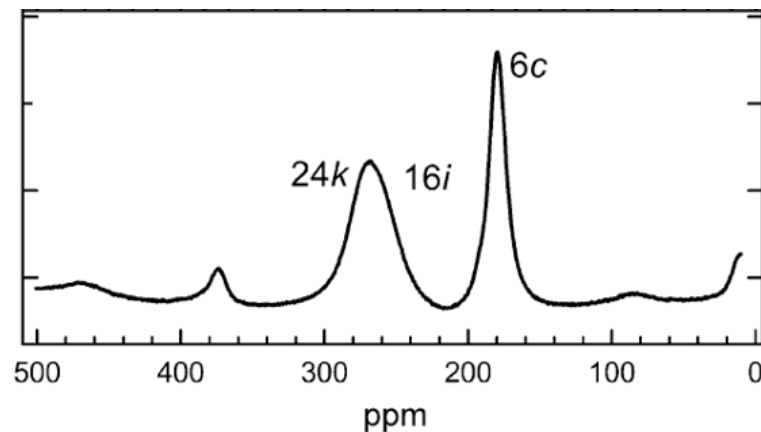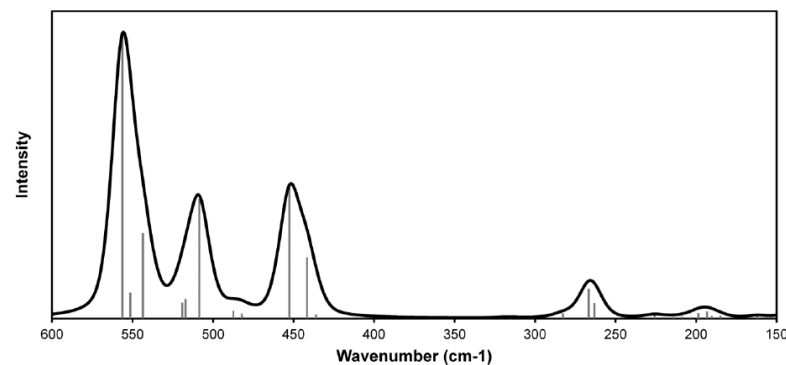# Lecture 8:
Spectroscopies and thermal analysis

- Spectroscopic methods
  - Infrared and Raman spectroscopy
  - Solid-state NMR spectroscopy
  - X-Ray and electron spectroscopies (*extra material*)

- Thermal analysis
  - Thermogravimetry (TG)
  - Differential thermal analysis (DTA)
  - Differential scanning calorimetry (DSC)
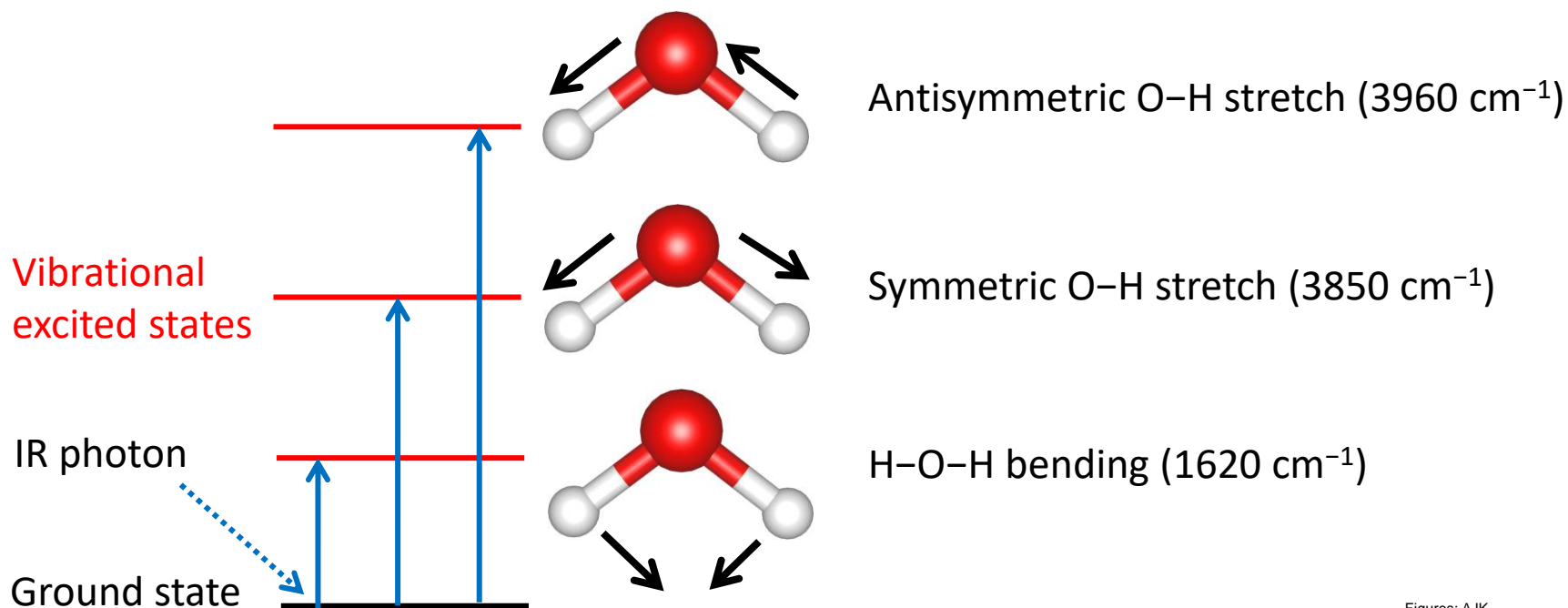
Figures: AJK

Spectroscopies

- Information on **local** structure. Some spectroscopies can be used for fingerprinting.
- Investigate bonding and defects / impurities
- Structural characterization when structure cannot be (fully) solved by XRD
    - Solid solutions, amorphous materials, thin films, complex hybrid materials

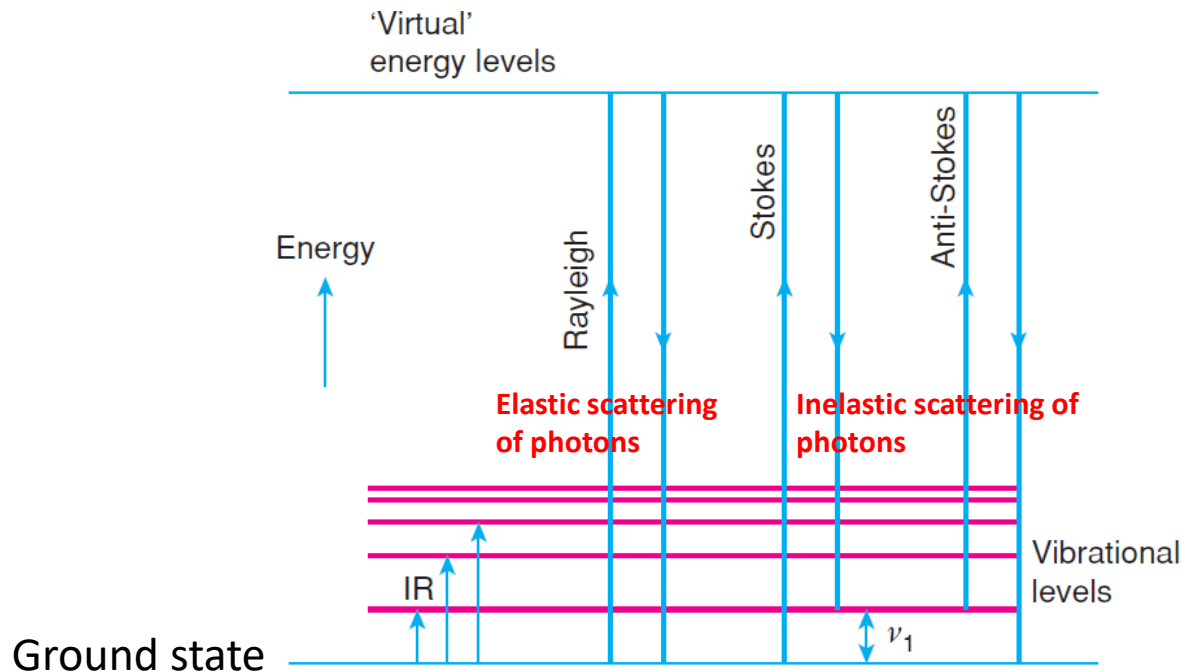| Freq. (Hz)	Energy (kJ/mol)	Radiation	Spectroscopies	What is probed
10^{18}	400 000	X-rays	X-ray spectroscopies	Inner shell electrons
10^{17}	40 000			
10^{16}	4 000	Ultraviolet	UV-Vis	Valence shell electrons
10^{15}	400	Visible		
10^{14}	40			
10^{13}	4	Infrared	IR, Raman	Molecular vibrations
10^{12}	0.4			
10^{11}		Microwaves		
10^{10}			ESR	Electron spin
10^{9}				
10^{8}		Radio waves	NMR	Nuclear spin

Vibrational spectroscopies

Infrared spectroscopy (IR)

- Materials have vibrational energy levels that can be excited with IR radiation
- IR spectrometer measures how much the material absorbs IR radiation
  - One can also measure the inverse quantity, transmission
- Typical energy range: 40–4000 cm^{-1} (1–100 THz)
  - The IR wavenumbers below have been calculated for a gas-phase water molecule (at DFT-PBE0/TZVP level of theory)
  - **Jmol can visualize vibrational modes (MyCourses -> Software -> Jmol docs)**

Antisymmetric O–H stretch (3960 cm^{-1})

Symmetric O–H stretch (3850 cm^{-1})

Vibrational excited states

IR photon

H–O–H bending (1620 cm^{-1})

Ground state

Figures: AJK

4

Vibrational spectroscopy: Raman

- In Raman spectroscopy, the material is excited by laser

- Most of the emitted photons have the same energy as the original photons (elastic scattering)

- Some of the emitted photons are shifted with respect to the laser wavelength due to coupling with vibrational levels -> Raman scattering

  - Raman spectrometer measures the shift of the emitted photons (v_1)

- The studied vibrational excited states are similar as in IR spectroscopy

'Virtual' energy levels

Energy

Rayleigh

Stokes

Anti-Stokes

Elastic scattering of photons

Inelastic scattering of photons

Vibrational levels

IR

v_1

Ground state

Selection rules (1)

- IR and Raman spectra of a material can be rather different
  - The two techniques are governed by different **selection rules**
  - Only those vibrational modes that are IR or Raman active can be observed
- In H_2O, all three modes are IR and Raman active, but the intensities differ

IR spectrum of H_2O molecule

Figures: AJK

Raman spectrum of H_2O molecule
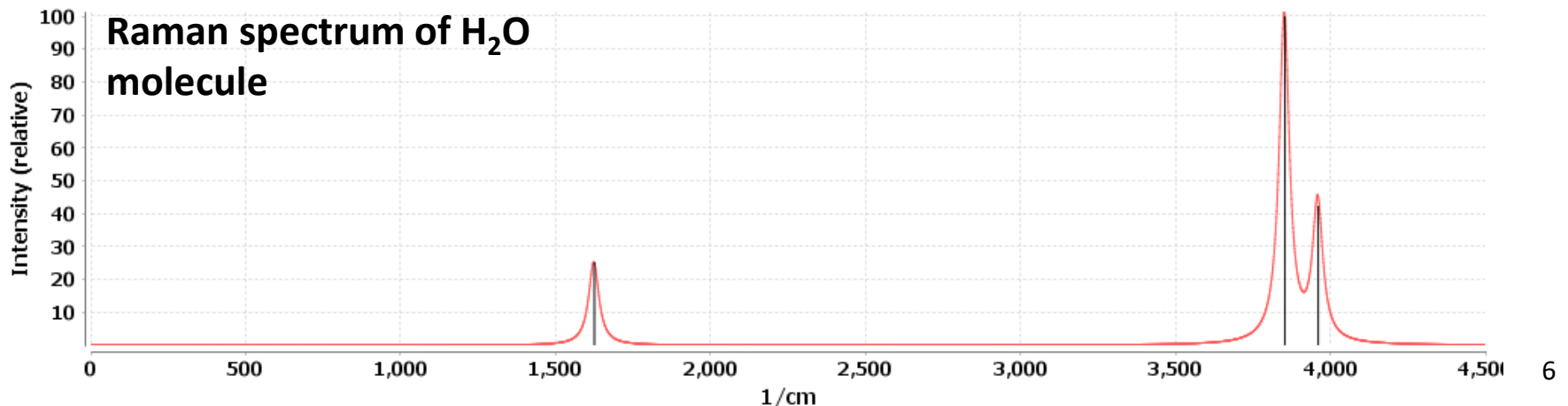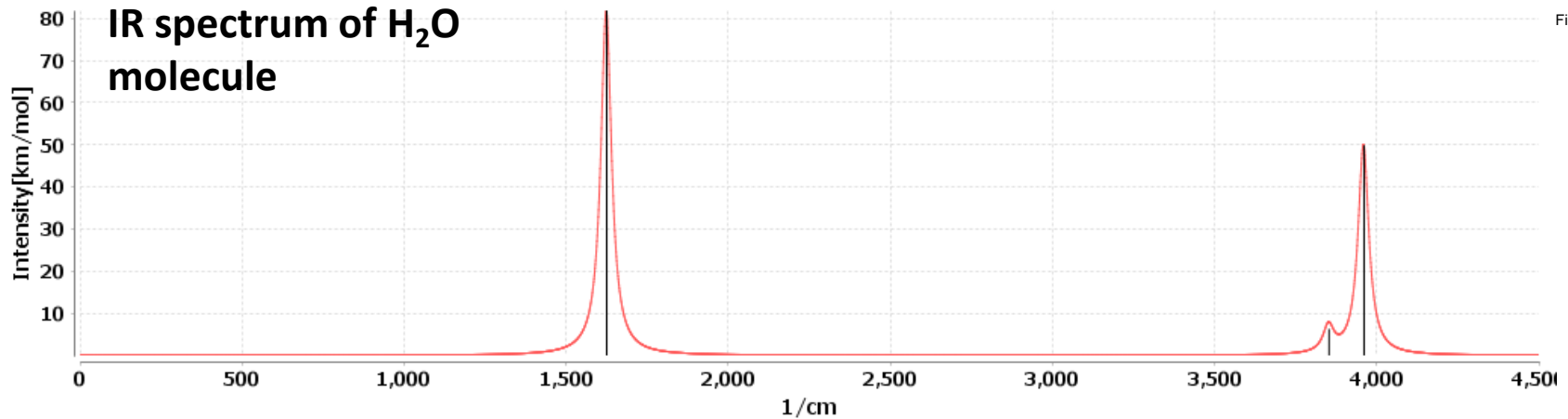
Selection rules (2)

- A vibrational mode is **IR active** if the dipole moment of the system changes
  - Consequently, centrosymmetric vibrational modes are IR inactive
  - For example, symmetric C–H stretching of methane (CH_4) is not IR active
  - The larger the change of the dipole moment, the higher the intensity

- A vibrational mode is **Raman active** if the polarizability of the system changes
  - Polarizability = the ability to form instantaneous dipoles
  - The symmetric C – H stretching of methane CH_4 is Raman active
  - The larger the change of polarizability, the higher the intensity

Figure: AJK

- For selection rules of point groups, see http://symmetry.jacobs-university.de/
  - IR active representations possess a linear function (*x*, *y*, *z*)
  - Raman active representations possess a quadratic function (x^2, y^2, z^2, etc.)
- Interpretation of solid-state IR/Raman spectra is not as easy as for molecules
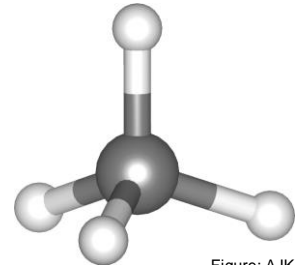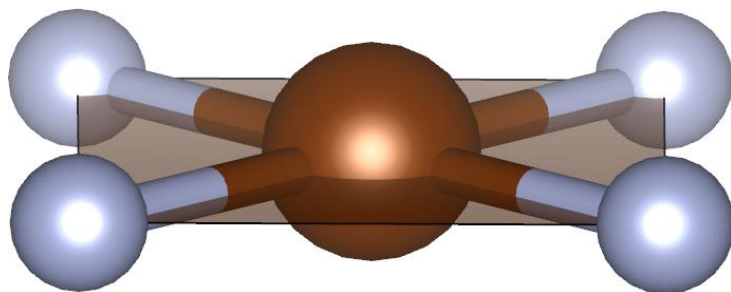 - Nowadays facilitated by quantum chemical calculations

7

Interpretation of Raman and IR spectra: $Ba(BrF_4)_2$

Synthesis and Characterization of Barium Tetrafluoridobromate(III) $Ba(BrF_4)_2$
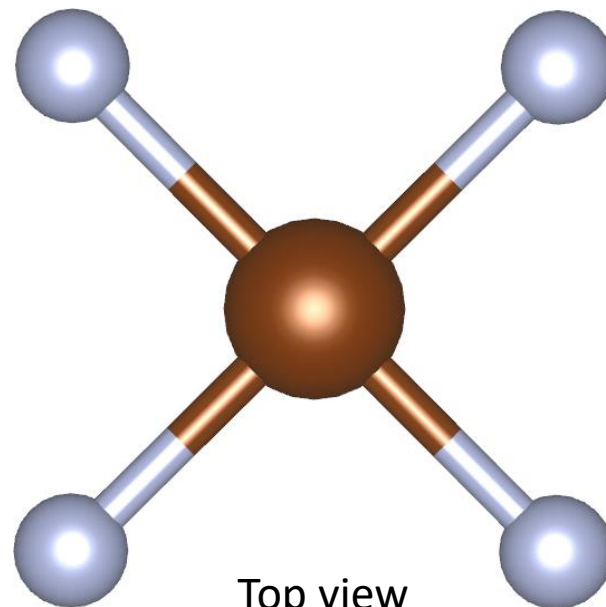
Sergey Ivlev,[a] Vasily Sobolev,[a] Markus Hoelzel,[b] Antti J. Karttunen,[c] Thomas Müller,[d] Ivan Gerin,[a] Roman Ostvald,*[a] and Florian Kraus*[d]

[BrF4]− anion (D_{4h})

Side view

Top view
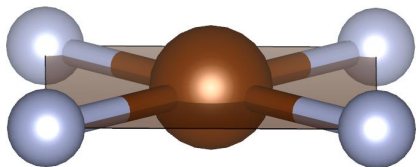
Figures: AJK

Ba(BrF$_4$)$_2$ Raman

Experiment

**Theory
(DFT-PBE0/SVP)**

Pseudo-Voigt broadening
(FWHM 16 cm^{-1})
Grey peaks show the raw
data without broadening

Figures: AJK

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Ba(BrF$_4$)$_2$ Raman and IR interpretation

Table 3. Assignment of IR and Raman bands of Ba(BrF$_4$)$_2$. The interpretation of the bands is straightforward and agrees well with the calculated Raman and IR intensities. The only thing "missing" in the experimental spectrum is the Br–F out-of-plane mode at about 300–320 cm^{-1} (the calculated intensity of this mode is about 50% of the mode at 546 cm^{-1}).

IR frequency [cm^{-1}]	Raman exp. frequency [cm^{-1}] (rel. intensity)	Raman calcd. frequency [cm^{-1}] (rel. intensity)	Mode symmetry for point group D_{4h}	Assignment of the vibrational mode
546 s	549 (10.0)	555 (10)	A_{1g}	symmetric BrF$_4$ stretch
485 vs	491 (2.3)	509 (4.3)	E_u	antisymmetric BrF$_4$ stretch
416 s	450 (2.0)	452 (4.7)	B_{2g}	antisymmetric BrF$_4$ stretch
	273 (1.6)	266 (1.3)	B_{1g}	F scissoring
	195 (0.3)	196 (0.4)	B_{1u}	F rocking (+ twisting)

**Complete assignment of the spectrum enabled by quantum chemistry!**

Table S2. Interpretation of the theoretical Raman data. The assignment of the peaks was carried out by visual inspection of the normal modes (Jmol program package[7]). The wavenumbers have been scaled by a factor of 0.95 (see the caption of Figure S4 for details). The intensities have been scaled so that the largest intensity is 1000. While the ideal point group symmetry of the BrF$_4^-$ anion is D_{4h}, the point group symmetry is reduced to the subgroup S_4 in the space group I–4. Every D_{4h} vibrational mode is split into a set of three modes in S_4 (A, B, and E; the doubly degenerate E_u modes in D_{4h} split into two sets of A, B, E modes). All irreducible representations of the S_4 point group are Raman active, B and E are IR active. The red and blue shading are used to visually clarify the grouping of the raw frequencies. The vibrational modes of molecular BrF$_4^-$ were inspected with the help of the TURBOMOLE and TmoleX program packages.[6]

Fitted Raman peak (cm^{-1})	Raw frequencies (cm^{-1})	Raman Intensity (arb. units)	IR intensity (arb. units)	Irrep in S_4	Irrep in D_{4h} (Raman/IR active)	Assignment
	556	1000.0	0.0	A		
555	551	88.5	78.6	B	A_{1g} (Raman active)	Symmetric BrF$_4$ stretch
	544	300.4	420.0	E		

10

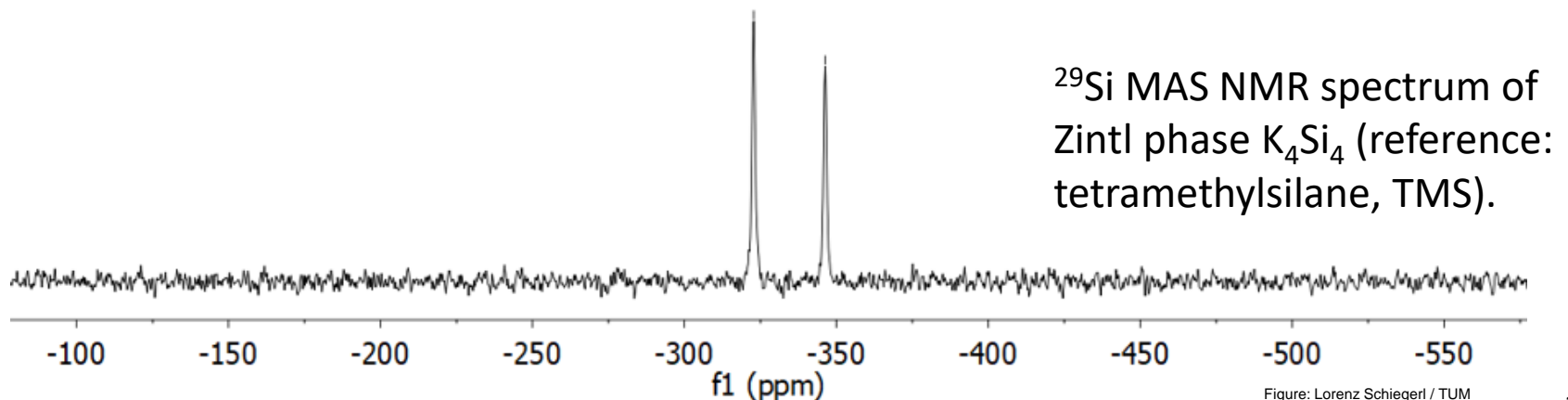# Solid-state NMR spectroscopy

Solid-state NMR spectroscopy (1)

- Nuclear Magnetic Resonance (NMR) is an extremely important specroscopic tool for the determination of molecular structure
  - Bonding, coordination numbers, next nearest neighbors, *etc*.
- NMR utilizes the magnetic spin energy of atomic **nuclei**
  - The magnetic energy levels split into two groups, depending on whether the nuclear spins are aligned parallel or antiparallel to applied magnetic field
  - The energy difference between the parallel and antiparallel spin states is in the radiofrequency region of the electromagnetic spectrum
  - The magnitude of the energy change and the associated frequency of absorption depends on the element and its chemical environment

$m_S = -1/2$

Energy

$\Delta E = E_{-1/2} - E_{+1/2}$

$m_S = +1/2$

$B_0 = 0$ $B_0 \neq 0$ Magnetic Field
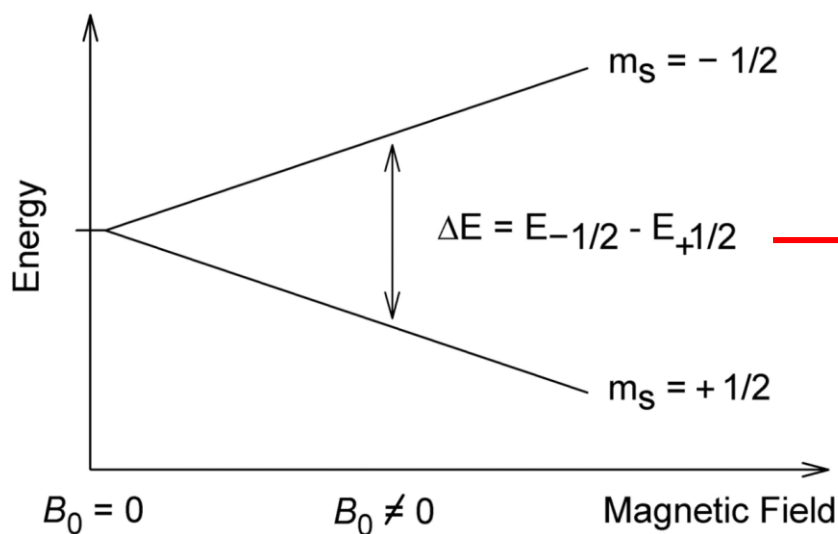
1. Nuclear spins are aligned with an external magnetic field
2. The spins are excited by radiofrequencies
3. The energy difference ΔE is measured

Figure: Wikipedia

Solid-state NMR spectroscopy (2)

- Solid-state NMR is not as routine as solution-state NMR
  - In solution there is thermal motion of molecules and atoms, resulting in averaged NMR spectra that are rather straightforward to interpret
  - In solid state, the averaging effect of thermal motion is much smaller
- Solid-state NMR is enabled by **Magic Angle Spinning** (MAS)
  - The sample is rotated at a high velocity at a critical angle of 54.74° to the applied magnetic field
  - Chemical shifts are averaged so that interpretation becomes possible
  - First applications were on silicates ([29]Si, *J. Am. Chem. Soc.*, **1980**, *102*, 4889)

^{29}Si MAS NMR spectrum of Zintl phase K_4Si_4 (reference: tetramethylsilane, TMS).

Figure: Lorenz Schiegerl / TUM
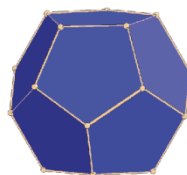
Solid-state NMR for $A_8Al_8Si_{38}$ (A=K, Rb, Cs)

A Combined Metal–Halide/Metal Flux Synthetic Route towards Type-I Clathrates: Crystal Structures and Thermoelectric Properties of $A_8Al_8Si_{38}$ (A = K, Rb, and Cs)

Volodymyr Baran,[a] Anatoliy Senyshyn,[b] Antti J. Karttunen,[c] Andreas Fischer,[d] Wolfgang Scherer,[d] Gabriele Raudaschl-Sieber,[a] and Thomas F. Fässler*[a]
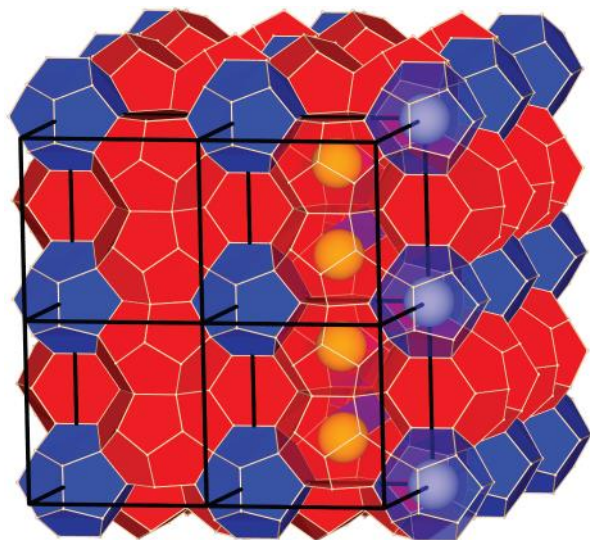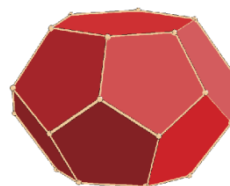
M_{20} cage M_{24} cage

(**M** = Si, Ge, Sn)

8 Al atoms distributed in 46 framework sites

Clathrate I (*Pm*-3*n*)

^{27}Al MAS NMR spectra

- Si and Al **cannot be distinguished by XRD** due to similar X-Ray scattering (neighboring elements, 13/14 electrons)

- Combination of neutron diffraction, ^{27}Al MAS NMR, and computational solid-state NMR (DFT-PBE) enables a complete structural characterization of the Si/Al occupancy
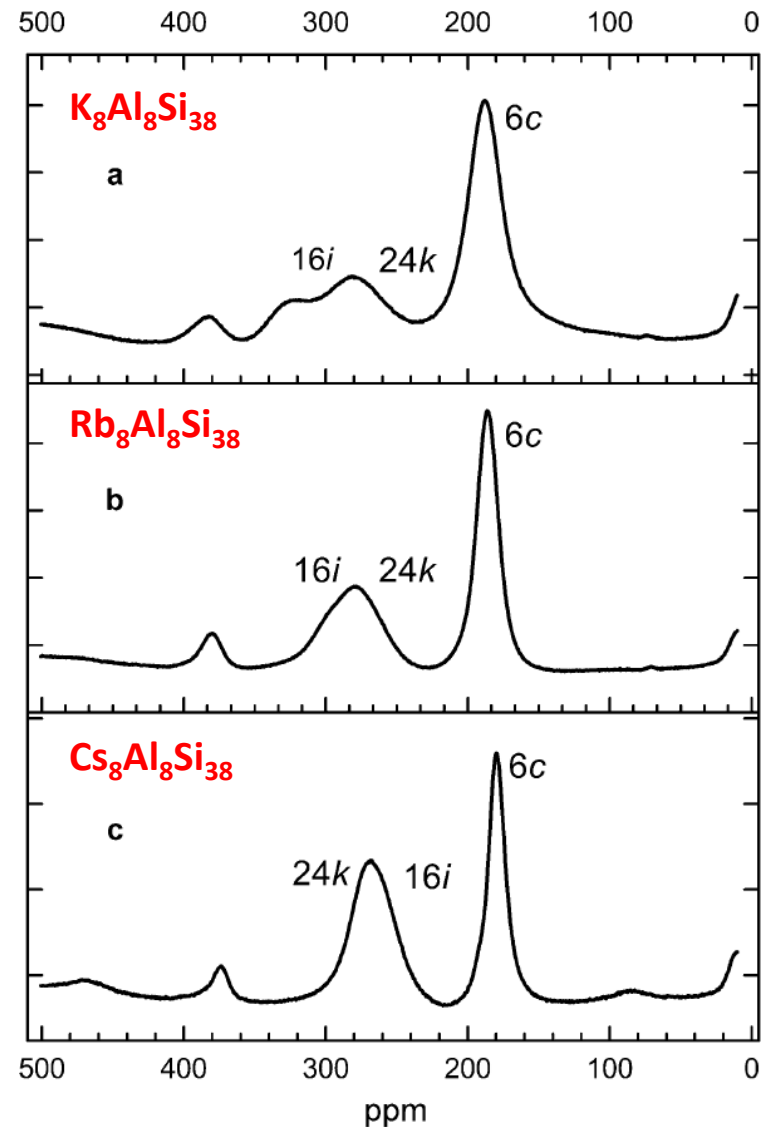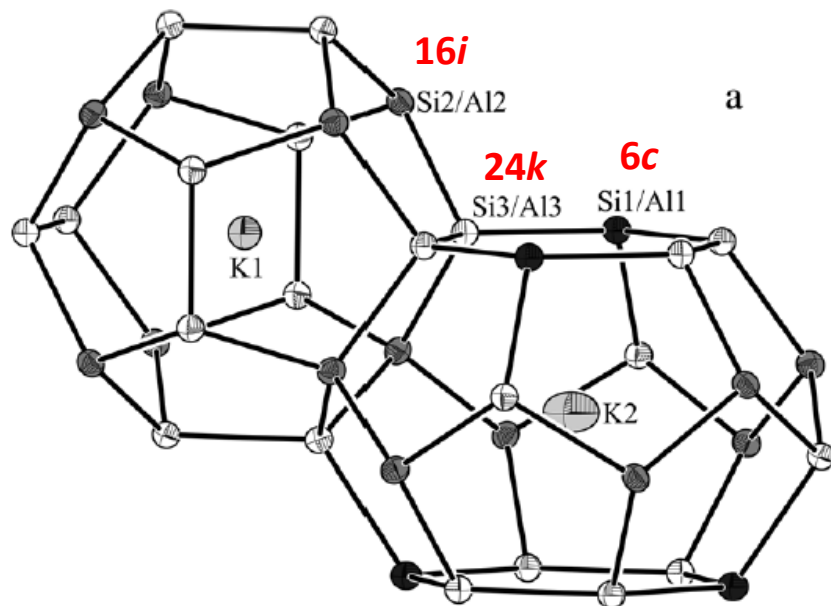
Peak area ratio -> Al occupancy of sites

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Thermal analysis

Thermal analysis (TA)

- Measurement of certain physical and chemical properties as a function of T
  - Mainly enthalpy, heat capacity, mass, and coefficient of thermal expansion
- In solid state chemistry, thermal analysis can be used for the study of:
  - Solid state reactions
  - Thermal decompositions
  - Phase transitions
  - Determination of phase diagrams.
- The main thermal analysis techniques are:
  - Thermogravimetry (**TG**), which records the mass of a sample as a function of temperature or time.
  - Differential thermal analysis (**DTA**), which measures the difference in temperature between a sample and an inert reference material as a function of temperature (-> detects changes in heat content).
  - Differential scanning calorimetry (**DSC**) is a technique closely related to DTA. In DSC, the equipment is designed for a quantitative measurement of the enthalpy changes that occur.

Ref: West p. 314

Thermogravimetry (1)

- TG measures the change in mass of a substance as a function of T or time
- The results appear as a continuous record as shown in Figure below
- The sample is heated at constant rate and has a constant mass M_i, until it begins to decompose at temperature T_i.
- Under conditions of dynamic heating, decomposition usually takes place over a range of temperatures, T_i to T_f, and a second constant-mass plateau is observed above T_f, which corresponds to the mass of the residue M_f.
- The masses M_i and M_f and the difference ΔM are fundamental properties of the sample and can be used for quantitative calculations of compositional changes, etc.
- By contrast, the temperatures T_i and T_f depend on variables such as heating rate, nature of the solid (e.g. its particle size) and **atmosphere** above the sample

Figure 6.42 Schematic TG curve for a single-step decomposition reaction.
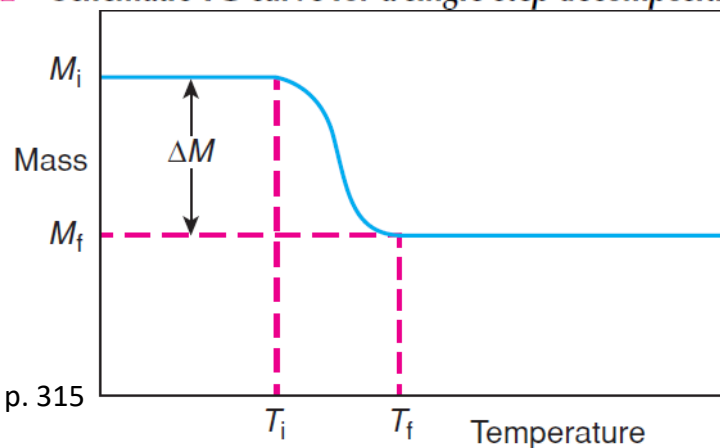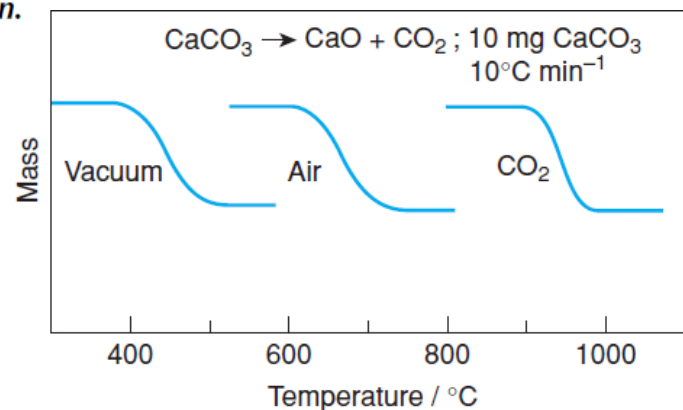

Ref: West p. 315

Figure 6.43 Decomposition of $CaCO_3$ in different atmospheres.

18

Thermogravimetry (2)

- In multistage decomposition processes, TG, either alone or in conjunction with DTA, may be used to separate and determine the individual steps.

- Figure below illustrates the decomposition of **calcium oxalate monohydrate**.

- Decomposition occurs in three stages giving, as intermediates, **anhydrous calcium oxalate** and **calcium carbonate**.

Ref: West p. 320   *Figure 6.49*   *Schematic, stepwise decomposition of calcium oxalate hydrate by TG.*
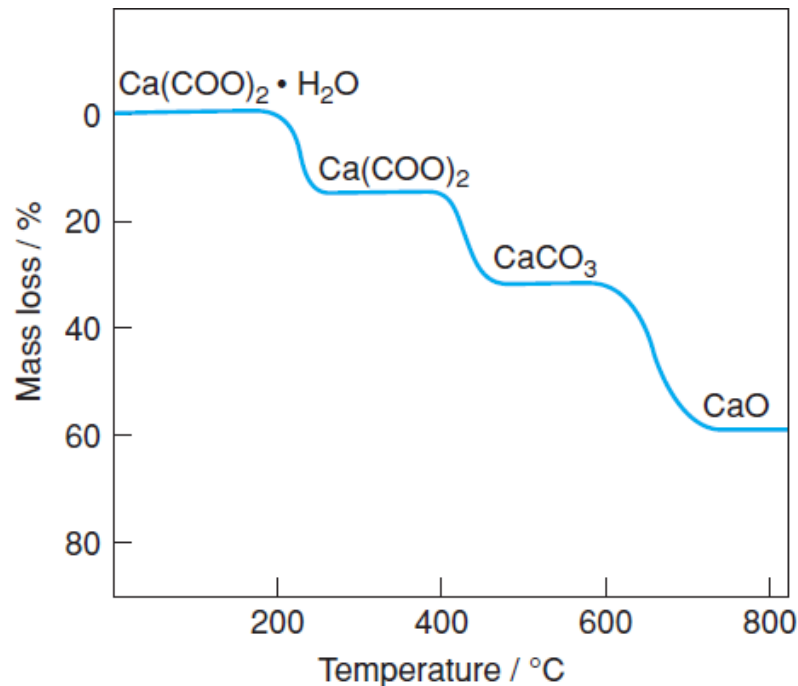
Differential thermal analysis (DTA)

- In DTA, the temperature of a sample is compared with that of an inert reference material during a programmed change of temperature

- The temperatures should be the same until some thermal event, such as melting, decomposition, or change in crystal structure, occurs

- In this case, the sample temperature either:

  - Lags behind the reference temperature (if the change is endothermic) or

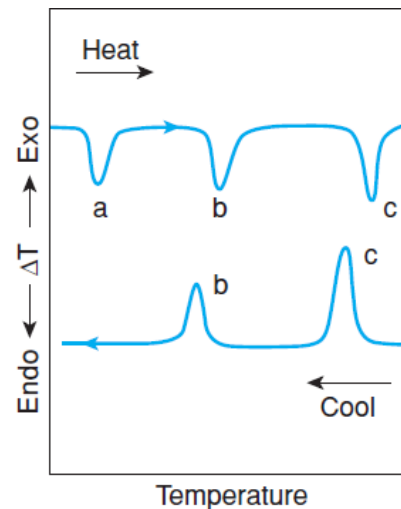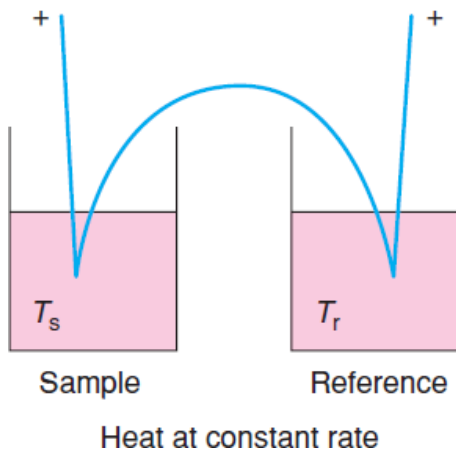 - Leads the reference temperature (if the change is exothermic)

Figure 6.46   *Some schematic reversible and irreversible changes: (a) dehydration, (b) polymorphic transition and (c) melting/solidification.*

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Extra slides

"Nice-to-know"-type material that is not needed for completing the exercises

Summary of various characterization methods

Strategy to identify, analyze, and characterize unknown solids

- The next two slides summarize how various characteriation methods can be applied to find out the composition and structure of an unknown solid
- The table does not include any property measurement techniques and their uses for the characterization of solids, for example:
  - Magnetic properties such as magnetic moment give information on the unpaired spins (-> electronic structure)
  - Electrical properties such as conductivity give information on the electronic structure, oxidation states, and the effect of dopants or defects
  - Optical property measurements can also give information on oxidation states and d / f electron configurations
- Numerous **physical property** measurement techniques are not discussed here. Just to list a few examples:
  - Mechanical/elastic properties (elastic moduli, hardness, …)
  - Permittivities, refractive indices
  - Thermo-, piezo-, pyro-, and ferroelectric properties
  - Thermal conductivity, thermal expansion, heat capacity
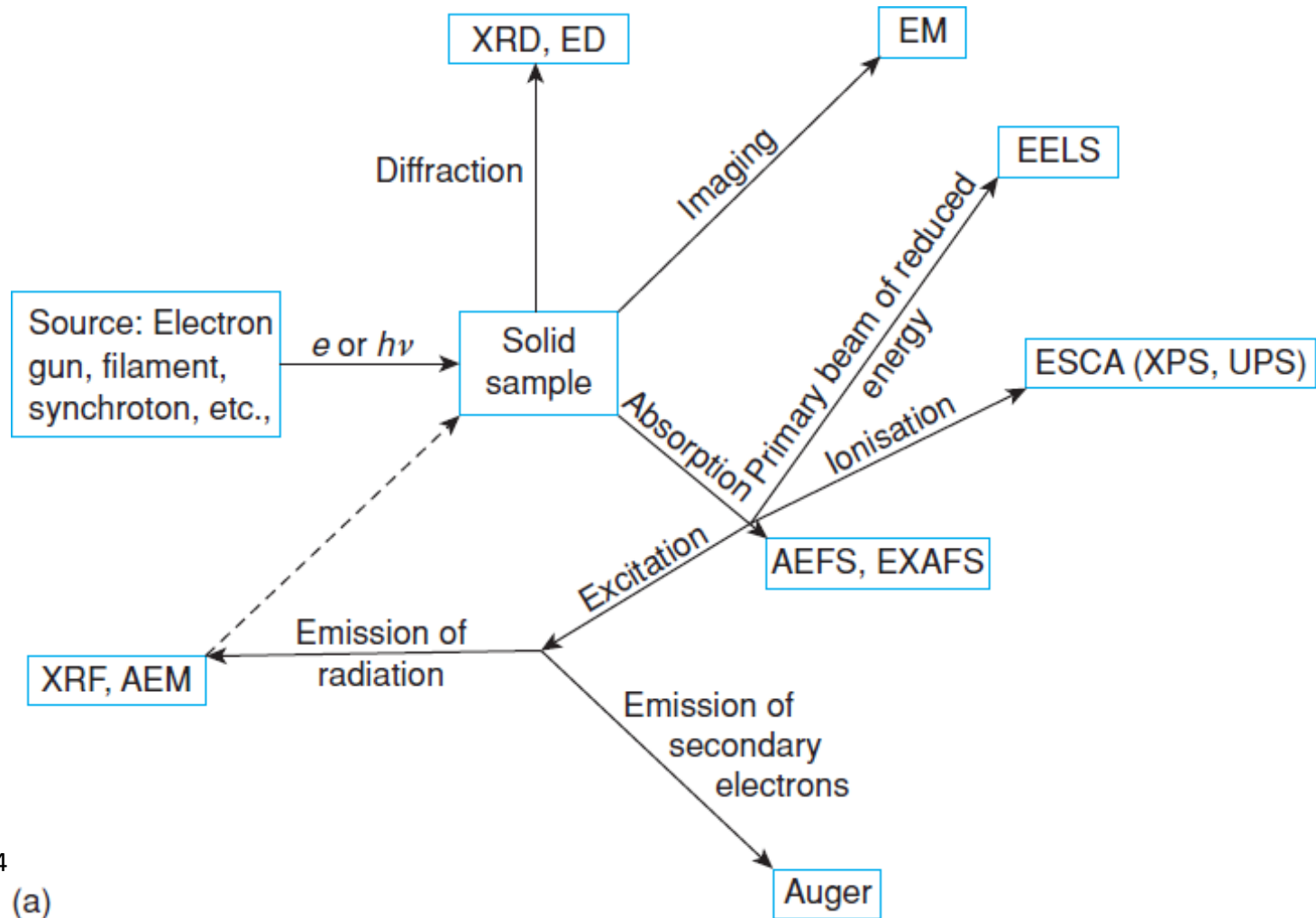
Ref: West p. 321

Table 6.1 *Strategy and overview for identification, analysis and structure determination of solids*

Technique	Information sought	Notes
	1. What is it (in general terms?)	
Optical microscopy	• Is it amorphous/glassy or crystalline? • Are the particles at least micron-size or submicron/nano?	An invaluable, quick, first-look technique. If the solid is crystalline, follow-up characterisation of crystal symmetry is possible: are all the particles similar or is there a phase mixture?; are the crystals twinned?; is the crystal quality good (sharp extinction)?. If particles are submicron size, move on to SEM
Powder X-ray diffraction	• Crystalline phase identification; phase purity	The most important general technique for fingerprinting solids. Should tell what crystalline phase(s) is present, but not its chemical composition. Can identify individual phases in a mixture. Requires access to database and assumes that all possible phases are in the database
	2. What is its chemical composition?	
Atomic absorption spectroscopy; inductively-coupled plasma mass spectrometry	• Bulk chemical analysis of dissolved sample	Gives overall chemical composition but no information on phase identity or purity. Dissolution prior to analysis may be easy or may require fusion in e.g. Na_2CO_3 or B_2O_3, followed by dissolution
X-ray fluorescence	• Bulk chemical analysis of solids	A non-destructive technique although the sample may be embedded within a glass matrix. Also, only gives overall composition. Not suitable for light elements
C, H, N analysis	• Composition of organic solids or organic component of organometallic compounds	Relevant to molecular organic-based materials. Linked to spectroscopic techniques (NMR, mass spectrometry, IR) for structure determination. Separate branch of chemistry; not considered further here
Electron probe microanalysis; energy-dispersive analysis of X-rays; high-angle, annular darkfield/Z-contrast imaging	• Elemental analysis of individual particles from micron to ångström-level	For micron-sized particles, use EPMA for quantitative analysis (excluding H, Li). For semiquantitative analysis to nanometre level, use SEM–EDX/EDS. For atomic-level analysis, use Z-contrast STEM
	3. What is its structure?	
Single-crystal X-ray diffraction	• Crystal structure: atomic coordinates of unit cell contents	The standard technique for structure determination. For molecular materials, gives both solid state packing arrangement and molecular configuration. Crystals as small as 1–10 μm can be studied with synchrotron XRD
Powder X-ray and neutron diffraction (ND)	• Crystal structure: atomic coordinates of unit cell contents	An increasingly powerful technique using synchrotron XRD but one needs access to national facilities for this and for ND. Assumes either prior knowledge of unit cell and space group or determination of these during earlier stages of data processing; not always possible, therefore. ND also gives magnetic structure
Electron diffraction: selected area and convergent beam	• Unit cell and space group	Invaluable aid to structure determination if unit cell cannot be determined *ab initio* by powder XRD/ND. Full structure determination and refinement not usually possible with ED as diffraction intensities are unreliable

High-resolution and Z-contrast electron microscopy	• Lattice imaging	Under favourable circumstances, lattice planes can be imaged by HREM. Invaluable for shear structures, layered intergrowths and homologous series of phases. Z-contrast imaging gives 2D structural projections directly, without focusing problems, at atomic level. Crystallites need to be oriented correctly
X-ray spectroscopies	• Local structure information on bulk materials	Diffraction techniques give crystal structure information averaged over many unit cells. This is complemented by local structure information given by a wide range of spectroscopic techniques including XANES (for oxidation states) and EXAFS (for coordination numbers of specific elements and bond lengths)
Mössbauer spectroscopy	• Coordination numbers and oxidation states of selected elements	Very powerful local structure probe but limited to a few elements: Fe, Sn, I
Electron spectroscopies	• Local structure information especially at surfaces	The shallow escape depth for low-energy electrons gives surface-specific information. XPS provides rapid overview data for solid samples. EELS and Auger are electron microscope-based. EELS gives atomic-level bonding information when used in conjunction with Z-contrast imaging. Auger is particularly useful for light elements which give simpler spectra
NMR spectroscopy	• Element-specific local structure information	Provides bulk information using the solid state, MAS technique. Particularly useful for amorphous materials such as aluminosilicate and borosilicate glasses and for characterising intermediate-range structural features (such as next nearest neighbours)
ESR spectroscopy	• Element-specific local structure information	Specific to paramagnetic species; very high sensitivity
IR and Raman spectroscopy	• Identification of functional groups	For non-carbon-containing materials, IR is useful for identifying functional groups such as oxyanions and H-species. Raman has uses for phase fingerprinting of e.g. C polymorphs

4. Is it stable to temperature/atmosphere?

Thermogravimetry	• Determine thermal stability, susceptibility to atmospheric attack	TG detects weight loss from specific compounds such as hydrates or carbonates or the effects of atmospheric attack, mainly by H_2O, CO_2. Link TG to MS for evolved gas analysis. Drying conditions for chemical reagents can be established. Avoid possible instrument damage and contamination by separate prior heating tests on samples to maximum TG temperature. Use of TG to determine oxygen stoichiometries by H-reduction TG
Differential thermal analysis and differential scanning calorimetry	• Determine melting points, phase transitions and their modification with dopants/impurities	DSC/DTA detect thermal events on heat/cool cycles. Combine with TG to separate effects involving weight loss. Determine reversibility of changes on heat/cool cycles.

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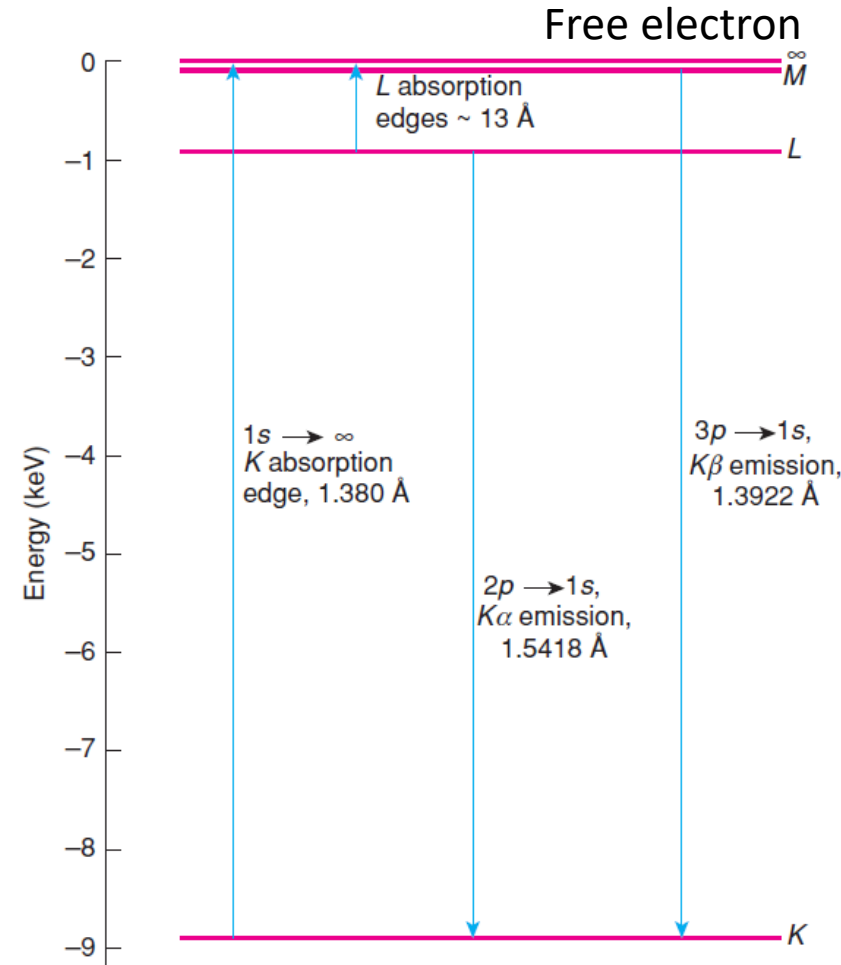# X-Ray and electron spectroscopies

X-Ray and electron spectroscopies

Ref: West p. 304

(a)

The following slides summarize some key X-ray and electron specroscopies, but these are not core contents of the course.
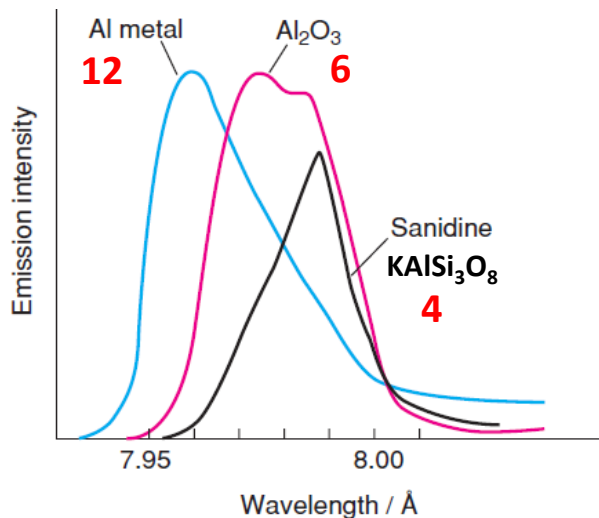
X-Ray spectroscopies

- X-Rays are very useful for the chemical and structural characterization of solids

- **Emission**: Utilize the characteristic *X-ray emission spectra* of elements generated by bombardment with high-energy X-Rays or electrons.
  - Mainly used for chemical analysis
  - Also some uses in determination of local structure and coordination

- **Absorption**: Measure the absorption of X-rays by samples, especially at energies in the region of absorption edges.
  - Powerful techniques for studying local structure but usually require a high-energy X-ray source such as a synchrotron

Free electron

Energy (keV)

- *L* absorption edges ~ 13 Å
- $1s \longrightarrow \infty$ *K* absorption edge, 1.380 Å
- $2p \longrightarrow 1s$, *Kα* emission, 1.5418 Å
- $3p \longrightarrow 1s$, *Kβ* emission, 1.3922 Å

Electronic transitions responsible for emission and absorption X-ray spectra. **Wavelengths for Cu**.

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X-Ray emission spectroscopies

- X-ray fluorescence spectroscopy (**XRF**, see [Solid State Chemistry Wiki](#))
  - A solid sample is bombarded with high-energy X-Rays
  - The resulting emission spectrum is recorded
  - From the spectral peak positions, the elements present can be identified
  - From their intensities, a quantitative analysis can be made
- Peak positions vary slightly with local environment
  - Determination of local structure such as coordination numbers, bond distances
- XRF is a **bulk** technique, while micron- or submicron-sized particles can be analyzed with Analytical Electron Microscopy, AEM (EPMA / EDAX / EDS)
 - In conjunction with **SEM** / **TEM** measurement, utilizing emitted X-Rays


Al Kβ emission spectra of three Al-containing materials

Al coordination number in red

X-Ray absorption spectroscopies (1)

- Atoms give characteristic X-ray absorption spectra in addition to characteristic emission spectra

- X-ray Absorption Near Edge Structure (**XANES**)
  - (Absorption edge fine structure, AEFS)
  - The exact peak positions depend on details of oxidation state, site symmetry, surrounding ligands and the nature of the bonding

Cu
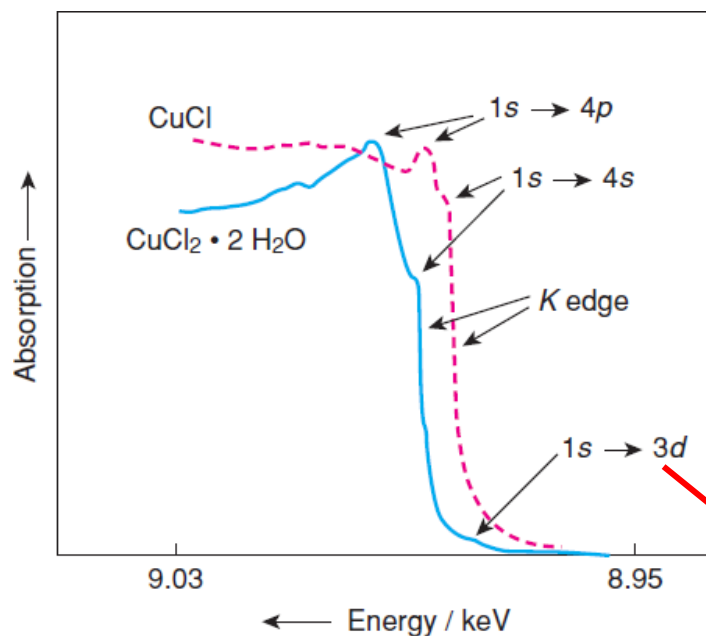
Only for CuCl$_2$ with d^9 Cu(II)
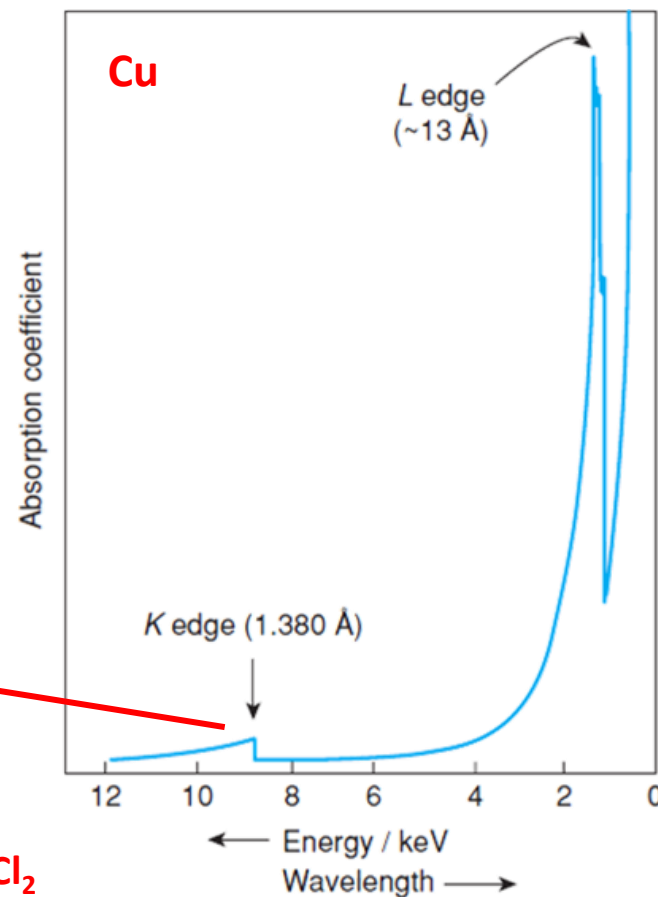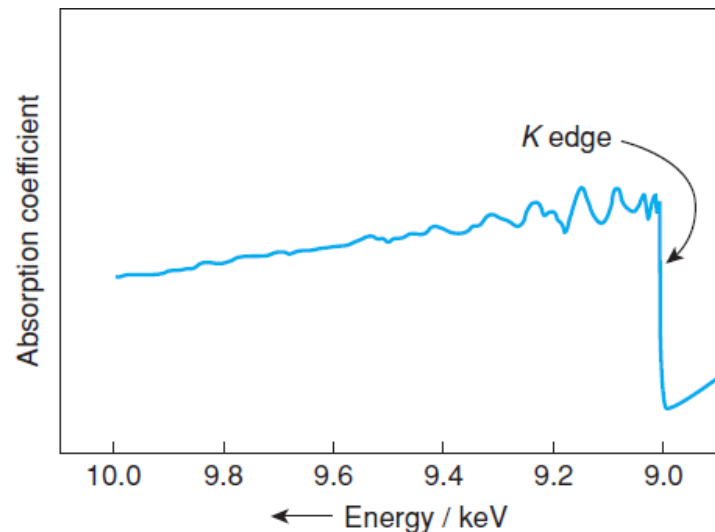
Ref: West p. 306

Figure 6.31 *AEFS spectra of CuCl and CuCl$_2$·2H$_2$O.*

X-Ray absorption spectroscopies (2)

- Extended X-ray Absorption Fine Structure (**EXAFS**) examines the variation of absorption with energy over a much wider range compared to XANES
  - From the absorption edge to higher energies by up to ~1 keV
  - See [Solid State Chemistry Wiki](#)
- The absorption usually shows a ripple, known also as the Kronig fine structure, from which information on local structure and bond distances may be obtained
- Often used to determine **interatomic distances** in amorphous materials

Ref: West p. 306

Figure 6.32 EXAFS spectrum of Cu. Reproduced with permission from E. A. Stern 'The Analysis of Materials by X-Ray Absorption' Scientific American, 234(4):96 © 1976 Scientific American, a division of Nature America, Inc.

Electron spectroscopies (1)

- Based on the kinetic energy of electrons that are emitted from matter because of bombarding it with ionizing radiation or high-energy particles
- Electron Spectroscopy for Chemical Analysis (ESCA)
  - X-Rays as ionizing radiation -> XPS (X-ray photoelectron spectroscopy)
  - UV-light as ionizing radiation -> UPS (ultraviolet photoelectron spectroscopy)
  - Auger electron spectroscopy (AES)
  - Electron energy loss spectroscopy (EELS, particularly useful for light atoms)
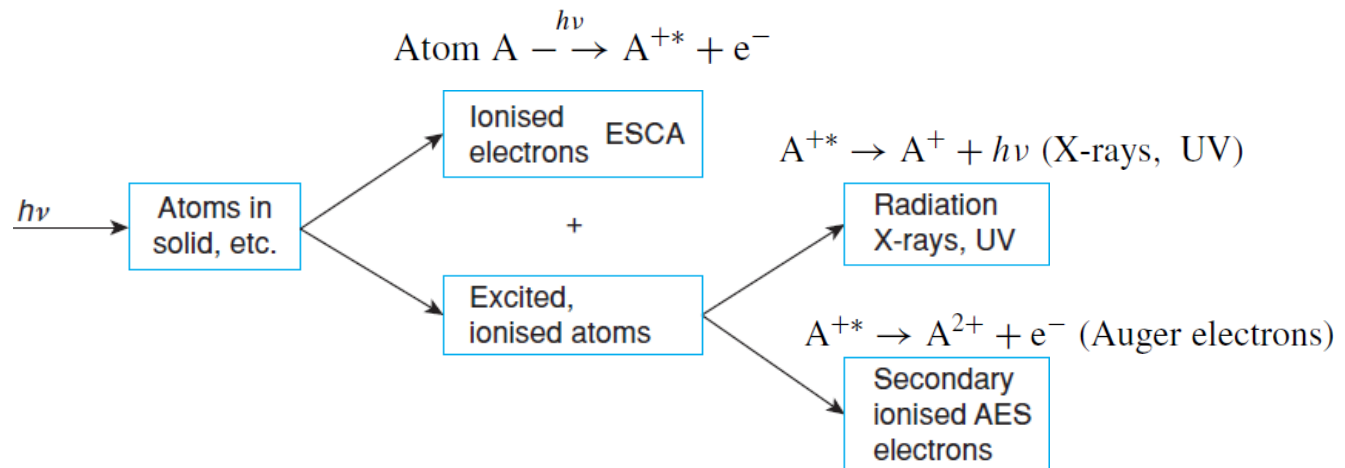
$$\text{Atom A} \xrightarrow{h\nu} A^{+*} + e^-$$

$$A^{+*} \rightarrow A^+ + h\nu \ (\text{X-rays, UV})$$

$$A^{+*} \rightarrow A^{2+} + e^- \ (\text{Auger electrons})$$

Ionised electrons ESCA

$h\nu \rightarrow$ Atoms in solid, etc.

+

Excited, ionised atoms

Radiation X-rays, UV

Secondary ionised AES electrons

Figure 6.34 *Origins of ESCA and Auger spectra.*

Ref: West p. 309

Electron spectroscopies (2)

- XPS can be used to probe the local structure of solids (see [Solid State Chemistry Wiki](#))
- This is possible because the binding energies of electrons may vary depending on the immediate environment of the particular atom and its charge or oxidation state
- In sodium thiosulfate, $Na_2S_2O_3$, the two types of S atom may be distinguished.
- Peaks are of equal height, indicating equal numbers of each. Assignment of the peaks of higher kinetic energy to the terminal S atom is made on the basis that this atom carries more negative charge than the central atom and is, therefore, easier to ionize
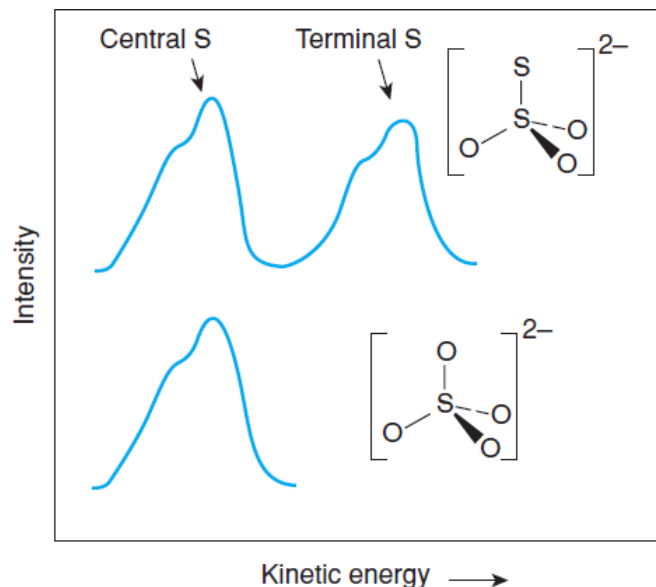
Ref: West p. 310

Figure 6.36 *Schematic XPS 2p spectra of $Na_2S_2O_3$ and Na_2SO_4. Each peak is a doublet because of the two spin–orbit states, 1/2 and 3/2, of the 2p electron.*

Electron spectroscopies (3)

- KCr_3O_8 is a mixed valence compound better written as $KCr^{III}(Cr^{VI}O_4)_2$. Its XPS spectrum shows doublets for Cr 3s and 3p electrons.

- The intensities are in the ratio 2:1 and the peaks are assigned to the oxidation states Cr^{VI} and Cr^{III}.

- This fits with the formula and with the expectation that ionization potential is greater for Cr^{VI} than for Cr^{III} (the latter is easier to ionize, emitted e⁻ more energetic)
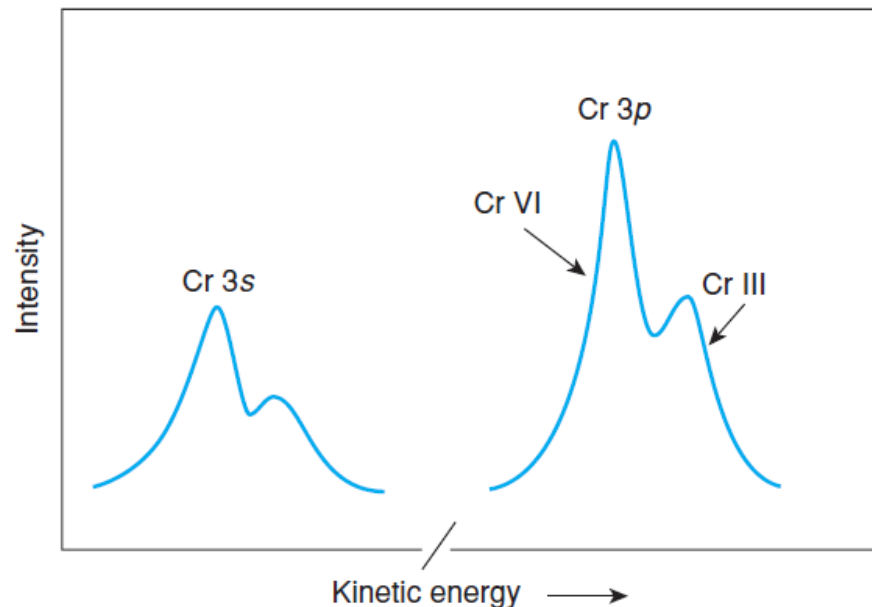

Figure 6.37   *XPS spectrum of Cr 3s, 3p electrons in KCr₃O₈.*