

Chapter-20: Infrared spectroscopy (Identifying Compounds or ligands)

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An IR spectrum can be visualized in a graph of infrared light absorbance (or transmittance) on the vertical axis (y axis) vs. frequency or wavelength on the horizontal axis (x axis). Typical units of frequency used in IR spectra are reciprocal centimeters (sometimes called wave numbers), with the symbol cm^{-1} . The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared. **Among these regions, the mid-infrared, approximately $4000\text{--}400\text{cm}^{-1}$ ($2.5\text{--}25\text{ }\mu\text{m}$) may be used to study the presence of different moieties or groups present in certain compounds or ligands.**

Classification different moieties or groups in the different regions of i.r. spectrum w.r.t their frequency (cm^{-1}):

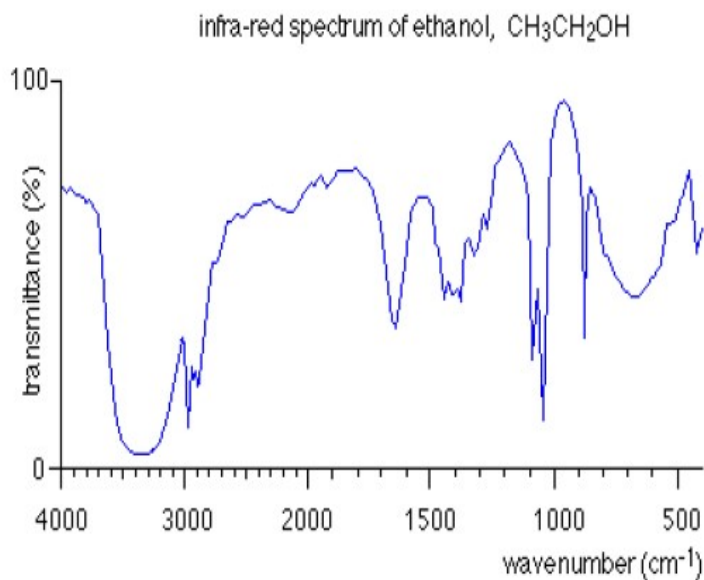
Table.1: IR frequency of alcoholic -OH, carboxylic -OH, carbonyl, alcoholic C-O and C-H of hydrocarbons

Bond	Functional group	Absorbance (cm^{-1})
O - H	Alcohols	3200 - 3600 / strong and broad*
O - H	Carboxylic acids	2500 - 3200 / medium and very broad*
C=O	Aldehydes / ketones / carboxylic acids/ esters	1680 - 1750 / strong and sharp
C-O	Alcohols / esters / ethers	1050 - 1300 / medium
C-H	Alkanes / alkenes etc	2850 - 3100 / medium

* Broad peak occurs due to H-bonding between O-H groups

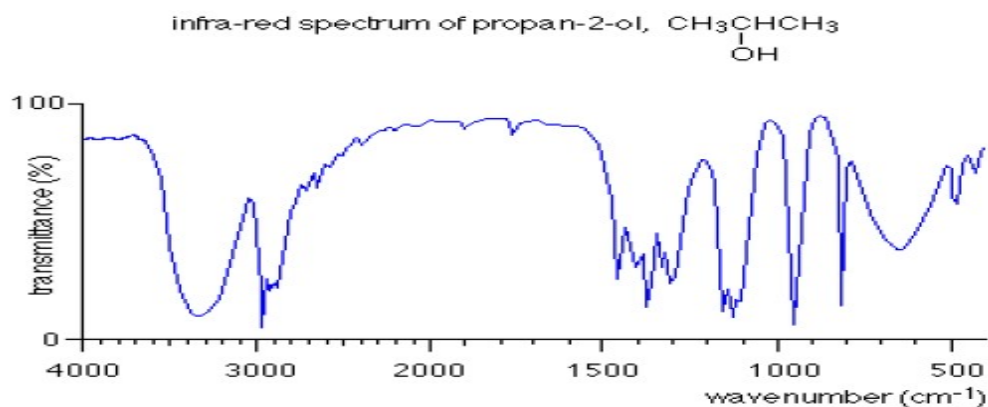
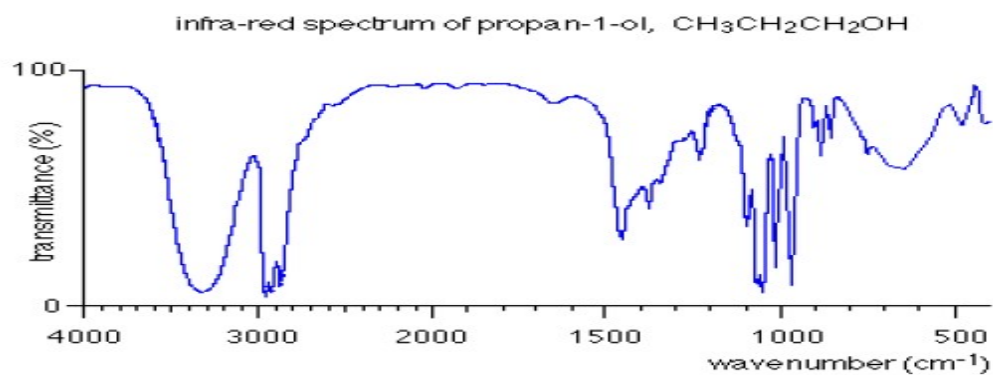
IR spectra of Alcohol (R-OH):

The O-H bond in an alcohol absorbs at a higher wave number than it does in an ethanoic acid - somewhere between $3230 - 3550 \text{ cm}^{-1}$.

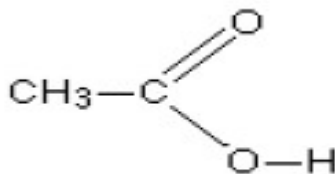


IR spectra of propan-1-ol and propan-2-ol:

Compare the infra-red spectra of propan-1-ol and propan-2-ol. Both compounds contain exactly the same bonds. Both compounds have very similar troughs in the area around 3000 cm^{-1} - but compare them in the fingerprint region between 1500 and 500 cm^{-1} .



IR spectra of Ethanoic acid (CH_3COOH):



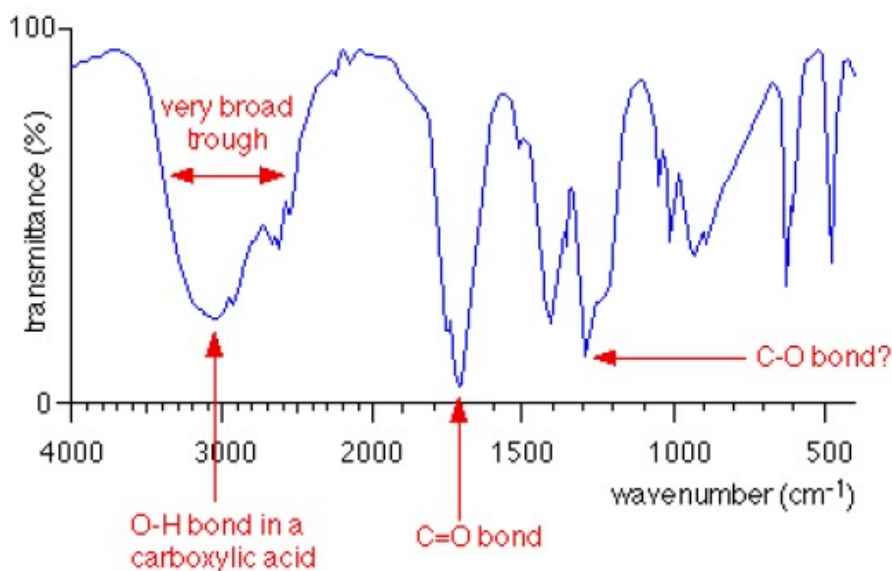
It contains the following bonds:

carbon-oxygen double, $\text{C}=\text{O}$; carbon-oxygen single, $\text{C}-\text{O}$; oxygen-hydrogen, $\text{O}-\text{H}$; carbon-hydrogen, $\text{C}-\text{H}$; carbon-carbon single, $\text{C}-\text{C}$.

The carbon-carbon bond ($\text{C}-\text{C}$) has absorptions which occur over a wide range of wave numbers in the fingerprint region - that makes it very difficult to pick out on an infra-red spectrum. The **carbon-oxygen single bond ($\text{C}-\text{O}$)** also has an absorption in the fingerprint region, varying **between 1000 and 1300 cm^{-1}** depending on the molecule it is in.

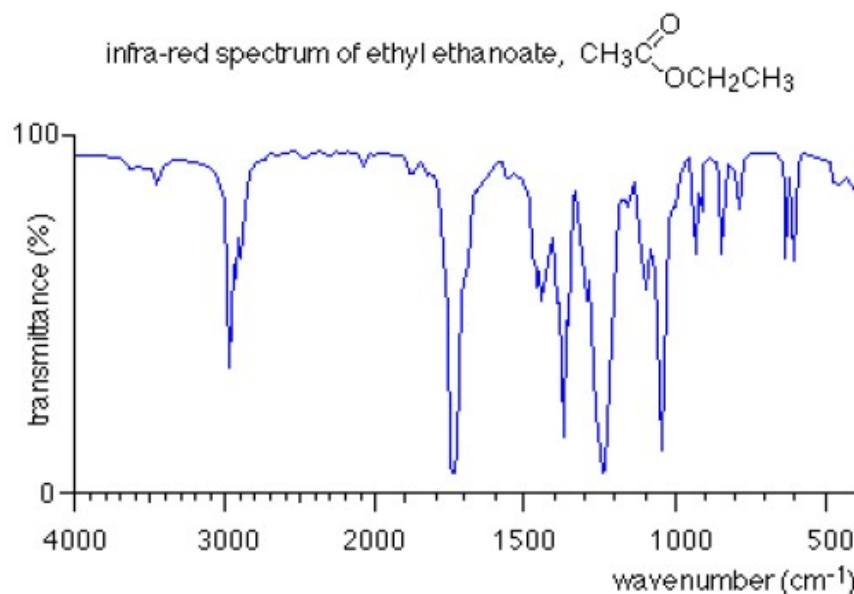
The other bonds in ethanoic acid have easily recognized absorptions outside the fingerprint region. **The $\text{C}-\text{H}$ bond** (where the hydrogen is attached to a carbon which is singly-bonded to everything else) absorbs somewhere **in the range from 2853 - 2962 cm^{-1}** . **The carbon-oxygen double bond, $\text{C}=\text{O}$** , is one of the really useful absorptions, found **in the range 1680 - 1750 cm^{-1}** . Its position varies slightly depending on what sort of compound it is in. The other really useful bond is the **$\text{O}-\text{H}$ bond**. This absorbs differently depending on its environment. It is easily recognised in an acid because it produces a **very broad peak in the range 2500 - 3300 cm^{-1}** .

infra-red spectrum of ethanoic acid, CH_3COOH



THE INFRARED SPECTRUM FOR AN ESTER (ETHYL ETHANOATE):

- In this case, the O-H absorption is missing completely. Don't confuse it with the C-H band fractionally less than 3000 cm^{-1} . The presence of the C=O double bond is seen at about 1740 cm^{-1} .
- The C-O single bond is the absorption at about 1240 cm^{-1} because C-O single bonds vary anywhere between 1000 and 1300 cm^{-1} depending on what sort of compound they are in. An absorption band from $1230 - 1250\text{ cm}^{-1}$ is the C-O bond in an ethanoate.

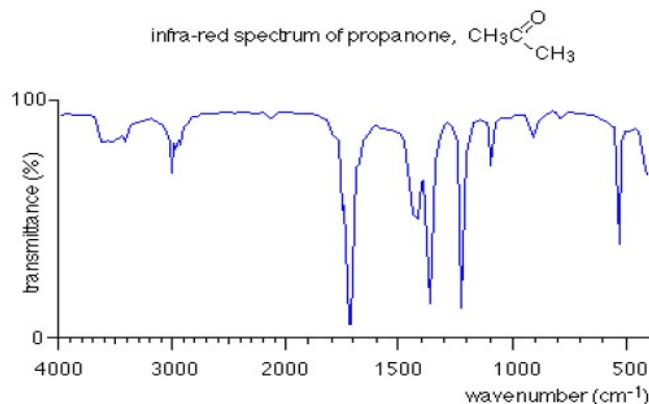


INFRARED SPECTRUM FOR A KETONE (PROPANONE):

It is very similar to the infra-red spectrum for ethyl ethanoate, an ester.

Again, there is no band due to the O-H bond, and again there is a marked absorption at about 1700 cm^{-1} due to the C=O.

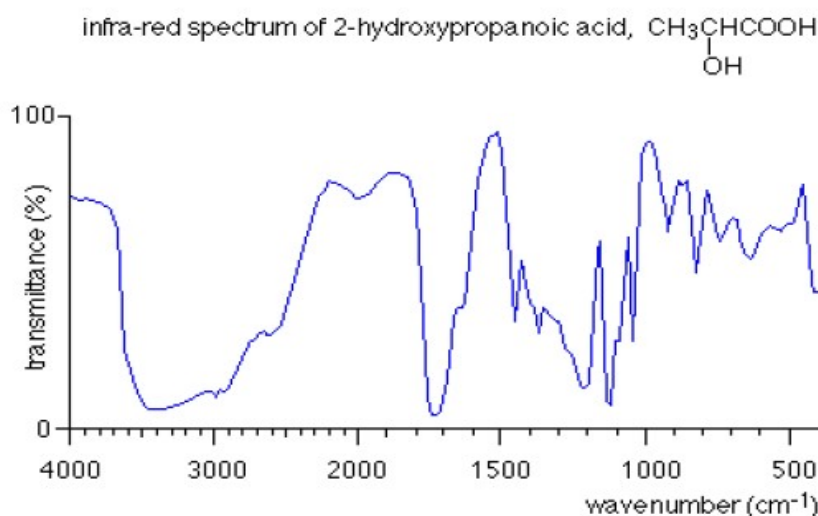
Confusingly, there are also absorptions which look as if they might be due to C-O single bonds - which, of course, aren't present in propanone. Aldehydes will have similar infra-red spectra to ketones.



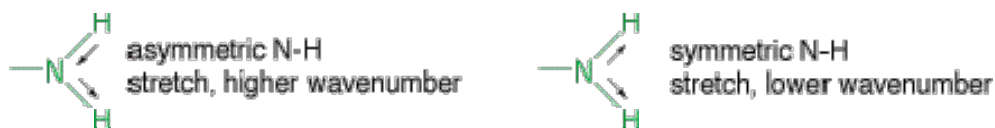
THE INFRARED SPECTRUM FOR A HYDROXY-ACID 2-HYDROXYPROPANOIC ACID (LACTIC ACID):

This is interesting because it contains two different types of O-H bond: the one -OH is in the -COOH group and the other -OH is in the "alcohol" type in the chain attached to the central atom.

The O-H bond in the acid -COOH group absorbs between 2500 and 3300 cm^{-1} , the other -OH group in the chain absorbs between 3230 and 3550 cm^{-1} . Taken together, that gives this immense peaks covering the whole range from 2500 to 3550 cm^{-1} that peak as well will be absorptions due to the C-H bonds. Notice also the presence of the strong C=O absorption at about 1730 cm^{-1} .



INFRARED SPECTRUM OF AMINE:



The N-H stretches of amines are in the region 3300-3000 cm^{-1} . These bands are weaker and sharper than those of the alcohol O-H stretches which appear in the same region.

In primary amines (RNH_2), there are two bands in this region (3300-3000 cm^{-1}), the asymmetrical N-H stretch and the symmetrical N-H stretch.

Secondary amines (R_2NH) show only a single weak band in the 3300-3000 cm^{-1} region, since they have only one N-H bond.

Tertiary amines (R_3N) do not show any band in this region since they do not have an N-H bond.

A shoulder band usually appears on the lower wave number side in primary and secondary liquid amines arising from the overtone of the N–H bending band. This can confuse interpretation. **Eg. IR spectrum of aniline**

The N–H bending vibration of primary amines is observed in the region $1650\text{--}1580\text{ cm}^{-1}$. Usually, secondary amines do not show a band in this region and tertiary amines never show a band in this region. This band can be very sharp and close enough to the carbonyl region.

Another band attributed to amines is observed in the region $910\text{--}665\text{ cm}^{-1}$. This strong, broad band is due to N–H wag and observed only for primary and secondary amines.

The C–N stretching vibration of aliphatic amines is observed as medium or weak bands in the region $1250\text{--}1020\text{ cm}^{-1}$.

In aromatic amines, the band is usually strong and in the region $1335\text{--}1250\text{ cm}^{-1}$.

Key bands:

N–H stretch $3400\text{--}3250\text{ cm}^{-1}$

1° amine: two bands from $3400\text{--}3300$ and $3330\text{--}3250\text{ cm}^{-1}$

2° amine: one band from $3350\text{--}3310\text{ cm}^{-1}$

3° amine: no bands in this region

N–H bend (primary amines only) from $1650\text{--}1580\text{ cm}^{-1}$

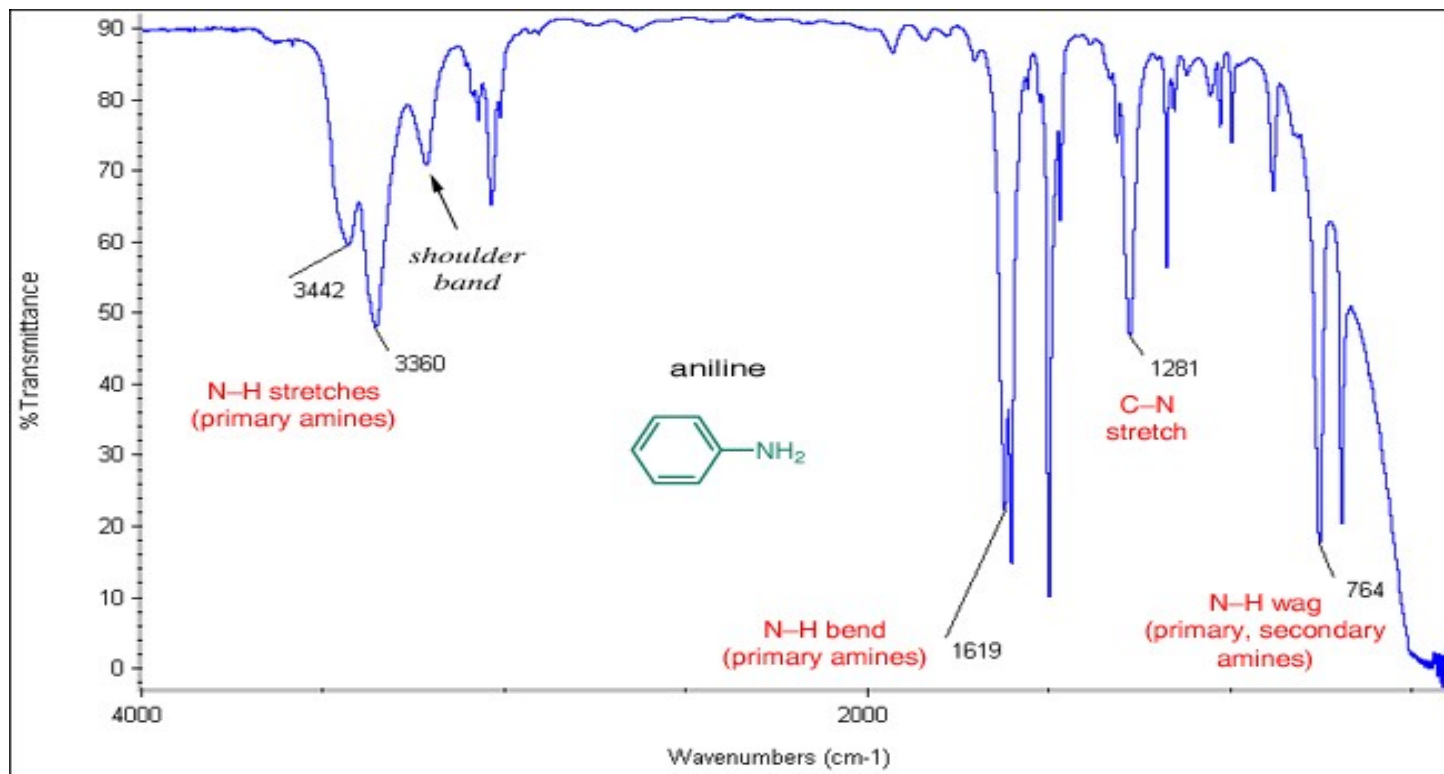
C–N stretch (aromatic amines) from $1335\text{--}1250\text{ cm}^{-1}$

C–N stretch (aliphatic amines) from $1250\text{--}1020\text{ cm}^{-1}$

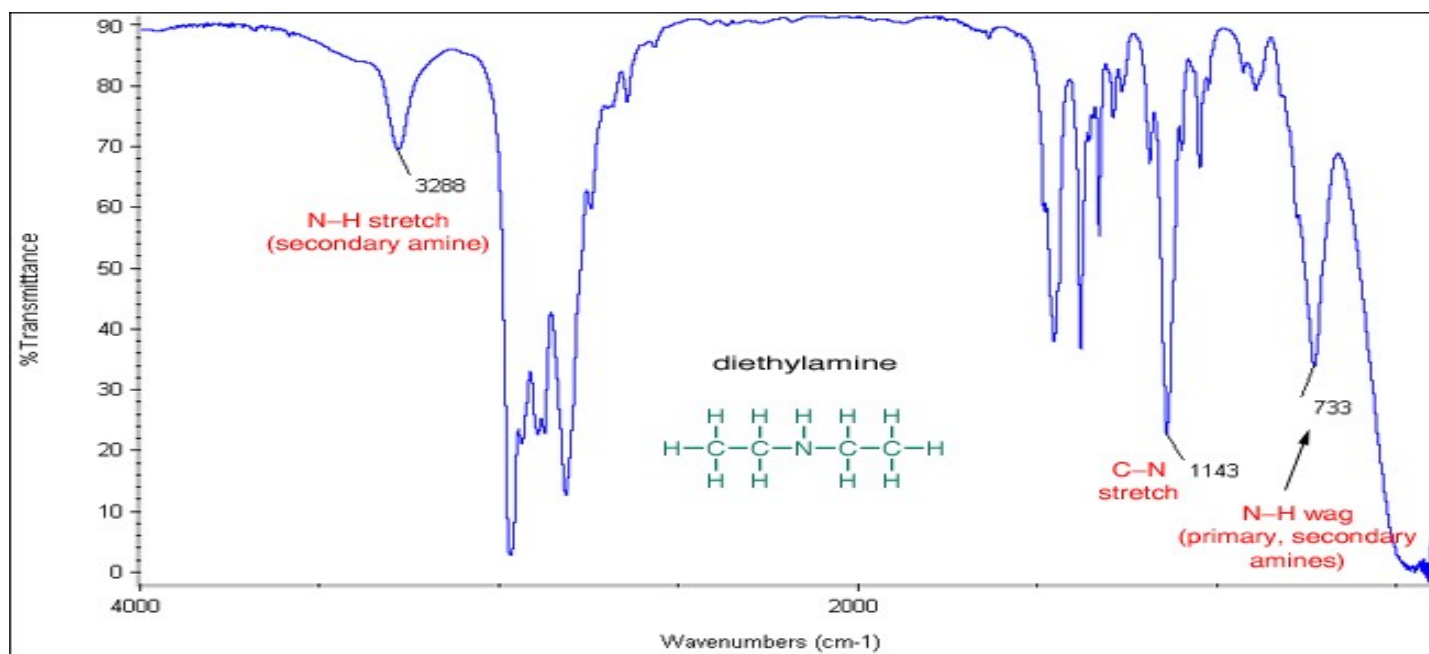
N–H wag (primary and secondary amines only) from $910\text{--}665\text{ cm}^{-1}$

Few examples on i.r. spectrum of amines are given below:

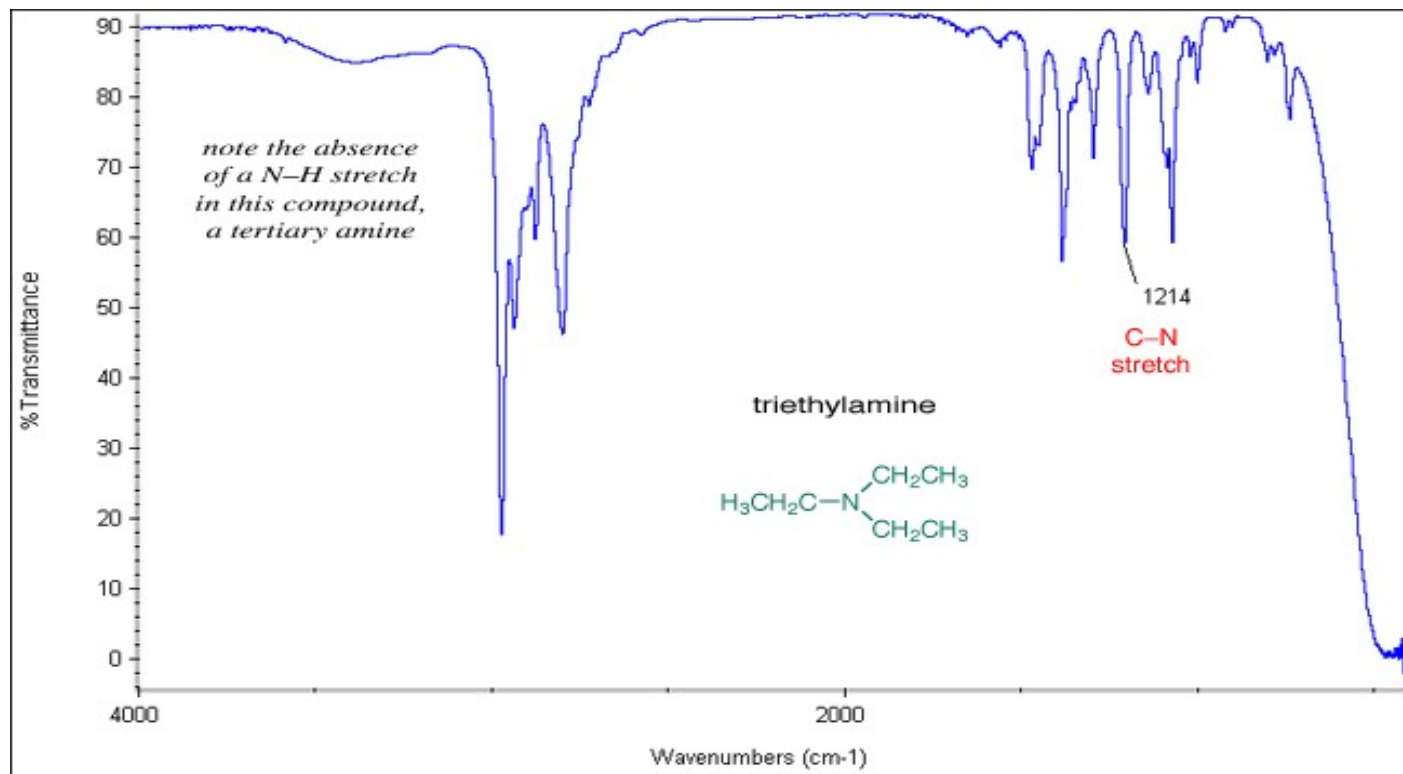
The i.r. spectrum of aniline (aromatic primary amine) shows two N–H stretches (3442, 3360); note the shoulder band, which is an overtone of the N–H bending vibration. N–H bend at 1619. The C–N stretch appears at 1281 rather than at lower wavenumbers because aniline is an aromatic compound.



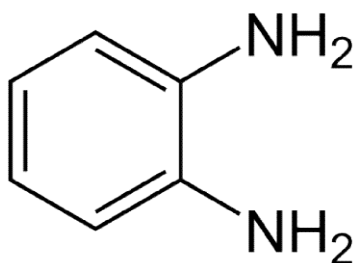
The i.r. spectrum of diethylamine (secondary amine) shows only one N–H stretch (3288cm⁻¹). The C–N stretch is at 1143cm⁻¹, in the range for non-aromatic amines (1250-1020cm⁻¹). Diethylamine also shows an N–H wag (733cm⁻¹).

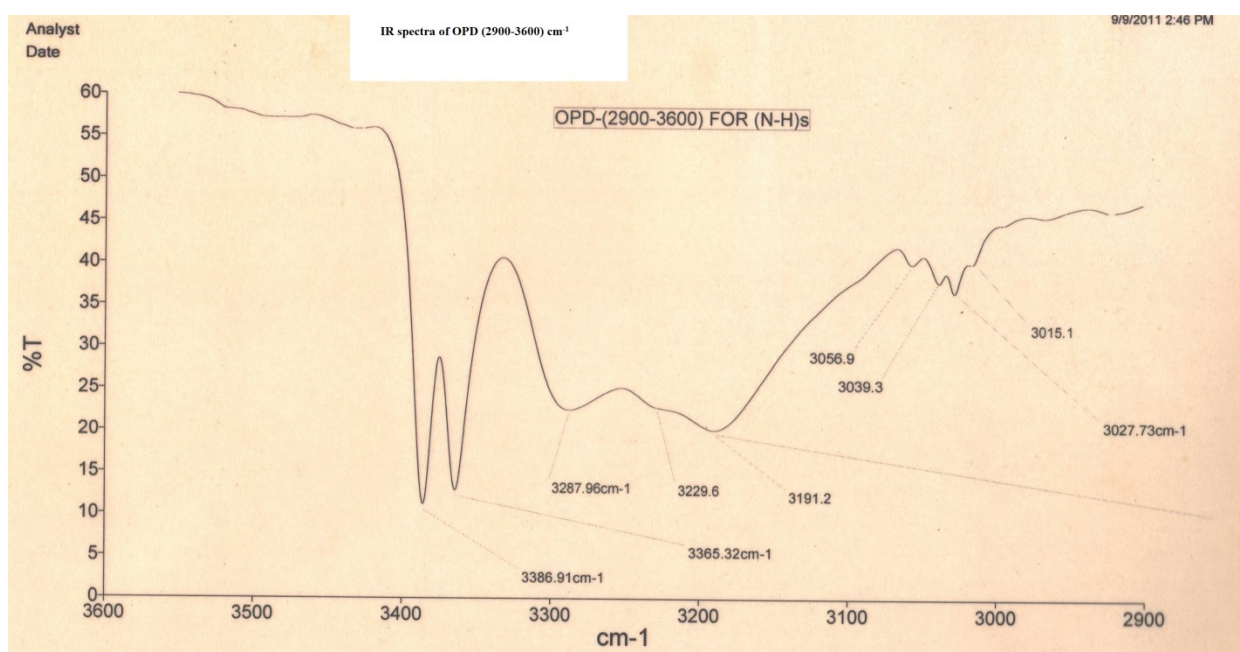
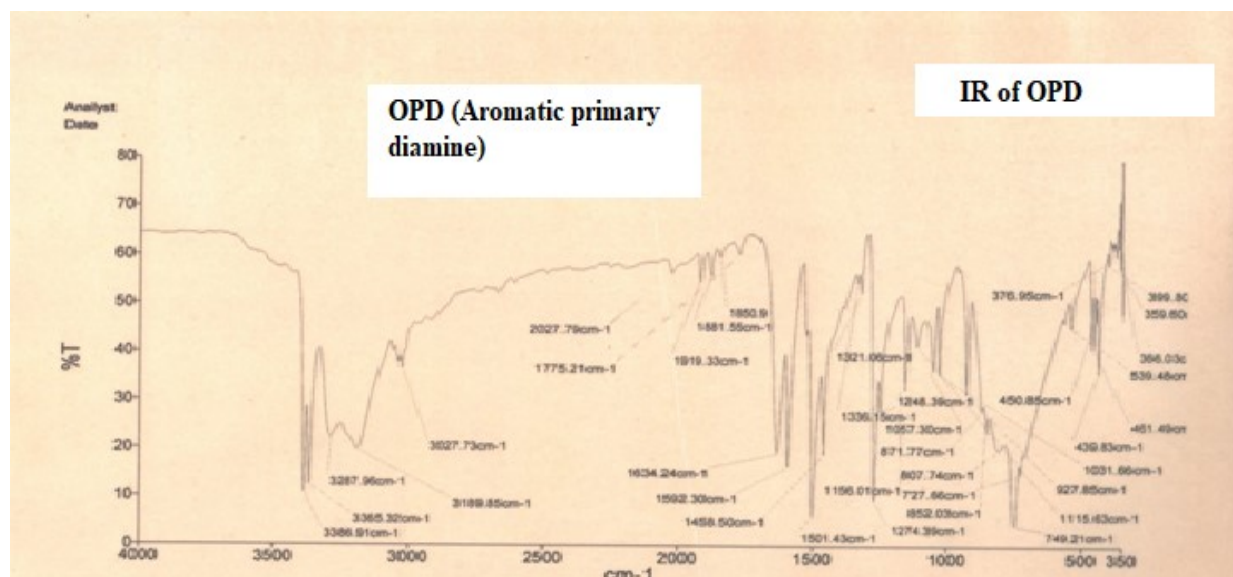


Triethylamine is a **tertiary amine** and does not have an N–H stretch, nor an N–H wag. The C–N stretch is at 1214 cm^{-1} (non-aromatic).

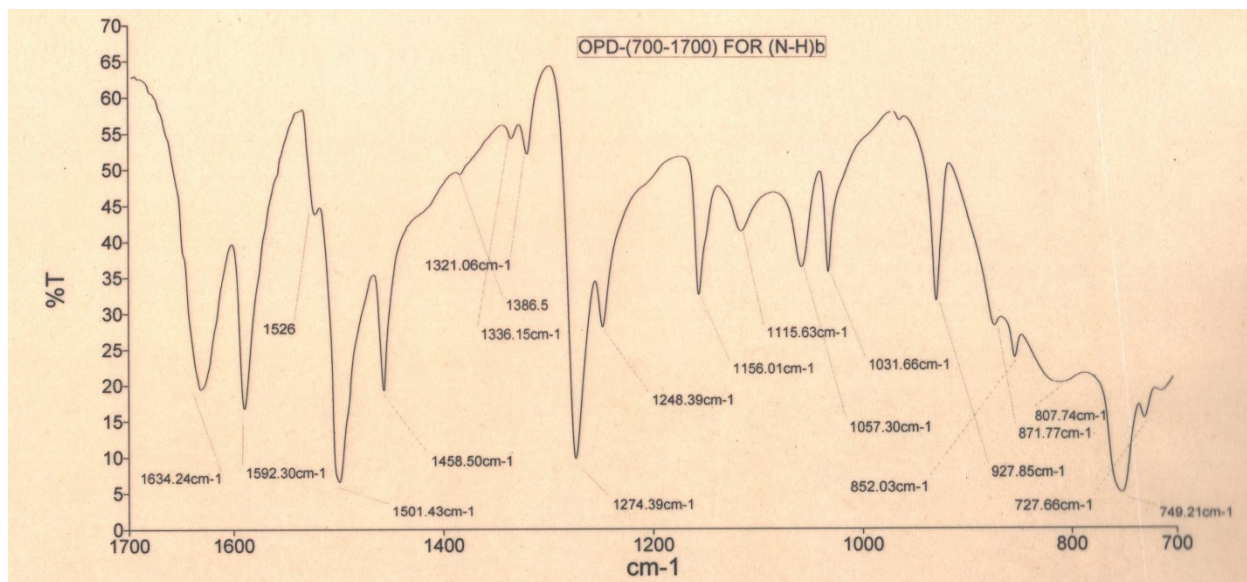


IR spectrum of orthophenylenediamine (OPD)



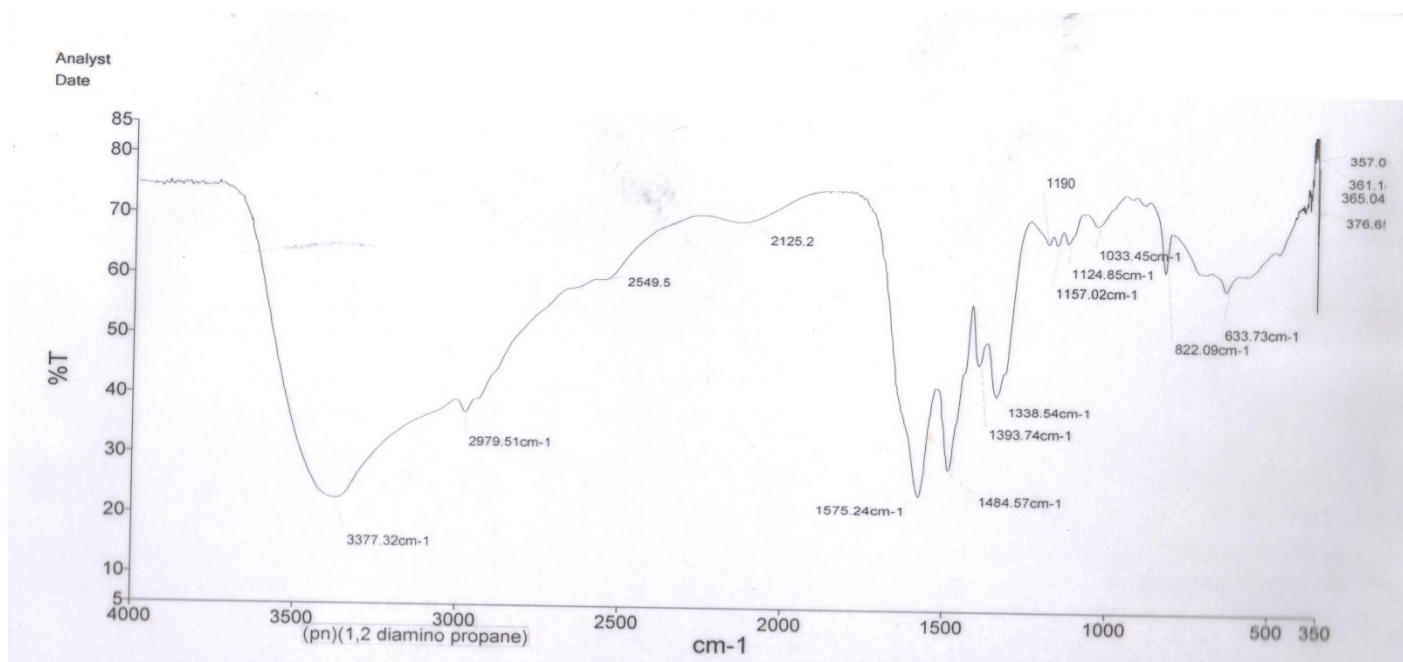


A broad band in the region $3000 - 3600 \text{ cm}^{-1}$ which are due to $\nu(\text{N} - \text{H})$. A group of broad bands in the range $3300 - 3400 \text{ cm}^{-1}$ attributed to $\nu(\text{N} - \text{H})$ (asymmetric and symmetric) stretching modes from the ligand, *o*-phenylenediamine.

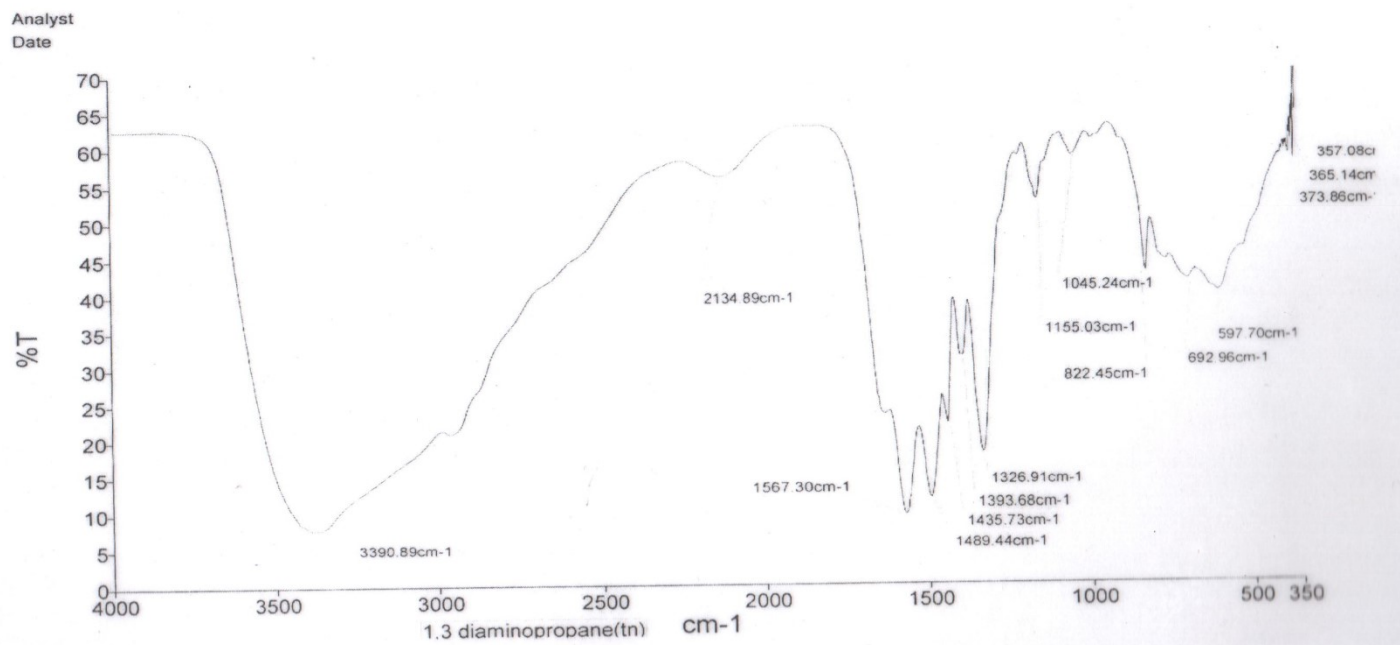


Multiple bands have been found in the region $1587 - 1720 \text{ cm}^{-1}$ which correspond to the N – H bending (scissoring) mode of vibration from diamine. The $\nu(\text{C} - \text{N})$ bending mode observed in OPD at 1274 cm^{-1} . A strong absorption band found at 749 cm^{-1} in the spectrum of OPD attributable to out of plane C – H ring (aromatic) bending mode, characteristic of substituted benzene. The $\nu(\text{C} - \text{H})$ (aromatic ring) arising from aromatic ligands is observed as weak band(s) in the region $3000 - 3100 \text{ cm}^{-1}$.

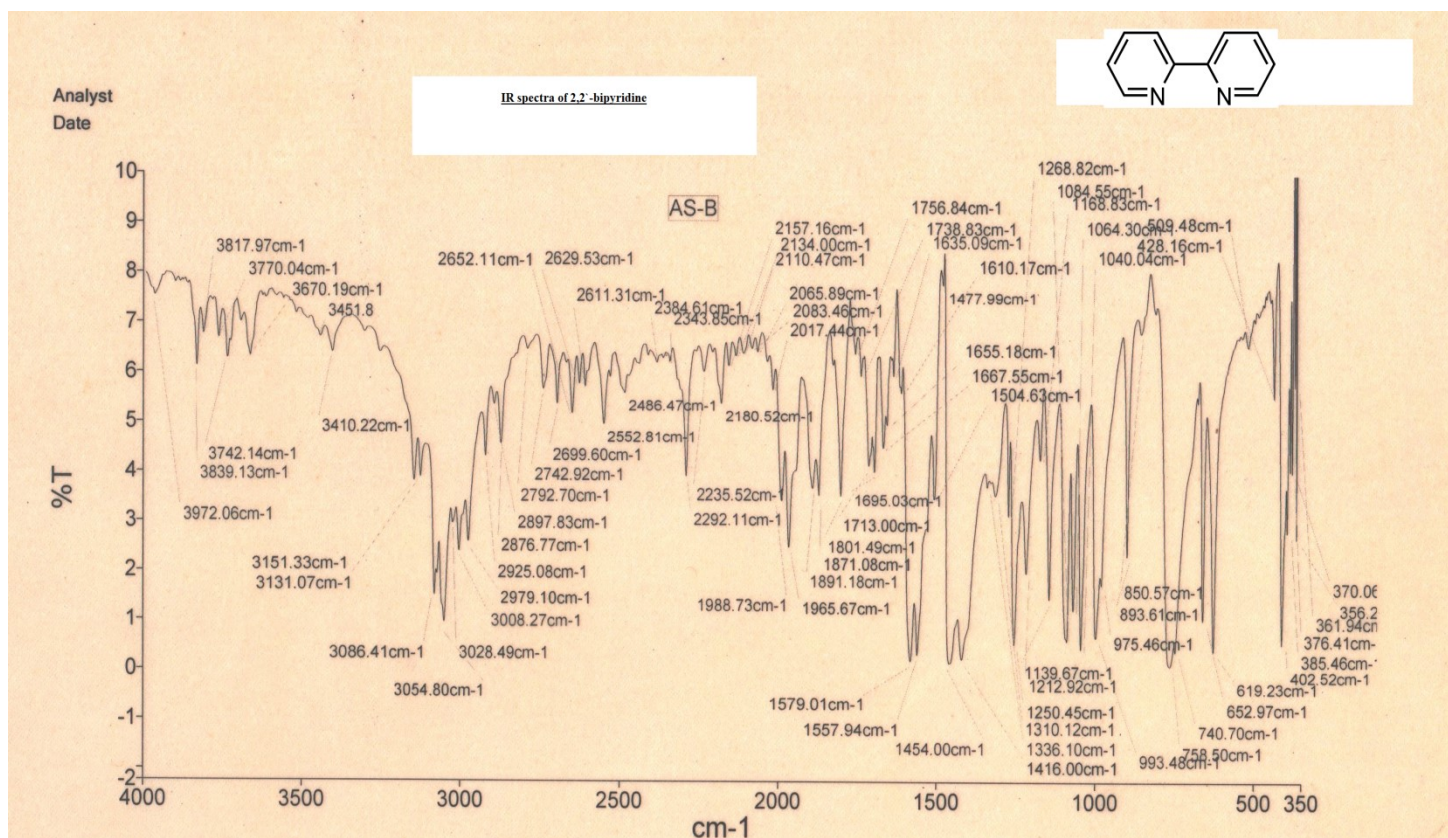
IR spectrum of 1,2-diamino propane (pn)



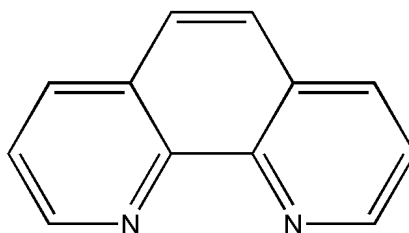
IR spectrum of 1,3-diamino Propane (tn)



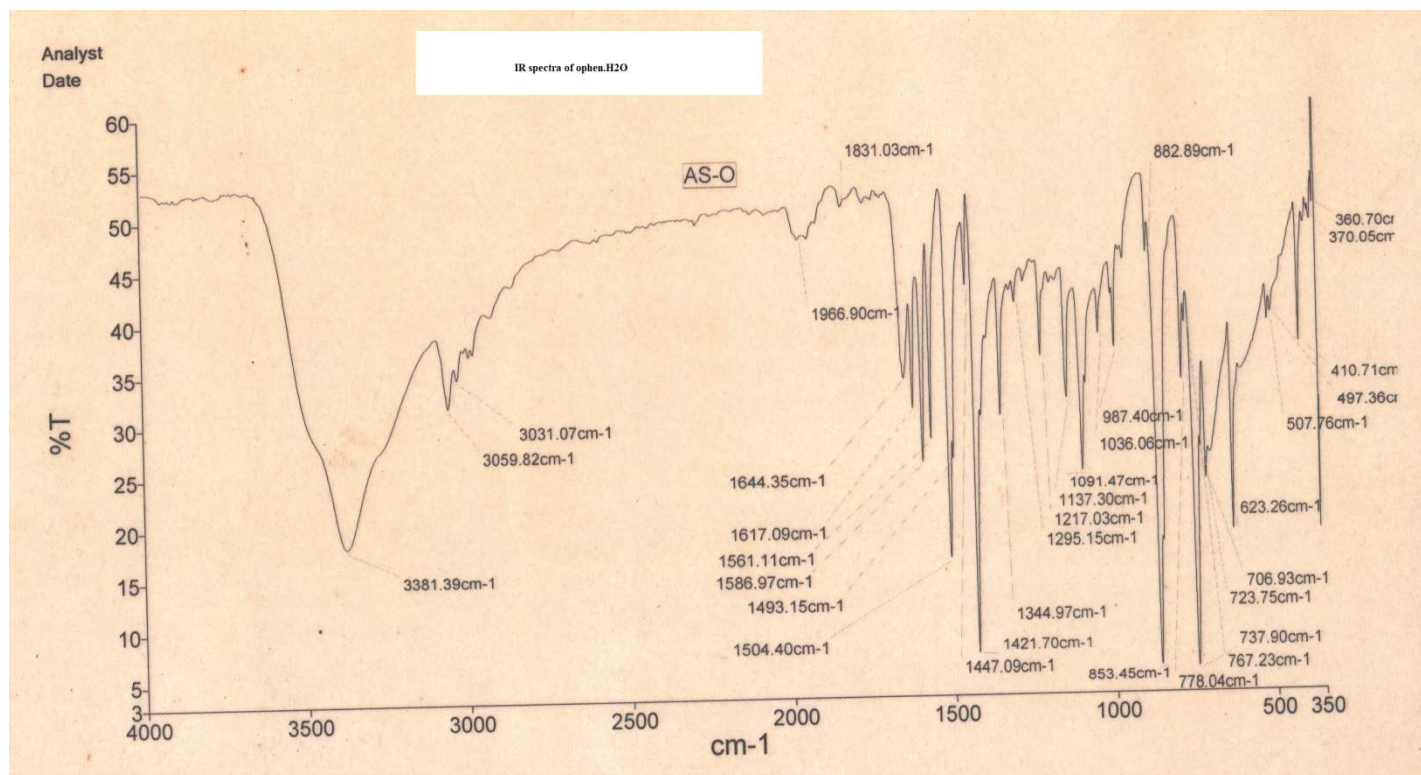
IR spectrum of 2,2'-bipyridine (bipy)



IR spectrum of 1,10-phenanthroline (ophen.H₂O)



. H₂O



Related Questions:

Q.1. How many bands for N-H stretches observed in the primary amine, secondary amine and tertiary amine?

Q.2. Explain why two bands for N-H stretches observed in the primary amine while only one band for N-H stretch observed in the secondary amine?

Q.3. Explain why i.r. O-H band will be broad in nature?

Reference Books:

1. *Fourier Transforms in NMR, Optical and Mass Spectroscopy*, Alan G. Marshall, Francis R. Verdun, Elsevier, 1990.
 2. *Practical Fourier Transform Infrared Spectroscopy*, John R. Ferraro, K. Krishnan, Academic Press, 1990
 3. *Infrared Spectroscopy: Fundamentals and Applications*, Barbara H. Stuart, John Wiley & Sons, Ltd, 2004.
 4. *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory and Applications in Inorganic Chemistry, Sixth Edition*, Kazuo Nakamoto, John Wiley & Sons, Ltd, 2008.
 5. *Infrared and Raman spectroscopy principles and spectral interpretation*, Peter Larkin, Elsevier, 2011.
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