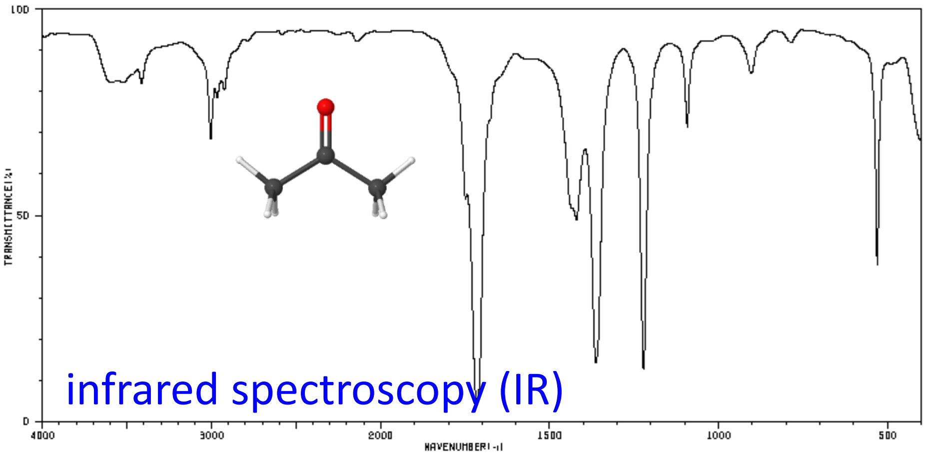
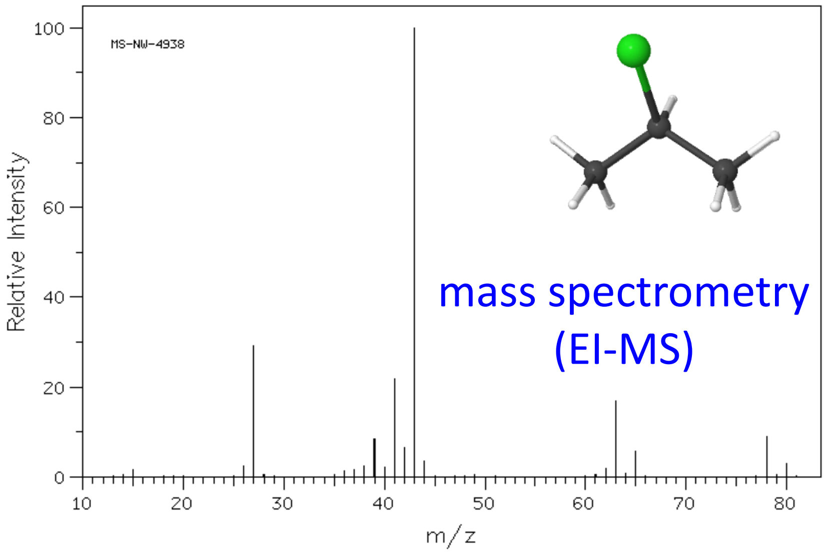
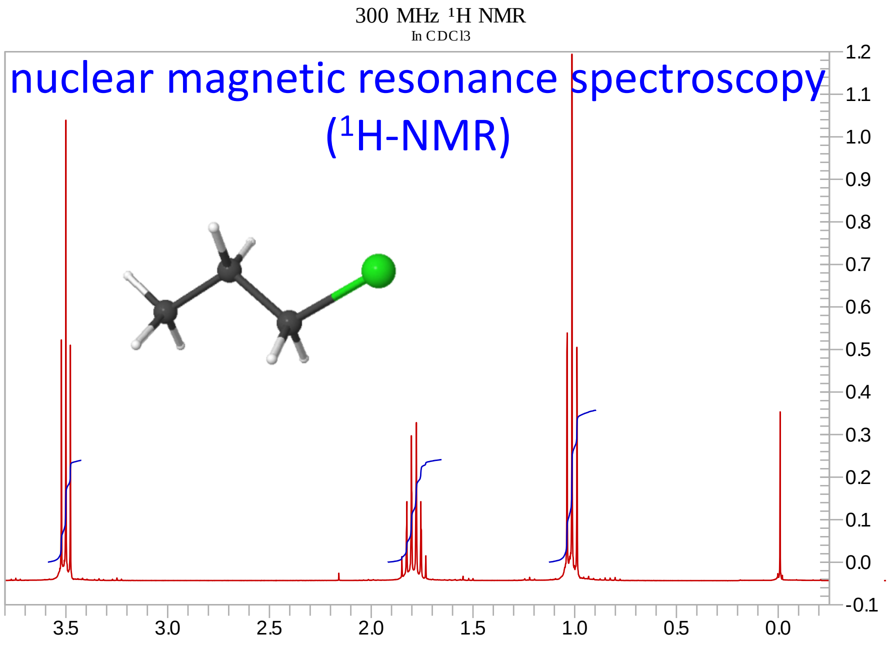
CHEM 344/345 – Spectroscopy and Spectrometry in Organic Chemistry



infrared spectroscopy (IR)

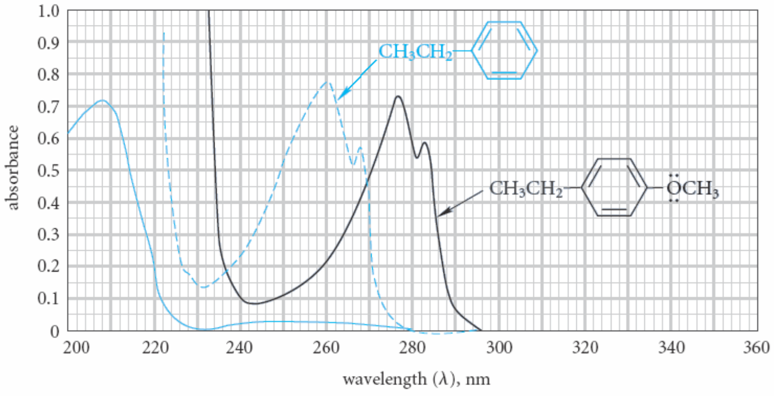


mass spectrometry (EI-MS)



nuclear magnetic resonance spectroscopy (^{1}H-NMR)

ultra-violet and visible light absorption spectroscopy (UV-vis)



Spectroscopy and Spectrometry in Organic Chemistry

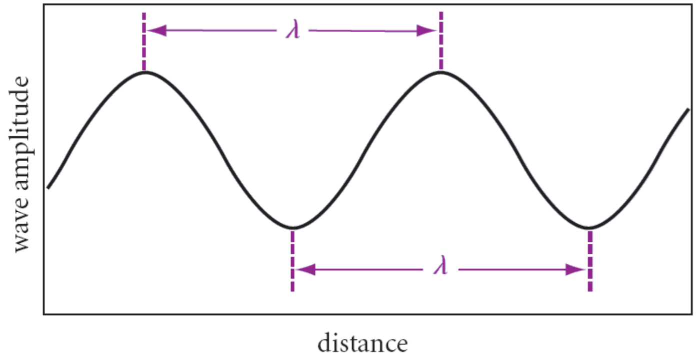
1. **U**ltra-**v**iolet and **vis**ible (**UV/Vis**) spectroscopy provides information about the electronic structure of a molecule through the excitation of electrons. (15.2, 16.3D, 19.3D)

2. **I**nf**r**ared (**IR**) spectroscopy can be used to determine functional groups and bond strengths based upon molecular vibrations. (12.1 – 12.5, 14.3B, 16.3A, 19.3A, 20.3A, 21.4A, 23.4A, & A-3 – A-4)

3. **M**ass **S**pectrometry (**MS**) ionizes and energizes a molecule to determine its mass and connectivity through fragmentation. (12.6, 19.3E, 26.8A)

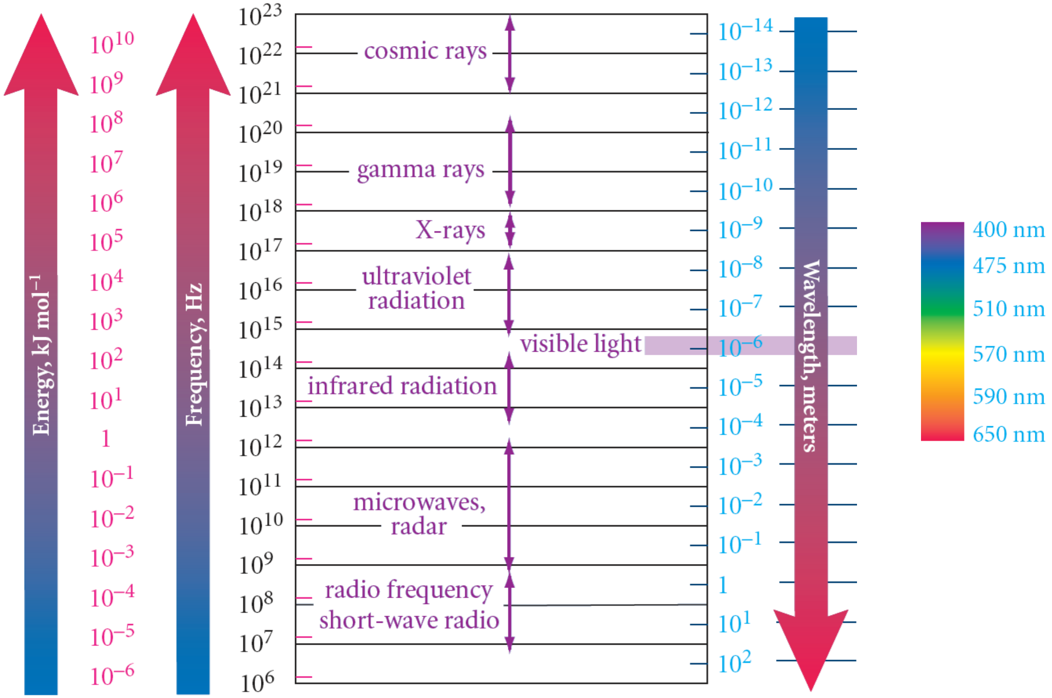
4. **N**uclear **M**agnetic **R**esonance (**NMR**) spectroscopy provides detailed information about the structure of a molecule by its interaction with a magnetic field and a radio frequency pulse. (13, 14.3C, 16.3B – 16.3C , 19.3B – 19.3C, 20.3B, 21.4B, 23.4A, & A-5 – A-8)

Electromagnetic Radiation



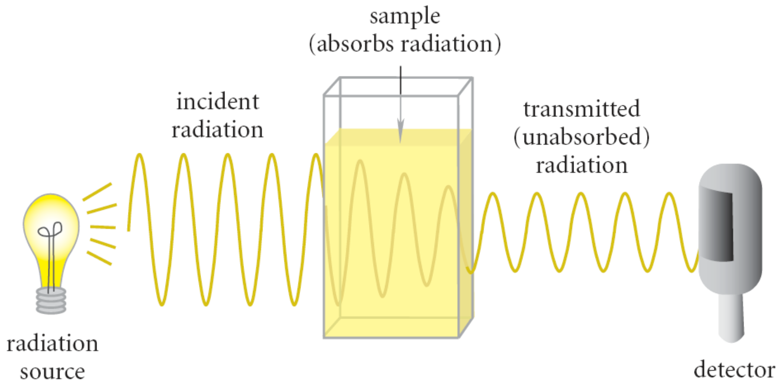
$$E = h\nu = \frac{hc}{\lambda}$$

$$h = 6.625 \times 10^{-34}\ \text{J s}$$



Absorption spectroscopy in 3 easy steps.

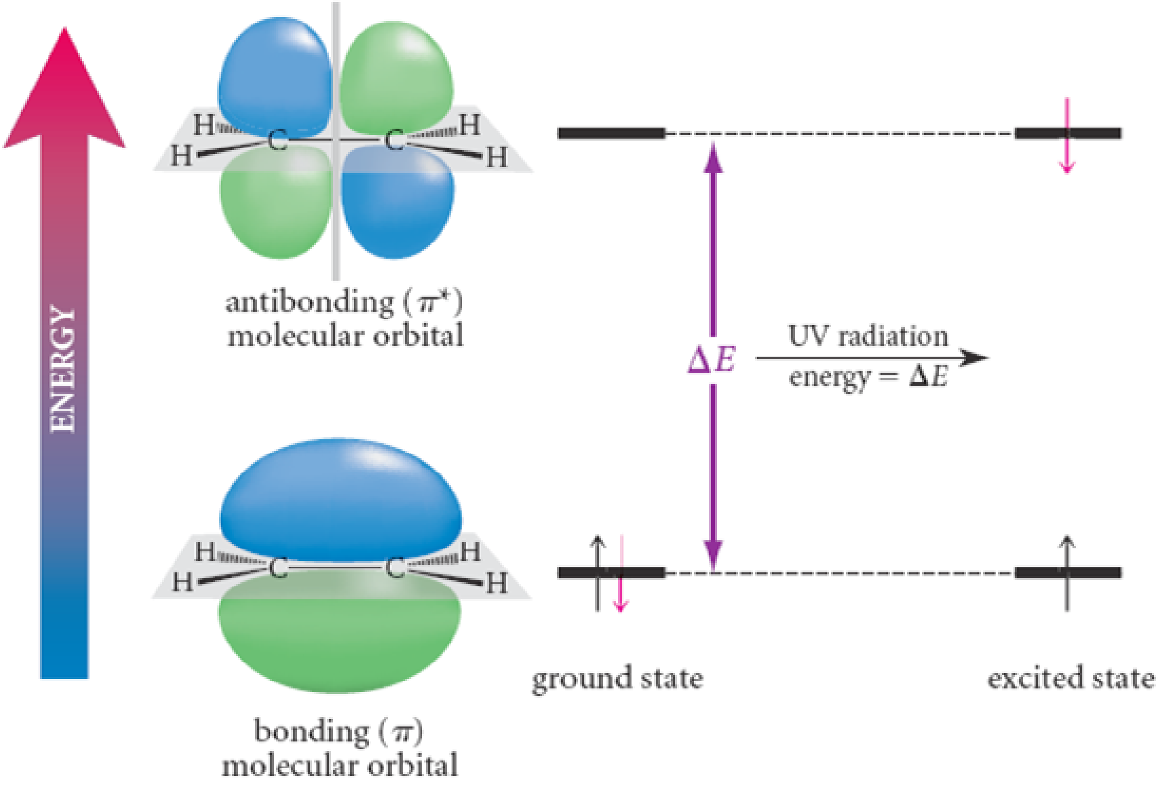
1) Make light.
2) Pass light through sample.
3) Check for absorption.



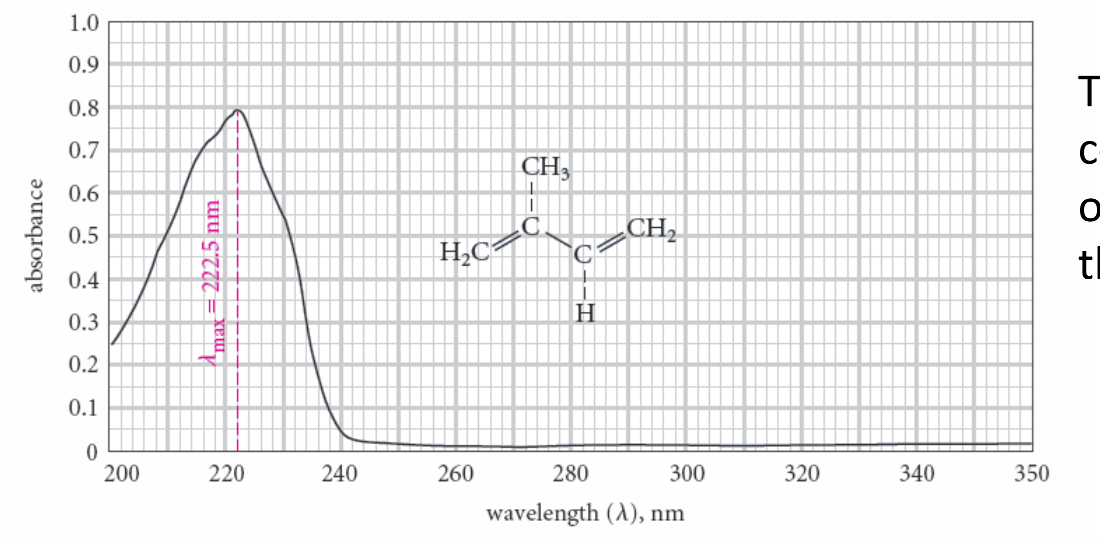
UV/Vis Absorption Spectroscopy

Ultra-**v**iolet and **vis**ible (**UV/Vis**) spectroscopy provides information about the electronic structure of a molecule – particularly useful for conjugated π systems.

UV/Vis photons excite electrons to an excited state if $E_{photon} = E_{LUMO\text{-}HOMO}$.

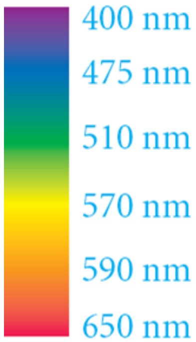


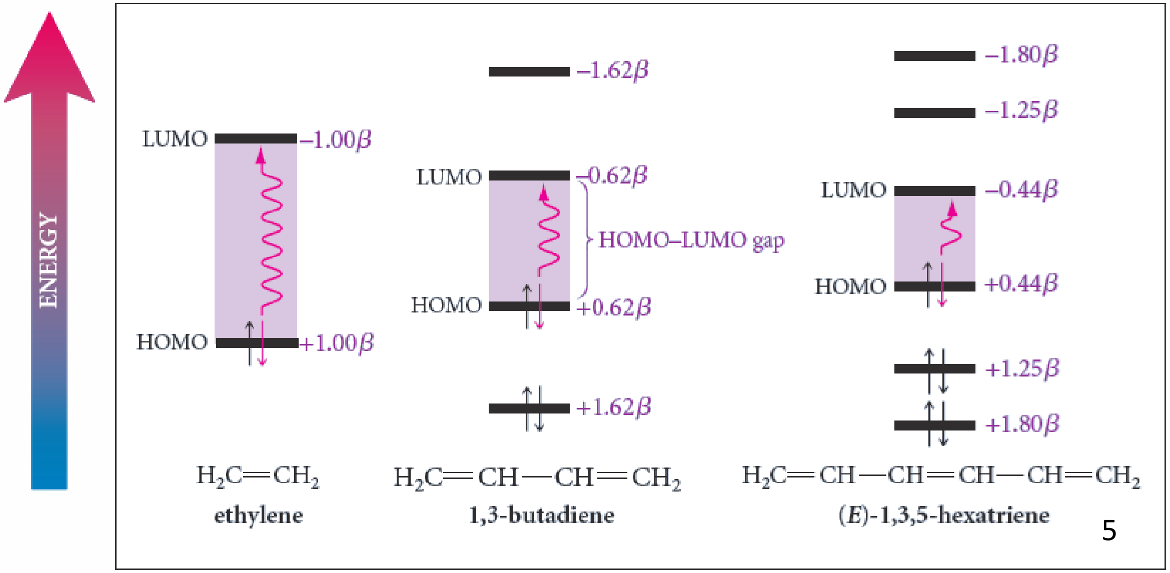
UV/Vis Absorption Spectroscopy



This explains why many organic compounds tend to be boring (white or off-white powders or crystals) in the visible spectrum.

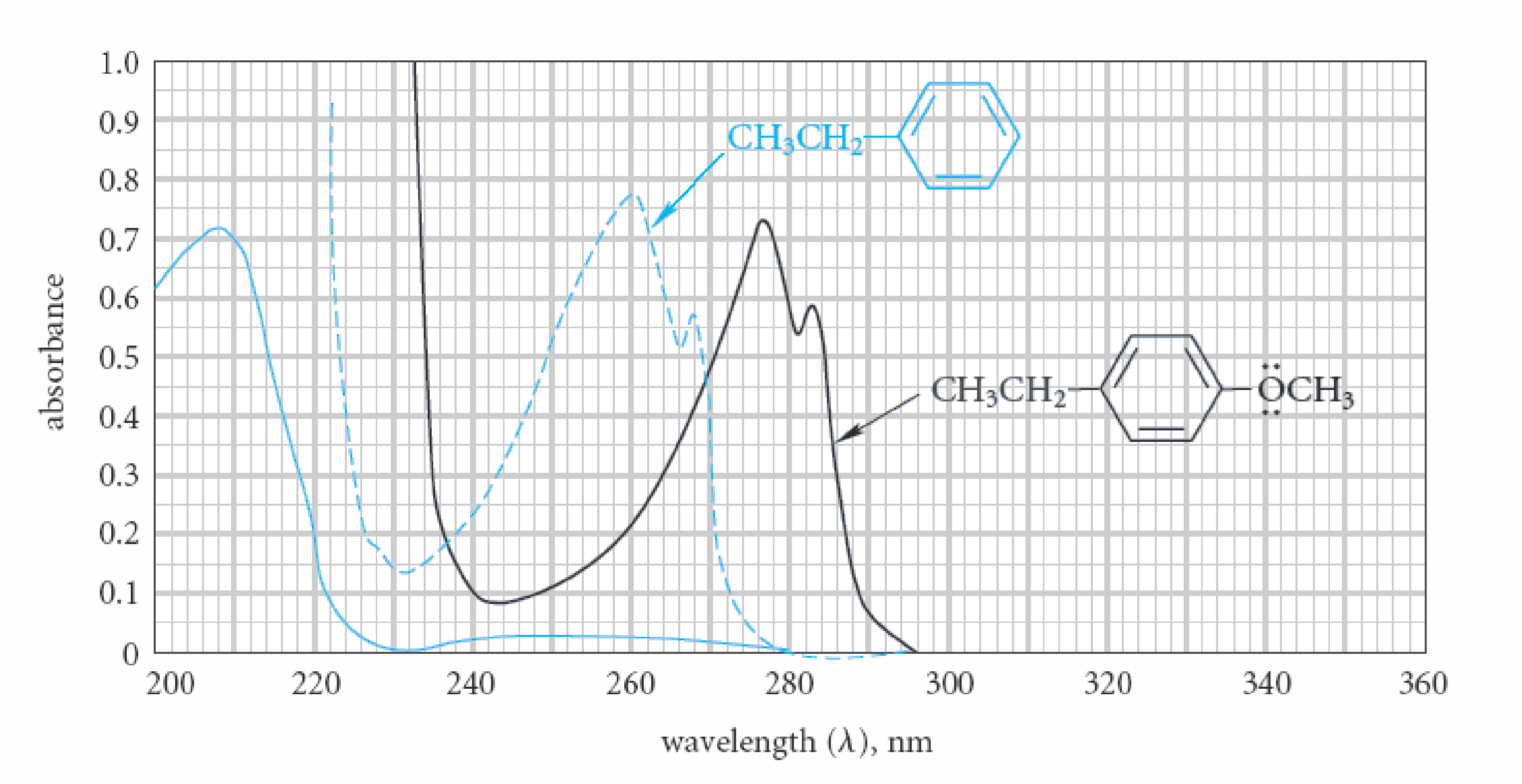
Molecules need to absorb in the visible range in order to be colored.





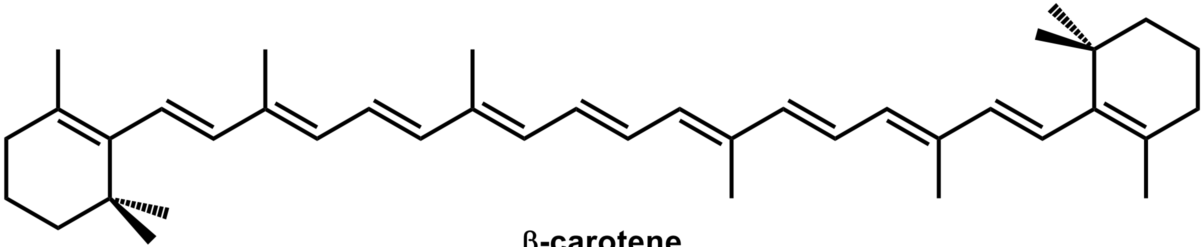
Conjugation in 4-ethylanisole

The more conjugated the π-system, the lower the HOMO-LUMO gap, the larger the λ_{max} will be.

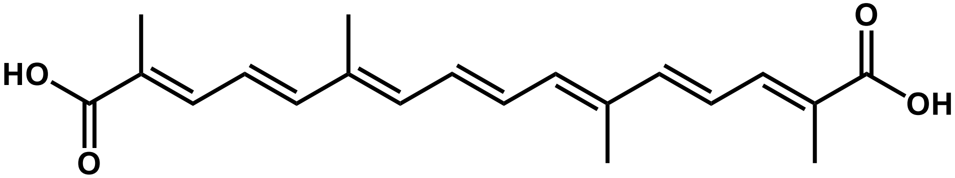


The p-orbital lone pair of the oxygen atom conjugates to the aromatic ring π-system.

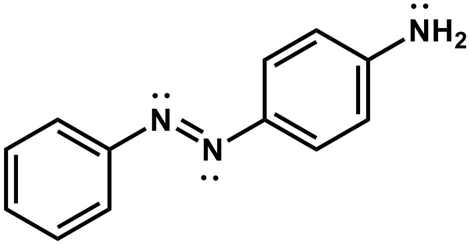
Brightly Colored Organic Molecules



β-carotene

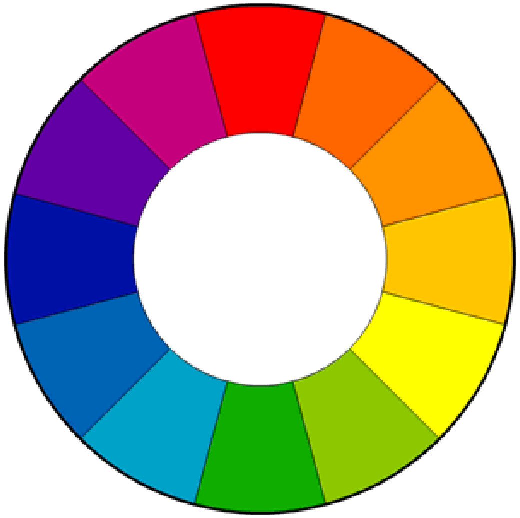


Crocetin

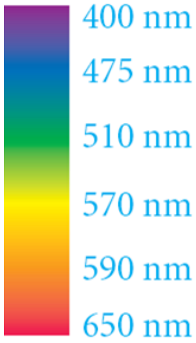


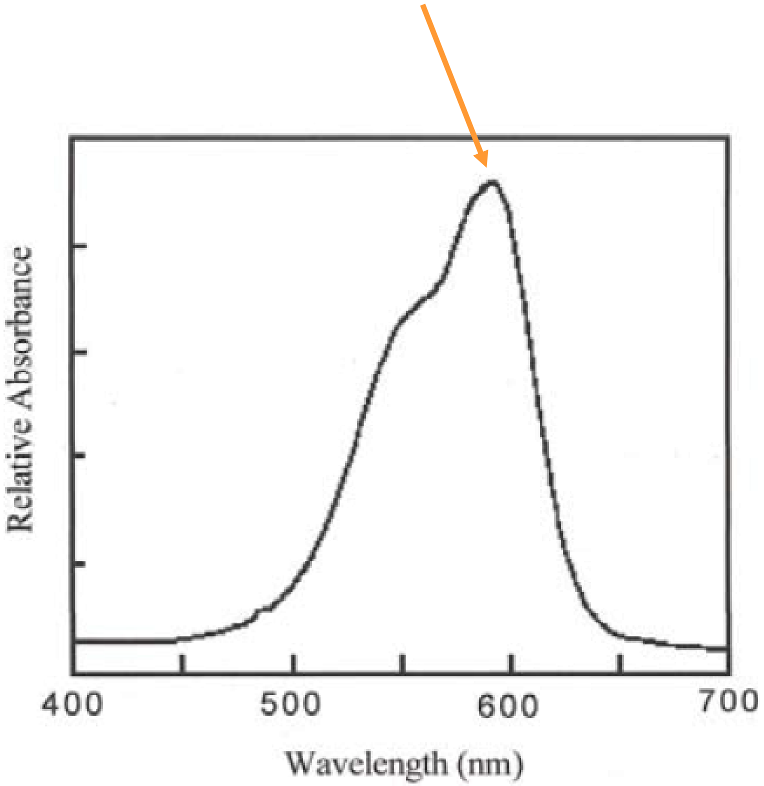
Aniline Yellow

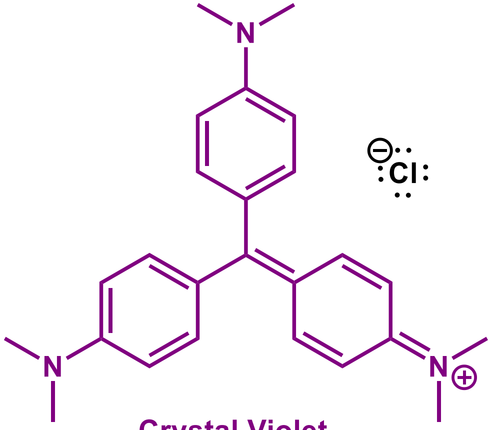
UV/Vis Spectrum of Crystal Violet



Molecules need to absorb in the visible range in order to be colored.



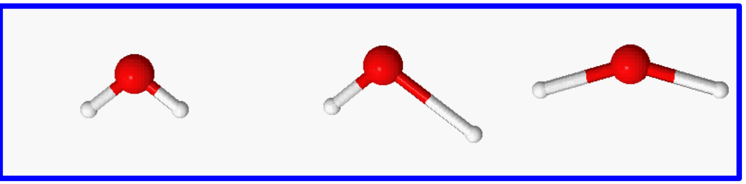

λ_{max} = 590 nm



Crystal Violet

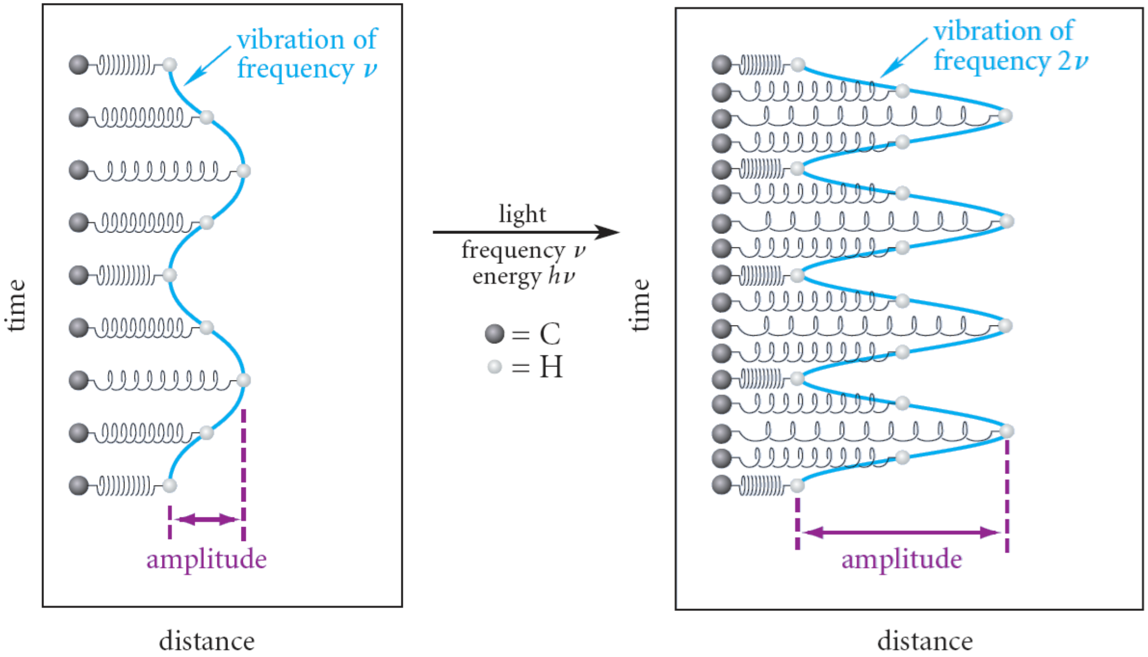
Physical Basis for IR Spectroscopy

Chemical bonds are not rigid, but in continuous states of vibration.



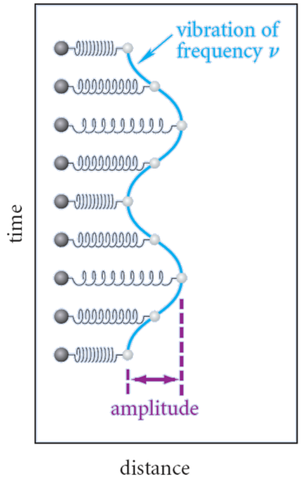
3585 cm^{-1} 3506 cm^{-1} 1885 cm^{-1}

Normal modes of vibration of water



If a molecule absorbs a photon of a frequency of light that matches the frequency of a vibration, an absorption occurs and that vibrational state is excited.

Factors that Affect IR Absorption Frequency



$$\nu = \frac{1}{2\pi}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$$

Chemical bonds can be approximated to be springs.

Hooke’s Law governs the energy of vibration.

The frequency (ν) is dependent on the force constant (*k* ~ bond strength) and the masses of the nuclei.

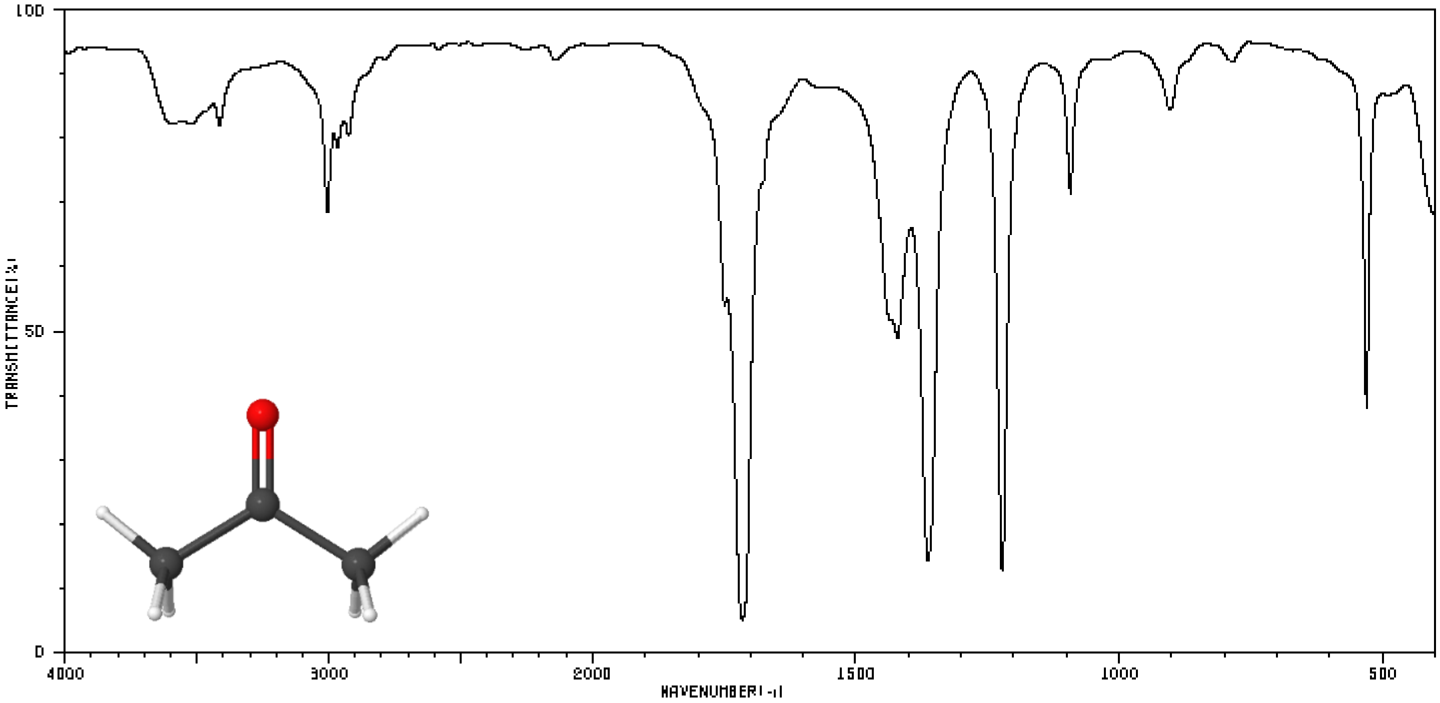
Bond	Approximate vibrational frequency
C–C	1000 cm^{-1}
C=C	1600 cm^{-1}
C≡C	2200 cm^{-1}

Bond	Approximate vibrational frequency
C(sp)–H	3300 cm^{-1}
C(sp^2)–H	3100 cm^{-1}
C(sp^3)–H	2900 cm^{-1}

Bond	Approximate vibrational frequency
C(sp^3)–D	2200 cm^{-1}
C(sp^3)–H	2900 cm^{-1}

IR Spectrum of Acetone

Vertical axis in %Transmittance (most often) in IR spectra.

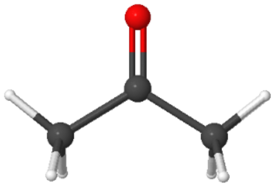


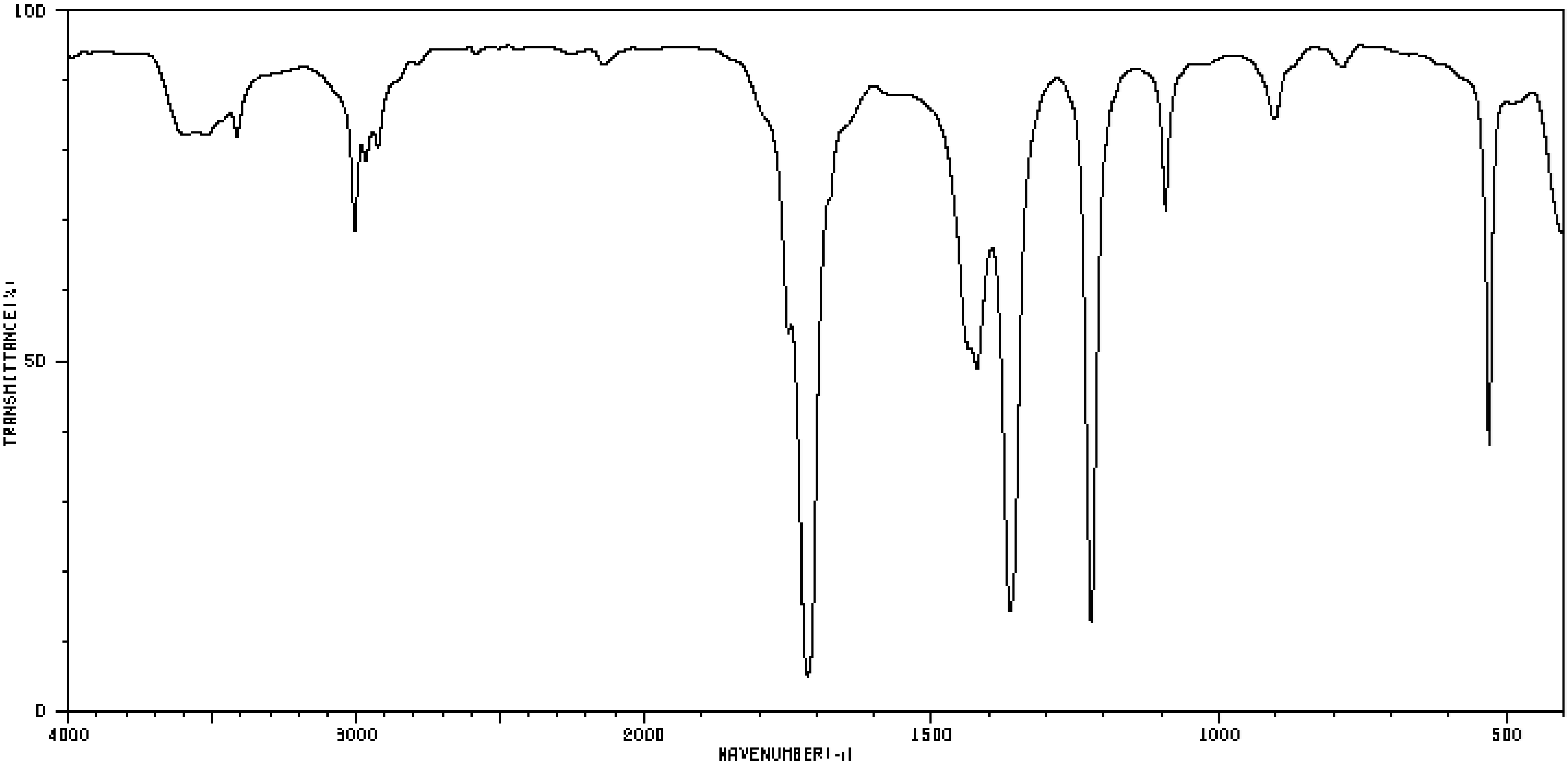
Horizontal axis in wavenumber (cm^{-1}) for most IR spectra.

Absorptions are observed as sharp or broad reductions in the % of light transmitted.

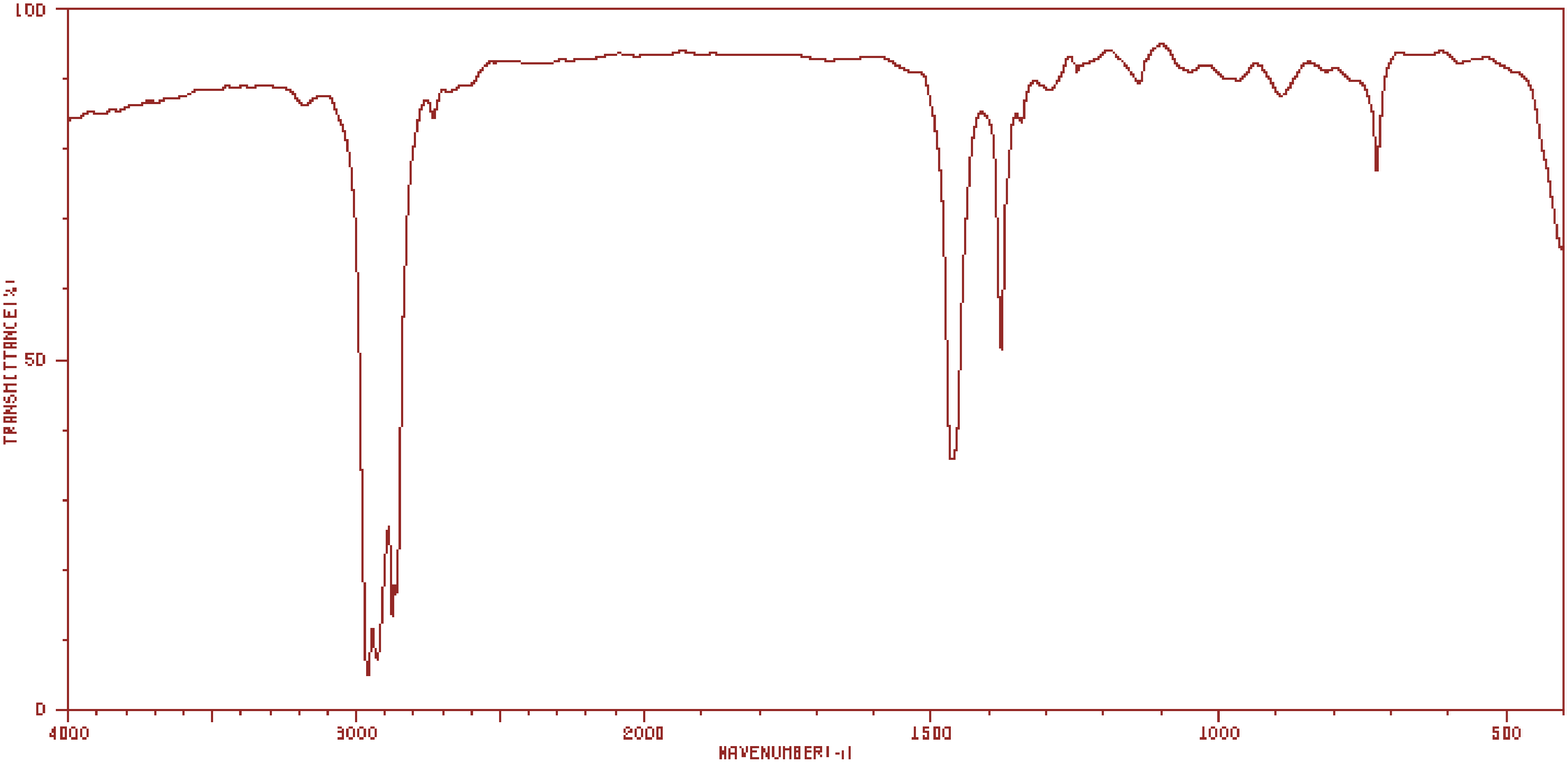
12.4 & 19.3A

IR Spectrum of Acetone



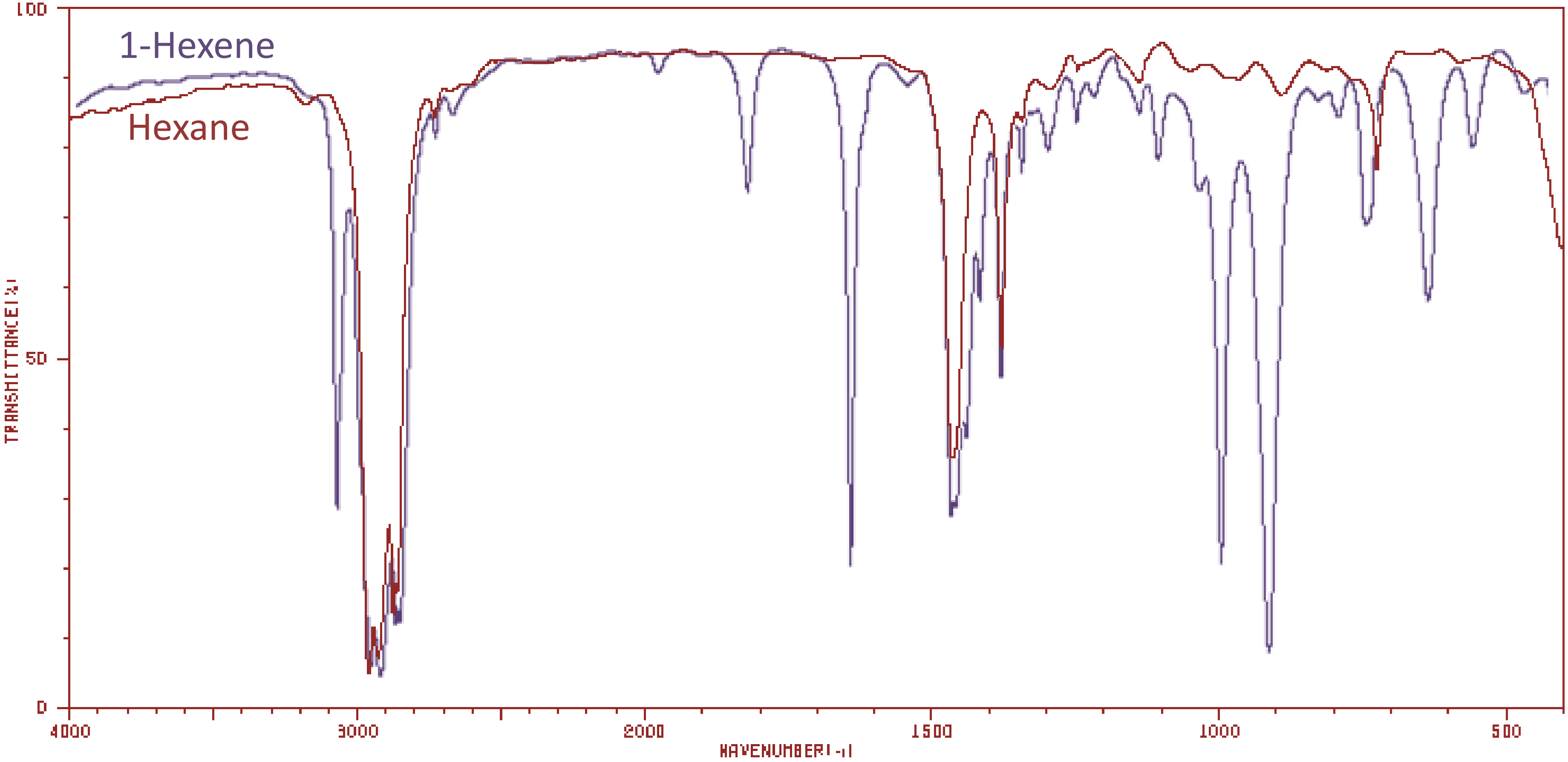


IR Spectrum of **Hexane**

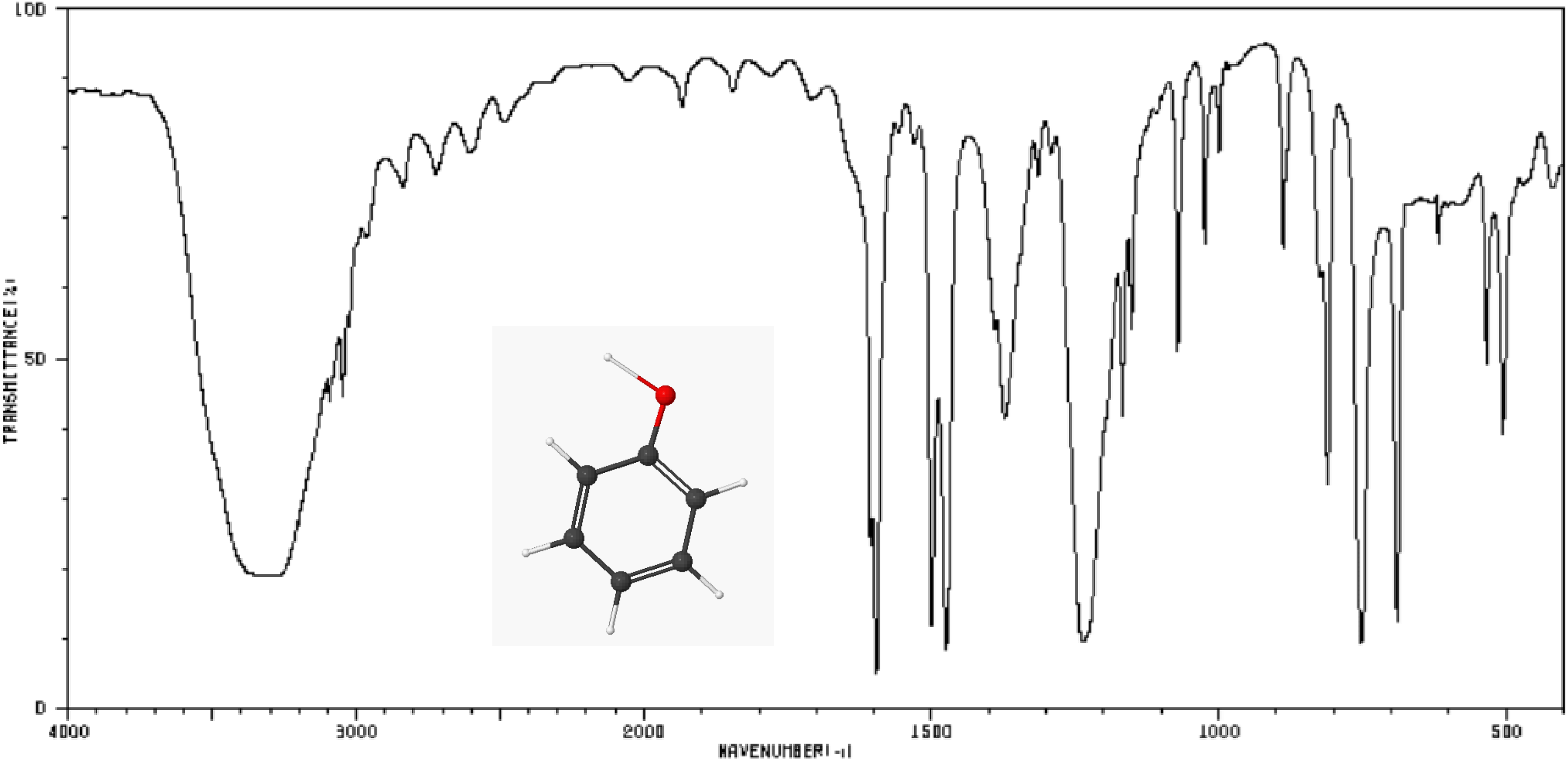


This is a pretty boring IR spectrum due to the lack of functional groups in an alkane.

IR Spectrum of Hexane vs. 1-Hexene



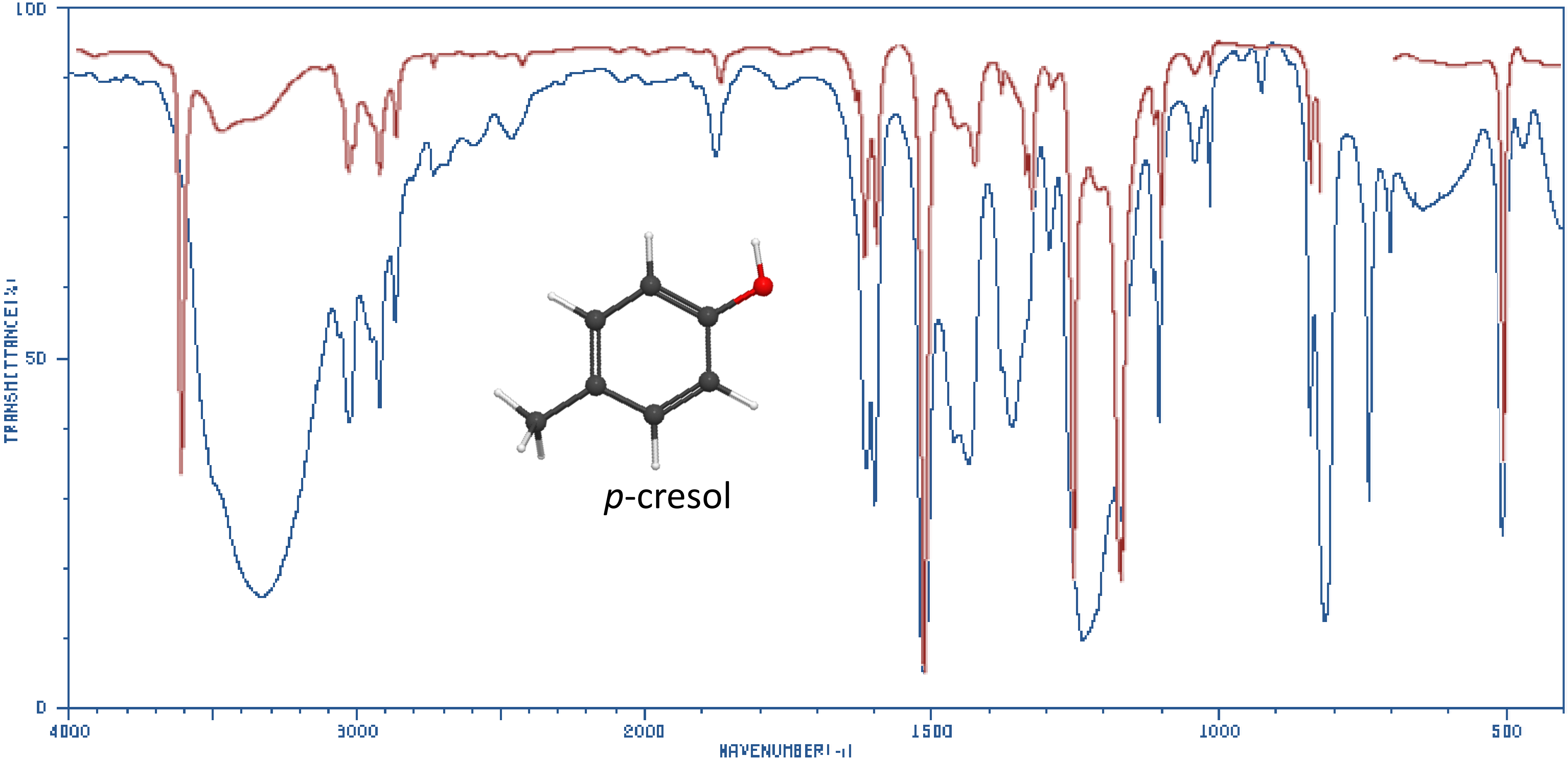
IR Spectrum of Phenol



Broad and intense signals in this region are diagnostic for H-atoms connected to N or O atoms that are involved in hydrogen bonding.

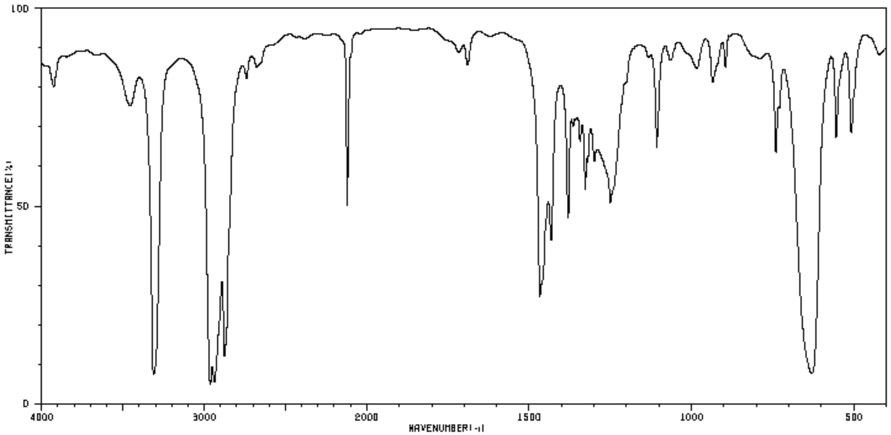
Infrared Observation of Hydrogen Bonding – *p*-Cresol

Appearance of O–H stretches are dependent on conditions. Below, the blue spectrum is of a pure liquid with H-bonding. Below, the red spectrum is of a sample dilute in CCl_4.

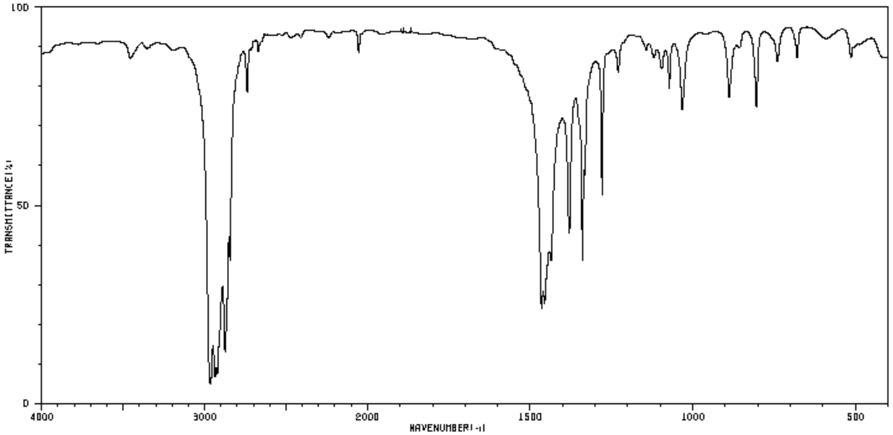


Three Isomeric Hexynes

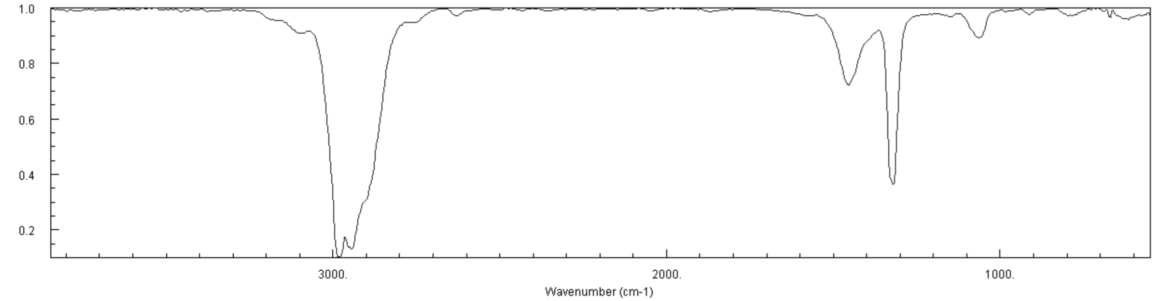
1-Hexyne



2-Hexyne



3-Hexyne



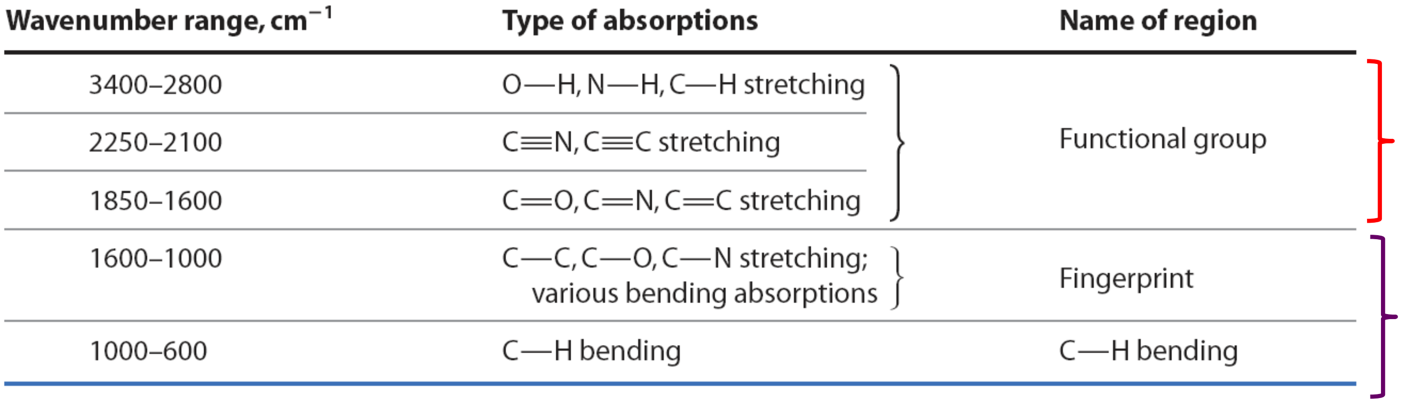
IR intensity depends on the change in the bond dipole moment during vibration.

The more asymmetric a bond, the greater the intensity.

12.3

Functional Group Identification with Correlation Tables

IR spectra provide confirmation of the presence of a functional group or a partial structure determination when used in tandem with other analyses.



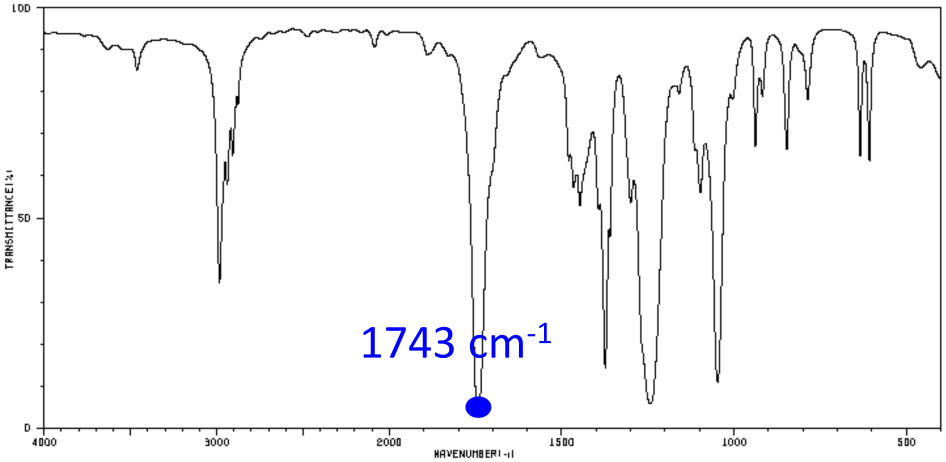
Wavenumber range, cm^{-1}	Type of absorptions	Name of region
3400–2800	O—H, N—H, C—H stretching	Functional group
2250–2100	C≡N, C≡C stretching	
1850–1600	C=O, C=N, C=C stretching	
1600–1000	C—C, C—O, C—N stretching; various bending absorptions	Fingerprint
1000–600	C—H bending	C—H bending

- 3400 – 2800: great for detecting O–H or N–H stretching.
- 2250 – 2100: great for detecting asymmetric triple bonds R–C≡N, R–C≡C–R’.
- 1880 – 1600: great for detecting C=O, C=N, C=C and aromatic rings.

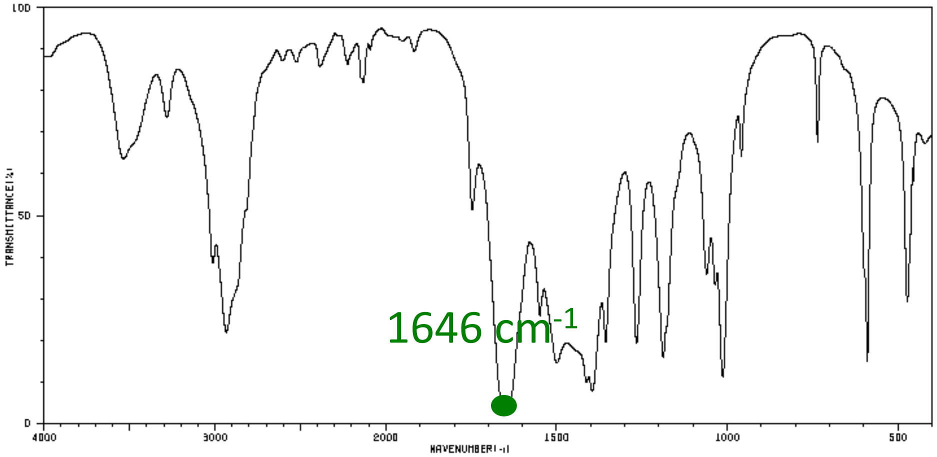
Functional Group Identification with Correlation Tables

Double Bond Stretching Vibrations

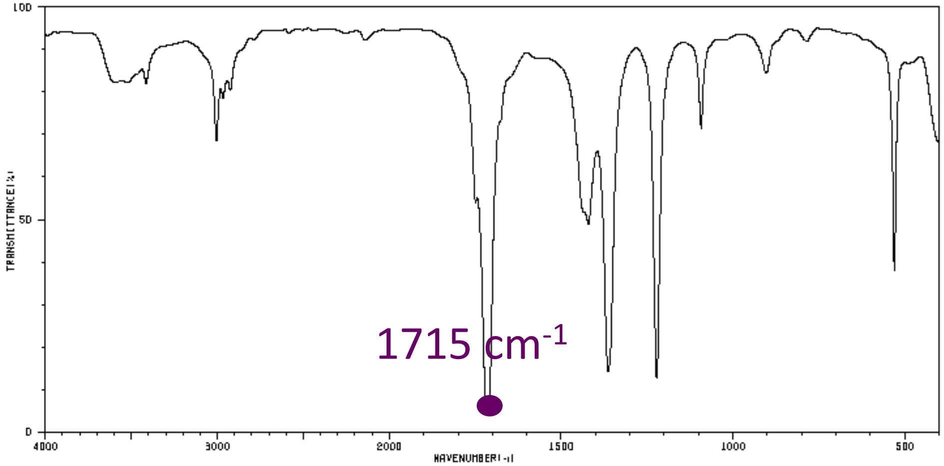
1710 cm^{-1}	Aldehyde or ketone
1680	Conjugated ketone
1745	Cyclopentanone
1780	Cyclobutanone
1730	α-Hydroxy ketone
1740	Ester
1660	Amide
1800	Acid chloride
1810 and 1760	Acid anhydride
1700	Carboxylic acid
1680-1500	C=C stretch
1675-1590	Aromatic C=C stretch



1743 cm^{-1}

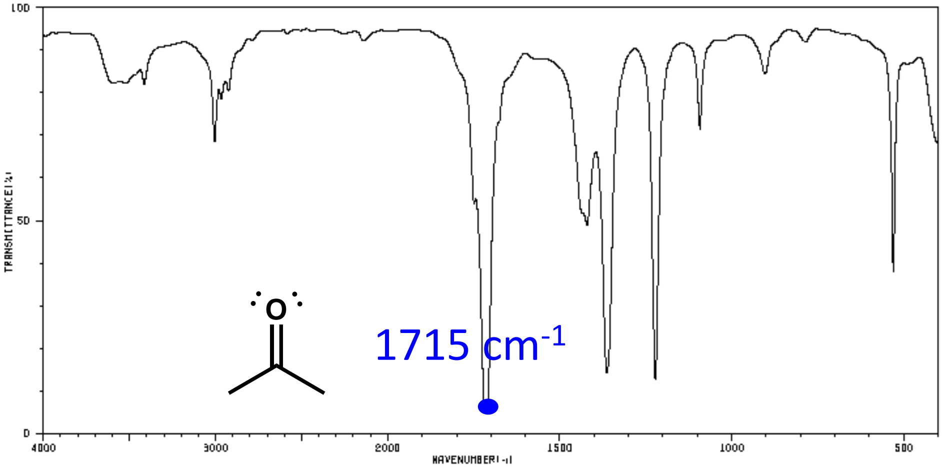


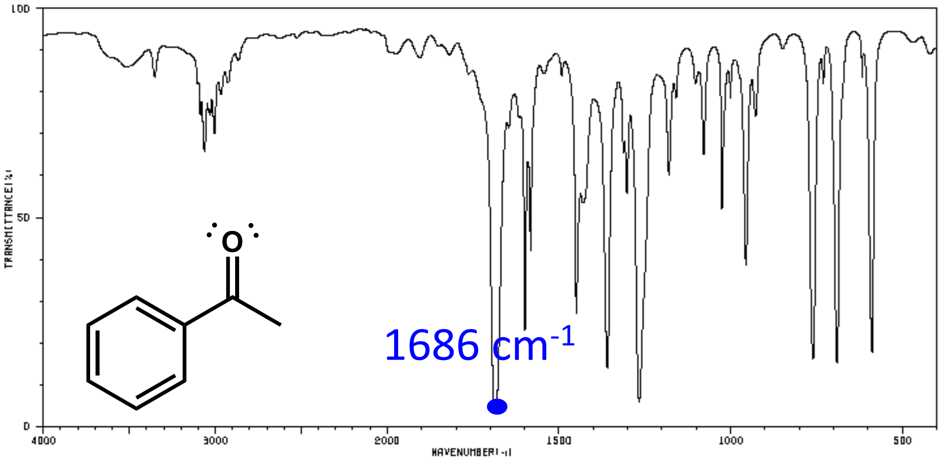
1646 cm^{-1}



1715 cm^{-1}

Functional Group Identification with Correlation Tables

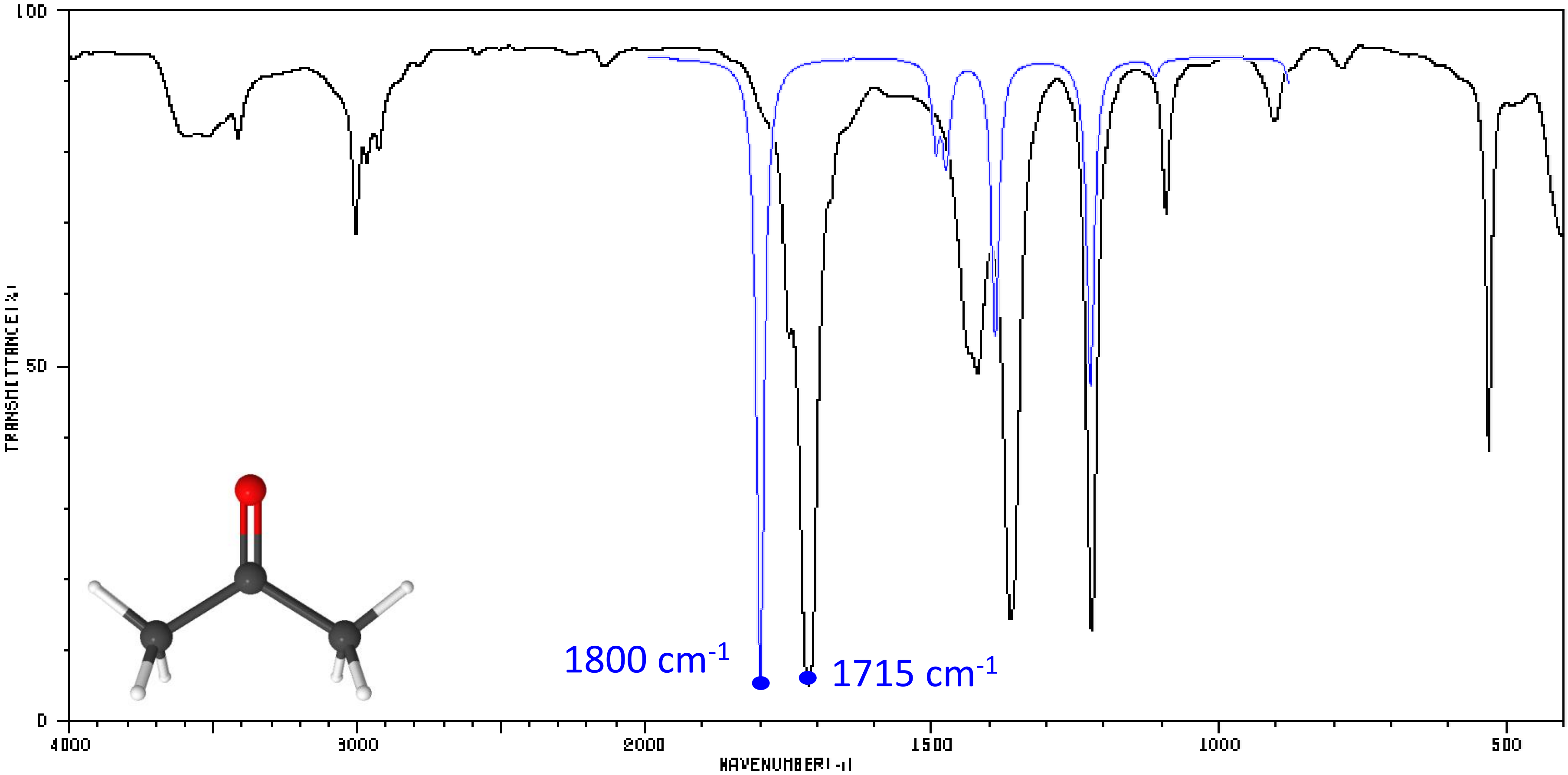




Conjugation of the C=O π bond with the aromatic π system increases the C–O length by decreasing the C=O double bond character and increasing the C–O single bond character.

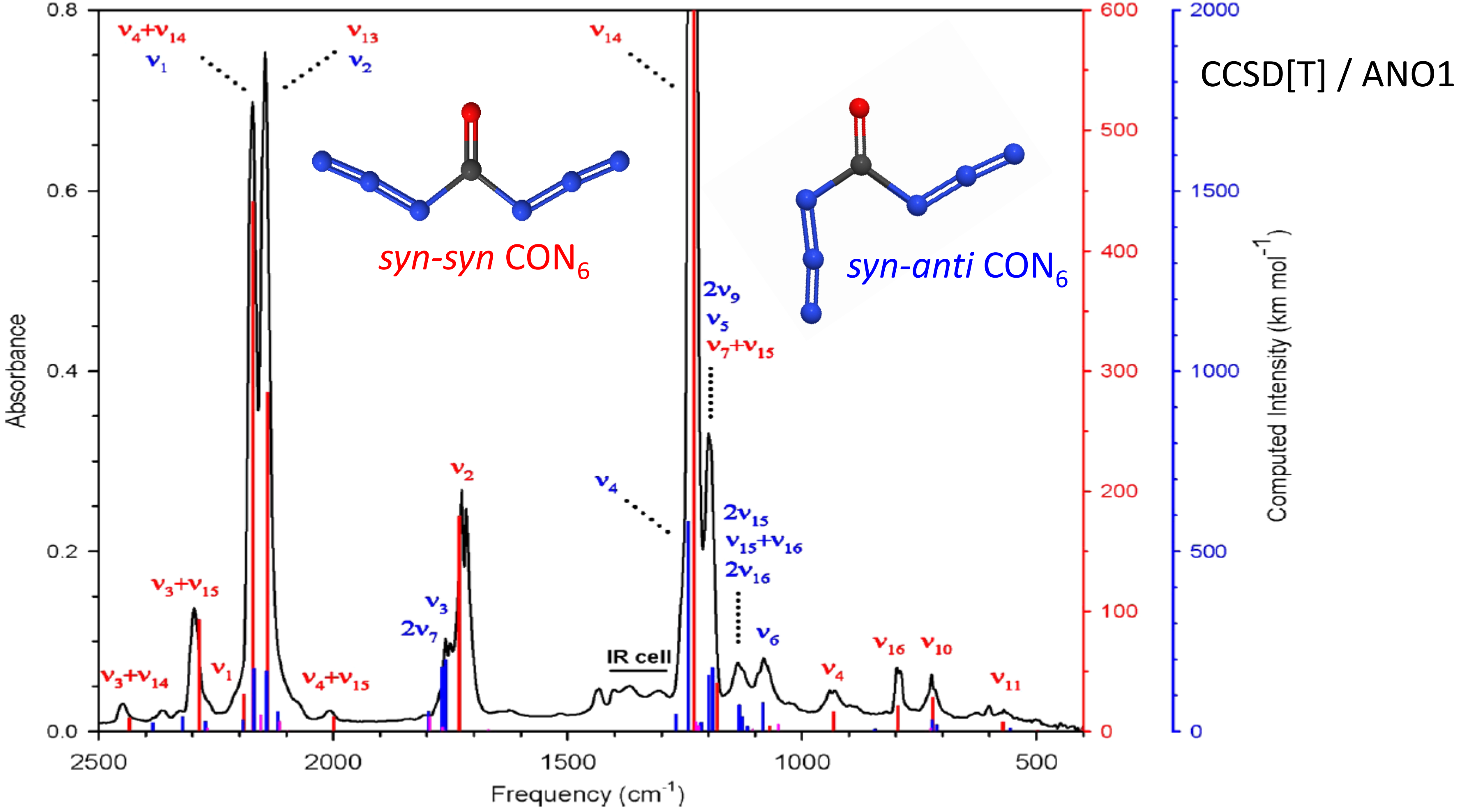
Bond	Approximate vibrational frequency
C–C	1000 cm^{-1}
C=C	1600 cm^{-1}
C≡C	2200 cm^{-1}

Infrared Prediction with Computational Chemistry



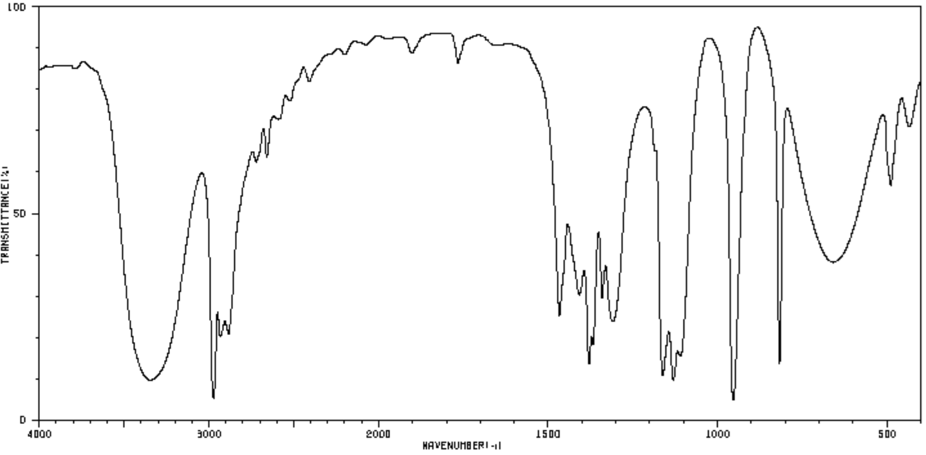
A quick (~ 1 min) calculation using Gaussian09 with B3LYP/6-31G(d) overestimates the absorption frequencies. (More sophisticated calculations can predict more accurately.)

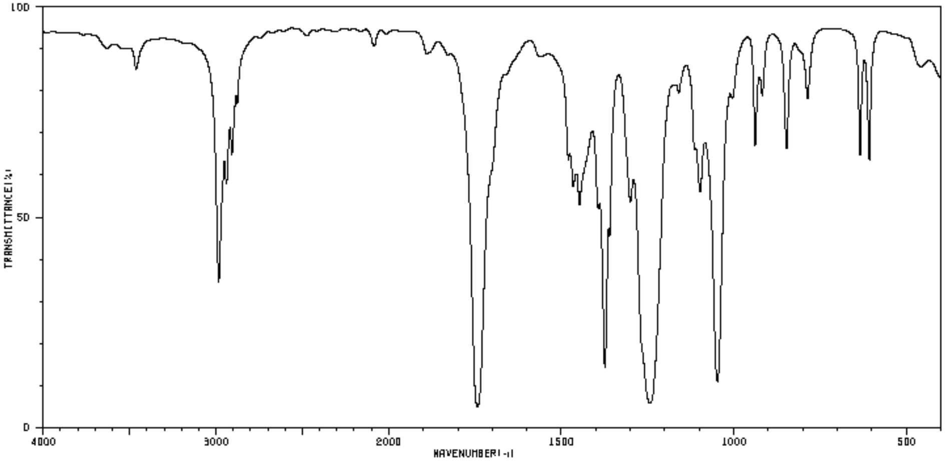
Fully Assigned IR spectrum – CON_6

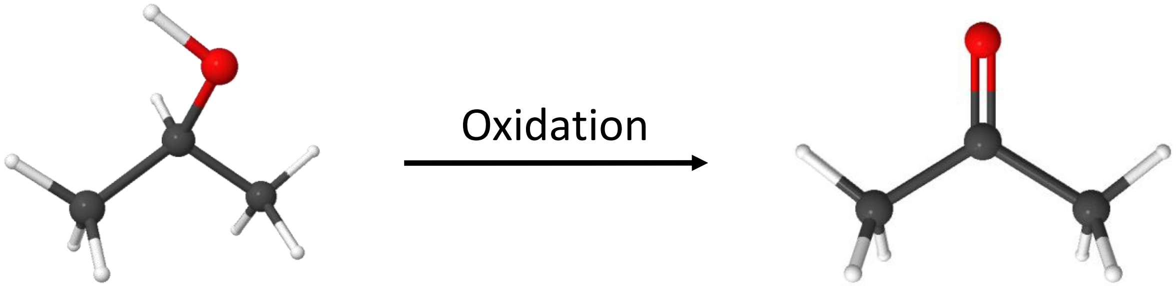


Nolan, A. M.; Amberger, B. K.; Esselman, B. J.; Thimmakondu, V. S.; Stanton, J. F. ; Woods, R. C.; McMahon, R. J., Carbonyl Diazide, $OC(N_3)_2$: Synthesis, Purification, and IR Spectrum. *Inorg. Chem.* **2012**, *51,* 9846-9851.

IR Spectroscopy to Observe Reactions





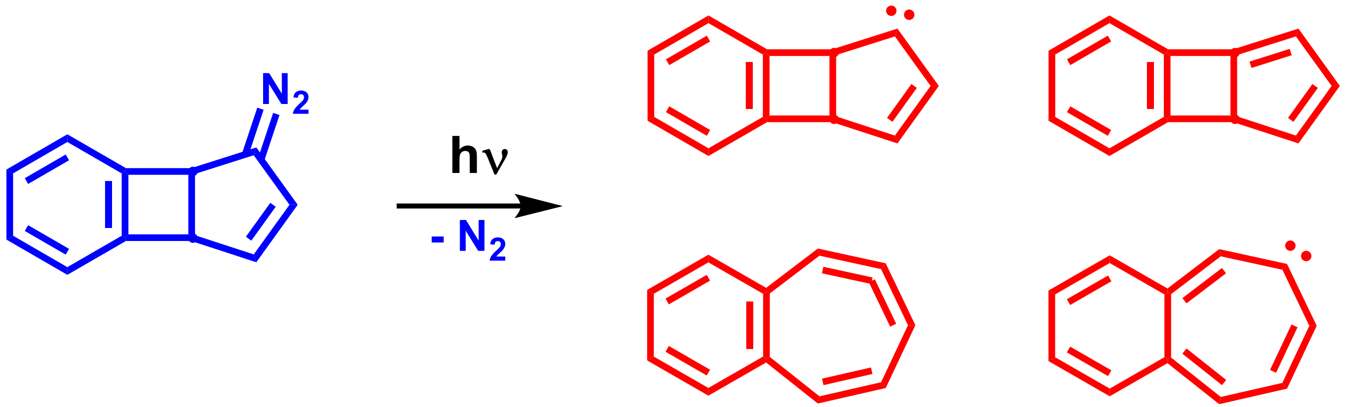


Reaction progress can be monitored by looking for the disappearance or appearance of spectral features associated with the changing functional group.

IR Spectroscopy in Photochemistry

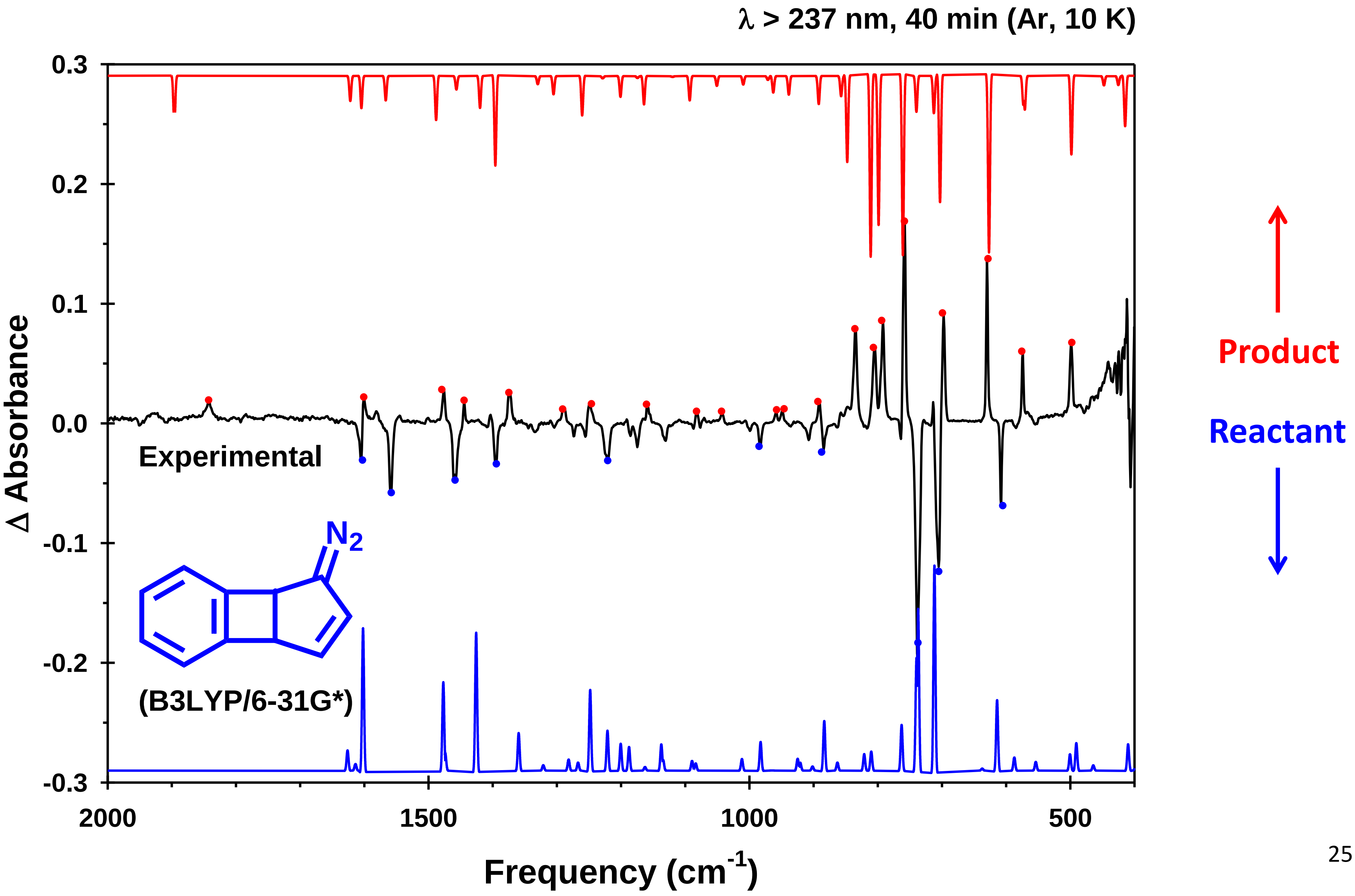
How to determine which product is formed?

- *Predict (calculate)* the IR spectrum of *each* product.
- Compare experimental IR spectrum to all of the computed IR spectra.
- A good match between experimental and computed IR spectra establishes the identity of the product.



Bonvallet, P. A.; McMahon, R. J., Generation, Characterization, and Rearrangements of 4,5-Benzocyclohepta-1,2,4,6-tetraene. *J. Am. Chem. Soc.* **2000,** *122* (38), 9332-9333.

IR Spectroscopy in Photochemistry



IR Spectroscopy – Summary

Inf**r**ared (**IR**) spectroscopy can be used to determine functional groups and bond strengths based upon molecular vibrations.

Frequency of the IR absorptions is dependent upon the bond strengths and the masses of the atoms in the molecule.

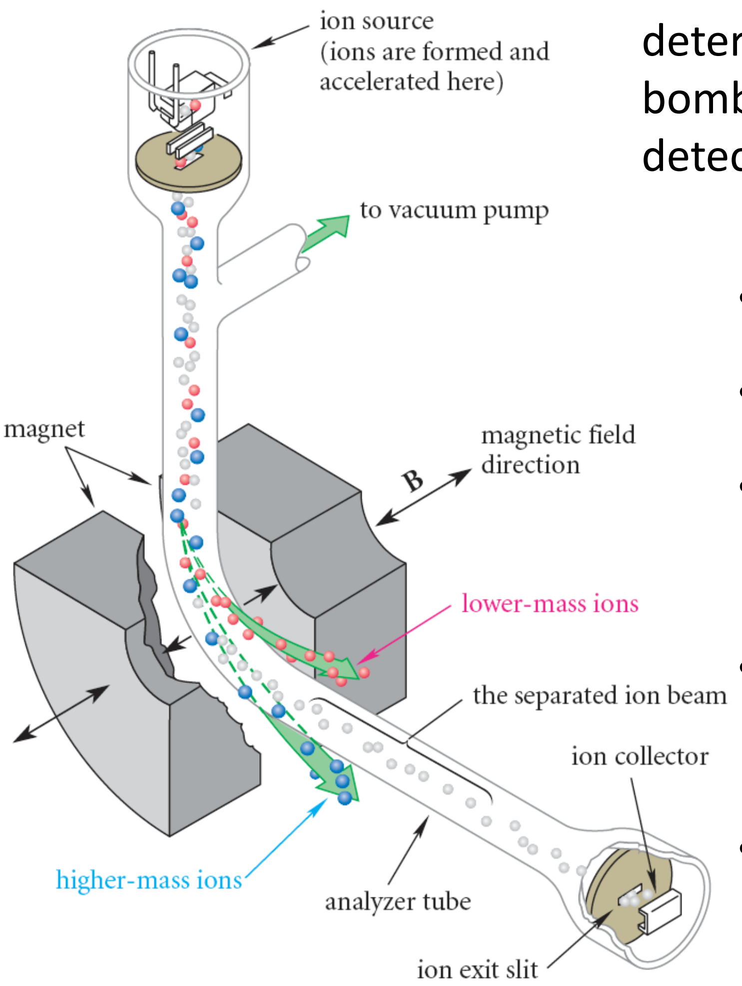
IR intensity is related to a change in dipole upon vibration.

IR spectra can be used to easily identify functional groups.

- O–H, N–H, and C–H
- C≡N and C≡C
- C=C, C=N, C=O

Much of the spectra less than 1500 cm^{-1} can be ignored at the Chem 344/345 level, but can be assigned with a deeper analysis using computational chemistry.

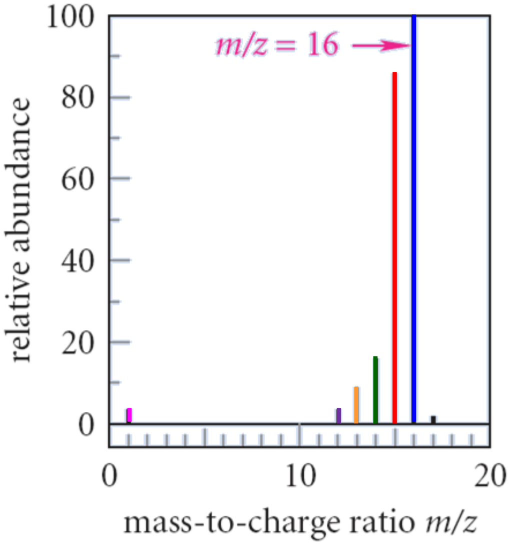
Electron Impact Mass Spectrometry (EI-MS)



Electron-Impact Mass Spectrometry (EI-MS) is used to determine molecular masses and connectivity by bombarding a molecule with high energy electrons and detecting the masses of the resulting fragments.

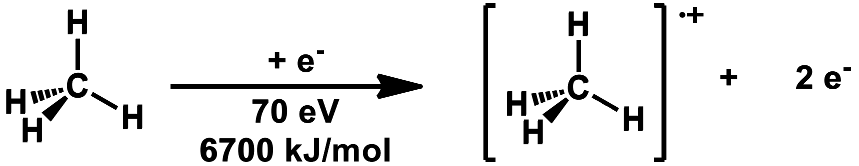
- Highly sensitive and destructive.
- Ionization from a 70 eV beam of electrons.
- Ions formed are controlled by a magnetic field, mass selected, and detected at an ion collector.
- Detection does not use electromagnetic radiation (not spectroscopy).
- Fragmentation provides structural and molecular mass information.

EI-Mass Spectrum of Methane



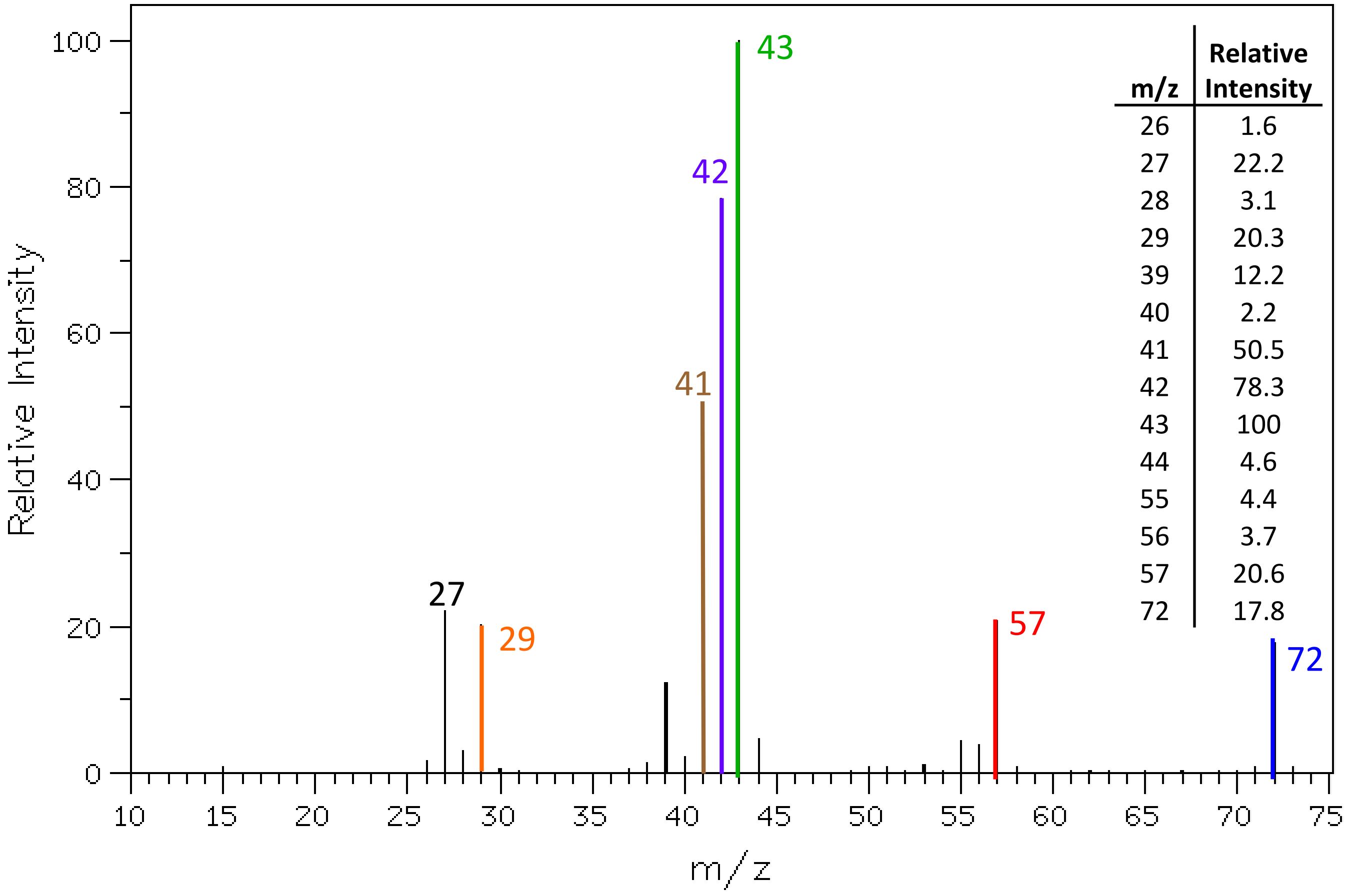
m/z	relative abundance	
1	3.36	
12	2.80	
13	8.09	
14	16.10	
15	85.90	
16	100.00	(base peak)
17	1.17	

molecular ion



radical cation

EI-Mass Spectrum of Pentane

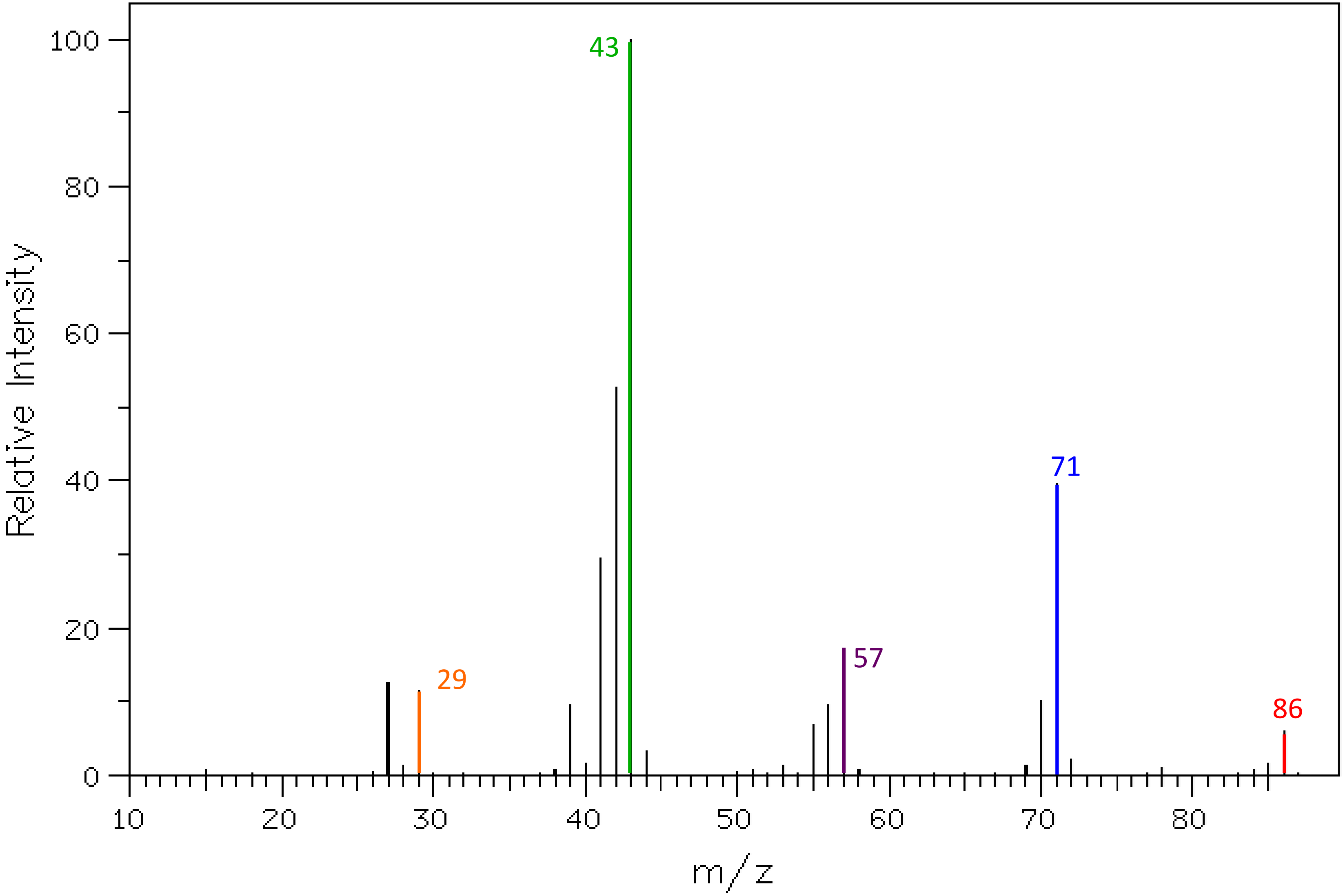


m/z	Relative Intensity
26	1.6
27	22.2
28	3.1
29	20.3
39	12.2
40	2.2
41	50.5
42	78.3
43	100
44	4.6
55	4.4
56	3.7
57	20.6
72	17.8

Often many different cation fragments appear in the mass spectrum of a single molecule.

Neutral fragments do not respond to the magnetic field and are not detected.

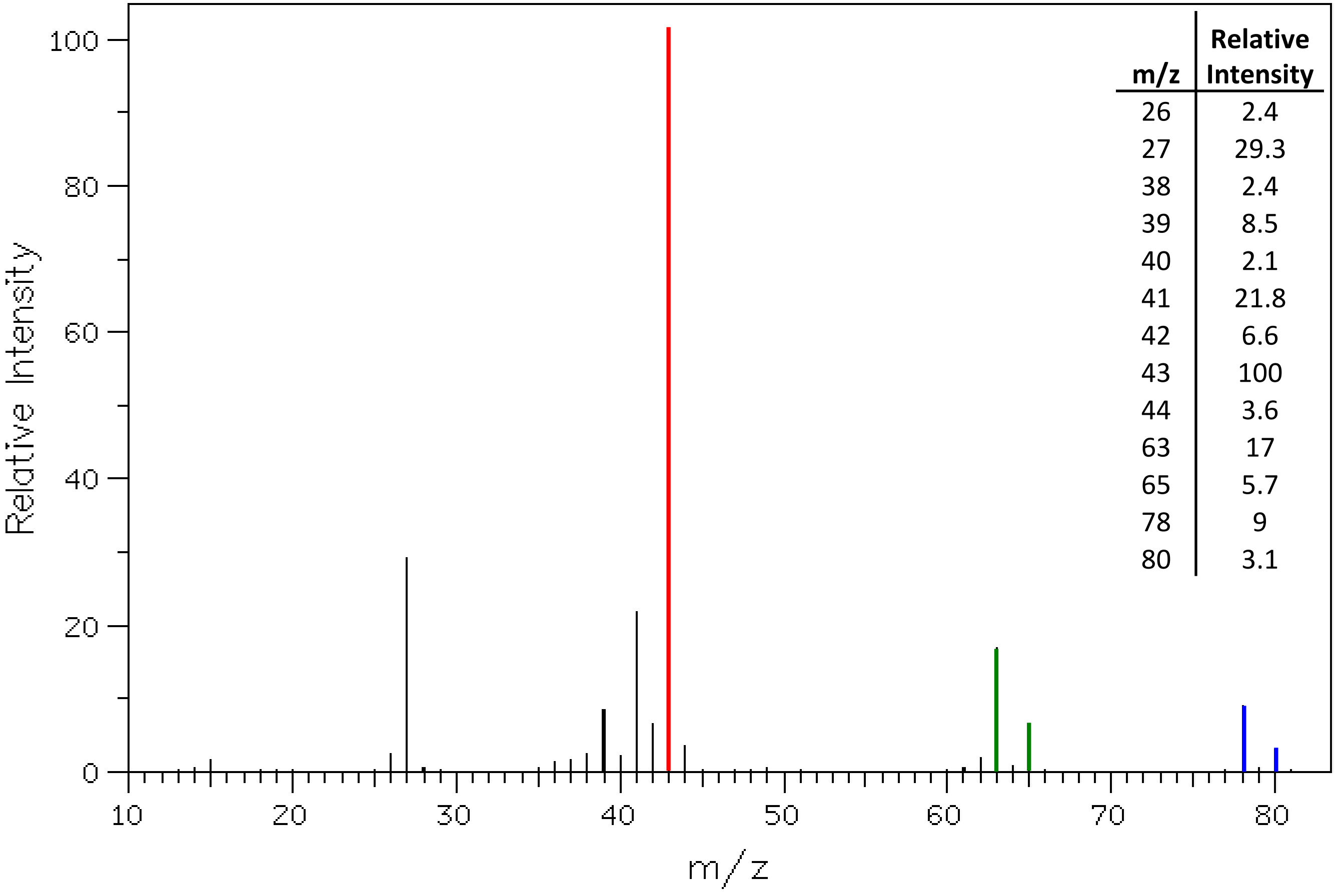
EI-Mass Spectrum of 2-Methylpentane



Isotopic Abundance and Masses for Selected Elements

Element	Isotope	Exact Mass	Abundance %
Hydrogen	^{1}H	1.007825	99.985
	^{2}H or D	2.0140	0.015
Carbon	^{12}C	12.0000	98.90
	^{13}C	13.00335	1.10
Nitrogen	^{14}N	14.00307	99.63
	^{15}N	15.00011	0.37
Oxygen	^{16}O	15.99491	99.759
	^{17}O	16.99913	0.037
	^{18}O *	17.99916	0.204
Fluorine	^{19}F	18.99840	100.0
Silicon	^{28}Si	27.97693	92.21
	^{29}Si	28.97649	4.67
	^{30}Si	29.97377	3.10
Phosphorus	^{31}P	30.97376	100.0
Sulfur	^{32}S	31.97207	95.0
	^{33}S	32.97146	0.75
	^{34}S	33.96787	4.22
Chlorine	^{35}Cl	34.96885	75.77
	^{37}Cl	36.96590	24.23
Bromine	^{79}Br	78.91834	50.69
	^{81}Br	80.91629	49.31
Iodine	^{127}I	126.90447	100.0

EI-Mass Spectrum of Isopropyl Chloride



m/z	Relative Intensity
26	2.4
27	29.3
38	2.4
39	8.5
40	2.1
41	21.8
42	6.6
43	100
44	3.6
63	17
65	5.7
78	9
80	3.1

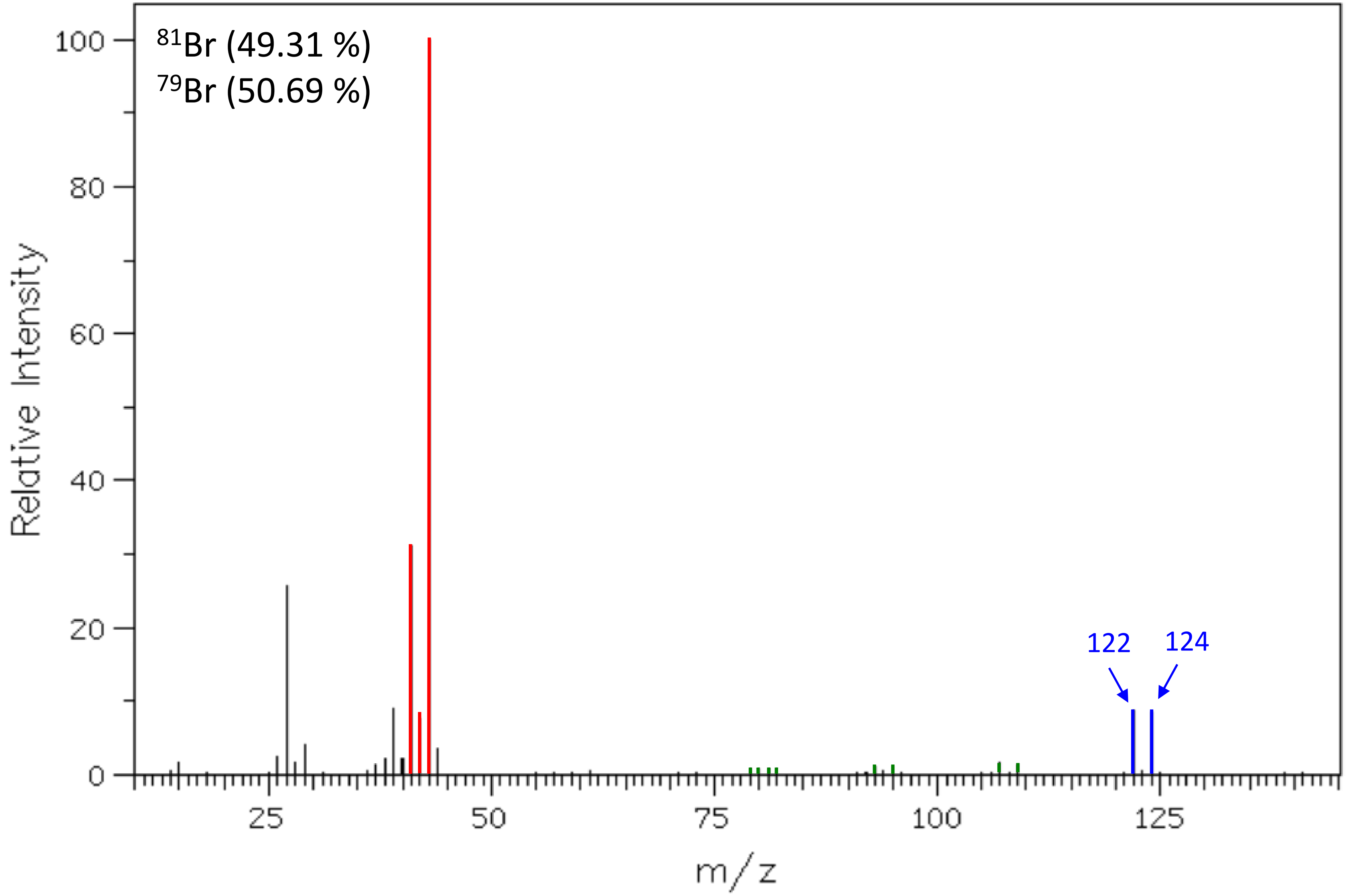
There are two easily recognizable molecular ion signals for isopropyl chloride.

Chlorine has two highly-abundant, naturally-occurring isotopes.

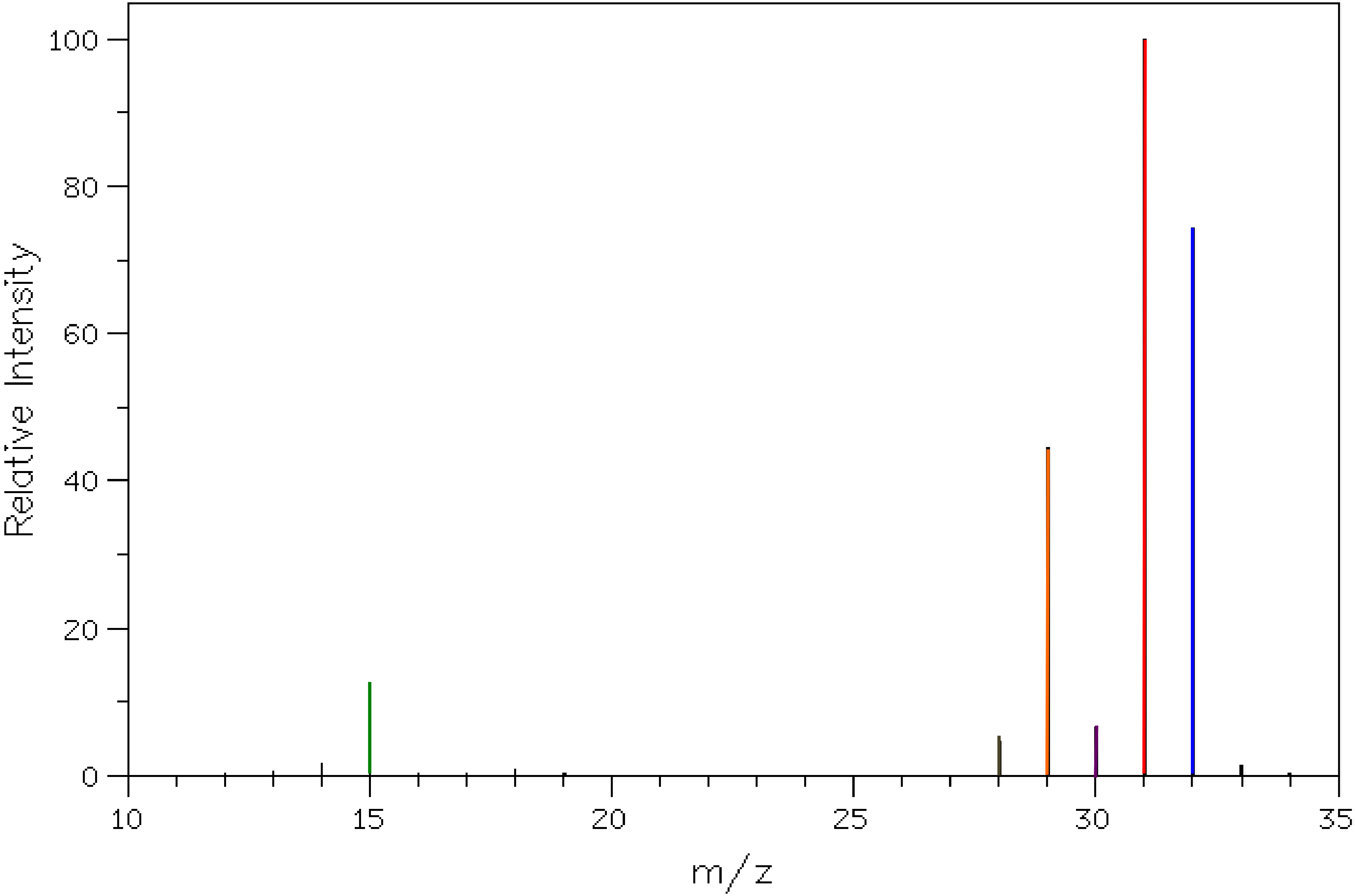
^{35}Cl (75.77 %)
^{37}Cl (24.23 %)

The isotope ratio is 3:1 which roughly matches the observed intensity ratio.

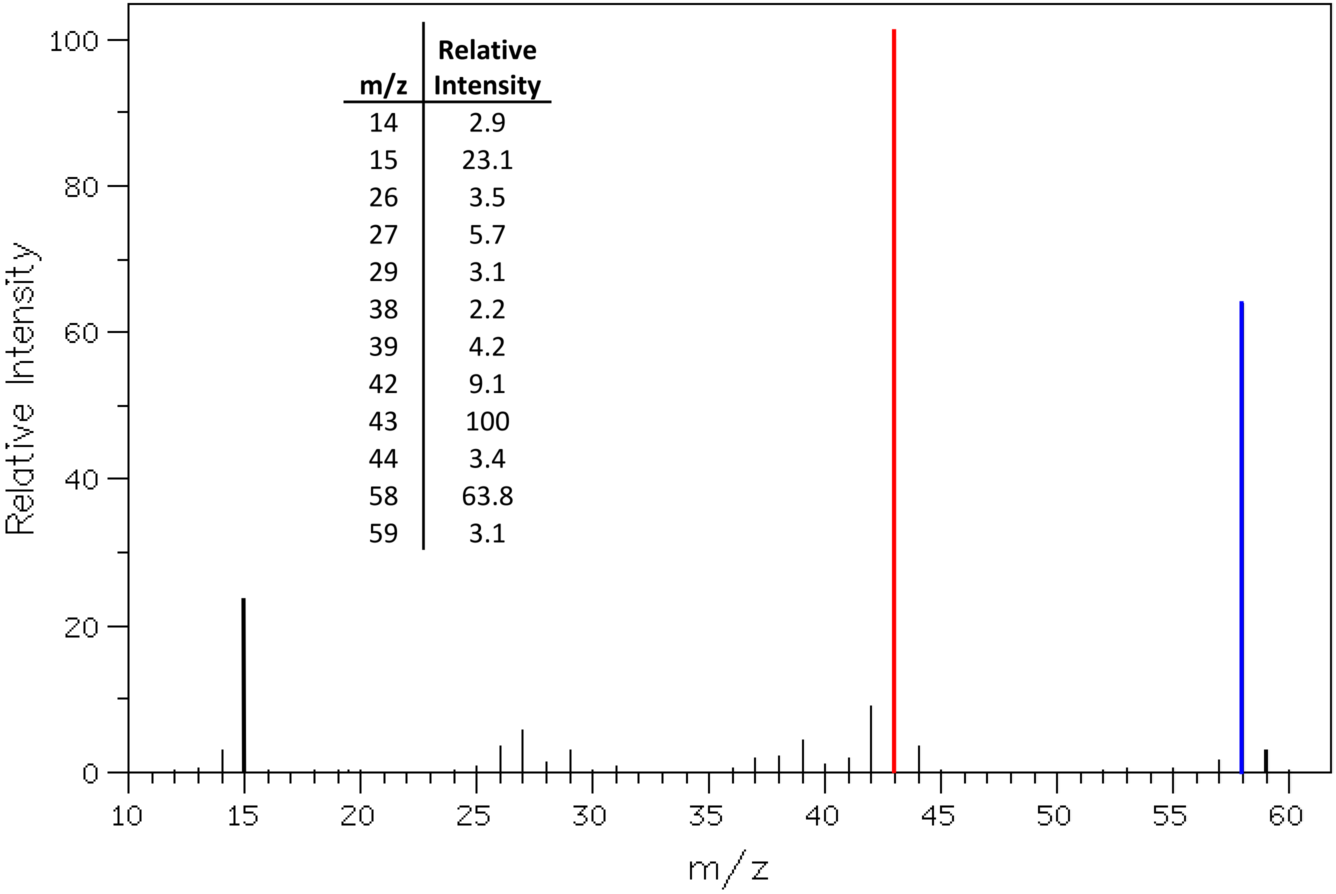
EI-Mass Spectrum of Propyl Bromide



EI-Mass Spectrum of Methanol



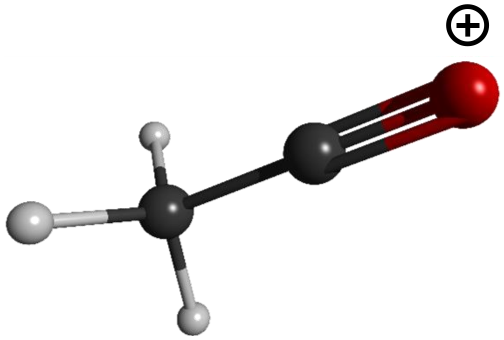
EI-Mass Spectrum of Acetone



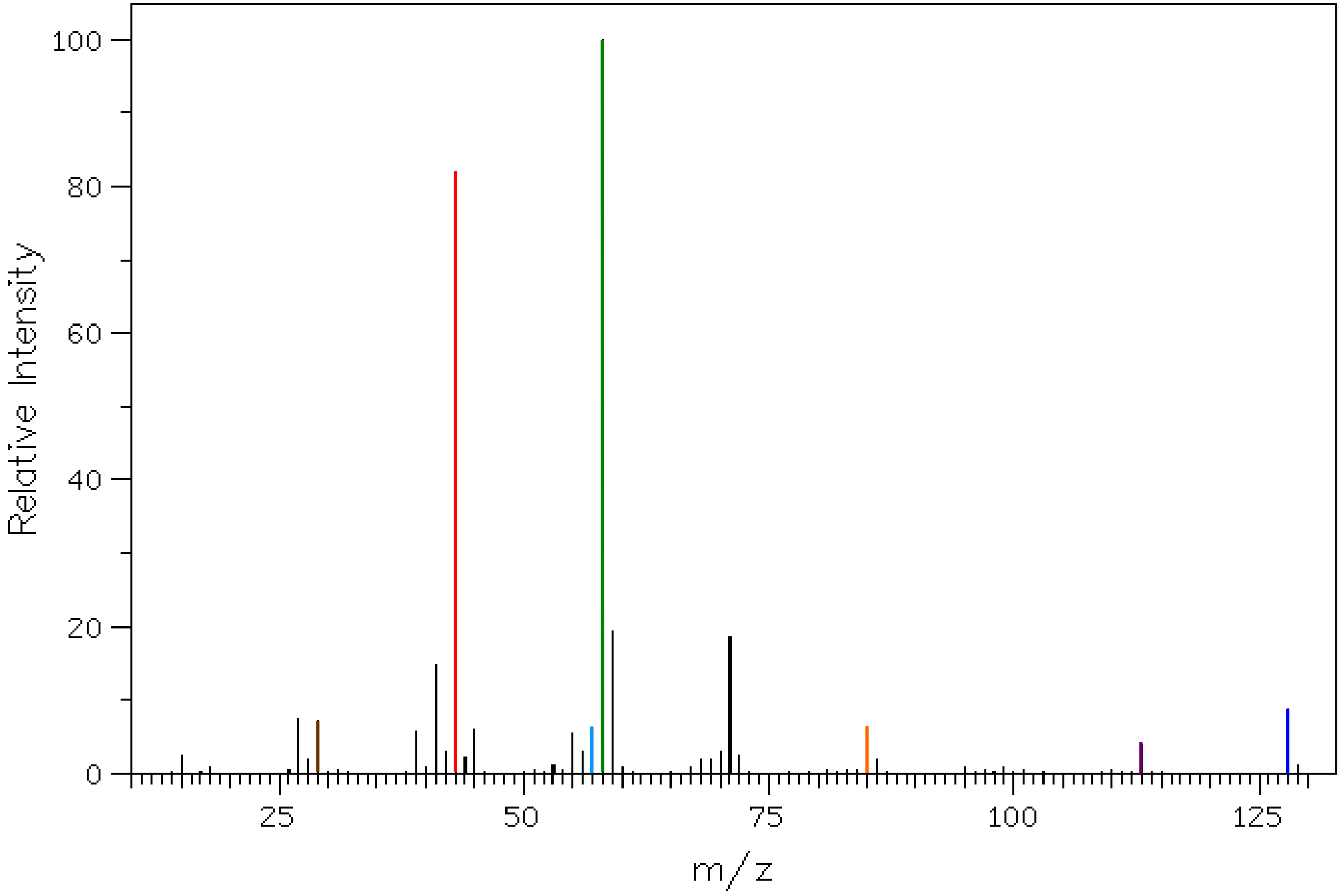
m/z	Relative Intensity
14	2.9
15	23.1
26	3.5
27	5.7
29	3.1
38	2.2
39	4.2
42	9.1
43	100
44	3.4
58	63.8
59	3.1

Acylium-type cations are common MS fragments produced from carbonyl containing compounds.

Acylium is also a reactive intermediate in EAS (Friedel–Crafts) acylation reactions.



EI-Mass Spectrum of 2-Octanone



Mass Spectrometry – Summary

Mass **S**pectrometry (**MS**) ionizes and energizes a molecule to determine its mass and connectivity through fragmentation. Electron Impact – Mass Spectrometry (EI-MS) uses high energy electrons to ionize the molecules.

$$\text{Molecule} \xrightarrow{70\text{ eV } e^-} [\text{Molecule}]^{\oplus\bullet} \longrightarrow \text{Fragments}$$

Only cationic fragments are responsive to the magnetic field and detected.

Abundance of ions detected is dependent upon their rate of formation and their rate of fragmentation.

More stable ions that are easy to form tend to be responsible for more intense signals.

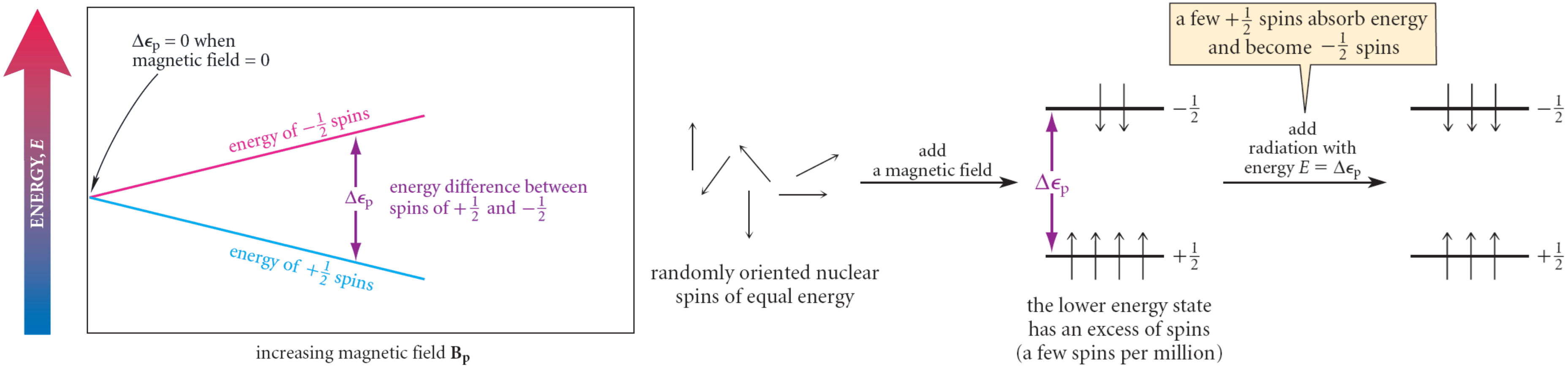
^{1}H-NMR & ^{13}C-NMR Spectroscopy

Nuclear Magnetic Resonance Spectroscopy takes advantage of the magnetic spin properties of some nuclei to provide detailed structural information about molecules.

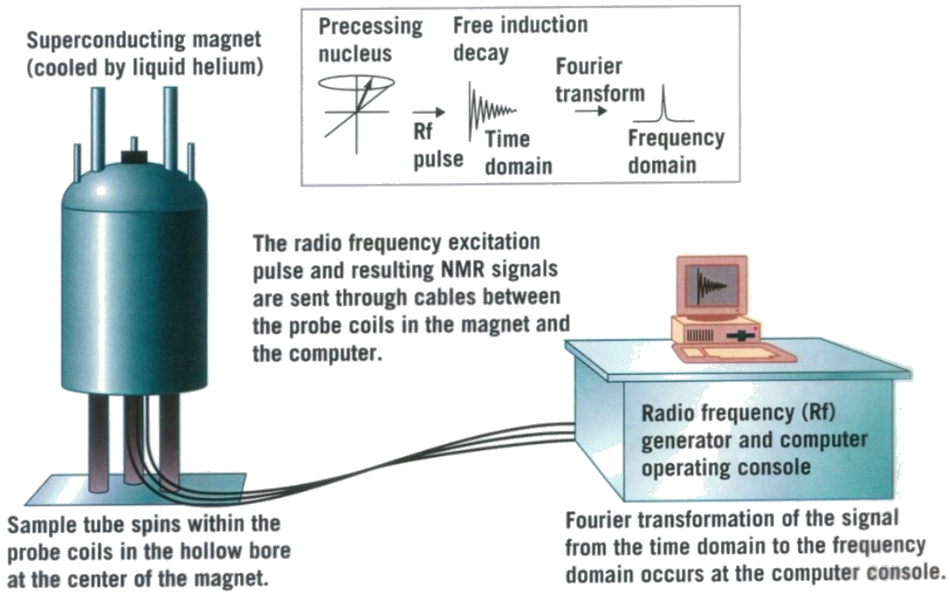
Nuclei which have an odd number of protons and/or neutrons are NMR active and can be studied by NMR.

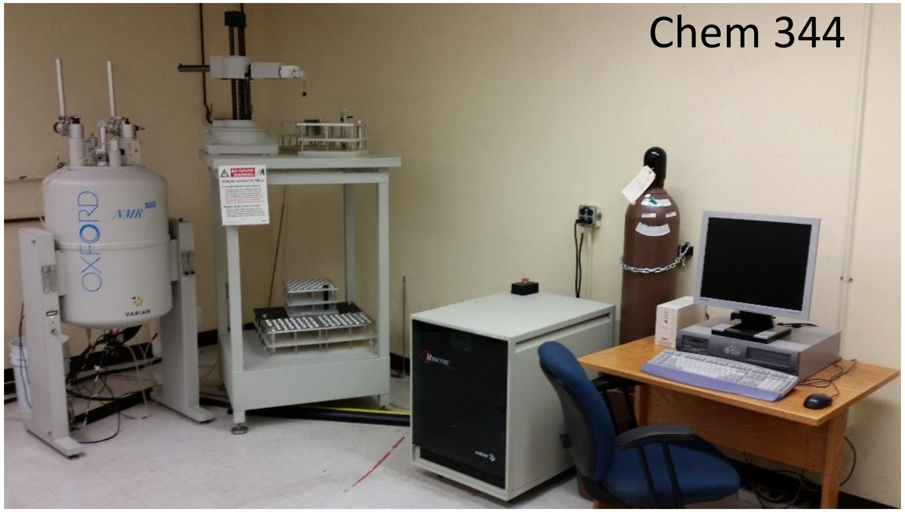
NMR active nuclei: ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P most common NMR experiments

NMR inactive nuclei: ^{12}C, ^{16}O, ^{32}S



^{1}H-NMR & ^{13}C-NMR Spectroscopy

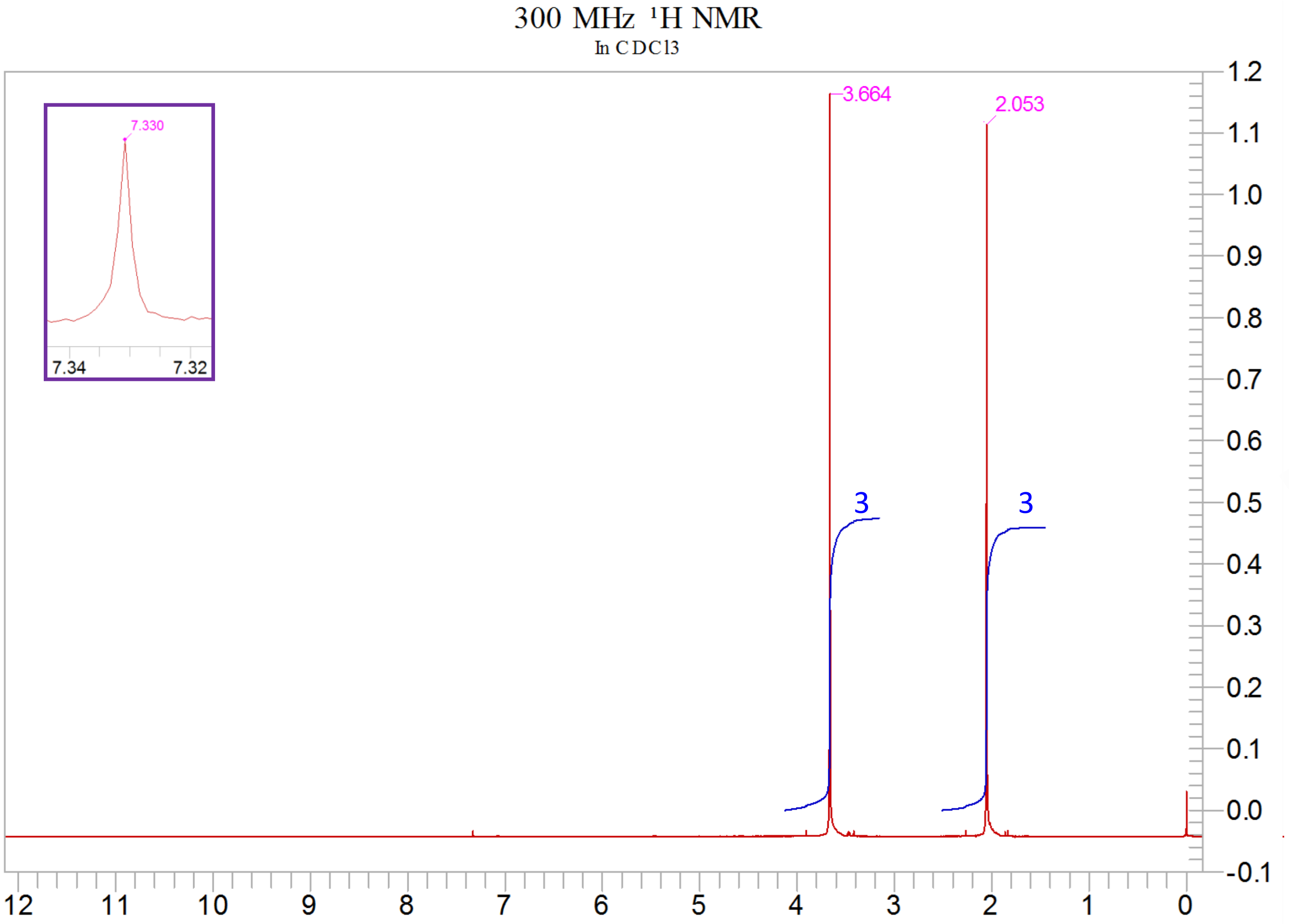


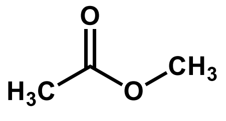


The modern NMR experiment typically involves:

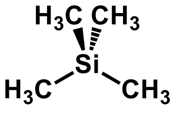
1) putting the sample in a magnetic field, usually a He-cooled super-conducting magnet
2) bombarding the sample with a radio frequency pulse sequence
3) detecting the relaxation of the sample back to its previous state
4) applying FFT to convert the signal from time space to frequency space
5) interpreting the output

^{1}H-NMR Interpretation





methyl acetate



TMS

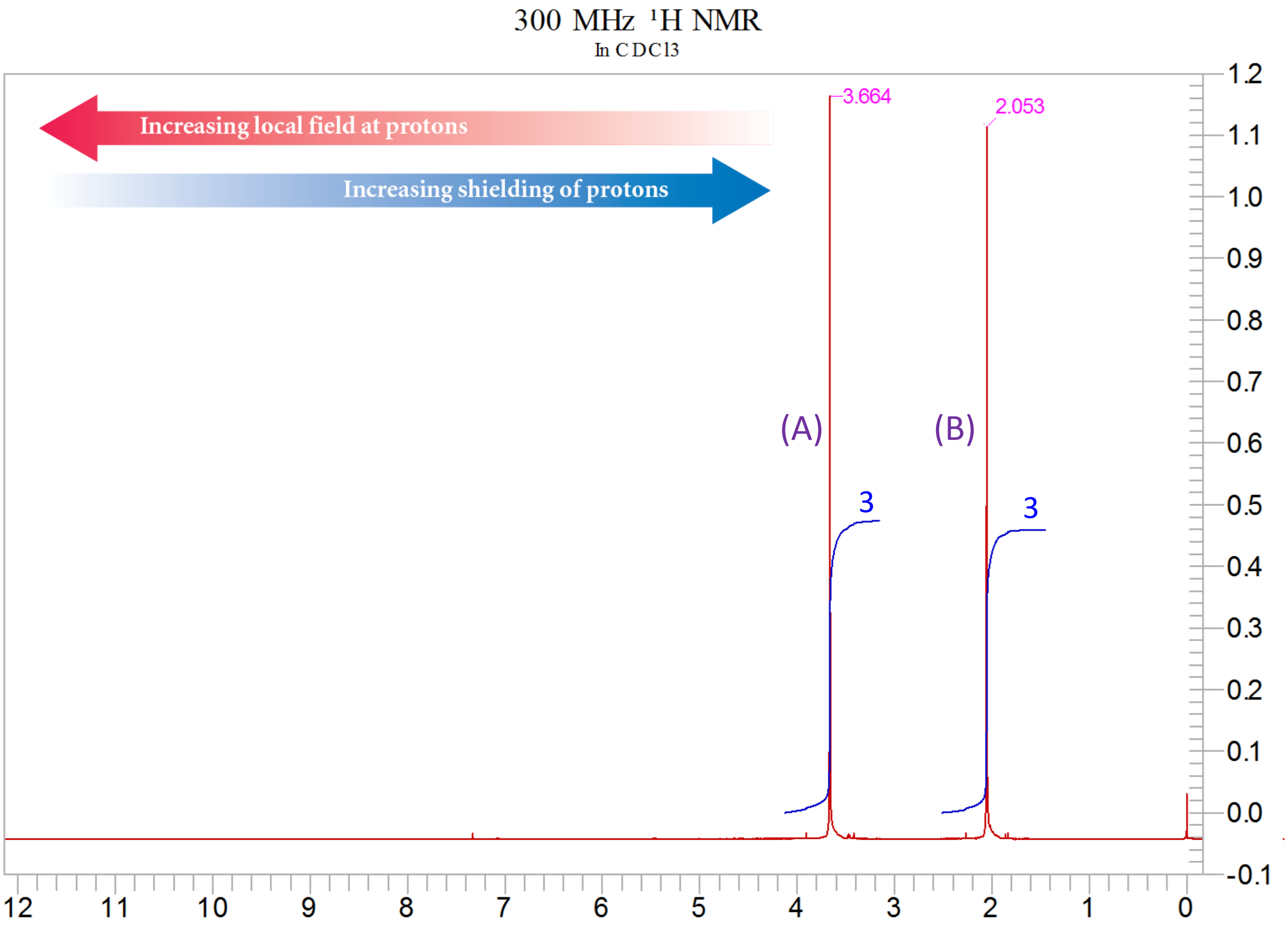
^{1}H-NMR Interpretation

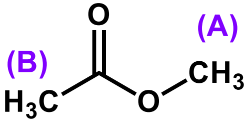
---

^{1}H-NMR spectra are filled with useful information about the sample molecule(s).

- The number of separate signals indicate the number of distinct environments in the molecule(s) in which H atoms are located. (# of signals)
- The type of environment is indicated by the upfield or downfield chemical shift of the signals. (chemical shift in ppm)
- The integration of all of the peaks in a signal provides the relative number of atoms that are making that signal. (integration value)
- The couplings or splitting patterns indicate the number of hydrogen atoms in close proximity in the molecule that are in nonequivalent environments. (coupling pattern)
- The substitution pattern or stereochemistry can often be unambiguously determined by the size of the coupling constants. (coupling constant value)
- The purity or relative abundance of two molecules in the sample can be determined by comparing the integration of two signals in separate molecules.

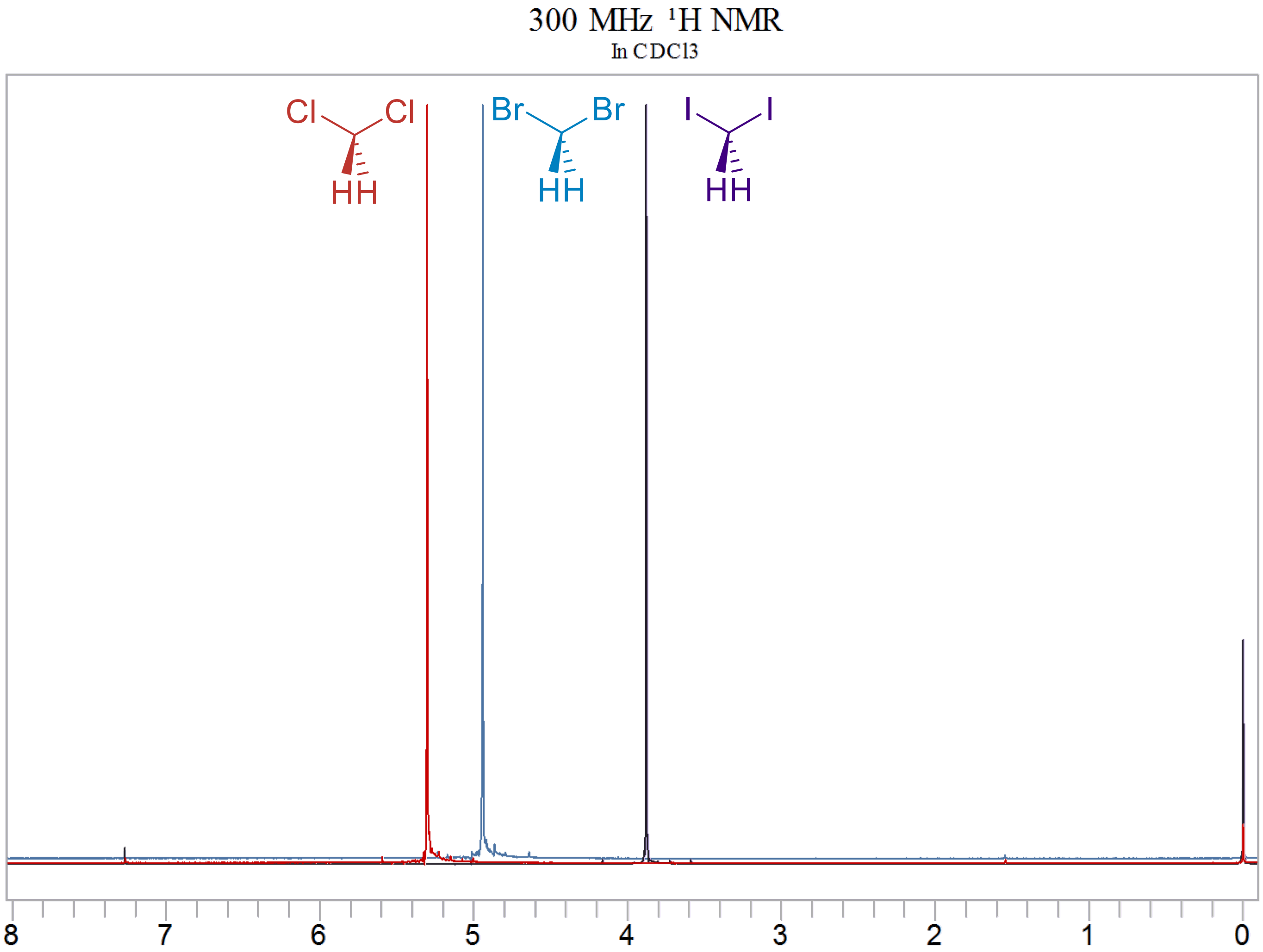
^{1}H-NMR Chemical Shift





methyl acetate

^{1}H-NMR Chemical Shift

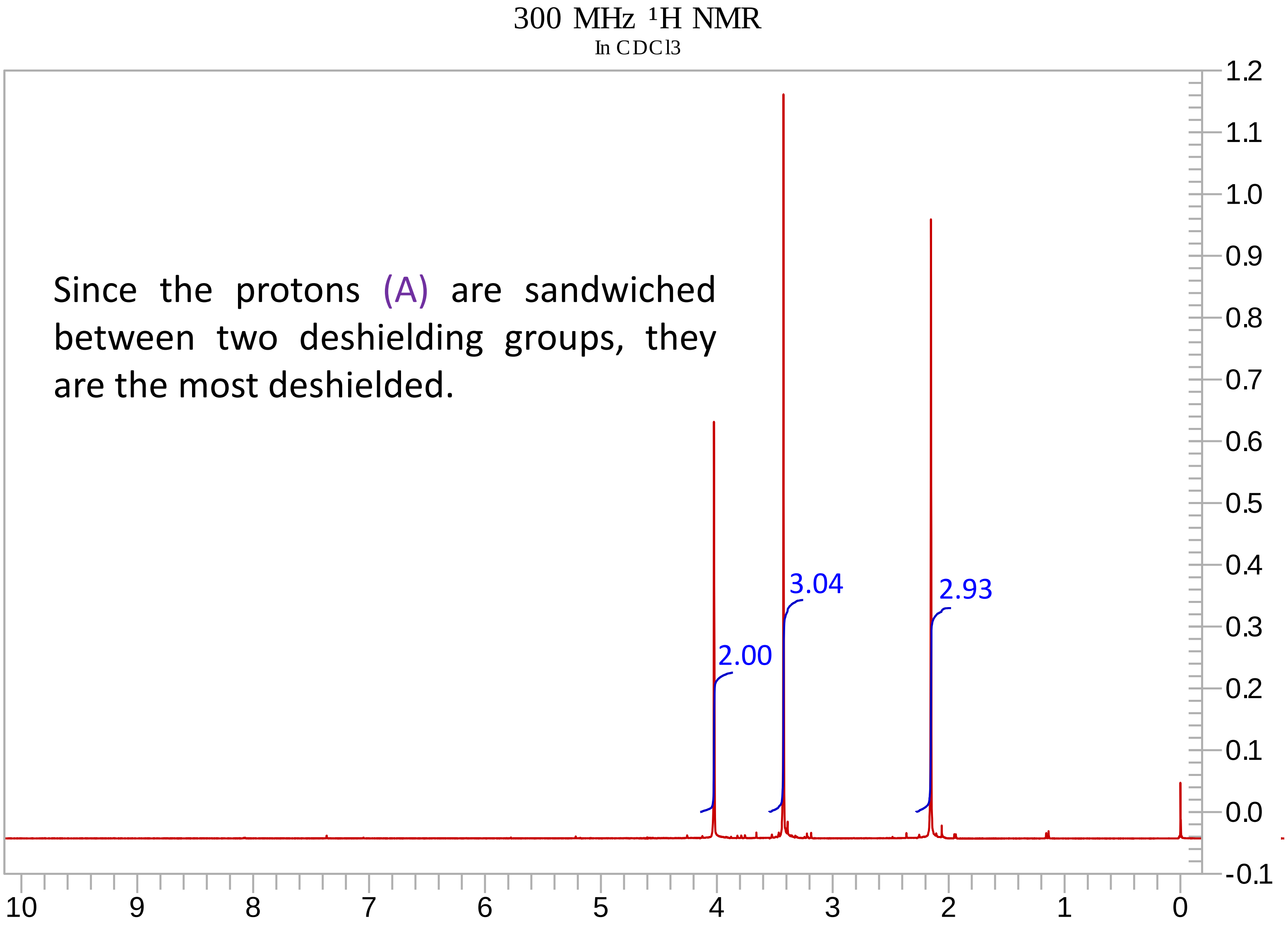


EWG's tend to be deshielding and cause a downfield shift.

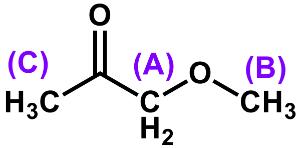
Pauling
Electronegativities
F = 4.0
Cl = 3.16
Br = 2.96
I = 2.66

CH_2F_2 ^{1}H-NMR
= δ 5.45 ppm

^{1}H-NMR Chemical Shift

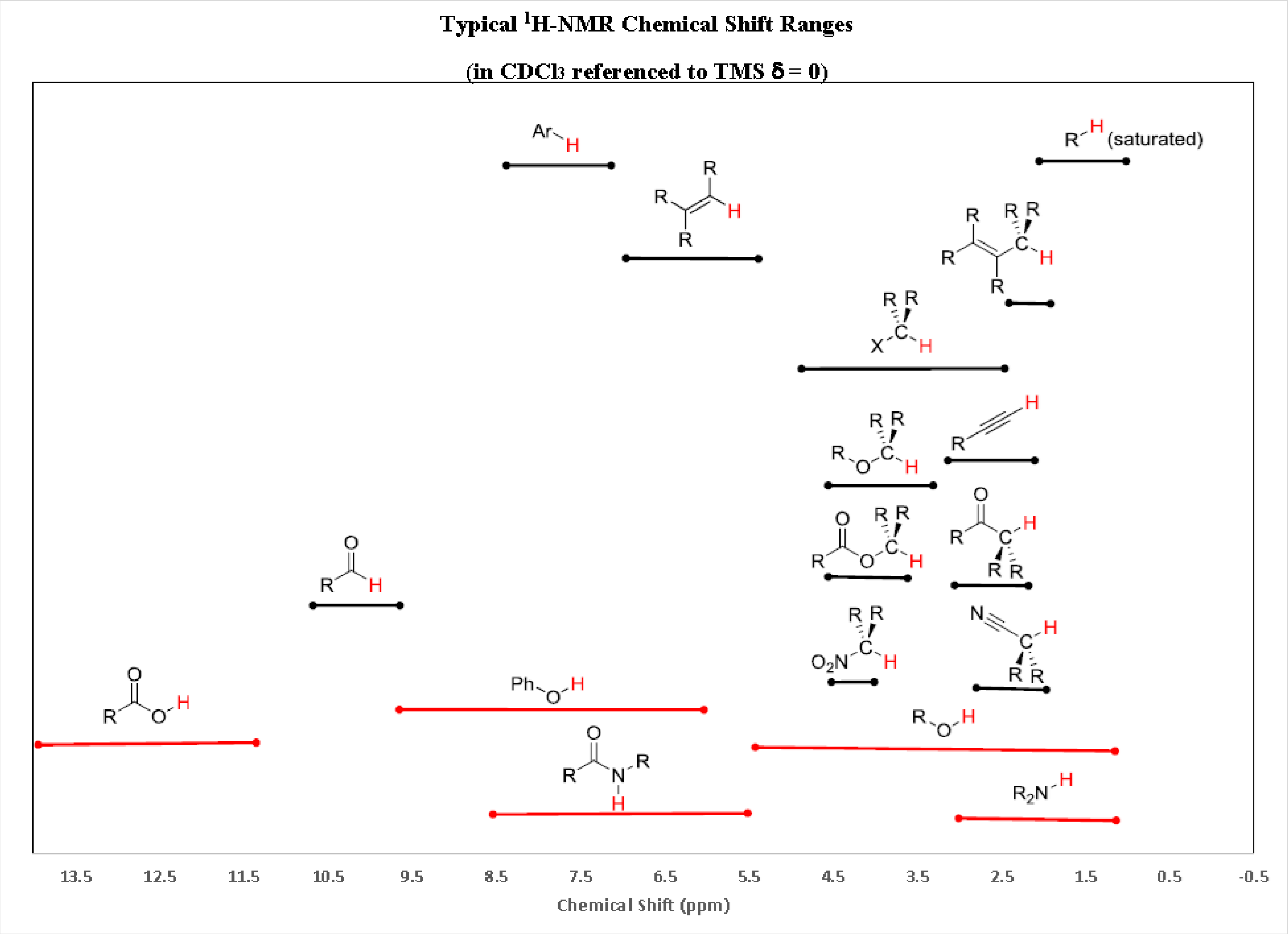


Since the protons (A) are sandwiched between two deshielding groups, they are the most deshielded.



methoxyacetone

^{1}H-NMR Chemical Shift



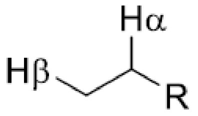
Typical ^{1}H-NMR Chemical Shift Ranges

(in $CDCl_3$ referenced to TMS δ = 0)

^{1}H-NMR Chemical Shift

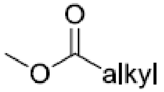
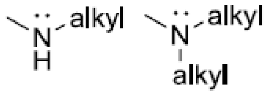
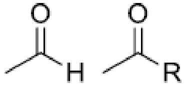
Curphy-Morrison Additivity Constants for Proton NMR

α and β Substituent Effects on:

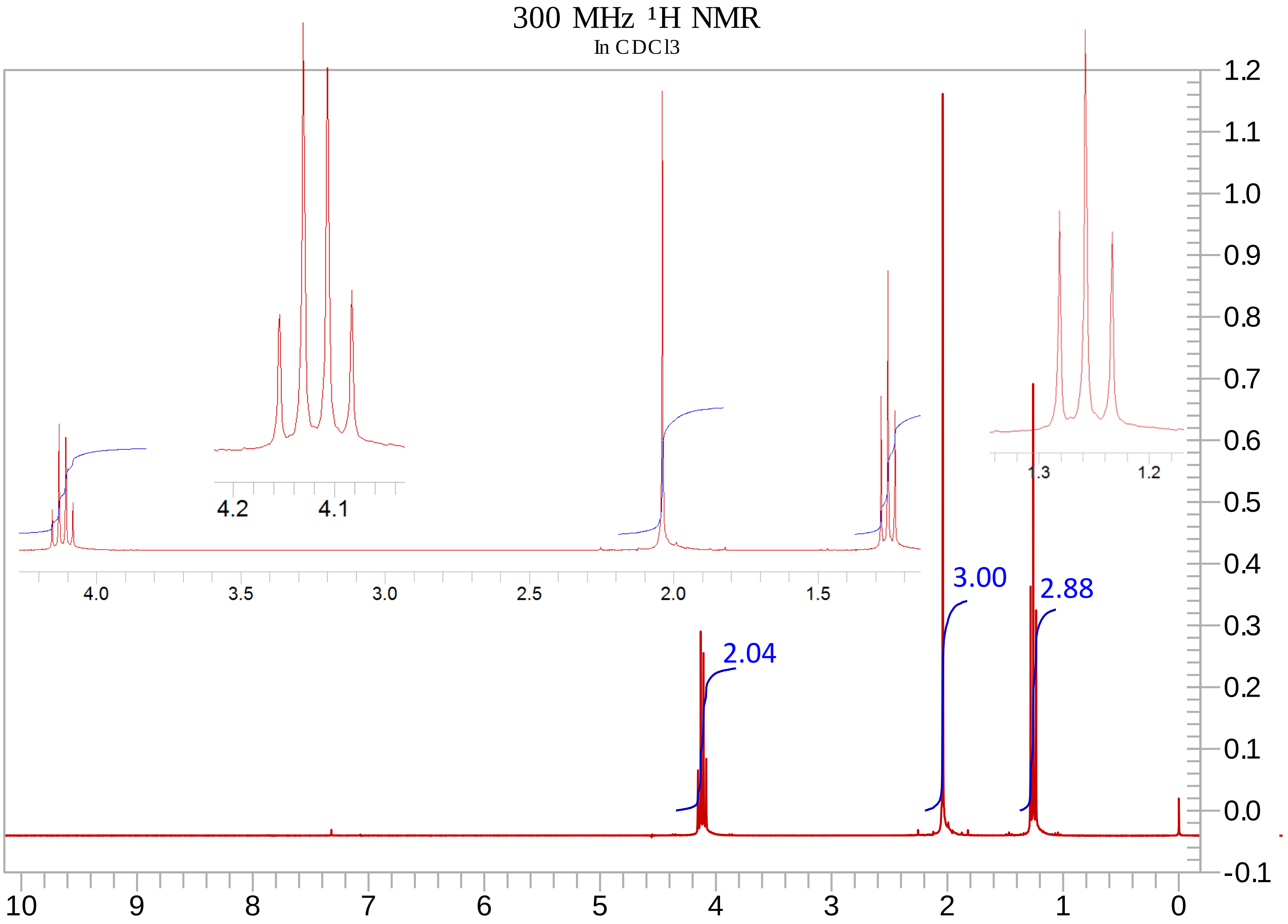


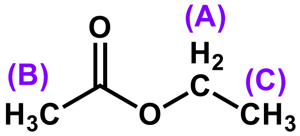
Standard Shift: Methyl ($-CH_3$) 0.90 δ, Methylene ($-CH_2-$) 1.20 δ, Methine (-CH-) 1.55 δ

Shift Estimate: δ_H = Standard Shift + $\Sigma_{\alpha\text{-shifts}} + \Sigma_{\beta\text{-shifts}}$

Substituent (R)		α-shift	β-shift	Substituent (R)		α-shift	β-shift
Cl	$-CH_3$	2.30	0.60		$-CH_3$	2.90	0.40
	$-CH_2-$	2.30	0.55		$-CH_2-$	2.95	0.45
	-CH-	2.55	0.15		-CH-	3.45	----
Br	$-CH_3$	1.80	0.80		$-CH_3$	2.84	0.39(1)
	$-CH_2-$	2.15	0.80		$-CH_2-$	2.66(6)	0.28(5)
	-CH-	2.20	0.25		-CH-	3.16(3)	0.32(2)
I	$-CH_3$	1.80	0.80		$-CH_3$	3.01	0.47(2)
	$-CH_2-$	2.15	0.80		$-CH_2-$	2.90(5)	0.43(2)
	-CH-	2.20	0.25		-CH-	2.64(1)	0.61(1)
Aryl	$-CH_3$	1.45	0.35		$-CH_3$	1.25	0.20
	$-CH_2-$	1.45	0.55		$-CH_2-$	1.40	0.15
	-CH-	1.35	----		-CH-	1.35	----
	$-CH_3$	1.25	0.25		$-CH_3$	2.08(8)	0.28(10)
	$-CH_2-$	1.10	0.30		$-CH_2-$	2.03(12)	0.34(2)
	-CH-	0.95	----		-CH-	2.33(2)	?

^{1}H-NMR Coupling





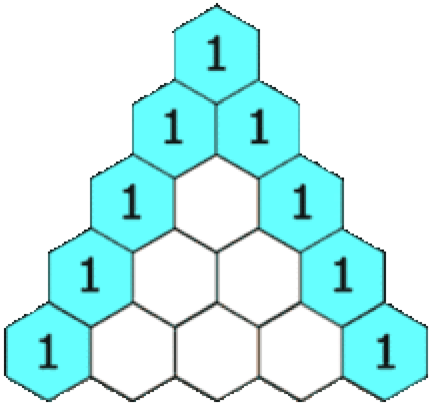
ethyl acetate

^{1}H-NMR Coupling

The *simplest* coupling patterns (resulting from equal coupling constants) in ^{1}H-NMR can be interpreted by the *n+1 rule* where the number of peaks in a signal is equal to the number of nonequivalent vicinal hydrogen atom neighbors plus one.

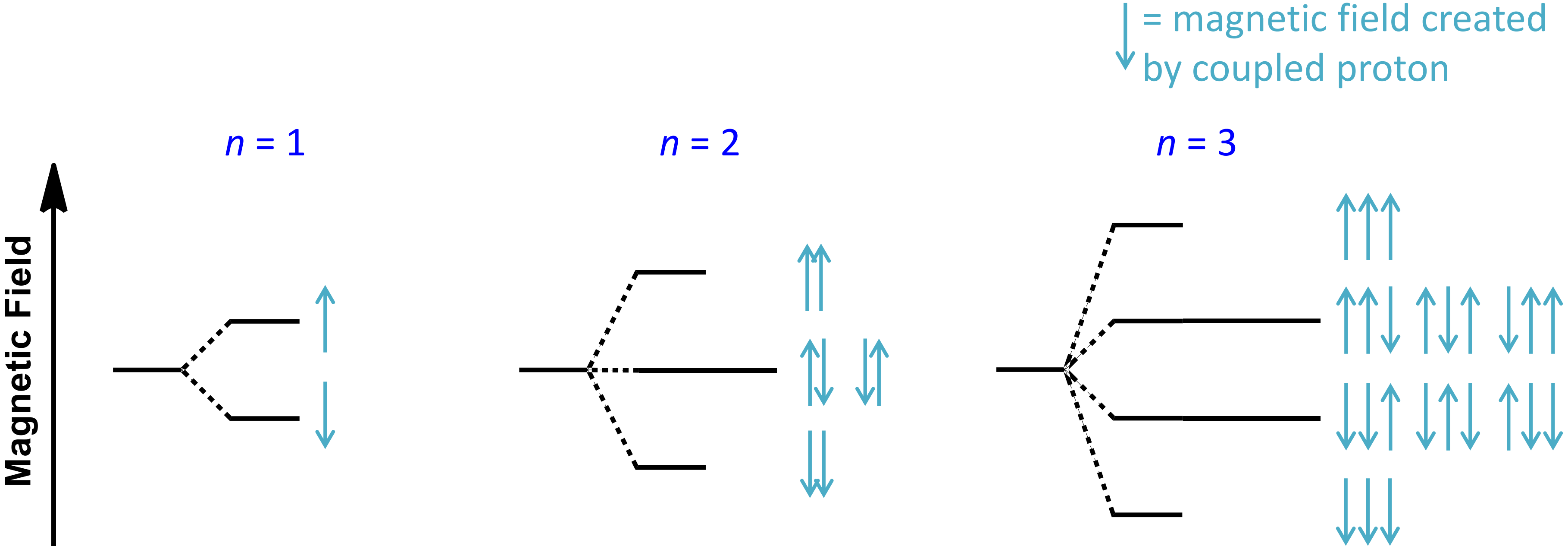
$$peaks = n + 1,$$

n	**Number of lines in splitting pattern (name)**	**Relative line intensity within splitting pattern**
0	1 (singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

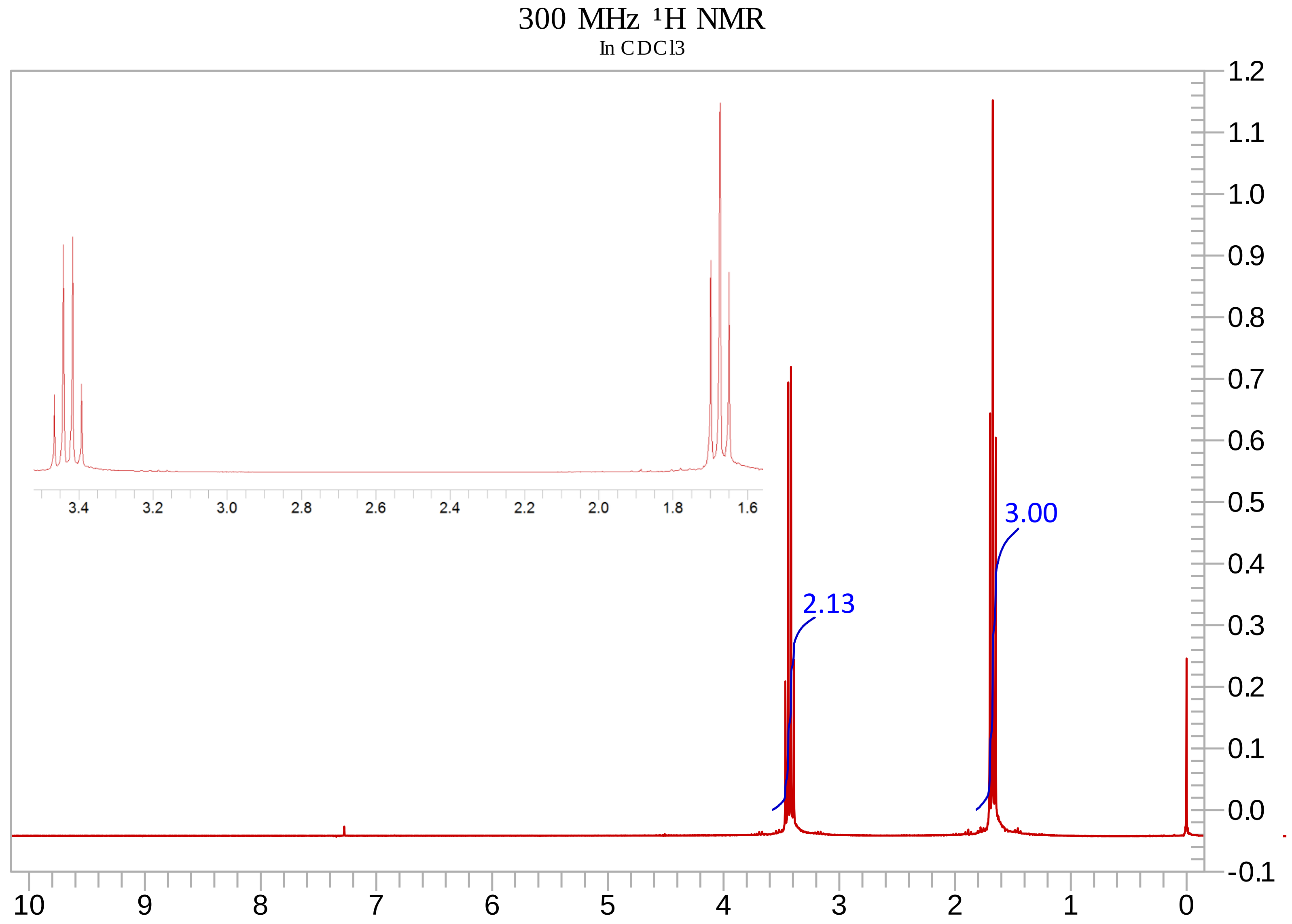


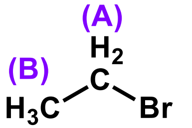
^{1}H-NMR Coupling

The coupling of vicinal protons is due to the magnetic field created by each proton due to its spin. Each vicinal proton can either align parallel or anti-parallel to the external magnetic field which alters the resonance of individual protons.



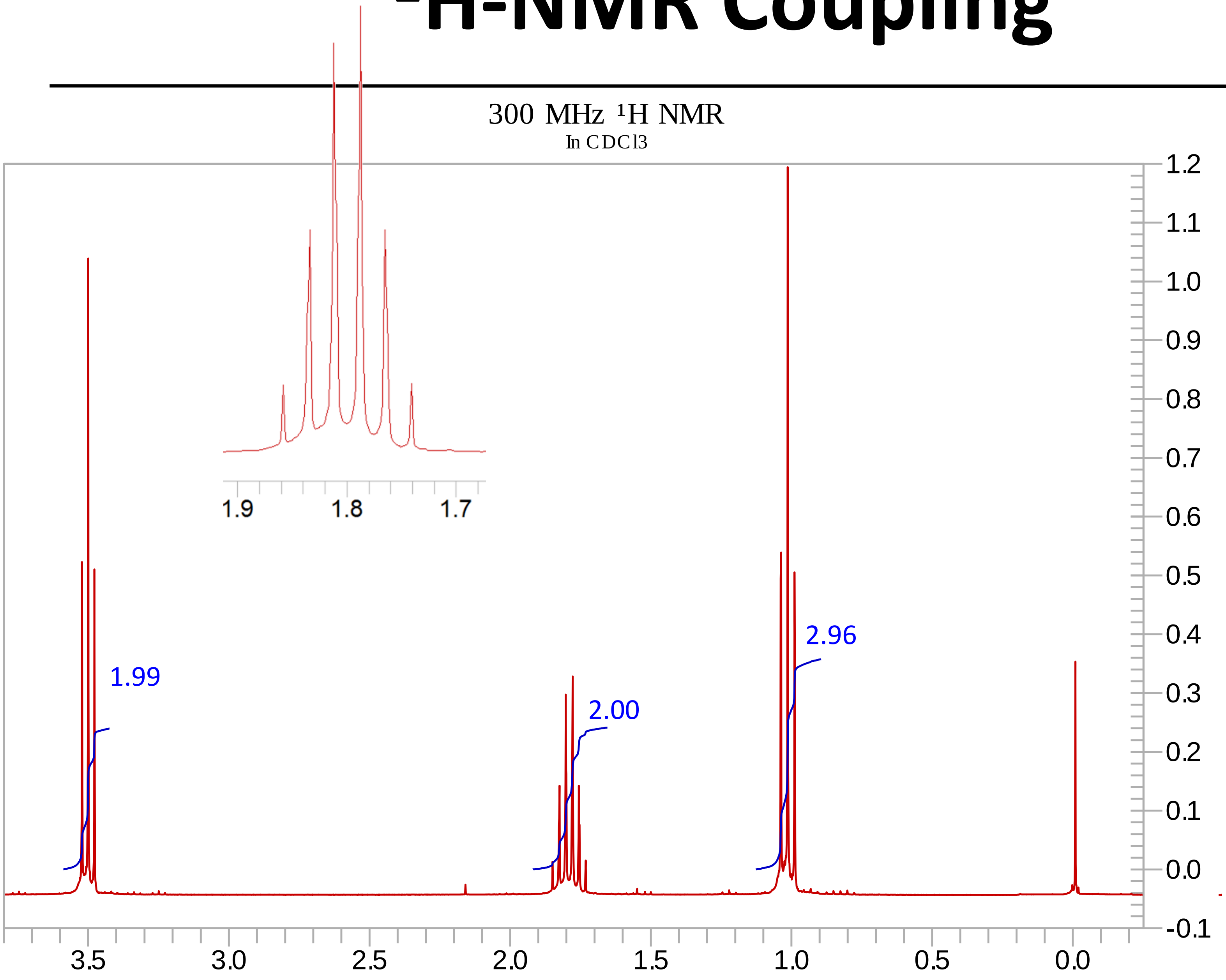
^{1}H-NMR Coupling

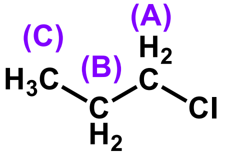




ethyl bromide

^{1}H-NMR Coupling

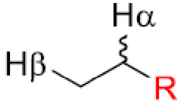




propyl chloride

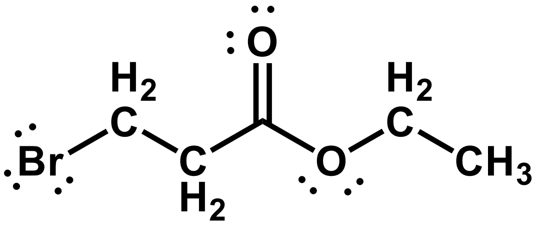
Estimating Chemical Shift via Curphy - Morrison parameters

α and β Substituent Effects on:

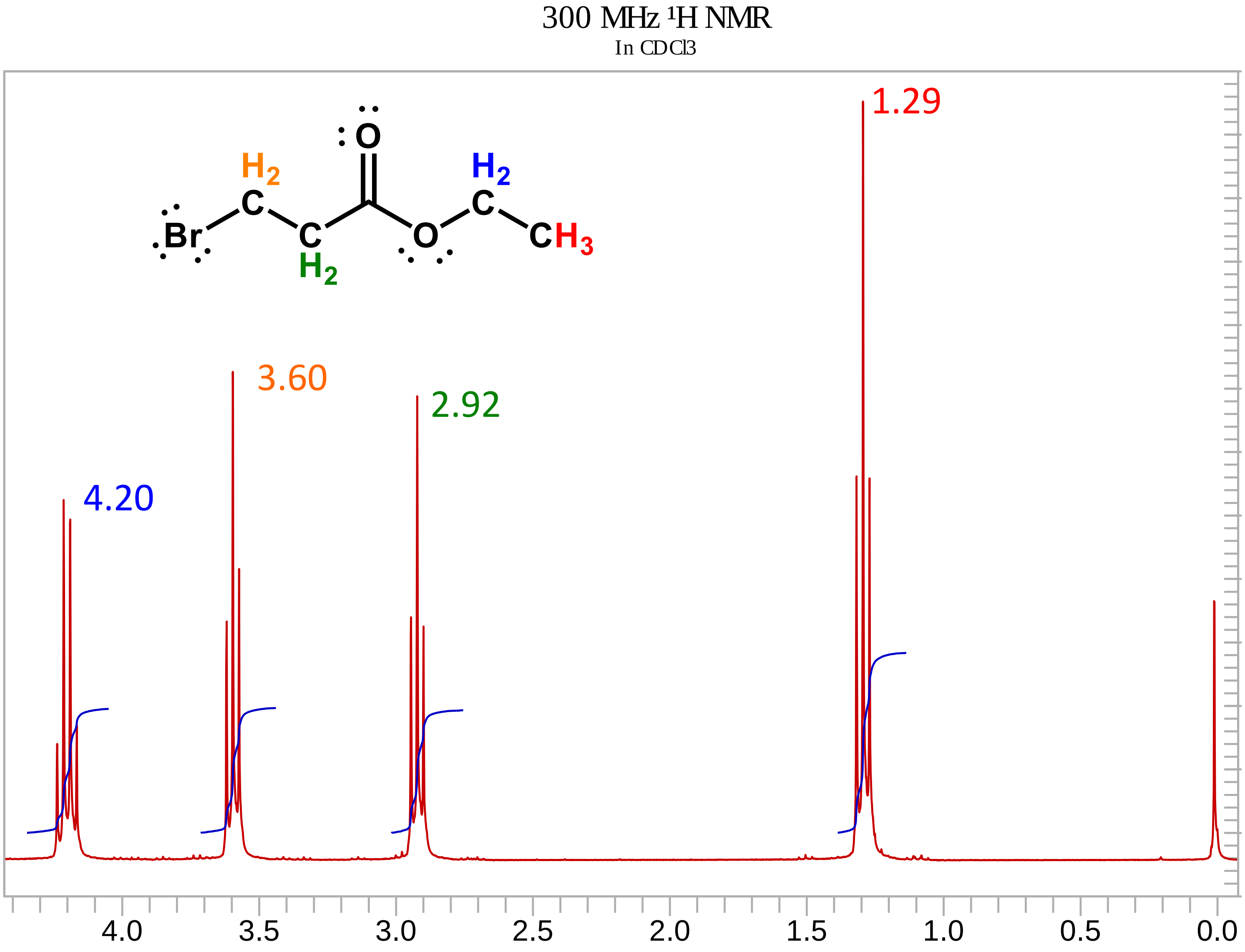


Standard Shift: Methyl (-CH_3) 0.90 δ, Methylene (-CH_2-) 1.20 δ, Methine (-CH-) 1.55 δ

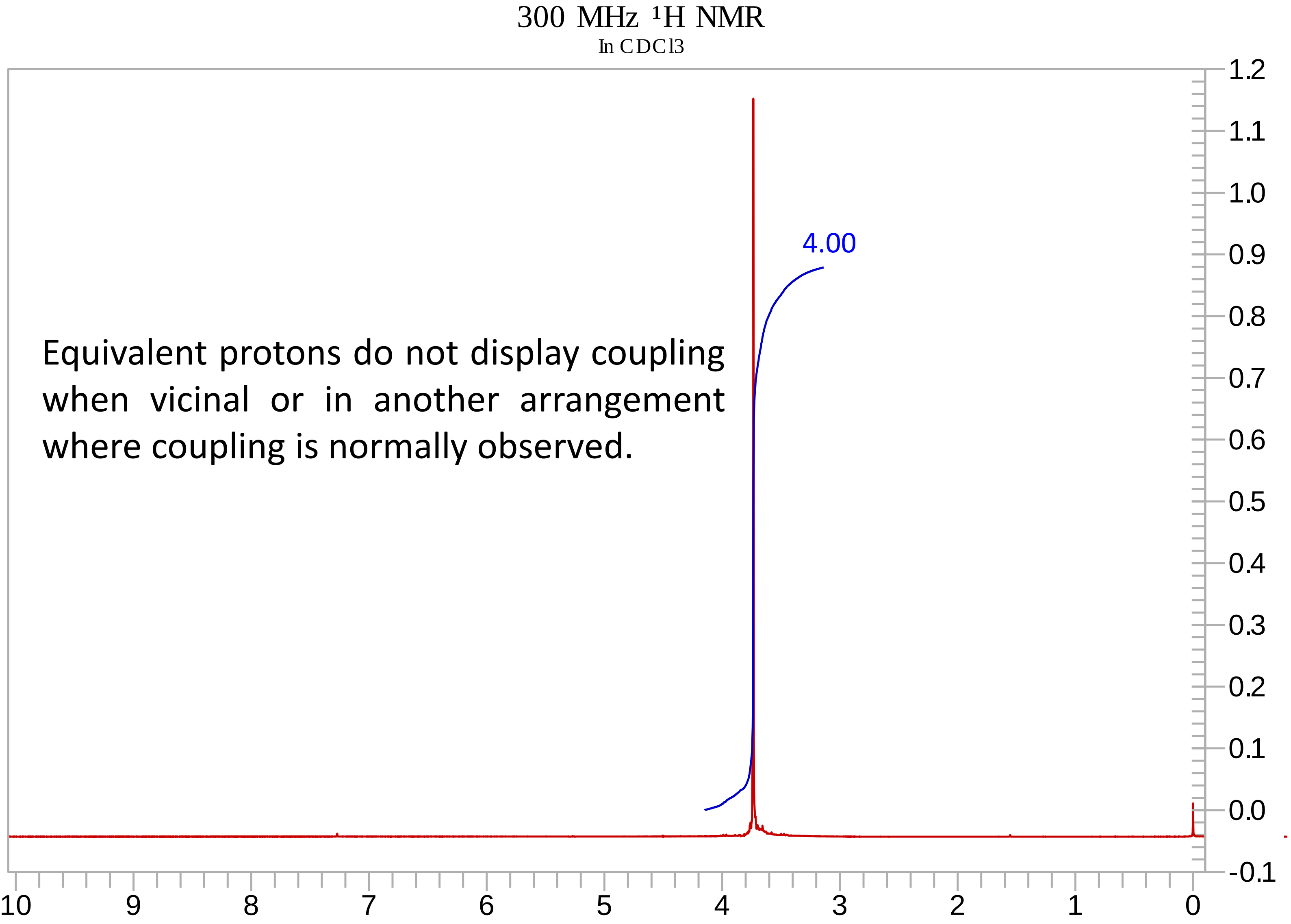
Shift Estimate: δ_H = Standard Shift + $\Sigma_{\alpha\text{-shifts}}$ + $\Sigma_{\beta\text{-shifts}}$



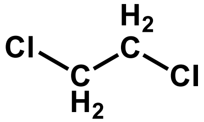
Estimating Chemical Shift via Curphy - Morrison parameters



^{1}H-NMR Coupling – Or Lack Thereof…

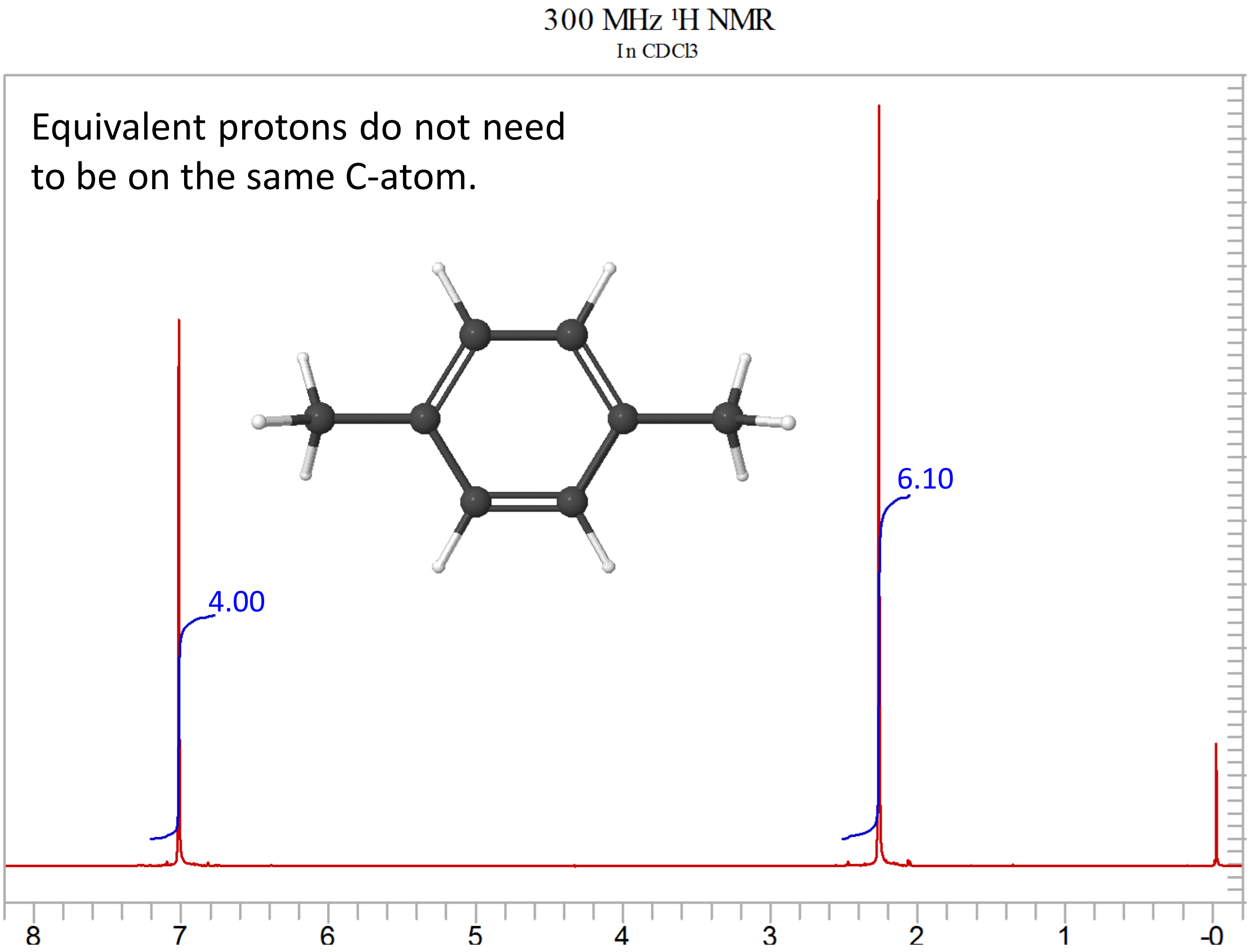


Equivalent protons do not display coupling when vicinal or in another arrangement where coupling is normally observed.

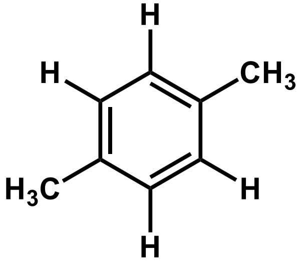


1,2-dichloroethane

^{1}H-NMR Coupling – Or Lack Thereof…



Equivalent protons do not need to be on the same C-atom.



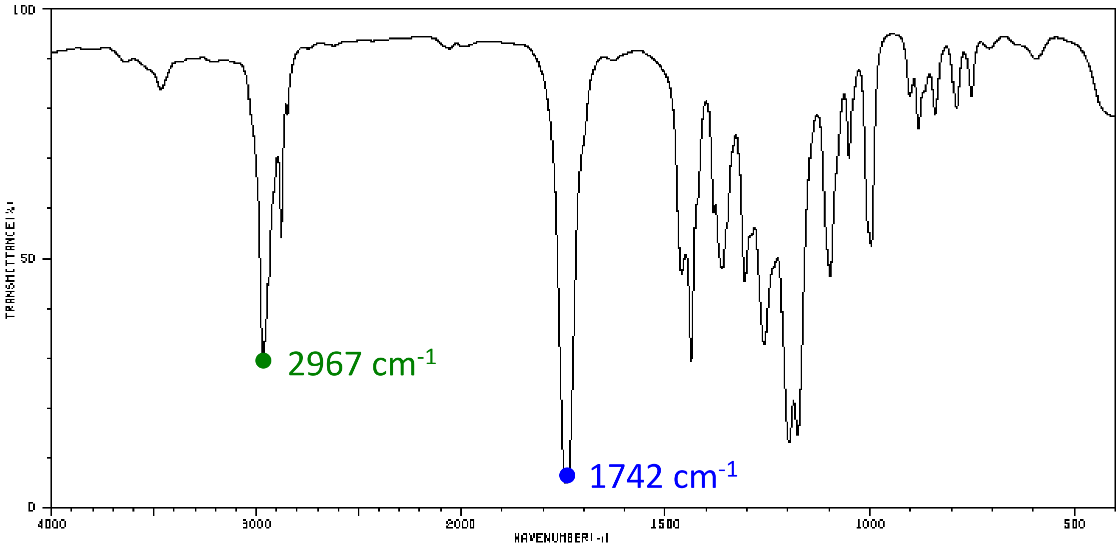
***p*-xylene**

Structure Determination – $C_5H_{10}O_2$

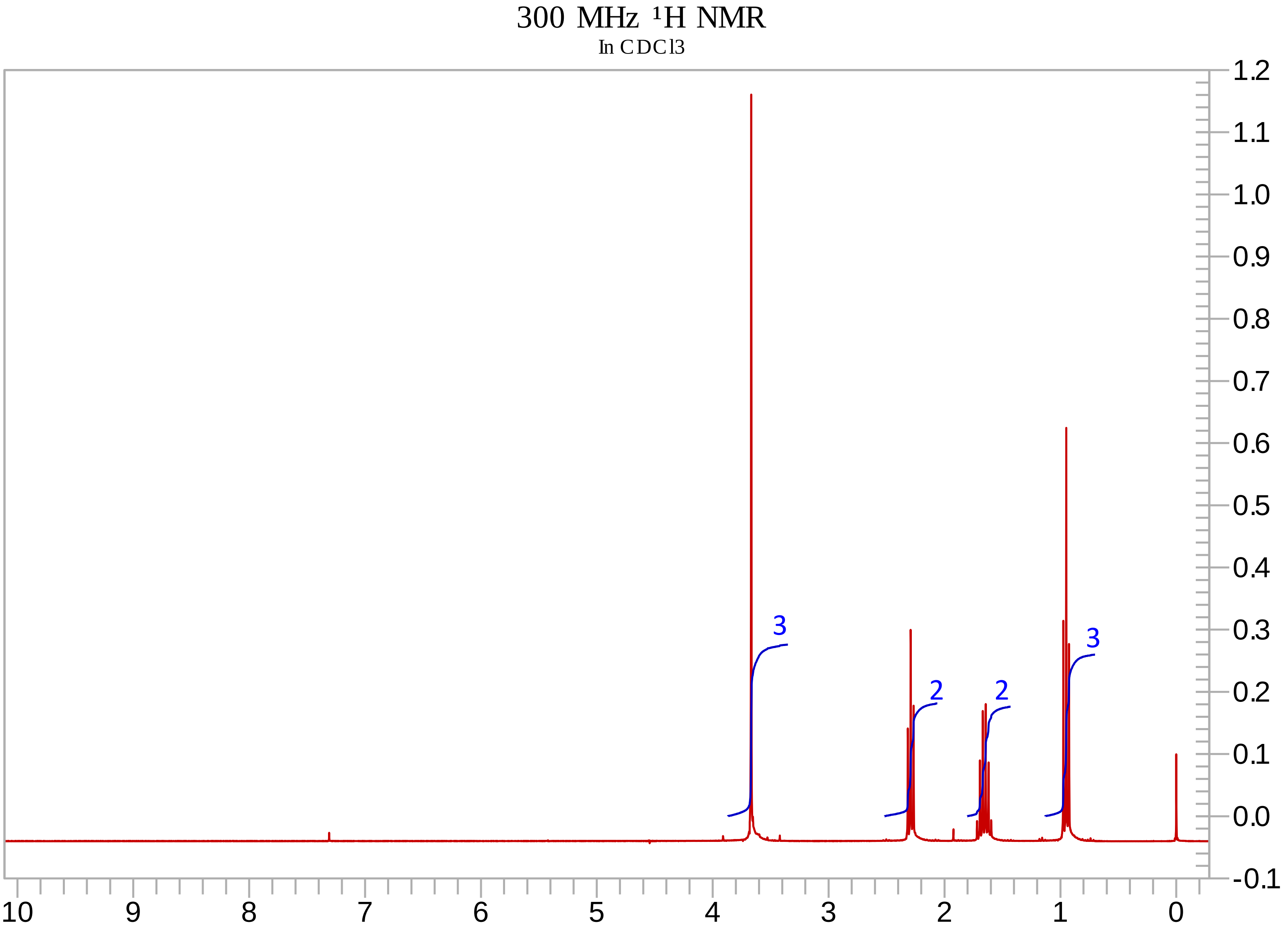
With a chemical formula of $C_5H_{10}O_2$, what types of functional groups are possible?

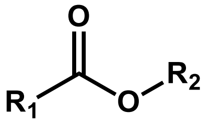
- alkenes
- aldehydes
- ketones
- carboxylic acids
- esters
- alcohols
- peroxides
- ethers
- cyclic alcohols
- cyclic ethers
- epoxides

$$U = \frac{2C + 2 + N - H - X}{2} = \frac{2(5) + 2 - (10)}{2} = 1$$



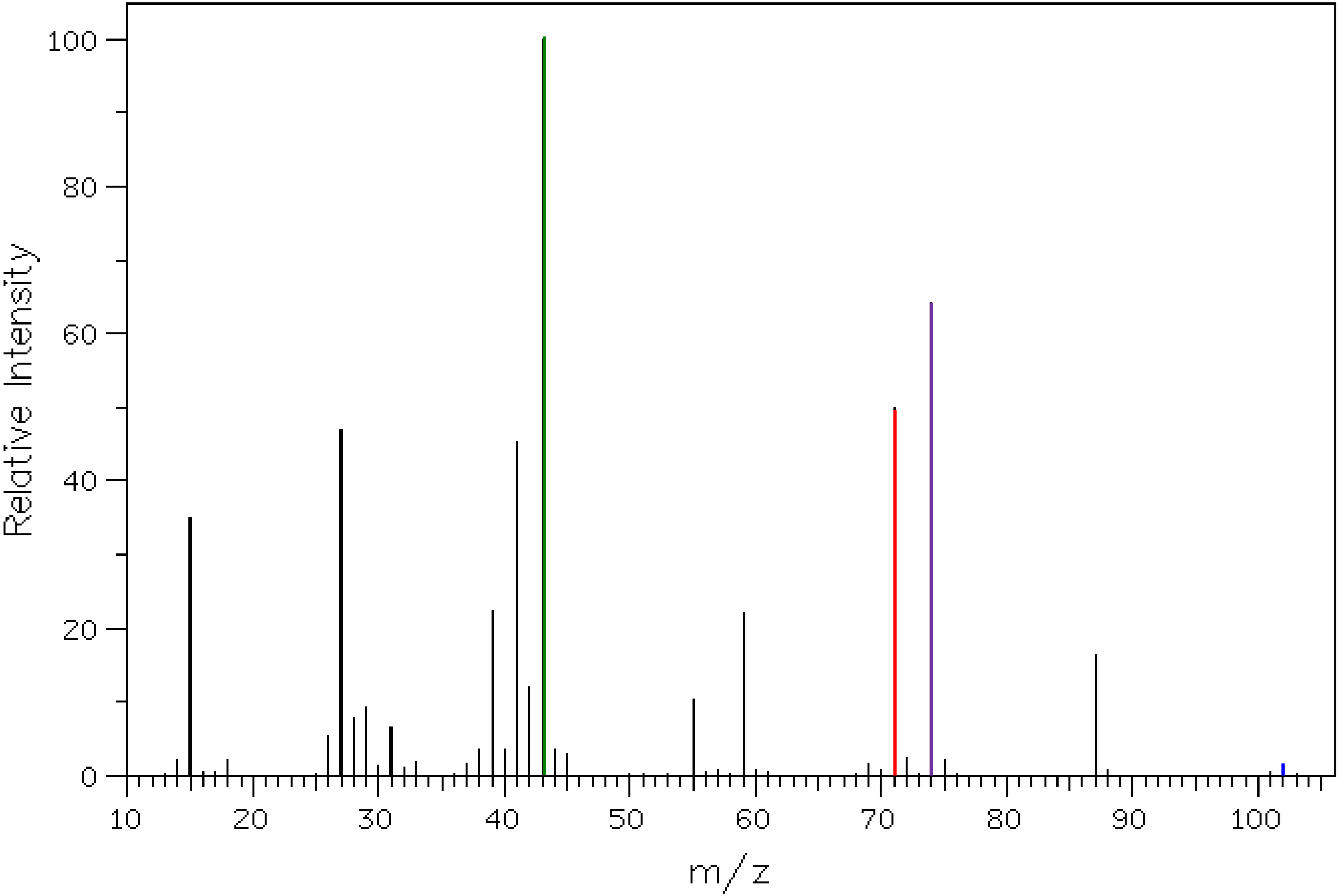
Structure Determination – $C_5H_{10}O_2$





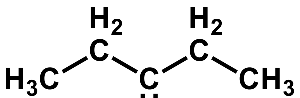
ester from IR

Structure Determination – $C_5H_{10}O_2$

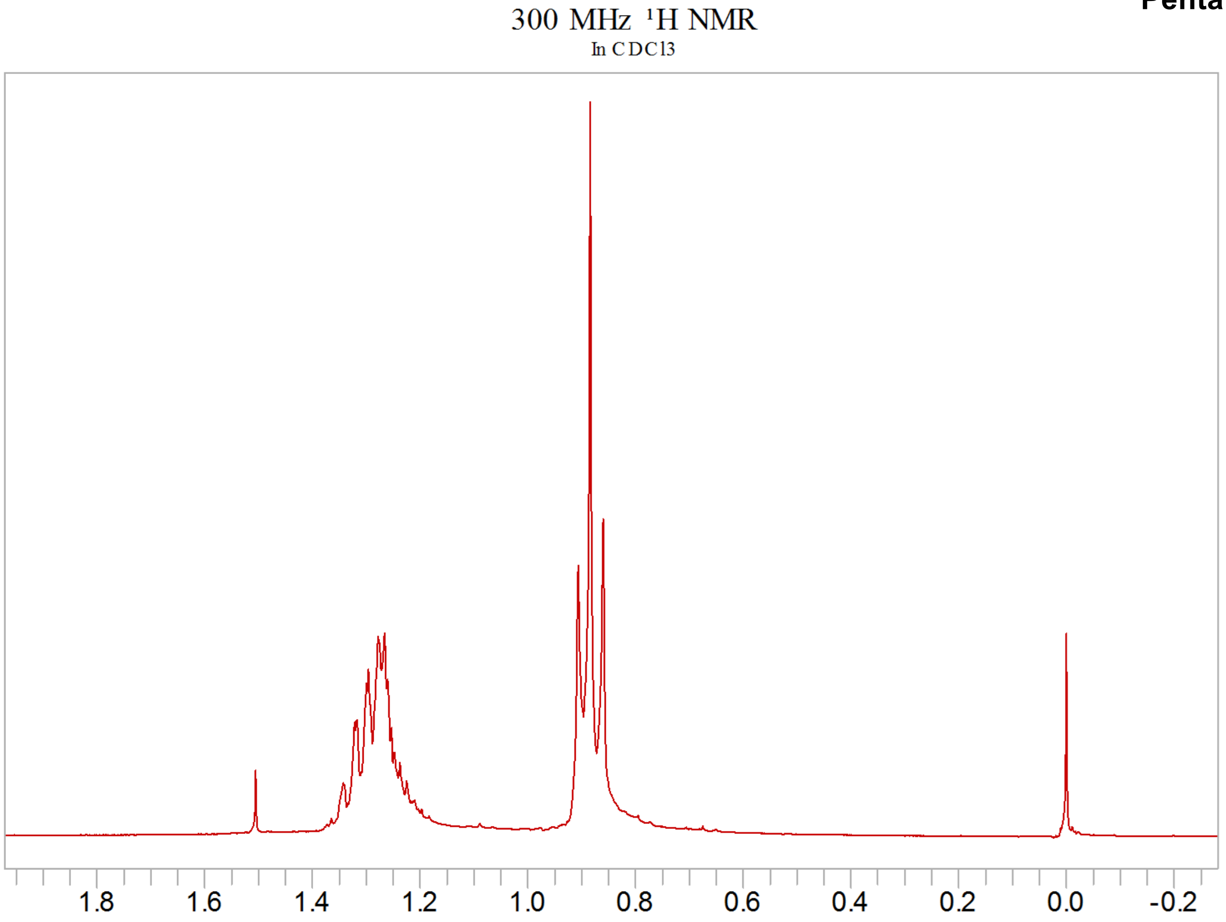


^{1}H-NMR Coupling – Or Lack Thereof…

When non-equivalent ^{1}H-atoms are very close together in chemical shift, the coupling becomes unrecognizable or disappears.



Pentane



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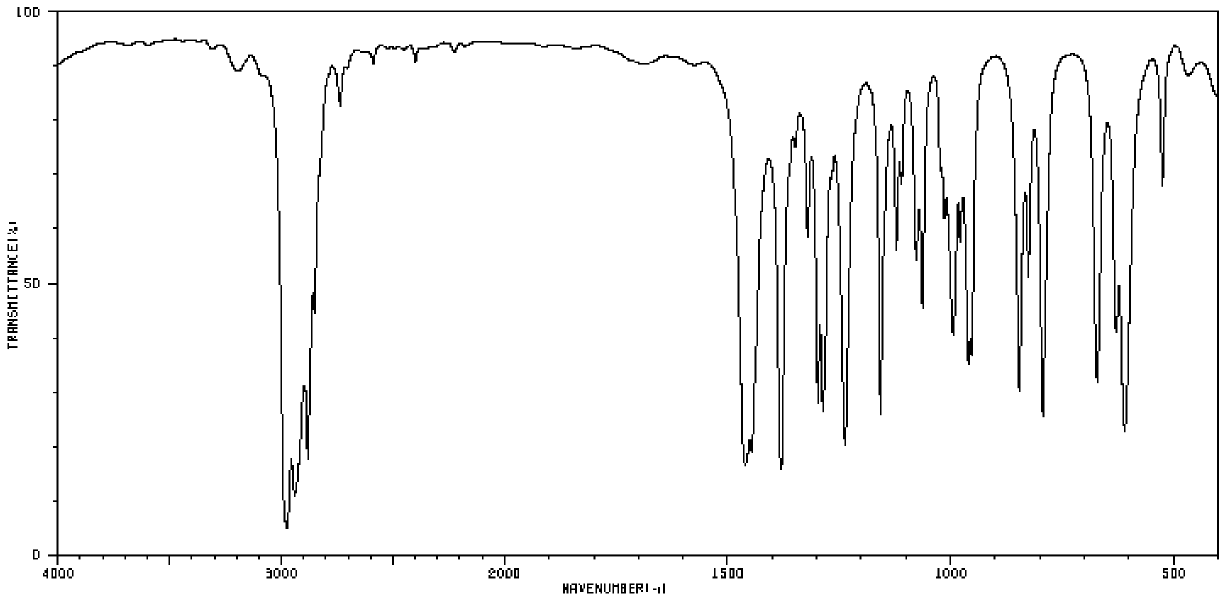
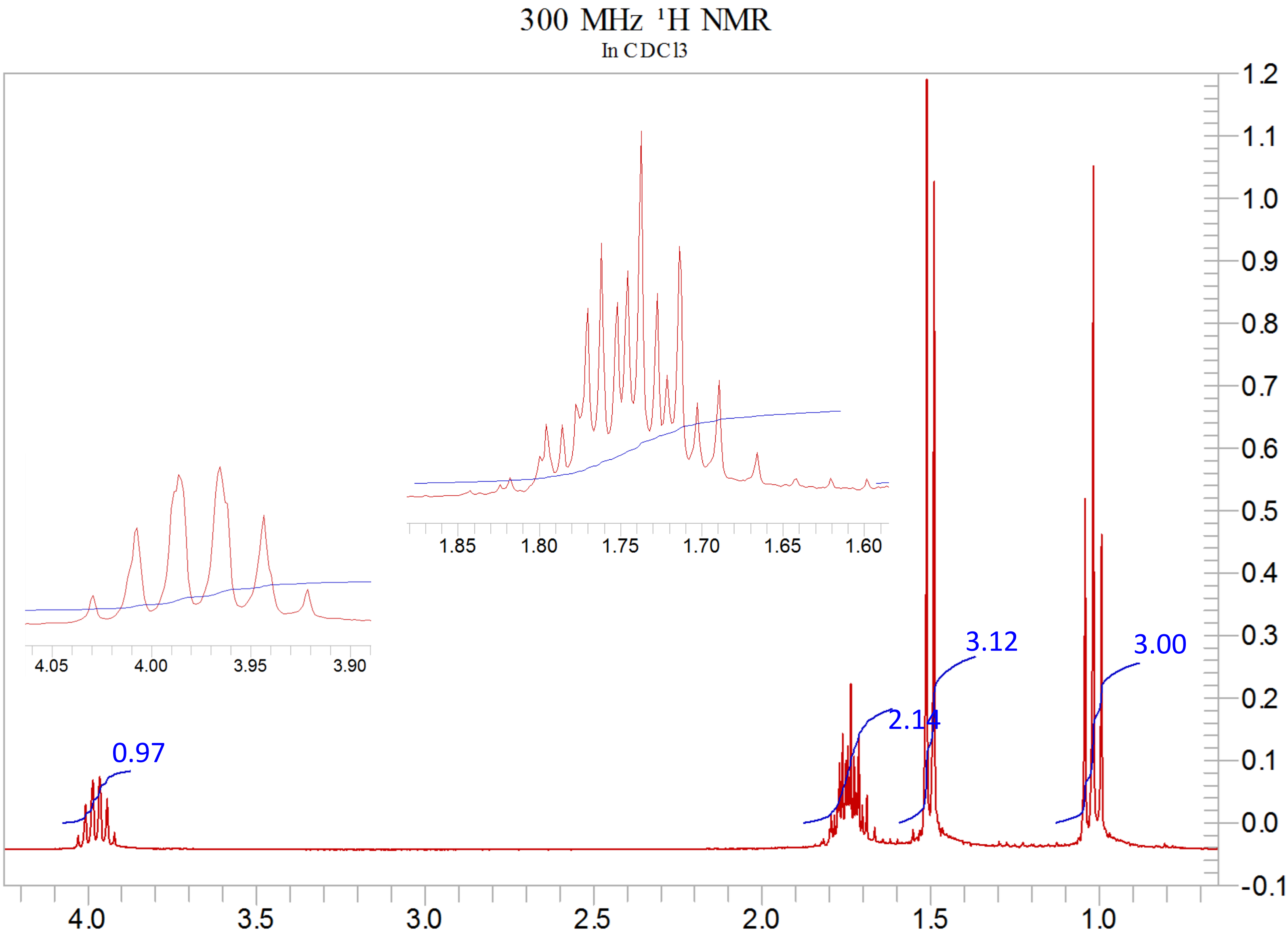
Structure Determination – C_4H_9Cl

$$U = \frac{2C + 2 + N - H - X}{2} = \frac{2(4) + 2 - (9) - (1)}{2} = 0$$



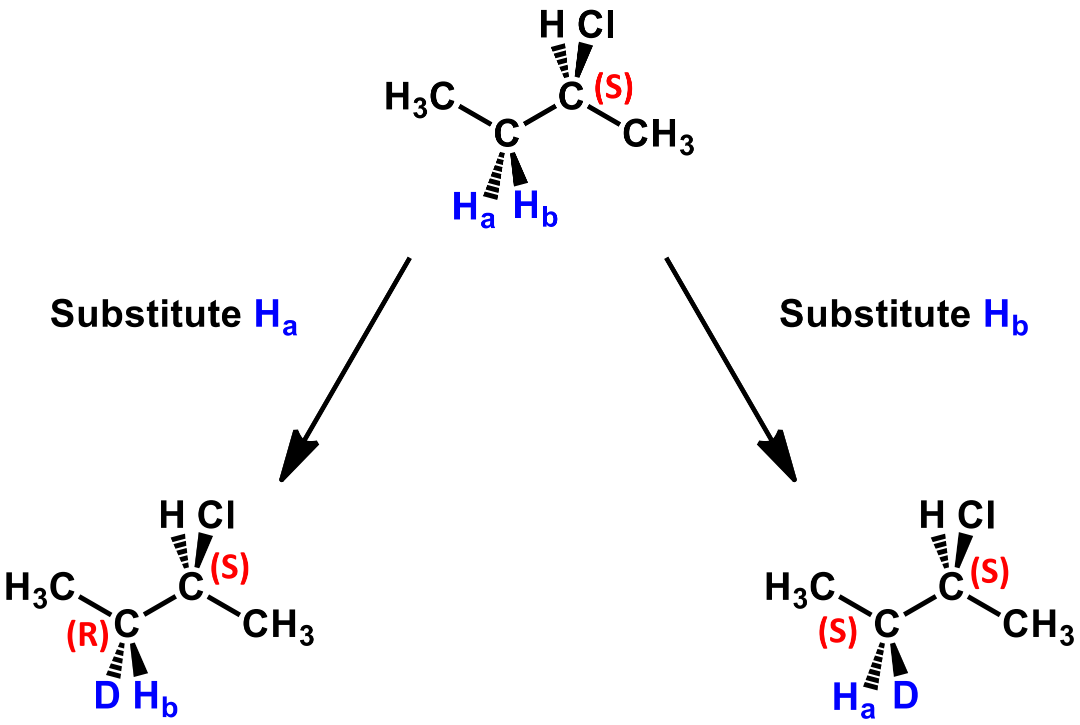
Structure Determination – C_4H_9Cl



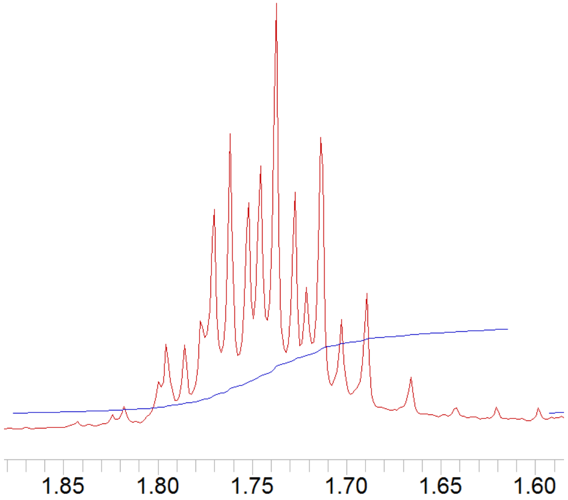
^{1}H-NMR – Diastereotopic Protons & 2nd Order Coupling

2nd order coupling is a term applied to coupling patterns where the *n*+1 rule breaks down. This is likely to occur when there are 2 protons that are coupled together that have close, but not equal, chemical shifts.

Diastereotopic protons are a great example of this. The substitution test is a great way to identify diastereotopic protons that may lead to more exciting couplings.



The substitution test confirms that H$_a$ and H$_b$ are in different, but nearly equal magnetic environments. And in this case, it leads to an exciting coupling.

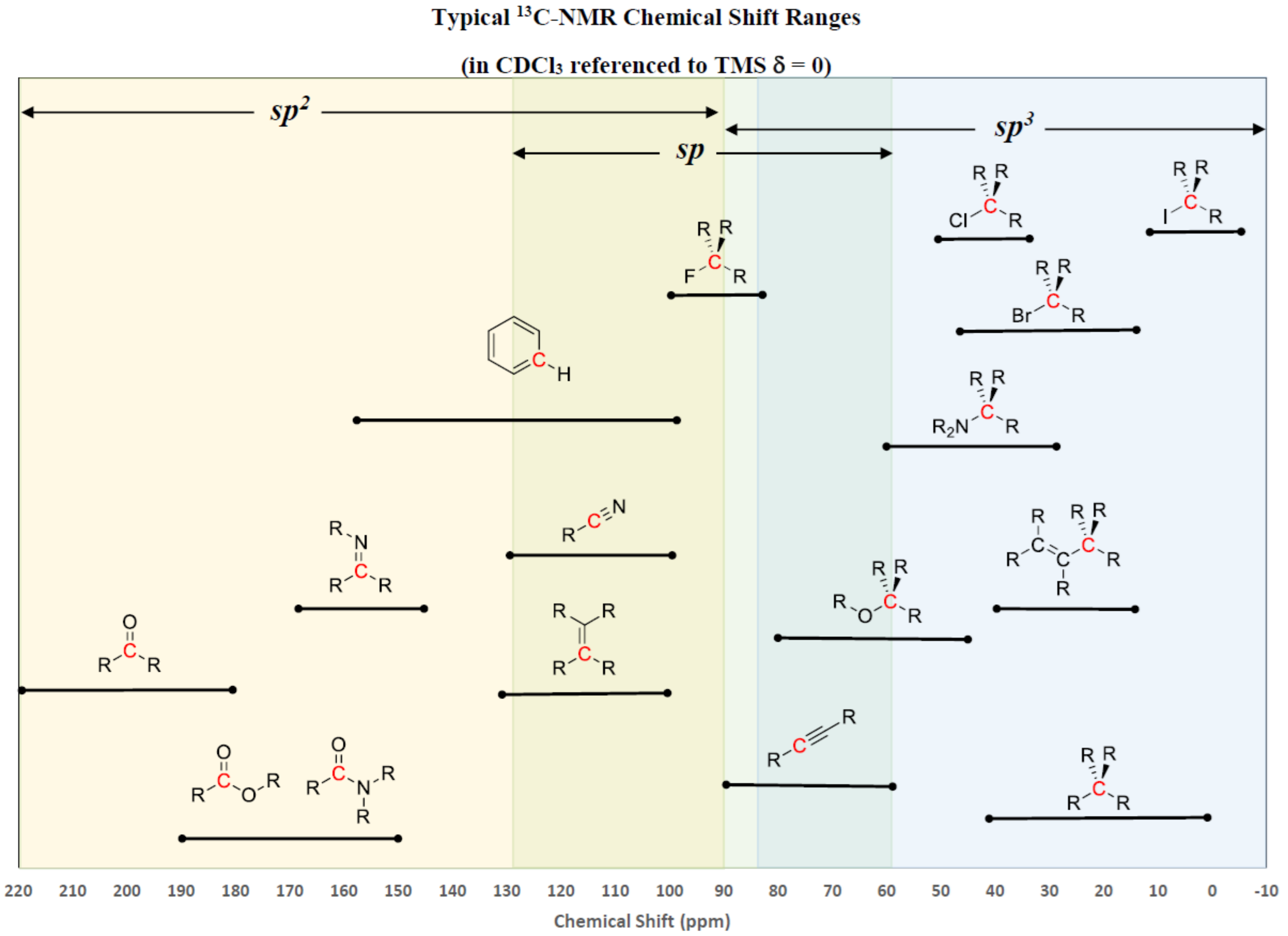


^{13}C-NMR Interpretation

^{13}C-NMR spectra are almost always decoupled and show no splitting or coupling. Since ^{13}C is not highly abundant, ^{13}C-NMR spectra are usually nosier. Signal integrals are not directly related to the number of atoms making the signal.

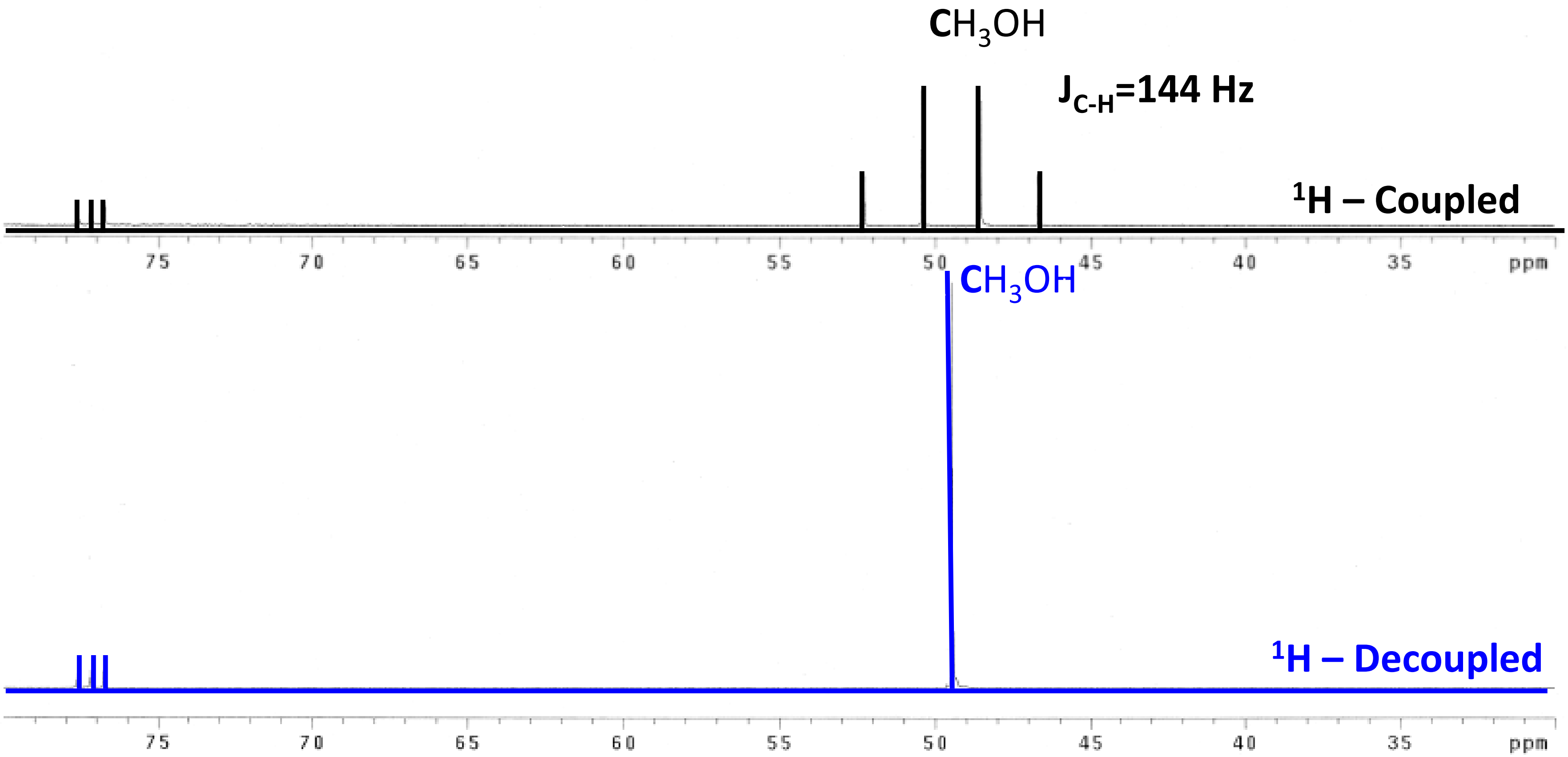
- The number of separate signals indicate the number of distinct environments in the molecule(s). (# of signals)
- The type of environment is indicated by the upfield or downfield chemical shift of the signals. (chemical shift in ppm)

^{13}C-NMR Chemical Shift

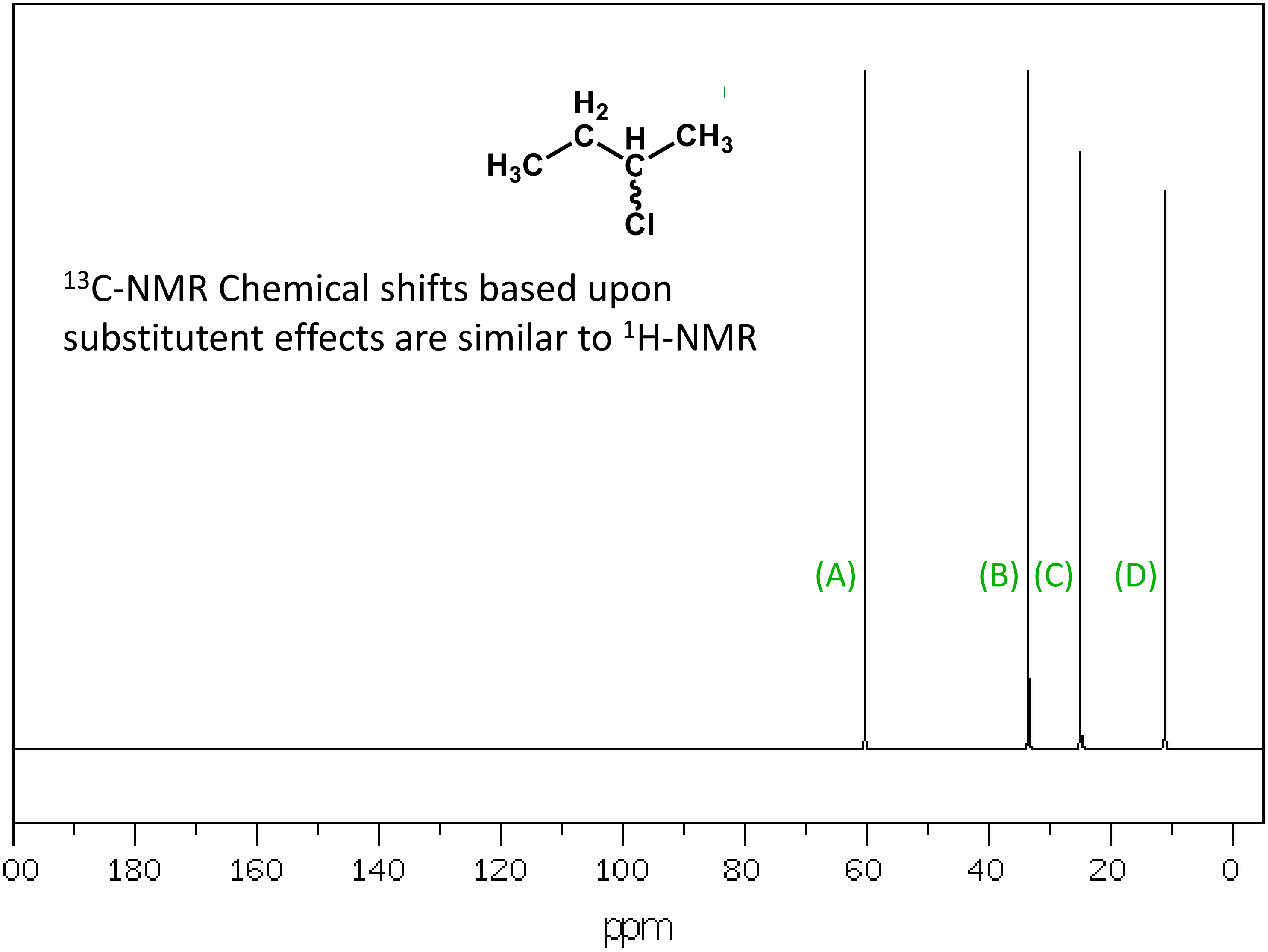


^{13}C-NMR Interpretation - Methanol

^1H is > 99% abundant; it couples strongly to ^{13}C –atom it is attached to ($^1J_{HC}$ = 100-210 Hz) with normal *n+1 rule* splitting.

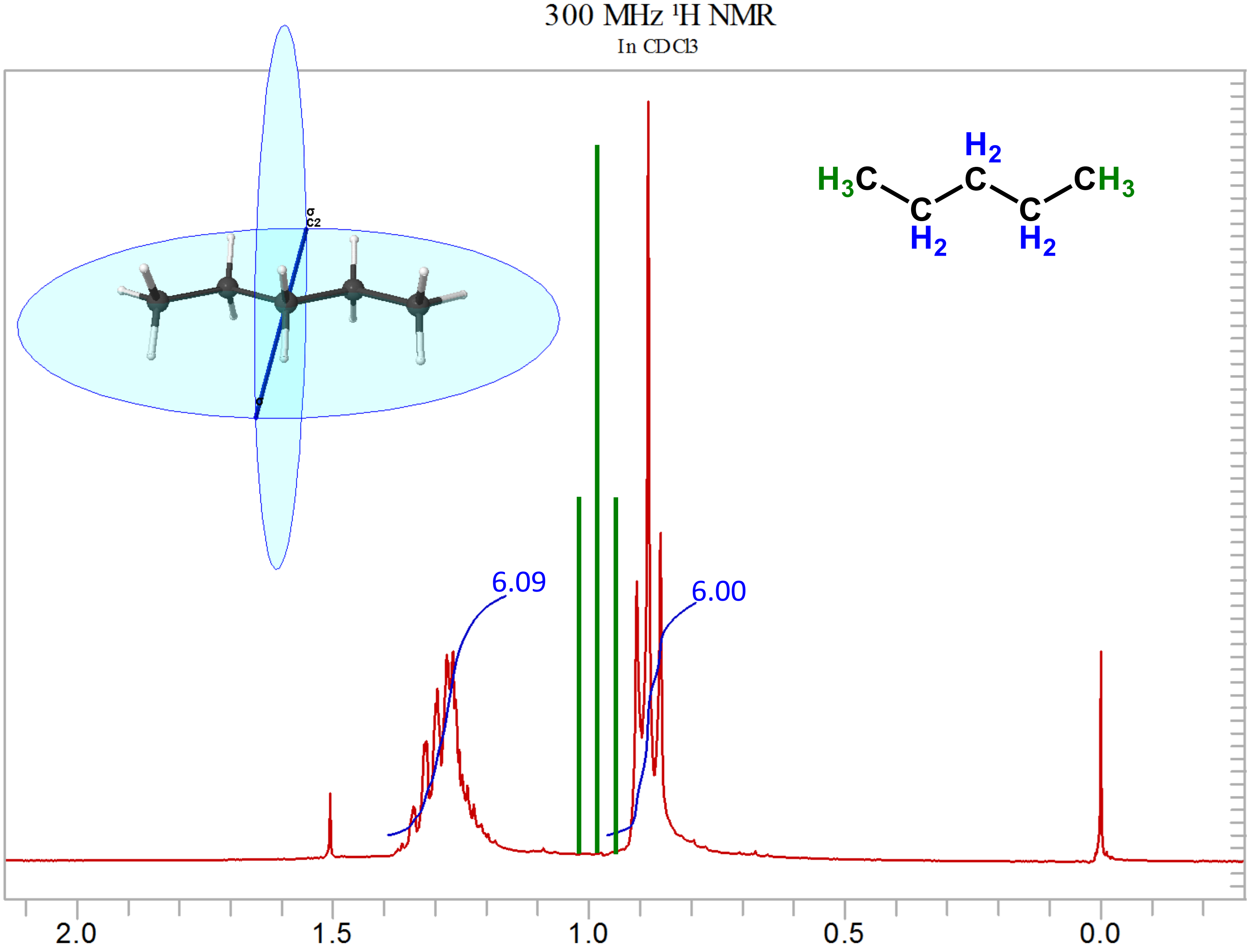


^{13}C-NMR Interpretation – 2-Chlorobutane

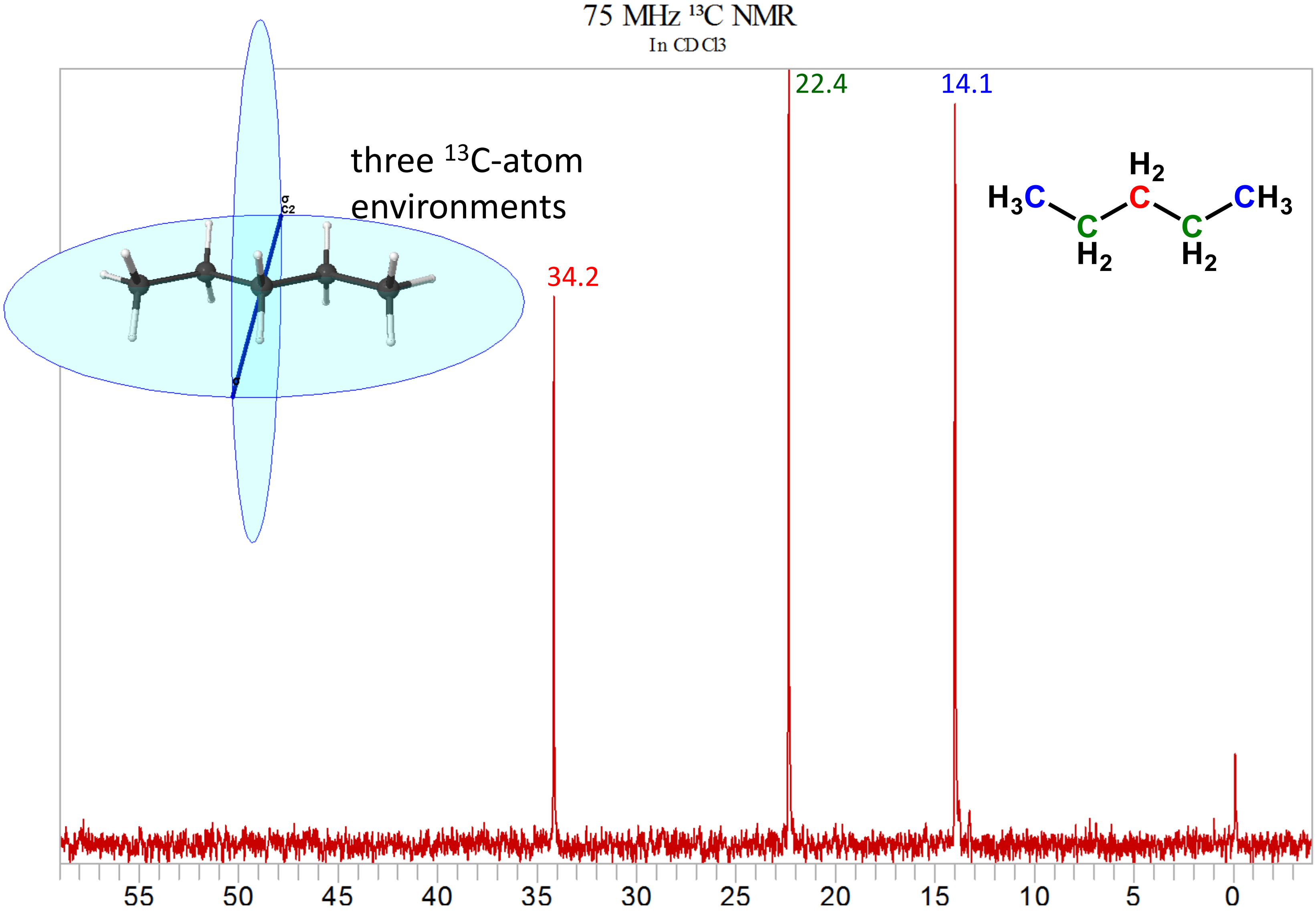


^{13}C-NMR Chemical shifts based upon substitutent effects are similar to ^{1}H-NMR

^{1}H-NMR Spectrum of *n*-pentane

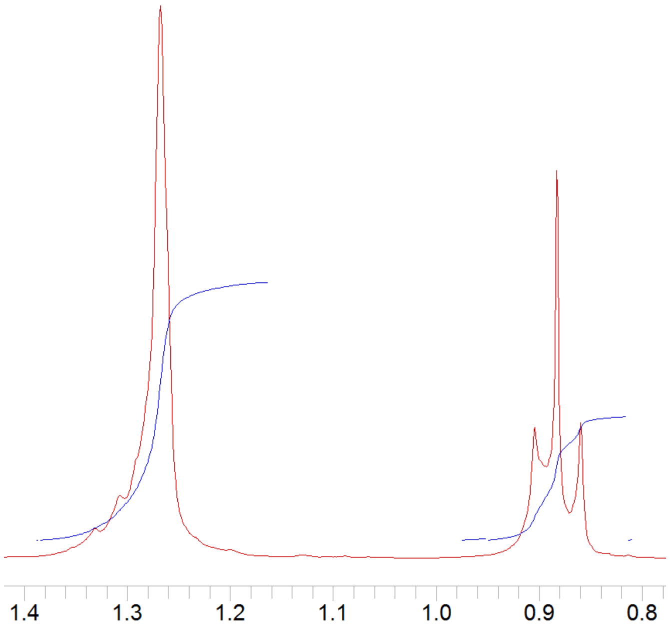


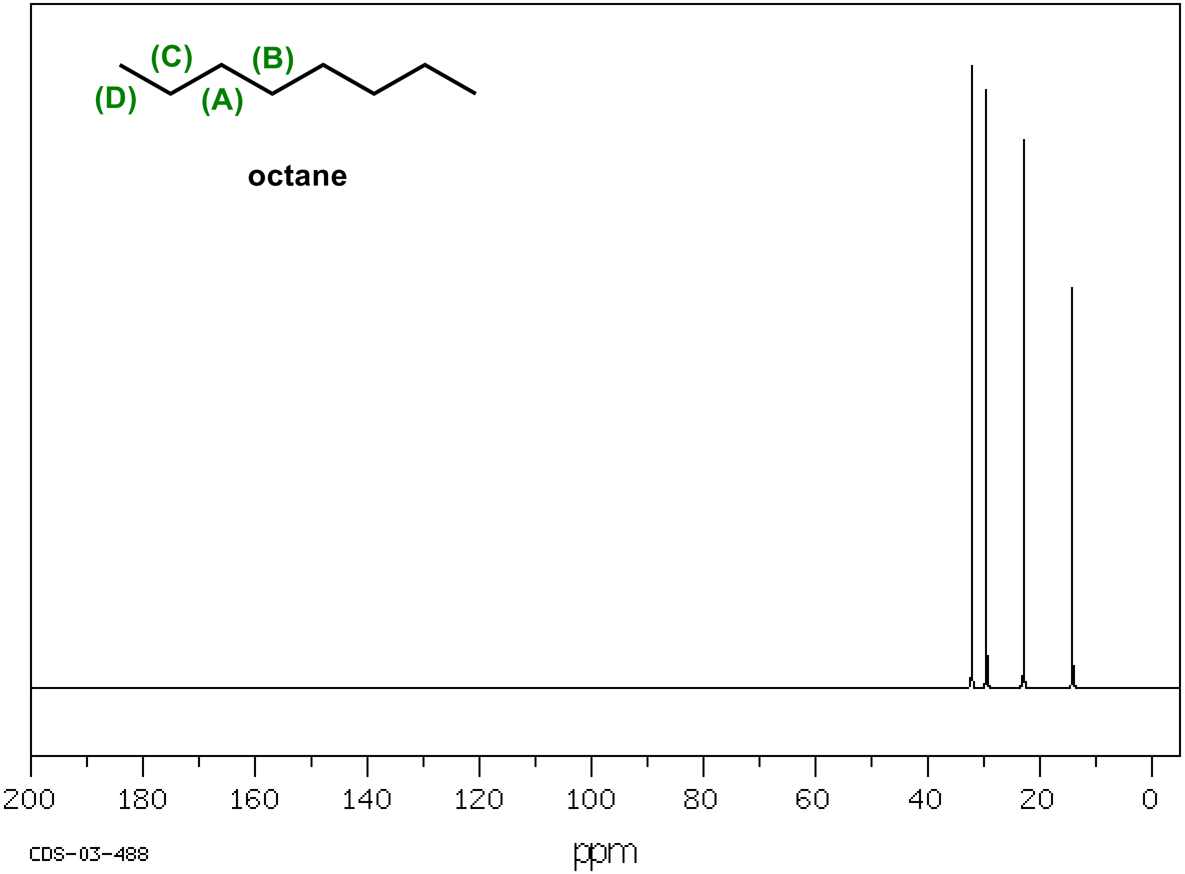
^{13}C-NMR Spectrum of *n*-pentane



three ^{13}C-atom environments

^{13}C-NMR Interpretation





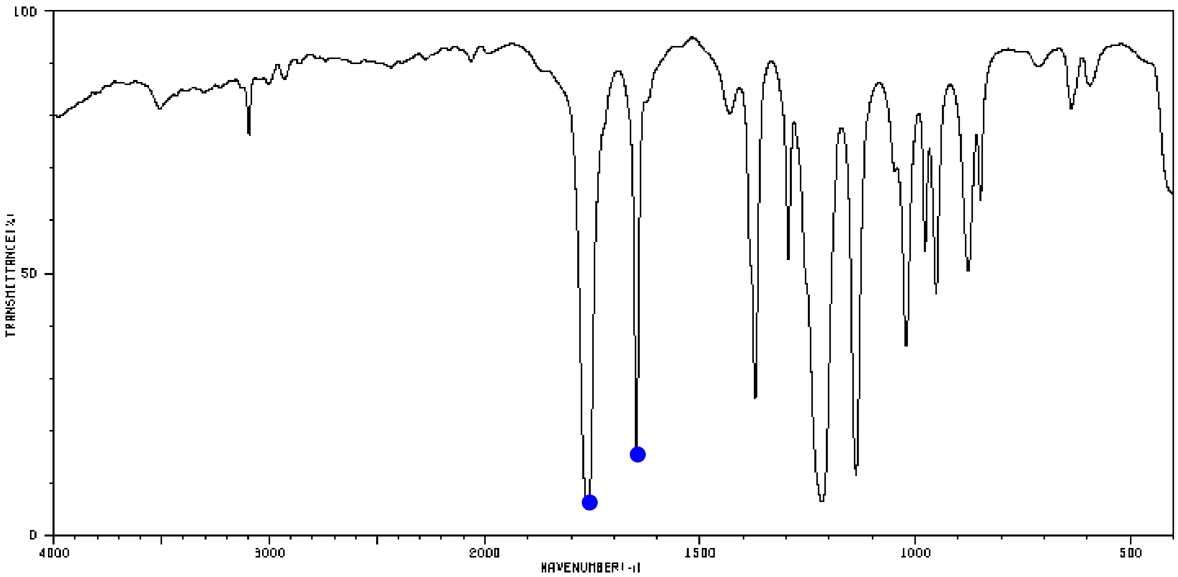
Due to its increased chemical shift range, ^{13}C-NMR provides a lot more useful information about octane than ^{1}H-NMR provides.

Structure Determination – $C_4H_6O_2$

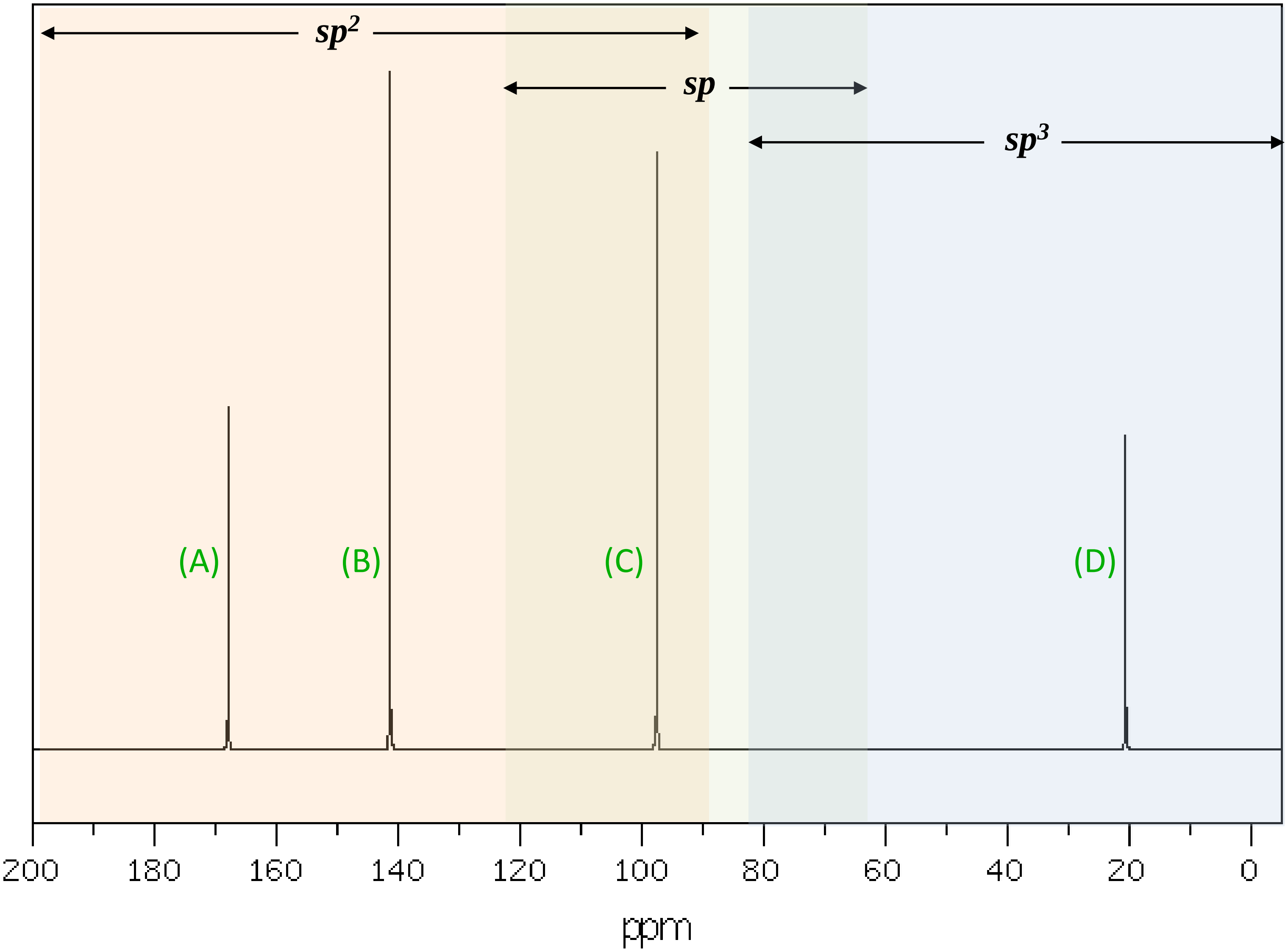
With a chemical formula of $C_4H_6O_2$, what types of functional groups are possible?

- alkenes
- aldehydes
- ketones
- carboxylic acids
- esters
- alcohols
- peroxides
- ethers
- cyclic alcohols
- cyclic ethers
- epoxides

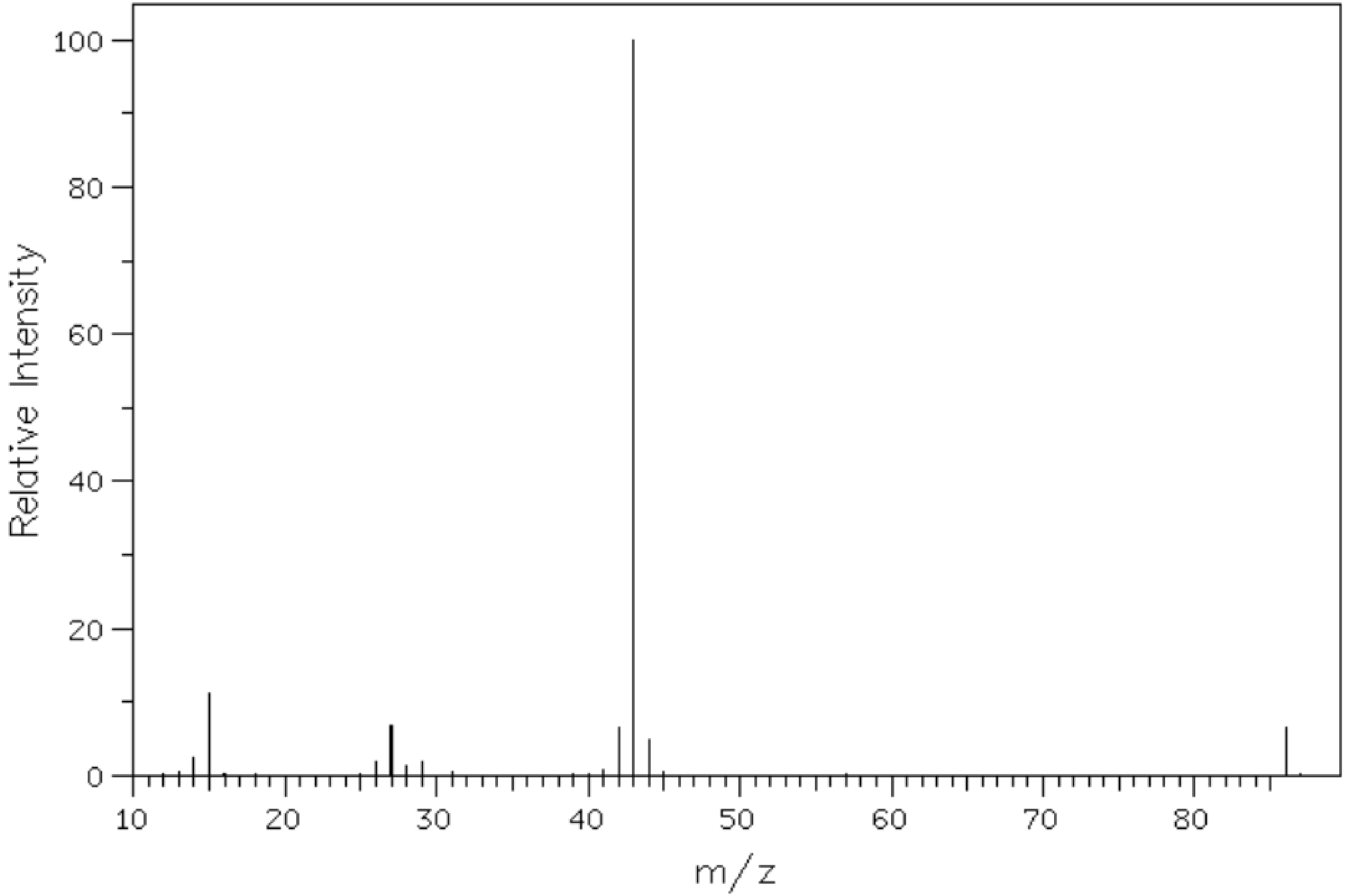
$$U = \frac{2C + 2 + N - H - X}{2} = \frac{2(4) + 2 - (6)}{2} = 2$$



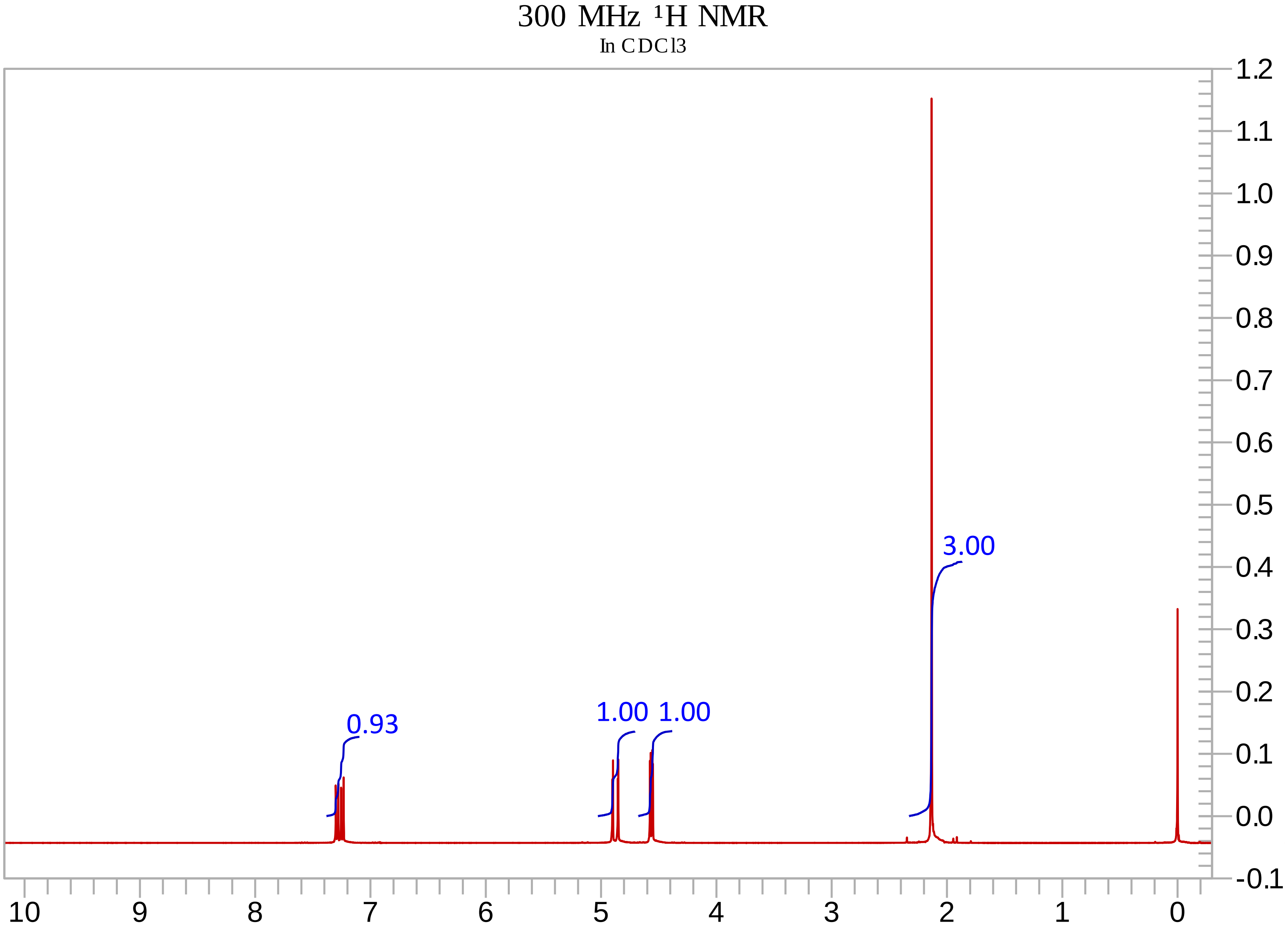
Structure Determination – $C_4H_6O_2$



Structure Determination – $C_4H_6O_2$

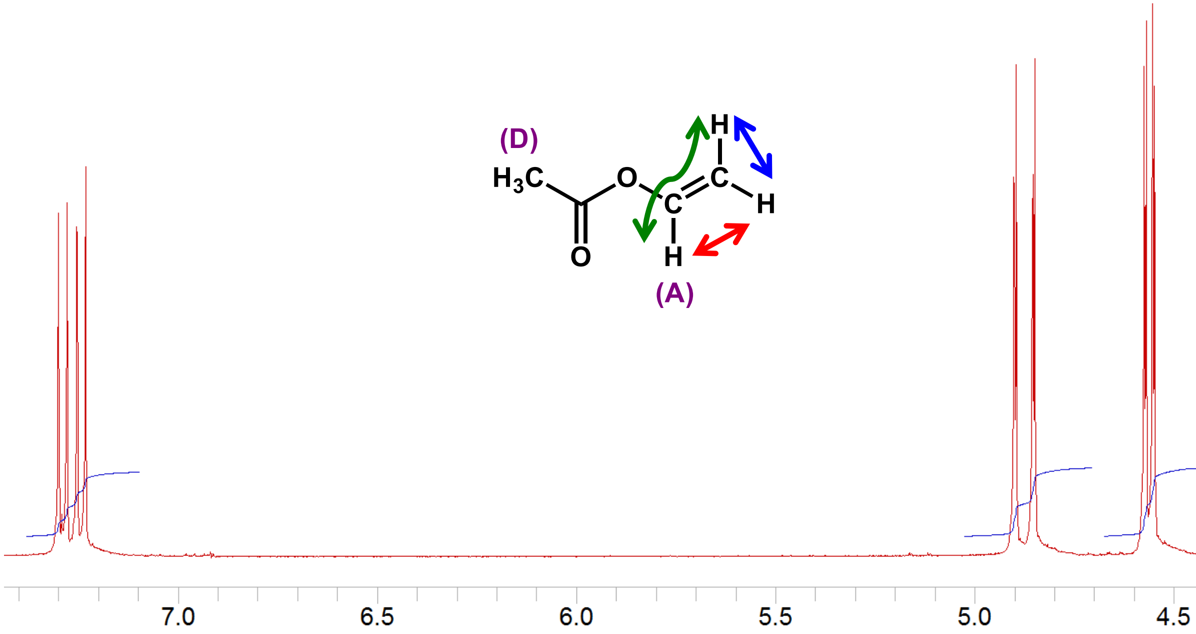


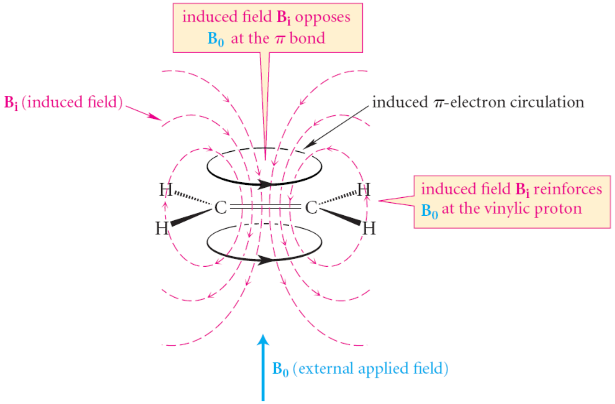
Structure Determination – $C_4H_6O_2$



^{1}H-NMR Vinyl Region

Due to the magnetic field of the electrons in the π bond, ^{1}H-atoms attached to double-bonded C-atoms experience an enhanced magnetic field resulting in a significant downfield shift to about δ 5.8 ± 1.5 ppm.

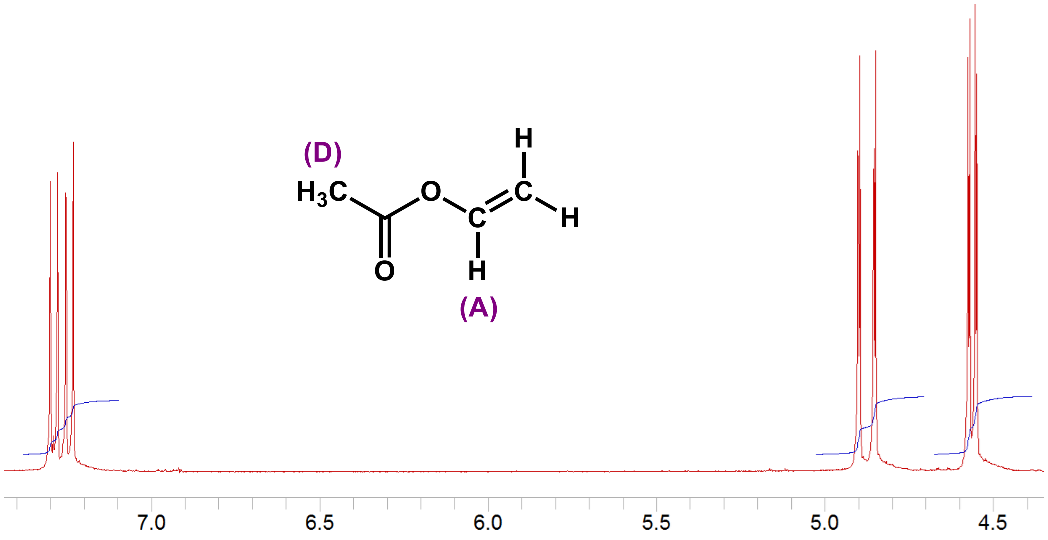




- Chemical shift varies with substitution.
- Coupling constants vary from ***trans***, ***cis***, and ***geminal*** protons.

^{1}H-NMR Vinyl Region

The two remaining signals can be assigned knowing the typical couplings constants for vinyl protons. $J_{trans} = 12 - 18$ Hz $> J_{cis} = 6 - 12$ Hz $> J_{gem} = 1 - 3$ Hz



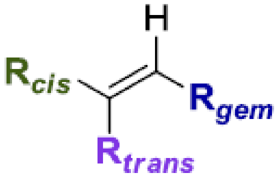
- For couplings with different coupling constants, apply them independently to interpret a splitting pattern.

- Coupling trees can be quite instructive; draw them.

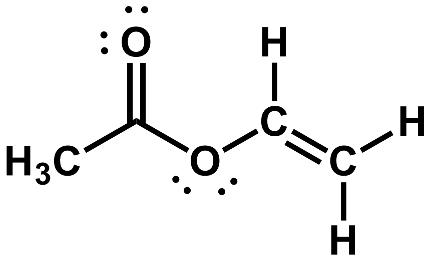
- All three signals are differently-spaced doublets of doublets.

Estimating Chemical Shift via Curphy - Morrison parameters

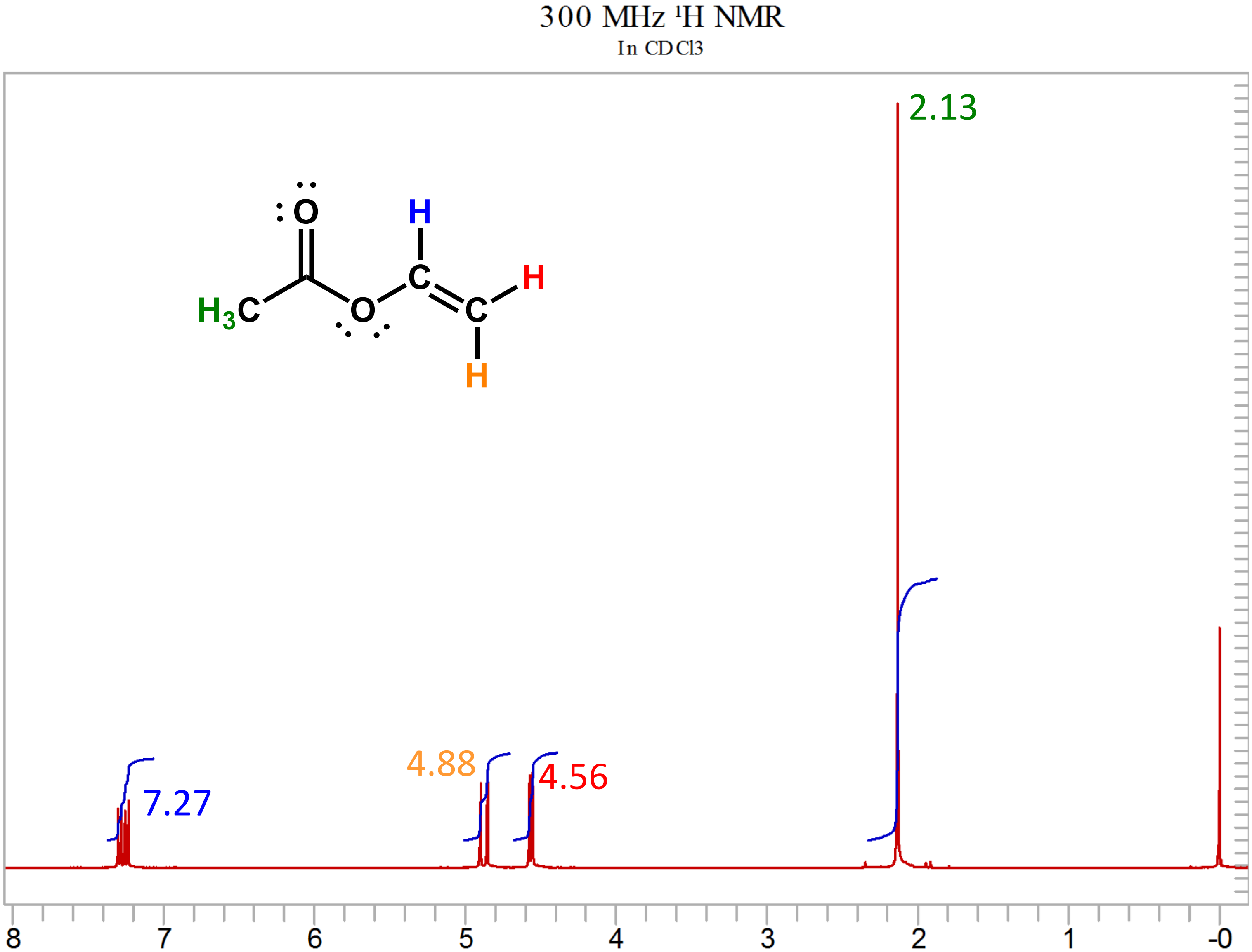
Substituent Effects on:



Shift Estimate: $\delta_{H\,(vinyl)} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$

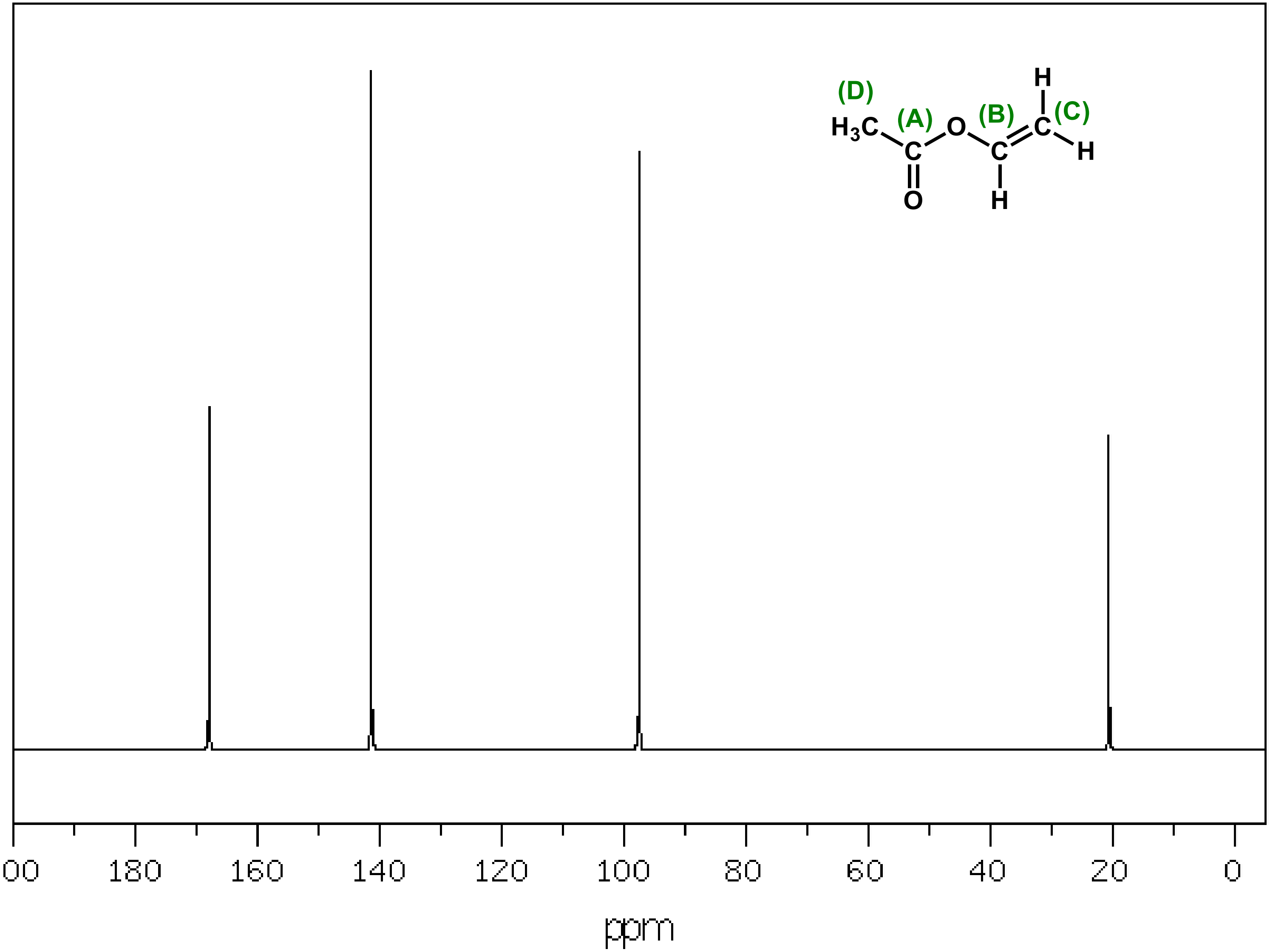


Estimating Chemical Shift via Curphy - Morrison parameters

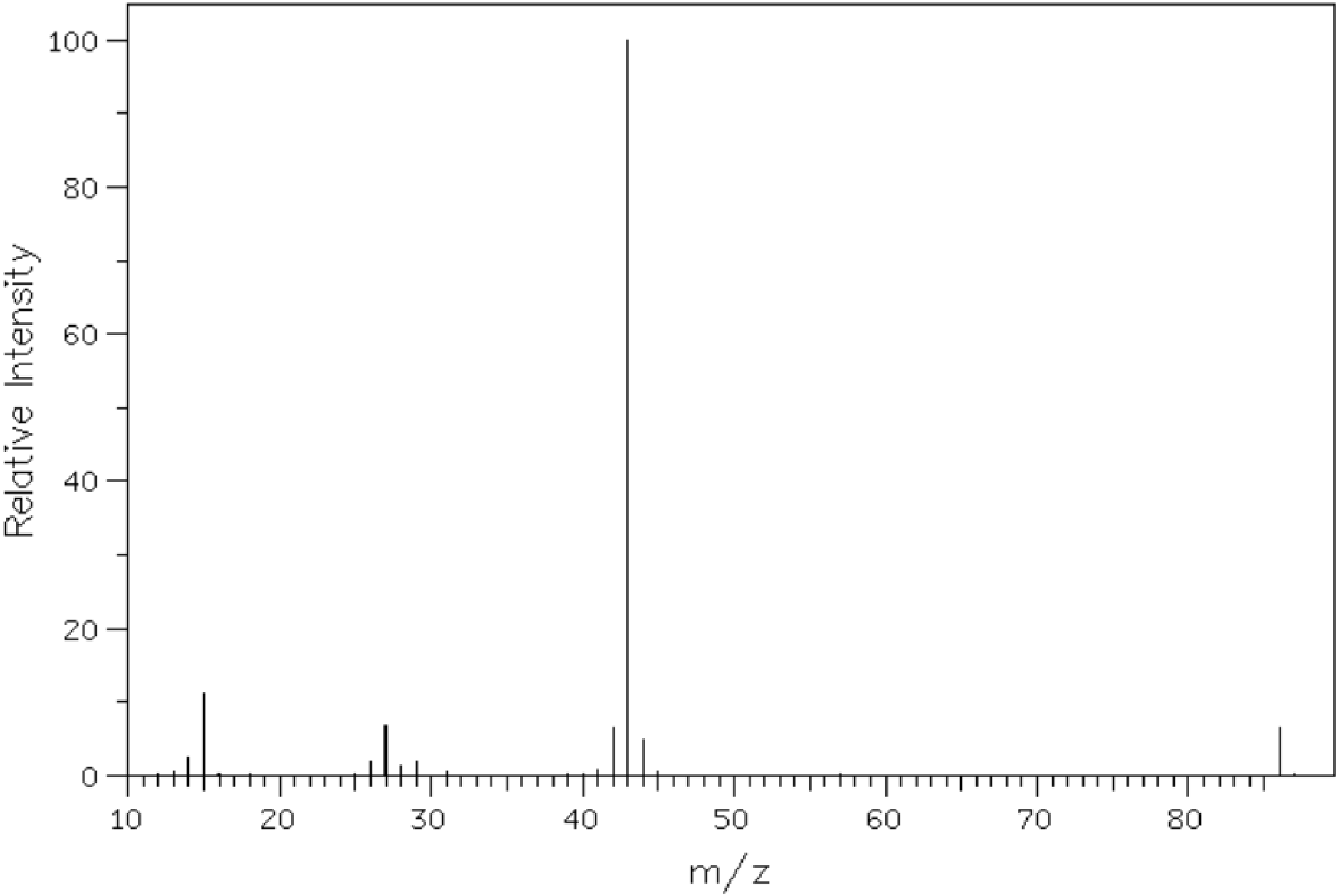

300 MHz ^{1}H NMR

In CDCl3

Structure Determination – $C_4H_6O_2$



Structure Determination – $C_4H_6O_2$

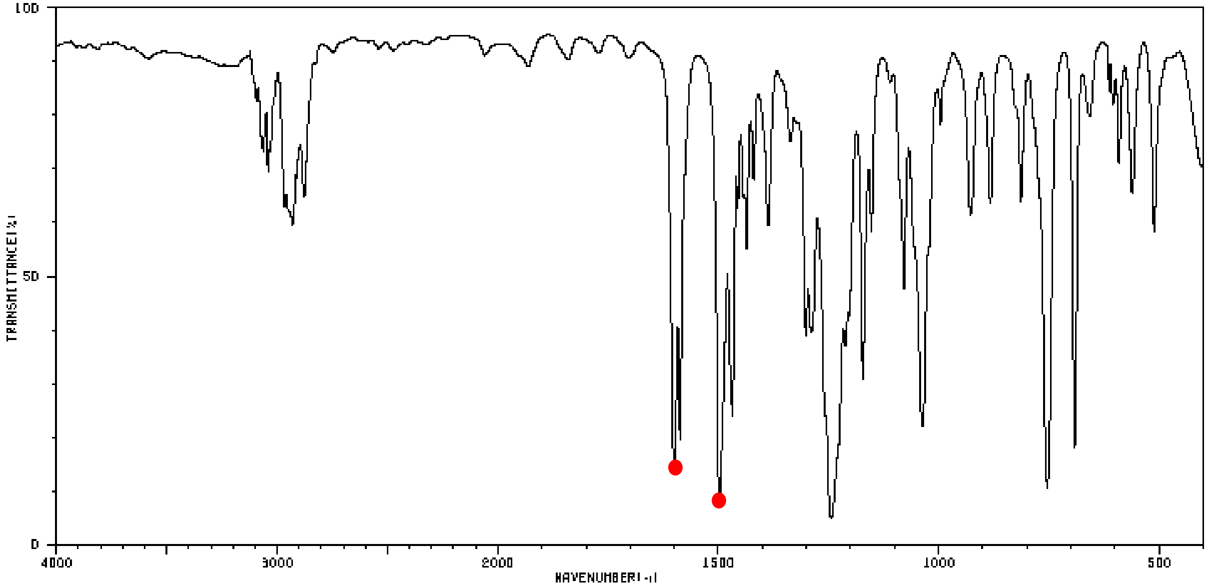


Structure Determination – $C_9H_{11}OBr$

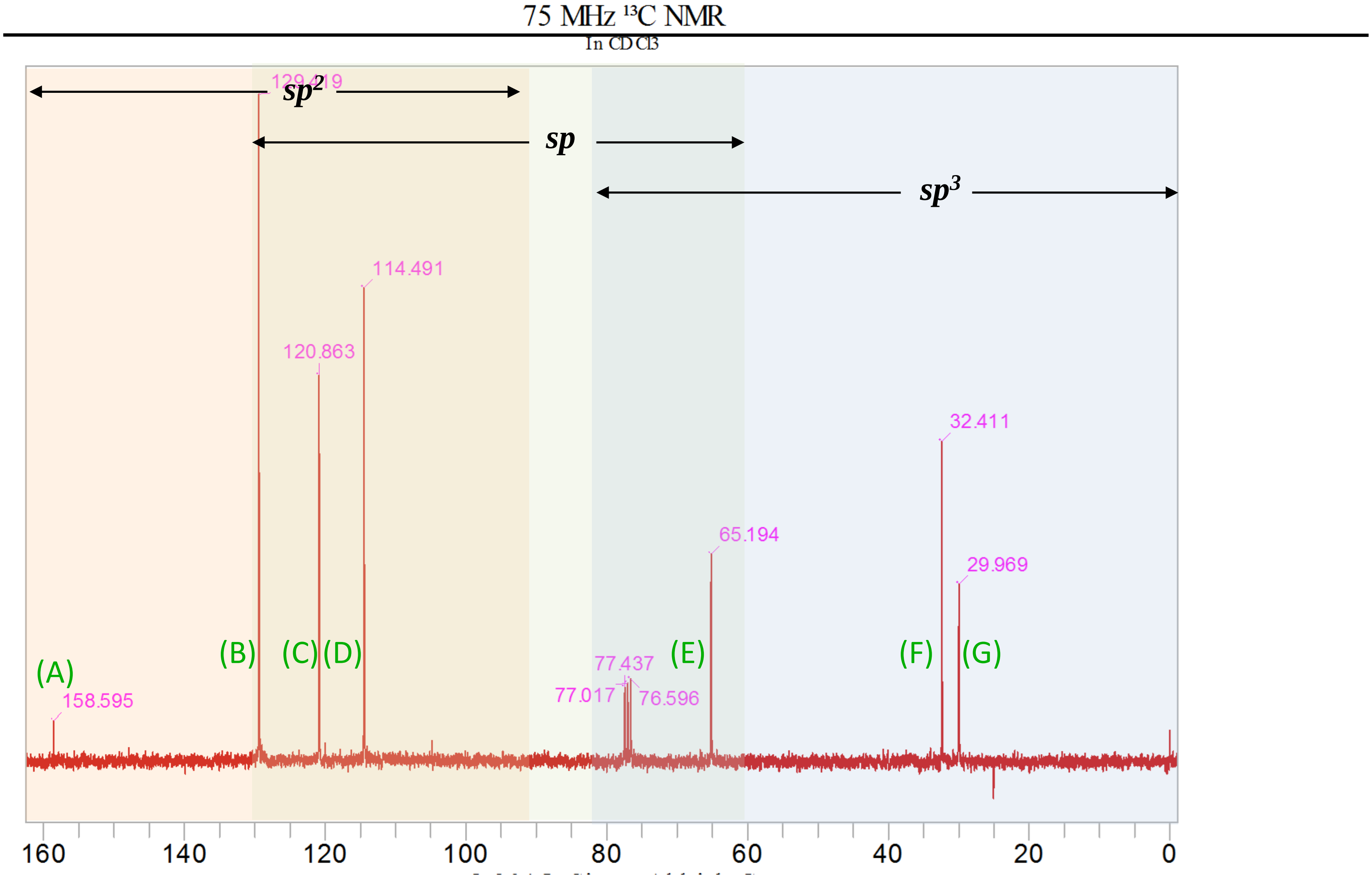
With a chemical formula of $C_9H_{11}OBr$, what types of functional groups are possible?

- alkenes
- alkynes
- arenes
- aldehydes
- ketones
- alcohols
- ethers
- cyclic alcohols
- cyclic ethers
- epoxides
- etc

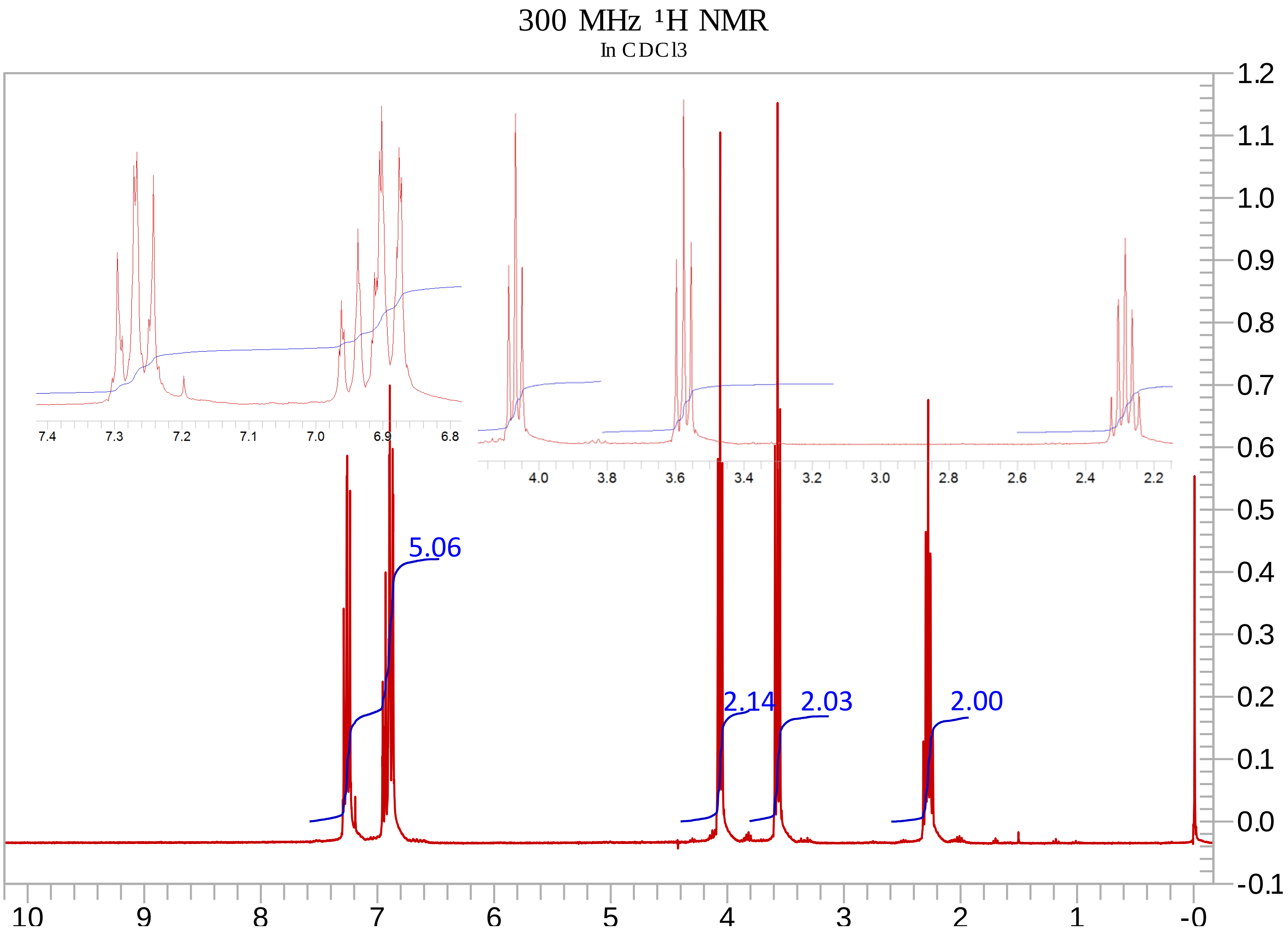
$$U = \frac{2C + 2 + N - H - X}{2} = \frac{2(9) + 2 - (11) - (1)}{2} = 4$$



Structure Determination – $C_9H_{11}OBr$

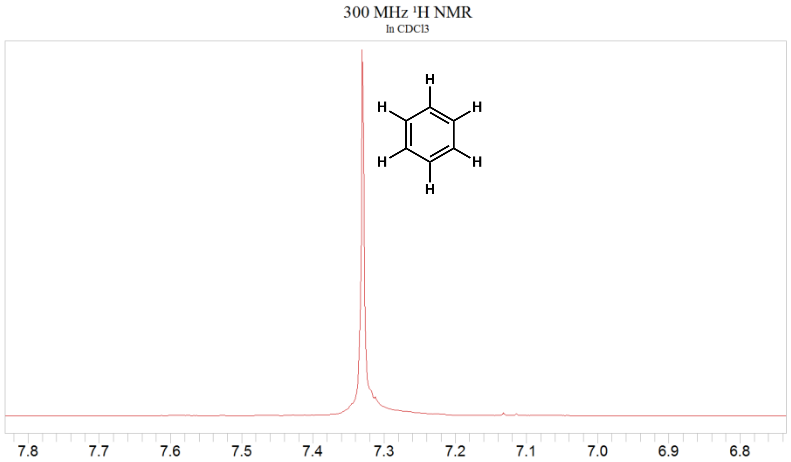


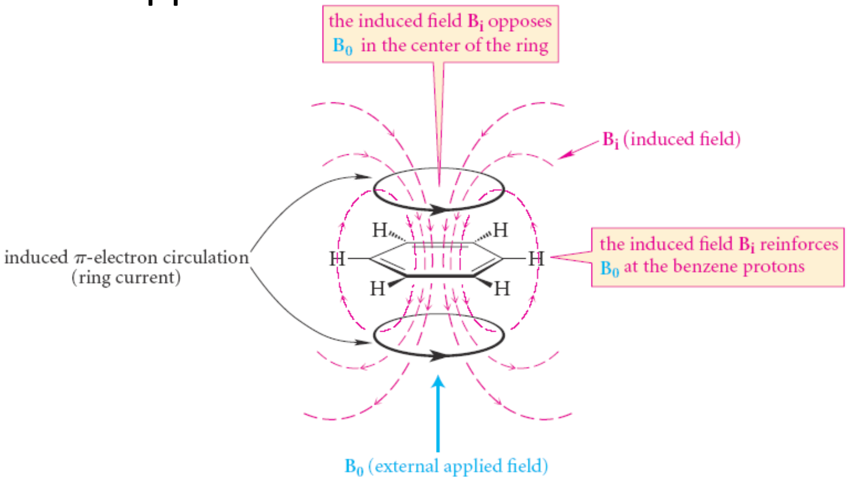
Structure Determination – $C_9H_{11}OBr$



^{1}H-NMR Aromatic Region

Due to the local magnetic field created by the diatropic aromatic ring current, ^{1}H-atoms attached to C-atoms that are part of a aromatic ring experience an enhanced magnetic field resulting in a significant downfield shift to about δ 7.5 ± 1 ppm.

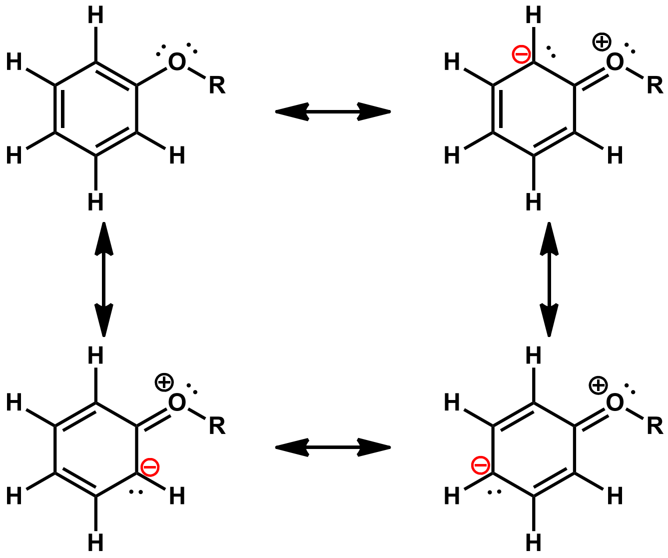


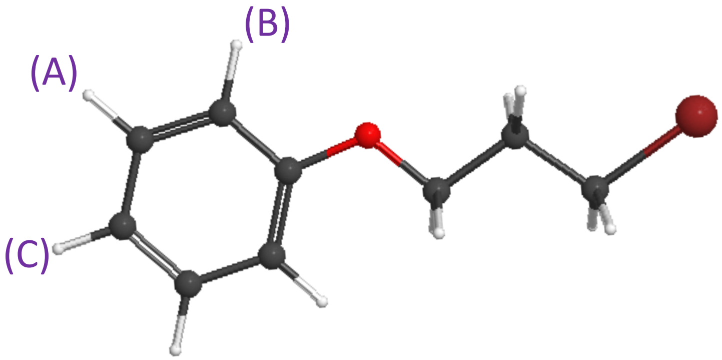


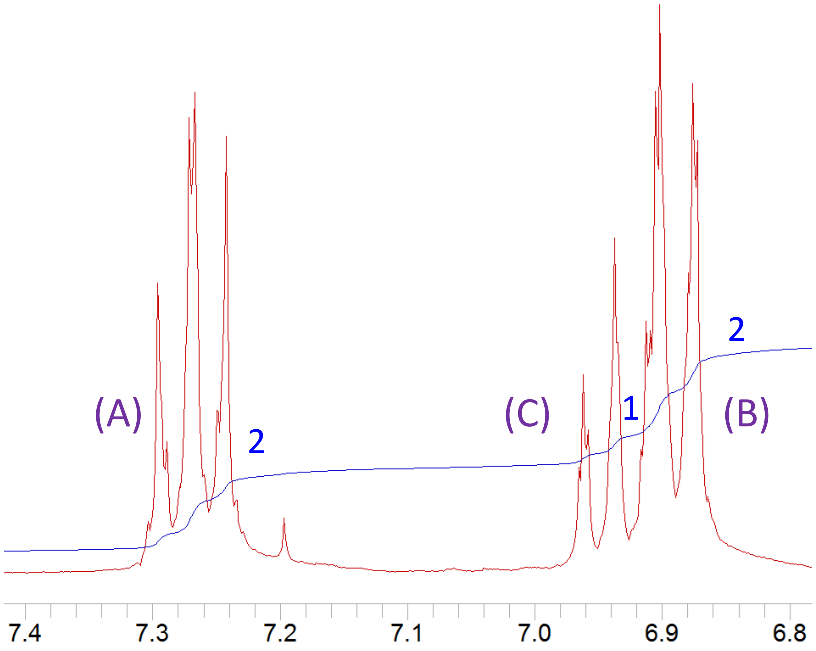
- Shift is much further downfield than for typical CH protons without multiple strong EWGs.
- Shift is further downfield than an H-atom on an alkene or conjugated diene; aromaticity is important.
- No coupling is observed for benzene as all protons are equivalent.

^{1}H-NMR Aromatic Region

EWG or EDG substituents on aromatic rings can alter the electron density at a carbon atom in the ring which in turn impacts the shielding for a particular proton. (more e$^-$ = more shielding)



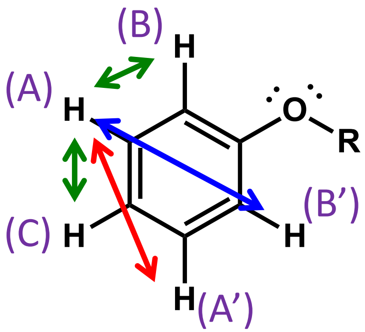




The coupling appears complicated, but can be interpreted without too much difficulty using the *ortho* couplings.

^{1}H-NMR Aromatic Region

The coupling constants of protons on aromatic rings follow some predictable trends.



J_{ortho} = 6 – 12 Hz > J_{meta} = 1 – 3 Hz > J_{para} = 0 – 1 Hz

Ignore…

For couplings with different coupling constants, apply them independently to interpret a splitting pattern.

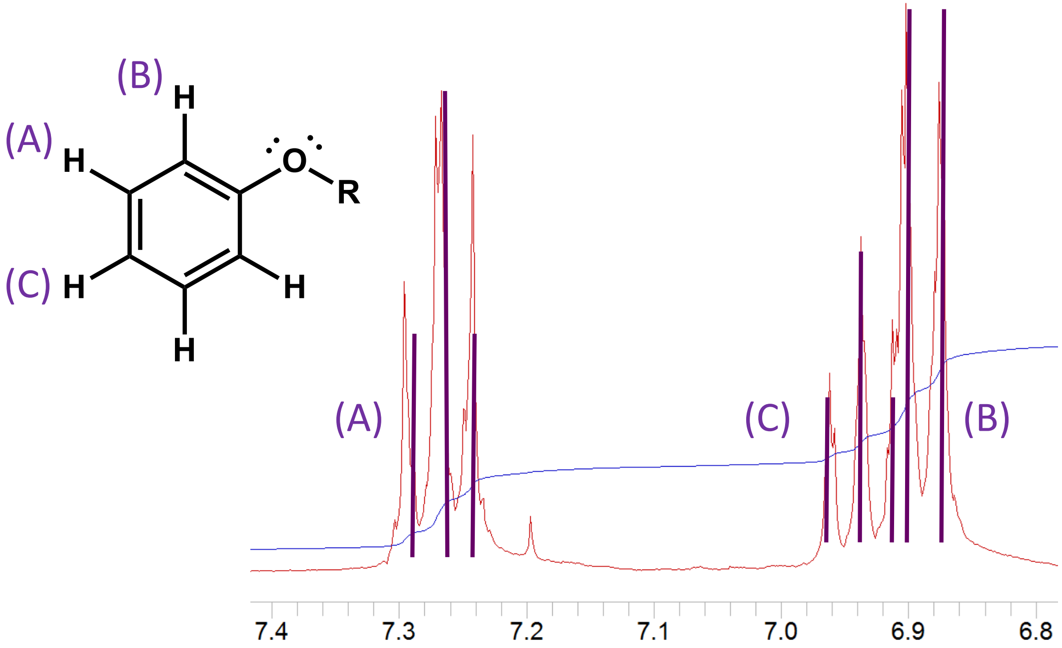
For (A):
2 ortho H atoms (B & C)
1 meta H atom (A')
triplet of doublets

For (B):
1 ortho H atom (A)
2 meta H atoms (C & B')
doublet of triplets

For (C):
2 ortho H atoms (A & A')
2 meta H atoms (B & B')
triplet of triplets

(Shows oversimplification of coupling patterns; true pattern is AA'BB'C.)

^{1}H-NMR Aromatic Region



This approach is an over-simplification of the coupling, but works well enough in most *simple* cases to make assignments.

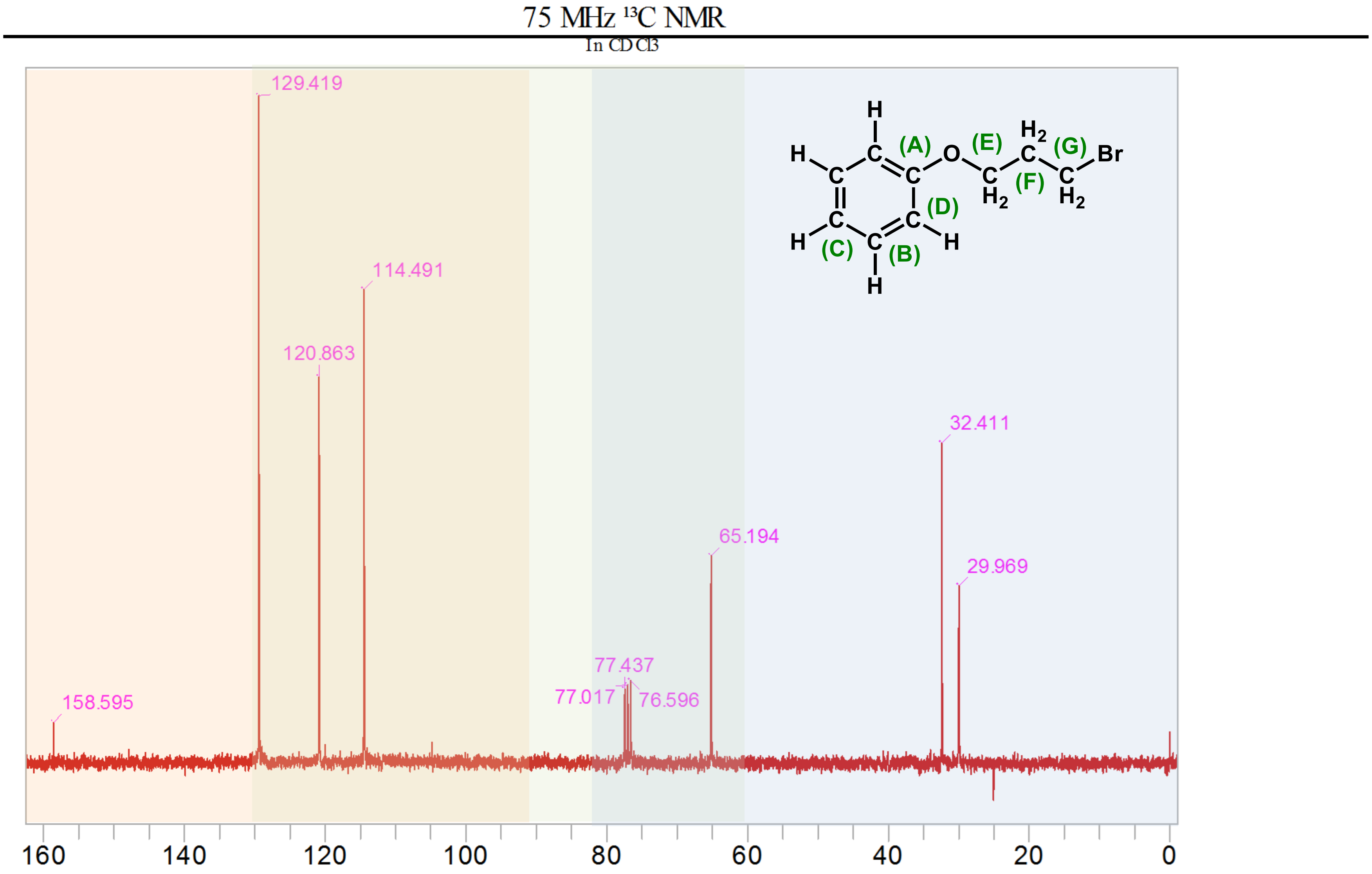
Usually assignments can be made from the *ortho* couplings alone; focus on them.

(A): *triplet of doublets*

(B): *doublet of triplets*

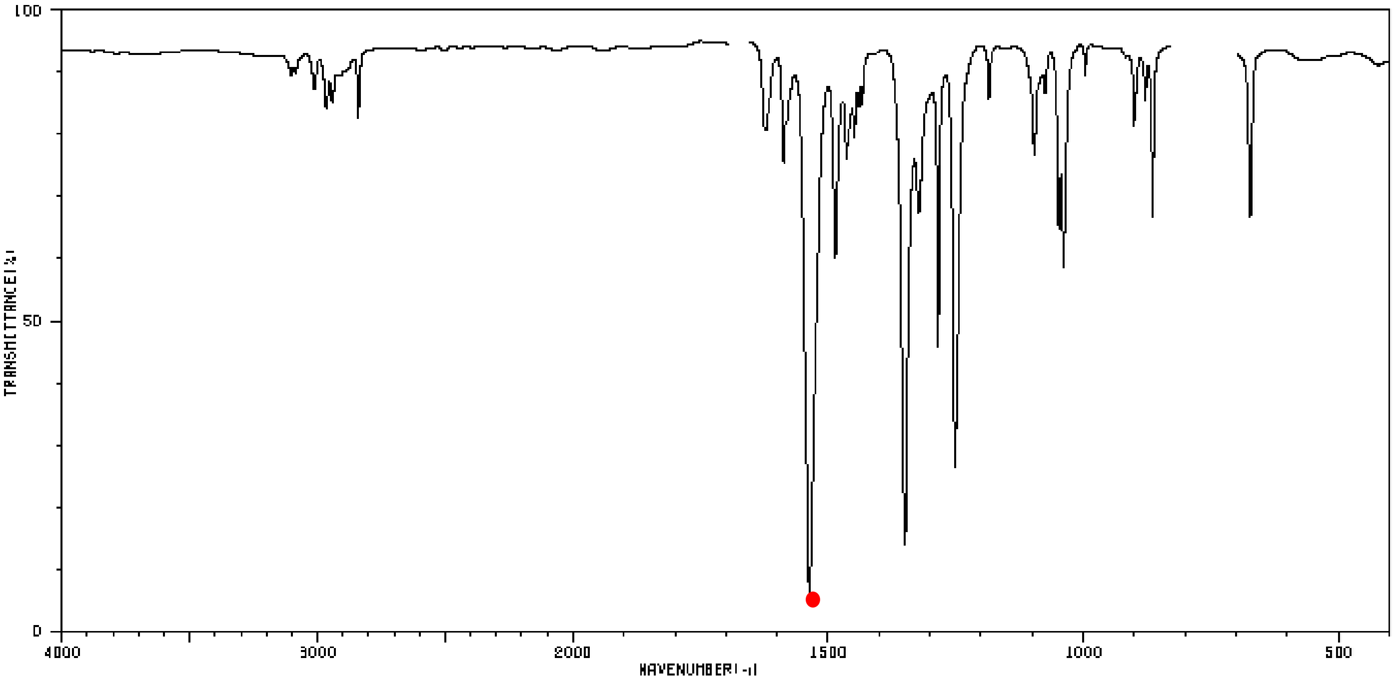
(C): *triplet of triplets*

Structure Determination – $C_9H_{11}OBr$

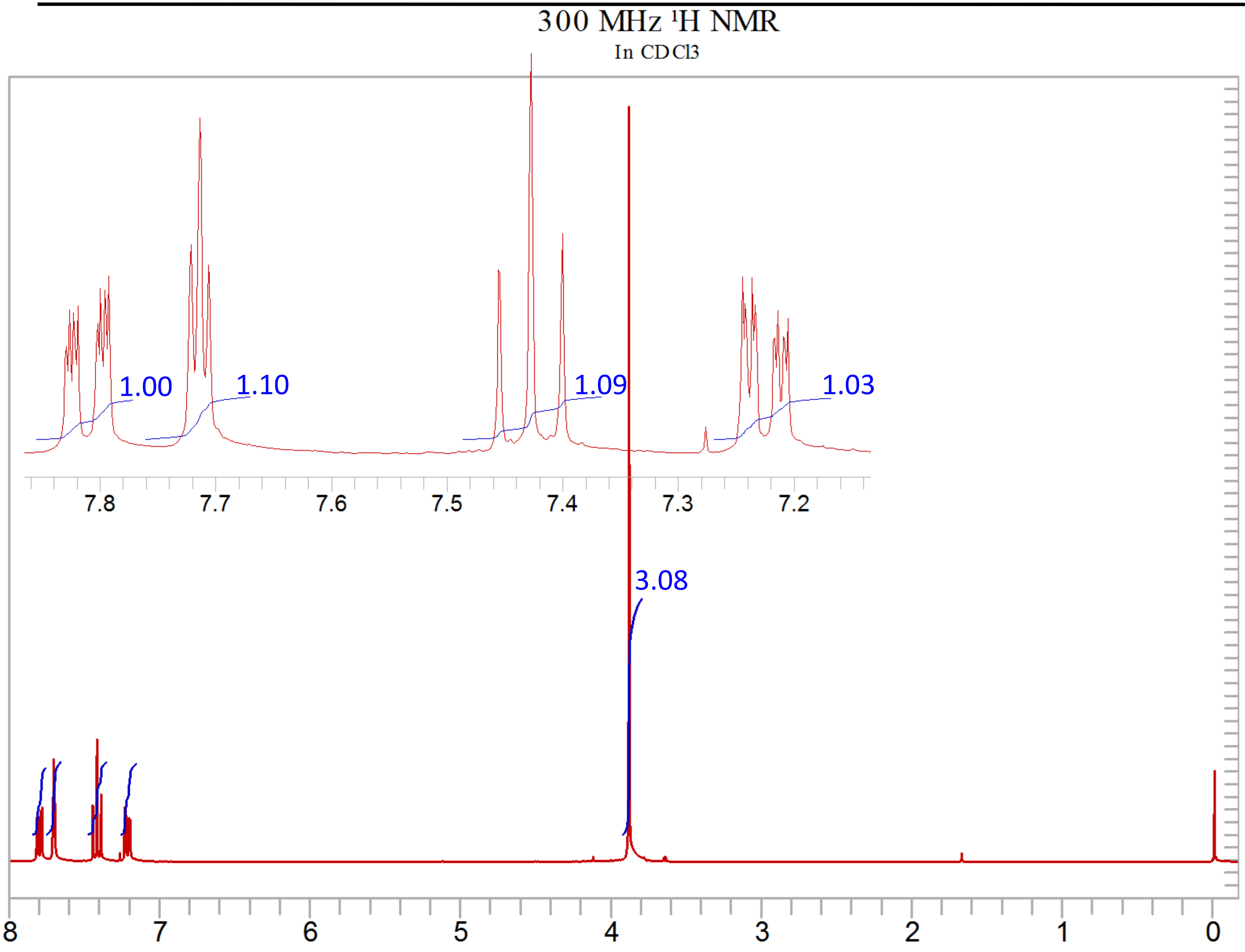


Structure Determination – $C_7H_7NO_3$

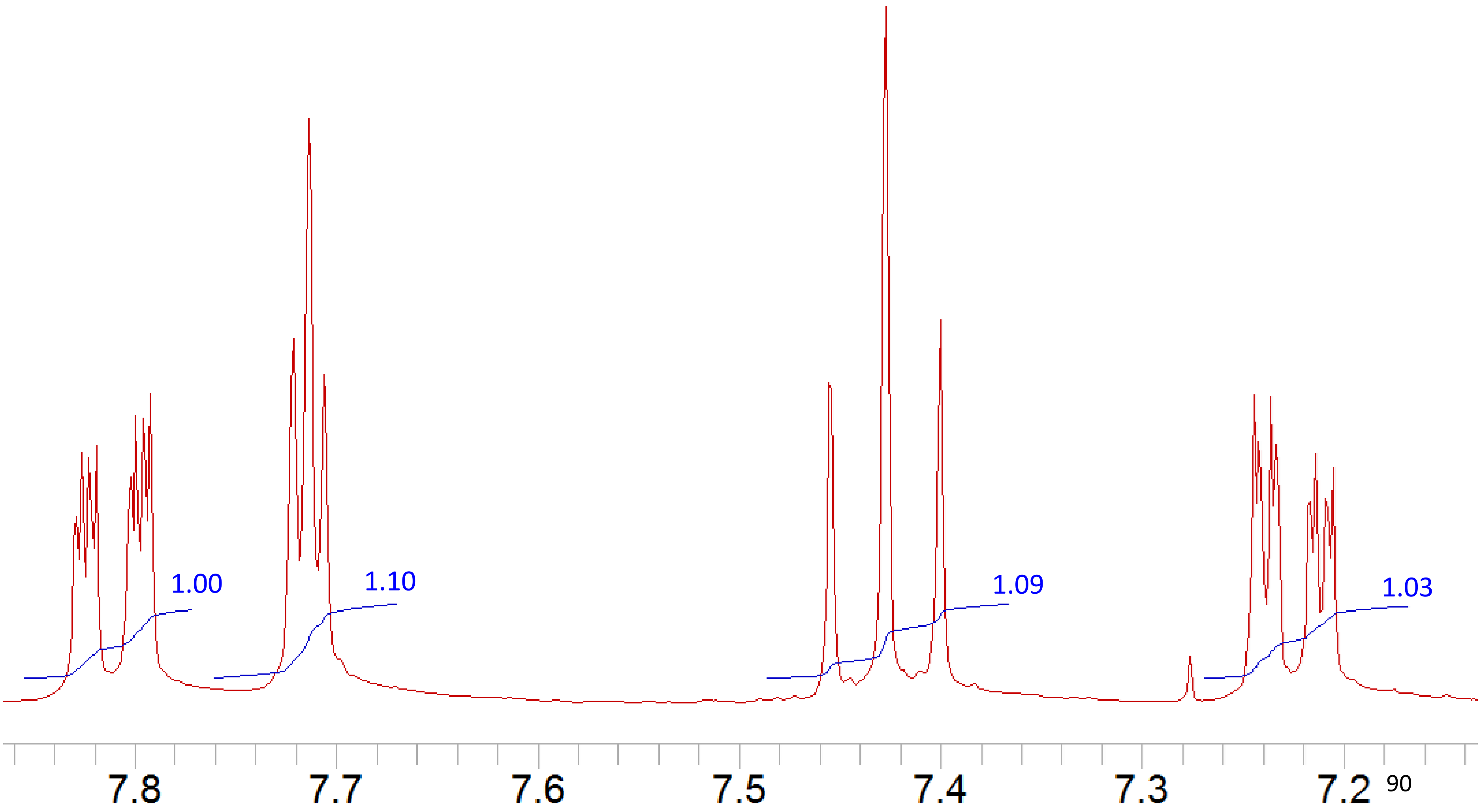
$$U = \frac{2C + 2 + N - H - X}{2} = \frac{2(7) + 2 + (1) - (7)}{2} = 5$$



Structure Determination – $C_7H_7NO_3$

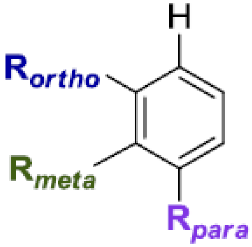


Structure Determination – $C_7H_7NO_3$



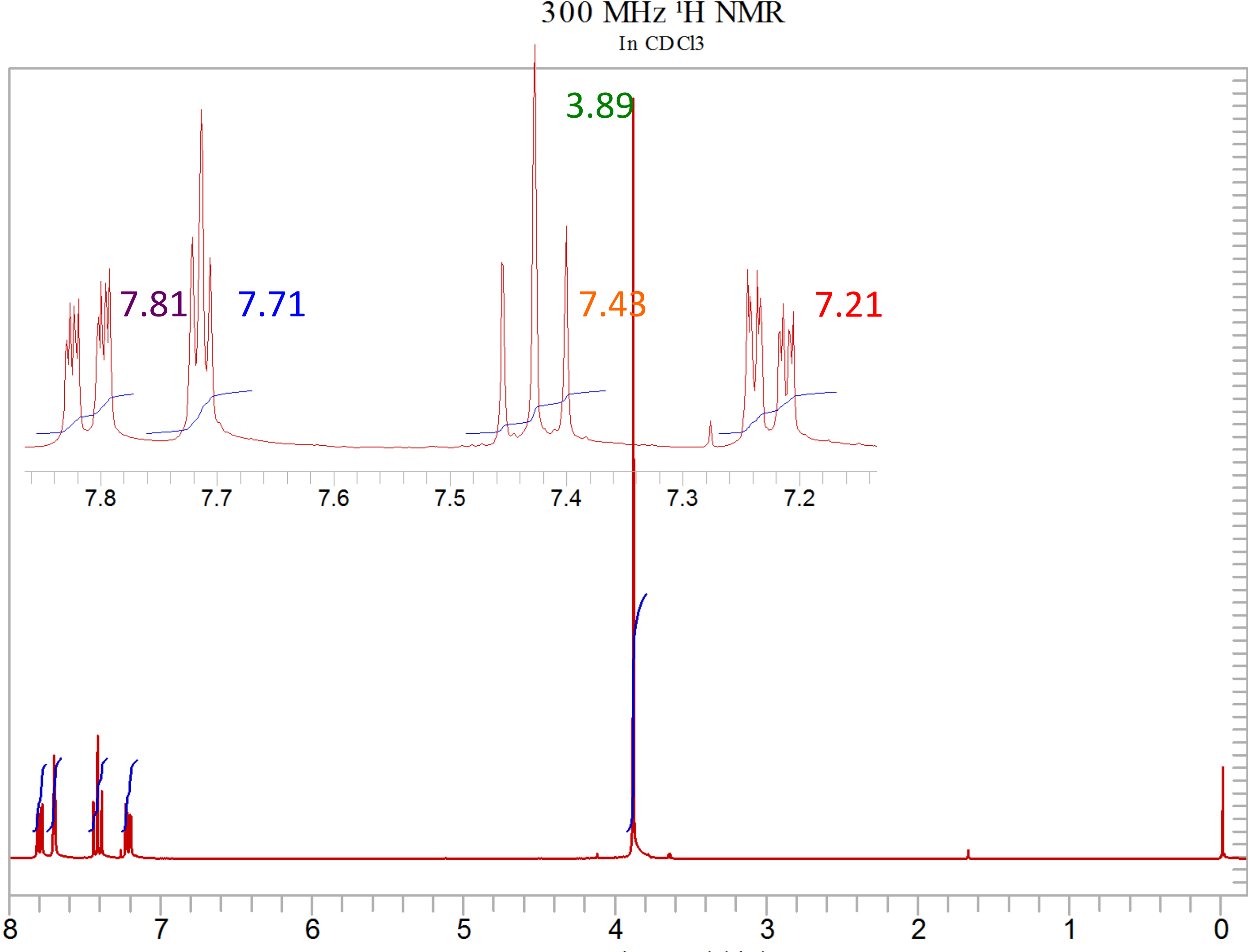
Estimating Chemical Shift via Curphy - Morrison parameters

Substituent Effects on:

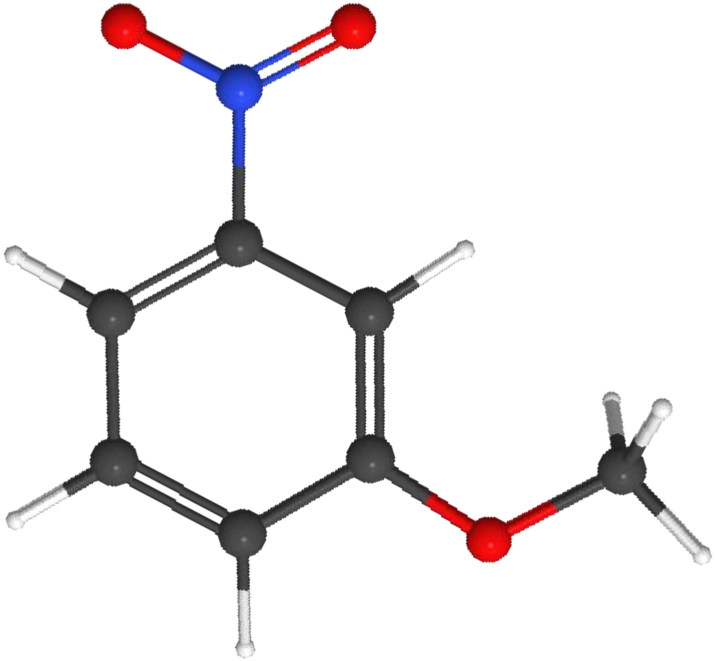


Shift Estimate: $\delta_{H\ (vinyl)} = 7.36 + Z_{ortho} + Z_{meta} + Z_{para}$

Estimating Chemical Shift via Curphy - Morrison parameters

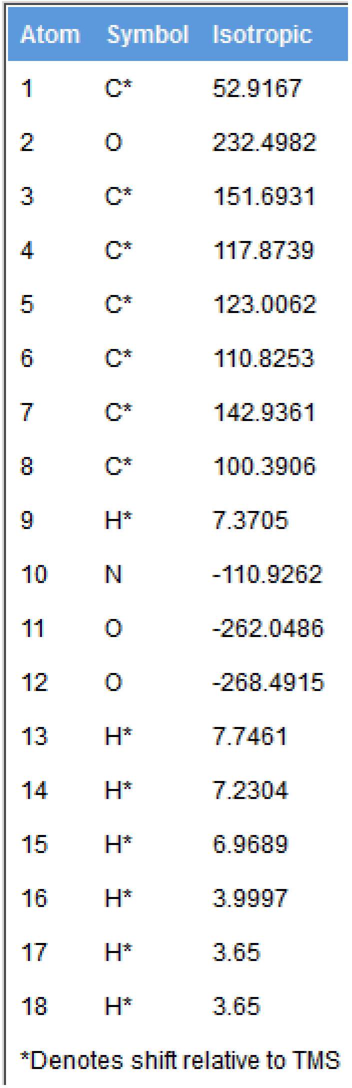


^{1}H-NMR Chemical Shift Prediction with Computational Chemistry



Absolute NMR Shifts

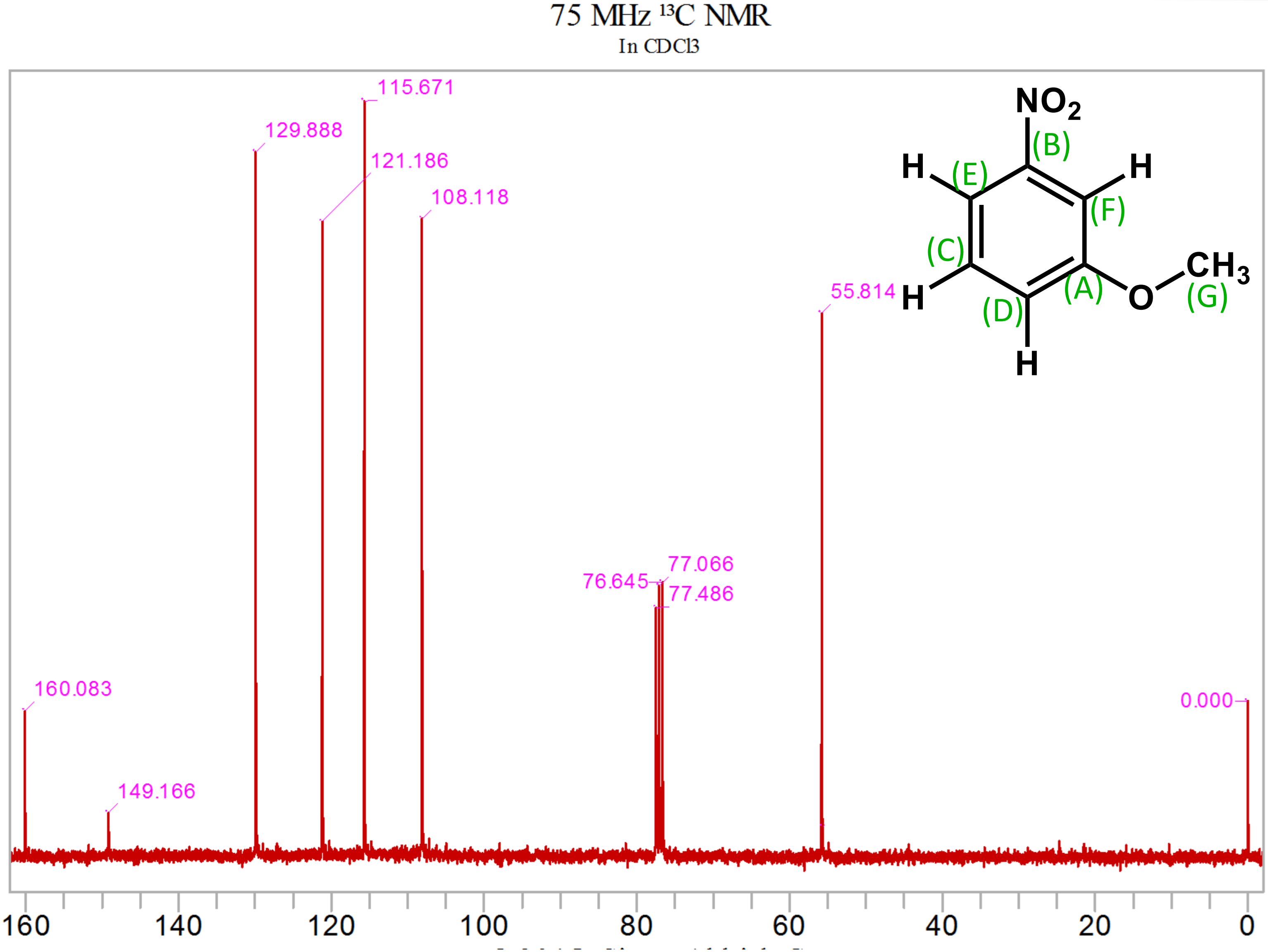
B3LYP/6-31G(d)



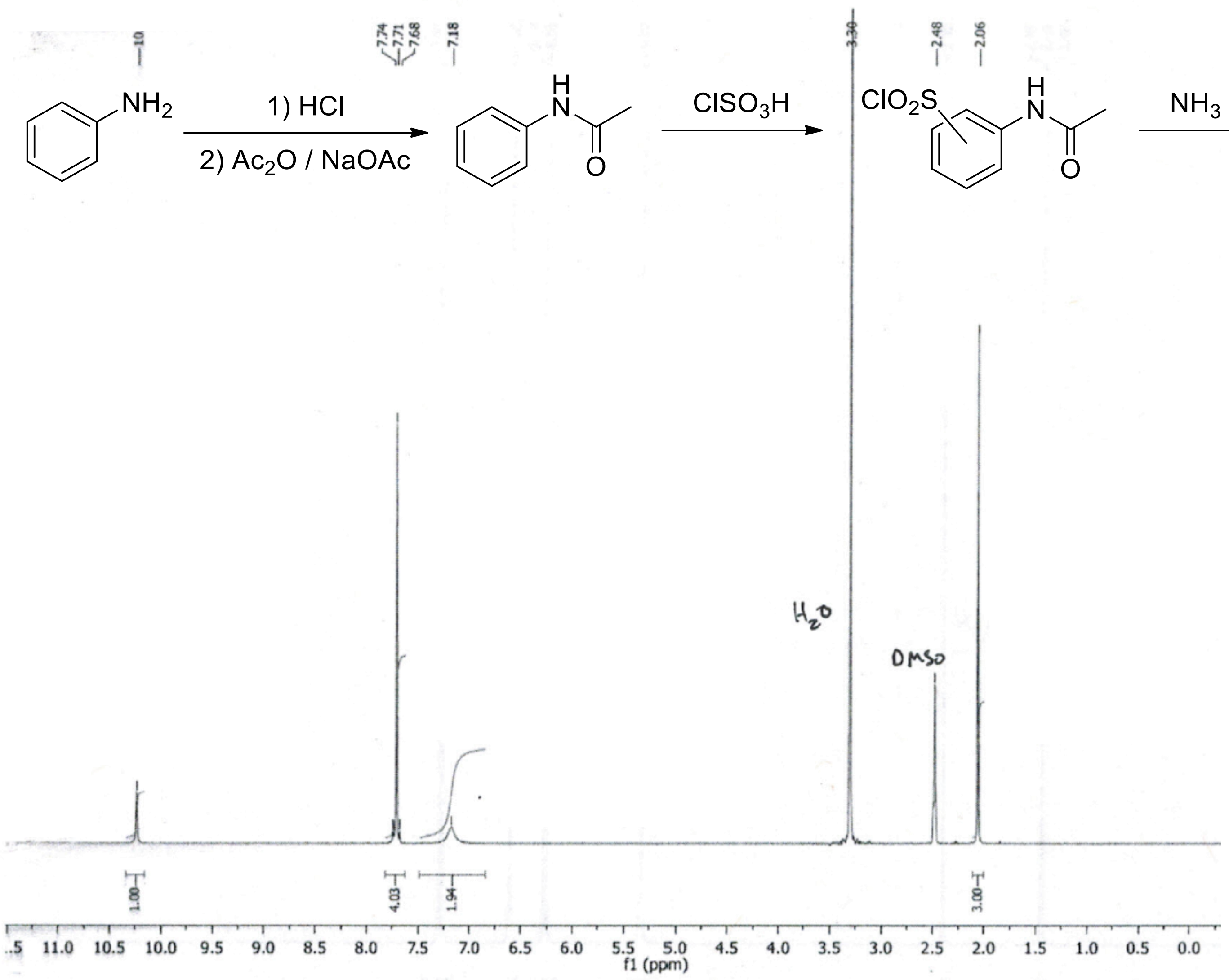
Atom	Symbol	Isotropic
1	C*	52.9167
2	O	232.4982
3	C*	151.6931
4	C*	117.8739
5	C*	123.0062
6	C*	110.8253
7	C*	142.9361
8	C*	100.3906
9	H*	7.3705
10	N	-110.9262
11	O	-262.0486
12	O	-268.4915
13	H*	7.7461
14	H*	7.2304
15	H*	6.9689
16	H*	3.9997
17	H*	3.65
18	H*	3.65

*Denotes shift relative to TMS

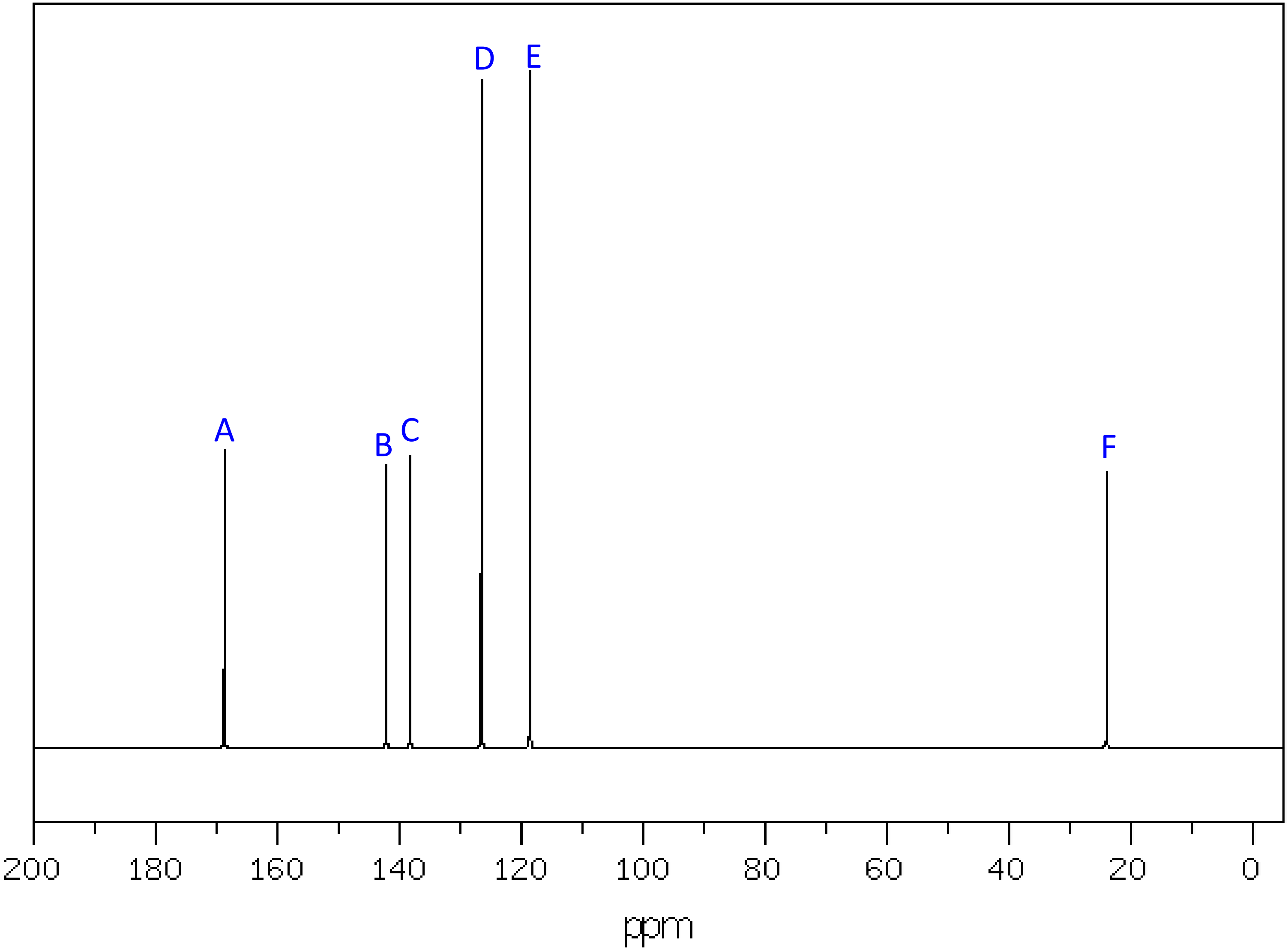
Structure Determination – $C_7H_7NO_3$



^{1}H-NMR Interpretation – 4’-sulfamoylacetanilide



^{13}C-NMR Interpretation – 4’-sulfamoylacetanilide



NMR Spectroscopy – Summary

^{1}H-NMR and ^{13}C-NMR spectra are very useful for structural determination of sample molecule(s).

- NMR techniques are based upon the interaction between radio frequency light and the magnetic properties of the nuclei in a molecule.
- ^{1}H-NMR and ^{13}C-NMR spectra commonly use TMS as a 0 ppm standard.
- Important information is found in the # of signals, chemical shift in ppm, integration value, coupling pattern, and coupling constant value.
- For 1st order ^{1}H-NMR spectra, the *n+1* rule is highly useful for interpreting coupling patterns.
- The size of the coupling constants can be used to interpret stereochemical and regiochemical relationships of protons.

References and Acknowledgements

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1) All computational values were calculated in WebMO running Gaussian 09 using B3LYP/6-31G(d). Atomic charges were calculated using NBO 6.0 unless otherwise noted.

2) All ^{1}H-NMR spectra were obtained from the Sigma-Aldrich Spectral Viewer unless otherwise noted.

3) Vibrational potential surface taken from http://www.chemtube3d.com/spectrovibwater1-CE-final.html

4) All MS, IR and ^{13}C-NMR spectra were obtained from the Spectral Database of Organic Compounds (SDBS). National Institute of Advanced Industrial Science and Technology (AIST) http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng

5) Many images were obtained from Loudon 5th edition 2009.

6) Amberger, B. K.; Esselman, B. J.; Woods, R. C.; McMahon, R. J., Millimeter-wave spectroscopy of carbonyl diazide, $OC(N_3)_2$. *J. Mol. Spectrosc.* **2014**, 295, 15-20.

7) Bonvallet, P. A.; McMahon, R. J., Generation, Characterization, and Rearrangements of 4,5-Benzocyclohepta-1,2,4,6-tetraene. *J. Am. Chem. Soc.* **2000,** *122* (38), 9332-9333.