

H3 CHEMISTRY SPECTROSCOPY

TABLE OF CONTENTS

GENERAL IDEAS & FORMULA LIST	1
1. UV/VIS SPECTROSCOPY	3
2. IR SPECTROSCOPY	5
IR REFERENCE VALUES	9
3. NMR SPECTROSCOPY	10
NMR REFERENCE VALUES	20

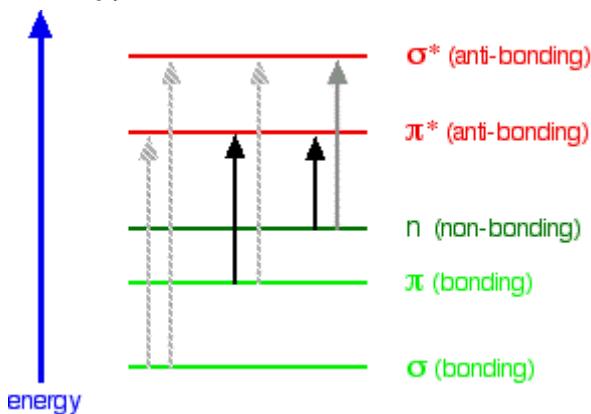
General Ideas & Formula List

Formulae	
Photon Energy	$E = hf = \frac{hc}{\lambda} = h\nu$ <ul style="list-style-type: none"> • E: J • f: Hz • ν: Hz/cm • λ: m • h: $6.63 \times 10^{-34} \text{ Js}$
Transmittance	$T = \frac{I}{I_0} \times 100\%$ <ul style="list-style-type: none"> • I: the intensity of emerging radiation • I₀: the intensity of incident radiation
Absorbance	$A = -\lg\left(\frac{I}{I_0}\right) = \lg\left(\frac{I_0}{I}\right) = \epsilon cl$ <ul style="list-style-type: none"> • ε: the molar extinction coefficient, or molar absorptivity ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) • C: [compound] (in mol dm^{-3}) • l: path length of the absorbing solution (in cm^3) <ul style="list-style-type: none"> ○ Usually 1.0 cm
Chemical shift value	$\delta_x = \frac{(f_x - f_{TMS})}{F}$ <ul style="list-style-type: none"> • δ_x: chemical shift of proton x • f_x: frequency of absorption of proton x • f_{TMS}: frequency of absorption of the proton in TMS • F: frequency of irradiation in MHz
	$\nu = \frac{\mu B_0}{2\pi}$ <ul style="list-style-type: none"> • In practice, ν is kept constant and B is varied

1. UV/Vis Spectroscopy

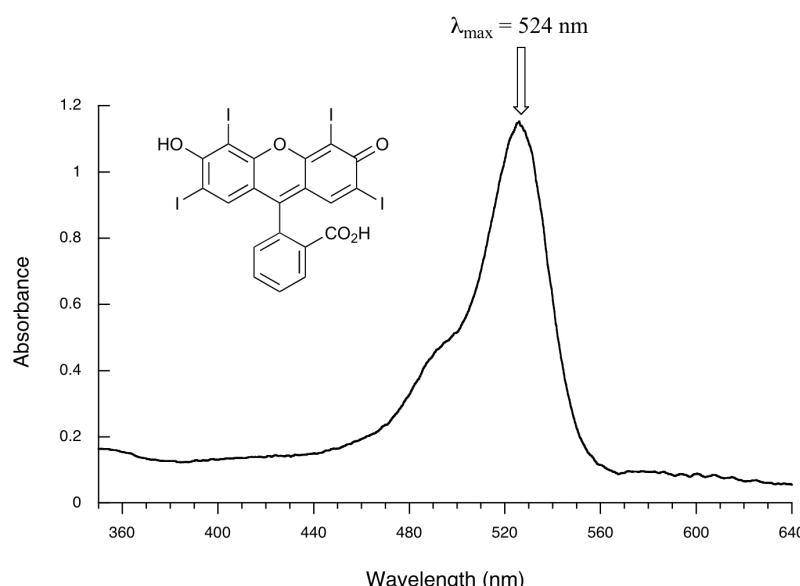
- ❖ A system containing the electrons responsible for the absorption of radiation is called a chromophore. This system is either an isolated double bond or a conjugated system of double bonds.

Principles of UV/Vis Spectroscopy



- UV spectroscopy makes use of energy from ultraviolet light. Photons are absorbed by the analyte to promote an electron from π to π^* and n to π^* (and n to σ^*) molecular orbital.
- The difference in the energy gap between two orbitals matches the wavelength of the UV light and shows as a signal in the UV spectrum. **OR**
- When a photon of UV light is absorbed by a molecule, an electron gains the photon's energy and is promoted to a higher energy orbital.
- The lowest energy electronic transition is between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).
- Absorption in the UV region corresponds to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. [2]

UV/Vis Spectrum



- Beer-Lambert Law: $A = \epsilon c l$

- Each peak represents a different electronic transition.
- Conjugation of π bonds reduces the energy gap between the HOMO and LUMO (or $\pi \rightarrow \pi^*$ orbitals), and hence shifts the absorption towards the longer wavelength.
- The incorporation of an atom with a lone pair of electrons can cause a major shift of absorbance to longer wavelengths since the $n \rightarrow \pi^*$ energy gap is smaller than the $\pi \rightarrow \pi^*$ gap.
 - The wavelength of absorption will be higher. Overlap of the phenolic hydroxyl oxygen lone pair and the phenyl π system results in more extended conjugation which lowers the HOMO \rightarrow LUMO energy gap.

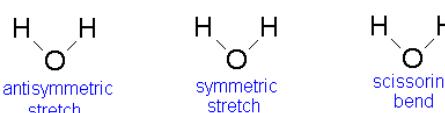
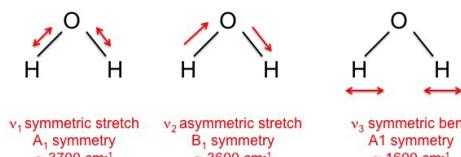
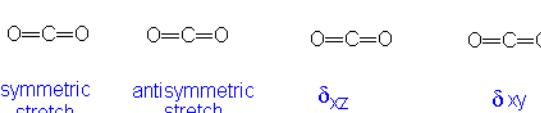
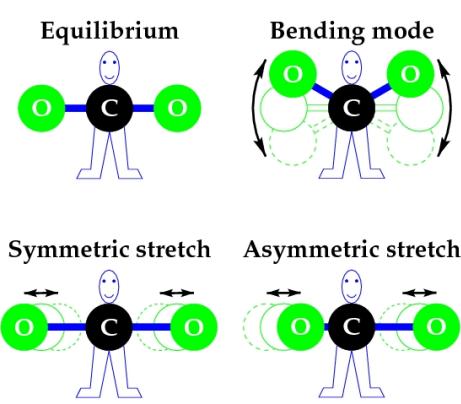
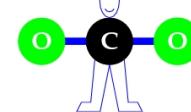
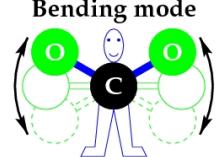
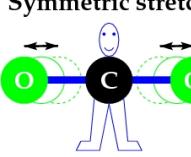
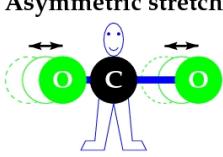
Ultraviolet Absorptions of some Conjugated Molecules

Name	Structure	λ_{\max} (nm)
2-methylbuta-1,3-diene		220
cyclohexa-1,3-diene		256

- P-orbitals are held more rigidly in the ring structure \rightarrow greater conjugation effect \rightarrow lower E

2. IR Spectroscopy

Degree of freedom of a molecule with n-atoms	3n
Translation and rotations of the molecule itself	6
Degrees of vibrational freedom for a non-linear molecule	3n - 6
Degrees of vibrational freedom for a linear molecule	3n - 5

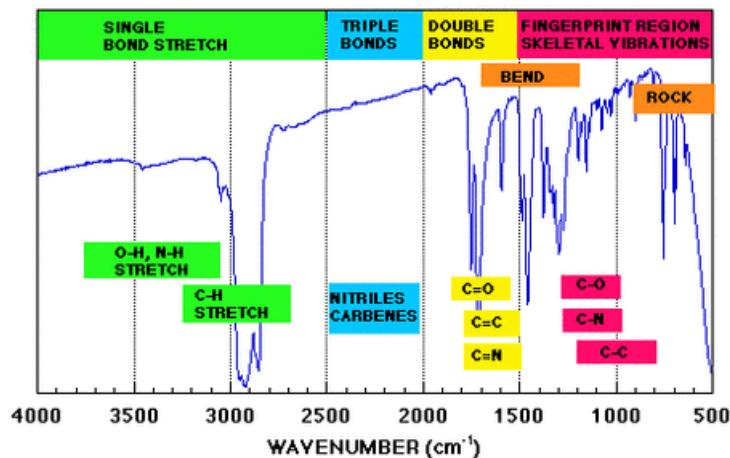
Molecule	H ₂ O	CO ₂
Degrees of freedom	3(3) = 9	3(3) = 9
Degrees of vibrational freedom	9 - 6 = 3	9 - 5 = 4
Molecular vibrational modes	 <p>Three fundamental modes of vibration for water</p>  <p> v_1 symmetric stretch A_1 symmetry $\sim 3700 \text{ cm}^{-1}$ </p> <p> v_2 asymmetric stretch B_1 symmetry $\sim 3600 \text{ cm}^{-1}$ </p> <p> v_3 symmetric bend A_1 symmetry $\sim 1600 \text{ cm}^{-1}$ </p>	 <p> $O=C=O$ symmetric stretch inactive no dipole change </p> <p> $O=C=O$ antisymmetric stretch active </p> <p> $O=C=O$ δ_{xz} $O=C=O$ δ_{xy} degenerate same energy one band </p>  <p> Equilibrium  </p> <p> Bending mode  </p> <p> Symmetric stretch  </p> <p> Asymmetric stretch  </p>

Principles of IR Spectroscopy

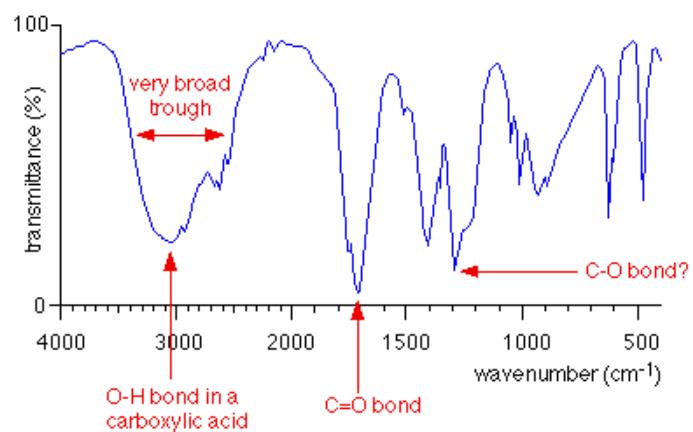
- The absorption of IR radiation is associated with vibrational energy levels of bonds in a molecule.
- For a molecule to absorb IR, the vibrations within a molecule must cause a net change in the dipole moment of the molecule.
- If the frequency of the radiation matches the energy gap between vibrational energy levels of the molecule then radiation will be absorbed.

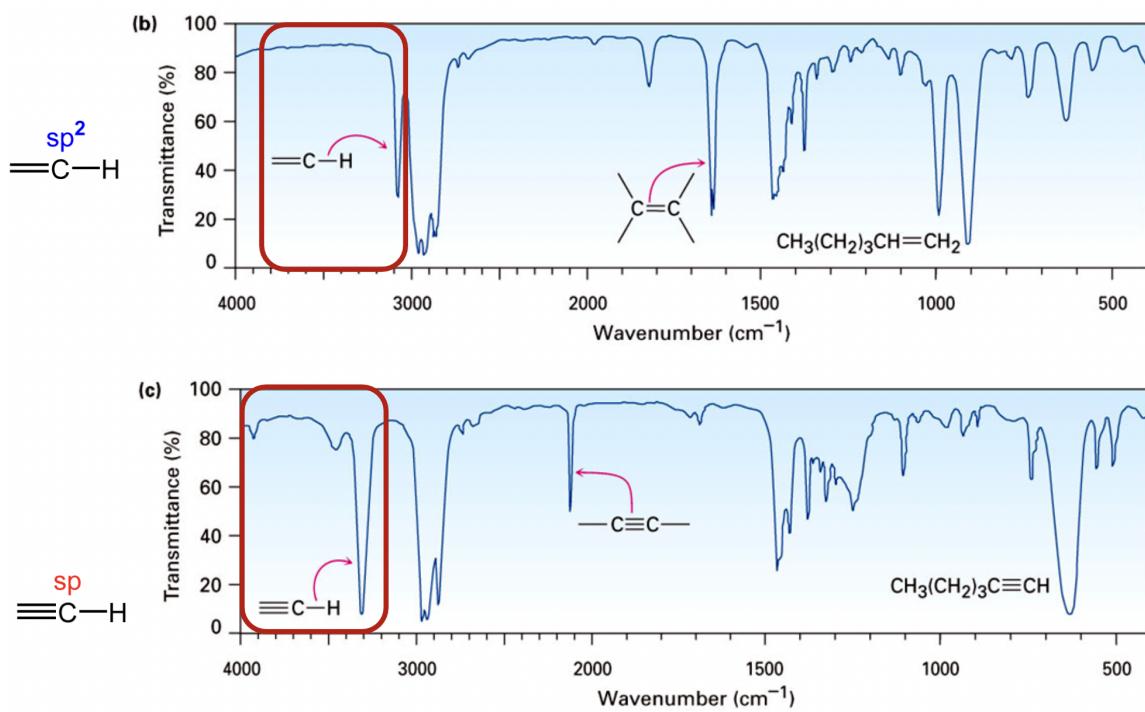
- The energy of other frequencies will be transmitted. Using information on the absorption, IR spectroscopy can be used to identify specific functional groups present in a molecule.
- IR spectroscopy makes use of energy from infrared waves which are absorbed by the analyte as the molecule exhibits various modes of vibration such as stretching and bending which result in a change in dipole moment.

IR Spectrum



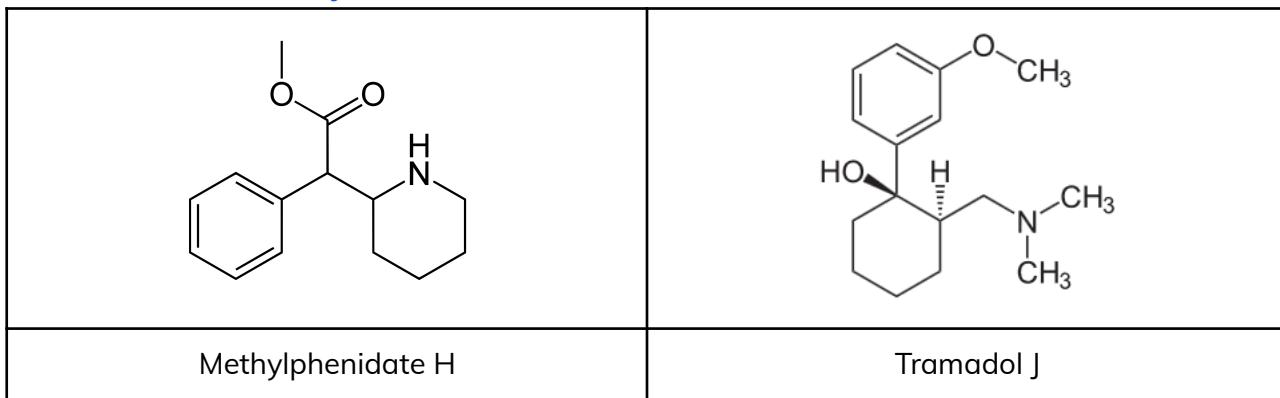
infra-red spectrum of ethanoic acid, CH_3COOH





Questions:

1. Describe the differences between the IR spectra of CO and SO₂.
 - o Carbon monoxide being a diatomic molecule shows 1 absorption signal due to the C≡O stretch.
 - o Sulfur dioxide being a bent triatomic molecule shows 3 absorption signals due to symmetrical stretch, asymmetric stretch and bend mode.
2. Predict the no. of absorption in the IR spectrum of O=C=S and describe the vibrations that give rise to these absorptions.
 - o Carbon oxysulfide is predicted to show 3 absorption signals due to symmetrical stretch, asymmetric stretch and degenerate bends. Despite being a linear molecule, symmetrical stretch will result in a change in dipole moment for O=C=S.
3. Describe the differences in IR Spectra of these 2 molecules.
 - o Presence of a sharp signal at wavenumber 1710-1750 cm⁻¹ for H due to ester C=O stretch but not in J.
 - o Presence of a weak signal at wavenumber 3300-3500 cm⁻¹ for H due to amine N-H stretch but not in J.
 - o Presence of a broad signal at wavenumber 3200-3600 cm⁻¹ due to alcohol O-H stretch in J but not in H



IR Reference Values

Hydro-carbon	Vibration	Wavenumber (cm ⁻¹)	Intensity	
Alkane				
C-H	Stretching	2850 - 3000	Medium	
CH ₂	Bending	1450-1475	Medium	
CH ₃	Bending	1375 and 1450	Weak to medium	
C-C	(Not useful for interpretation - too many bands)			
Alkene				
C-H	Stretching	3000 - 3100	Weak to medium	
Bond order = 2 → C=C	Stretching	1600 - 1680	Weak to medium	
Alkyne				
C-H	Stretching	3300	Medium to strong	
Bond order = 3 → C≡C	Stretching	2100-2250	Weak	
Arene				
C-H	Stretching	3030	Weak to medium	
Bond order = 1.5 → C=C	Stretching	1450-1600	Medium	
	C-H	Bending	690-900	Strong

Correlation Tables

- IR stretching frequencies of selected functional groups:

	Stretching	
Wavenumber	Frequency (cm ⁻¹)	Intensity
O-H	3200-3650	weak to strong
N-H	3100-3550	medium
C-H	2700-3300	weak to medium
C=C	1600-1680	weak to medium
C=O	1630-1820	strong
C-O	1000-1250	strong
C-N	1000-1250	medium
C=N	1640-1690	medium to strong
C≡N	2240-2260	medium to strong

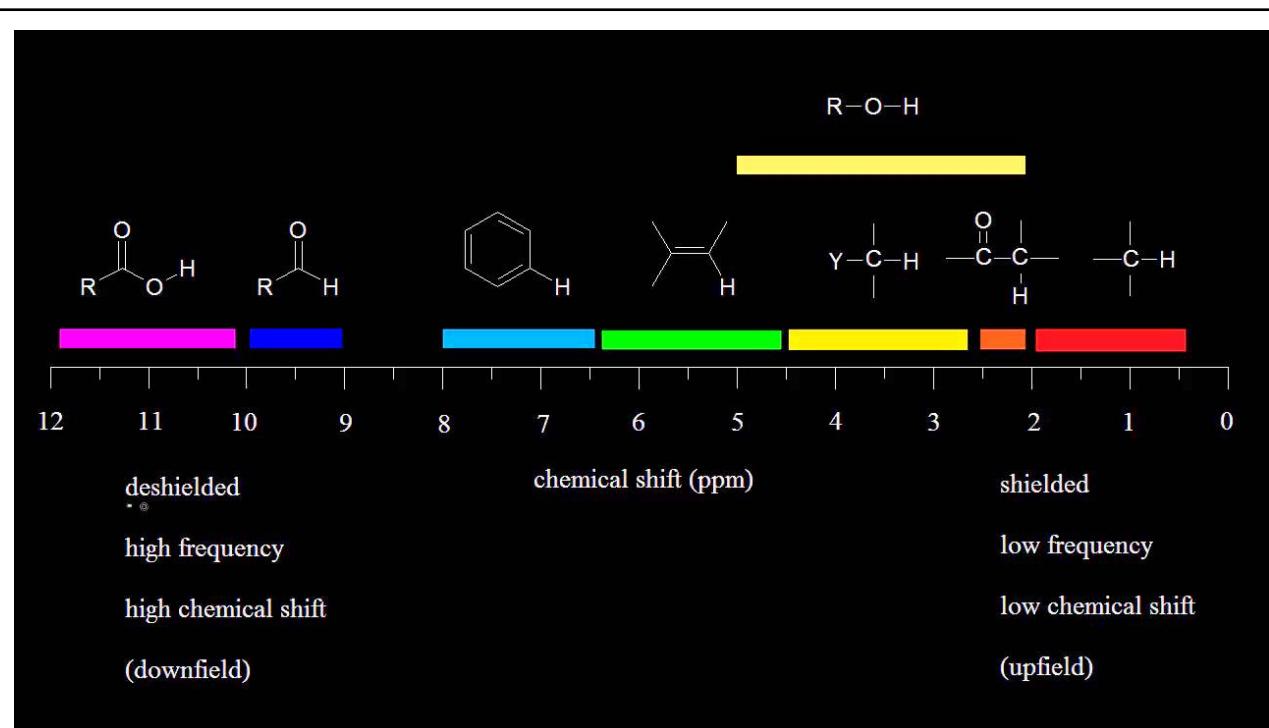
- Normally aldehyde C=O absorbs at relatively higher wavenumber than ketone C=O, but usually cannot be differentiated easily

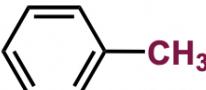
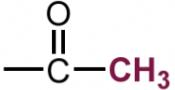
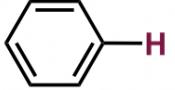
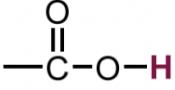
3. NMR Spectroscopy

Principles of NMR Spectroscopy

- NMR spectroscopy relies on subjecting the analyte molecule to the influence of an external magnetic field which creates two quantum states in particular nuclei. The nuclei will be also subjected to radiofrequency set in sweeping mode and the frequency that matches the energy gap of the two quantum states will be absorbed thereby promoting the electron up to a higher energy level. The relaxation of the electron will be detected as a signal in the spectrum. The structure of the molecule will be deduced by examining the splitting pattern of the signal.
- For example, if a particular proton has a neighbouring methyl group only, then the signal will show a splitting pattern that resembles a quartet.
- In addition, certain functional groups such as alkene, benzene and electronegative element can cause the signal to be downshifted. For example, an aromatic proton is more downshifted than protons in a methyl group. The integral ratio obtained can also inform the relative ratio of H atoms at each signal in the spectrum.
- Finally, certain protons for instance hydroxyl protons can be ascertained by running the analysis in deuterated solvent and noting the loss of signal by comparing it with the spectrum obtained with non-deuterated solvent. [5]
- [NMR Spectroscopy is based upon the spin of nuclei in an external magnetic field.](#)
- [In the absence of a magnetic field, the nuclear spins are oriented randomly. Once a strong magnetic field is applied, they reorient their spins, i.e. aligned with the field or against the field.](#)
- [Orientation parallel to the alignment of the applied force is lower in energy.](#)
- [When nuclei are radiated with radio waves, the lower energy nuclei flip to high state and nuclei are said to be in resonance.](#)
- [Nuclei in different chemical environment will have different energy gap between the two spin states and hence they will absorb the radiation at different frequencies.](#)

Equivalent Protons	Non-Equivalent Protons
<ul style="list-style-type: none">• Same chemical environment• Absorb similar amount of energy at resonance• Produce same signal in an NMR spectrum	<ul style="list-style-type: none">• Different chemical environment• Absorb different amount of energy at resonance• Produce different signals in an NMR spectrum
<ul style="list-style-type: none">• Draw electrons away from the proton (electronegative atoms, alkenes, benzenes) ⇒ the proton is less shielded from the external magnetic field<ul style="list-style-type: none">◦ More deshielded protons ⇒ higher frequency	



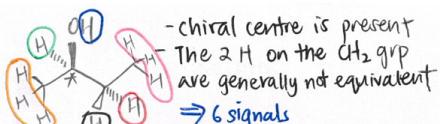
Functional Group		Chemical Shift
$\text{R}-\text{CH}_3$	Alkyl	0.8 – 1.2
$\text{C}=\text{C}-\text{CH}_3$	Allylic	1.6
	Benzyllic	2.3
	Carbonyl	2.2
$-\text{N}-\text{CH}_3$	Amine	2.3
$-\text{O}-\text{CH}_3$	Alkoxy	3.3
$\text{Cl}-\text{CH}_3$	Alkyl halide	3.6
$\text{C}=\text{C}-\text{H}$	Vinyl	4.5 – 6.0
	Benzene	6.0 – 9.0
$\text{R}-\text{O}-\text{H}$	Hydroxyl	0.5 – 4.5 (broad)
	Carboxyl	9.0 – 15.0

No. of equiv. adjacent protons (n)	No. of peaks due to splitting (n+1)	Splitting pattern	Intensity ratio	E.g.
0	1	Singlet (s)	1	No adj proton
1	2	Doublet (d)	1 : 1	Adj -CH
2	3	Triplet (t)	1 : 2 : 1	Adj -CH ₂
3	4	Quartet (q)	1 : 3 : 3 : 1	Adj -CH ₃
4	5	Quintet (qt)	1 : 4 : 6 : 4 : 1	2 adj -CH ₂
6	7	Septet	1 : 6 : 15 : 20 : 15 : 6 : 1	2 adj -CH ₃ 3 adj -CH ₂
-	Multiple	Multiplet (m)	-	Aromatic protons in benzene ring At least 2 groups of non-equiv adj protons (e.g. -CH ₂ and -CH ₃) Note: due to small diff, may overlap and appear as a singlet

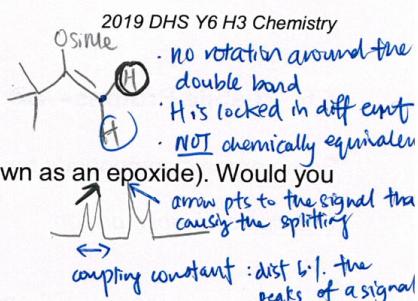
No. of signals	No. of non-equivalent protons
Relative peak area	Relative no. of equivalent protons (H on adjacent C)
Chemical shift values	Chemical environment of each type of proton
Splitting pattern	No. of adjacent protons + 1

TMS	<ul style="list-style-type: none"> TMS is used as an internal reference. <ul style="list-style-type: none"> Non-toxic, inert, cheap and volatile (can be vapourised to get back pure sample) It shows a sharp singlet assigned $\delta=0$. <ul style="list-style-type: none"> Gives strong sharp reference signal at a lower frequency than most ¹H absorptions, so its peak does not interfere with the other peaks. The chemical shifts of protons are calculated using the difference between proton absorption frequency and that of TMS, divided by the irradiating frequency. $\delta_x = \frac{(f_x - f_{TMS})}{F}$
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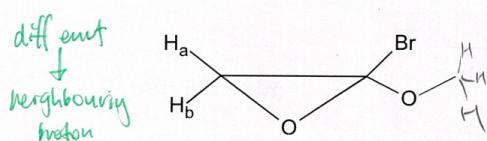
Deuterated Solvent	<ul style="list-style-type: none"> Deuterated solvent is used to dissolve the sample. Since the deuterium nuclei does not absorb in the same frequency range as ^1H nuclei, the solvent does not complicate the NMR spectra.
D₂O	<ul style="list-style-type: none"> D₂O allows identification of labile protons. Rapid exchange with deuterium occurs, removing absorption peaks of labile protons from the NMR spectra.
Non-visible NH and OH chemical shifts	<ul style="list-style-type: none"> These protons are labile and undergo rapid exchange with D₂O. The deuterium nucleus does not absorb in the same frequency as ^1H, hence these chemical shifts are not visible in the spectrum.



NMR Spectra of Cyclic Compounds



Consider the two protons labelled in the compound below (known as an epoxide). Would you expect them to be chemically equivalent? Explain.



How would you expect the ^1H NMR spectrum to look like?

- 2 doublets
- 1 singlet (CH_3)

E.g. 6 Explain how ^1H NMR spectroscopy would allow the *E* and *Z* isomers of the compound below to be distinguished.



The *E* isomers will show 2 signals because there are 2 different environments.

Both CH_2 protons are in the same environments.

The *Z* isomers will show 3 signals because there are 3 different environments.

One of the CH_2 protons is on the same phase to both Br atoms while the other CH_2 protons are on the opposite phase/trans.

5.6 Labile Protons—Deuterium Exchange

Some organic compounds have **labile protons** (also known as exchange protons).

Examples of labile protons:

Alcohols, Phenols & Carboxylic Acids	Amines and Amides
$\text{R}-\text{O}-\text{H}$ $\text{R}-\text{C}(=\text{O})-\text{O}-\text{H}$	$\text{R}-\text{N}-\text{H}$

These labile protons readily undergo rapid exchange with neighbouring molecules under normal conditions.



- * **No coupling effect** could be observed *original splitting pattern is gone*
 - * **No splitting pattern** of signals due to them or their adjacent protons
- ⇒ Labile protons appears as a broad singlet in the NMR spectrum

Deuterium oxide (D_2O where D is ${}^2\text{H}$ isotope) is used to **identify labile protons**.

resonate at a diff freq. range

After addition of deuterium oxide, D_2O :

- * All labile protons are **replaced by deuterium (deuterium exchange)**
- * Signals originally corresponding to labile protons **disappear** from the NMR spectrum

Question 7

Gamma-aminobutyric acid (GABA) is a neurotransmitter used in the central nervous system. The ${}^1\text{H}$ NMR spectrum of GABA (dissolved in D_2O) at 200 MHz is summarized in the table.

GABA	chemical shift (δ , ppm)		
	1.99	b	
	2.28	m	v
	3.01	a	

- Explain why the chemical shifts corresponding to the NH and OH protons are not visible in the spectrum.
- Deduce which chemical shifts correspond to the protons H_a , H_b and H_c , explaining your answers.
- State the relative intensities for the signals corresponding to H_a , H_b and H_c .
- State the multiplicity of each of the signals corresponding to H_a , H_b and H_c .

splinting pattern

[N17/1(d)]

Question 7

- (i) These protons are labile and undergo rapid exchange with D₂O. The deuterium nucleus does not absorb in the same frequency as ¹H, hence these chemical shifts are not visible in the spectrum.

(ii)

Proton	δ / ppm	explanation
a	2.28	deshielded by adjacent C=O group
b	1.99	most shielded of the three as H _b is the furthest from the C=O and -NH ₂ groups.
c	3.01	deshielded by adjacent electronegative N atom

- (iii) The relative intensity is 1:1:1

(iv)

proton	multiplicity
a	triplet
b	doublet of doublets / multiplet / quintet
c	triplet

Example 12

IR spectrum

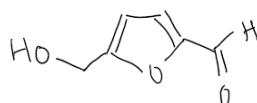
Broad absorption ~3400 cm⁻¹ O-H stretch

Sharp absorption ~1700 cm⁻¹ C=O stretch

NMR spectrum

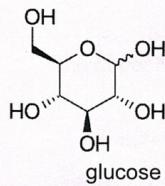
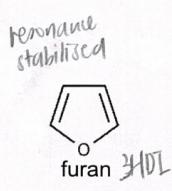
δ / ppm	No. of H	Splitting	deductions
3.8	1	singlet	Labile -OH proton
4.7	2	singlet	-CH ₂ - deshielded by ring current or adjacent electronegative atom. There are no protons on adjacent C
6.5	1	singlet	aromatic proton on furan ring
7.1	1	singlet	aromatic proton on furan ring
9.6	1	singlet	aldehyde -CHO proton. There are no protons on adjacent C

The structure of HMF is



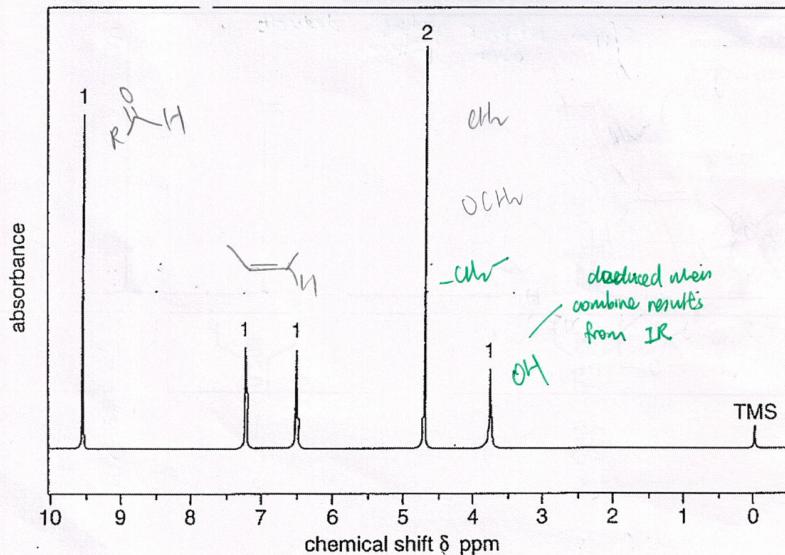
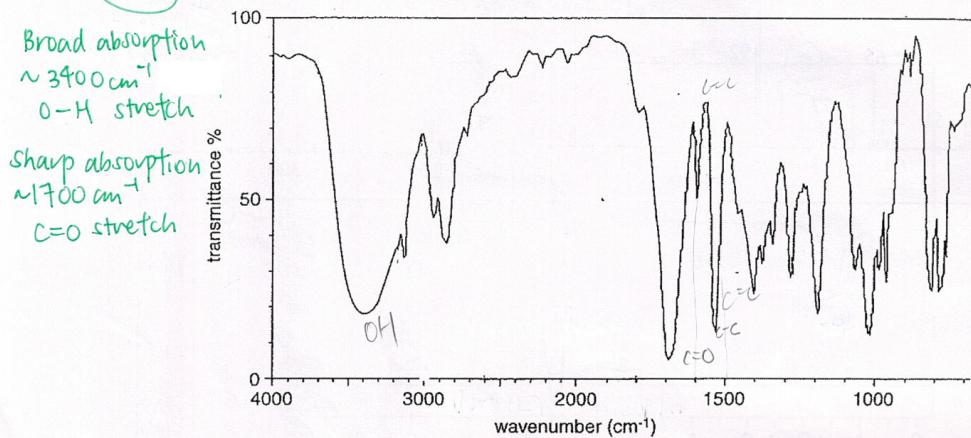
Question 12

Furan is an aromatic compound. HMF, $C_6H_6O_3$, is a furan derivative formed during cooking by the heating of sugars such as glucose.



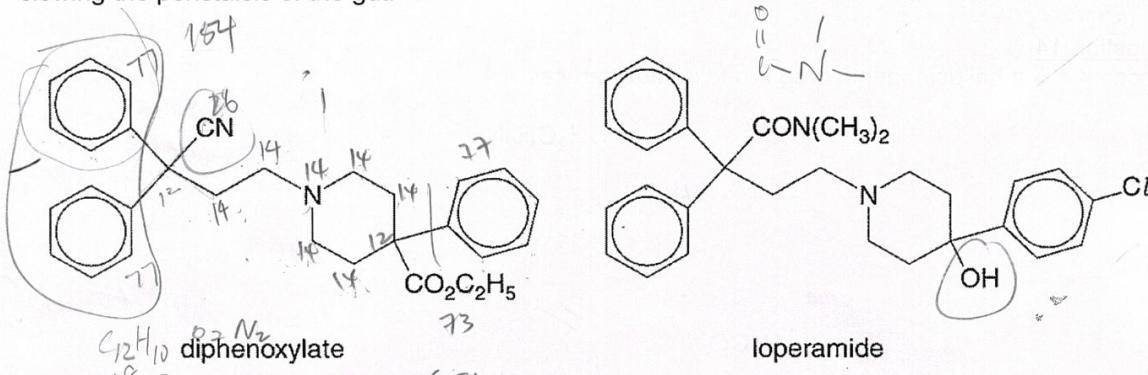
Table

Deduce the structure of HMF using the IR and NMR spectra given.



Question 13

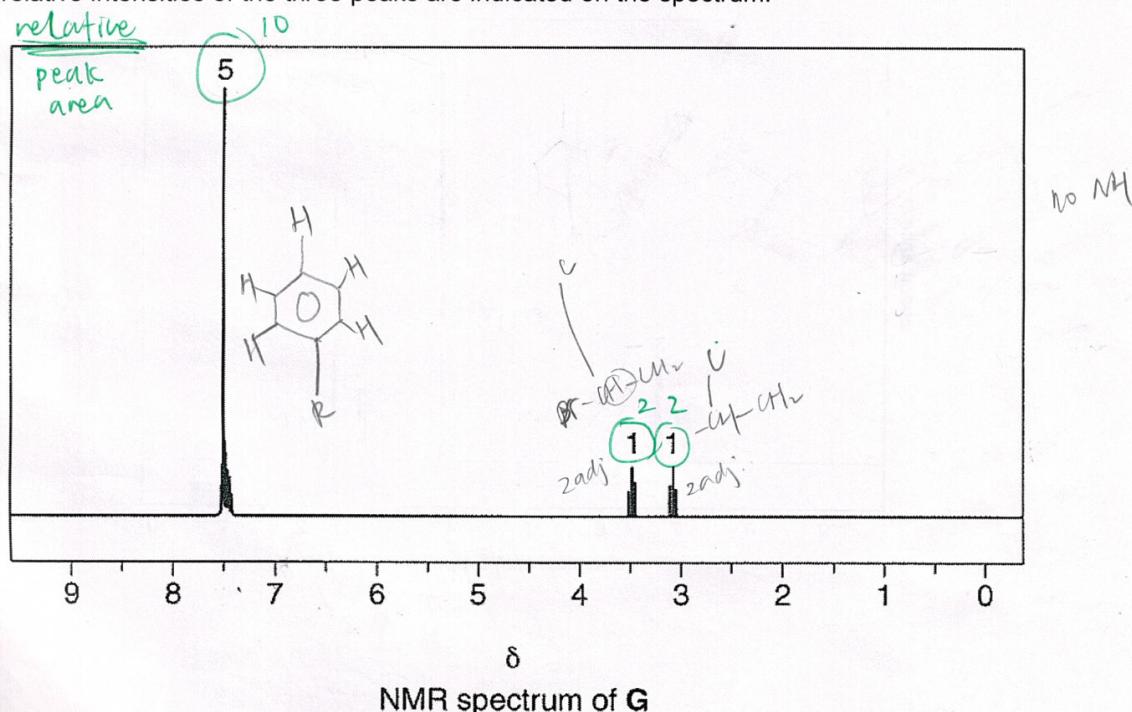
Diphenoxylate and loperamide are two opioid agonists that are used in the treatment of diarrhea, slowing the peristalsis of the gut.



- (a) By studying their molecular structures, state **two** differences in the IR spectra of diphenoxylate and loperamide that will allow you to distinguish between them. Identify the wavenumbers of the absorptions and functional groups involved.

- Diphenoxylate will show a weak signal at $2200-2250 \text{ cm}^{-1}$ while loperamide would not due to the presence of nitrile CN stretch.
- Loperamide will show a broad signal at $3200-3600 \text{ cm}^{-1}$ owing to the presence of tertiary alcohol O-H stretch and it may show a signal at $700-800 \text{ cm}^{-1}$ due to the aryl chloride C-Cl stretch. These are absent for diphenoxylate.

Compound G is an intermediate in the synthesis of diphenoxylate. Its NMR spectrum is shown below. The relative intensities of the three peaks are indicated on the spectrum.



Compound G contains the elements C, H and N, together with one halogen atom per molecule. The major peaks in its mass spectrum are as follows.

m/e	% abundance
192	100
299	30
301	30

$452 - 301 = 151$

- (b) Use the NMR spectrum, the mass spectroscopy data and the structure of diphenoxylate to deduce the structure of G. Explain your answer fully.

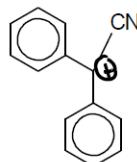
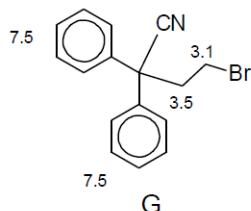
Mass Spectrometry Data:

- The Mr of G is likely 299.
- Since the relative abundance of m/e 299 : 301 (M : M+2) peaks is 1:1, G contains a Br atom.

NMR Spectrum:

- The relative intensities of the three peaks in NMR spectrum represents a ratio of 5:1:1 and not indicative that there are only 7 H atoms in G.
- The signal at about 7.5 ppm of the NMR spectrum is indicative of aromatic protons. Since there cannot be 3 benzene rings in G, it is more likely that G contains 2 benzene rings and hence 14 H atoms (7 relative no. of protons $\times 2$).
 - $7 \times 5 = 35$ H atoms which is more than number of H atoms in diphenoxylate
 - the requirement that there are 6 protons (2 relative no. of protons $\times 3$) that gives a pair of triplet is not observed in the structure of diphenoxylate.
- By inspecting the structure of diphenoxylate, the quaternary carbon containing two benzene rings is likely to be in G.
- In addition, since G is expected to have one bromine atom, it serves as a convenient electrophilic centre that can undergo nucleophilic substitution with a piperidine to form diphenoxylate.

δ / ppm	integral	multiplicity	deductions
7.5	5	multiplet	Two mono-substituted phenyl rings
3.5	1	triplet	-CH ₂ - bonded to electronegative Br atom, next to -CH ₂ -
3.1	1	triplet	-CH ₂ - adjacent to -CH ₂ Br

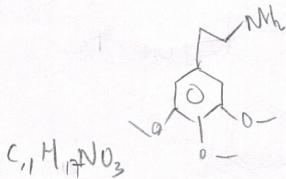
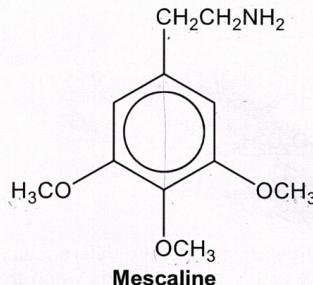


fragment m/e 192 is very stable due to the mesomeric effect exerted by 2 benzene ring and the CN group



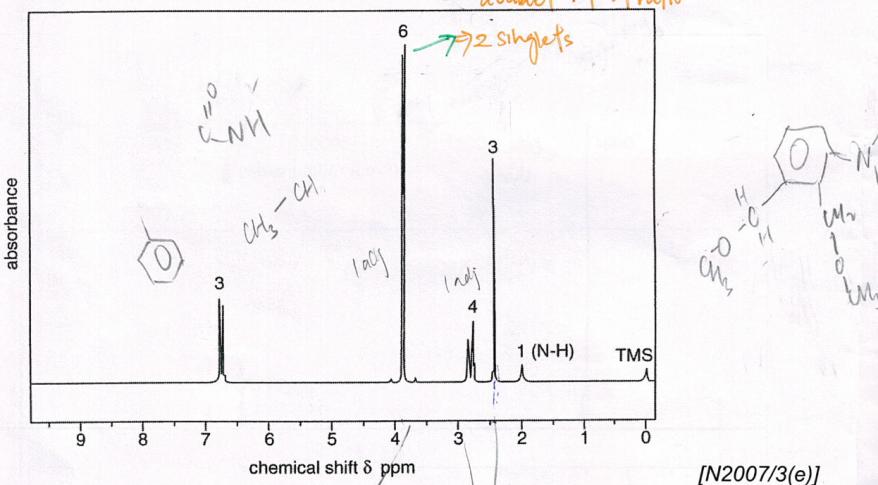
Question 14

Mescaline is a hallucinogenic drug found in Mexican cacti.



^{4HDL}
use Mescaline as the base
Compound A, $C_{11}H_{17}NO_2$, is structurally related to mescaline. The NMR spectrum of compound A is given below. Deduce a structure for compound A, and explain your reasoning. [5]

doubtful : 1 : 1 ratio



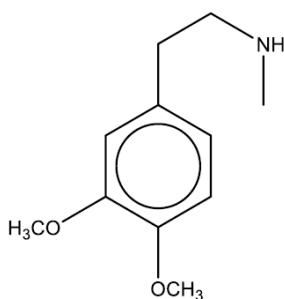
[N2007/3(e)]

Example 14

The ^1H NMR shows that there are 5 proton environments:

δ / ppm	Rel. peak area	Splitting pattern	Deductions
2	1	broad s	-NH- proton on 2° amine (unlike mescaline, which contains a 1° amine)
2.4	3	s	- CH_3 protons deshielded by adjacent electronegative N atom
2.75	4	2 s	2 distinct - CH_2- units
3.8	6	2 s	2 distinct - CH_3 units adjacent to electronegative O atom \Rightarrow 1 of the 3 - OCH_3 units on mescaline is lost
6.75	3	d	3 aromatic protons on a tri-substituted phenyl ring

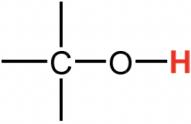
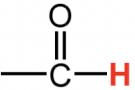
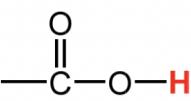
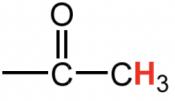
Using the structure of mescaline as the starting point, possible structure of compound A is:



note: 3 aromatic protons appear as a doublet due to overlapping signals with very similar δ values.

NMR Reference Values

Correlation of ^1H chemical shift with electronic environment:		
Type of hydrogen		Chemical shift (δ)
Reference	$(\text{CH}_3)_4\text{Si}$	0
Alkyl (1°)	---CH_3	0.7-1.3
Alkyl (2°)	$\text{---CH}_2\text{---}$	1.2-1.6
Alkyl (3°)	$\begin{array}{c} \\ \text{---CH---} \end{array}$	1.4-1.8
Allylic	$\begin{array}{c} & & \\ & \text{C}=\text{C} & \text{---C---H} \\ & & \end{array}$	1.6-2.2
Alkynyl	---\equiv---H	2.5-3.0
Vinylic	$\begin{array}{c} & & \text{H} \\ & \diagup & \diagdown \\ & = & \\ & \diagdown & \diagup \\ & & \text{H} \end{array}$	4.5-6.5
Aryl	Ar---H	6.5-8.0
Alkyl halide	$\begin{array}{c} \text{H} \\ \\ \text{---C---X} \\ \end{array}$	2.5-4.0
Alcohol, ether	$\begin{array}{c} \text{H} \\ \\ \text{---C---O---} \\ \end{array}$	3.3-4.5

Alcohol		2.5-5.0
Aldehyde		9.7-10.00
Carboxylic Acid		11.0-12.0
Alkyl (1°)	---CH_3	0.7-1.3
Methyl ketone		2.0-2.4
Aromatic methyl	Ar---CH_3	2.4-2.7

Electromagnetic range	Type of spectroscopy	E1-E2 Transition between
Ultraviolet-Visible	UV-Vis	Electronic energy levels
Infrared	IR	Vibrational energy levels
Radio waves	NMR	Nuclear spin states