University of Babylon

College of Science

Department of Chemistry

Course No. Chsc 424

Undergraduate Studies

Physical chemistry
Fourth year - Semester 2
Credit Hour: 3 hrs.
Scholar units: Three units

Lectures of Molecular Spectroscopy

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Lecture No. 3: Infrared Spectroscopy

1-Introudction.

IR technique is proved information about the structure of a chemical compounds and as an analytical tool to assess the purity of a compound.

They found main points in IR- spectroscopy:

- Chemical bond is electrical combination between two electrical charged compartments (energetic process).
- As soon as chemical bond formation as rotational- vibrational motions occurs spontaneously through center of mass.
- Differences in electrical charge distribution along the chemical bonds lead to form a permanent electric dipole moment onto the chemical species.
- Interaction between a permanent electric dipole moment of active Species and electrical force field of light produced energy absorption and excitation occurs in higher vibration energy levels.
- Rotational transitions occurs simultaneously within each two vibrational energy level of transition.

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The IR region is dived into three regions: the near, mid, and far IR as shown in figure 1. The mid IR region is of greatest practical using.

Region	Wavelength (λ) Range, μm	Wavenumber ($\bar{\nu}$) Range, cm^{-1}	Frequency (ν) Range, Hz
Near	0.78 to 2.5	12,800 to 4000	3.8×10^{14} to 1.2×10^{14}
Middle	2.5 to 50	4000 to 200	1.2×10^{14} to 6.0×10^{12}
Far	50 to 1000	200 to 10	6.0×10^{12} to 3.0×10^{11}
Most used	2.5 to 15	4000 to 670	1.2×10^{14} to 2.0×10^{13}

Figure 1. Classification of infrared regions.

2-Theory of Infrared Absorption.

- The molecules must be polar to be active, because they possess a permanent dipole moment.
- A molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule.
- The alternating electrical field of the radiation interacts with fluctuations in the dipole moment of the chemical bond.
- If the frequency of the radiation matches, the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration.

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Conditions IR absorbance to occur:

- A change in the dipole moment of the ***chemical bond*** that allows interaction with the alternating electrical component of the IR radiation wave. **(Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment.)**
- The radiation frequency matches the natural frequency of the vibration **(the IR photon energy is absorbed and the amplitude of the vibration increases)**.

3-Molecular transitions

There are three main types of molecular transitions, which occur in IR

- Rotational transitions

When an asymmetric molecule rotates about its center of mass, the dipole moment seems to fluctuate. ΔE for these transitions correspond to $n < 100$ cm^{-1} .Quite low energy, show as sharp lines that subdivide vibrational peaks in gas phase spectra.

- Vibrational-rotational transitions

Complex transitions that arise from changes in the molecular dipole moment due to the combination of a bond vibration and molecular rotation.

- Vibrational transitions

The most important transitions observed in qualitative mid-IR spectroscopy.

4- Molecular Vibrations:

There are two main types of molecular vibrations, which are stretching and bending vibrations, since actual case of bond lengths and angles represent the **average positions** about which atoms vibrate.

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- A molecule consisting of *n* atoms has a total of 3*n* degrees of freedom, corresponding to the Cartesian coordinates of each atom in the molecule.
- A nonlinear molecule, has 3 of these degrees are rotational and 3 are translational and the remaining corresponds to fundamental vibrations;
- A linear molecule, has 2 degrees are rotational and 3 are translational. The net number of fundamental vibrations for nonlinear and linear molecules is therefore:

Molecular degrees of freedom (nonlinear 3*n*– 6*)* and *(linear* 3*n*– 5)

The symmetrical stretch of CO_2 is inactive in the IR because this vibration produces no change in the dipole moment of the molecule. In order to be IR active, a vibration must cause a change in the dipole moment of the molecule.*(The reason for this involves the mechanism by which the photon transfers its energy to the molecule.

((***The dipole moment is define as the product of the charge and the distance of separation. The distance has direction; therefore, dipole moments are vectors.***)) Of the following linear molecules, carbon monoxide and iodine chloride absorb IR radiation, while hydrogen, nitrogen, and chlorine do not. In general, the larger the dipole change, the stronger the intensity of the band in an IR spectrum.

C≡O I—Cl H_2 N_2 Cl_2

Absorbed in IR *do not absorb in IR*

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Only two IR bands (2350 and 666 cm^{-1}) are found for carbon dioxide, instead of four corresponding to the four fundamental vibrations. Carbon dioxide is an example of why one does not always see as many bands as implied by our simple calculation. In the case of CO_2, two bands are degenerate, and one vibration does not cause a change in dipole moment. Other reasons why fewer than the theoretical number of IR bands are include:

1- An absorption is not in the 4000–400 cm^{-1}range.

2- An absorption is too weak to observe.

3- Absorptions are too close to each other to be resolved on the instrument.

4- Weak bands, which are overtones or combinations of fundamental vibrations, are observe.

The stretching and bending vibrations for the important organic group, $–CH_2$, are illustrated in Figure .2 (The 3*n*–6 rule does not apply since the $–CH_2$group represents only a portion of a molecule.) Note that bending vibrations occur at lower frequencies than corresponding stretching vibrations.

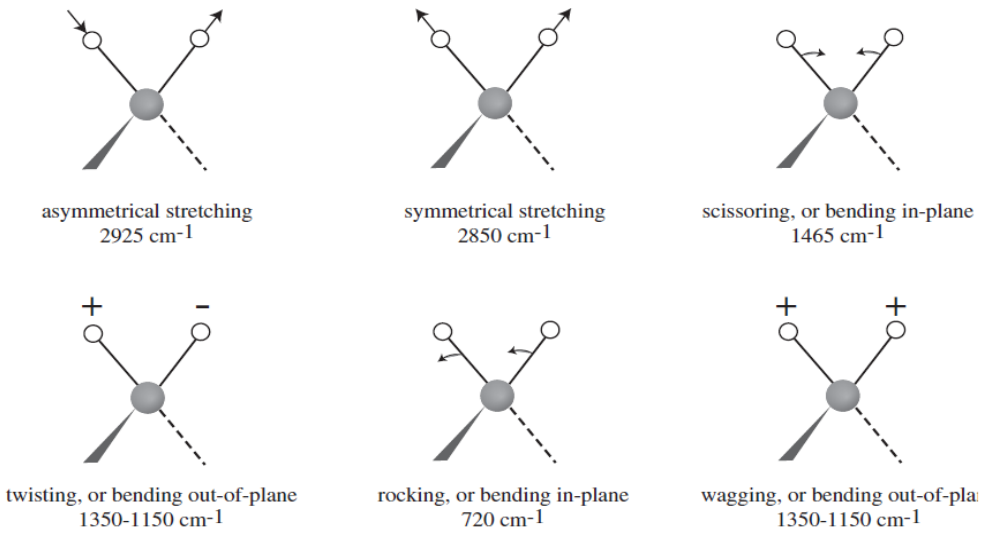

Figure 2. Stretching and bending vibrational modes for a CH_2 group.

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5- Stretching Vibrations.

Hooke's Law can approximate the stretching frequency of a bond. In this approximation, two atoms and the connecting bond are treated as a simple harmonic oscillator composed of two masses (atoms) joined by a spring. The energy curve for a simple harmonic oscillator is illustrate in Figure 3. According to Hooke's law, the frequency of the vibration of the spring is relate to the mass and the force constant of the spring, ***k***, by the following formula

$$\upsilon = \frac{1}{2\pi}.\sqrt{\frac{k}{\mu}}$$

Where ***k*** is the force constant ***μ*** is the reduced mass ***ν*** is the frequency of the vibration. In the classical harmonic oscillator,

$$E = 1/2\boldsymbol{k}x^2$$

Where x is the displacement of the spring.

The energy or frequency is dependent on how far one stretches or compressed the spring, which can be any value. If this simple model were true, a molecule could absorb energy of any wavelength.

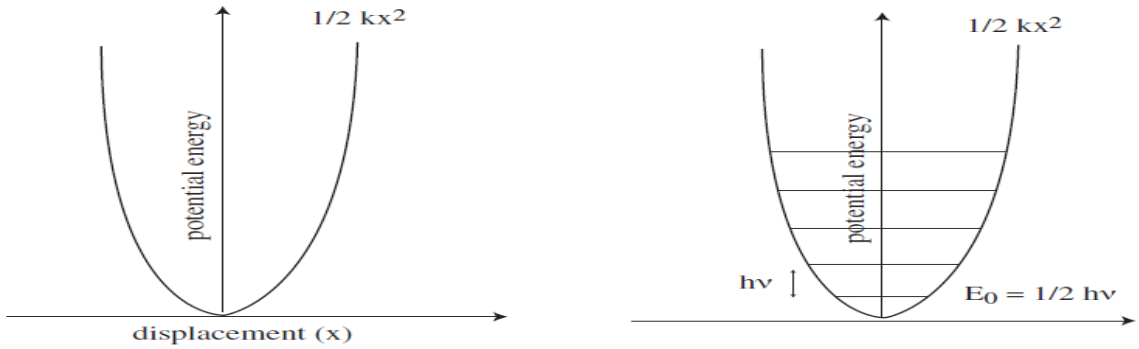

Figure 3. Energy curve for a vibrating spring (left) and energy constrained to quantum mechanical model (right).

However, vibrational motion is quantized, it must follow the rules of quantum mechanics, and the only transitions which are allowed fit the following formula: $E_v = (v+\frac{1}{2})h\nu$

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Where ν is the frequency of the vibration and **v** is the vibration quantum number (0, 1, 2, 3, . . .).

$$E_v = (v+\frac{1}{2})G\bar{\nu}_{osc} \quad \text{by joule units.}$$

$$\varepsilon_v = E/hC = (v+\frac{1}{2})G\bar{\nu}_{osc} \quad \text{by } Cm^{-1}$$

$G\bar{\nu}_{osc}$ is oscillator frequency, selection rule is $\Delta v = \mp 1$.

The lowest energy level is $E_0 = 1/2\ h\nu$, the next highest is $E_1 = 3/2\ h\nu$. According to the selection rule, only transitions to the next energy level are allows; therefore, molecules will absorb an amount of energy equal to 3/2 – 1/2 hν or hν. This rule is not inflexible, and occasionally transitions of 2 hν, 3 hν, or higher are observed. These correspond to bands called overtones in an IR spectrum. They are of lower intensity than the fundamental vibration bands.

A molecule is actually an inharmonic oscillator. As inter atomic distance increases, the energy reaches a maximum, as seen in Figure 5. Note how the energy levels become more closely spaced with increasing inter atomic distance in the inharmonic oscillator. The allowed transitions, hν, become smaller in energy. Therefore, overtones can be lower in energy than predicted by the harmonic oscillator theory. The following formula is derive from Hooke's law. For the case of a diatomic molecule, (ν has been substituted for ν, recall that ν = cν from equations).

The energy value for this modulation is

$$\varepsilon_v = E/hC = (v+\frac{1}{2})G\bar{\nu}_e - (v+\frac{1}{2})^2 G\bar{\nu}_e.\chi_e - (v+\frac{1}{2})^3 G\bar{\nu}_e.\chi_e \ldots\ldots \text{exc by } Cm^{-1}$$

Since $G\bar{\nu}_e$ is oscillator frequency, and χ_e is a harmonist constant with value did not exceeded 0.01. Selection rule for corrected state is involved long transition, selection rule is $\Delta v = \mp 1, \mp 2, \mp 3, \mp 4 \ldots..$

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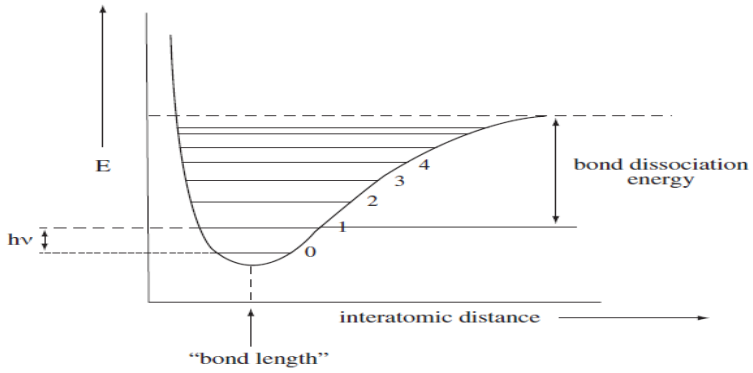

Figure 4. Energy curve of vibrating bond of inharmonic oscillator model.

Final Equation shows the relationship of bond strength and atomic mass to the wave number at which a molecule will absorb IR radiation. As **the force constant increases, the vibration frequency (wave number) also increases**.

As the mass of the atoms increases, the vibration frequency decreases. Using the following mass values: C, carbon 12/6.02 x 10^{23}. H, hydrogen 1/6.02 x 10^{23}.

6-Applications.

Example 1: Calculate the fundamental frequency of hydrogen molecules if you know that's the atomic mass of hydrogen atom is 1.0079AMU and the force constant of hydrogen molecule equal to573.4 Nm^{-1} .

Solution:-

$$\begin{aligned} m_H &= 1.0079 \text{ amu} \\ &= 1.0079 \cdot 1.6606 \cdot 10^{-27} \text{ kg} \\ &= 1.673710^{-27}\text{kg}. \end{aligned}$$

The reduced mass of the hydrogen molecule is

$$\begin{aligned} \mu &= \frac{m_H \cdot m_H}{m_H + m_H} \\ &= \frac{1}{2} m_H = 8.3686 \cdot 10^{-28} \text{ kg}. \end{aligned}$$

the frequency of the vibration is related to the mass and the force constant of the spring, ***k***,

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$$\upsilon = \frac{1}{2\pi}.\sqrt{\frac{k}{\mu}}$$

The force constant of the chemical bond in the hydrogen molecule is $f = 573.4\ \mathrm{Nm}^{-1}$. Therefore the fundamental frequency is

$$\nu_e = \frac{1}{2\pi}\sqrt{\frac{573.4\ \mathrm{Nm}^{-1}}{8.3686 \cdot 10^{-28}\ \mathrm{kg}}}$$
$$= 1.317 \cdot 10^{14}\ \mathrm{Hz}.$$

The most common energy unit in vibrational spectroscopy is the wavenumber. In these units the fundamental frequency is

$$\tilde{\nu}_e = \frac{\nu_e}{c} = \frac{1.317 \cdot 10^{14}\ \mathrm{Hz}}{2.99792458 \cdot 10^{10}\ \mathrm{cm\,s}^{-1}} = 4395\ \mathrm{cm}^{-1}.$$

Example2: the infrared spectrum of $^{39}K^{35}Cl$ has a single intense line at 378.0 cm^{-1}. What is the force constant?

Solution:-

Our first step is to convert the wavenumber to frequency, using. This yields $\nu = c\nu$-

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ν = 378 cm^{-1} x 3.00 x 10^{10} cm/s = 1.134 x 10^{13} s^{-1}.

The reduced mass of $^{39}K^{35}Cl$ is
μ KCl =(35AMUx39AMU) / (35AMU +39AMU) x1.67x 10^{-27}kg /AMU
= 3.08x 10^{-26}kg
Rewriting our frequency equation to solve for force constant yields
k = $(2\pi\nu)^2$ μ = (2 π 1.134 x 10^{13}) ^{2} x 3.08 x 10^{-26} = 156 N/m.

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