PartII分子光谱习题

1. Sketch on the same graph the potential energy functions for the harmonic oscillator with three different values of k. How do you interpret the meaning of k?

2. Describe qualitatively how the average bond length changes with increasing vibrational energy for a vibrating diatomic using (a) the harmonic oscillator model and (b) the Morse model.

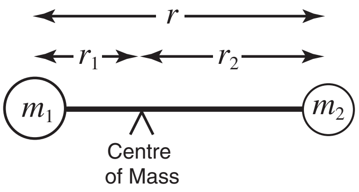
3. The far infrared spectrum of $^{39}K^{35}Cl$ has an intense line at 278.0 cm^{-1}. Calculate the force constant for KCl.

4. The force constant of $^{79}Br_2$ is 240 N m^{-1}. Calculate the fundamental vibrational frequency and the zero-point energy of $^{79}Br_2$.

5. From the data in the spectrum of carbon monoxide shown on page 12, determine ω and x_e and hence k_M, D_e, D_0 and β, and explain what each of these terms means.

6. Using your answers to question 5, calculate the relative populations of the vibrational levels $v = 0$ and $v = 1$ for carbon monoxide at room temperature and 600 K. How would the rotation-vibration of carbon monoxide change at higher temperatures?

7. The moment of inertia, I, of a molecule is defined as $\sum_i m_i r_i^2$ where m_i is the mass of atom i and r_i is the distance of atom i from the centre of mass of the molecule.



For the diatomic molecule shown left, show that $r_2 = (m_1 r)/(m_1 + m_2)$. Find (or write!) a similar expression for r_1 and hence show that

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

where μ is the reduced mass of the molecule.

8. Which of the following molecules will show a rotational spectrum?

CH_4, CH_2Cl_2, H_2O, HCl, C_2H_2, O_3, CO_2, SO_2, N_2O, *cis* and *trans* ClHC=CHCl?

9. Without calculating the specific values, arrange the following molecules in order of increasing value of their rotational constants, B:

HF, DF, H–C≡C–C≡C–C≡N, HD, $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, ClCN.

10. Calculate the value of the rotational constants for $^{12}C^{16}O$ and $^{13}C^{16}O$ assuming a bond length of 1.128 Å. Express your answers in J, Hz and cm^{-1}.

11. The rotational constant for $H^{35}Cl$ is observed to be 10.5909 cm^{-1}. What are the values of B for $H^{37}Cl$, and for $D^{35}Cl$?

12. Calculate the value of the rotational constant for $^{35}ClCN$. (r_{ClC} = 1.629 Å; r_{CN} = 1.160 Å)

13. Show that the J value for the energy level with the maximum population, J_{max}, is given by:

$$J_{max} \approx \sqrt{\frac{kT}{2hc\tilde{B}}} - \frac{1}{2}$$

14. A 476.5 nm argon ion laser was used to record the rotational Raman spectrum of $^{14}N_2$. The spectrum shows a series of regularly spaced lines, the first of which are 11.937 cm^{-1} either side of the peak due to the Rayleigh scattering of the laser. What is the separation of the remaining lines from these first ones? At what frequencies do the S_{10} peaks occur in the Stokes and anti-Stokes branches? Calculate the bond length N_2.

15. The rotational spectrum of $^{79}Br^{19}F$ shows a series of equidistant lines 0.71433 cm^{-1} apart. Calculate the rotational constant, B, and hence the moment of inertia and the bond length of the molecule. Determine the wavenumber of the $J = 9 \rightarrow J = 10$ transition and find the transition which gives rise to the most intense spectral line at room temperature (say 300 K). State any assumptions you make. Calculate the number of revolutions per second which the BrF molecule undergoes when in (a) the $J = 0$ state, (b) the $J = 1$ state, and (c) the $J = 10$ state.

16. The following data are obtained from the vibration-rotation spectrum of $H^{79}Br$. Determine B_0, B_1, and B_e from these data and their corresponding bond lengths.

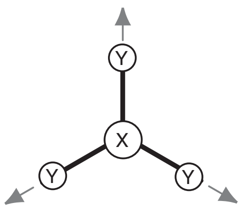
Line	Frequency /cm^{-1}
R_0	2642.60
R_1	2658.36
P_1	2609.67
P_2	2592.51

17. Sketch the normal modes for (a) H_2S and (b) HCN. Classify each mode as parallel or perpendicular.

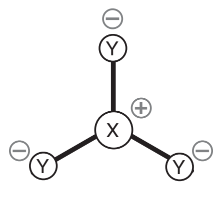
18. Classify each of the vibrational normal mode in acetylene shown on page 29 as parallel or perpendicular. Which are Raman active and which are IR active?

19. Both N_2O and NO_2 exhibit three different fundamental vibrational frequencies; each molecule has some vibrational modes at the same frequencies in both the infrared and Raman spectra. The bands in NO_2 show complex rotational structure while bands in N_2O show only simple PR structures (no Q branches). What can be deduced about the structure of each molecule?

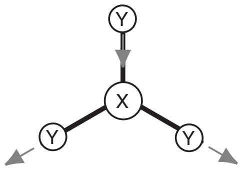
20. The non-degenerate normal modes for a trigonal planar XY_3 structure are shown below. Which modes will be IR active and which will be Raman active?



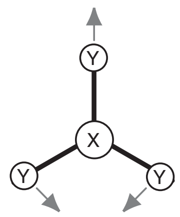
ν_1



ν_2

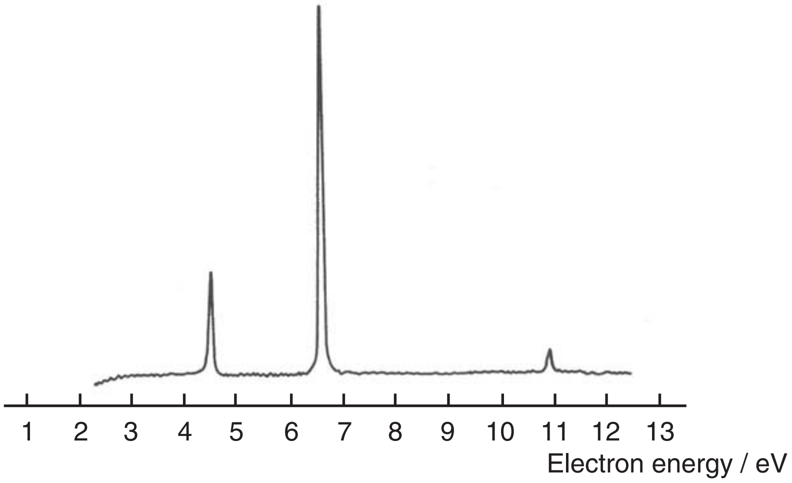


ν_3



ν_4

21. Shown below is the PES spectrum of mercury vapour. The x-axis gives the kinetic energy of the ejected electrons, as determined by the instrument, rather than the more usual ionization energies. The incident photons used to ionize the sample are from a helium resonance lamp and are of wavelength 584 Å.



a) What is is the energy of the incident radiation in eV?

b) What are the approximate ionization energies leading to each of the peaks in the spectrum?

c) The peaks in the spectrum correspond to removing electrons from the valence shell of the mercury atom, i.e. from the 5d shell or the 6s shell. Give the term symbols for the possible ions formed by by the ejection of a single electron from either the 5d or 6s shell in Hg.

d) By considering the degeneracies of each of these levels, what should the expected ratios of the peak intensities in the spectrum be? Assign the appropriate term symbol to each of the peaks in the spectrum.

It is also highly recommended that you try (at some point) Question A4 from Tripos papers 2002-2007.