SPECTROSCOPIC ANALYSIS OF ORGANIC COMPOUNDS

PART-3, PPT-3, SEM-5, CC-12P

Dr. Kalyan Kumar Mandal
Associate Professor
St. Paul's C. M. College
Kolkata

CONTENTS

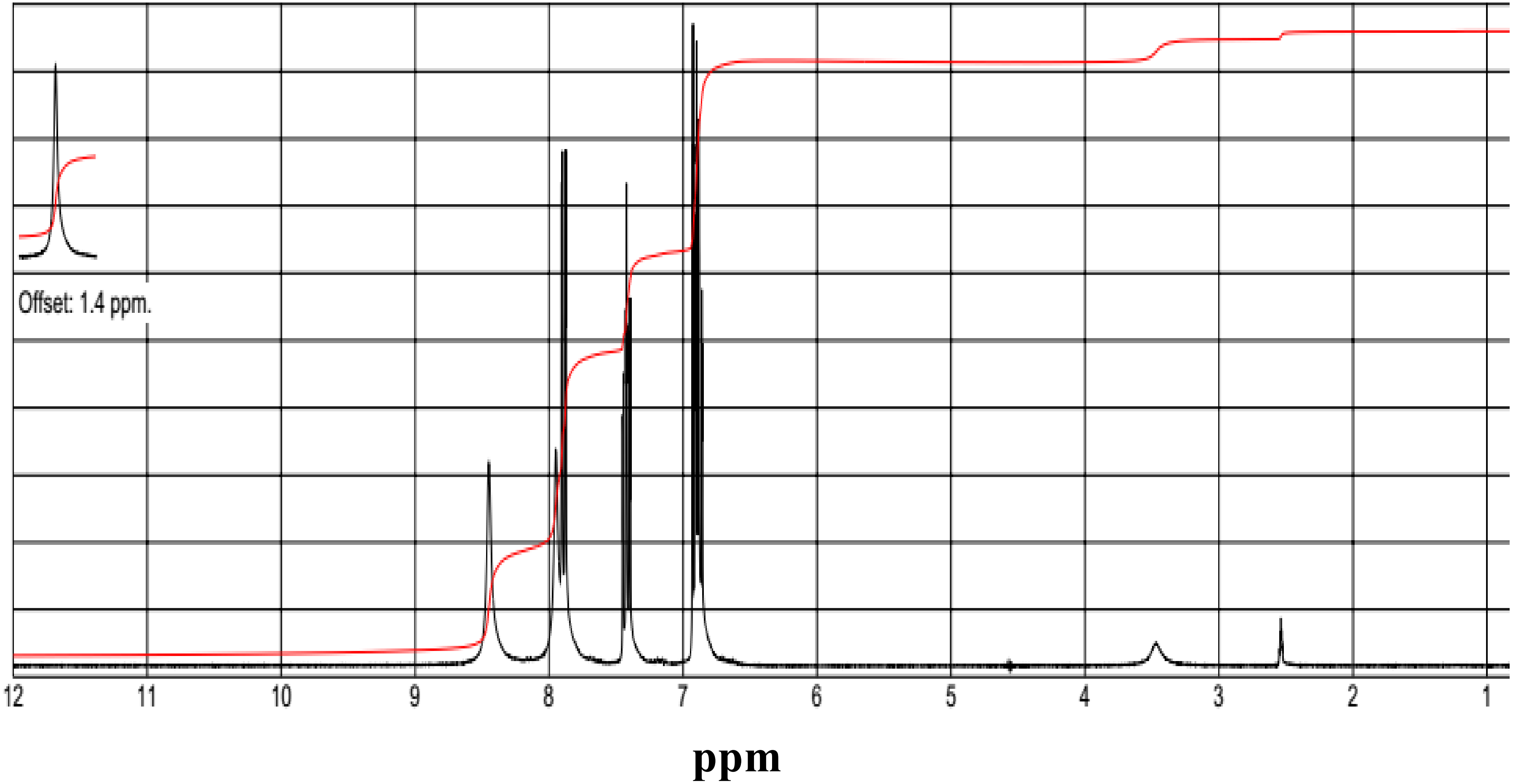
SPECTROSCOPIC ANALYSIS, PART-3

^{1}H NMR and IR Spectral Analysis of

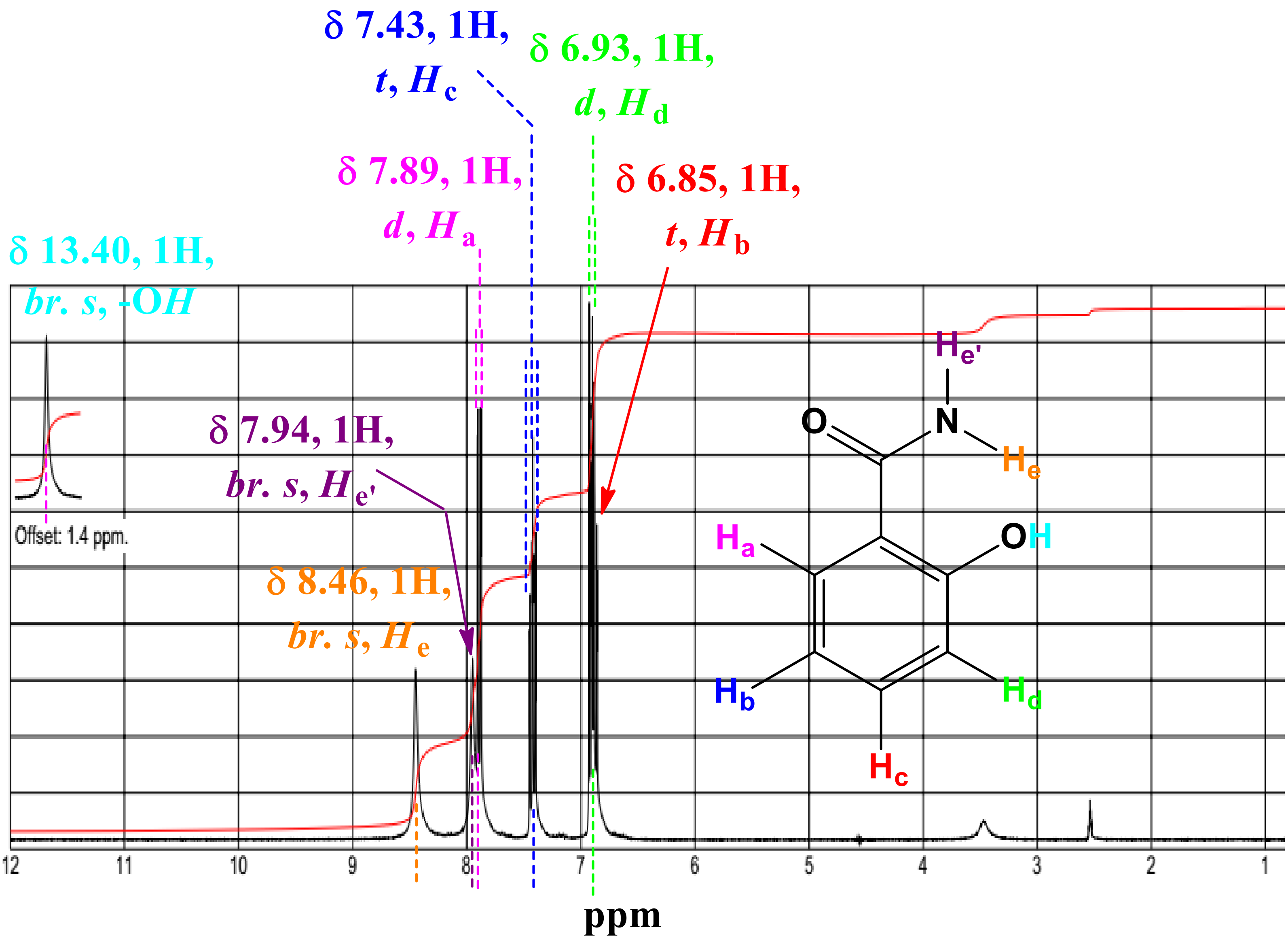
1. ***Salicylamide***
2. ***2'-Hydroxyacetophenone***

^{1}H NMR Spectrum of Salicylamide

300 MHz, DMSO-d6: δ (in ppm): 13.40, 8.46, 7.94, 7.89, 7.43, 6.93, 6.85



^{1}H NMR Spectrum of Salicylamide



δ 7.43, 1H, *t*, H_c

δ 6.93, 1H, *d*, H_d

δ 7.89, 1H, *d*, H_a

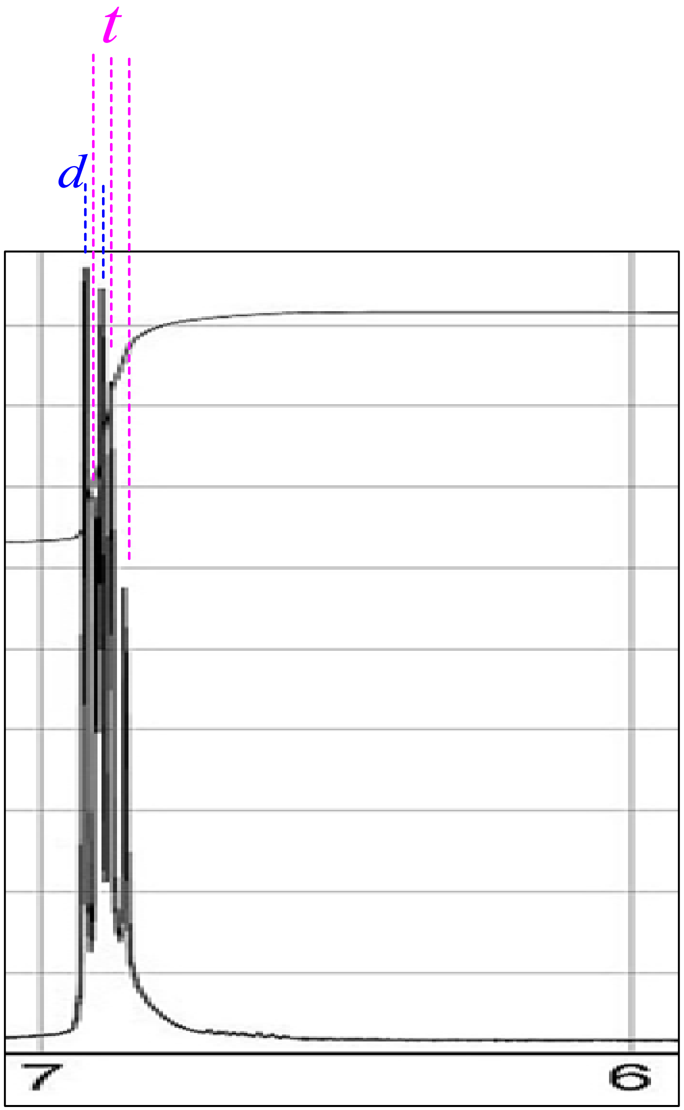
δ 6.85, 1H, *t*, H_b

δ 13.40, 1H, *br. s*, -O*H*

δ 7.94, 1H, *br. s*, $H_{e'}$

δ 8.46, 1H, *br. s*, H_e

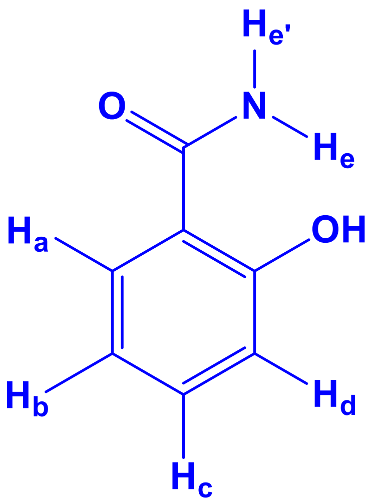
^{1}H NMR Spectrum of Salicylamide



^{1}H NMR Spectral Analysis of Salicylamide

- Spectrum is recorded in 300 MHz instrument in DMSO-d_6 using TMS as internal standard

Chemical shift (δ in ppm)	Number of hydrogens	Splitting pattern	Probable assignment
13.40	1H	*br. s*	-*OH*
8.46	1H	*br. s*	H_e
7.94	1H	*br. s*	$H_{e'}$
7.89	1H	*d*	H_a
7.43	1H	*t*	H_c
6.93	1H	*d*	H_d
6.85	1H	*t*	H_b



This Lecture is prepared by Dr. K. K. Mandal, SPCMC, Kolkata

^{1}H NMR Spectral Analysis of Salicylamide

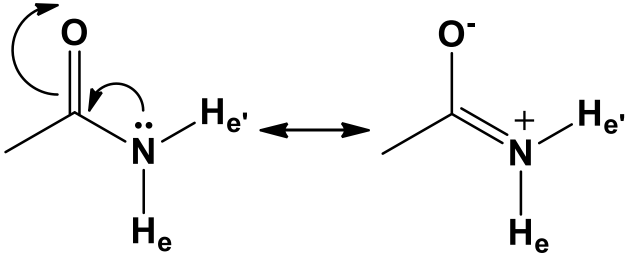
1. **δ 13.4: 1H, *br. s*, Ar-OH:** This proton is deshielded due to anisotropy of aromatic ring and conjugation that draws away the electron density from the oxygen of the phenolic-OH group. Attachment to electronegative oxygen atom (local diamagnetic effect) and intramolecular H-bonding also contribute to make this proton the most deshielded one.

- Broadness of the signal is due to hydrogen bonding and intermediate to rapid rate of proton exchange.

2. **δ 8.46 and 7.94: Protons attached to N-atom of -NH_2 group; 1H each, *br. s*, H_e (lies *trans* to O-atom of -$CONH_2$ group) and $H_{e'}$ (lies *cis* to O-atom of -$CONH_2$ group) respectively:** Deshielding of these protons is due to the EW effect of C=O and local diamagnetic anisotropy of electronegative N-atom.

^{1}H NMR Spectral Analysis of Salicylamide

2. Due to mesomeric interaction within the amide moiety, the C-N bond acquires partial double bond character which is why the two amide protons **H_e** and **$H_{e'}$** are in different chemical environment and they are non equivalent. Thus **H_e** and **$H_{e'}$** resonate at different chemical shift values. The proton **$H_{e'}$** is shielded compared to **H_e** proton due to anisotropy of C=O bond.



- Both these protons appear as a broad singlet (***br, s***). The broadness of signal is due to (i) intermediate rate of proton exchange, and (ii) the protons couple to each other, and (iii) inherent broadening associated with spin active nitrogen nucleus.

^{1}H NMR Spectral Analysis of Salicylamide

3. **δ 7.89:1H, *d*, *H*$_a$, proton *ortho* to -CONH$_2$:** ***H***$_a$ is deshielded due to diamagnetic anisotropic effect of (i) the aromatic moiety (ring current effect) and ii) the amide carbonyl group. This is further deshielded by the EW (**-R** and **-I**) -CONH$_2$ group.

- ***H***$_a$ appears as a ***doublet*** as it couples with adjacent ***H***$_b$ proton. (***ortho***-coupling).

4. **δ 7.43: 1H, *t*, *H*$_c$, proton *para* to -CONH$_2$ group:** ***H***$_c$ proton is deshielded by the diamagnetic anisotropy of the aromatic moiety (ring current effect) and EW (**-R** and **-I**) -CONH$_2$ group which is ***para*** to it.

- ***H***$_c$ proton appears as a ***triplet*** as it couples with two ***ortho*** protons ***H***$_b$ and ***H***$_d$ with respect to it.

^{1}H NMR Spectral Analysis of Salicylamide

5. **δ 6.93: 1H, *d*, *H_d*, proton *ortho* to -OH group:** Though this proton is deshielded by the (i) diamagnetic anisotropy of the aromatic moiety (ring current effect) and (ii) EW effect of –$CONH_2$ group, yet, it is strongly shielded by the electron donating (+R > -I) phenolic-OH group. Therefore, ***H_d*-proton** resonates at a higher field compared to both ***H_a*** and ***H_c*** protons.

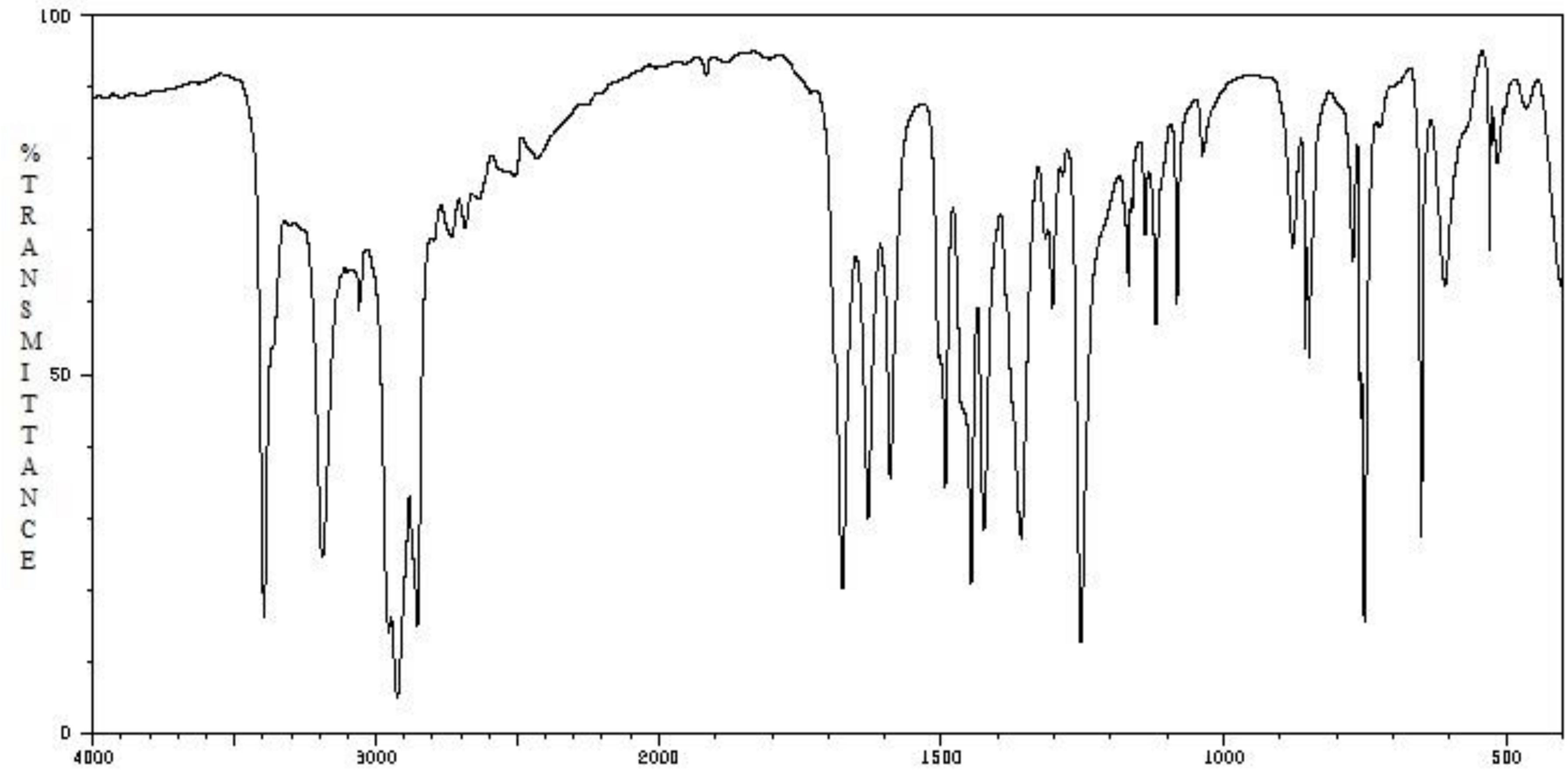
- ***H_d***-proton appears as a ***doublet*** since it couples with the proton ***H_c*** (***ortho***-coupling).

6. **δ 6.85: 1H, *t*, *H_b*, proton *para* to -OH group:** Though this proton is deshielded by the (i) diamagnetic anisotropy of the aromatic moiety (ring current effect) and (ii) EW -$CONH_2$ group, yet, it is strongly shielded by the electron donating (+R > -I) phenolic-OH group.

- ***H_b***-proton appears as a ***triplet*** since it couples with the protons ***H_a*** and ***H_c*** (both are ***ortho***-coupling).

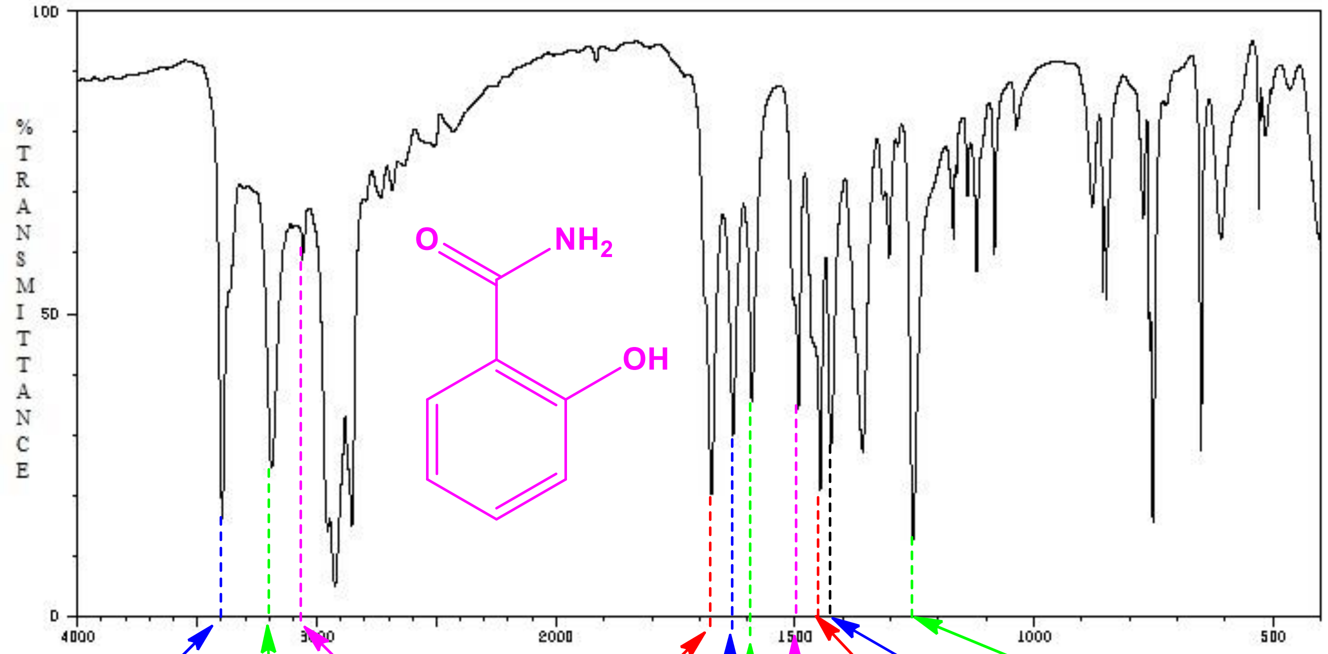
IR Spectrum of Salicylamide

FT-IR (CCl_4): Wavenumbers (cm^{-1}): 3390, 3200, 3060, 1680, 1630, 1595, 1495, 1450, 1425, and 1250



Wavenumbers (in cm^{-1})

IR Spectral Analysis of Salicylamide



3390, *s*,
N-H *str.*
Asymmetric

3200, *m*,
N-H *str.*
Symmetric

3060, *w*,
C_{sp2}-H *str.*
Aromatic

1680, *s*,
C=O *str.*
Amide I

1630, *m*,
N-H *bend.*
Amide II

1595, *m*,
C=C *str.*
Aromatic

1495, *m*,
C=C *str.*
Aromatic

1450, *s*,
C=C *str.*
Aromatic

1425, *m*,
C-N *str.*

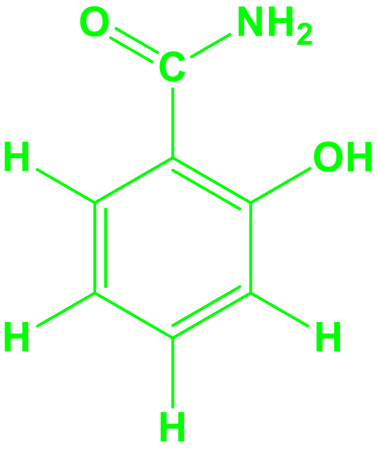
1250, *s*,
C-O *str.*
Ar-OH

This Lecture is prepared by Dr. K. K. Mandal, SPCMC, Kolkata

IR Spectral Analysis of Salicylamide

- **Spectrum is recorded in CCl_4 solution.**

Wavenumbers (cm^{-1})	**Nature**	**Probable Assignment**
3390, 3200	***s, m***	**N-H stretchings; Asymmetric and Symmetric**
3060	***w***	**C_{sp2}-H; Aromatic**
1680	***s***	**Aromatic C=O stretching; Amide-I**
1630	***m***	**N-H bending; Amide-II**
1595, 1495, 1450	***m, m, s***	**C=C stretchings; Aromatic skeletal vibrations**
1425	***m***	**C-N stretching**
1250	***s***	**C-O stretching; Ar-OH**



This Lecture is prepared by Dr. K. K. Mandal, SPCMC, Kolkata

IR Spectral Analysis of Salicylamide

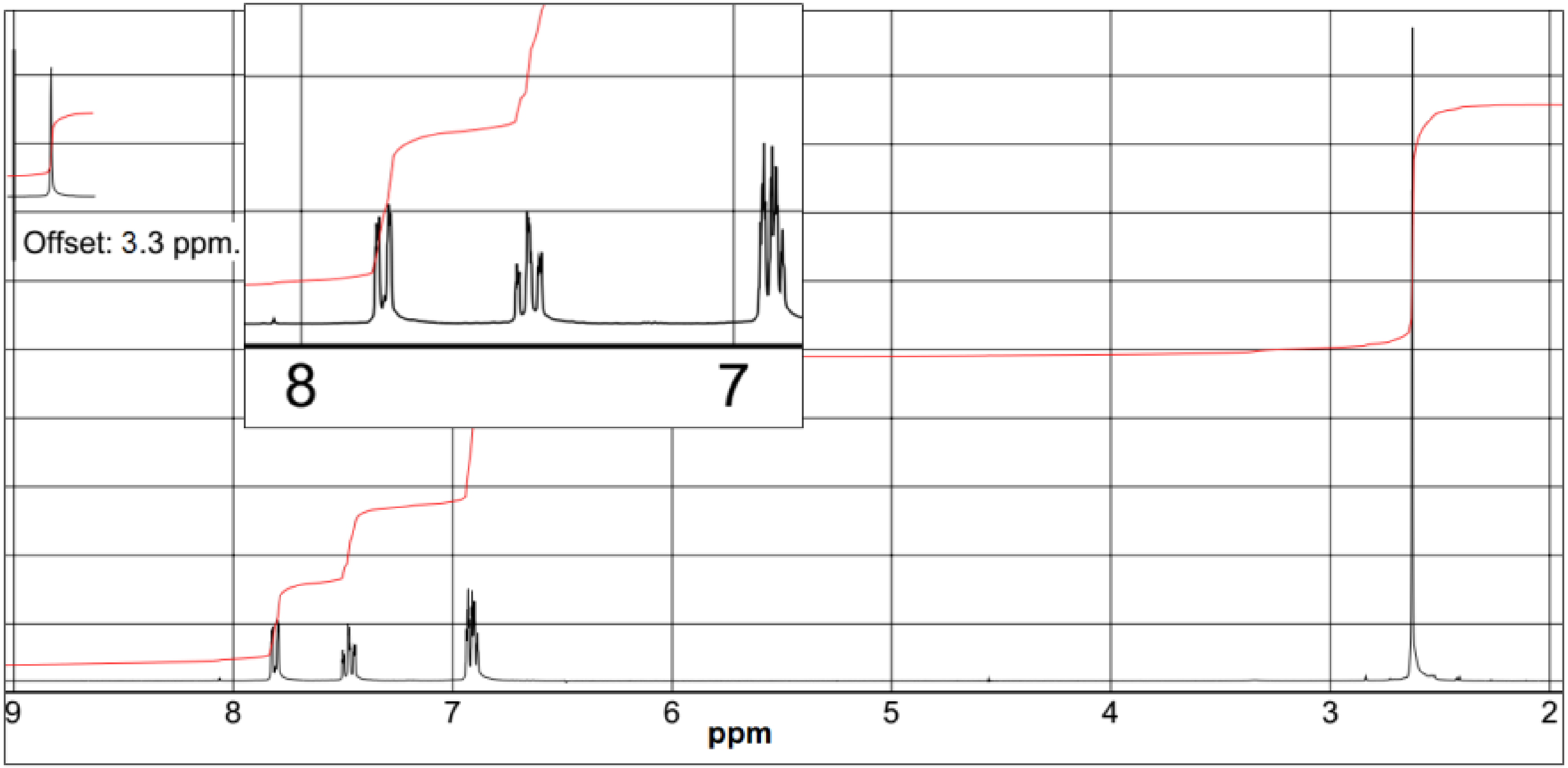
1. **3390, 3200: N-H stretchings, Asymmetric and Symmetric:** These are the characteristic absorptions for AB_2 type of grouping ($-NH_2$) present in the molecule. Two bands are due to vibrational coupling. This absorption occurs at a higher wave number region because N-H bond contains a small atom H, so frequency (***v***) and hence wavenumber increases by Hooke's law.
2. **3060: C_{sp2}-H stretching:** These absorptions are due to strong **C_{sp2}-H** bonds. The absorption at a higher region is due to the presence of small atom in the bond on one hand and hydrogen atom is attached to a ***sp*^{2}** hybridized carbon atom on the other.
3. **1680: Aromatic C=O stretching:** Carbonyl group is conjugated with nitrogen lone pair via the conjugative group, an aromatic ring in this case. As a result, due to mesomeric interaction, C=O bond assumes single bond character in the charged canonical form. Bond order of C=O decreases, and hence C=O absorption occurs at lower than 1715 cm^{-1}.

IR Spectral Analysis of Salicylamide

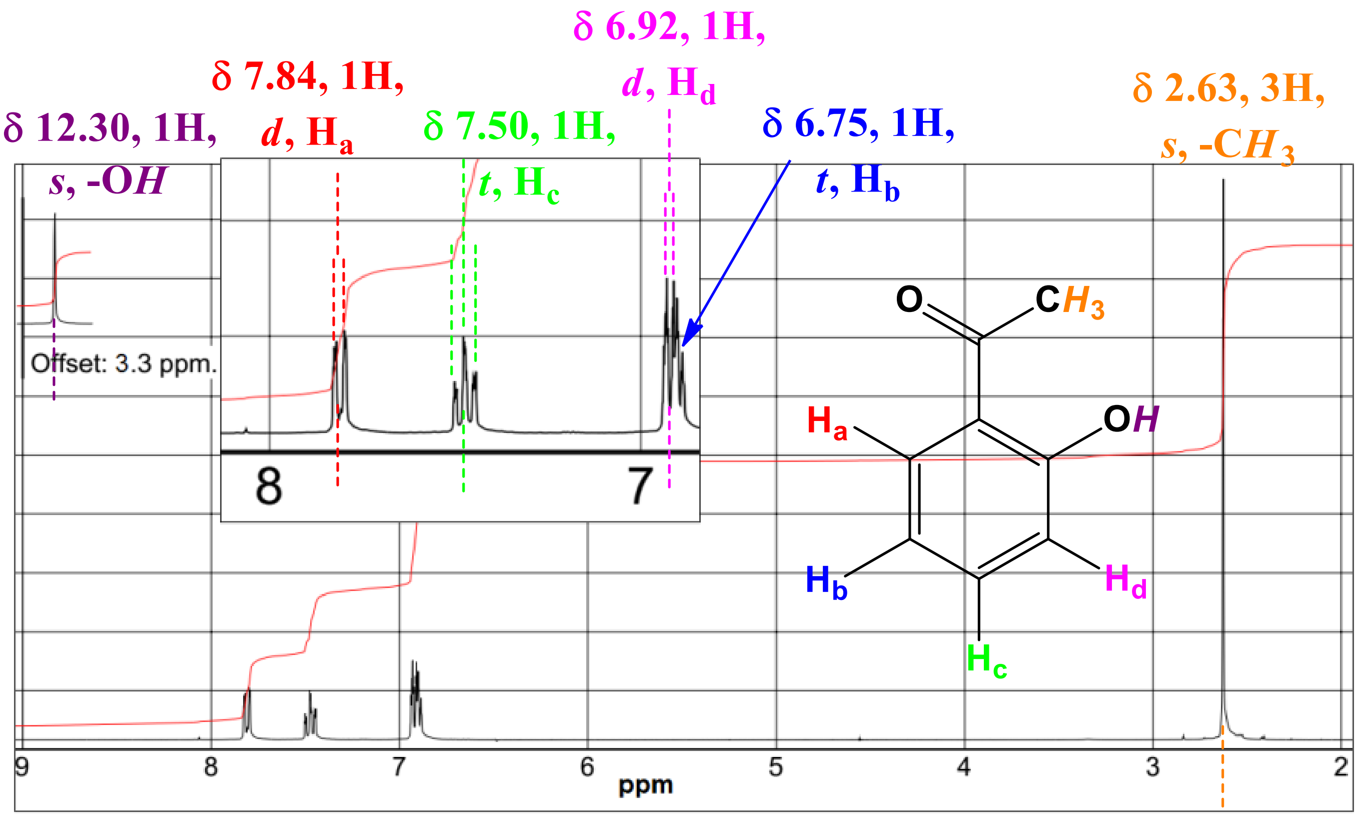
4. **1630: N-H bending, Amide-II:** This absorption is due to a bending vibration (N-H) and appears at a lower wave number region than than that of C=O stretching.
5. **1600, 1495, 1450: C=C stretchings:** The vibration due to the conjugated aromatic system (***aromatic skeletal vibrations***) appears at a lower wavenumber than that of the nonconjugated system due to lowering of C=C bond strength.
6. **1425: C-N stretching:** This absorption appeared at lowerwave number region as (i) it is a single bond and (ii) the bond involves a higher reduced mass. However, this bond is stronger as carbon atom is a part of the aromatic ring.
7. **1250: C-O stretching of Ar-OH:** Appearance at lower wave number of this bond is due to (i) the vibration involves a single bond and (ii) masses of both the constituent atoms are relatively large unlike C-H, O-H, etc.

^{1}H NMR Spectrum of 2'-Hydroxyacetophenone

300 MHz, $CDCl_3$ + DMSO-d6: δ (in ppm): 12.30, 7.84, 7.50, 6.92, 6.75 and 2.63

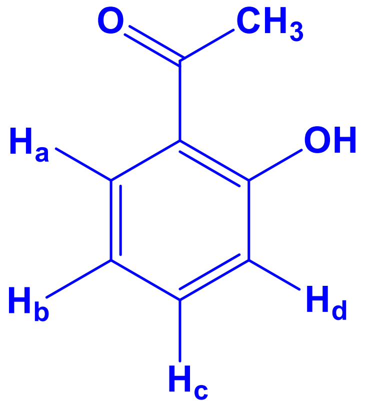


^{1}H NMR Spectral Analysis of 2'-Hydroxyacetophenone



^{1}H NMR Spectral Analysis of 2'-Hydroxyacetophenone

- Spectrum is recorded in 300 MHz instrument in $CDCl_3$ + DMSO-d6 using TMS as internal standard



Chemical shift (δ in ppm)	Number of hydrogens	Splitting pattern	Probable assignment
12.30	1H	*s*	-O*H*
7.84	1H	*d*	H_a
7.50	1H	*t*	H_c
6.92	1H	*d*	H_d
6.75	1H	*t*	H_b
2.63	3H	*s*	$-COCH_3$

^{1}H NMR Spectral Analysis of 2'-Hydroxyacetophenone

1. **δ 12.3: 1H, *s*, Ar-O*H*:** This proton is deshielded due to anisotropy of aromatic ring and conjugation that draws away the electron density from the oxygen of the phenolic-OH group. Attachment to electronegative oxygen atom (local diamagnetic effect) and intramolecular H-bonding also contribute to make this proton the most deshielded one.

- This proton appears as a ***singlet*** due to the absence of neighbouring interacting proton.

2. **δ 7.84: 1H, *d*, H_a (proton *ortho* to –$COCH_3$ group):** This proton is deshielded by the combined effect of diamagnetic anisotropy of the neighbouring carbonyl group and that of the aromatic ring (ring current effect), as well as the EW (-I and -R) effect of the –$COCH_3$ group.

- It appears as a ***doublet*** due to coupling with the proton **H_b** (***ortho*-**coupling).

^{1}H NMR Spectral Analysis of 2'-Hydroxyacetophenone

3. **δ 7.5: 1H, *t*, H_c (proton *para* to -$COCH_3$ group):** This proton is deshielded by the (i) diamagnetic anisotropy of aromatic ring (ring current effect), and EW (**-I** and **-R**) effect of the –$COCH_3$ group. It is less deshielded than **H_a** because it does not fall in the deshielding zone of the keto group.

- It appears as a ***triplet*** due to coupling with the two ***ortho*** protons, **H_b** and **H_d** with respect to it.

4. **δ 6.92: 1H, *d*, *H_d*, proton *ortho* to -OH group:** Though this proton is deshielded by the (i) diamagnetic anisotropy of the aromatic moiety (ring current effect) and (ii) EW effect of –$COCH_3$ group, yet, it is strongly shielded by the electron donating (+R > -I) effect of phenolic-OH group. Therefore, ***H_d*-proton** resonates at a higher field compared to ***H_a*** and ***H_c*** protons.

- ***H_d***-proton appears as a ***doublet*** since it couples with the proton ***H_c*** (***ortho***-coupling).

^{1}H NMR Spectral Analysis of 2'-Hydroxyacetophenone

5. **δ 6.75: 1H, *t*, *H_b*, proton *para* to -OH group:** Though this proton is deshielded by the (i) diamagnetic anisotropy of the aromatic moiety (ring current effect) and (ii) EW effect of –$COCH_3$ group, yet, it is strongly shielded by the electron donating (+R > -I) effect of phenolic-OH group.

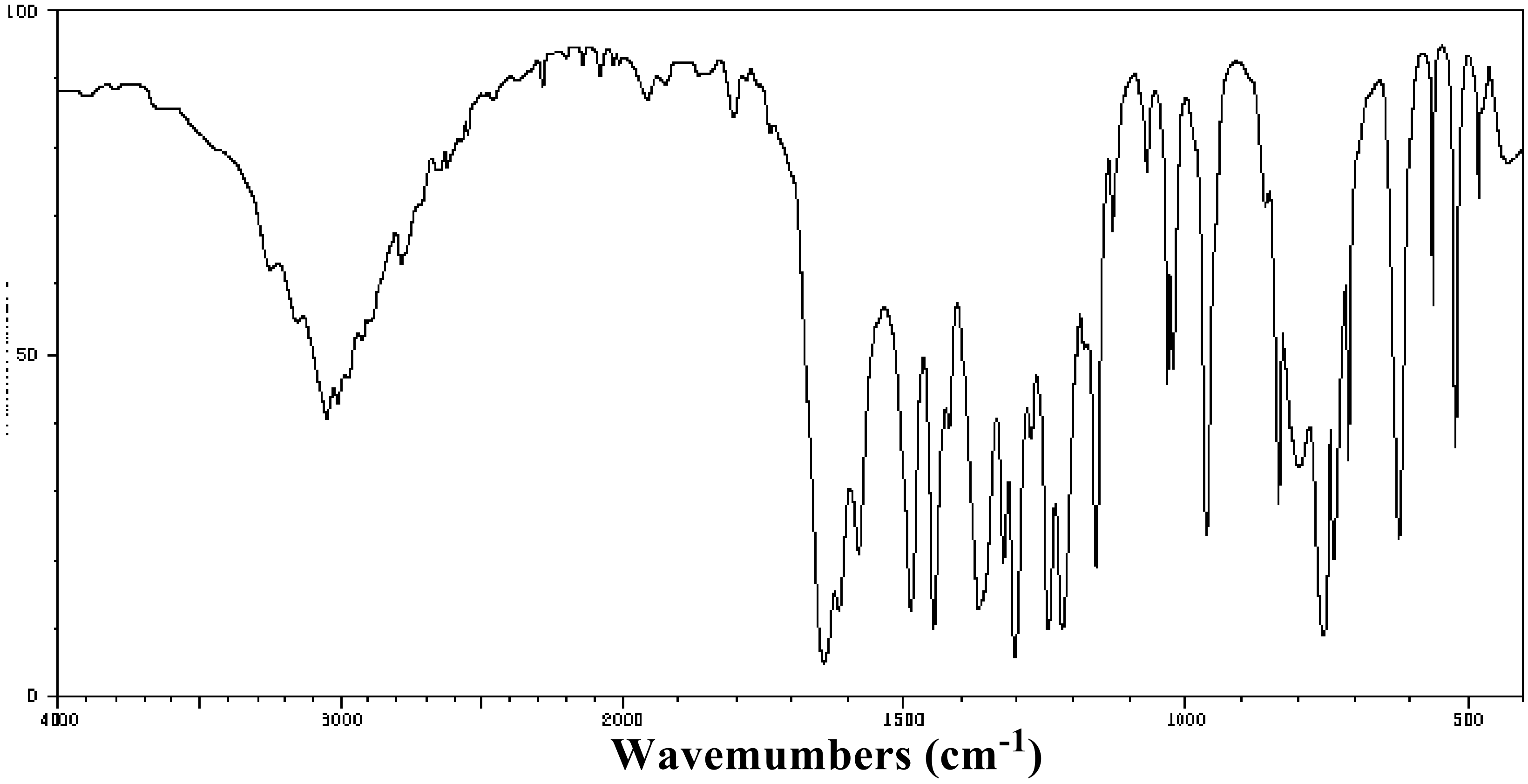
- ***H_b***-proton appears as a ***triplet*** since it couples with the protons ***H_a*** and ***H_c*** (both are ***ortho***-coupling).

6. **δ 2.58: 3H, *s*, -COC*H_3*:** The ketomethyl protons are deshielded due to EW effect (**-I** and **-R**) of C=O group of -$COCH_3$ group. Diamagnetic deshielding effect of the C=O group of -$COCH_3$ also plays a part.

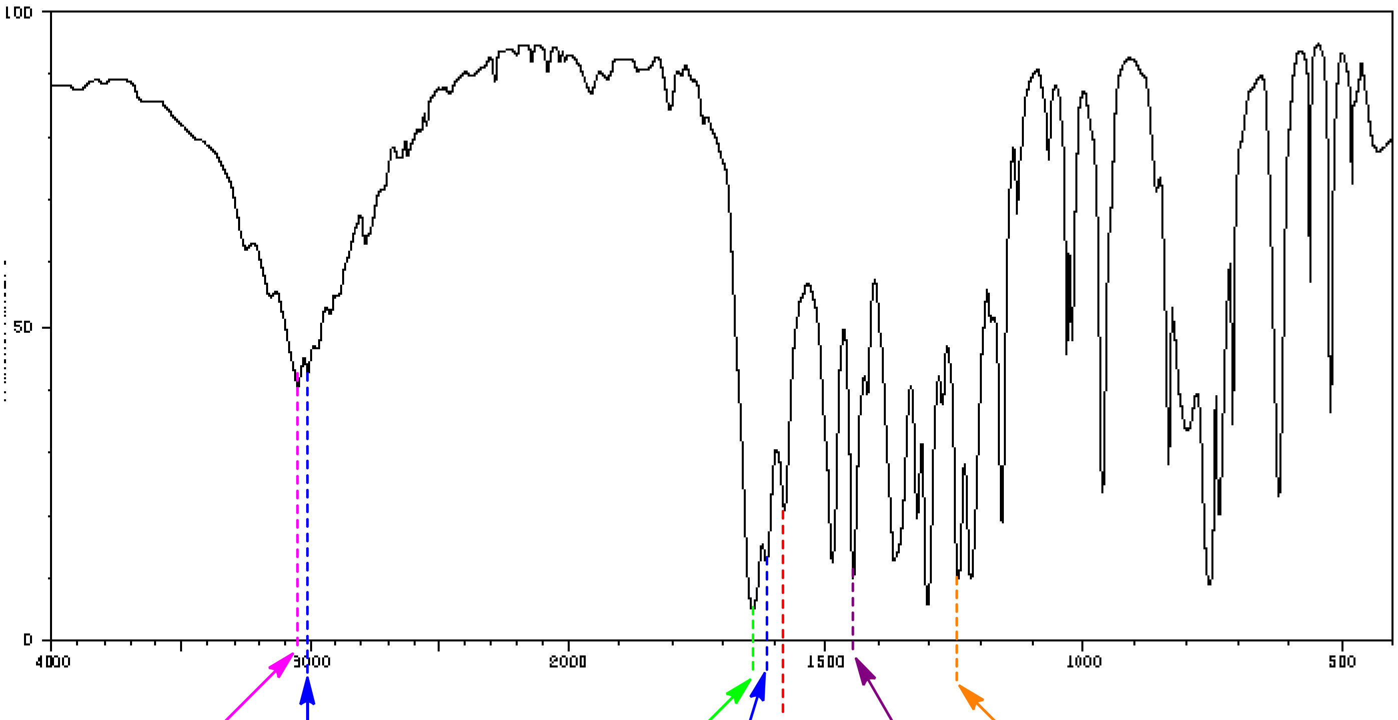
- This protons appear as a ***singlet*** as they have no neighbouring hydrogen to couple with.

IR Spectrum of 2'-Hydroxyacetophenone

FT-IR (Liquid Film): Wavenumbers (cm^{-1}): 3300-2700, 3050, 1643, 1617, 1582, 1448, and 1245



IR Spectral Analysis of 2'-Hydroxyacetophenone



3050, *m*,
C_{sp2}-H str.

3010, Central position of broad O-H str. 3300-2700

1643, *s*,
C=O str.
Conjugated

1617, *s*,
C=C str.
Aromatic

1582, *m*,
C=C str.
Aromatic

1448, *s*,
C=C str.
Aromatic

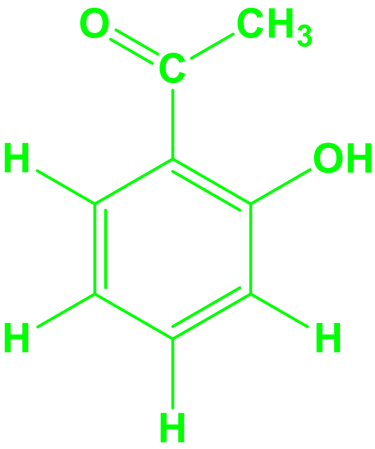
1245, *s*,
C-O str.

This Lecture is prepared by Dr. K. K. Mandal, SPCMC, Kolkata

IR Spectral Analysis of 2'-Hydroxyacetophenone

- **Spectrum is recorded in liquid film solution.**

Wave Numbers (cm^{-1})	Nature	Probable Assignment
3300-2700	***broad***	**O-H stretching for the dimer centred at 3010 cm^{-1}**
3050	***w***	**C_{sp2}-H; Aromatic**
1643	***s***	**Conjugated C=O stretching**
1617, 1482, 1448	***s, m, s***	**C=C stretchings; Aromatic skeletal vibrations**
1245	***s***	**C-O stretching; Ar-OH**



IR Spectral Analysis of 2'-Hydroxyacetophenone

1. **3300-2700: O-H stretching of the dimer:** This broad absorption band for O-H bond centres near 3010 cm^{-1}. Vibrational frequency associated with the O-H bond is very high because (i) O-H bond is very strong and (ii) this bond contains a small atom hydrogen (reduced mass decreases, frequency increases). Broad signal is due to H-bonding. Hydrogen bonding causes lengthening of the original O-H bond and it becomes weaker. Hence force constant of O-H bond decreases.

2. **3050: C$_{sp2}$-H stretching:** These absorptions are due to strong **C$_{sp2}$-H** bonds. The absorption at a higher region is due to the presence of small atom in the bond on one hand and hydrogen atom is attached to a sp^2 hybridized carbon atom on the other.

IR Spectral Analysis of 2'-Hydroxyacetophenone

3. **1643: Conjugated C=O stretching:** Carbonyl group is conjugated with nitrogen lone pair via the conjugative group, an aromatic ring in this case. As a result, due to mesomeric interaction C=O bond assumes single bond character in the charged canonical form. Bond order of C=O bond decreases and hence C=O absorption occurs at lower than 1715 cm^{-1}.
4. **1617, 1582, 1448: C=C stretchings:** The vibration due to the conjugated aromatic system (***aromatic skeletal vibrations***) appears at a lower wave number than that of the nonconjugated system due to lowering of C=C bond strength.
5. **1245: C-O stretching of Ar-OH:** Appearance at lower wave number of this bond is due to (i) the vibration involves a single bond and (ii) masses of both the constituent atoms are relatively large unlike C-H, O-H, etc.