CHM 411

PART C

PHYSICAL TECHNIQUES IN INORGANIC CHEMISTRY

DIFFRACTION METHODS:

The method allows for the unambiguous determination of the position of the atoms and ions that make up a molecular or ionic compound and description of structures in terms of features such as bond lengths and angles relative positions of ions and molecules in a unit cell.

Structural data obtained are useful in interpretation of ionic and atomic radii useful in prediction of structures and trends in many properties.

X-RAY DIFFRACTION:-

Diffraction is the interference between waves that occurs as a result of an object in their path. X-rays are scattered by the electrons in atoms and diffraction can occur for a periodic array of scattering centres separated by distances similar to the wave length of the radiation of approximately 100pm, such as exist in a crystal.

Diffraction is equivalent to a reflection from two adjacent parallel planes separated by a distance, d, the angle after which constructive inference occurs between waves of wave length, λ is given by the Bragg equation.

$$2d\sin\theta = \lambda \qquad (1)$$

Intensity of diffraction depends on the details of the crystal structure and the identities of the atoms. How well an electron scatters x-ray is related to how many electrons it possesses and its location in the unit cell.

Measurements of diffraction angles and intensities allow backward workings of structural information.

TECHNIQUES

POWDER METHOD:

This method is used for phase identification and determination of lattice parameters and lattice type

The sample is a powder made up of enormous number of very small crystallites of approximately 001 to 10μ in dimension of random orientation.

X- ray beam strikes a poly crystalline sample, scattering in all possible directions. Each plane of atoms is separated by different lattice spacing in the crystal, giving rise to a cone of diffraction intensity.
Each cone consists of a set of closely spaced dots, each one of which represents diffraction from a single crystallite within the powder sample. With very diffraction large number of crystallites, these dots combine to form the diffraction cone.
Useful data are obtained by determining the positions of the various diffraction cones using either a photographic film or a detector sensitive to x-ray radiation.
A powder diffractometer uses an X-ray detector to measure the various diffraction beams. Scanning the detector around the sample along the circumference of a circle cuts through the diffraction cones at the various diffraction maxima and the intensity of the x-rays detected is recorded as a function of the detector angle

DIAGRAM

Fig: powder diffraction pattern obtained for a mixture of T_1O_2 polymorphs.
The number and position of the diffraction maxima i.e. reflections depend on the cell parameters, crystal system, lattice type and λ used in data collection, the peak intensities depend on the types of atoms present and their positions.
The presence or absence of certain reflections in the diffraction pattern permits the determination of the lattice type.

APPLICATION OF POWDER X-RAY DIFFRACTION METHOD

APPLICATION	TYPICAL USE OF INFORMATION EXTRACTED
Identification of unknown materials	Rapid identification of most crystalline phases
Determination of sample purity	Monitoring the progress of a chemical reaction occurring in the solid state.
Determination of refinement of lattice parameters	Phase identification and monitoring structure as a

	function of composition.
Investigation of phase diagrams/ new materials	Mapping out compositions and structure particle size measurement and uses in metallurgy
Structure refinement	Extraction of crystallographic data from a known structure type
Structure determination	Structure determination at high precisions
Phase changes/ expansion coefficients	Studies as a function of temperature (cooling or heating) and a large range. 100-1200k, observation of structural transitions

SINGLE- CRYSTAL X-RAY DIFFRACTION

This is an important method of obtaining the structures of inorganic solids, provided the compound of interest can be grown as a crystal of sufficient size and quality. Data provide definitive information on molecular or extended lattice structure. Technique of data collection involves using a laboratory-based four-circle or area detector diffractometer. For very small crystals, x-ray beams obtained at synchrotron sources can be used.
A four-circle diffractometer uses a scintillation detector to measure the diffracted x-ray beam intensity as a function of the four angles shown in the diagram below

DIAGRAM

A computer controls the location of the detector as the four angles are changed systematically.

NEUTRON DIFFRACTION

Scattering of neutrons by crystals yields diffraction data that give additional information on structure, particularly on light atom positions. Diffraction from crystals for any particle with a velocity associated with λ through de Broglie relation

$\lambda = h/ m\upsilon$ is comparable to the separations of the atoms/ions in the crystal. Neutrons and electrons can have λ of the order 100 – 200pm and thus undergo diffraction by crystalline inorganic compounds.

Neutron beams of appropriate wavelength are generated by moderating (slowing down) neutrons generated in nuclear reactors or through a process known as spallation in which the neutrons are chipped off the nuclei of heavy elements by accelerated beams of protons. Instrumentation used for collection of data and analysis of data of single crystals/powder neutron diffraction patterns is similar to that used for X-ray diffraction. The scale is much larger, because neutron beam fluxes are much lower than laboratory X-ray sources.

The advantages of neutron diffraction stem from the fact that neutrons are scattered by nuclei rather than by the surrounding electrons. As a result, neutrons are sensitive to structural parameters that often complement X – rays. The scattering is not dominated by the heavy elements which can be a problem with X – ray diffraction for most inorganic compounds, e. g locating the position of a light element like it, H, Li, in a material that also contain Pb is impossible with X-ray diffraction, as almost all the e-density is associated with Pb atoms with neutrons in contrast, scattering from light atoms is often similar to that of heavy elements, so, neutron diffraction is frequently used in conjunction with X – ray diffraction techniques to define a structure more accurately.

Typical applications include studies of the complex oxides of heavier metals such as the high temperature super conductors where accurate oxide ion positions are required in the presence of metals such as barium and thallium and systems where hydrogen positions are of interest.

ABSORPTION SPECTROSCOPY

Absorption of electromagnetic radiation by a molecule or material at a characteristic frequency corresponding to the energy of a transition between vibrational or electronic energy levels; the intensity of absorption is related to the probability of the transition occurring, which in turn is determined by the symmetry of the molecule.

UV – Visible (electronic) spectroscopy:

Energy is used to excite species (electrons) to higher electronic state by applying electromagnetic radiation in the UV - Visible regions of the spectrum

Sample is usually a solution (or a gas) contained in a cell or cuvette (an optically transparent material)

Cell is placed in the beam from a light source and the optical transmission is measured at a detector.

Incident light, beam is split into two, one passing through the sample and the other through the reference; the beams (sample and reference) are compared at the detector – a photodiode.

Absorbance 'A' of the sample is defined as

$$\log = (I_o / I) \qquad (2)$$

Where Io is incident intensity, I measure the intensity after passing through the sample.

The Beer – Lambert law is used to relate the absorbance to the molar concentration J of the absorbing species, l, and the optical path length

$$A = \varepsilon [J]l \qquad (3)$$

ε is the molar absorptivity or the extinction coefficient, it ranges from $> 10^5$ dm^3 $mol\text{-}^1$ $cm\text{-}^1$ for allowed transitions and less than $1dm^3mol\text{-}^1m\text{-}^1$ for forbidden transitions.

The energies and intensities of transition provide information on electronic structure and chemical environment: changes in spectral properties are used to monitor the progress of reactions.

Spectrophotometry: involves the measurement of absorbance rather than the energy of transitions provided one of the species has a suitable absorption band. A spectrophotometric titration is carried out and the extent of reaction is monitored by measuring the concentrations of the components.

Proportionality between absorbance and concentration provides a way to measure properties that depend on concentration e.g. equilibria and rate constants. Spectra changes during titrations provide information on the number of species that form during its progress.

The appearance of one or more isosbestic points, wavelengths at which two species have equal values of their molar absorption coefficients, during a reaction or titration. At this point it is unlikely that a third species will have the same molar absorption coefficient. The retention of isosbestic points in a titration or during the course of a reaction is evidence that only two species dominant i.e. reactant and product are in the solution.

Example is the isosbestic points observed in the spectral changes during reactions of HgTPP (TPP = tetra phenyl porphyrin) with Zn^{2+} in which Zn replaces Hg in the macrocycte. The initial and final product, which indicates that free TPP does not reach a detectable concentration during the reaction.
Techniques:

- Stopped – flow method initiated by mixing reactants with half – lives of between 1 ms and 10 s.
- Photochemically initiated ultrafast laser pulse technique is used to monitor slow reactions over long hours or days.

Infrared and Raman spectroscopy

Vibrational spectroscopy is used to characterize compounds, measure bond strength and force constants.
Principle : bonds in a molecule behave like a spring stretching through a distance X with a restoring force F, for small displacements, the restoring force is proportional to the displacement.

$$F = - kX \tag{4}$$

Where k is the force constant

$$\varepsilon\upsilon = (\upsilon + 0.5)\, \hbar\, \omega \tag{5}$$

$\omega = (k/\mu)\ 0.5$

$\upsilon = 0, 1, 2, ...$

υ is the vibrational quantum number and μ is the effective mass of the oscillator, for a diatomic molecule composed of two atoms of masses ma and mb

$\mu = m_a\ m_b\ /\ m_a + m_b$

ω = frequeny

$\upsilon = \omega / 2\pi c$, value υ lies between 300 - 3800 cm-1

vibrational energies are expressed in terms of wave number $\bar{\upsilon}$.

A nonlinear molecule consisting N atoms vibrates in 3N – 6 ways and a linear molecule 3N – 5 ways. These vibrations are referred to as normal modes, which correspond to a changing electric dipole moment that can interact with infrared radiation. These modes are IR active. In addition to the fundamental transitions of $\Delta\upsilon \pm 1$, vibrational spectra may also show bands arising from double quanta ($\Delta\upsilon = +2$, at $2\bar{\upsilon}$) known as overtones, and combinations of two different vibrational modes e.g. $\upsilon1 + \upsilon2$. Overtones often arise even when fundamental transition is not allowed by the selection rule.
Technique:

IR spectroscopy:

compound is exposed to IR radiation and the variation of the transmission frequency obtained recorded. Spectrum is extracted from an interferogram by Fourier transformation which converts the information in the time domain based on the interference of waves travelling along paths of different length to the frequency domain.

Raman spectroscopy: sample is exposed to intense laser radiation in the visible region of the spectrum. Most of the photons are scattered with no change of frequency while some are scattered giving of some of their energy to excite vibrations with photons having frequencies different from the incident radiation by amounts equivalent to vibrational frequencies of the molecule. No molecule with a centre of symmetry can be IR and Raman active.

Only vibrational modes corresponding to a changing polarizability of the molecule are Raman active, however, a mode may be inactive in both.

Raman spectroscopy can be studied in aqueous solutions.

Applications of IR / Raman spectroscopy

- Excellent method for studying molecules trapped in inert matrices, a technique known as matrix isolation.
- Incorporated into rapid kinetic technique – ultrafast laser photolysis and stopped – flow methods used for identification of transient intermediates in reactions that involve changes in vibrational spectra, such as those involving the addition or loss of CO ligands.
- Study of d – block compounds with carbonyl (CO) group. The CO group is a strong oscillator with intense absorption bands. Free CO absorbs at 2143cm-1, when coordinated with a compound, the stretching frequency and wave number is lowered by an amount that depends on the extent to which the electron density is transferred into the 2π orbital by back donation from the metal. CO stretch absorption allows distinction to be made between terminal and bridging ligands occurring at lower frequency.

RESONANCE TECHNIQUE

The use of NMR and ESR/EPR

NUCLEAR MAGNETIC RESONANCE

- It’s a suitable technique for studying compounds containing elements with magnetic nuclei, particularly those containing hydrogen
- Sensitivity of method is dependent on several parameters including the abundance of the isotope and the size of its nuclear magnetic moment
- NMR techniques for ^{1}H, ^{19}F, ^{31}P are easy to observe because of the abundance of the elements and their sensitivities.
- A common limitation for exotic nuclei is the presence of a nuclear quadrupole moment, a non – uniform distribution of electric charge (present for all nuclei $I > ½$), which broadens the signals and degrades spectra. Nuclei with even atomic number have zero spin and are invisible to NMR.

  A nucleus of spin I take up $2I + 1$orientations relative to the direction of an applied magnetic field.
- Energy separation of the two levels of a spin – ½ nucleus (e.g. ^{1}H or ^{13}C) is $E = \hbar\gamma B_o$, where B_o is the applied magnetic field, γ is the magnetogyric ratio of the nucleus, the ratio of its magnetic moment to its spin angular momentum
- The frequency of an NMR transition depends on the local magnetic field experienced by the nuclei and it is expressed in terms of the chemical shift δ, the difference between resonance frequency of the nuclei in the sample and that of a reference compound tetramethylsilane.
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$$\delta = \frac{v - vref}{vref}\ x\ 10^{6}$$

- $\delta < 0$, nucleus is shielded
- $\delta > 0$, nucleus is deshielded
- the higher the electron density around a nucleus the greater the shielding effect e.g. H bound to a closed shell, low oxidation state, d – block element from group 6 to 10 e.g.$[HCo(CO)_4]$ is highly shielded. An oxoacid like sulphuric acid is deshielded

- chemical shifts are different for the same elements in equivalent positions within the molecule as in ClF_3, ^{19}F NMR for equatorial ^{19}F is different for axial ^{19}F
- structural assignments are done by coupling of nuclei which gives rise to multiplex in the spectra. The spin – spin coupling constant J is the strength of the coupling
- a multiplex of 2I + 1lines is obtained when a spin - ½ nucleus or a set of symmetry related spin, - ½ nuclei is coupled to a nucleus of spin 1
  e.g GeH_4, 4 equivalent H atoms, Ge I= 0, GeH_4 I = 9/2.
  Lines generated = 2 x 9/2 + 1 = 10
- the integrated intensity of a signal arising from a set of symmetry related nuclei is proportional to the number of the number ofnuclei in the set
- Relative intensities of the 2N +1 lines in a multiplex that arises from coupling to N equivalent spin – ½ are given by Pascal's triangle. 3 equivalent H gives 1:3:3:1, 2 H, I = 1, 2I + 1 = 3 orientations
- NMR of compounds can be measured by varying temperature and also in the solid state.

ELETRON PARAMAGNETIC RESONANCE:

- Technique can e used to study compounds with unpaired electrons in d –block metals. It is used in identification of Fe and Cu at the active sites of metalloenzymes. S for unpaired electron is - ½
- An external magnetic field B produces a change in between m_s – ½ and + ½ states
- $\Delta E = g\mu_o B$, g is g- value, μ_o is Bohr magneton
- G – value for a free electron = 2.0023 and it is altered by spin – orbit coupling, g – value for d – metal complexes maybe highly anisotropic such that the resonance conditions depends on the angle the paramagnetic species makes with the applied field
- The hyperfine structure of a spectrum is due to the magnetic nuclei present. Coupling with spin I split EPR line into 2I + 1 lines of the same intensity.
- Hyperfine structure is due to coupling to the nucleus of the atom on which the unpaired electron is primarily located

- Superfine coupling is the coupling to ligands nuclei. It is used to measure the extent of electron delocalisation and covalence in metal complexes.

MOSSBAUER SPECTROSCOPY

- This technique is based on the resonant absorption of gamma radiation by nuclei. It exploits the fact that nuclear energies are sensitive to the electronic environment.
- Mossbauer Effect is the recoil free emission of gamma radiation by a nucleus.
- If the emitting nucleus recoils as it emits the gamma ray photon, its frequency is shifted by the Doppler effect.
- The recoil is avoided when ^{57}Fe* nuclei are pinned down into a rigid lattice so, that the reaction is highly monochromatic.
- A sample of ^{57}Fe is placed near a ^{57}Co source. The monochromatic recoil free gamma emitted by^{57}Fe* is expected to be absorbed by the ^{57}Fe nuclei.
- Resonance absorption may not occur if the electronic environment of the receiver ^{57}Fe is different from that ^{57}Fe* transmitter. The two nuclei can be brought to resonance by moving the target nucleus relative to the transmitter and relying on the Doppler shift to match the absorption frequency to the transmitted frequency.
- A Mossbauer spectrum portrays the resonant absorption peaks that occur as the velocity of the sample is changed.
- Mossbauer spectrum of a sample containing Fe is expected to consist of a single signal due to absorption of radiation at the energy required (ΔE) to excite the nucleus from the ground to the excited state.
- The difference between the ΔE of the sample and that of the metallic ^{57}Fe is known as the isomer shift, expressed in terms of the velocity(mm/s) that is required to achieve resonance by Doppler shift

- ΔE value depends on the electron density at the nucleus, though the effect is primary because of the s electrons (ψ = 0 at the nucleus)
- ΔE is sensitive to shielding effects of p and d electrons.
- Oxidation states of Fe (II), Fe (III) and Fe (IV) can be distinguished as well as ionic and covalent bonding.
- Element most suitable for Mossbauer spectroscopy is Fe
- ^{57} Fe*, I = 3/2, electronic quadrupole moment provided the environment is not isotropic, splits into 2 lines with separation ΔE_q. The splitting depends on the oxidation state and the distribution of d electron density
- Other elements suitable for technique includes ^{119}Sn, ^{129}I, ^{197}Au

ATOMIC ABSORPTION SPECTROSCOPY

- AAS is used to determine quantitatively most metallic elements using absorption characteristics.
- Principle is similar to Uv/ visible spectroscopy except that the absorbing species are free ions/atoms
- Transitions occur between electronic energy levels
- Spectra are sharply defined lines, not broad bands
- Energy of photons is the same as that absorbed by the unbound atoms/ions of the same element
- Differences in instrumentation arise from different methods used for the conversion of analyte.
- Discuss Flame atomisation and Electro thermal atomisation techniques.

REFERENCE /TEXT

Shriver and Atkins
Inorganic Chemistry 4th Edition