

**COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH**  
**UNIVERSITY GRANTS COMMISSION**

CHEMICAL SCIENCES

CODE:01

**2.6.1 Molecular spectroscopy**

**At a Glance**

Different type of Molecular spectra, Mutual exclusion principle, Harmonic and Anharmonic Oscillator Model, Application of IR, Raman spectra.



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### Key Statement

**Basic Key Points:** Absorption and emission spectra (2.6.1), Different type of molecular spectra (2.6.2), Conditions for various types of spectra (2.6.4/5/6), Selection rule for the vibration transition of a SHO (2.6.9), Moment of inertia (2.6.14), Kinetic energy of rotation (2.6.15), Frequency of spectral line (2.6.16), Rotational spectrum of spectral lines (2.6.17)

**Standard Key Point:** Mutual exclusion principle (2.6.7), Vibrational spectra of diatomic molecule (2.6.8), Vibrational – Rotational spectra of diatomic molecule (2.6.10), Application of IR spectroscopy (2.6.12), Isotopic effect (2.6.19)

**Advance Key Point:** Anharmonic Oscillator model (2.6.11), Frank – Condon principle (2.6.13), Intensity of rotational spectral lines (2.6.18), Classical theory of Raman spectra (2.6.21)



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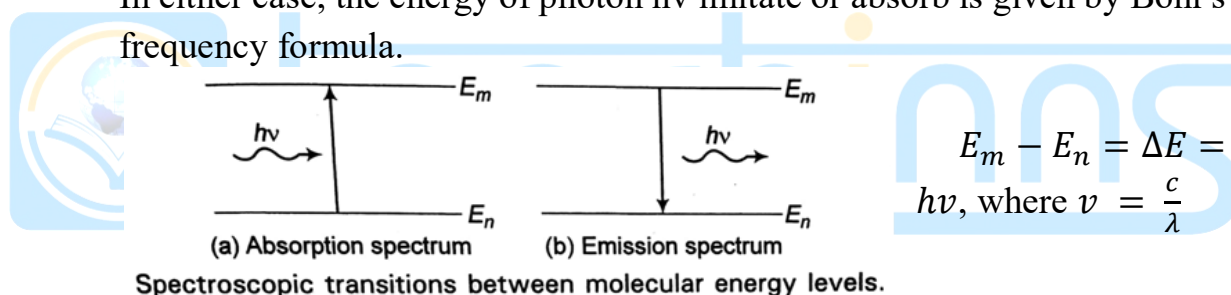
### Key Facts

#### 2.6.1. Absorption and emission spectrum:

Any atom or molecule has a number of energy levels which are quantized. The transitions takes place only between these energy levels according to certain rules called selection rules. Transition between any two energy levels can take place in either of the following two ways:

- The transition may take place from lower energy level to higher energy level why absorption of energy from photon. It is then called absorption spectroscopy and the result obtained as a result of number of such transitions is called absorption spectrum.
- The transition may take place from higher energy level to a lower energy level by emitting the excess energy as a Photon. It is called emission spectroscopy and the result obtained as a result of number of such transitions is called emission spectrum.

In either case, the energy of photon  $h\nu$  imitate or absorb is given by Bohr's frequency formula.



#### 2.6.2. Different types of molecular spectra:

- Pure Rotational or microwave spectra:

If the energy absorbed by the molecules is so low that it can cause transition only from one rotational level to other within the same vibrational level, molecular spectrum obtained in this case is called the rotational spectrum. These spectra are there observe in the far infrared region or in the microwave region energies are extremely small (wave number =  $1\text{-}100\text{cm}^{-1}$ ). The spectra obtained are therefore also called microwave spectra.

- **Vibrational rotational or IR spectra:**

If the energy absorbed by the molecules is comparatively large so that it can cause it transition from one vibrational level to other within the same electronic level, both type of transition will take place. The spectrum obtained in this case is called vibrational rotational spectra. Such spectra are observed in near IR region ( $\bar{\nu} = 500\text{-}400\text{cm}^{-1}$ ) and are also called infrared spectra.

- **Electronic spectra/UV visible spectra:**

If the energy absorbed by the molecules is higher such that it can cause transition from one electronic level to another, then this will also be accompanied by vibrational level changes and each of these further accompanied by rotational level changes. For each vibrational change, a set of closely spaced lines is observed due to rotational level changes. A group of closely spaced rotational lines is called a **band**. Thus for a given electronics transition, a set of bands is observed. The spectrum obtained in the case is called electronic band spectra. Such spectra are observed in the visible region ( $12500\text{-}25000\text{cm}^{-1}$ ) and ultraviolet region ( $25000\text{-}70000\text{cm}^{-1}$ ).

- **Raman spectra:**

This is also a type of vibrational rotational spectrum but is based on scattering of radiation and not on the absorption of radiation by the sample. So, it is emission spectra.

It is based upon the principle that when a sample is hit by monochromatic radiation of the visible region, scattering is observed at right angles to the direction of the incident beam. If the frequency of the scattered radiation is equal to that of the incident beam, it is called **Rayleigh scattering** and if the frequency of scattered beam is different from that of incident beam, it is called **Raman scattering**. The difference in the frequencies of the incident beam and that of the scattered beam are called Raman frequencies and the spectra obtained in this case is called Raman spectra. Raman spectra are observed in the visible region ( $12500\text{-}25000\text{ cm}^{-1}$ )

**2.6.3. Note:**

A body has three principal moment of inertia, one about each axis, usually designated  $I_A$ ,  $I_B$  and  $I_C$ .

- For linear molecules [e.g., HCl, carbon oxysulfide ( $O=C=S$ )]  
 $I_B = I_C$ ,  $I_A = 0$
- For symmetric top molecules (e.g.,  $CH_3F$ ,  $BCl_3$ )  
 $I_B = I_C \neq I_A$  and  $I_A \neq 0$   
If  $I_B = I_C > I_A$ , then the molecule is called a Prolate symmetric top (e.g.,  $CH_3F$ ).  
If  $I_B = I_C < I_A$ , then the molecule is called oblate symmetric top (e.g.,  $BCl_3$ ).
- For spherical top molecules  $I_A = I_B = I_C$  (e.g.,  $CH_4$ ).
- For asymmetric top molecules  $I_A \neq I_B \neq I_C$  (e.g.,  $H_2O$ )

**2.6.4. Condition for Rotational spectra:**

The condition for obtaining a pure rotational spectrum is that the molecule must have a permanent dipole moment so that it can interact with the electromagnetic radiation and absorb or emit a photon. Thus pure rotational spectrum is given only by polar molecules.

Homo nuclear diatomic molecules ( $H_2$ ,  $O_2$ ,  $N_2$  etc.) and symmetrical linear molecules like  $CO_2$  or symmetrical molecules like  $C_6H_6$ ,  $CH_4$  non-polar. So these molecules will not give rotational spectra.

Molecules like HCl,  $CH_3Cl$ , CO possess a permanent dipole moment. So, these molecules will show spectra.

**2.6.5. Condition for vibration spectra (IR spectra):**

The condition for obtaining vibrational spectra is that the dipole moment of the molecule must change when the atoms are displaced due to vibration. Homo nuclear diatomic molecules like  $H_2$ ,  $O_2$ ,  $N_2$ , which have only stretching mode of vibration, no bending mode of vibration are infrared active i.e., do not show vibrational spectra because the dipole moment of these molecules do not change during vibration.

On the other hand, hetero-nuclear diatomic molecules like HCl, CO, NO and polyatomic molecules like CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, which show change in dipole moment in some mode of vibration give vibrational spectra and are said to be infrared active.

#### 2.6.6. Condition for rotational vibrational Raman spectra:

The selection rule for a molecule to give rotational vibrational Raman spectrum is that the polarization of the molecule must change as the molecule vibrates.

Both types of diatomic molecules (homo-nuclear and hetero-nuclear) give rotational vibrational Raman spectra. Homo nuclear diatomic molecules such as H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> which do not show IR spectra there dipole moment does not change during vibration, do show Raman spectra since their vibration accompanied by a change in polarizability of the molecules.

#### 2.6.7. Mutual exclusion principle:

For centrosymmetric molecules the vibration which is active in IR, is inactive in Raman and the vibration which is active in IR, is active in Raman spectra.

- Diatomic molecules like H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> are centrosymmetric. Their vibrations are IR inactive and Raman active.
- For CO<sub>2</sub> molecule among the three modes of vibrations asymmetric stretching and bending modes is IR active but Raman inactive. Symmetric stretching of vibration is IR inactive Raman active.
- For H<sub>2</sub>O molecule all the three modes of vibration are IR and Raman active.
- As SO<sub>2</sub> molecule has no centre of symmetry, all three fundamental modes of vibration are IR and Raman active.
- For planer AB<sub>3</sub> molecule (BF<sub>3</sub>), symmetric stretching vibration is IR active but Raman inactive, out-of-plane symmetric deformation is IR active but Raman inactive, asymmetric stretching and asymmetric information are both Raman and IR active.
- For pyramidal AB<sub>3</sub> (NH<sub>3</sub>) all 4 vibrations are both IR and Raman active.

2.6.8. **Vibrational spectra of diatomic molecule:** Classically the vibrational frequency of the molecule is given by the relation

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

Where,

$\mu$  is the reduced mass

$k$  is the force constant

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

The solution of the Schrodinger equation for a simple harmonic oscillator gives the quantized vibrational energy levels.

$$E_{vib} = \left(v + \frac{1}{2}\right) h\nu; v = 0, 1, 2, 3, \dots$$

Where  $v$  is the vibrational quantum number and  $\nu$  is the vibrational frequency.

At the lowest vibrational level ( $v = 0$ ),

$$E_0 = \frac{1}{2} h\nu$$

This energy is called **zero point energy**. In other words the molecules can never have zero vibrational energy i.e., atoms can never be at absolute rest.

When,  $v = 1$ ,  $E_v = \frac{3}{2} h\nu$

$v = 2$ ,  $E_v = \frac{5}{2} h\nu$

$v = 3$ ,  $E_v = \frac{7}{2} h\nu$

$v = 4$ ,  $E_v = \frac{9}{2} h\nu$

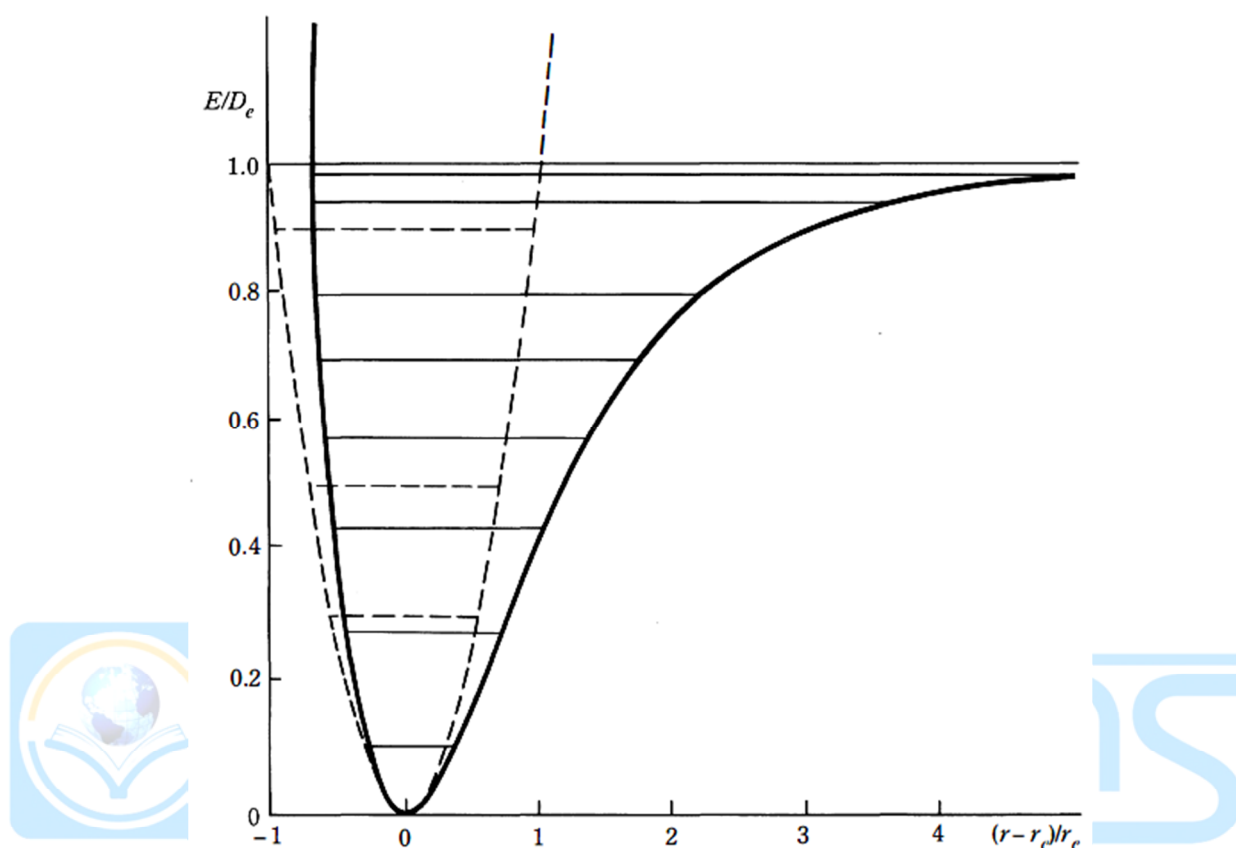
$$E_{v(1 \leftarrow 0)} = E_{v=1} - E_{v=0} = h\nu$$

The frequency observed for this transition is called fundamental frequency ( $\nu_0$ )

So,  $\nu = \nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$  and  $E_{vib} = \left(v + \frac{1}{2}\right) h\nu_0$



The spacing between the adjacent vibrational levels is always equal to  $h\nu_0$  i.e., the vibrational levels of simple harmonic oscillator are equidistant.



#### 2.6.9. Selection rule for vibrational transition of a simple harmonic oscillator:

The transition in vibrational energy levels is limited to only adjacent vibrational levels of a simple harmonic oscillator. Show the selection rule is  $\Delta v = \pm 1$

During transition in vibrational energy levels, there is also transition in rotational energy levels. So the selection rule for vibrational rotational spectra is  $\Delta J = \pm 1$  and  $\Delta v = \pm 1$ .



### 2.6.10. Vibrational rotational spectra of diatomic molecule:

During vibrational motions of the simple harmonic oscillator, there is also rotational motion. Hence the total energy of the molecule is given by

$$E_{\text{total}} = E_{\text{vib}} + E_{\text{rot}} = \frac{(E_v + E_j)}{hc} cm^{-1}$$

Considering the molecule executing rotational and vibrational motions simultaneously and neglecting the centrifugal distortion effect,

$$E_{v,J} = \left[ BJ(J+1) + \left(v + \frac{1}{2}\right) h\nu_0 \right] cm^{-1}$$

$$B = \frac{h}{4\pi^2 IC}$$

$$J = 0, 1, 2, 3, \dots$$

$$v = 0, 1, 2, 3, \dots$$

The selection rule is  $\Delta J = \pm 1$  and  $\Delta v = \pm 1$

The energy change for the transition from  $(v', J')$  to  $(v'', J'')$  levels is given by

$$\begin{aligned} \Delta E_{v,J} &= \Delta E_{v'',J''} - \Delta E_{v',J'} \\ &= [B\{J''(J''+1) - J'(J'+1)\} + (v'' - v')\bar{\nu}_0] cm^{-1} \end{aligned}$$

At lower temperature, the molecules are generally in their lowest vibrational level ( $v = 0$ ). Hence the transition would be essentially from  $v = 0$  to  $v = 2$

In this case,

$$\begin{aligned} \Delta E_{v,J} &= \{2B(J+1) + \bar{\nu}_0\} cm^{-1} \text{ [Considering } \Delta J = +1] \\ &= \{-2B(J+1) + \bar{\nu}_0\} cm^{-1} \text{ [considering } \Delta J = -1] \end{aligned}$$

- $\bar{\nu}_0$  is called band origin or band centre.
- The spectral lines corresponding  $\Delta J = -1$  i.e., at lower frequency side of  $\bar{\nu}_0$  are called P branch lines.
- The spectral lines corresponding  $\Delta J = +1$  i.e., at higher frequency side of  $\bar{\nu}_0$  are called R branch lines.

2.6.11. **Anharmonic oscillator model:** The expression of vibrational energy of anharmonic oscillator is,

$$E_{vib} = \left[ \left( v + \frac{1}{2} \right) h\bar{\nu}_e + \left( v + \frac{1}{2} \right)^2 h\bar{\nu}_e x \right] cm^{-1}$$

$\bar{\nu}_e$  = equilibrium oscillation frequency

x = anharmonicity constant. It has small magnitude.

**Selection rule:** Because of the anharmonicity, the vibrational transitions are not confined to two adjacent levels only, but may also occur between different levels. So the selection rule is  $\Delta v = \pm 1, \pm 2, \pm 3, \dots$

The transitions from  $v = 0$  is most probable at room temperature because at room temperature only lowest vibrational level is occupied.

- The lines appearing due to transition from  $v = 0$  to  $v = 1$  is called **fundamental band**.
- $v = 0$  to  $v = 2$  transition the line called **first overtone band**.
- $v = 0$  to  $v = 3$  transition gives the line called **second overtone band**.
- $v = 1$  to  $v = 2$  transition give the line called **hot band** as the type of transition is possible only at higher temperature.

2.6.12. **Application of IR spectroscopy:**

- **Calculation of force constant:** The force constant is the restoring force per unit displacement. the fundamental frequency is related with the force constant by the following equation:

$$\bar{\nu}_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Or,  $k = 4\pi^2 C^2 (\bar{\nu}_0)^2 \mu$

k = force constant of the bond.

$\bar{\nu}_0$  = fundamental vibrational rotational frequency in terms of wave number.

$\mu$  = reduced mass of the molecule.

C = velocity of light.

The k value increases from a single to double and from double to triple bond. Hence k gives usual information regarding the type of Bond.

- **Identification of the compound:**

Every pure substance has its own characteristic IR spectrum, different from that of any other substance. The spectral picture thus helps in confirming and identifying an unknown sample.

- **Purity of the sample:** Purity of a particular compound can be checked by comparing the IR spectrum of the sample with the IR spectrum of the compound.

2.6.13. **Franck-Condon principle:** According to this principle, “During the electronic transition, the inter-atomic distance remain unaltered, because the time required for electronic transition (of the order of  $10^{-16}$  sec) is very short, as compared to the time of vibration(of the order of  $10^{-13}$  sec).”

2.6.14. **Moment of inertia:** The moment of inertia of a rigid rotator model is given by the equation,

$$I = \frac{m_1 m_2}{(m_1 + m_2)} r^2 = \mu r^2$$

Where  $\mu$  = Reluctant or reduced mass of the system

2.6.15. **Kinetic energy of rotation:**

$$E_J = \frac{h^2}{8\pi^2 I} [J(J + 1)] \text{ ergs}$$

J = rotational quantum number having integral values 0, 1, 2,....

2.6.16. **Frequency of spectral line:**

$$\Delta E_J = \frac{h^2}{8\pi^2 I} [J''(J'' + 1) - J'(J' + 1)]$$

2.6.17. **Rotational spectrum of spectral lines.**

$$\bar{\nu}_{\text{rot}} = B [J''(J'' + 1) - J'(J' + 1)]$$

Rotational spectrum is a concept of a series of spectral lines with frequency separation of  $2B \text{ cm}^{-1}$  between the two consecutive lines.

**2.6.18. Intensity of rotational spectral lines:**

$$J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

$k$  = Boltzmann constant

$T$  = temperature

$B = h/8\pi^2IC$

$c$  = velocity of light

$h$  = planck's constant

$I$  = moment of inertia of diatomic molecule.

**2.6.19. Isotope effect on the rotational spectra:** The diatomic molecule having different isotopes of the same element such as HCl, DCl show different rotational spectra. This is because of the fact that masses of isotropic atoms are different and hence the reduced mass, moment of inertia as well as frequencies of rotation would be different. It has been established that

$$B \propto \frac{1}{\mu}$$

Thus spectrum of heavier species which shows smaller values of  $B$  and hence smaller separation between the spectral lines. This fact has been used in the evolution of precise atomic weights.

**2.6.20. The energy of rotation for non rigid rotator model:**

$$E_j = \frac{h^2}{8\pi^2I} [J(J + 1)] - D[J^2(J + 1)^2] \text{ ergs}$$

$D$  = the centrifugal distortion constant and is of order of  $10^{-4}$  B. It is given by

$$D = 4B^3/(\bar{\nu}_0)^2$$

**2.6.21. Classical theory of Raman spectra:**

$$\mu = \alpha_0 E_0 \sin 2\pi\nu_0 t + \frac{1}{2} \left( \frac{\partial \alpha}{\partial x} \right) x_0 E_0 \cos 2\pi(\nu_0 - \nu_m)t - \frac{1}{2} \left( \frac{\partial \alpha}{\partial x} \right) x_0 E_0 \cos 2\pi(\nu_0 + \nu_m)t$$

Thus the type of movement has three components depending upon three distinct sequences with which it oscillates. The first term gives scattering of radiation without change in frequency  $\nu_0$ . This gives Rayleigh scattering. The second and the third terms give scattering with frequencies  $(\nu_0 - \nu_m)$  for anti stokes line and  $(\nu_0 + \nu_m)$  for stokes lines respectively.

**2.6.22. Note:**

- The frequency of scattered light or limited photon which is either higher or lower than that of the incident photon is called Raman frequency.
- The frequency of scattering line is less than that of the incident light. This gives stokes line of Raman spectra.
- Anti stokes line of Raman spectra where frequency of scattered light is more than that of incident light.
- The Raman shift is independent of the frequency of incident lines i.e., incident light maybe at any frequency.
- Stokes line are more intense than anti stokes line as stokes lines are caused by molecules of low energy level which is more populated and hence have more intensity of absorption. Anti stokes lines are caused by molecules of higher energy level which is less populated and hence less intense.
- Ordinarily less than one part in  $10^6$  of incident light undergoes inelastic scattering. So Raman lines in the spectrum are very weak as compared to Rayleigh line of scattering. Therefore long exposures are required with conventional light source. However, the uses of laser-a powerful monochromatic source have considerably reduced the time and solve this problem.
- The molecule must possess anisotropic polarizability which should change during molecular rotation or vibration for rotational or rotation vibrational Raman spectra.

**NET JUNE 2016**

**Q. Q.** Upon application of a weak magnetic field, a line in the microwave absorption spectrum of rigid rotor splits into 3 lines. The quantum number (J) of the rotational energy level from which the transition originates is

- (a) 0                      (b) 1                      (c) 2                      (d) 3

**Ans.**

As we know that the selection rule,  $\Delta J = 0, \pm 1$

**Correct option is (a).**

**NET DEC 2016**

**Q.** The rotational constant and the fundamental vibrational frequency of HBr are, respectively,  $10\text{cm}^{-1}$  and  $2000\text{cm}^{-1}$ . The corresponding values for DBr approximately are

- (a)  $20\text{cm}^{-1}$  and  $2000\text{cm}^{-1}$                       (b)  $10\text{cm}^{-1}$  and  $1410\text{cm}^{-1}$   
(c)  $5\text{cm}^{-1}$  and  $2000\text{cm}^{-1}$                       (d)  $5\text{cm}^{-1}$  and  $1410\text{cm}^{-1}$

**Ans.**  $\bar{\nu}_{DBr} = \frac{\bar{\nu}_{HBr}}{\sqrt{2}} = \frac{2000}{\sqrt{2}} = 1410$ ;  $B_{DBr} = \frac{B_{HBr}}{2} = \frac{10}{2} = 5$

**Correct option is (d).**

**Q.** Among the following, both microwave and rotational Raman active molecule is

- (a)  $\text{CH}_4$                       (b)  $\text{N}_2\text{O}$                       (c)  $\text{C}_2\text{H}_4$                       (d)  $\text{CO}_2$

**Ans.**

$\text{N}_2\text{O}$  is microwave and rotational Raman active.

**Correct option is (b)**

**NET JUNE 2017**

**Q.** The  $v = 0$  to 1 vibration-rotation spectrum of a diatomic molecule exhibits transitions for R(0), R(1), P(1) and P(2) lines at 2241, 2254, 2216 and 2203  $\text{cm}^{-1}$ , respectively. From this data, we can conclude that the molecule

- (a) has rigid rotation and harmonic vibration
- (b) has anharmonic vibration
- (c) has rotational-vibrational interaction
- (d) is affected by nuclear spin-statistics

**Ans.** Since due to vibrational – rotational interaction P and R lines are obtained and molecule behave as a diatomic vibrating rotor

$$E = BJ(J + 1) + \left(v + \frac{1}{2}\right) \bar{\omega}_e + \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e x_e$$

**Correct option is (c).**

**Q.** The first electronic absorption band maximum of a polar and relatively rigid aromatic molecule appears at 310 nm but its fluorescence maximum in acetonitrile solution appears with a large Stokes shift at 450 nm. The most likely reason for the Stokes shift is

- (a) large change in molecular geometry in the excited state
- (b) increase in dipole moment of the molecule in the excited state
- (c) decrease in polarizability of the molecule in the excited state
- (d) lowered interaction of the excited molecule with polar solvent

**Ans.** The electronic absorption band of a polar and relatively rigid aromatic molecule appears at 310nm but its fluorescence maximum in acetonitrile solution appears with a large stokes shift at 450nm. The reason for stokes shift increasing dipole moment of the molecule in the excited state.

**Correct option is (b).**



**NET DEC 2017**

**Q.** The molecule that will show Raman spectrum, but not IR spectrum, among the following is

- (a)  $H_2$                       (b)  $HCl$                       (c)  $BrCl$                       (d)  $CS_2$

**Ans.** Molecules having zero dipole moment is unable to show IR spectra but having ability to show polarizability in Raman active.

**Correct option is (a).**

**Q.** The pair that contains a spherical top and a symmetric top, among the following, is

- (a)  $CH_4$ ,  $CH_2Cl_2$                       (b)  $CH_2Cl_2$ ,  $CH_3Cl$   
(c)  $CH_3Cl$ ,  $CH_4$                       (d)  $CH_4$ ,  $C(CH_3)_4$

**Ans.**

For spherical top molecules  $I_A = I_B = I_C$ .

For symmetric top molecules  $I_B = I_C \neq I_A$  and  $I_A \neq 0$

**Correct option is (c).**

## NET JUNE 2018

**Q.** In the pure Raman rotational spectrum of  $^{16}\text{O}_8$ , whose electronic ground state is  $^3\Sigma_g^-$ , transitions to/from

- (a) Even J levels are missing                      (b) Odd J levels are missing  
(c) All J levels appear                              (d) None of the J levels appear

**Ans.** To make total wave function symmetric J – levels must be anti-symmetric. Levels with odd J will be present while levels with even J will be missing.

**Correct option is (a).**

**Q.** A symmetric top molecule, among the following, is

- (a) Ethylene    (b) allene  
(c) butatriene    (d) hexatriene

**Ans.** For symmetric top molecules  $I_B = I_C \neq I_A$  and  $I_A \neq 0$

**Correct option is (b).**

**Q.** Assuming harmonic approximation, the energy change for the reaction  $\text{HCl} + \text{D}_2 \rightarrow \text{DCl} + \text{HD}$  in  $\text{cm}^{-1}$  is (the vibrational frequency data in  $\text{cm}^{-1}$  is given in the table below),

HCl	D <sub>2</sub>	DCl	HD
2885	2990	1990	3627

- (a) -258                      (b) +258                      (c) -129                      (d) +129

**Ans.**

$$\Delta E = \frac{(E_{\text{DCl}} + E_{\text{HD}})}{2} - \frac{(E_{\text{HCl}} + E_{\text{H}_2})}{2} = \frac{(1990 + 3627)}{2} - \frac{(2885 + 2990)}{2} = -129 \text{ cm}^{-1}.$$

**Correct option is (c).**