

CHEM 355

EXP 5

Infrared Spectroscopy

Infrared spectroscopy is the spectroscopy that helps us identify the functional parts of the molecule, then the molecule itself, by using the fact that each functional part absorbs a specific portion of the infrared light. These absorptions occur because a certain bond or a group or the molecule itself as a whole does a periodic motion with a frequency that is resonant to the vibrational excited state energy level achieved by the absorbed light. Absorption of the light results in the excitation of an electron from one quantum state to another.

There are three types of excitations that a molecule can experience; electronic, vibrational and rotational. Electronic transition require high energy usually corresponding to a wavelength in UV or visible region, and results in an electron transition from one electronic energy level to another, in simple terms to a different orbital (see Figure 1 A and B group transitions). Vibrational excitations and rotational excitations occur between vibrational and rotational energy levels. (Figure 1 C and D transitions) Number of allowed vibrational transitions depends on the possible vibrational modes (periodic motions that result in a net dipole change) of a group or a molecule. As the number of constituent atoms increases so does the number of vibrations a molecule can do. Thus a molecule with a very large number of atoms will have many different vibrational energy transitions. Rotational transitions are only experienced by the molecules that have different center of mass and center of charge. Therefore, completely symmetric (like H_2 , O_2 , etc), molecules do not have any rotational transitions thus any rotational spectra since their center of mass and charge is the same point in space and application of field do not cause a rotation of the molecule.

Normal modes of vibrations:

Molecular vibrations depend on vibrational modes. For nonlinear molecules having N atoms, vibrational modes are $3N-6$ and for linear molecules vibrational modes are $3N-5$. As an example H_2O , a non-linear molecule, will have $3 \times 3 - 6 = 3$ degrees of vibrational freedom, or modes.

Simple diatomic molecules have only one bond and only one vibrational band, simple stretching motions of the two atoms similar to a two end loaded spring. If the molecule is symmetrical, e.g. N_2 , the band is not observed in the IR spectrum since the oscillations do not result in a net dipole change. However, an asymmetrical diatomic molecule, e.g. CO , does absorb in the IR spectrum since the symmetry is broken. More

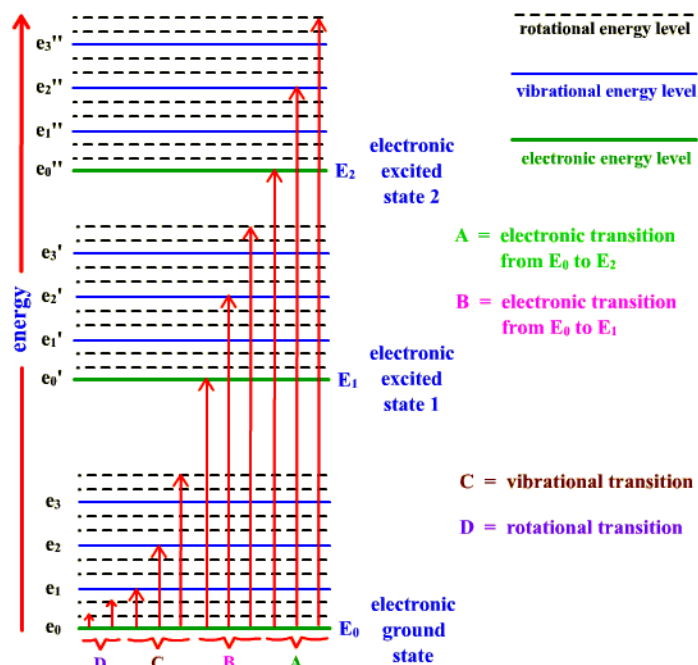


Figure 1. Some of the possible electronic, vibrational, and rotational transitions of a molecule.

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

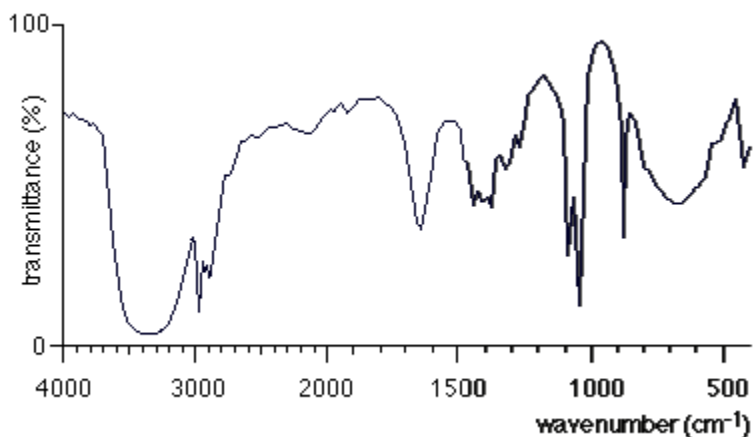


Figure 2. Infrared spectrum of ethanol

Types of vibrations:

A molecule vibrates in $3N-6$ different way (or $3N-5$ ways if linear) but all have a common basic motions of the atoms attached to the central atom; stretching and bending. Stretching vibration leads to bond length change during vibration. If more than one bond stretching is coupled in a vibrational mode than it is grouped into two; symmetric and asymmetric. Bending vibrational modes cause change in bond angle. Figure 3 shows six vibrational modes that can be achieved by CH_2 group of a molecule.

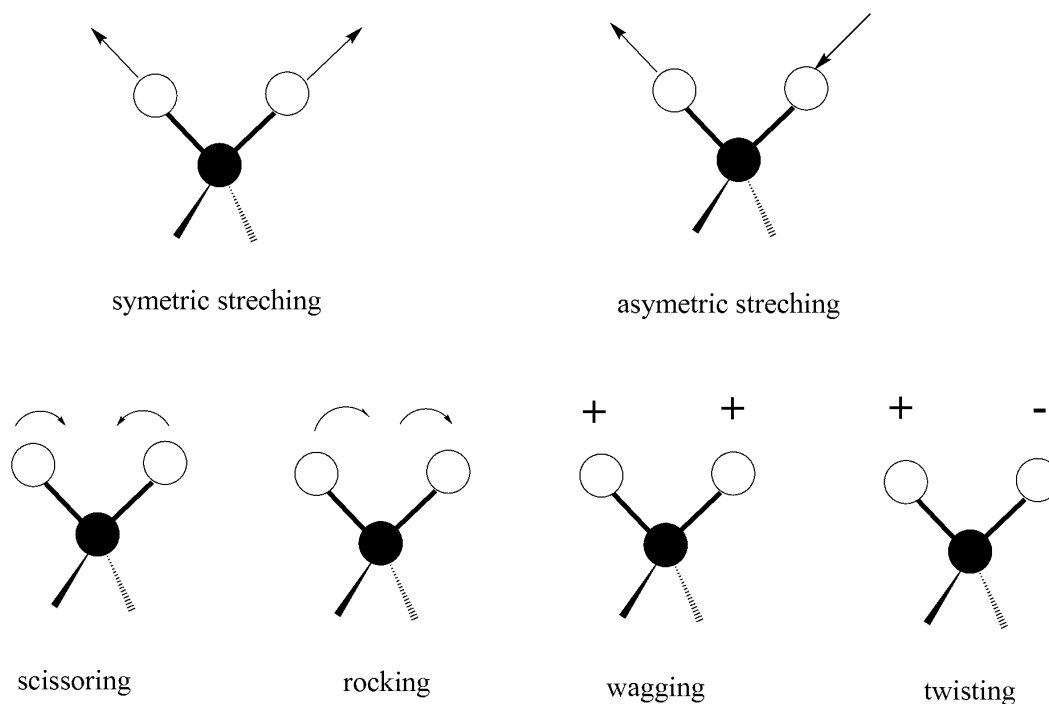


Figure 3. Stretching and Bending Vibrations (+ means out of the plane, - means in the plane)

Vibrational transition of a diatomic molecule: Vibrational spectrum of the diatomic molecule is evaluated by using harmonic oscillator quantum mechanics. The energy is defined as Eq. (1)

$$E_v = \left(v + \frac{1}{2}\right) h\nu_0 \quad (1)$$

where v is the vibrational quantum number that can be 1,2,3.....

ν_0 is the frequency of the vibration

The frequency of a given stretching vibration in an IR spectrum can be related to three factors;

1. masses of bonded atoms, light atoms vibrate at higher frequency than heavier one
2. relative stiffness, triple bonds vibrate at higher frequencies than double bonds
3. force constant

Dependence of frequency of the vibration to force constant is given by following Eq. (2)

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \text{where } k \text{ is in } \frac{N}{m} \text{ and } \mu \text{ is in } kg \quad (2)$$

Rotational transition of a diatomic molecule: To evaluate the rotational spectrum of the diatomic molecules it is considered as a rigid rotor. Rotational energy is equal to

$$E_J = B J \cdot (J + 1) \cdot \frac{h^2}{8\pi^2 I} \quad (3)$$

where B is the rotational constant and is also given by Eq.(4)

$$B = \frac{h^2}{8\pi^2 I c} \quad (4)$$

where I is moment of inertia that is defined as $I = \mu r^2$, μ is reduced mass, r is bond length.

When transition between rotational levels is thought, it is seen that they are equally spaced and its magnitude is 2B. Therefore calculation of moment of inertia and bond length becomes possible.

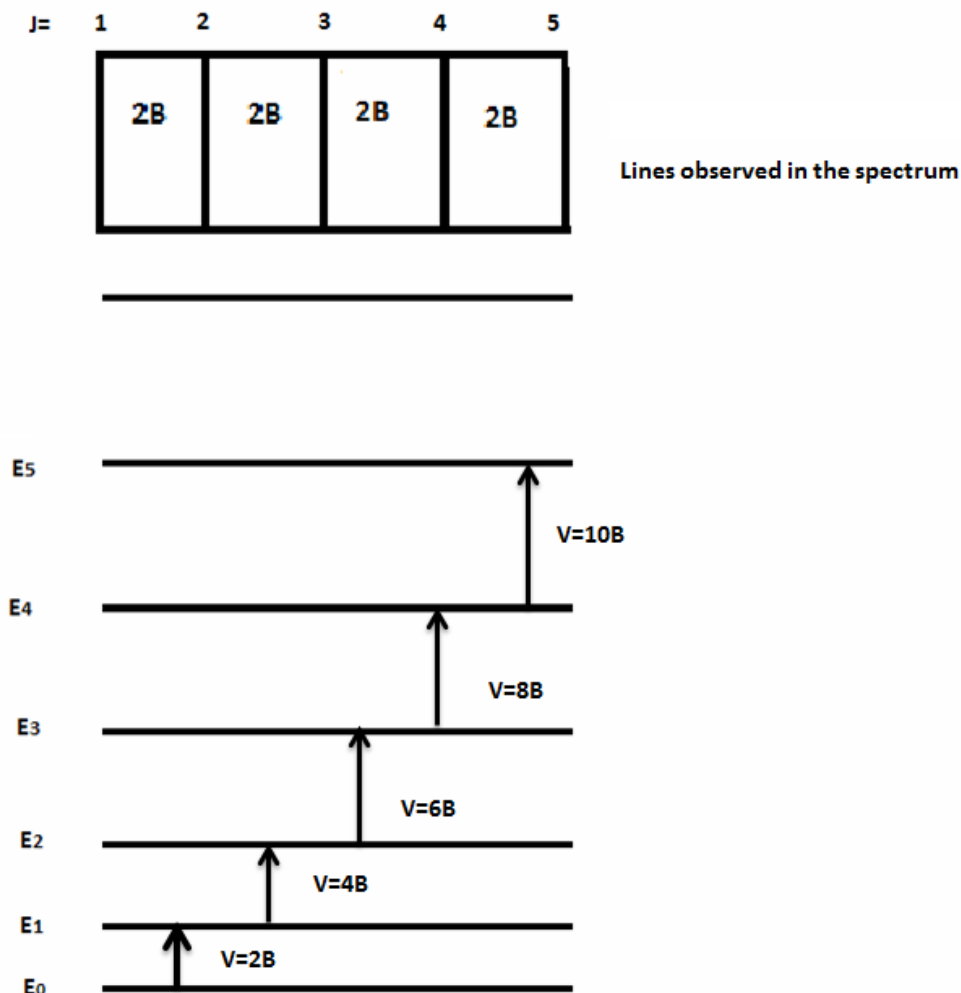


Figure 4. Rotational energy levels and lines observed in the spectrum.

Notice that difference between the rotational energy levels are always $2B$.

Selection rule for vibrational and rotational transition:

In infrared spectroscopy, under harmonic oscillator approximation selection rule for a vibrational transition is $\Delta v = \pm 1$; thus, only allowed transition that starts from a ground state ($v=0$) is to be to the first excited state. All others ($\Delta v > 1$) are not allowed transitions. However in reality the molecular systems are not an exact harmonic oscillators and behave as anharmonic oscillator in most of the time. In that case all Δv is allowed but transitions $\Delta v > \pm 1$ is weakly observed. Selection rule for an allowed rotational transition is $\Delta J = \pm 1$. In some cases $\Delta J = 0$ is also allowed especially for nonlinear molecules.

Vibrational and rotational spectra of molecules:

IR spectra consist of both vibrational and rotational transitions of molecules because in most cases vibrational and rotational transitions are coupled (see Figure 1). Therefore, vibrational and rotational energy are added and expressed as depicted in Eq.(5)

$$E_{v,j} = \left(v + \frac{1}{2}\right)h\nu_0 + BJ(J + 1) \quad (5)$$

The rotational-vibrational spectrum of HCl molecule are divided into three classes, P, R and Q branch, corresponding to $\Delta J = -1$, $\Delta J = +1$ and $\Delta J = 0$ respectively (Figure 5 and 6). Since HCl is a linear molecule $\Delta J = 0$ is not allowed transition.

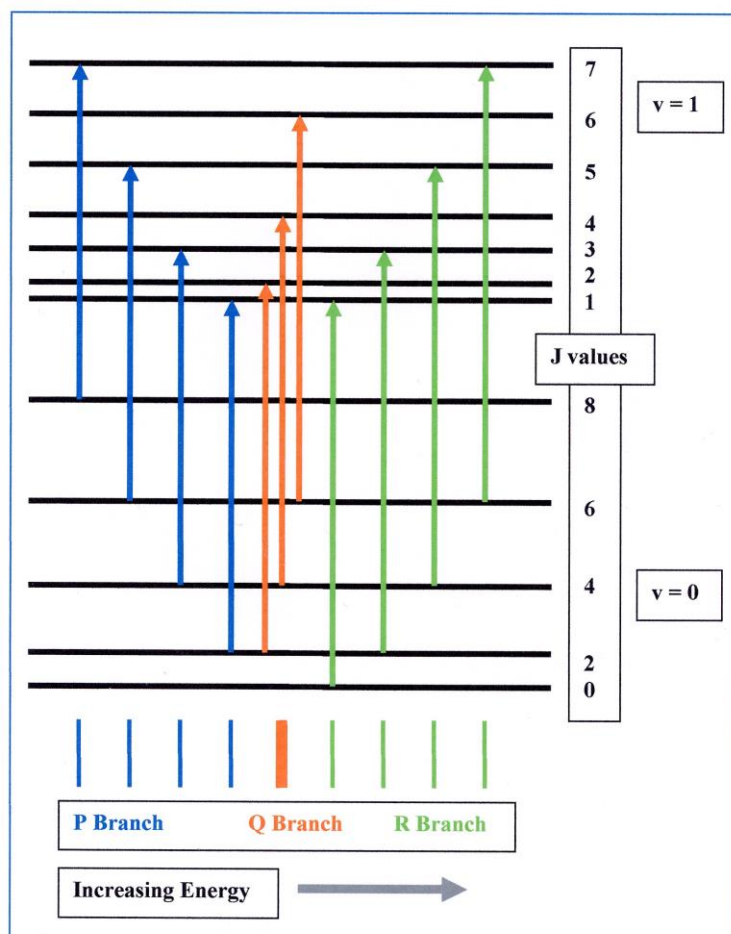


Figure 5. Vibrational and rotational energy level and possible transitions.

Notice that Q branch has $\Delta J=0$, P branch and R branch has $\Delta J=\pm 1$.

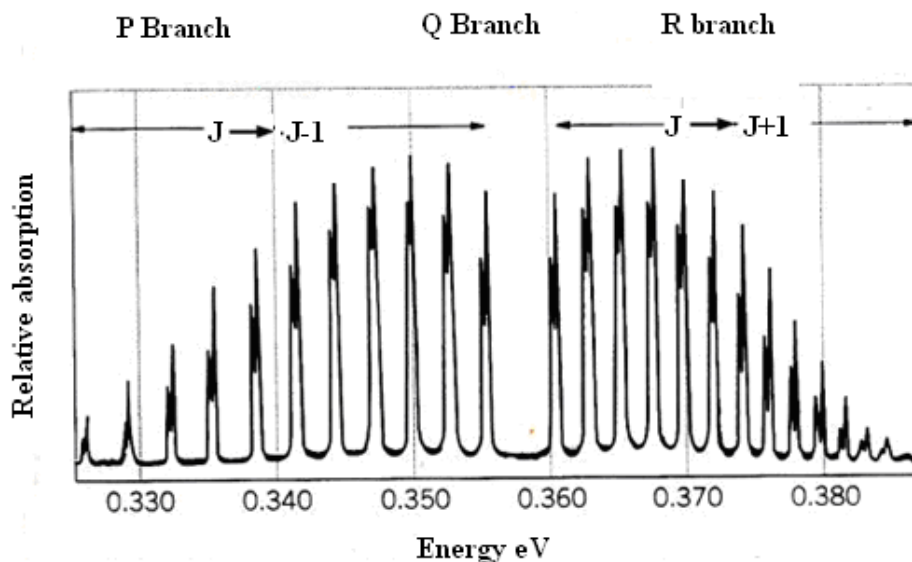


Figure 6. The molecular absorption spectrum of HCl

Chemical and apparatus

FTIR spectrometer, IR gas cell, concentrated HCl and vacuum pump.

Procedure

1. Evacuate the IR cell and take background spectrum.
2. After taking background spectrum, IR cell is evacuated and IR cell is exposed to HCl vapor after opening one of inlet.
3. Take IR spectrum of HCl gas.
4. Print out spectrum

Treatment of data

1. Calculate force constant, rotational constant, moment of inertia and bond length of HCl.
2. Compare theoretical and experimental results.

Questions

1. Discuss the allowed and forbidden transitions and explain the reason why there is no peak in bond origin.
2. Label R, P and Q branches on the spectrum and discuss the intensity of R and P branches.
3. Explain the reason why the gas phase is used.
4. Explain the reason why KBr glass is used.