VOLUME-19 Part B and C

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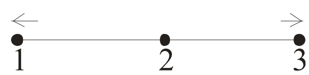
VIII.8.2 Near Infra-Red Spectroscopy (Vibrational Rotational Spectra)

1. Introduction

The molecular motion that has the next higher energy level spacing after the rotation of molecules in vibration of the atoms of the molecule with respect to one another. It will be shown that the study of absorption of radiation resulting from transitions among the vibrational energy levels leads to further detailed insight into the nature of molecules.

Vibrational motion is a periodic, concerted displacement of the nuclei in a molecule which leaves the centre of mass unaltered in laboratory space. The appropriate linear combination of the displacement of each nucleus from its equilibrium position is called the vibrational coordinate, q and is used to describe a particular vibrational motion.

In linear molecule, CO_2, the symmetric stretching coordinate q_1 involves the displacement of two O atoms away from (or towards) each other. There is no contribution from c atom to the vibrational coordinate because it remains fixed at the centre of the mass.



$$q = \Delta Z_3 - \Delta Z_1$$

Figure 1. The vibrational coordinate q_1 which describes the symmetric stretching vibration of the CO_2 molecule.

Poly atomic molecules have several, distinct vibrational modes but a diatomic molecule has only one. The motion in this case is stretching of the bond between the two atoms. Many alternative definitive of the vibrational coordinate for a diatomic molecule are possible but the simplest is

$$q = r - r_c$$

where r and r_c are the instantaneous and equilibrium bond lengths respectively.

We will first discuss the spectrum due to the vibration of a diatomic molecule and afterwards will take the diatomic molecules which undergo vibration and rotation simultaneously.

2. Energy change in vibration

It can be shown by wave-mechanical treatment that the energy of a vibrational levels is given by

$$\varepsilon_{vib} = \left(v + \frac{1}{2}\right) h\nu \text{ ergs} \qquad \ldots 1$$

where v is the vibrational quantum number having values 0, 1, 2,…. and ν is the frequency in cycles/sec and is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}} \qquad \ldots 2$$

where, f = force constant (dynes/cm) which gives the idea of toughness or the strength of the bond

μ = reduced mass $= m_1 m_2 / m_1 + m_2$; m_1 and m_2 are the masses of the atoms of a bond.

It can be easily seen from the ε_{vib} expression (1) that energy difference, $\Delta\varepsilon_{vib'}$ in successive vibrational levels will be given by

$$\Delta\varepsilon_{vib} = \frac{h}{2\pi}\sqrt{\frac{f}{\mu}} \text{ ergs}$$

$$= \frac{h}{2\pi \times hc}\sqrt{\frac{f}{\mu}} cm^{-1} \qquad \ldots 3$$

$$= \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}} cm^{-1}$$

At room temperature, the value of kT is sufficiently small compared with typical values of $\Delta\varepsilon_{vib}$ so that most of the molecules are in the lowest allowed vibrational state. In a spectroscopic study, therefore, one investigates the absorption of radiation by these $v = 0$ state molecules.

3. Selection rules

Electromagnetic radiation can induce transitions among the vibrational energy levels only when the vibration of a molecule leads to an oscillating dipole moment and a vibrational spectrum can be expected. This means that molecules like H_2, N_2, O_2 etc. with not give infrared spectrum whereas molecules like HCl, H_2O, NO_2 etc. will give infrared spectrum. Also, during transition, change in vibrational quantum number can be only ± 1 *i.e.,* $\Delta_v = \pm 1$. Vibrational spectra are usually determined by absorption spectroscopy, and then the rule $\Delta_v = \pm 1$ is the only part of this selection rule which is pertinent.

4. Stretching and bending modes of vibration

There are two kinds of fundamental vibration for molecules: stretching in which the distance between two atoms increases or decreases, but the atoms remain in the same bond axis; and bending (or deformation), in which the position of the atoms changes relative to the original bond axis. The various stretching and bending vibrations of a bond occur at certain quantized frequencies. When infrared light of the same matching frequency is incident on the molecule, energy is absorbed and the amplitude of the vibration is increased. When the molecule reverts from the excited state to the original ground state, the absorbed energy is released as heat.

Some of the various stretching and bending vibrations that can exist within a molecule are shown schematically in Figure 9.2. Bending vibrations generally require less energy and occur at longer wavelengths (lower v) than stretching vibrations. Stretching vibrations are found to occur in the order of bond strengths. For example, $v_{C-C} < v_{C=C} < v_{C\equiv C}$.

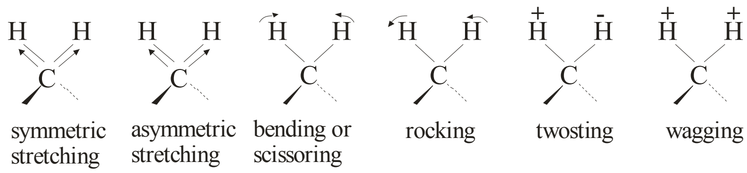


Figure 2. Different modes of vibrations of methylene group.

5. Number of fundamental vibrations

A polyatomic non-linear molecule having n atoms has a total of $3n$ degrees of freedom and since 3 of these are overall translational degrees of freedom and 3 (or 2 if the molecule is linear) are rotational degrees of freedom, there will be $3n - 6$. ($3n - 5$ for a linear molecule) vibrational degrees of freedom. There are, therefore, $3n - 6$ (or $3n - 5$) energy-level patterns, each with its own spacing (i.e., $v = 0$ to $v = 1$ transition for each of the modes of vibration will normally have energies that are different from each other). If the vibrations corresponding to all these patterns are associated with oscillating dipole moments, there will be $3n - 6$ (or $3n - 5$) observed absorption centred at 1595, 3652, 3756 cm^{-1}. For a molecule with many atoms, $3n - 6$ becomes large and one expects very many vibrational transitions and a very complicated spectral pattern.

6. Overtones and combination bands

Additional (not-fundamental) absorption bands may occur because of the presence of overtones (or harmonics) that occur with greatly reduced intensity, at $1/2, 1/3$.....of the wave lengths (twice, thrice…..the wave number for fundamental vibration), combination bands (the sum of two or more) different wave numbers for fundamental vibration), and difference band (the difference of two or more different wave numbers for fundamental bands).

7. Spectral range

The ordinary infrared region extends from 2.5-15μ (4000 – 667 cm^{-1}); the region from 0.8 – 2.5μ (12500 – 4000 cm^{-1}) is called the near infrared and the region from 15-200μ (657 – 50 cm^{-1}) is called the far infrared.

8. Vibrating diatomic molecule as a harmonic oscillator

Frequency of vibration: To calculate it, let us suppose the bond gets distorted from its equilibrium length r_C to the instantaneous length r, in such a case the restoring force on each atom of a diatomic molecule are

$$M_1 \frac{d^2 r_1}{dt^2} = -K(r - r_C)$$

and $$M_2 \frac{d^2 r_2}{dt^2} = -K(r - r_C)$$

where K is proportionality constant called force constant, force constant is a measure of the stiffness of the bond, r_1 and r_2 are the position of atoms 1 and 2 relative to the centre of mass of the molecule we know that

$$r_1 = \frac{m_2 r}{m_1 + m_2},$$

$$r_2 = \frac{m_1 r}{m_1 + m_2},$$

Putting the values of r_1 in first equation of motion, we get

$$\frac{m_1 m_2}{m_1 + m_2}\frac{d^2 r}{dt^2} = -K\left(r - r_e\right) \qquad \ldots 1$$

Since r_e is constant, its differentiation with respect to t will be zero, so that we can write

$$\frac{d^2 r}{dt^2} = \frac{d^2\left(r - r_e\right)}{dt^2}$$

Putting in equation (1),

$$\frac{m_1 m_2}{m_1 + m_2}\frac{d^2\left(r - r_e\right)}{dt^2} = -K\left(r - r_e\right) \qquad \ldots 2$$

Let us put

$$r - r_e = x, \text{ and } \frac{m_1 m_2}{m_1 + m_2} m'$$

where x would then represent that displacement of the bond length from its equilibrium position. Therefore, equation (2) gives

$$m'\frac{d^2 r}{dt^2} = -Kx$$

or $$\frac{d^2 x}{dt^2} + \frac{K}{m'}x = 0.$$

or $$\frac{d^2 x}{dt^2} + \omega^2 x = 0$$

which is the equation of simple harmonic motion with frequency of vibration, expressed in cm^{-1} unit (wave number),

$$= \frac{1}{c}\sqrt{\frac{K}{m'}}$$

or $$\nu_{classical} = \frac{1}{2\pi c}\sqrt{\frac{K}{m'}} m^{-1}$$

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