Common techniques for structural studies

Information sought	Phase of sample: Gas	Liquid or solution	Solid
Fingerprint[a]	IR *Microwave Mass spec. UV/vis *UPS	IR, R NMR Mass spec.[b] UV/vis	IR, R Powder X-ray diffraction Mass spec.[b] UV/vis
Groups present	IR Mass spec. NMR	IR, R Mass spec.[b] NMR	IR, R Mass spec.[b] *NMR *Mössbauer
Molecular symmetry	IR[c] *Microwave **ED	IR, R NMR	IR, R *NMR **NQR Single crystal X-ray diffraction
Bond lengths and angles	IR, R[d] *Microwave **ED	***EXAFS LCMNR	Single crystal X-ray diffraction ***Neutron diffraction
Electronic structure[e]	UV/vis *UPS ESR	UV/vis ESR *XPS	UV/vis *UPS *XPS *Mössbauer **NQR Single crystal X-ray and neutron diffraction

Common techniques for structural studies

Comparison of some physical techniques for structural studies

Technique	Nature of the Effect	Information	Interaction time	Sensitivity	Comments
X-ray diffraction	Scattering, mainly by electrons, followed by interference ($\lambda = 0.01$–1 nm)	Electron density map of crystal	10^{-18} s but averaged over vibrational motion	crystal *ca.* 10^{-3} cm^3	Location of light atoms or distinction between atoms of similar scattering factor difficult in presence of heavy atoms
Neutron diffraction	Scattering, mainly by nuclei, followed by interference ($\lambda = 0.1$ nm)	Vector internuclear distances	10^{-18} s but averaged over vibrational motion	crystal *ca.* 1 cm^3	Extensively used to locate hydrogen atoms. May give additional information due to spin $\frac{1}{2}$ on neutron leading to magnetic scattering
Electron diffraction	Diffraction (atom or molecule) mainly by nuclei, but also by electrons ($\lambda = 0.01$–0.1 nm)	Scalar distances due to random orientation	10^{-18} s but averaged over vibrational motion	100 Pa (1 Torr)	Thermal motions cause blurring of distances. Preferably only one (small) species present. Heavy atoms easy to detect
Microwave	Absorption of radiation due to dipole change during rotation ($\lambda = 0.1$–30 cm; 300–1 GHz in frequency)	Mean value of r^{-2} terms; potential function	10^{-10} s	10^{-2} Pa (10^{-4} Torr)	Mean value of r^{-2} does not occur at r_e even for harmonic motion. Dipole moment necessary. Only one component may be detected. Analysis difficult for large molecules of low symmetry
Vibrational infrared	Absorption of radiation due to dipole change during vibration ($\lambda = 10^{-1}$–10^{-4} cm)	Qualitative for large molecules	10^{-13} s	100 Pa (1 Torr)	Useful for characterization. Some structural information from number of bands, position and possibly isotope effects. All states of matter

Common techniques for structural studies

Comparison of some physical techniques for structural studies

Technique	Nature of the Effect	Information	Interaction time	Sensitivity	Comments
Vibrational Raman	Scattering of radiation with changed frequency due to polarizability change during a vibration (λ = visible usually)	Qualitative for large molecules	10^{-14} s	10^4 Pa (100 Torr) (v^4 dependent)	Useful for characterization. Some structural information from number of bands, position, depolarization ratios, and possibly isotope effects. All states of matter
Electronic	Absorption of radiation due to dipole change during an electronic transition ($\lambda = 10$–10^2 nm)	Qualitative for large molecules	10^{-15} s	1 Pa (10^{-2} Torr)	Useful for characterization. Some structural information from number of bands and position. All states of matter
Nuclear magnetic resonance	Interaction of radiation with a nuclear transition in a magnetic field ($\lambda = 10^2$–10^7 cm; 3 KHz to 300 MHz)	Number of magnetically equivalent nuclei in each environment	10^{-1}–10^{-9} s	10^3 Pa (10 Torr (^{1}H))	Applicable to solutions and gases. In conjunction with molecular weight measurements may be possible to choose one from several possible models
Mass spectrometry	Detection of fragments by charge/mass	Mass number, plus fragmentation patterns	—	10^{-9} Pa (10^{-11} Torr)	Useful for characterization of species in a vapour, complicated by reactions in spectrometer. Does not differentiate isomers directly. Important for detecting hydrogen in a molecule

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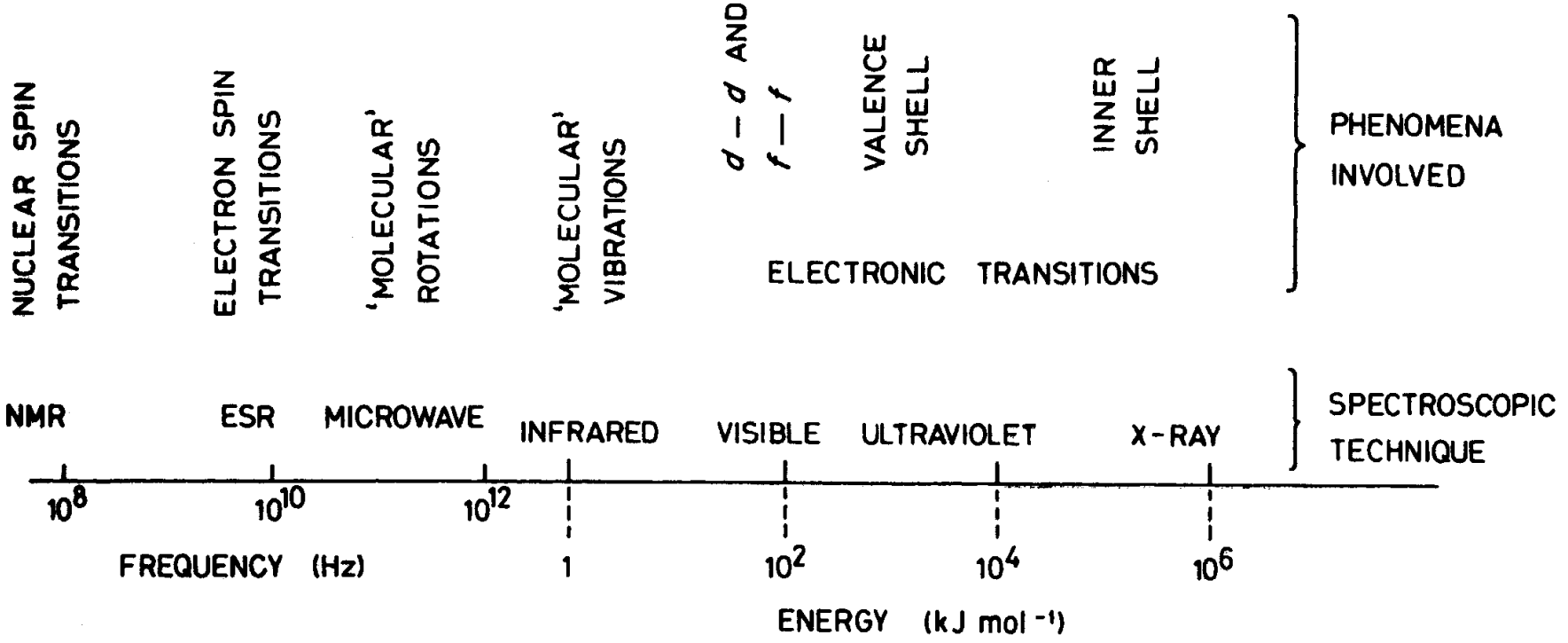
Structure determination techniques and electromagnetic radiation



Structure determination techniques and electromagnetic radiation