

Organic Spectroscopy

Second Year, Michaelmas term, 8 lectures: Dr TDW Claridge & Prof BG Davis

Lectures 1-4 highlight the importance of spectroscopic methods in the structural elucidation of organic molecules starting with an introduction to the NMR phenomenon; these four lectures will enable you to interpret ^1H and ^{13}C spectra of simple organic molecules and to identify simple organic structures from their NMR spectra.

Content: (1) Organic absorption spectroscopy, nuclear spin and resonance, chemical shifts; (2) factors that influence ^1H chemical shifts, spin-spin coupling, coupling patterns and resonance multiplicities, coupling to chemically equivalent spins, weak and strong coupling; (3) chemical and magnetic equivalence, ^1H spin couplings and chemical structure—geminal, vicinal and long-range couplings, chirality and NMR, chiral solvating agents; (4) ^{13}C NMR spectroscopy, NMR instrumentation, Fourier transform NMR, interpretation.

Lectures 5-7 will introduce those aspects of UV (0.5 lect.), IR (1.5 lect.) and MS techniques (1 lect.) that you will need in order to suggest candidate structures given raw experimental data in each case. Coverage of the underlying theory and instrumentation associated with each method will be kept to a bare minimum since these aspects are covered elsewhere. In modern research laboratories, NMR spectroscopy and MS are usually the first choice method for gaining structural information, with IR information routinely acting in a supporting capacity and UV spectra only being required in specialised circumstances (e.g. polymers, porphyrins). Lecture 8 will show how IR and MS data can be used in combination with NMR spectra to assign structures in a selection of real examples.

Previous examination questions for practice

Part IA: 2004 (Q7), 2005 (Q2), 2006 (Q1), 2007 (Q8), 2008 (Q9), 2009 (Q1)

Bibliography

- Introduction to Organic Spectroscopy: LM Harwood & TDW Claridge

Basic text for this course

- Spectrometric Identification of Organic Compounds (7th ed): RM Silverstein, FX. Webster & DJ. Kiemle

Comprehensive description of IR, MS and NMR with many problems: highly recommended

- Spectroscopic Methods in Organic Chemistry (5th Edn): DH Williams & I Fleming

Broad coverage of UV, IR, NMR and MS

- Organic Structures from Spectra: LD Field, S Sternhell & JR Kalman

Workbook of ^1H and ^{13}C NMR spectra of increasing complexity

- Structure Elucidation by NMR in Organic Chemistry: E Breitmaier

Workbook of example NMR spectra

- Experimental Organic Chemistry (2nd Edition): L M Harwood, C J Moody & J M Percy

Chapter 5 and Appendix 3 provide useful background and reference tables

InfraRed (IR), UltraViolet (UV) Spectroscopy and Mass Spectrometry (MS)

V-VII

First lectures are aimed at providing a basic introduction to the use of IR and UV in Organic Chemistry. This should enable you to interpret (and even predict key fundamental features of) IR and UV spectra of simple organic molecules as a supporting method to identifying their structures.

This will be followed by an introduction to the methods behind Mass Spectrometry and the interpretation of spectra based in part upon insight into chemical processes in the gas phase under the conditions of MS. Again this provides another invaluable method in structure elucidation; MS is probably now the second most valuable technique after NMR to the small molecule organic chemist and arguably the most valuable to the larger molecule organic chemist or biological chemist.

Finally, we will work through some illustrative examples for you to see the process of associating a given set of spectroscopic and spectrometric data with a molecular structure. The generation of a mutually consistent set of convincing data of this kind (NMR, MS, IR, UV, optical rotation, melting point....) is often referred to as compound characterization.

Content

IR

Organic Spectroscopy of Spectrometry

Re-cap of Basics of Absorption Spectroscopy

Stretching and Bending; Hooke's Law

Sample Preparation

Spectral Range; Hydrocarbons, Alcohols, Carbonyls; Tables

Structural Insight Through Changes (Playing with k / bond order)

Examples

UV

Electronic Transitions

Beer-Lambert Law

Sample Preparation

Common Transitions and Functional Groups

Conjugation

Woodward-Fieser Rules

Examples

MS

Fundamentals

Traditional Methods of Ionization: EI, CI,

Fragmentation of Ions; Charge Location, Bond Strength, Stability

Fragmentation Types: Heteroatom cleavage, α -cleavage, Rearrangements

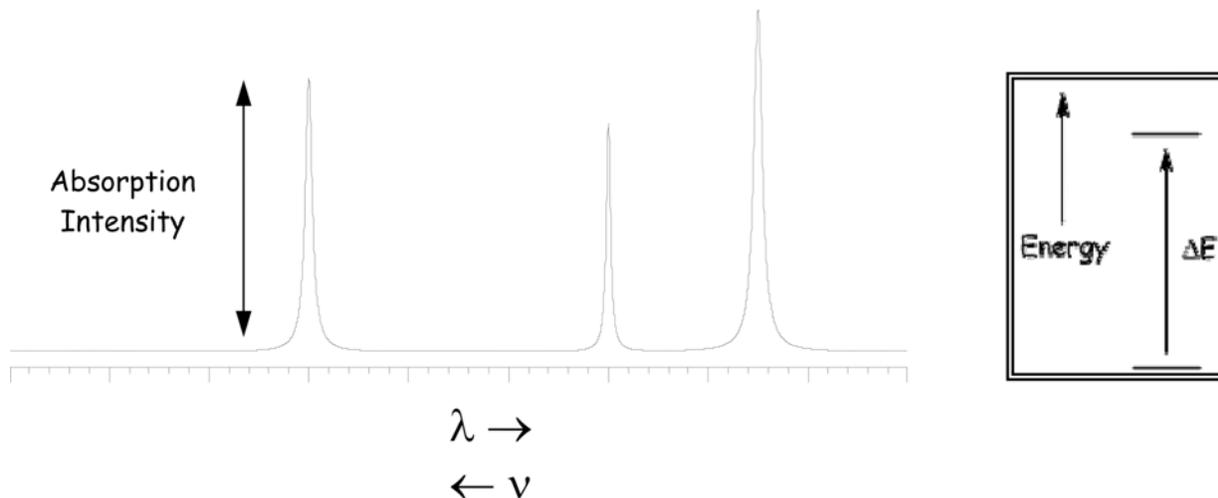
Examples: Hydrocarbons, Alcohols, Ethers, Halogens, Carbonyls

Other Ionization Methods: ES, FD, FAB/SIMS, LDI/MALDI

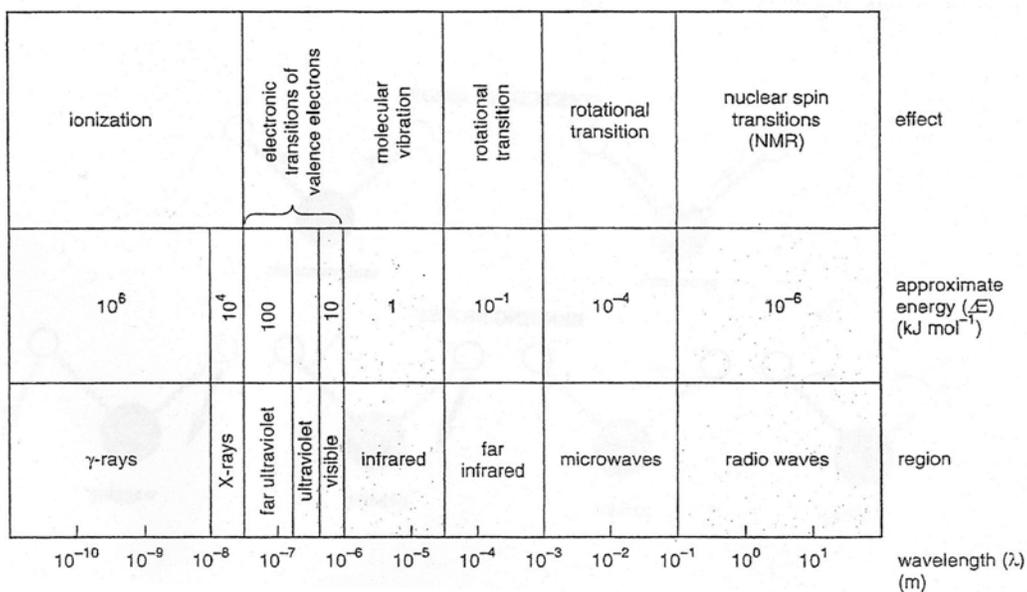
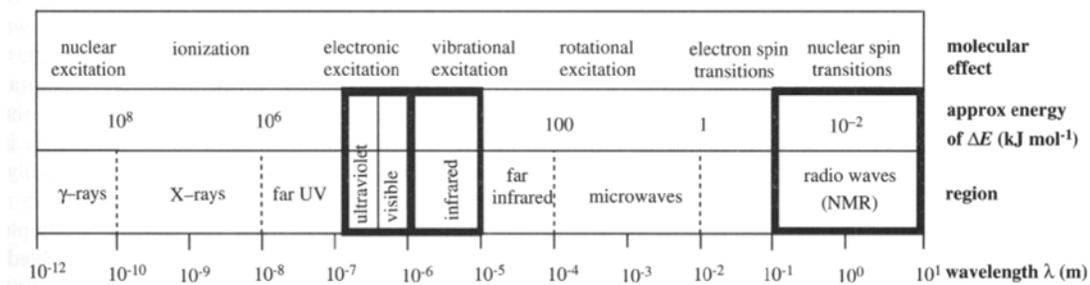
Accurate and High Resolution MS

$c = \nu\lambda$ where ν = frequency (Hz); λ = wavelength (m), c = speed of light ($3 \times 10^8 \text{ m s}^{-1}$)
 $\Delta E = h\nu$ where E = energy (J), h = Planck's constant ($6.626 \times 10^{-34} \text{ J s}$)
 $\Delta E = 1.19 \times 10^5 / \lambda \text{ kJ mol}^{-1}$ (wavelength in nm)

Absorption spectroscopy

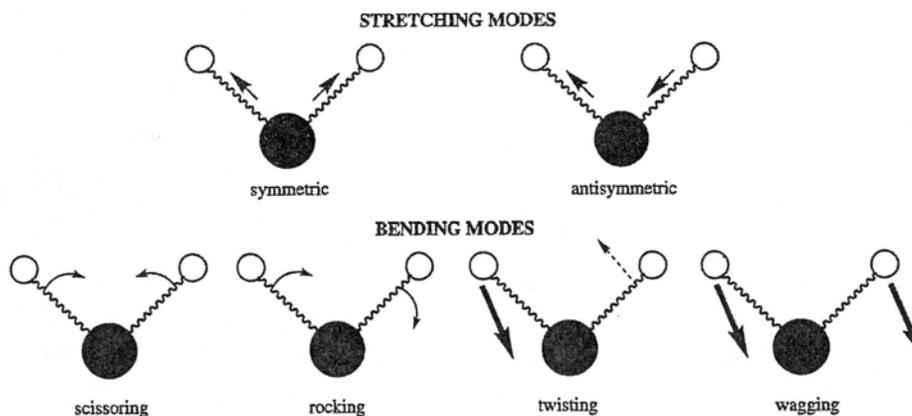


Electromagnetic spectrum



Stretching and Bending

- Molecular vibrations as a source of bonding information
- Dipole moment change needed



- Hooke's Law for simple harmonic motion:

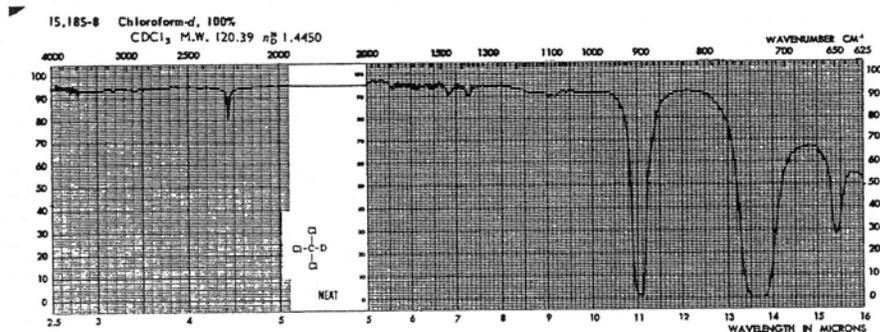
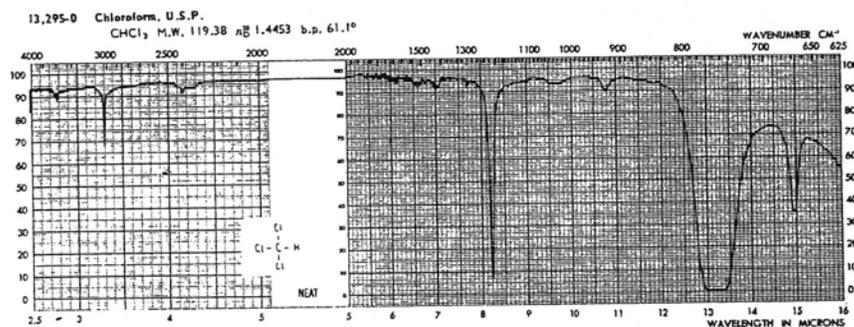
with ν = frequency of oscillation

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\bar{m}}}$$

k = force constant of bond

$$\bar{m} = \text{reduced mass} = \frac{m \cdot M}{m + M}$$

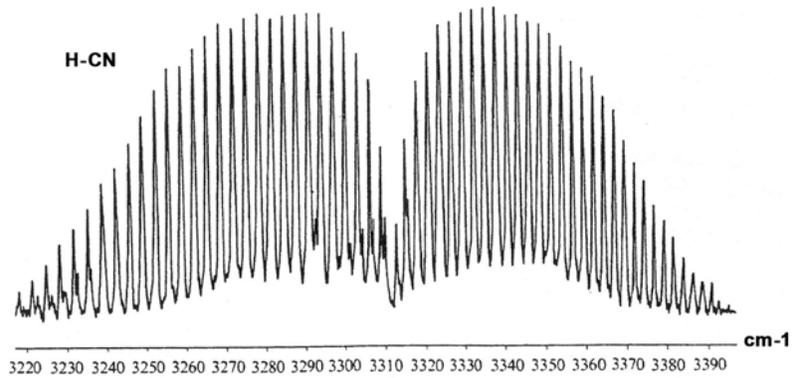
- Importance of m illustrated by comparison of IR data for CHCl_3 and CDCl_3



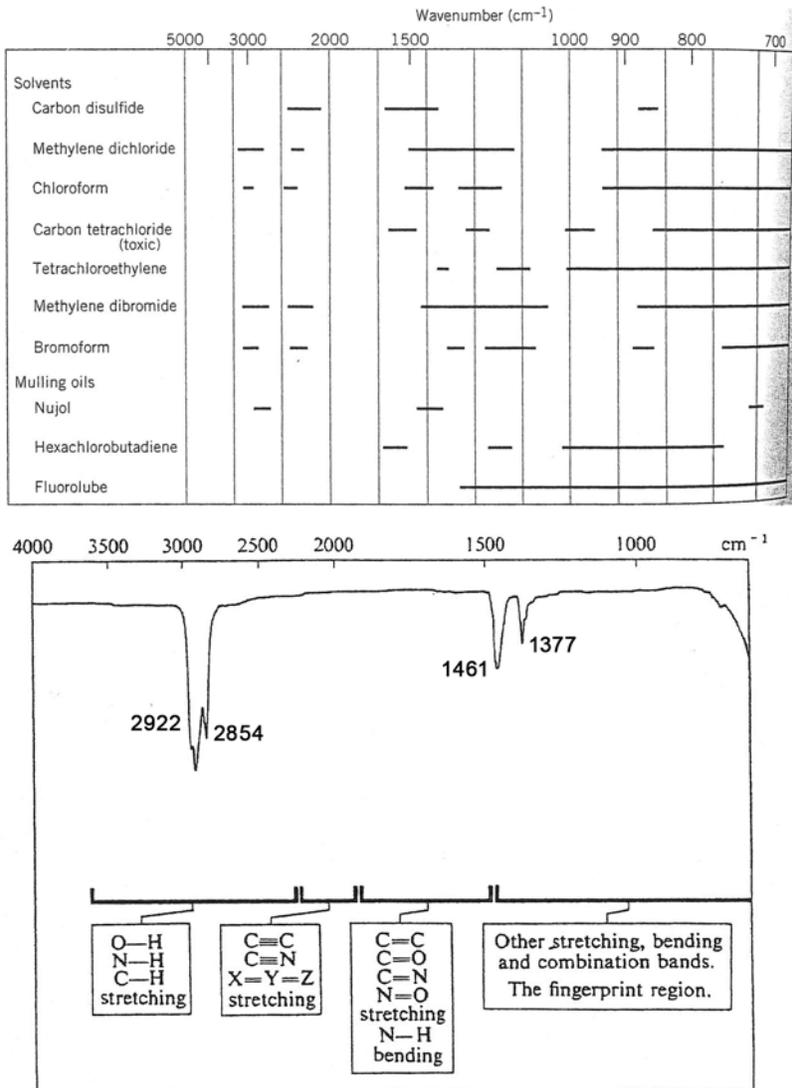
- Measured and reported now only in wavenumbers: cm^{-1}
- Spectra read 'right to left' as a hangover from wavelength origins

Sample Preparation

- Gas phase show rotational fine structure

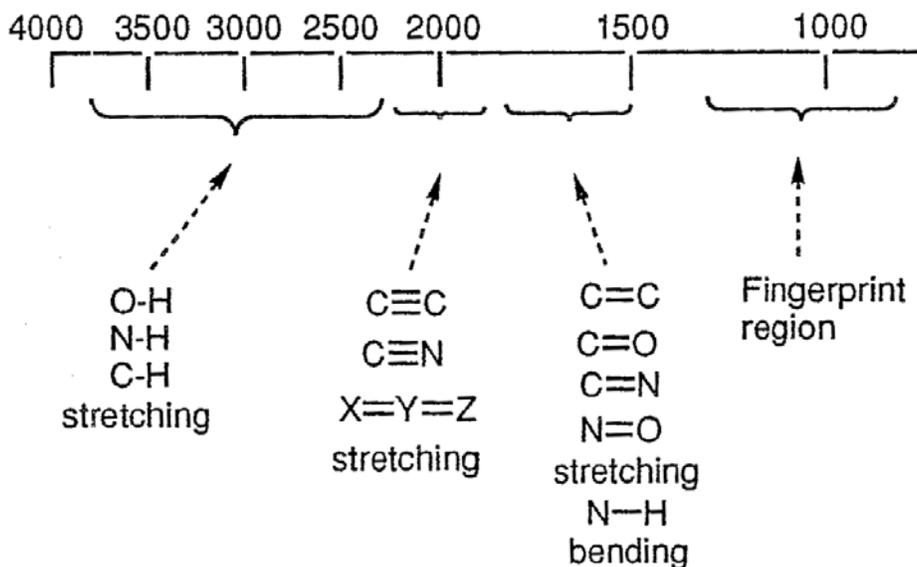


- Solution, Solid or Mull - IR transparency of sample 'surround' key



Spectral Regions

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$



Hydrocarbons

C-C	1500
C=C	1650
C≡C	2100
C-H	3000

Alcohols

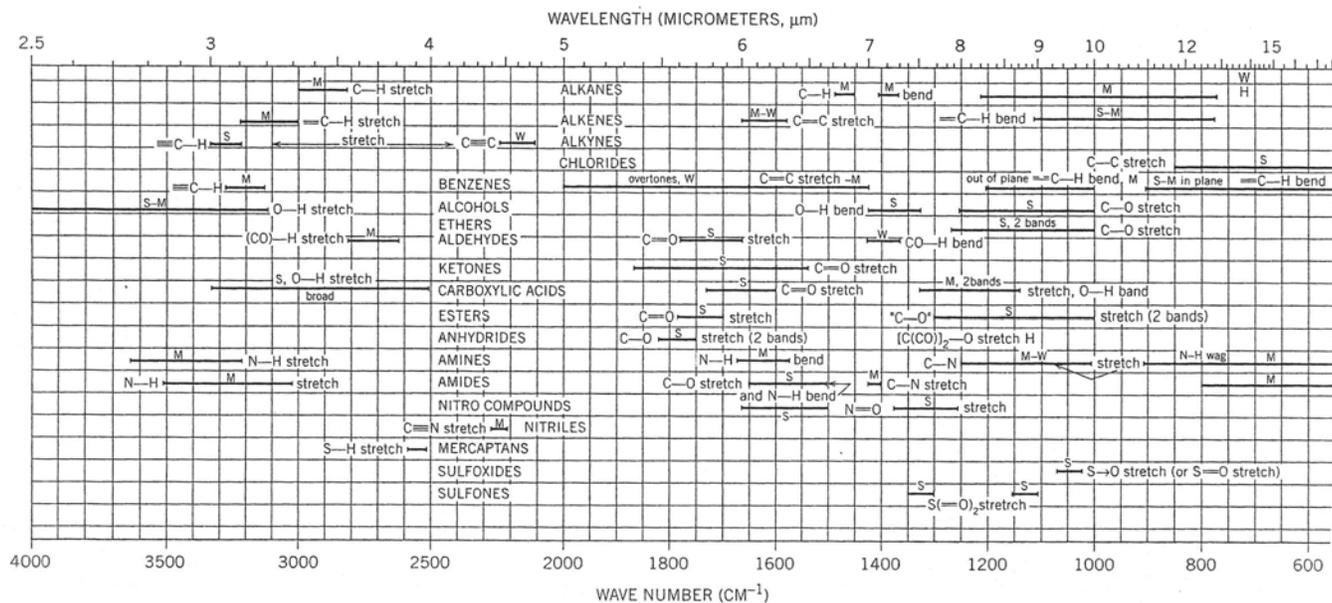
O-H	3200-3600 (broad)
C-O	1100

Carbonyl

For RC(O)X , the more electronegative X, the higher the absorption frequency (thus, acid chlorides, anhydrides and esters absorb at a higher frequency than ketones). Conversely, the more electron releasing by resonance is X, the lower the frequency (this is because the C=O is weakened, i.e. has more single bond character and therefore is more near the "normal" C-O resonance at 1100):

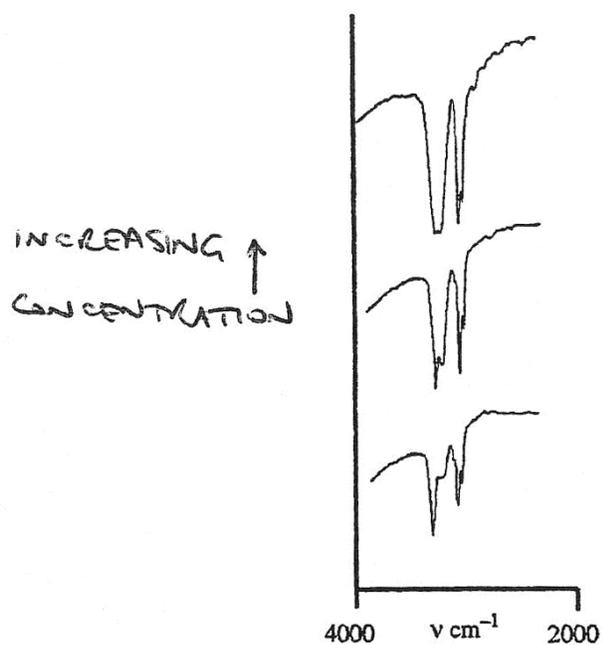
RC(O)O(O)R	RC(O)Cl	$\text{RC(O)OR}'$	RCHO	RC(O)R	$\text{RC(O)NR}'_2$
1850	1800	1750	1740	1720	1690

ν (cm ⁻¹)	Functionality	Comment
4000–2500 region		
3600	O–H	Free non H–bonded is sharp
3500–3000	O–H	H–bonded, broad
	N–H	Usually broad, amine or amide
3300	≡C–H	Sharp and strong
3100–2700	C–H	Variable, usually strong for sp ³ , weak for sp ² hybridized C–H
3500–2500	CO ₂ H	Broad, H–bonded carboxylic acid OH
2500–1900 region		
2350	CO ₂	Path length imbalance not sample
2200	C≡C, C≡N	Usually weak. If a terminal alkyne, shows a peak at 3300 cm ⁻¹
2200–1900	X=Y=Z	Strong, allene, isocyanate, azide, diazo
1900–1500 region		
1850–1650	C=O	Strong α , β -unsaturation 1650–1690 cm ⁻¹ , small ring ketones (≤ 5 membered) and α -electron withdrawing groups (eg halogen) 1750–1850 cm ⁻¹
1650–1500	C=C, C=N	Usually weak. Stronger if conjugated. Absent for symmetrical alkenes
1600	C=C (arom)	Variable. Usually associated with peaks in the fingerprint region.
1550	NO ₂	Strong
1500–600 (Fingerprint) region		
1350	NO ₂	Strong
	–SO ₂ –	Strong, also a peak at 1150 cm ⁻¹
1300–250	P=O	Strong
1300–1000	C–O	Strong, alcohol, ether, ester.
1150	–SO ₂ –	Strong, see above
850–700	C–H (arom)	Indicates substitution pattern (p. 33)
800–700	C–Cl	Strong, obscured by CHCl ₃



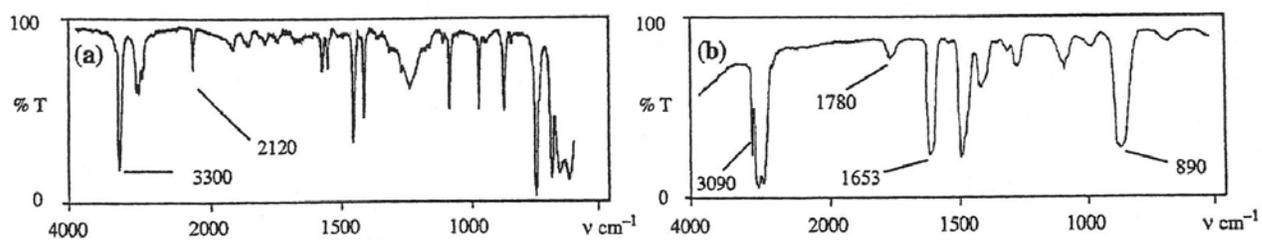
Structural Insight Through Changes (Playing with k / bond order)

- Conjugation to $C=C$ lowers $C=O$ frequency by $15-40\text{cm}^{-1}$
- Ring strain raises frequency (smaller ring, higher frequency): 6-rings 'normal'
- Hydrogen bonding to the $C=O$ lowers frequency by about 50cm^{-1}
- Hydrogen bonding of NH , OH to 'map' interactions

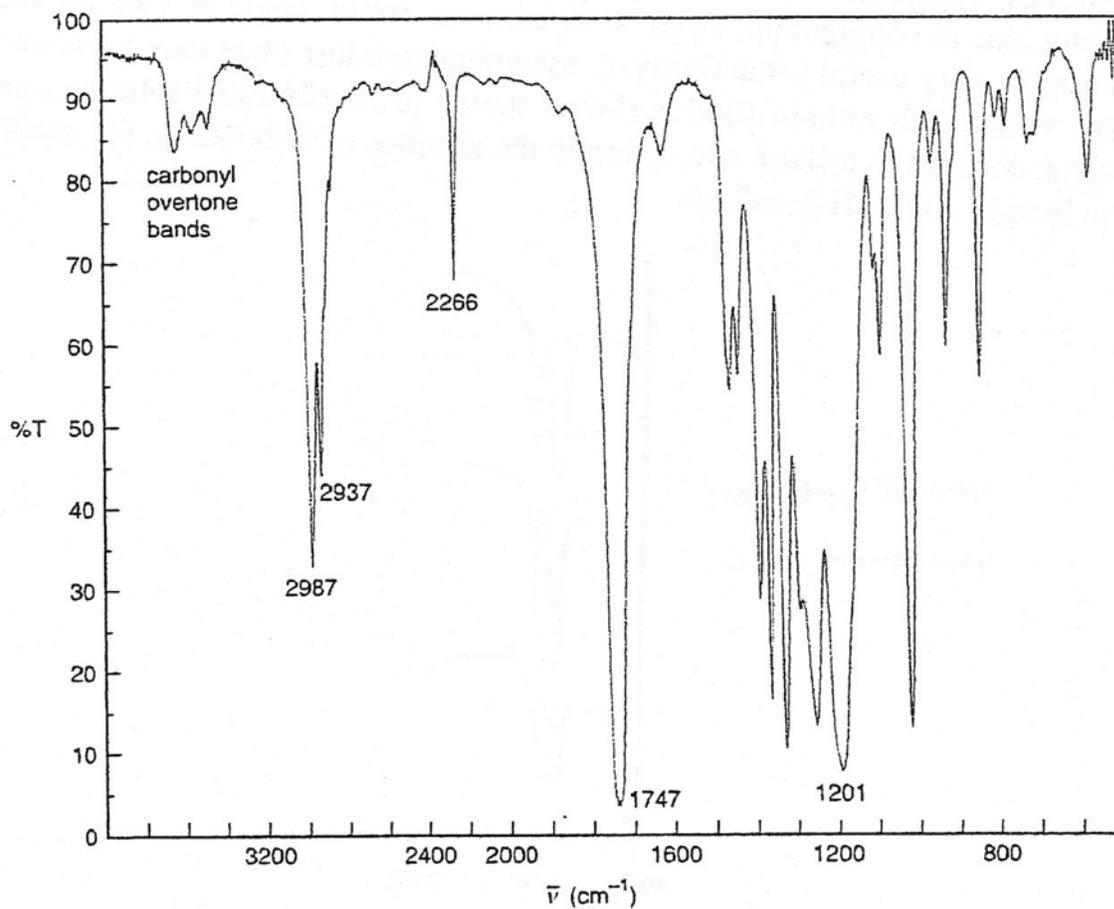


NOTE: Overtones can appear (at twice the frequency of the fundamental)

Example 1: (a) $\text{PhC}\equiv\text{CH}$; (b) $\text{Me}_2\text{C}=\text{CHBu}$



Example 2: $\text{EtO}_2\text{CCH}_2\text{CN}$



Example 3: Assign the spectra

