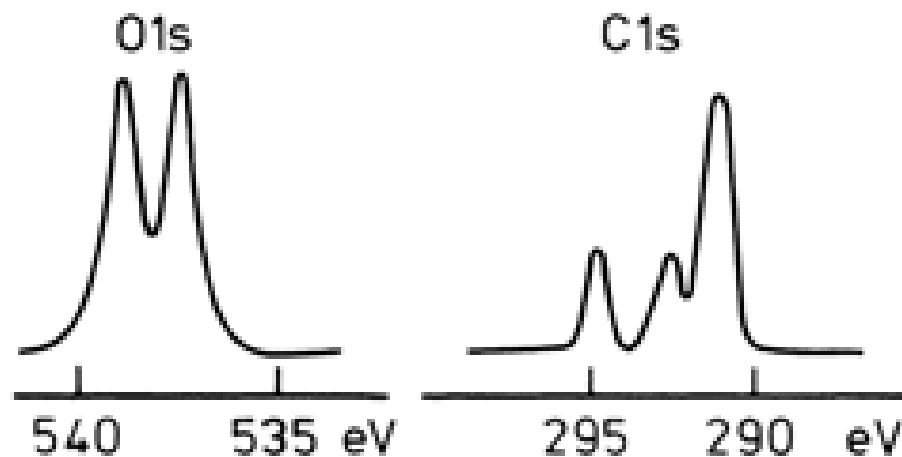
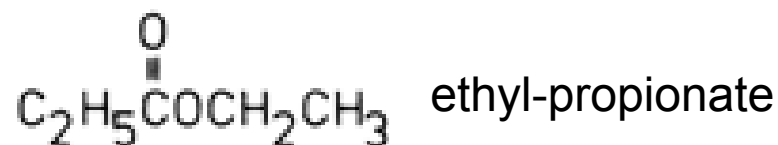
1.174 9 Å



1.074 Å



X-ray photoelectron spectra of molecules



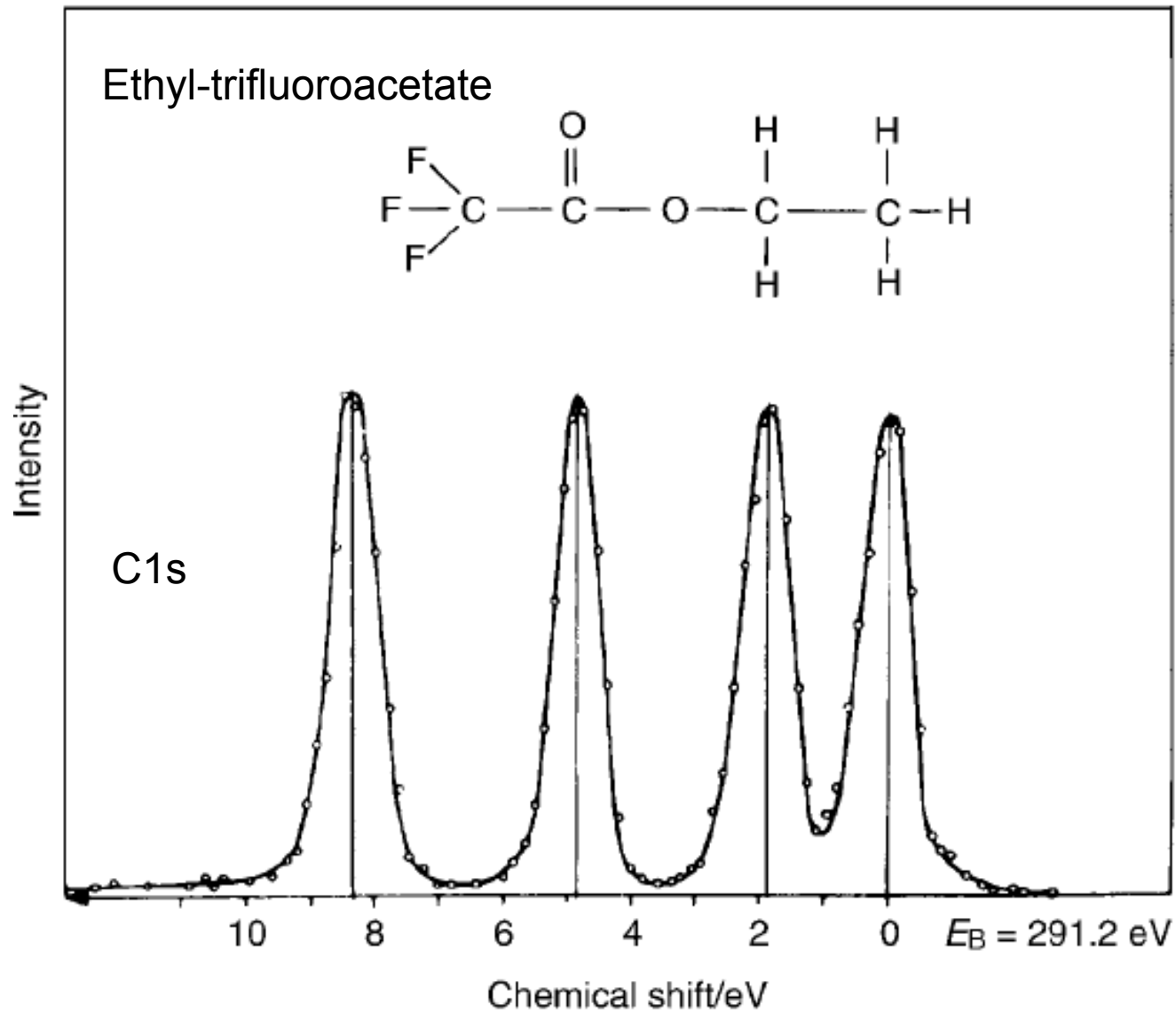
Potential energy of e_i :
$$E_{\text{pot}}^{(i)} = - \sum_{k=1}^p \frac{q_k e}{4\pi\epsilon_0 r_{ik}} = - \left(\sum_k \frac{q_k e}{4\pi\epsilon_0 r_{ik}} \right)_A - \left(\sum_j \frac{q_j e}{4\pi\epsilon_0 r_{ij}} \right)_N$$

In the final state:
$$E_{\text{pot}}^{(f)} = - \left(\sum_{k=1}^{p-1} \frac{q_k e}{4\pi\epsilon_0 r_{ik}^*} \right)_{A^+} - \left(\sum_j \frac{q_j e}{4\pi\epsilon_0 r_{ij}^*} \right)_N$$

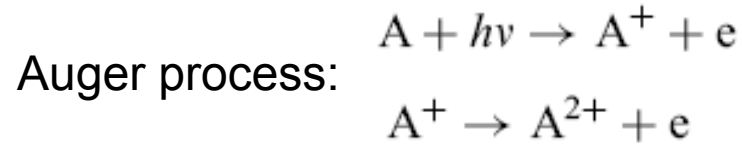
Chemical shift: ΔE

Core orbitals are influenced by valence orbitals and their shift relates to the local chemical environment.

X-ray photoelectron spectra of molecules



Auger electron spectroscopy



The energy of the Auger electron is characteristic of the element that emitted it.

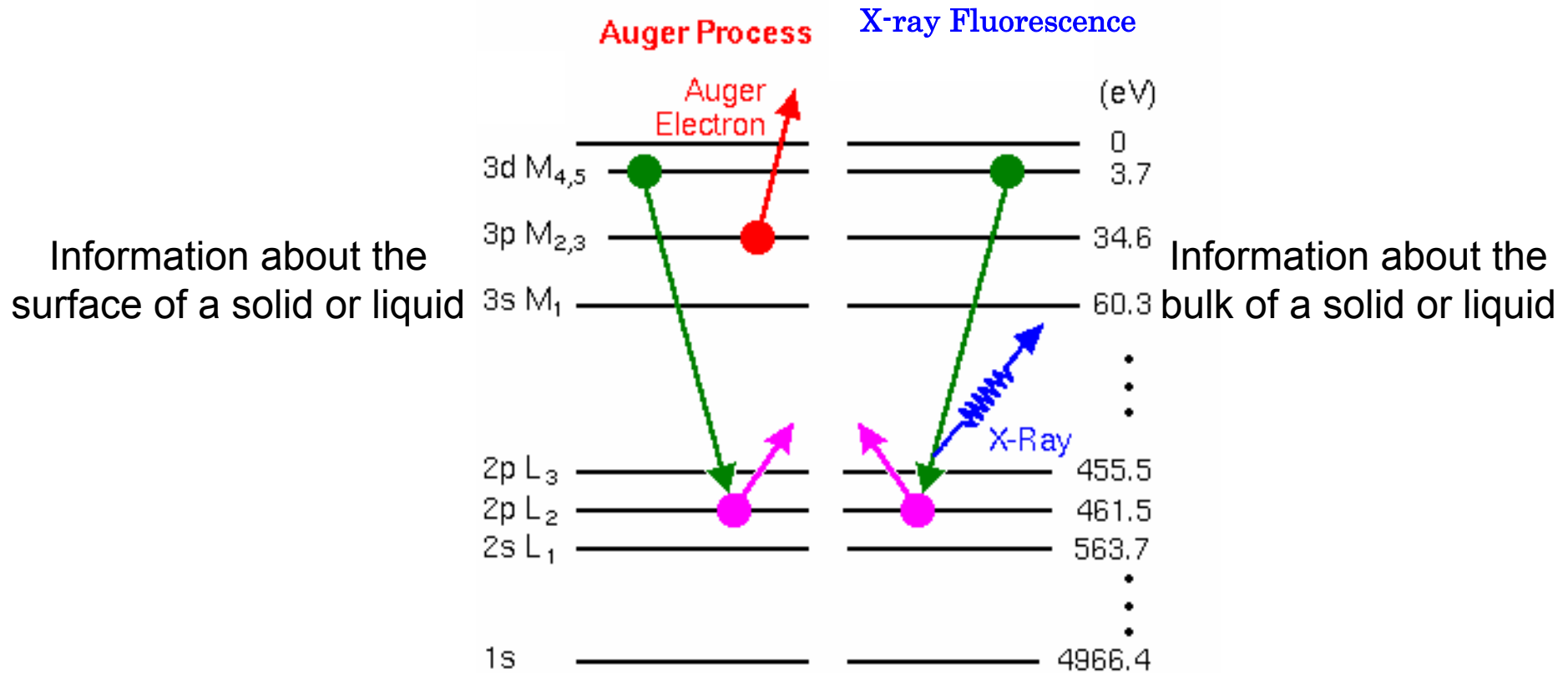
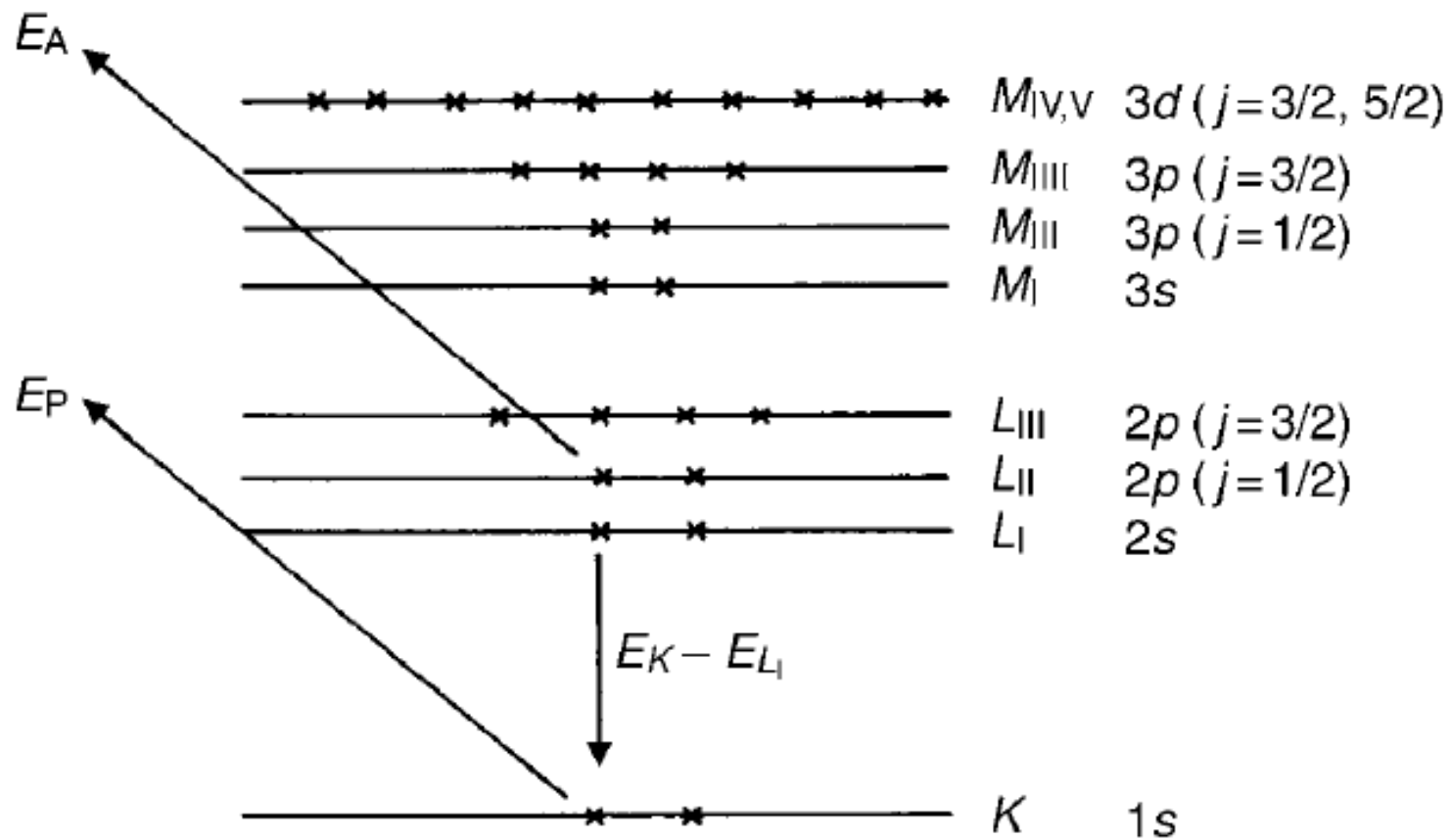


Illustration of a KL_1L_{II} Auger process

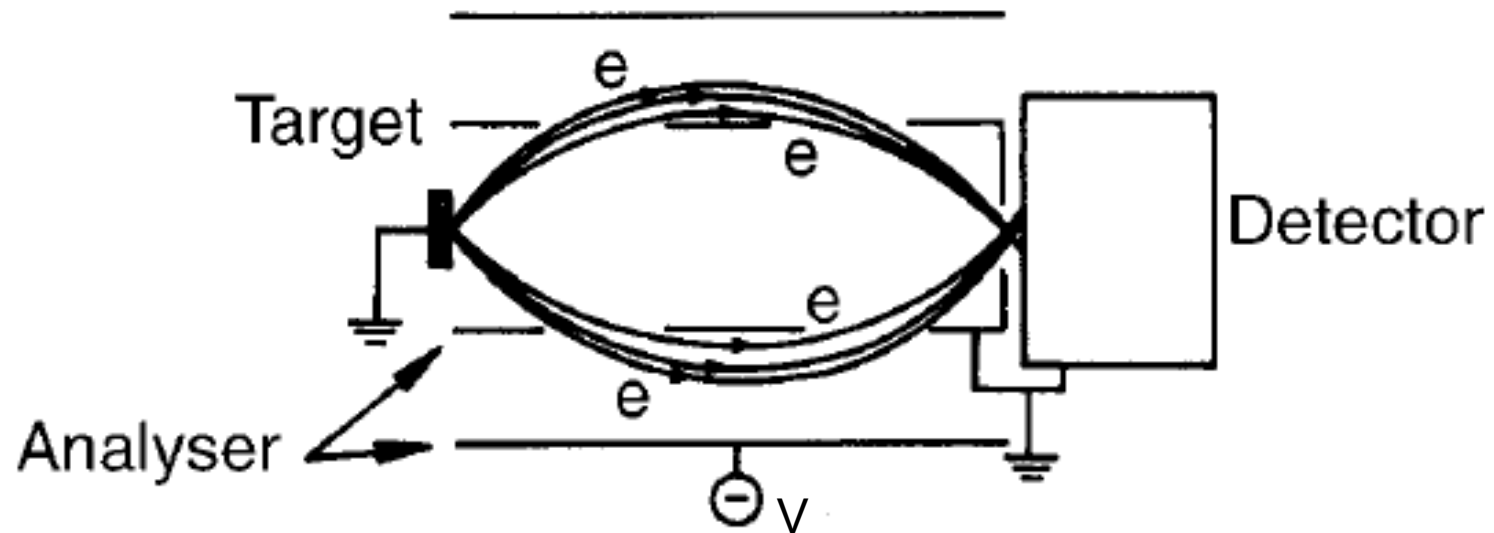


The Auger electron kinetic energy E_A : $E_A = E_K - E_{L_I} - E'_{L_{II}}$

E_K and E_{L_I} : binding energies for the neutral atom

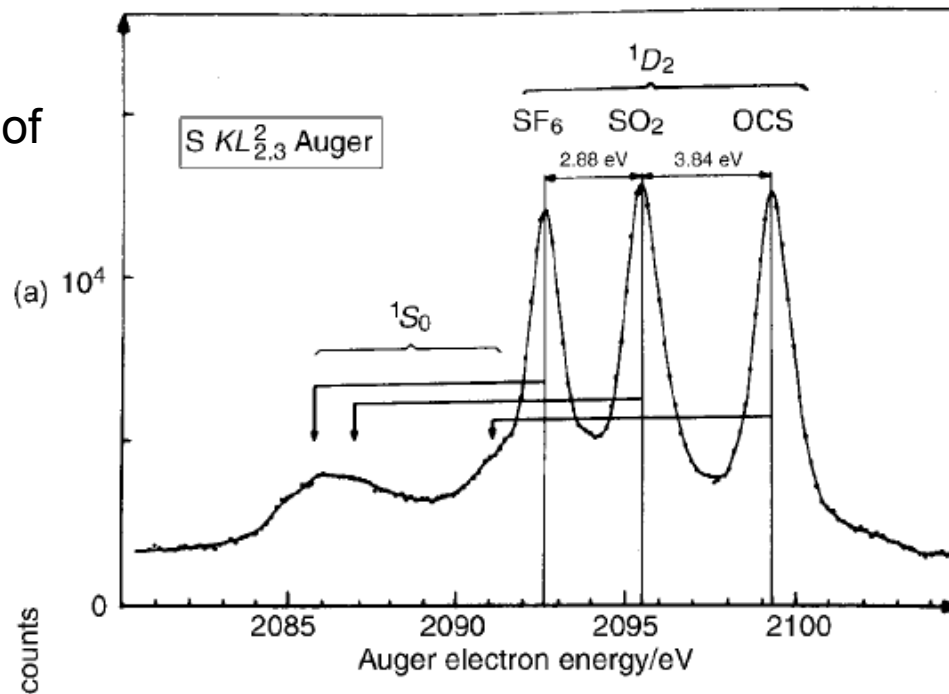
$E'_{L_{II}}$: binding energy of an electron in L_{II} of the ion with a single charge in L_I .

Experimental method

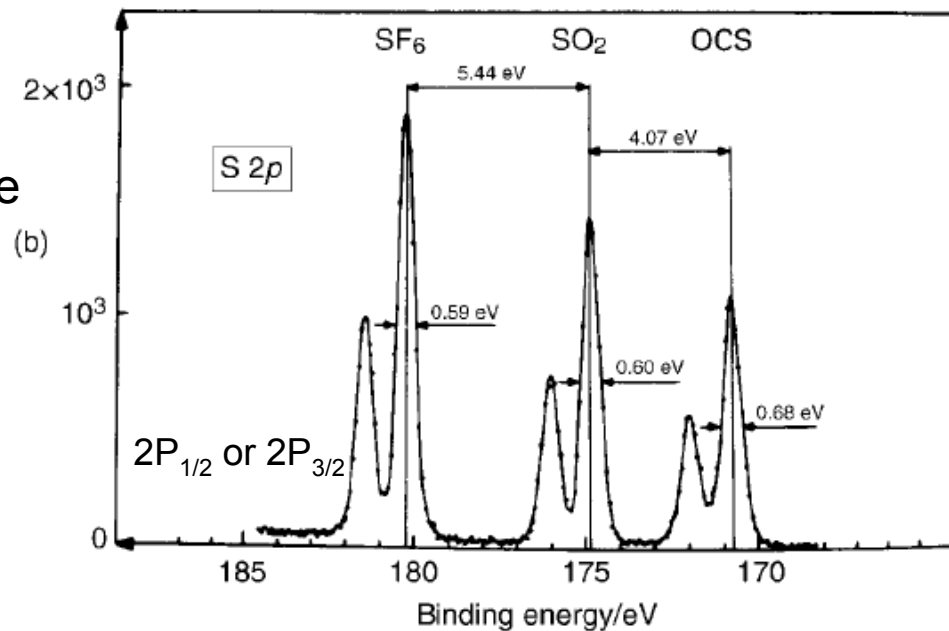


The Auger electron spectrum:
the number of electrons reaching the detector as a function of V .

Auger spectrum of a gaseous mixture of SF₆, SO₂ and OCS



S 2p XP spectrum of a gaseous mixture of SF₆, SO₂ and OCS



The electric properties of molecules

Molecular response to electric fields:

The electric polarizability of a molecule α is a measure of the ease of displacement of positive charge relative to negative charge in the molecule as response to an electric field (acquire an electric dipole moment μ).

The perturbation caused by an electric field \mathcal{E} :

$$H^{(1)} = -\mu \cdot \mathcal{E} \quad \mu = \sum_i q_i r_i \quad (1)$$

The uniform electric field is applied in the z-direction: $\mathcal{E} = \mathcal{E}k$

$$H^{(1)} = -\mu_z \mathcal{E} \quad (2)$$

Molecular response parameters

The Hellmann–Feynman theorem:

the hamiltonian depends on parameter P

$$\frac{dE}{dP} = \left\langle \frac{\partial H}{\partial P} \right\rangle \quad (3)$$

The wavefunction is normalized to 1 for all values of P:

$$E(P) = \int \psi(P)^* H(P) \psi(P) d\tau$$

Proof:

$$\begin{aligned} \frac{dE}{dP} &= \int \left(\frac{\partial \psi^*}{\partial P} \right) H \psi d\tau + \int \psi^* \left(\frac{\partial H}{\partial P} \right) \psi d\tau + \int \psi^* H \left(\frac{\partial \psi}{\partial P} \right) d\tau \\ &= E \int \left(\frac{\partial \psi^*}{\partial P} \right) \psi d\tau + \int \psi^* \left(\frac{\partial H}{\partial P} \right) \psi d\tau + E \int \psi^* \left(\frac{\partial \psi}{\partial P} \right) d\tau \\ &= E \frac{d}{dP} \int \psi^* \psi d\tau + \int \psi^* \left(\frac{\partial H}{\partial P} \right) \psi d\tau \end{aligned}$$

0

$$H = H^{(0)} + Px, \text{ then } \partial H / \partial P = x \quad \frac{dE}{dP} = \langle x \rangle$$

Molecular response parameters

The parameter P is the electric field strength \mathcal{E} :

$$\frac{dE}{d\mathcal{E}} = \left\langle \frac{\partial H}{\partial \mathcal{E}} \right\rangle \quad (4)$$

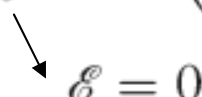
$$\frac{\partial H}{\partial \mathcal{E}} = \frac{\partial H^{(0)}}{\partial \mathcal{E}} + \frac{\partial H^{(1)}}{\partial \mathcal{E}} = \frac{\partial H^{(1)}}{\partial \mathcal{E}} = \frac{\partial}{\partial \mathcal{E}} (-\mu_z \mathcal{E}) = -\mu_z$$

The variation of the energy with the electric field strength:

$$\frac{dE}{d\mathcal{E}} = -\langle \mu_z \rangle \quad (5)$$

Taylor expansion of the energy, E, of the molecule in the presence of the electric field:

$$E = E(0) + \left(\frac{dE}{d\mathcal{E}} \right)_0 \mathcal{E} + \frac{1}{2!} \left(\frac{d^2E}{d\mathcal{E}^2} \right)_0 \mathcal{E}^2 + \frac{1}{3!} \left(\frac{d^3E}{d\mathcal{E}^3} \right)_0 \mathcal{E}^3 + \dots \quad (6)$$


 $\mathcal{E} = 0$

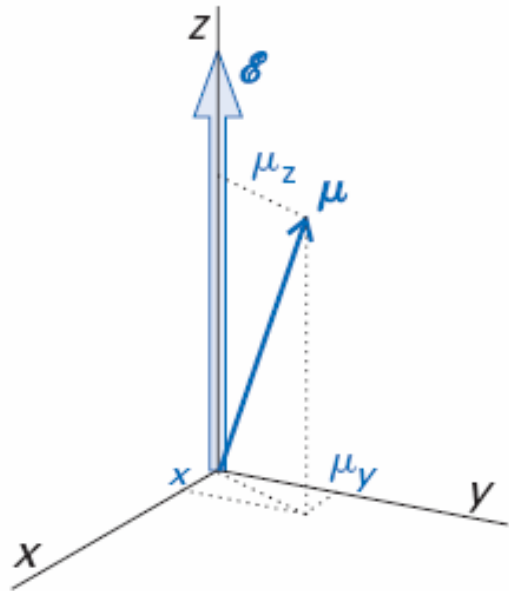
From (5) and (6):

$$\langle \mu_z \rangle = - \left(\frac{dE}{d\mathcal{E}} \right)_0 - \left(\frac{d^2E}{d\mathcal{E}^2} \right)_0 \mathcal{E} - \frac{1}{2} \left(\frac{d^3E}{d\mathcal{E}^3} \right)_0 \mathcal{E}^2 - \dots \quad (7)$$

Molecular response parameters

The expectation value of the electric dipole moment in the presence of the electric field: the sum of the permanent dipole moment and the contribution induced by the field.

$$\langle \mu_z \rangle = \mu_{0z} + \alpha_{zz} \mathcal{E} + \frac{1}{2} \beta_{zzz} \mathcal{E}^2 + \dots \quad (8)$$



$$\mu_q = \alpha_{qz} \mathcal{E} \quad q = x, y, z \quad (9)$$
$$\alpha_{zz} > \alpha_{xz}, \alpha_{yz}$$

Three directions relative to the molecule that, when the field is applied along them, give rise to strictly parallel induced dipole moments: **principal axes of polarizability**.

Molecular response parameters

$$\langle \mu_z \rangle = - \left(\frac{dE}{d\mathcal{E}} \right)_0 - \left(\frac{d^2 E}{d\mathcal{E}^2} \right)_0 \mathcal{E} - \frac{1}{2} \left(\frac{d^3 E}{d\mathcal{E}^3} \right)_0 \mathcal{E}^2 - \dots$$

$$\langle \mu_z \rangle = \mu_{0z} + \alpha_{zz} \mathcal{E} + \frac{1}{2} \beta_{zzz} \mathcal{E}^2 + \dots$$

$$\mu_{0z} = - \left(\frac{dE}{d\mathcal{E}} \right)_0 \quad \alpha_{zz} = - \left(\frac{d^2 E}{d\mathcal{E}^2} \right)_0 \quad \beta_{zzz} = - \left(\frac{d^3 E}{d\mathcal{E}^3} \right)_0 \quad (10)$$

The Taylor expansion of energy (6) in terms of molecular properties

$$E = E(0) - \mu_{0z} \mathcal{E} - \frac{1}{2} \alpha_{zz} \mathcal{E}^2 - \frac{1}{6} \beta_{zzz} \mathcal{E}^3 + \dots \quad (11)$$

The static electric polarizability

The perturbation expression
for the energy:

$$E_0 = E_0^{(0)} + \langle 0|H^{(1)}|0\rangle + \sum_n' \frac{\langle 0|H^{(1)}|n\rangle\langle n|H^{(1)}|0\rangle}{E_0^{(0)} - E_n^{(0)}} + \dots \quad (12)$$

$$H = H^{(0)} + \lambda H^{(1)}$$

$\searrow -\mu \cdot \mathcal{E}$

$$E_0 = E_0^{(0)} - \langle 0|\mu_z|0\rangle \mathcal{E} + \left\{ \sum_n' \frac{\langle 0|\mu_z|n\rangle\langle n|\mu_z|0\rangle}{E_0^{(0)} - E_n^{(0)}} \right\} \mathcal{E}^2 + \dots \quad (13)$$

The first derivative with respect to \mathcal{E} for $\mathcal{E} = 0$

$$\mu_{0z} = -\left(\frac{dE_0}{d\mathcal{E}}\right)_0 = \langle 0|\mu_z|0\rangle \quad (14)$$

permanent electric dipole moment of the molecule

The static electric polarizability

The second derivative in (13) after setting $\mathcal{E} = 0$

$$\alpha_{zz} = -2 \sum_n' \frac{\langle 0 | \mu_z | n \rangle \langle n | \mu_z | 0 \rangle}{E_0^{(0)} - E_n^{(0)}} \quad (15)$$

μ_z transforms as z , α_{zz} transforms as z^2 ;

In (15) make the notations: $\Delta E_{n0} = E_n^{(0)} - E_0^{(0)}$ $\langle m | \mu_z | n \rangle$ as $\mu_{z,mn}$

$$\alpha_{zz} = 2 \sum_n' \frac{\mu_{z,0n} \mu_{z,n0}}{\Delta E_{n0}} \quad (16)$$

The mean polarizability α (molecule rotates in a fluid) :

$$\alpha = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = \frac{2}{3} \sum_n' \frac{|\mu_{n0}|^2}{\Delta E_{n0}} \quad (17)$$

$$|\mu_{n0}|^2 = \mu_{0n} \cdot \mu_{n0} = \mu_{x,0n} \mu_{x,n0} + \mu_{y,0n} \mu_{y,n0} + \mu_{z,0n} \mu_{z,n0}$$

Polarizability volume

Polarizability is expressed in $\text{C}^2 \text{m}^2 \text{J}^{-1}$

Polarizability volume α' :

$$\alpha' = \frac{\alpha}{4\pi\epsilon_0} \quad (18)$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{J}^{-1} \text{C}^2 \text{m}^{-1}$$

vacuum permittivity

	μ/D	$\alpha'/(10^{-30} \text{m}^3)$
CCl_4	0	10.3
H_2	0	0.819
H_2O	1.85	1.48
HCl	1.08	2.63
HI	0.42	5.45

similar in magnitude to actual molecular volumes

Polarizability volume correlates with the HOMO–LUMO separations in atoms and molecules.

Polarizability volume

When the electric field is increased by $d\mathcal{E}$, the energy of a molecule changes by $-\mu^*d\mathcal{E}$

The change in energy
$$\Delta E = -\int_0^{\mathcal{E}} \mu^* d\mathcal{E} = -\int_0^{\mathcal{E}} \alpha \mathcal{E} d\mathcal{E} = -\frac{1}{2} \alpha \mathcal{E}^2$$

$$\hat{H}^{(1)} = -\hat{\mu}_z \mathcal{E}$$

An expression proportional to \mathcal{E}^2 : second-order contribution to the energy

$$\begin{aligned} E^{(2)} &= \sum_{n \neq 0} \frac{|\int \psi_n^* \hat{H}^{(1)} \psi_0 d\tau|^2}{E_0^{(0)} - E_n^{(0)}} = \mathcal{E}^2 \sum_{n \neq 0} \frac{|\int \psi_n^* \hat{\mu}_z \psi_0 d\tau|^2}{E_0^{(0)} - E_n^{(0)}} \\ &= \mathcal{E}^2 \sum_{n \neq 0} \frac{|\mu_{z,0n}|^2}{E_0^{(0)} - E_n^{(0)}} \end{aligned}$$

Polarizability volume

The polarizability of the molecule in the z-direction

$$\alpha = 2 \sum_{n \neq 0} \frac{|\mu_{z,0n}|^2}{E_n^{(0)} - E_0^{(0)}}$$

↑
eR
↓
HOMO–LUMO separation

Then:

$$\alpha \approx \frac{2e^2 R^2}{\Delta E}$$

The excitation energy: the energy needed to remove an electron to infinity from a distance R from a single positive charge

$$\Delta E \approx e^2 / 4\pi\epsilon_0 R$$

Substituting in the equation of α

$$\alpha' \approx R^3$$

Polarizabilities and molecular spectroscopy

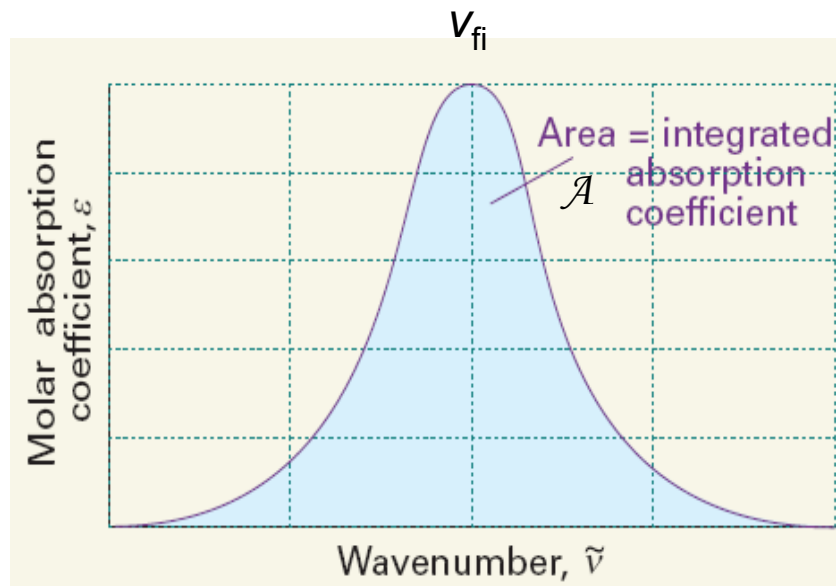
$$\mathcal{A} = \int \varepsilon(\nu) d\nu = \left(\frac{h\nu_{fi}}{c} \right) N_A B \quad B = \frac{|\mu_{fi}|^2}{6\varepsilon_0\hbar^2}$$

$$\mathcal{A} = \frac{\pi\nu_{fi}N_A|\mu_{fi}|^2}{3\varepsilon_0\hbar c}$$

Oscillator strength f :
(dimensionless)

$$f = \left(\frac{4\pi m_e \nu_{fi}}{3e^2\hbar} \right) |\mu_{fi}|^2$$

$$f = \left(\frac{4m_e c \varepsilon_0}{N_A e^2} \right) \mathcal{A}$$



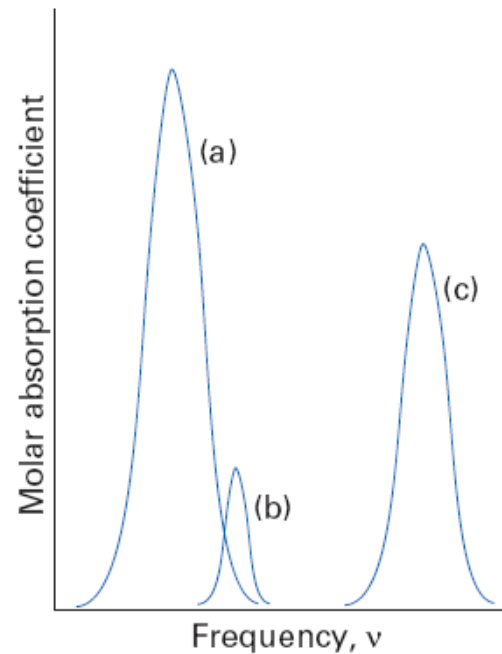
Polarizabilities and molecular spectroscopy

The oscillator strength of the transition 0-n:

$$f_{n0} = \left(\frac{4\pi m_e}{3e^2 \hbar} \right) \nu_{n0} |\mu_{n0}|^2$$

Molecular polarizability:

$$\alpha = \frac{\hbar^2 e^2}{m_e \Delta E^2} \sum_n' f_{n0}$$



Kuhn–Thomas sum rule:

$$\sum_n' f_{n0} = N_e \quad \longrightarrow$$

$$\alpha \approx \frac{\hbar^2 e^2 N_e}{m_e \Delta E^2}$$

Molecules composed of heavy atoms to be strongly polarizable.