

GENERAL INORGANIC PHYSICAL METHODS NOTES

Preparation, Separation, and Purification

Preparation

The principle methods of preparation are as follows:

Oxidation –

Agents: halogens, O₂, H₂O₂, MnO₄⁻, anodic oxidation, etc.

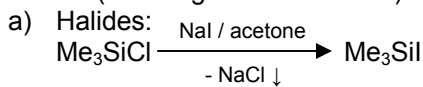
e.g. Xe + nF₂ → XeF_{2n}

Reduction –

Agents: H₂, element, alkali metal, organometallics, Zn/HCl, cathodic reduction, etc.

e.g. 2 GaCl₃ + Ga → 3 GaCl₂

Metathesis (exchange or substitution) –



b) Oxides / Hydroxides: controlled hydrolysis + elimination of H₂O.

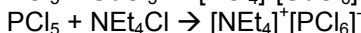
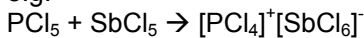
e.g. XeF₆ in H₂O → OXeF₄, XeO₃

c) Other types – e.g. amides, hydrides, organometallics, complexation.

Acid-Base Reactions –

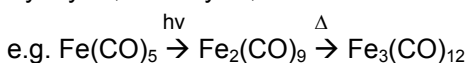
Addition, elimination or displacement without change of oxidation state.

e.g.



Decomposition Processes –

Pyrolysis, Photolysis, etc.



Separation and Purification

There are four main methods for separating and purifying the products of chemical reactions, the choice depending on the physical and chemical properties of the reaction mixture.

- Distillation or Sublimation, for volatile molecular compounds.
- Crystallisation, e.g. NBU₄⁺ICl₄⁻ (solvent choice critical).
- Chromatography (Gas or Liquid) for separation molecular compounds. Also includes Ion Exchange for separating charged species.
- Solvent-Extraction.

Detection and Identification

Distinctive tests for a compound depending on its physical and/or chemical properties.

Chemical Methods

Redox Reactions, e.g. starch-iodide paper for oxidising gases, or Cr(VI) paper for reducing ones.

Precipitations, e.g. Ag⁺ → AgCl(s).

Complexations, e.g. Cu²⁺ → [Cu(NH₃)₄]²⁺ - deep blue.

Acid-Base properties, e.g. SF₄ vs. SF₆ (former complexes to BF₃).

Physical Methods

- + Vapour Pressure.
- + Molecular Weight (Mass Spectrometry).
- + Nuclear Decay (for radioactive nuclei).
- + UV-Visible Absorption or Emission Spectra.
- + IR Spectrum or Raman Spectrum (Vibrational).
- + NMR Spectrum.
- + EPR Spectrum (for paramagnetic systems).
- + Magnetic Susceptibility (usually for paramagnets).
- + X-ray Powder Diffraction.
- + X-ray Fluorescence and Photoelectron Spectroscopy.
- + Retention Time (chromatography).
- + Electrochemical Properties (includes Transport, Cyclic Voltammetry, solution conductivity).
- + Electrical Conductivity of Solids.

Quantitative Analysis

Determining elemental composition or its concentration. Again, there are chemical or physical methods available.

Chemical Methods

- + Usually based on the same reaction types listed above, e.g.
- + Redox – titration with MnO_4^- .
- + Precipitation – AgCl or BaSO_4 , then gravimetric analysis (with sparingly soluble salt).
- + Complexation – e.g. EDTA ligand for the estimation of Ca^{2+} in tap water.
- + Acid-Base Properties – titrations with acid/base.

Physical Methods

- + UV-Visible Absorption and Emission – particularly important is atomic spectroscopy.
- + X-ray Fluorescence Spectrophotometry – atomic composition of solid samples.
- + IR Spectrophotometry – concentrations of strongly absorbing species, e.g. metal carbonyls. Monitoring chemical reactions.
- + Raman Spectrophotometry – lacks sensitivity, but can be used to determine concentrations and monitor chemical changes.
- + NMR Spectroscopy – useful for following changes of concentration and chemical reactions.
- + Electrochemical Measurements.
- + Nuclear Decay Properties – amounts of trace amounts of materials.

Uses of some Physical Techniques in characterising inorganic compounds:

Information Sought	Phase of Sample		
	Gas	Liquid / Solution	Solid
Fingerprint	IR. Mass Spec. UV/Vis.	IR, Raman. NMR. Mass Spec. UV/Vis.	IR, Raman. Powder X-ray. Mass Spec. UV/vis
Groups / Atoms present	IR. Mass Spec. Atomic absorption. Nuclear Decay.	IR, Raman. Mass Spec. NMR, EPR. Atomic absorption. Nuclear Decay.	IR, Raman. Mass Spec. NMR, EPR. X-ray emission. X-ray PES. Nuclear Decay.
Molecular Symmetry	IR. Microwave.	IR, Raman. NMR, EPR.	IR, Raman. NMR, EPR.

Bond lengths and angles	Electron Diffraction. EPR.		Single-crystal X-ray Diffraction.	
	IR, Raman. Microwave. Electron Diffraction.	IR. NMR. EXAFS.	Single-crystal X-ray Diffraction. Neutron Diffraction. NMR. EXAFS.	
Electronic structure	IR UV/Vis. UV PES. EPR.	IR UV/Vis. X-ray PES. EPR.	IR. UV/Vis. UV and X-ray PES. Single-crystal X-ray and Neutron Diffraction	

Mass Spec requires gas phase – can be used for solution / solid providing ionised first (without using electron bombardment!).

Solid State NMR requires special conditions (see later).

EPR only works on paramagnetic samples.

Microwave Spectrum requires a permanent electric dipole moment in the ground electronic state.

- No one method is universally applicable! -

Limitations

FACTOR	COMMENTS
Selection Rules	Essential restrictions on the appearance, or at least the intensity, of a spectroscopic transition or diffraction feature. <ul style="list-style-type: none"> ✚ need dipole moment for rotational transitions. ✚ Vibrational transitions are active IR absorption or Raman scattering (case of centrosymmetric molecules). ✚ Systematic absences in X-ray powder patterns.
Sensitivity (minimum amount of material that can be detected)	For spectroscopic transitions, this depends on the probability. In UV/vis/IR spectra – determined by extinction coefficient (small for d-d transitions, large for most charge-transfers for $\nu(\text{CO})$ modes in IR). High Sensitivity: nuclear decay > mass spec and EPR. Low sensitivity: NMR and Raman, although there are ways of enhancing. X-ray Diffraction.
Specificity (how selective is the method)	Depends on sharpness, number and ease of interpretation of the measured features. For fingerprinting, the more features the better.
Scale (amount of material needed)	Techniques vary widely in the amount of sample they need, although most can cope with at least mg quantities. Magnetic Susceptibility, NMR, neutron diffraction and electron diffraction tend to need lots.
Phase	IR, Raman and UV/vis are among the few techniques that can be applied relatively freely to all phases. <ul style="list-style-type: none"> ✚ Structure determination based on rotational transitions or ED patterns confined to the gas phase. ✚ X-ray and neutron diffraction confined to crystalline solids. ✚ NMR best suited to liquids (lack of sensitivity limits gas). ✚ Mass spec requires special methods of ionisation. ✚ Specialised methods are needed to determine bond lengths and interbond angles in the liquid phase, or in amorphous solids, e.g. NMR, EXAFS or Vibrational Spectroscopy.
Intrusion (does the method involve destruction of the sample)	Elemental analysis, e.g. by atomic absorption, usually destroys the sample. Many methods require special preparation (e.g. alkali halide discs for IR, solutions for NMR and UV/vis). Non-intrusive methods include Raman and various fluorescence techniques, NMR

	and EPR studies of pure liquids/solids, diffraction of solids.
Susceptibility to Interference (are the features liable to be masked or otherwise affected by the presence of other compounds)	The widths and number of spectroscopic / diffraction features will determine how susceptible the measurements are to interference from other active components, and how suitable the method is for studying mixtures. The contribution of solvents may be a major limiting factor (e.g. water absorbs in IR strongly).
Special Requirements of the Sample	Possible problems: <ul style="list-style-type: none"> • The sample may need to be handled under air and/or moisture free conditions. • A compound may be highly dependent on choice of solvent, pH, pressure, temperature, etc. • Practical problems: e.g. alkali halide windows in IR studies susceptible to attack, or HF solutions which etch glass apparatus.
Timescale	Lifetime of the compound and the timescale associated with the physical method.

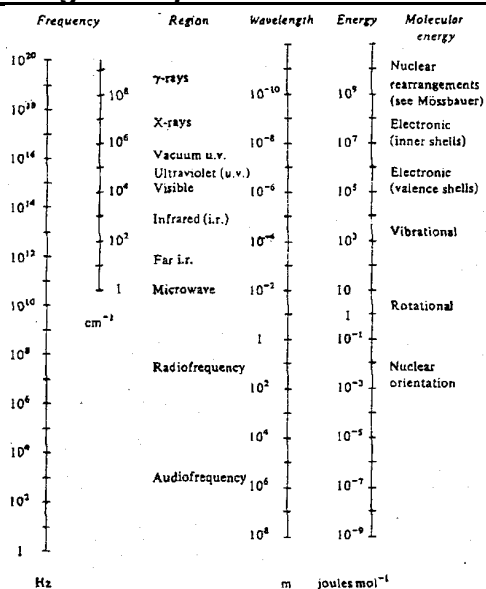
Timescales

There are at least four timescale that concern us:

- 1) Interaction Time [1 / energy of excited state]
- 2) Lifetime of Excited State [relaxation time]
- 3) Lifetime of species being studied.
- 4) Total time of the experiment.

Technique	Energy of excited state / Hz	Relaxation time / s	Linewidth / Hz
NMR (solution)	10^8	10	10^{-1}
ESR (solution)	10^{10}	10^{-5}	10^5
Vibrational (gas)	10^{14}	10^{-8}	10^8
Electronic (solution)	10^{16}	10^{-15}	10^{15}
Diffraction Methods	$10^{18} - 10^{20}$	-	-

Regions of the Electromagnetic Spectrum and Associated Molecular Energies



Useful approximations: $1 \text{ cm}^{-1} \approx 10 \text{ J mol}^{-1}$
 $\approx 3 \times 10^{16} \text{ Hz}$
 $1 \text{ eV} \approx 8000 \text{ cm}^{-1} \approx 100 \text{ kJ mol}^{-1}$

Fourier Transform Techniques

Simplest way of recording a spectrum is to use a tunable monochromatic source. However, few of these can be tuned over a wide range of frequencies are available, so spectra are commonly recorded using a broad-band source, whose output contains all frequencies of interest.

The problem then becomes how to separate out the information about intensities at each frequency from the overall transmission. The usual method (at least in the range UV to IR) is to use a diffraction grating (or similar device) to spatially separate the radiation at different frequencies.

There is another way of separating the information according to frequency, and this involves the interference phenomena that are also responsible for the dispersive effect of a diffraction grating. If interference effects can be made to alter the amplitude of the total radiation reaching the detector as a function of *time*, a Fourier transform will convert the record of amplitude A(t) into the desired spectrum I(v). This is carried out using a computer, which can also perform other functions such as controlling operation of the instrument and storage of spectra.

Fourier Transform (FT) techniques are now of great importance in two areas: NMR and IR. In NMR, interference is generated during the relaxation of nuclear spins, which gives beats of frequency which can be Fourier Transformed to generate a spectrum. In IR, the interference is generated by recombination of beams that have travelled different distances, and the path difference is Fourier Transformed this time.

Note that diffraction methods depend on interference effects as well, but for crystal data a 3D Fourier Transform is required to generate a three-dimensional map of the positions in the crystal. It is useful in fluid samples though.

The FT method enables spectra to be recorded much more rapidly than by direct observation of absorption. It may also offer major advantages of both sensitivity and resolution.

Glossary of Terms and Techniques

TECHNIQUE	DESCRIPTION	APPLICATION
AAS = atomic absorption spectrophotometry	Depends on electronic spectra of ATOMS in flames and selective absorption of light from atomic emission in the flame.	Primary method of elemental analysis.
COSY = correlation spectroscopy	2D NMR technique.	Gives information about couplings between nuclei.
CP-MAS = cross polarisation magic angle spinning	Method for narrowing lines in NMR spectra of nuclei in solids.	Important for high-res NMR studies of solids
ED = electron diffraction	Diffraction of monochromatic beam of electrons, usually by gases. Pattern recorded photographically.	Scattering by bonded and non-bonded atom pairs gives scalar interatomic distances. Vibrations broaden the features.
EDX = energy dispersive X-ray spectroscopy	X-ray fluorescence of solid samples when bombarded with electrons	Used in electron microscopes as a major tool for the analysis of solids
Electronic Spectroscopy	Absorption or emission of radiation, usually in visible and UV regions, accompanying changes in electronic state	Electronic energy spectra. For simple systems these may contain vibrational and rotational details for upper or lower states. Information about ligand-field phenomena, interelectron repulsion, and nature of valence-shell orbitals.
ENDOR = electron-	Observation of EPR spectrum while	Simplification and interpretation of EPR

nuclear double resonance.	irradiating nuclear spin transitions.	spectra.
EPR or ESR = electron paramagnetic/spin resonance spectroscopy	Observation of transitions between energy levels associated with unpaired electrons in a magnetic field. Microwave radiation employed.	Study of any species having at least one unpaired electron. Information about atomic constitution, symmetry, and bonding.
ESCA = electron spectroscopy for chemical analysis.	Another name for X-ray photoelectron spectroscopy.	
EXAFS = Extended X-ray Absorption Fine Structure	X-ray absorption spectra in region of absorption edge for particular element.	Gives distribution of interatomic distances around atoms of that element for solids, liquids, solutions, surfaces, etc.
INS = inelastic neutron scattering	Energy-loss spectroscopy using neutrons (cf. Raman)	Vibrational transitions observed unlimited by selection rules. Applicable to solids.
IR = infrared spectroscopy	Absorption or emission of radiation in the IR region, usually associated with changes in vibrational state.	Measurement of vibrational and rovibrational spectra. Information about vibrational frequencies, force constants, functional groups, molecular symmetry and structure.
LCNMR = liquid crystal nuclear magnetic resonance spectroscopy	NMR experiment using liquid crystals as solvents.	Gives geometrical information about the solute.
LIF = laser induced fluorescence	Fluorescence spectroscopy using laser source for excitation. If the source laser is tunable, extra information is obtainable about the excitation spectrum.	Simplification of electronic spectra. Information about vibrational properties of molecule in its electronic ground state.
MAS = magic angle spinning	Technique for narrowing NMR lines due to solids involving rapid rotation of the sample about an axis at an angle of 54.7° to the magnetic field.	Enables high-res NMR spectra of solids to be measured.
Mass Spectrometry	Analysis by mass and charge of molecular ions and their breakdown products. Often prefixed by a term describing the method of ionisation, e.g. FAB, SI, electrospray, etc.	Gives RMM's and fragmentation patterns may help in structure (connectivity) elucidation. Can also give bond dissociation energies, etc.
Matrix Isolation	Preparation of a sample of material trapped in a solid inert matrix (e.g. Ar) for ease of subsequent examination, e.g. by IR, EPR or electronic spectroscopy.	Study of reactive, unstable and short-lived species and reaction intermediates.
MCD = magnetic circular dichroism	Study of difference in absorption coefficients for left and right circularly polarised light caused by exposing the sample to a magnetic field.	Can reveal electronic transitions not resolved by conventional electronic spectroscopy, and provide information about electronic and magnetic properties of the excited and ground states
Microwave spectroscopy	Absorption spectroscopy of gaseous samples in the microwave region of the EM spectrum. Dipole moment necessary.	Measurement of pure rotational spectra of gaseous molecules. Accurate determination of rotational constants
Mossbauer Spectroscopy	Resonant absorption of nuclear γ -rays by nuclei, applicable to a limited number of atoms, e.g. Fe, Sn, I, Au	Gives information about chemical environment (e.g. Oxidation State), magnetic interactions and electric field gradient at the nucleus.
Neutron Diffraction	Diffraction of neutrons, mainly by crystalline solids	Structure determination, particularly useful for locating H and D atoms. May give additional information due to spin-1/2 on neutron leading to magnetic

		scattering.
NMR = nuclear magnetic resonance spectroscopy	Observation of transitions between energy levels associated with nuclear spins ($I > 0$) in magnetic field. Radiofrequency radiation employed.	Many applications, particularly in the identification and structural make-up of compounds, monitoring reactions, and kinetic studies.
NOESY = nuclear Overhauser Spectroscopy	2D NMR technique	Information about groups of protons that are close to one another in space in large molecules
NQR = nuclear quadrupole resonance spectroscopy	Involves energy levels arising from nuclear quadrupole moments of nuclei with $I > \frac{1}{2}$.	Information about environments of quadrupolar nuclei in solids, e.g. $\text{Ga}^+ \text{GaCl}_4^-$
PE, PES = photoelectron spectroscopy	General name for spectroscopic methods in which electrons are ejected as a result of absorption of radiation, and their energy distribution is analysed. UV PES is concerned with valence and X-ray PES with core electrons	Energies of occupied electronic levels determined (UV PES). Identity and environment of atoms in sample determined (X-ray PES)
Raman Spectroscopy	Observation of emitted radiation from sample irradiated by intense monochromatic light, usually in the visible region.	Rotational and vibrational spectra of sample measured, with selection rules different from those of IR spectroscopy
Rotational spectroscopy	Study of transitions involving changes in rotational quantum numbers of gas molecules using IR, Microwave, mm wave, sub-mm wave, and Raman techniques	Gives rotational constants of molecules and hence moments of inertia and molecular dimensions
Rovibrational spectroscopy	Study of rotational transitions associated with vibrational transitions of gas molecules using IR or Raman	Gives information about molecular symmetry, dimensions and vibrational assignments
RRS = resonance Raman spectroscopy	Raman spectroscopy involving excitation with radiation at a frequency that is absorbed by the sample	Enhanced signal, often involving one or a few bands, compared with normal Raman spectrum. May include progressions in one or more vibrational frequencies
UV/visible spectroscopy	Absorption or emission in UV or visible regions due to electronic transitions	Energies of electronic transitions. May also contain resolved vibrational or rotational detail. Information about 10Dq and interelectron repulsion for transition metal compounds
Vibrational spectroscopy	Study of changes in vibrational states, most often by IR absorption or Raman scattering	Many applications, including fingerprinting, identification of functional groups, molecular symmetry, force constants, etc
X-ray Diffraction	Diffraction of X-rays, usually by crystalline solids	Gives precise structural information (atom positions) and some information about atomic motions. Powder studies used for fingerprinting and determining unit cell symmetry and dimensions.
XRF = X-ray Fluorescence Spectroscopy	Emission of characteristic X-rays from solid samples excited by bombardment with electron beam	Detection and estimation of atomic composition of solids

EPR Spectroscopy

Essential Features:

The technique of electron paramagnetic resonance (EPR) spectroscopy can be applied only to species having one or more unpaired electrons, e.g. free radicals and many transition metal compounds. Observation of an EPR spectrum proves that at least part of the sample has

unpaired electrons, and the technique is particularly valuable for the study of unstable paramagnetic species which may be generated in situ, e.g. by electrochemical oxidation or reduction, or by irradiation.

EPR spectroscopy complements bulk magnetic susceptibility measurements as a means of studying paramagnetic compounds, but is usually concerned with short-range atomic or molecular properties, as opposed to the bulk properties of a paramagnetic ensemble.

The spin of an electron and its associated magnetic moment (possibly with some contribution from orbital angular momentum) are the basis of EPR Spectroscopy. The basis theory follows closely that of NMR Spectroscopy.

For radicals the g-factor is normally close to the free-electron value (2), but for transition metal compounds spin-orbit coupling and other factors can lead to major variations.

Transitions between such energy levels can be induced by the application of radiation with the appropriate frequency:

$$h\nu = g\mu_B B_0$$

The frequency required depends on B_0 (usually fields of 0.34T and 1.24T).

Hyperfine Interactions – the simple picture must be modified if the electron can interact with a neighbouring magnetic nucleus having a spin quantum number M_I . The energy levels become:

$$E = g \mu_B M_S B_0 + a M_S M_I$$

Where the constant is called the hyperfine coupling constant.

Relaxation can occur by various mechanism, via:

Spin-lattice, Spin-Spin and Chemical Exchange

Relaxation is typically efficient and fast (compared with NMR). Hence EPR signals are broad and are most easily recorded in practice their first-derivatives.

Photoelectron Spectroscopy

There are two distinct classes of experiment, using different sources.

XPES

Uses an X-ray source, e.g. Al $K\alpha_{1,2}$ lines. Effective resolution of only $\sim 1\text{eV}$, so typically poor for gaseous species (the linewidth is limited by the lifetime of the hole left by the transition, which is short). The mean free path in a solid is typically about 10\AA , so only electrons ionised from atoms near the surface reach the kinetic energy analyser without losing energy. These give sharp ionisation peaks. Hence, it is a surface-sensitive technique. Core ionisations from np and nd shells can have very pronounced spin-orbit splitting, when n is large.

XPES has two main applications:

a) ESCA (Electron-Spectroscopy for Chemical Analysis).

This examines the binding energies of core electrons, determined by effective nuclear charge. Responds to chemical environment through the charge distribution in the valence shell. Often a simple correlation can be made with the charge on the atom, which in turn depends on the oxidation state and the degree of covalency in bonding. This gives useful chemical information when structural data is not available, i.e. when the material is glassy or disordered, or when the surface of the solid does not have the same structure as the bulk solid.

b) Valence Shell Structure in solids.

The spectra give good representation of the energy distribution of filled states in the valence band, and can distinguish metallic compounds from insulators. Kinetic energies are always measured relative to the Fermi Level of the metallic components in the spectrometer. It is noticed that ionisation of the d-electrons are much more probable than the p-electrons – a

common feature of XPES. Ionisation probabilities depend on the radial distribution of the ionised electrons, and vary from shell to shell. The intensity of d-shell ionisations is obviously helpful in the study of the electronic structure of transition metal compounds.

UVPES

This uses hard UV photons from an electric discharge in helium gas. He(II) is commonly used as a source (brighter). Source linewidths are small and the resolution of the spectrum is usually limited by the quality of the electron kinetic energy analyser, typically ~10meV. Although the surfaces of solids can be studied, the resolution is most usefully and frequently employed in the gas phase. It is common to resolve vibrational features. Samples must have a reasonable vapour pressure. Species that can be easily studied are limited to smallish covalent molecules, and UVPES has been widely applied to elucidate the electronic structure of organometallic compounds. The spectrometer needs to be differentially pumped, to allow high vacuum in the electron analyser portion of the instrument.

Koopmans Theorem states that $I_j = -\epsilon_j$. This approximation relates the ionisation energy from the j^{th} orbital to the energy of an electron in that orbital calculated by self-consistent field methods. It is usually fairly accurate, as the neglect of the electron reorganisation energy following ionisation, which would lower the energy of the ionisation, is nearly offset by the increase in electron-electron repulsion energy due to the contraction of the orbitals in the ion.

Photoionisation Probability or Cross-Sections vary quite strongly with the energy of the outgoing photoelectrons, and in general decrease. For our purposes it is only necessary to know that d-shell and f-shell ionisations become considerably more intense relative to p-shell ionisations from the ligands in He(II) relative to He(I) spectra. This feature is used to assign the ionisations to these orbitals, or determine the proportion of metal character in a molecular orbital.

Bonding Character. The PES spectrum not only maps out orbital energies, but the vibrational structure (or its absence) is a good indicator of final state distortions, that are driven by the removal of the electron. Thus it can distinguish the degree of bonding or non-bonding character of the ionised electron. A particularly strong distortion can occur if the final state is Jahn-Teller unstable, and in this case the ionisation peak may split into two distinct components.

Spin-Orbit Coupling. If the ion contains a hole in a shell with orbital angular moment (i.e. not s), spin-orbit components may be resolvable. Since the splitting is very dependent on the atomic number it can be used to measure heavy atom contributions to the MO's, and thus to assign the features in the spectrum to particular orbitals.

Matrix Isolation

Matrix isolation involves the preparation of a rigid solid sample in which the molecular species of interest are at once isolated and effectively immobilised in an inert host lattice or matrix. The species are thus preserved, typically at high dilution and low temperatures (4-50K) and are thereby denied the opportunity for bimolecular collisions and the thermal energy for unimolecular decomposition. They key features are:

- Rigid Host (to immobilise the guest species).
- Inert Host (e.g. solid Ar, to minimise perturbation of the guest).
- High Dilution (for effective isolation).
- Low Temperatures (to minimise the thermal energy available to the molecule).

Lifetime – can extend lifespan of reactive molecules almost indefinitely.

Detection and Characterisation – various spectroscopic methods can be used to study the matrix. The most important methods in practice are those of Electronic, EPR, and particularly Infrared.

Reaction Intermediates – matrix isolation provides an alternative to flash photolysis, pulse radiolysis, and other time-resolved spectroscopic methods of studying reaction intermediates.

Apparatus – reaction carried out in situ, so that reactive intermediate can be effectively trapped.

Characterisation of an Unknown Molecule by IR Spectroscopy –

- By systematic variations of the conditions we aim to discover how many distinct species are present in the matrix.
- For each species we determine the number, relative intensities, and frequencies of the IR absorptions.
- We draw on the evidence of distinctive features, e.g. $\nu(\text{CO})$, and analogies with known molecules to deduce the likely nature of the unknown.
- Use of the vibrational selection rules may give vital clues to molecular symmetry.
- Isotopic Effects are likely to be vital for conclusive evidence of stoichiometry, geometry, and dimensions of the trapped molecule. Hence it may be possible via normal coordination analysis to determine force constants for the molecule.
- Theoretical calculations can now be carried out at a sufficiently high level to forecast the frequency and intensity patterns making up the IR spectrum of the molecule.
- Confirmation of identity may also be found by seeking independent routes to the compound.
- Sample-warming may also be helpful in identifying reactive molecules when diffusion provides the opportunity for simple bimolecular reactions to occur.

Optical Properties of Solids

For Solids:

- No rotations.
- Fixed orientation relative to polarised light.
- Fixed relative to oriented external perturbations – Magnetic Fields (Zeeman, Circular Dichroism), Electric Fields (Stark), Pressure.
- Low Temperatures (~1.5K) possible – no thermal vibrational energy, simplified spectrum, sharp transitions (long relaxation times).
- Well defined crystalline environment – well defined excitation energies.

Hence, spectra are sharp and have lots of information contained in them.