

# INFRARED SPECTROSCOPY

SEM-4, CC-8  
PART-6, PPT-12

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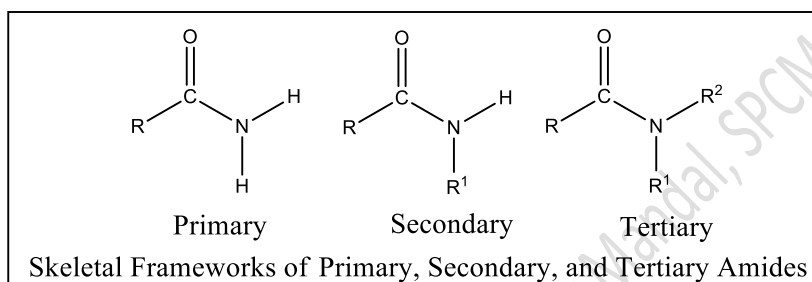
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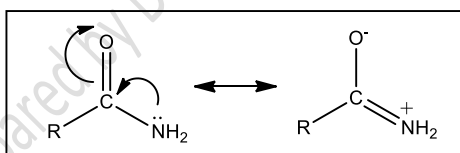
## INFRARED SPECTROSCOPY (PART-6, PPT-12)

### Absorptions of Amides (R-CO-NH<sub>2</sub>)

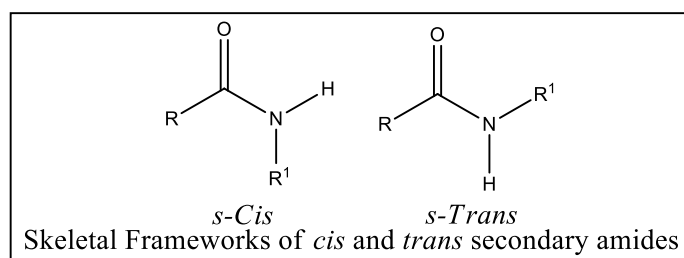
Amides are derivatives of carboxylic acids. An *amide* contains a carbonyl group with a carbon atom on one side and a nitrogen atom on the other side. All amides have at least one C-N bond, and are distinguished from each other by the total number of C-N bonds in the functional group. A *primary amide* has one C-N bond and two N-H bonds. A *secondary amide* has two C-N bonds and one N-H bond. A *tertiary amide* has three C-N bonds and no N-H bond.



The nitrogen in an amide contains a pair of nonbonding electrons that are in a *p*-type orbital, which points above the plane of the C=O bond. The carbonyl group has electrons in a similar orbital. The *p*-type electrons of the C=O group and the nitrogen atom in an amide can conjugate, allowing the electrons to delocalize along the C-N bond. The effect of conjugation is to lower the C=O stretching wavenumber for amides compared to ketones.



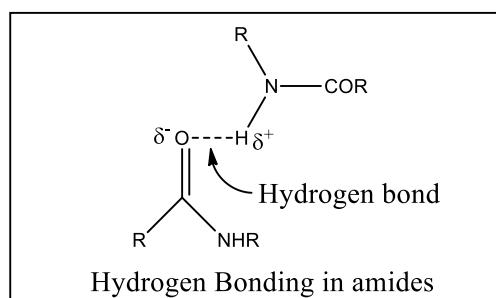
The effect of conjugation is that the C-N bond is "stiffer" than expected and has some double bond character. This stiff C-N bond prevents the nitrogen atom with the attached substituents from rotating about the C-N bond axis. In secondary amides, where the substituents attached to nitrogen are one hydrogen and one carbon atom, there exist *s-cis* and *s-trans* isomers of the molecule.



The N-H bond in primary and secondary amides is similar to the O-H bond found in alcohols, carboxylic acids, etc. Nitrogen is more electronegative than hydrogen, and the electrons in an

N-H bond have the highest probability of being found on the nitrogen atom. Consequently, there is a partial negative charge on the nitrogen and a partial positive charge on the hydrogen.

In amides, the C=O group is polar, with a partial negative charge on the oxygen and a partial positive charge on the carbonyl carbon. The positive end of an N-H bond of one molecule coordinates with the negative end of a C=O bond of another molecule to form a hydrogen bond in amides.

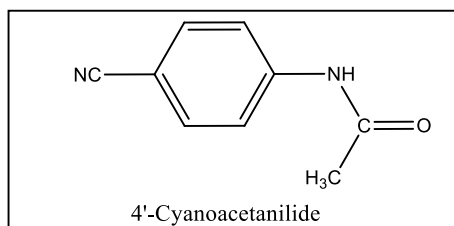


The dipole moment of a N-H bond is smaller than that of an O-H bond, so the hydrogen bonding in amides is weaker than in alcohols and carboxylic acids. The N-H stretching bands of an amide are of medium intensity compared to O-H stretches. The IR absorption bands of an amide are sensitive to the amount of hydrogen bonding taking place in a sample. Therefore, the positions of N-H stretch bands can shift over  $100\text{ cm}^{-1}$  in going from pure amide to dilute solution.

**C=O Stretching Vibrations (Amide I Band):** All amides show a C=O absorption band known as amide I band. Its position depends on the degree of hydrogen bonding and, thus, on the physical state of the compound. The C=O absorption of amides occurs at lower frequencies than “normal” C=O absorption of ketones due to the resonance effect.

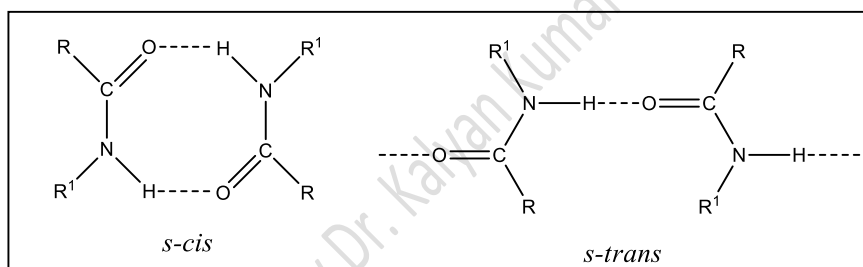
Primary amides (except acetamide, whose C=O bond absorbs at  $1694\text{ cm}^{-1}$ ) show a strong amide I band at  $\sim 1650\text{ cm}^{-1}$  in the solid state. In dilute solution, the absorption is shifted to a higher frequency, near  $1690\text{ cm}^{-1}$ . In more concentrated solutions, the C=O frequency is observed at some intermediate value, depending on the degree of hydrogen bonding. C=O stretch of benzamide appears at  $\sim 1656\text{ cm}^{-1}$ . Simple, open-chain, secondary amides ( $\text{R-CO-NH-R}^1$ ) absorb near  $1640\text{ cm}^{-1}$  in the solid state. In dilute solution, the frequency of the amide I band is raised and appears in the  $1700\text{-}1680\text{ cm}^{-1}$  region.

The C=O absorption frequency of *tertiary* amides ( $\text{R-CO-NR}_2$ ) is independent of the physical state, since hydrogen bonding with another tertiary amide group is impossible due to the absence of N-H bond. The C=O absorption occurs in the range of  $1680\text{-}1630\text{ cm}^{-1}$ . Electron withdrawing groups attached to the nitrogen increase the frequency of C=O absorption since they effectively compete with the carbonyl oxygen for the electrons of the nitrogen, thus increasing the force constant of the C=O bond. 4'-Cyanoacetanilide shows a strong C=O absorption band at  $1688\text{ cm}^{-1}$ .



**N-H Stretching Vibrations:** In dilute solution in non-polar solvents, primary amides show two moderately intense N-H stretching frequencies corresponding to asymmetrical and symmetrical N-H stretching vibrations. These bands occur near  $3520$  and  $3400\text{ cm}^{-1}$ , respectively. In the spectra of solid samples, these bands are observed near  $3350$  and  $3180\text{ cm}^{-1}$  by hydrogen bonding.

Secondary amides contain one N-H bond and exist mainly in the *s-trans* conformation. In dilute solutions, the single “free” N-H stretching vibration appears near  $3500\text{--}3400\text{ cm}^{-1}$ . In solid samples and in concentrated solutions, the “free” N-H band is replaced by multiple bands in the  $3330\text{--}3060\text{ cm}^{-1}$  region. Multiple bands are observed since the amide group can bond to produce dimers with an *s-cis* conformation, and polymers with an *s-trans* conformation.



**N-H Bending Vibrations (Amide II Band):** All primary amides show a sharp N-H bending absorption band in dilute solution (amide II band) at a somewhat lower frequency than the C=O band. This band appears in the  $1620\text{--}1590\text{ cm}^{-1}$  region and normally is separated from the amide I band. It has an intensity of one-half to one-third of the C=O absorption band.

In mulls and pellets, the band occurs near  $1655\text{--}1620\text{ cm}^{-1}$  and is usually under the envelope of the amide I band. Secondary acyclic amides in the solid state display an amide II band in the region of  $1570\text{--}1515\text{ cm}^{-1}$ . In dilute solution, the band occurs in the  $1550\text{--}1510\text{ cm}^{-1}$  region. This band results from interaction between the N-H bending and the C-N stretching of the C-N-H group. A second, weaker band near  $1250\text{ cm}^{-1}$  also results from interaction between the N-H bending and C-N stretching.

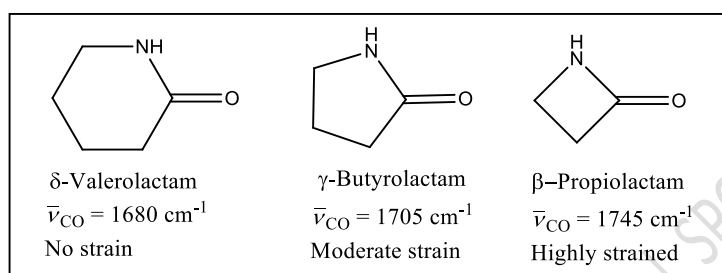
**N-H out-of-plane Bending Vibrations:** Primary and secondary amides show a broad, medium intensity band in the  $800\text{--}666\text{ cm}^{-1}$  region resulting from out-of-plane N-H wagging.

**C-N Stretching Vibrations:** The C-N stretching band of primary amides occurs near  $1400\text{ cm}^{-1}$ .

## Absorptions of Lactams

Cyclic amides of the amino acids are called lactams. In lactams of medium ring size, the amide group is forced into the *s-cis* conformation.

**C=O Stretching Vibrations:** The C=O absorptions in lactams depend upon the ring size. The C=O absorption with six-membered rings or larger appears near  $1680\text{ cm}^{-1}$ . Five membered ring ( $\gamma$ ) lactams absorb in the  $\sim 1705\text{ cm}^{-1}$  region. Four-membered ring ( $\beta$ ) lactams absorb in the  $1760\text{-}1730\text{ cm}^{-1}$  region.



**N-H Stretching Vibrations:** Solid lactams absorb strongly near  $3200\text{ cm}^{-1}$  because of the N-H stretching vibration. This band does not shift appreciably with dilution since the *s-cis* form remains associated at relatively low concentrations.

**N-H Bending Vibrations:** The N-H out-of-plane wagging in lactams causes broad absorption in the  $800\text{-}700\text{ cm}^{-1}$  region. Most lactams do not show a band near  $1550\text{ cm}^{-1}$  that is characteristic of *s-trans* acyclic secondary amides.

## Absorptions of Imides (-CO-NH-CO-)

*Imides* contain two carbonyl groups separated by a nitrogen atom. The carbons in the C=O bond are carbonyl carbons, and the nitrogen atom separating the two carbonyl groups is called the *imide nitrogen*. The most important imides are the cyclic imides, such as phthalimide. Straight chain imides have spectra very similar to secondary amides.

**C=O Stretching Vibration:** Straight chain imides give rise to one C=O stretching band in the  $1740\text{-}1670\text{ cm}^{-1}$  region. Cyclic imides, on the other hand, show two C=O absorptions corresponding to in-plane and out-of-plane stretching in the region of  $1790\text{-}1735\text{ cm}^{-1}$  and  $1750\text{-}1680\text{ cm}^{-1}$ , respectively. Phthalimide shows two C=O stretches at  $1774$  and  $1745\text{ cm}^{-1}$ . The band at lower wavenumber is more intense, which is typical of cyclic imides.

**N-H Stretching Vibration:** If an imide has an N-H bond, its N-H stretch appears in the  $3250\text{-}3150\text{ cm}^{-1}$  region. Phthalimide shows N-H stretch at  $3205\text{ cm}^{-1}$ .

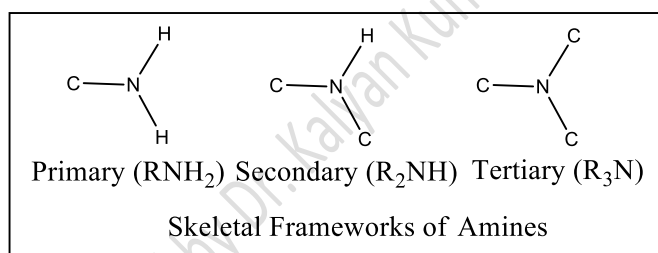
**N-H Bending Vibration:** In-plane N-H bending band of an acyclic imide is found at  $\sim 1505\text{ cm}^{-1}$ . In cyclic imides, this vibration is weak to non-existent.

**C-N Stretching Vibration:** C-N stretching vibration of an acyclic imide occurs in the  $1235\text{-}1165\text{ cm}^{-1}$  region. In cyclic imides, this vibration is weak to non-existent.

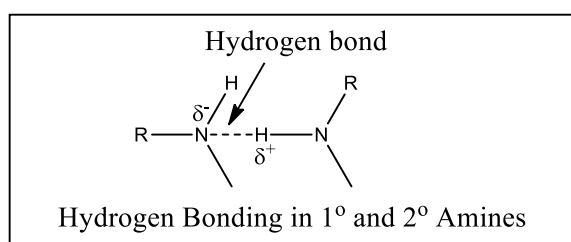
The Group Wavenumbers (in $\text{cm}^{-1}$ ) of Imides		
Vibration	Straight Chain	Cyclic
N-H Stretch	3250-3150	3250-3150
C=O Stretch	1740-1670 (1band)	1790-1735, 1750-1680 (2 bands)
N-H In-plane Bend	$\sim 1505$	-
C-N Stretch	1235-1165	-

### Absorptions of Amines

Amines contain only carbon, hydrogen, and nitrogen, and have at least one C-N bond. The number of C-N bonds in an amine determines the type of amine. A molecule with one C-N bond is a *primary amine*, a molecule with two C-N bonds is a *secondary amine*, and a molecule with three C-N bonds is a *tertiary amine*. The substituents on the nitrogen other than carbon atoms are always hydrogen atoms. The number of N-H bonds in primary, secondary, and tertiary amines is 2, 1, and 0, respectively.



The N-H bonds in primary ( $1^\circ$ ) and secondary ( $2^\circ$ ) amines are polar, with a partial positive charge on the hydrogen and a partial negative charge on the nitrogen. Because of these charges, the hydrogen of one amine molecule can coordinate with the nitrogen of a second amine molecule forming a hydrogen bond.

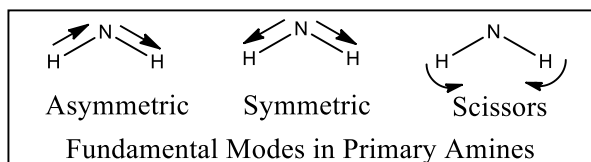


Like the O-H absorption bands in alcohols, the N-H absorption bands in primary and secondary amines are also broad due to hydrogen bonding. However, the hydrogen bonding in amines is weaker than in alcohols, so N-H stretching bands are not as broad or intense as O-H stretching bands.

The positions of N-H stretching and bending bands are sensitive to the amount of hydrogen bonding. Thus, the positions of these bands are different for pure samples of an amine versus a dilute solution.

### Absorptions of Primary Amines (R-NH<sub>2</sub>)

The structural feature of a primary amine is the presence of an NH<sub>2</sub> group. This moiety can stretch and bend.



The three important vibrations of the primary amine functional group are the asymmetric NH<sub>2</sub> stretch, symmetric NH<sub>2</sub> stretch, and NH<sub>2</sub> scissors mode. The asymmetric NH<sub>2</sub> stretch involves one hydrogen moving toward the nitrogen while the other hydrogen moves away from the nitrogen. The symmetric NH<sub>2</sub> stretch of a saturated primary amine involves both hydrogens simultaneously moving toward or away from the nitrogen.

### Absorptions of Amines (R-NH-R<sup>1</sup>)

**N-H Stretching Vibrations:** Primary amines, in dilute solutions, display two weak absorption bands: One near 3500 cm<sup>-1</sup> and the other near 3400 cm<sup>-1</sup>. These bands represent the “free” asymmetrical and symmetrical N-H stretching modes, respectively. These bands are shifted to lower wavenumbers by hydrogen bonding. Aliphatic primary amines (neat) absorb in the 3400-3330 and 3330-3250 cm<sup>-1</sup> region.

The aromatic primary amines absorb at slightly higher frequencies. The asymmetric N-H stretch appears in the 3500-3420 cm<sup>-1</sup> region, and the symmetric N-H stretch appears in the 3420-3340 cm<sup>-1</sup> region. The secondary amine contains one N-H bond. Consequently, it exhibits a single weak N-H stretching band in the 3350-3310 cm<sup>-1</sup> region. Tertiary amines have no N-H bonds. Consequently, there is no N-H stretching or bending band in the spectra of tertiary amines.

**N-H Bending Vibrations:** The bending of the primary amine NH<sub>2</sub> group can be in-plane or out-of-plane. The in-plane bending mode is a *scissoring* motion where the H-N-H bond angle gets bigger and smaller, like the opening and closing of a pair of scissors.

For primary amines, this band appears in the 1650-1580 cm<sup>-1</sup> region as a broad band. This band is medium to strong in intensity and is moved to slightly higher frequencies when the compound is associated. This mode in propylamine appears at 1606 cm<sup>-1</sup>. Secondary aromatic amines absorb near 1515 cm<sup>-1</sup>. The out-of-plane N-H bending vibration (*wagging*) of primary and secondary amines appears in the 900-700 cm<sup>-1</sup> region.

## Absorptions of Primary Amines (R-NH<sub>2</sub>)

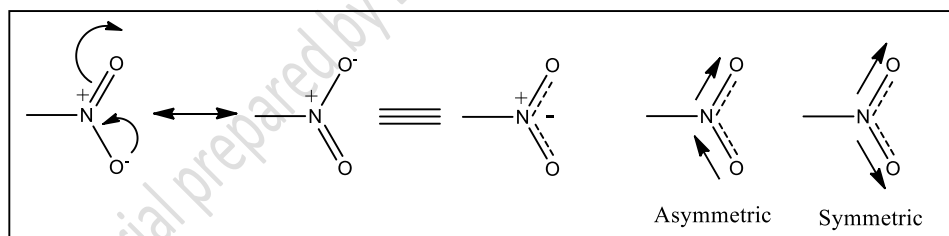
**C-N Stretching Vibrations:** Medium to weak absorption bands for the unconjugated C-N bond in primary, secondary, and tertiary aliphatic amines appear in the region of 1250-1020 cm<sup>-1</sup>. The vibrations responsible for these bands involve C-N stretching coupled with the stretching of adjacent bonds in the molecule (C-C-N vibrations).

Aromatic amines display strong C-N stretching absorption in the 1340-1250 cm<sup>-1</sup> region. The absorption appears at higher frequencies than the corresponding absorption of aliphatic amines because the force constant of the C-N bond is increased by resonance with the ring. C-N absorptions of secondary and tertiary aromatic amines appear in the region of 1350-1280, and 1360-1310 cm<sup>-1</sup>, respectively.

## Absorptions of Nitro Compounds

A *nitro* molecule contains the NO<sub>2</sub> group and organic nitro compounds have one carbon atom attached to the nitro group by a C-N bond. In reality, the N-O bonds in the nitro group are termed "bonds and a half" similar to the carboxylate C-O "bonds and a half". The electrons in the NO<sub>2</sub> bonds are spread out across both N-O linkages. This makes the two N-O bonds equivalent.

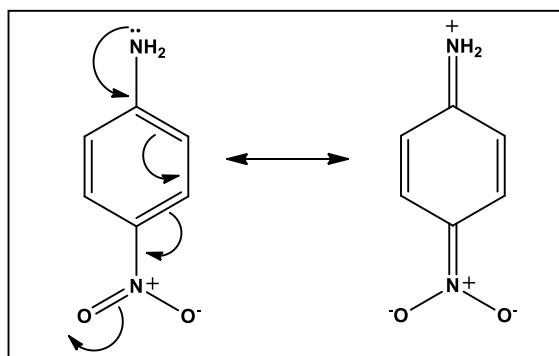
Depending on whether or not the alpha carbon is saturated, or part of an aromatic ring, nitro molecules can be divided into saturated and aromatic nitro compounds. The said N-O bonds of the nitro group give rise to two intense IR bands due to the asymmetric and symmetric stretching.



**Stretching Vibrations:** In the nitroalkanes, the asymmetric and symmetric stretching bands occur near 1550 and 1372 cm<sup>-1</sup>. Conjugation lowers the frequency of both bands. The asymmetric stretching of an aromatic nitro group gives rise to a very strong band in the 1550-1500 cm<sup>-1</sup> region. The symmetric stretch of the NO<sub>2</sub> group gives rise to a medium to strong intensity band in the 1390-1330 cm<sup>-1</sup>. Nitrobenzene absorbs at 1540 and 1350 cm<sup>-1</sup>. *m*-Nitrotoluene absorbs at 1527 and 1350 cm<sup>-1</sup>.

Because of strong resonance in aromatic systems containing NO<sub>2</sub> groups and electron donating groups such as the amino group, *ortho* or *para* to one another, the symmetrical NO<sub>2</sub> vibration is shifted to lower frequencies and increases in intensity. *p*-Nitroaniline absorbs at 1475 and 1310 cm<sup>-1</sup>.





Attachment of electronegative groups to the  $\alpha$  carbon of a nitro compound causes an increase in the frequency of the asymmetrical  $\text{NO}_2$  band and a reduction in the frequency of the symmetrical band, chloropicrin,  $\text{Cl}_3\text{CNO}_2$ , absorbs at  $1610$  and  $1307\text{ cm}^{-1}$ .

**C-N Stretching Vibration:** Nitro compounds show a C-N stretching vibrations near  $870\text{ cm}^{-1}$ . Nitrobenzene absorbs at  $852\text{ cm}^{-1}$ .

### Absorptions of Nitriles ( $\text{R-C}\equiv\text{N}$ )

A *nitrile* contains a carbon nitrogen triple bond,  $\text{C}\equiv\text{N}$ . If the alpha carbon of a nitrile is saturated, the compound is called a saturated nitrile. If the alpha carbon is part of a benzene ring, the molecule is denoted as an aromatic nitrile.

**$\text{C}\equiv\text{N}$  Stretching Vibrations:** The carbon nitrogen triple bond,  $\text{C}\equiv\text{N}$ , gives rise to an intense absorption band in a unique wavenumber range in the IR spectrum. For a saturated nitrile (aliphatic), the  $\text{C}\equiv\text{N}$  stretch appears in the region of  $2260\text{-}2240\text{ cm}^{-1}$ . Acetonitrile ( $\text{CH}_3\text{CN}$ ) absorbs at  $\sim 2252\text{ cm}^{-1}$ . Electron attracting group, such as oxygen or chlorine, attached to the carbon atom  $\alpha$  to the  $\text{C}\equiv\text{N}$  group reduce the intensity of absorption.

Conjugation, such as occurs in an aromatic nitrile, reduces the  $\text{C}\equiv\text{N}$  stretching frequency of absorption to  $2240\text{-}2220\text{ cm}^{-1}$  and enhances the intensity. Conjugation involves interactions between the  $\pi$  electrons of the nitrile group and the  $\pi$  electrons of an aromatic ring.

The  $p$ -orbitals for these electrons are next to each other, and a small amount of orbital overlap allows the electrons from the benzene ring and the  $\text{C}\equiv\text{N}$  to spread out across both functional groups. This lowers the force constant of the  $\text{C}\equiv\text{N}$  bond, causing the position of the  $\text{C}\equiv\text{N}$  stretch of an aromatic nitrile to be lowered about  $10$  to  $20\text{ cm}^{-1}$  compared to a saturated nitrile.

The $\text{C}\equiv\text{N}$ Stretches of Nitriles (all numbers in $\text{cm}^{-1}$ )		
Vibration	Saturated	Aromatic
$\text{C}\equiv\text{N}$ Stretch	2260-2240	2240-2220

### Absorptions of Imines and Oximes

The C=N bond of an imine (R-CH=N-R) has an  $sp^2$  carbon atom. Imines and related compounds absorb near where double bonds appear, 1690-1640  $\text{cm}^{-1}$ .

- An imine gives a C=N absorption in the 1690-1650  $\text{cm}^{-1}$  region.
- An oxime ( $\text{R}_2\text{C}=\text{N}-\text{OH}$ ) gives a C=N absorption in the range of 1690-1640  $\text{cm}^{-1}$ .
- Although the intensity of the C=N stretch is variable, it is usually more intense than the C=C stretch.

### Absorptions of Organic halogen Compounds

The strong absorption of halogenated hydrocarbons (RX) arises from the stretching vibrations of the carbon-halogen bond. The halogens are very electronegative, forming polar bonds with carbon atoms with large dipole moments. Therefore, carbon halogen stretches, or C-X stretches where X represents a halogen, are very intense.

Since halogens are generally heavier than the other atoms found in organic molecules, C-X stretches tend to appear at low wavenumber (a mass effect). In general, C-X stretching vibrational frequency goes down with increasing atomic mass.

**C-F Stretching Vibrations:** The fluorine atom shows the highest wavenumber C-X stretch since it is the lightest halogen. An alkyl fluoride shows strong band in the 1100-1000  $\text{cm}^{-1}$  region. Fluorobenzene displays a strong, narrow absorption band near 1230  $\text{cm}^{-1}$ .

**C-Cl Stretching Vibrations:** Chlorine is almost twice as heavy as fluorine. Consequently, C-Cl stretches occur at lower wavenumber than C-F stretches (a mass effect). Aliphatic C-Cl absorption is observed in the region of 850-600  $\text{cm}^{-1}$ . When several chlorine atoms are attached to the same carbon atom, the C-Cl band is more intense and the absorption frequency increases. Chloroform and carbon tetrachloride show intense C-Cl absorption bands at 758 and 797  $\text{cm}^{-1}$ , respectively. Chlorobenzene absorbs in the 1096-1089  $\text{cm}^{-1}$  region.

**C-Br and C-I Stretching Vibrations:** The heavier halogens, bromine and iodine, have C-X stretches at even lower wavenumber than C-Cl stretch. Bands due to C-Br and C-I stretching appear in the 690-515 and 600-500  $\text{cm}^{-1}$  region, respectively.