1. Distinguish between symmetric top (prolate and oblate), spherical top and asymmetric top molecules.
2. To which symmetric top, the benzene (C_6H_6) molecule belong?
3. Diatomic molecules such as CO, HF will show a rotational spectrum whereas N_2, O_2, H_2,... will not. Why? Will the molecule $^{17}O - {}^{16}O$ show a rotational spectrum?
4. The intensity of $J = 0 \rightarrow J = 1$ is often not the most intense rotational line. Why?
5. What is centrifugal distortion? Explain the effect of centrifugal distortion on the moment of inertia and energy of a diatomic molecule.
6. How knowledge of centrifugal distortion constant helps one to determine the force constant of a bond?
7. Outline the effect of isotopic substitution on the rotational spectra of molecules.
8. The observed rotational spectrum of HF shows decrease in the line separation on the high frequency side. Why?
9. What is Stark effect? Outline the importance of Stark effect studies in microwave spectroscopy?
10. What is nuclear quadrupole moment? How does it differ from nuclear quadrupole coupling constant?
11. Explain the construction details of Stark cell of microwave Stark modulation spectrograph.
12. Outline the importance of the study of quadrupole hyperfine interaction in microwave spectra.
13. Explain the difference between equilibrium internuclear distance r_e and internuclear distance r_0.

PROBLEMS

1. The bond length of HF molecule is 0.0927 nm (a) What is its moment of inertia ? (b) What is the value of rotational constant in joules and in cm^{-1}? (c) Find the wavenumbers of the first four-transitions. (d) Mention the spectral region in which these absorptions occur.
2. The average spacing between successive rotational lines of carbon monoxide molecule is 3.8626 cm^{-1}. Determine the transition which gives the most intense spectral line at temperature 300 K.
3. How many revolutions per second does a CO molecule make when $J = 3$? The CO bond length is 0.1131 nm.
4. How many revolutions per second does a CO molecule make when $J = 4$? The Rotational constant of CO molecule is 1.9313 cm^{-1}.
5. The microwave spectrum of CN radical shows a series of lines spaced by a nearly constant amount of 3.798 cm^{-1}. What is the bond length of CN?
6. The separation between lines in the rotational spectrum of HCl molecule was found to be 20.92 cm^{-1}. Calculate the bond length.
7. The rotational constant for $H^{35}Cl$ is found to be 10.5909 cm^{-1}. What is the value of B for $H^{37}Cl$ and for $D^{35}Cl$? Given that $m(^{35}Cl) = 35.45$ g/mol, $m(^{37}Cl)/m(^{35}Cl) = 1.056$.
8. Show that a substantial number of molecules of a gas are in excited rotational states at temperature 300 K.
9. The first line in the rotational spectrum of carbon monoxide has a frequency of 3.8424 cm^{-1}. Calculate (i) the moment of inertia of the molecule. (ii) its angular momentum and angular velocity in the $J = 3$ state. (iii) the wave number of the transition $J = 5 \rightarrow J = 6$.
10. In HCl a number of absorption lines with wave numbers 83.03, 103.73, 124.3, 145.03, 165.51 and 185.86 cm^{-1} have been observed. Are these vibrational or rotational transitions? If they are vibrational, what is the characteristic frequency? If they are rotational, give the J values of the 83.03 cm^{-1} transition and the moment of inertia of HCl. In that case estimate the internuclear distance.

1. Explain the effect of anharmonicity on the vibrational spectra of diatomic molecules.
2. Homonuclear diatomic molecules do not show vibrational spectra. Why?
3. What are hot bands? Why are they called so?
4. What parameters one can get from a study of the vibration-rotation spectrum of a heteronuclear diatomic molecule? How are they estimated?
5. Alternate lines of P and R branches of acetylene are less intense. Why?
6. The spacing between lines in the P and R branches of CO_2 is $4B$ instead of the expected $2B$. Why?
7. The spacing between lines in the P and R branches of $^{16}O–C–^{16}O$ is $4B$. What would be the corresponding spacing of $^{18}O–C–^{16}O$ and $^{18}O–C–^{18}O$?
8. The Q branch lines of CH_3I show the periodic variation of intensity strong, weak, weak; strong, weak, weak; ... Account for this variation.
9. How many normal modes would you expect to be observed in the infrared absorption spectra of H_2O and CO_2? Diagram the normal modes.
10. The IR spectrum of a symmetric XY_2 molecule gives 3 prominent lines. Check whether the molecule is bent or linear.
11. In the vibration rotation spectrum of HBr, the rotational lines at the high frequency end of the R-branch are closely spaced and those at the low frequency end of the P branch are widely spaced. Why?
12. The Q branch of the vibrational spectrum of CH_3Cl consists of a series of lines on both sides of the band center whereas that of a linear molecule is a single intense line. Explain.
13. Compare critically the mull and pellet techniques used for the recording of IR spectra.
14. Outline briefly the advantages of FTIR spectroscopy over the conventional procedure.
15. What is the ν_2 mode of ammonia molecule? Write a note on the inversion vibration of ammonia.

PROBLEMS

1. Calculate the amplitude of vibration in the $v = 0$ level of the molecule CO which has a force constant of 1870 N/m.
2. The HCl molecule gives the vibrational absorption line of wavelength 3.465×10^{-6} m. Calculate the force constant of the H–Cl bond.
   Given that $^1H = 1.0087\,u$, $^{35}Cl = 35.453\,u$ and $u = 1.67 \times 10^{-27}$ kg
3. What is the vibrational frequency corresponding to a thermal energy of kT at 298K? What is the wavelength of this radiation?
4. The fundamental vibration frequency of HCl is 2,989 cm^{-1}. Find the force constant of the HCl bond.
5. The fundamental vibration of $H^{35}Cl$ is $8{,}667 \times 10^{10}\ s^{-1}$. What would be the separation between the infrared absorption lines for $H^{35}Cl$ and $H^{37}Cl$. Given $m(^{37}Cl)/m(^{35}Cl) = 1.056$.