Subject: Chemistry

Semester VI

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Topic: IR Spectroscopy (Module-1I)

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Calculation of vibrational frequencies

The value of the stretching vibrational frequency of a bond can be calculated fairly accurately by the application of Hook's law which may be represented as:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{or} \quad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\frac{m_1 m_2}{m_1 + m_2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots..1$$

Where k – force constant of bond and relates with the strength of the bond. For single bond, it is approx. 5 x 10^5 gsec^{-2}, for double bond it is 10 x 10^5 gsec^{-2} and for triple bond it is 15 x 10^5 gsec^{-2}.

$\nu \longrightarrow$ frequency

$\mu \longrightarrow$ reduced mass

$m_1 \longrightarrow$ mass of atom 1

$m_2 \longrightarrow$ mass of atom 2

$\bar{\nu} = \frac{1}{\lambda}$ …………2; $\nu = \frac{c}{\lambda}$; therefore $\nu = c \times \frac{1}{\lambda}$ ……………3; and $\nu = c \times \bar{\nu}$ ……… ……4

Putting the value of ν in equation 1, we have

$$c \times \bar{\nu} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{therefore} \quad \bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots5$$

Equation 5 is used to calculate wavenumber for stretching vibrational frequency in IR spectroscopy. Thus the value of vibrational frequency or wave number depends upon: (i) Bond strength and (ii) reduced mass. The vibrational frequency of a band increases when the bond strength increases and also when the reduced mass of the system decreases.

For example, $C\equiv C$ (2150 cm^{-1}) absorbs at higher frequency than C=C stretching and C=C (1650 cm^{-1}) absorbs at higher frequency than C-C (1200 cm^{-1}) stretching. O-H stretching absorbs at higher frequency compared to C-C bond due to smaller value of reduced mass for O-H. Similarly, C = O (1715 cm^{-1}) absorbs at higher frequency than C = S (1350 cm^{-1}), C–H (3040 cm^{-1}) than C–D (2200 cm^{-1}) and the O-H (3570 cm^{-1}) bond absorbs at higher frequency than O-D (2630 cm^{-1}) bond. However, F-H group (4138 cm^{-1}) absorbs at higher frequency as compared to O-H and C-H due to higher electronegativity of fluorine. In general, functional groups that have a strong dipole give rise to strong absorptions in the infrared.

Number of fundamental vibrations

A molecule has as many degrees of freedom as the total degrees of freedom of its individual atoms. Consider a molecule containing n atoms we can refer the position of each atom in three Cartesian coordinates x, y and z, necessary to describe its position relative to other atoms in the molecule. Thus the total number of coordinate value is $3n$ and we can say the molecule has $3n$ degree of freedom. Since, molecule has three modes of vibrations: (i) Translational (ii) Rotational and (iii) Vibrational. Therefore

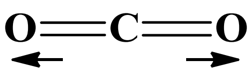
$3n$ degrees of freedom = Translational + Rotational + Vibrational

For a polyatomic atomic molecule whether it is linear or nonlinear there will be three degree of freedom for its translational motion in each case. But for the non linear molecule we need three coordinates to specify the center of gravity of molecule, so there will be three rotational degrees of freedom for nonlinear molecule about the center of gravity. Their rotation will be about three mutually perpendicular axes x, y and z. On the other hand, a linear molecule has only two independent rotational degrees of freedom about two mutually perpendicular axes which are perpendicular to the molecular axes. If we substract the translational and rotational degrees of freedom from the total $3n$ degrees of freedom, we find that we are left with $3n$-6 internal (vibrational motion) degree of freedom for a nonlinear molecule and $3n - 5$ internal (vibrational motion) degree of freedom for a linear molecule. These ($3n - 6$) and ($3n - 5$) vibrational motions for nonlinear and linear molecule, respectively, are also referred to as the normal modes of vibrations (or **fundamental vibrations**). Fundamental vibrations involve no change in the center of gravity of the molecule. For linear CO_2 molecule the number of vibrational degrees of freedom is 4 (9 - 5 = 4) and for nonlinear C_6H_6 molecule the vibrational degrees of freedom is 30 (3 x 12 – 6 = 30). Theoretically there should be 30 fundamental bands for benzene. But it has been observed that the theoretical number of fundamental vibrations are seldom obtained (never seen). Overtones (multiples of a given frequency) and combination bands (sum of two other vibrations) increase the number of bands, whereas other phenomena reduce the number of bands. The following will reduce the theoretical number of bands:

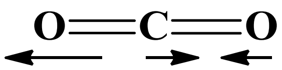
1. Fundamental frequencies that fall outside the region under investigation, i.e. 2.5 to 15 μ.
2. Fundamental bands that are too weak to be observed.
3. Fundamental vibrations that are so close that they overlap, i.e., degerate vibrations.
4. Certain fundamental vibrations fail to appear in the infrared because of lack of required change in dipole character of the molecule.

Example: Vibrational modes of CO_2.

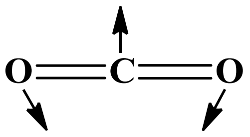
The symmetrical stretching vibration of CO_2 does not produce any change in dipole moment and is therefore infrared inactive (Raman active and appears in the Raman spectrum). While the asymmetric stretching and bending vibrations produce change in dipole moment and are therefore infrared active. The two bending modes have same frequency and are said to be degenerate. Thus, out of four normal modes of vibration for CO_2, there are only three different frequencies because of degeneracy of the two normal modes.



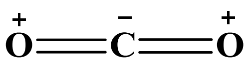
Symmetrical stretching
1340 cm^{-1}



Asymmetrical stretching
2350 cm^{-1}



bending
(in plane)
667 cm^{-1}



bending
(out of plane)
667 cm^{-1}

Overtone and Combination frequencies or bands (nonfundamental)

Additional absorption bands may occur as overtones at approximately twice, thrice and so on of the wavenumber of the fundamental mode. The fundamental vibrational frequencies of a molecule corresponds to transition from v=0 to v=1. An overtone bands occur when the molecule makes a transition from the ground state (v=0) to the second excited state (v=2), which is called the first overtone, or v=0 to v=3, which is called the second overtone. Fig. 1. shows the fundamental frequency for carbonyl stretch at 1717 cm^{-1} and overtone band at around 3414 cm^{-1} of almost twice the fundamental frequency.

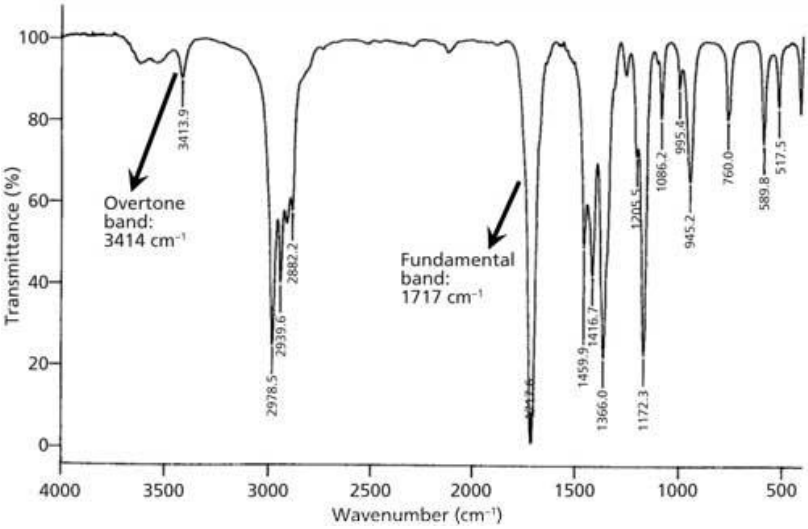


Fig. 1

Whereas, there may also be bands (or frequencies) arising from the addition (or combination) of two or more wave numbers (fundamental frequencies or overtones). These are known as combination bands. When two fundamental bands absorbing at ν_1 and ν_2 absorbs simultaneously then the new resulting bands (combination bands) may occur at $\nu_1 + \nu_2$, $2\nu_1 + \nu_2$ frequencies. Similarly, difference may occur at frequencies such as $(\nu_1 - \nu_2)$, $(2\nu_1 - \nu_2)$, etc are termed as difference band.

These overtone, combination and difference bands are normally less intense and weak than the fundamental bands.

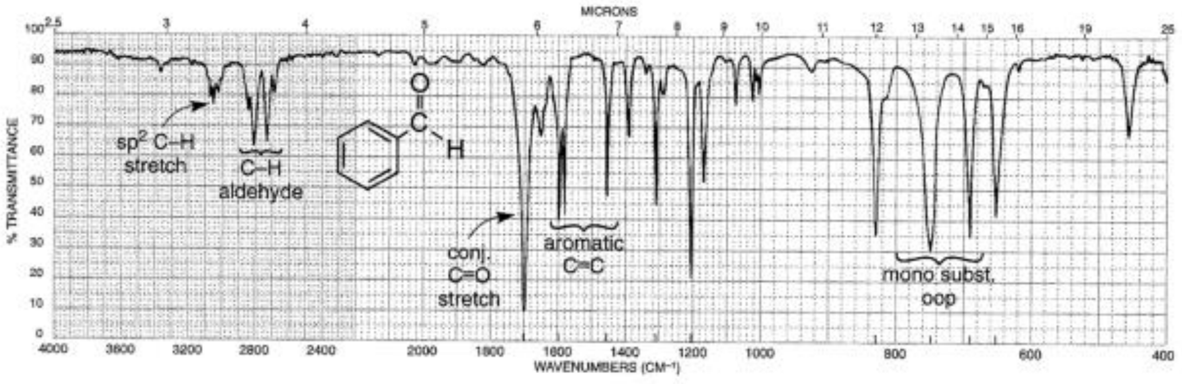
Factors affecting IR spectra: It may be noted that the vibrational frequency for a particular bond calculated by Hook's law is not always equal to its experimental value. The difference arises because of the influence of structural environment (for eg. electronic and steric effects) of the bond within the molecule. Some of the important factors which affects the vibrational frequency of a bond are as follows:

1. **Coupled vibrations**: In case of isolated C–H bond, only one C–H stretching frequency is expected but in case of methylene (–CH_2–), the C–H stretching vibrations combine together to produce two stretching vibrations, symmetric and asymmetric. Asymmetric vibrations occur at higher wavenumber than the symmetric stretching vibrations. These are known as coupled vibrations because these vibrations occur at different frequencies than that required for an isolated C–H stretching. Similarly, coupled vibrations of –CH_3 group take place at different frequencies as compared to –CH_2– group. Acid anhydrides show two C=O stretching absorptions between 1850-1800 and 1790-1740 cm^{-1} with a separation of about 65 cm^{-1}. These bands arise due to asymmetric and symmetric stretching.

2. **Fermi Resonance**: When a fundamental vibration couples with overtone or combination band, the coupled vibration is called a Fermi resonance. These two vibrational modes (or frequencies) having close vibrational frequencies, resonate and exchange energy resulting in two new frequencies, one higher and one lower than the original frequency. This phenomenon was explained by the Italian physicist Enrico Fermi. Fermi resonance requires that the vibrational levels be of the same symmetry species and the interacting groups be located in the molecule so that mechanical coupling is appreciable. It also involves sharing of intensity between the fundamental and an overtone, giving rise to a pair of transitions of equal intensity. Fermi resonance does not lead to additional bands in the spectrum, but rather shifts in bands that would otherwise exist.

   Example of Fermi resonance can be found in CO_2, the symmetrical stretching band of CO_2 appears at 1340 cm^{-1}. The fundamental bending vibration occurs at 667 cm^{-1} and the first overtone of this vibration occurs at 1334 cm^{-1} (2 x 667 cm^{-1}). The coupling between the fundamental stretching vibration (1340 cm-1) and the first overtone of the bending vibration (1334 cm-1) takes place to give two bands at frequencies 1285 cm^{-1} and 1385 cm^{-1}.

Another example of Fermi resonance is given by aldehydes in which C-H stretching absorption usually appears as a doublet near 2850 cm^{-1} and 2750 cm^{-1} due to the interaction between C-H stretching (fundamental) and the overtone of C-H deformation (bending).



3. **Electronic effects**: The absorption frequency of particular group changes, when the neighboring structural environment of that particular bond is changed. The electronic effect including inductive effect, mesomeric effect, field effect can cause changes in force constant or bond strength which leads to the shift in absorption frequency from the normal value.

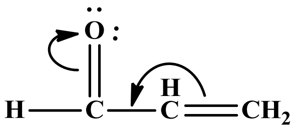
   In case of inductive effect, the +I effect **decreases wave number** (lengthening or weakening of bond occurs due to which force constant is decreased) and –I effect causes **increase in wavenumber** due to increase in force constant and decrease in bond length.

   Example: v(C=O) of formaldehyde HCHO occurs at higher wavenumber 1750 cm^{-1} than acetaldehyde (1745 cm^{-1}) due to +I effect of CH_3 group.

   Due to –I effect of chloro group, v(C=O) of chloroacetone (1725 cm^{-1}) occurs at higher wave number than acetone (1715 cm^{-1}).

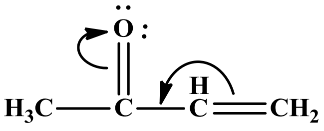
   Mesomeric effect also affect the absorption frequency of the particular group. In majority of cases, meosmeric effect works along with inductive effect. While in some cases, the inductive effect dominates mesomeric effect. For example, in case of acid chlorides –I effect of a halogen dominates over +M effect and as a result unconjugated acid chlorides display their C=O stretching in 1815-1785 cm^{-1} region.

Mesomeric effect causes lengthening of bond or weakening of bond resulting in decrease in wavenumber. For, example, conjugation of C=O group with olefinic or phenyl group causes a shift in C=O absorption to lower frequency. Consider the following compounds:



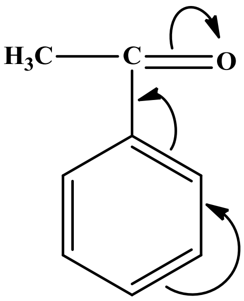
2-Butenal

νC=O 1690 cm^{-1}



Methyl Vinyl Ketone

νC=O 1686 cm^{-1}

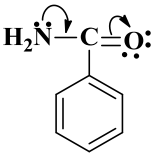


Acetophenone

νC=O 1693 cm^{-1}

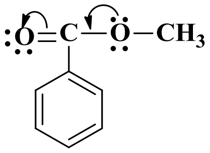
*ν(*C=O) of acetone (CH_3COCH_3) occurs at 1715 cm^{-1}.

Now, let us consider the C=O stretching frequency of amide and ester:



Benzamide

νC=O 1663 cm^{-1}

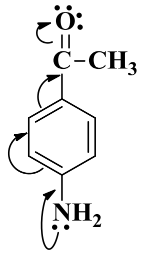


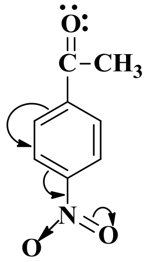
Methyl benzoate

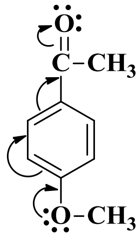
νC=O 1730 cm^{-1}

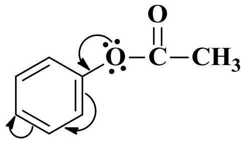
Oxygen atom of ester is more electronegative than nitrogen of amide. Therefore, lone pair of electrons on nitrogen atom of amide participates more in conjugation resulting in the decrease in absorption frequency of νC=O in amide as compared to that of ester.

In the example given below, due to the low electronegativity of nitrogen atom, the lone pair of electrons participates more in conjugation in compound I as compared to that compound III. Thus, in compound I, ν(C=O) absorption occurs at lower wave number compared to that in compound III. In compounds II and IV, inductive effect dominates over mesomeric effect and hence absorption takes place at comparatively higher frequencies. In compound IV, the non-bonding electrons on oxygen atom are partially drawn towards the benzene ring and thereafter their conjugation with C=O is minimized. Thus, C=O absorption band shifts to a higher frequency.


I


II


III


IV

p-amino-acetophenone	p-nitro-acetophenone	p-methoxy acetophenone	Phenyl acetate
νC=O 1677 cm^{-1}	νC=O 1700 cm^{-1}	νC=O 1684 cm^{-1}	νC=O 1770 cm^{-1}

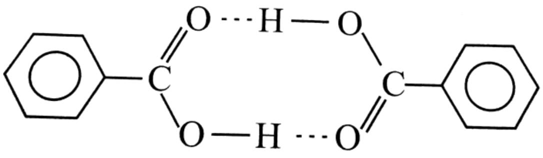
In ortho substitution, inductive effect, mesomeric effect along with steric effect is considered. In meta substituted compounds, only inductive effect is considered. In pare substitution, both inductive and mesomeric effects become important and wavenumber of absorption is decided by the dominant effect. In ortho substituted compounds, the lone pairs of electrons on two atoms influence each other through space interactions and depending upon the interactions wave number will increase or decrease. This effect is called field effect.

4. Hydrogen bonding:

The presence of hydrogen boding in the molecule changes the absorption frequency as well as shape of absorption band. Stronger the hydrogen bonding, greater the absorption shift towards lower wave number from normal value. The two types of hydrogen bonding (intramolecular and intermolecular) can be distinguished by the use of infrared spectroscopy. Intermolecular hydrogen bonding is concentration dependent and the absorption band shift on dilution. On the other hand intramolecular H-bonding is concentration independent. The intermolecular bonding gives rise to broad bands while the bands due to intra-molecular hydrogen bonding are sharp and well defined.

A free (unassociated) O-H bond (in vapour phase or in very dilute solutions) gives rise to stretching absorption at about 3610 cm^{-1}. While in dimeric or polymeric association the hydroxyl group absorbs as broad bands at lower frequency at around 3350 cm^{-1}.

Benzoic acid exists as dimer. The bridges formed are stabilized by resonance. The formation of dimer causes lowering in the force constant and lengthening of bonds. As a result absorption frequency for νC=O and νO-H decreases. The spectrum of benzoic acid displays broad and strong O-H stretching band at about 3000-2500 cm^{-1} and C=O stretching frequency at about 1685 cm$^{-1.}$



Dimerization in benzoic acid

Reference books

1. Spectrometric Identification of Organic Compounds by Robert M. Silverstein and Francis X. Webster, Wiley, Sixth edition (2006).
2. Applications of Absorption Spectroscopy of Organic Compounds by John R. Dyer (1987) Prentice Hall.
3. Elementary Organic Spectroscopy by Y. R. Sharma: Principles and Chemical Applications, S. Chand and Company Ltd.