

Chapter-17

Infrared spectroscopy (Vibrational Modes)

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Condition for IR active molecules:

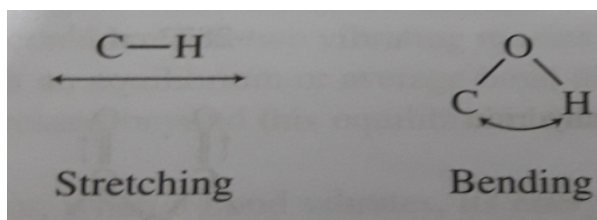
IR active molecules are polar. Polarity should be measured w.r.t. electronegativity difference $\text{END} \neq 0$ of each bond but not w.r.t. their permanent dipole moment ($\mu = 0 \text{ D}$).

Eg. CO_2 is IR active. CO_2 is a non-polar w.r.t. permanent dipole moment ($\mu = 0 \text{ D}$) but in this case each $\text{C}=\text{O}$ bond is polar ($\text{END} \neq 0$).

Molecular Vibrations be the basic principle of the IR spectra.

Types of vibrational motion in IR active molecule:

The simplest types or modes of vibrational motion in a molecule that are infrared (IR) active are the stretching and bending modes as follows:



Stretching and Bending Vibrations:

A. Stretching Vibrations:

Two (02) Types as follows

- i) Symmetric stretching ii) Asymmetric stretching**

In general, asymmetric stretching vibrations occur at higher frequencies than symmetric stretching vibrations.

In the same way, stretching vibrations occur at higher frequencies than bending vibrations
 Eg. $\text{C}-\text{H}$ stretching: $\sim 3000 \text{ cm}^{-1}$; $\text{C}-\text{H}$ bending: $\sim 1340 \text{ cm}^{-1}$.

B. Bending Vibrations:

Four (04) Types as follows

- i) Scissoring (just open a close scissor) ii) Rocking (moves forwards and backwards)
 iii) Wagging (move from side to side or up and down) iv) Twisting (having a lot of turns or changes of direction)

All these vibrations (Fig.1) are commonly used in the literature to describe the origins of IR bands.

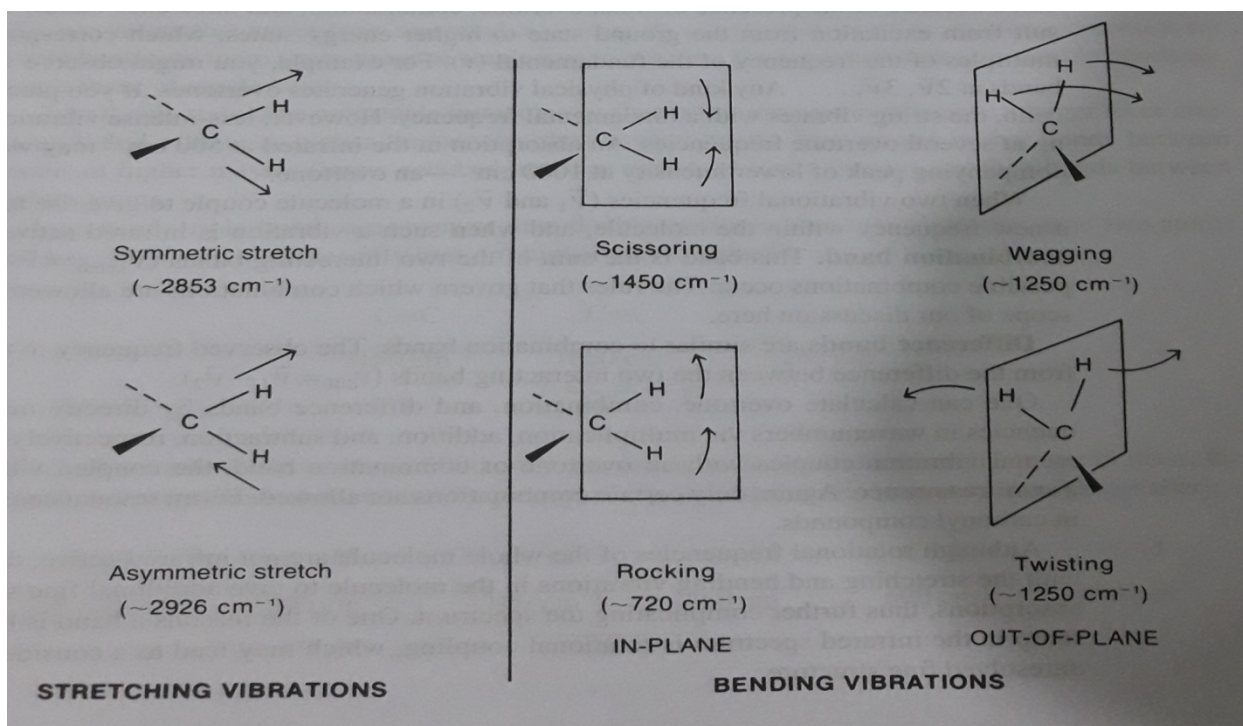


Fig.1: Pictorial diagram of all types of Stretching and Bending Vibrations For $>CH_2$ moiety

Occurrence of Symmetric and Asymmetric stretching vibrations within the functional group:

If any group or moiety contains three (03) or more atoms in which two atoms are identical, then this group exhibits two modes of stretching vibrations namely symmetric and asymmetric stretching vibrations.

Examples of such groupings are $-CH_3$, $-CH_2-$, $-NO_2$, $-NH_2$, and anhydrides. The methylene group ($-CH_2-$) gives rise to a symmetric stretching vibration at about 2853 cm^{-1} and an asymmetric stretching at about 2926 cm^{-1} .

Similar phenomenon occur in the methyl ($-\text{CH}_3$), anhydride $[(-\text{C}=\text{O})_2\text{O}]$, amino ($-\text{NH}_2$) and nitro ($-\text{NO}_2$) group (Fig.2) as follows:

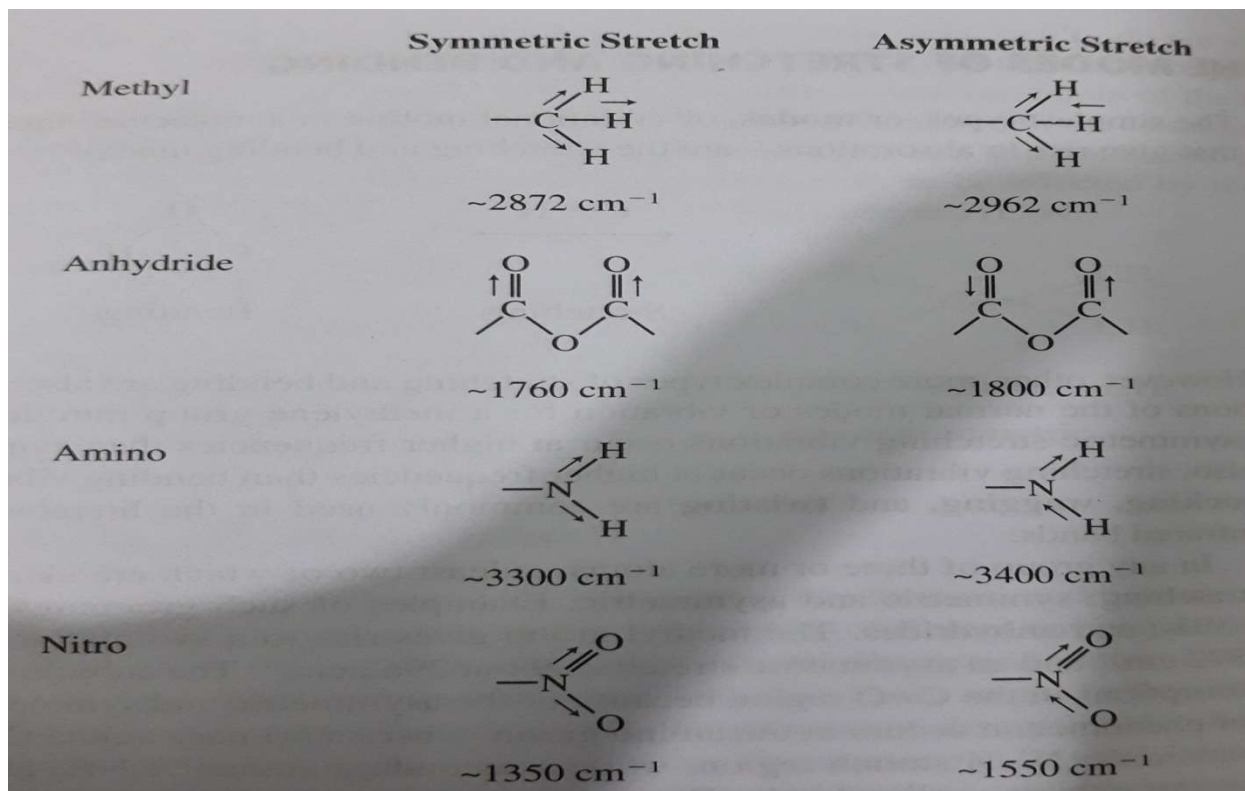


Fig.2: Symmetric and Asymmetric stretching vibrations in the methyl ($-\text{CH}_3$), anhydride $[(-\text{C}=\text{O})_2\text{O}]$, amino ($-\text{NH}_2$) and nitro ($-\text{NO}_2$) group.

In general, asymmetric stretching vibrations occur at higher frequencies than symmetric stretching vibrations.

Molecules show only stretching vibrational frequency:

Only stretching vibration occurs for linear molecules having atomicity 02. Molecules with more than 2 atoms (Fig.3 & Fig.4) can vibrate in different ways (stretching and also bending vibrations). e.g. sulphur dioxide (SO_2)

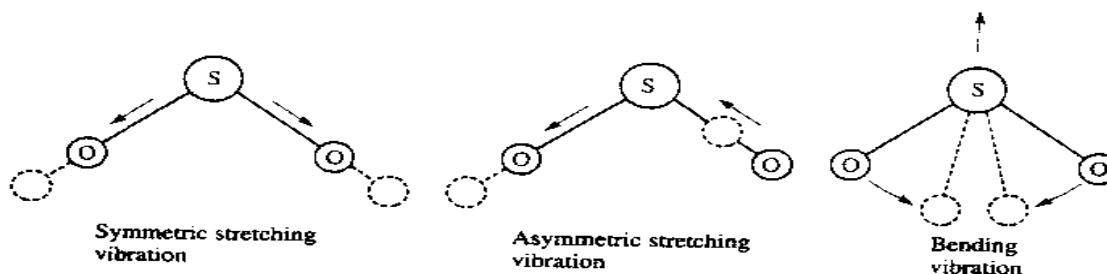


Fig.3: Stretching and bending vibration of SO_2 molecule

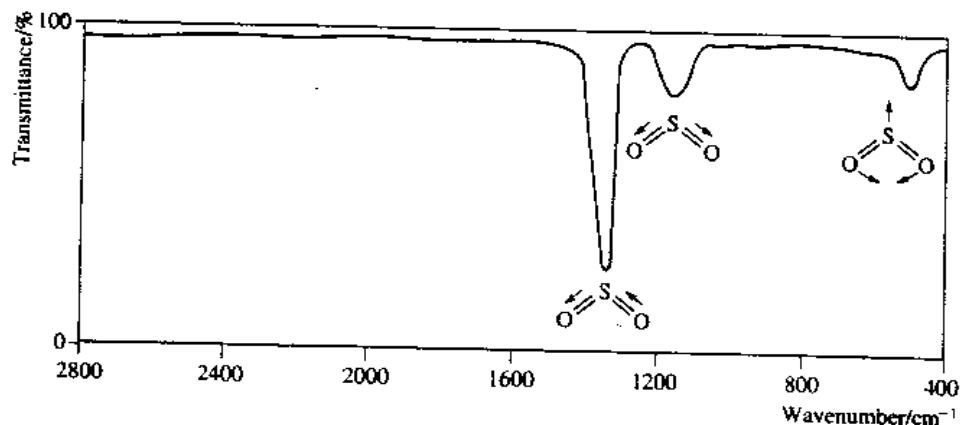


Fig.4: IR spectra of SO₂ molecule

Number of vibrational modes or vibrational degrees of freedom:

In order for a vibrational mode in a sample to be "IR active", it must be associated with changes in the dipole moment. A permanent dipole is not necessary, as the rule requires only a change in dipole moment.

A molecule can vibrate in many ways, and each way is called a *vibrational mode*.

- **Linear molecules with N number of atoms, have $3N - 5$ degrees of vibrational modes, whereas nonlinear molecules have $3N - 6$ degrees of vibrational modes (also called vibrational degrees of freedom).**
- Eg. CO₂ is a linear molecules, $N = 3$, will have $3 \times 3 - 5 = 4$ degrees of vibrational freedom, or modes. H₂O, a non-linear molecule, will have $3 \times 3 - 6 = 3$ degrees of vibrational freedom, or modes.

Homo nuclei diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, e.g. N₂ (END=0), the band is not observed in the IR spectrum. Asymmetrical heteronuclei diatomic molecules, e.g. CO (END \neq 0), absorb in the IR spectrum.

More complex molecules have many bonds, and their vibrational spectra are correspondingly more complex, i.e. big molecules have many peaks in their IR spectra.

Related Questions:

- Q.1. Q. How many types of vibrational motion occurs in the active molecule? Specify them.
- Q.2. Which types of groups exhibit two modes of stretching vibration? In between two modes of stretching vibrations which one shows higher frequency ?
- Q.3. Which types of molecules only show stretching vibrational frequency ?

Q.4. Draw the basic vibrational motions for SO₂.

Q.5. Assign the types of vibrational motion in the following molecules

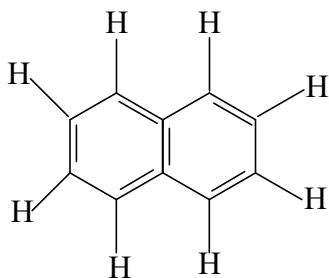
SO₂, CO₂, H₂S, H₂O, BCl₃, HCl, HBr, HI

Q.6. The number of normal modes of vibration in naphthalene is (IIT JAM 2017)

(a) 55 (b) 54 (c) 48 (d) 49

Ans:

(c)



naphthalene (non-linear)

Number of normal vibrational modes = $3n - 6$, where, n = Number of atoms

**Total number of atoms in naphthalene = 18, therefore, degrees of vibrational modes
= $3N - 6 = 3 \times 18 - 6 = 48$**

Q.7. IR active molecule(s) is/are (IIT JAM 2017)

(a) CO₂ (b) CS₂ (c) OCS (d) N₂

Ans: (a, b, c)

CO₂, CS₂, OCS molecules are IR active molecules because these molecules contain ionic character (END ≠ 0), and should have a change in dipole moment due to the vibration. N₂ is IR inactive (END = 0) but Raman active due to ionic character as well as non polarity.

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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