

INFRARED SPECTROSCOPY

SEM-4, CC-8
PART-2, PPT-8

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INFRARED SPECTROSCOPY (PART-2, PPT-8)

Effect of Deuteration

The C-H bond is a normal carbon-hydrogen bond where the hydrogen has an atomic mass of 1. The C-D bond represents a carbon-deuterium bond. Deuterium is an isotope of hydrogen, and has an atomic mass of 2. The reduced masses of these two bonds are different, but their force constants are the same. The C-H stretching vibration occurs at $\sim 3000 \text{ cm}^{-1}$, whereas a typical C-D bond has a stretching vibration around 2120 cm^{-1} .

By simply doubling the mass of the hydrogen atom, the C-H stretching vibration is reduced by over 800 cm^{-1} . A shift in band position caused by a change in reduced mass is called a mass effect. The Hooke's Law expression can be used to estimate the change in stretching frequency as the result of deuteration. The term $m_x m_y / (m_x + m_y)$ will be equal to $m_C m_H / (m_C + m_H)$ for the C-H compound. Since $m_C \gg m_H$, this term is approximately equal to $m_C m_H / m_C$ or to m_H .

$$\bar{\nu} = \frac{1}{2\pi c} \left[\frac{k}{m_x m_y / (m_x + m_y)} \right]^{1/2}$$

Thus, for the C-D compound the term is equal to m_D , and the frequency by Hooke's law application is inversely proportional to the square root of the mass of the isotope of hydrogen, and the ratio of the C-H to C-D frequency should equal $\sqrt{2}$.

Bond	C-H Stretch in cm^{-1}
C-H	~ 3000
C-D	~ 2120

From Hooke's Law, $\bar{\nu} = \frac{1}{2\pi c} \left[\frac{k}{m_x m_y / (m_x + m_y)} \right]^{1/2}$

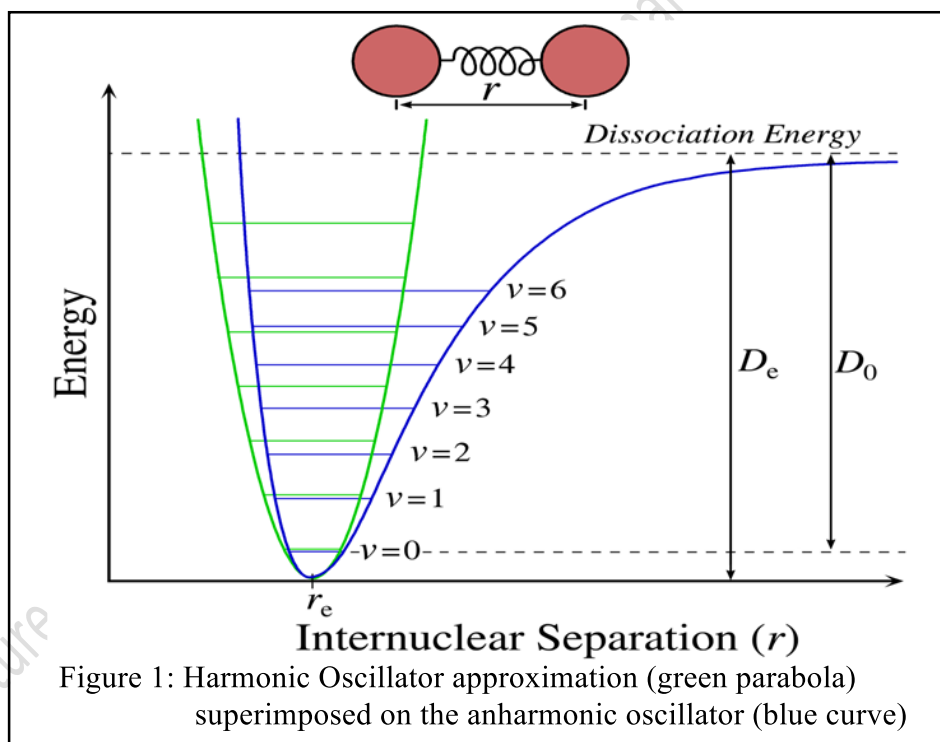
$$\bar{\nu}_{C-H} = \frac{1}{2\pi c} \left[\frac{k}{m_C m_H / (m_C + m_H)} \right]^{1/2} \quad \text{and} \quad \bar{\nu}_{C-D} = \frac{1}{2\pi c} \left[\frac{k}{m_C m_D / (m_C + m_D)} \right]^{1/2}$$

Considering, $m_C \gg m_H$, $m_C + m_H \approx m_C$ and $m_C \gg m_D$, $m_C + m_D \approx m_C$
 $m_C m_H / (m_C + m_H) \approx m_H$ and $m_C m_D / (m_C + m_D) \approx m_D$

$$\frac{\bar{\nu}_{C-H}}{\bar{\nu}_{C-D}} = \left[\frac{m_D}{m_H} \right]^{1/2} = 2^{1/2}$$

Therefore, $\bar{\nu}_{C-H} = \bar{\nu}_{C-D} \times 2^{1/2}$

A hypothetical plot of the molecular potential energy versus bond distance



Overtone Bands

In Figure 1, vibrational energy levels with vibrational quantum numbers of 0, 1, 2 and so on are seen. At room temperature, the vast majority of molecules are in the $\nu=0$ or ground vibrational state. When a molecule absorbs IR light and is excited to the first vibrational energy level ($\nu = 1$), it undergoes a fundamental transition. When a molecule is in the $\nu=1$

level, it is said to contain one quantum of vibrational energy. Fundamental vibrational frequencies of a molecule corresponds to transition from $\Delta\nu = \pm 1$.

Figure 1, also, shows that a molecule can be excited from the $\nu = 0$ level to the $\nu = 2, 3, 4$ and higher levels. This type of transition is called an overtone transition. If the molecule is excited to the $\nu = 2$ level, it contains two quanta of vibrational energy; if it is excited to the $\nu = 3$ level, it contains 3 quanta of vibrational energy.

In vibrational spectroscopy, an overtone band is the spectral band that occurs in a vibrational spectrum of a molecule when the molecule makes a transition from the ground state ($\nu = 0$) to the first ($\nu = 1$), second ($\nu = 2$) or higher excited vibrational energy level. Overtones give rise to very weak absorbance bands. A $\nu = 0$ to $\nu = 2$ transition is typically 10 times weaker than a fundamental band; a $\nu = 0$ to $\nu = 3$ transition is typically 100 times weaker than a fundamental band.

Until this point, it was assumed that the motions the atoms in a vibrating molecule undergo are harmonic. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator and anharmonic motion is the type of motion that really takes place in vibrating molecules. Anharmonicity causes the vibrational energy levels depicted in Figure 1 to be unevenly spaced and thus, the vibrational energy levels of a molecule are approximately equally spaced. Consequently, overtone bands are approximately rather than twice the energy of fundamental bands.

Overtones can be recognized because they are often at about twice the wavenumber of a fundamental band. Overtone bands (harmonics) appear at integer multiples of fundamental vibrations, so that strong absorptions at, say, 750 cm^{-1} and 1725 cm^{-1} will also give rise to weaker absorptions at about 1500 cm^{-1} and 3450 cm^{-1} , respectively.

Vibrational Coupling

The probable frequency or wavenumber of absorption can be calculated by the application of Hooke's Law. It has been found that the calculated value of frequency of absorption for a particular bond is never exactly equal to the experimental value. The difference arises from the fact that vibration of each group is influenced by the structure of the molecule in the immediate neighbour of the bond.

Many of the vibrations in most molecules involve more than one chemical bond. Since all parts of the molecule are connected by chemical bonds, exciting one bond often leads to partial excitation of another bond. This phenomenon is called vibrational interaction, and causes vibrational energy levels to be different from those calculated by simple harmonic oscillator theory.

Requirements for effective coupling interaction

1. For interaction to occur, the vibrations must be of the same symmetry species.

2. There must be a common atom between the groups for strong coupling between stretching vibrations.
3. Coupling between a stretching vibration and a bending vibration occurs if the stretching bond is one side of an angle varied by bending vibration
4. Interaction is greatest when the coupled groups absorb, individually, near the same frequency.
5. For coupling of bending vibrations, a common bond is necessary.
6. Coupling is negligible when groups are separated by one or more carbon atoms and the vibrations are mutually perpendicular.

Types of Vibrational Coupling

1. Coupling of two fundamental vibration modes (as in the coupled stretching vibrations of AX₂ and AX₃ groups) produces two new modes of vibration, with frequencies higher and lower than that observed in absence of interaction.
 - An isolated C-H bond has only one stretching frequency, but the stretching vibrations of C-H bonds in CH₂ groups combine together to produce two coupled vibrations of different frequencies- the asymmetric, $\bar{\nu}_{asy}$, and symmetric, $\bar{\nu}_{sym}$.
 - The spectra of alcohols have a strong band in the region between 1212 and 1000 cm⁻¹, which is designated as the "C-O stretching band". In case of methanol this band appears at 1034 cm⁻¹ whereas in the spectrum of ethanol it occurs at 1053 cm⁻¹. In ethanol, the C-O stretching mode is coupled with the adjacent C-C stretching vibration produces an asymmetric C-C-O stretching vibration.
2. Interaction can also take place between fundamental vibrations and overtones or combination tone of some other vibrations and such interactions are known as Fermi Resonance.
 - In Fermi resonance, two vibrations of similar wavenumber and proper symmetry "repel" each other, appearing at wavenumbers above and below where they are normally expected.
 - In aldehydes (-CH=O) the C-H stretching absorption usually appears as a doublet (~ 2820 cm⁻¹ and ~2720 cm⁻¹) because of interaction between the fundamental aldehydic C-H stretching vibration and the first overtone of the aldehydic C-H bending vibration that appear near 1390 cm⁻¹.
 - Another example of Fermi resonance is the doublet (1750 cm⁻¹ and 1746 cm⁻¹) appearance of the C=O stretch of cyclopentanone.

Combination/Difference Bands in IR

In addition to the fundamental vibrations, overtone bands, etc., IR spectrum of a compound also contains other absorption bands. Combination bands are observed when two or more fundamental vibrations are excited simultaneously. One reason a combination/difference band occurs is if a fundamental vibration does not occur because of symmetry. Combination implies addition of two frequencies, but it is also possible to have a difference band where the frequencies are subtracted. Combination bands: When two vibrational frequencies ($\bar{\nu}_1$ and $\bar{\nu}_2$) in a molecule couple to give rise to a vibration of a new frequency within the molecule, and when such a vibration is IR active, it is called a combination band. This band is the sum of the two interacting bands ($\bar{\nu}_{comb} = \bar{\nu}_1 + \bar{\nu}_2$). Not all possible combinations occur. Difference band: The observed frequency in this case results from the difference between the two interacting bands ($\bar{\nu}_{diff} = \bar{\nu}_1 - \bar{\nu}_2$)

Fingerprint Region

The region 1470-910 cm^{-1} in the IR spectra of a compound is known as *Fingerprint region*. This region of the spectrum is particularly rich in absorption bands and shoulders. This region contains much important absorption caused by bending vibrations (particularly C-H) as well as absorptions caused by C-C, C-O, and C-N single bond stretching vibrations. Some absorption bands due to benzene rings are also found in this wavenumber region.

Significance

The utility of the fingerprint region is that the many bands there provide a fingerprint for a molecule. No two molecules, *except the enantiomers*, in the universe have the same IR spectrum, and there is no better way to determine whether two samples are the same than by comparing their fingerprint regions. The pattern of absorptions in this region is unique to any particular compound just as a person's fingerprints are unique and distinguishable. The absorption bands appear in this region is characteristic of a particular compound.

Mechanics of Measurement

IR source: A common light source for IR radiation is the Nernst Glower. It is a molded rod containing a mixture of rare-earth oxides - zirconium oxide (ZrO), yttrium oxide (YtO), and erbium oxide (EbO). When the rod is electrically heated at $\sim 1500^\circ\text{C}$, it emits IR light.

Cell: The glass as well as quartz absorb strongly throughout most of the IR region. So, these are not used as cell containers. So, metal halides, such as, NaCl, KBr, CsCl, etc., are commonly used for these purpose. The spectrum may be determined if the sample is a gas, a solid, a liquid, or in solution. The sample should be dry, because water absorbs strongly near 3710 cm^{-1} (O-H stretching) and near 1630 cm^{-1} (O-H bending). These absorptions may obscure absorptions of the substance being examined and may lead to erroneous assignments.

The spectrum of a solid sample is best determined as an alkali halide "pellet" (KBr is commonly used). Since Potassium bromide does not absorb IR light in the region, $4000\text{-}667\text{ cm}^{-1}$, a complete spectrum of the sample is obtained. The spectrum of a solid sample may

also be determined conveniently as a mull. The most commonly used mulling agent is nujol, a mixture of high molecular weight liquid paraffinic hydrocarbons; absorptions present are caused C-H stretching (3030-2860 cm^{-1}) and C-H bending ($\sim 1460 \text{ cm}^{-1}$ and $\sim 1378 \text{ cm}^{-1}$). Clearly, when nujol is used as the mulling agent, no information can be derived about absorptions of the sample in these regions.

It is frequently desirable to determine the spectrum of a substance in solution. All solvents absorb strongly in at least several regions of the IR spectrum. The most commonly used solvents in IR spectroscopy are carbon tetrachloride, carbon disulphide, and chloroform. The most commonly used cell for solution spectra have a path length of 0.1 mm. A 10% solution generally gives a satisfactory spectrum.

Scale of IR Spectrum

The absorbance (A) of a sample at a particular frequency is defined as $A = \log(I_0/I_t) = \epsilon cl$, where I_0 and I_t are the intensities of the light before and after interaction with the sample, respectively, ϵ is the molar absorptivity, c is the molar concentration of the solute, and l is the path length (in cm). Absorbance is, therefore, a logarithmic ratio.

The transmittance (T) of a sample is defined as, $T = I_t/I_0$. Transmittance, therefore, bears a reciprocal and logarithmic relationship to absorbance: $A = \log(1/T) = -\log T$

Most IR spectra record the intensities of bands as a linear function of percentage transmittance (% T). A plot of measured IR radiation intensity versus wavenumber (on the X-axis) is known as an IR spectrum. Common convention in IR spectra of plotting increasing transmittance on the Y-axis (transmittance spectrum) which makes IR spectra appear 'upside-down' compared with other spectra.

