Quantum Physics（量子物理）習題
Robert Eisberg（Second edition）
CH 12：Molecules

12-01、From the following data, find the energy required to dissociate a KCl molecule into a K atom and a Cl atom. The first ionization potential K is 13.4eV; the electron affinity of Cl is $3.82eV$; the equilibrium separation of KCl is 2.79Å. (Hint: Show that the mutual potential energy of K^+ and Cl^- is $-\frac{14.40}{R}eV$ if R is given in Angstroms.)

ANS：$4.64eV$

12-02、The first ionization potential for K is $4.3eV$; the ion Br^- is lower in energy by $3.5eV$ than the neutral bromine atom. Compute the largest separation of K^+ and Br^- ions that gives a bound KBr molecule.

ANS：$18\overset{0}{A}$

12-03、For a system which executes simple harmonic motion about a position of stable equilibrium, the force, F, is given by $F=-(\frac{\partial^2 V}{\partial R^2})_{R_0}(R-R_0)$. Where V is the potential energy and $R-R_0$ is the deviation from equilibrium. Show that the zero-point vibration of a molecule is given by $\frac{1}{2}h\nu_0=\frac{h}{4\pi\mu^{1/2}}[(\frac{\partial^2 V}{\partial R^2})_{R_0}]^{1/2}$.

ANS：

12-04、The potential energy V of $NaCl$ can be described empirically by $V=-\frac{e^2}{4\pi\varepsilon_0 R}+Ae^{-\frac{R}{\rho}}$ where R is the internuclear separation. The equilibrium separation of the nuclei R_0 is 2.4Å and the dissociation energy is $3.6eV$. (a) Calculate A and $\frac{\rho}{R_0}$, neglecting zero-point vibrations. (b) Sketch V and each of the terms in V on one graph. (c) Give the physical significance of A and ρ.

ANS：

12-05、(a) Show that the ratio of the number of molecules in rotational level r to the number in the $r=0$ level, in a sample at thermal equilibrium, is a maximum for the level specified by $r=(\frac{kTI}{\hbar^2})^{\frac{1}{2}}-\frac{1}{2}$. (b) For HCl, what is the most populated level at $600^0 K$?

ANS：(b) $r=4$

12-06、Taking the rotational inertia of H_2 from Table 1-1, find the temperature at which the average translational kinetic energy of an H_2 molecule equals the energy between the ground rotational state and first excited rotational state. What can you conclude about the occupation of rotational excited states in H_2 at room temperature?

ANS：$120^0 K$

12-07、Determine δ, the zero-point vibrational energy, for a $NaCl$ molecule, given that is fundamental vibrational frequency is $1.14\times10^{13} vib/\sec$.

ANS：

12-08、(a) Show that, if E_d is the dissociation energy of a molecule, the fraction of the molecules that dissociate at a temperature T is $e^{-\frac{E_d}{kT}}$. (b) It is found (from electron diffraction studies) that as T increase, the internuclear separation increases. Example what effect this has on the potential energy curve and on the result of part (a).

ANS：

12-09、For $NaCl$, the separation of two vibrational levels is about $4\times10^{-2} eV$. Using Table 12-1, and noting that the rotational levels are not equally spaced, show that there are about 40 rotational levels between a pair of vibrational levels.

ANS：

12-10、The potential energies of two diatomic molecules of the same reduced mass are shown in Figure 12-14. From the graph determine which molecule has the large (a) internuclear distance, (b) rotational inertia (moment of inertia), (c) separation between rotational energy levels of the same r and v, (d) binding energy, (e) zero-point energy (Hint: See Problem 3). (f) separation between low-lying vibrational states.

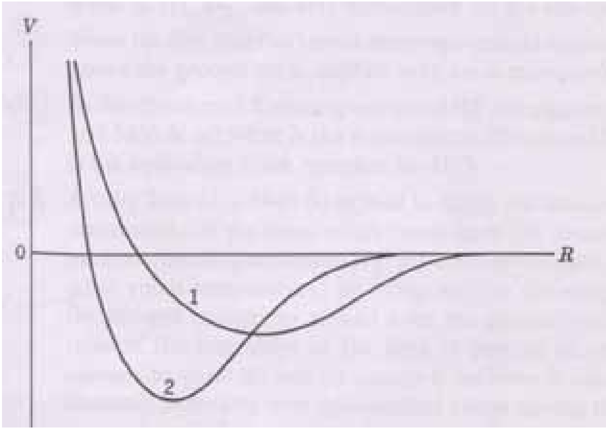

Figure 12-14 Potential energy curves considered in Problem 10.

ANS：(a) 1 (b) 1 (c) 2 (d) 2 (e) 2 (f) 2

12-11、(a) What fraction of HCl molecules at $1000^0 K$ will be found in the first excited vibrational state? (Hint: Use the Boltzmann factor.) (b) Find the ratio of HCl molecules in the first excited rotational state to those in the first excited vibrational state at $1000^0 K$. (Hint: Remember the degeneracy factors.)

ANS：(a) $\frac{1}{72}$ (b) $\frac{210}{1}$

12-12、(a) Derive an expression giving the ration of the energy of a transition from the lowest to the first excited vibrational levels to the energy of a transition from the lowest to the first excited rotational level for a diatomic molecule. (b) What is this ratio for $NaCl$? For H_2? (Hint: See Example 12-3.)

ANS：

12-13、(a) Show that the relative frequency shift of a spectral line in a rotational band arising from a mixture of two isotopic diatomic molecules is given by $\frac{\Delta \nu}{\nu} = -\frac{\Delta \mu}{\mu}$, where μ is the reduced mass of the molecule. (b) What is this ratio for a mixture of HCl^{35} and HCl^{37}?

ANS：

12-14、Show that the ratio R of the total number of molecules in all excited vibrational states to the number in the ground vibratinal state is $R = (e^{\frac{h\nu_0}{kT}} - 1)^{-1}$ provided that the levels are assumed to be equally spaced.

ANS：

12-15、What is the amplitude of vibration of HCl in the first excited vibrational state?

ANS： $0.190\overset{0}{A}$

12-16、(a) Use data from Example 12-3 to predict the reciprocal wavelength of the zero-point vibration of HCl given in Table 12-1. (b) What must be the force constant to given exact agreement?

ANS：

12-17、From the value $2940.8cm^{-1}$ for the reciprocal wavelength equivalent to the fundamental vibration of a molecule Cl_2, each of whose atoms has an atomic weight 35, determine the corresponding reciprocal wavelength for Cl_2 in which one atom has atomic weight 35 and the other 37. What is the separation of spectral lines, in reciprocal wavelengths, due to this isotope effect?

ANS： $2900cm^{-1}$， $40cm^{-1}$

12-18、(a) Specify the resolution, $\frac{\Delta\lambda}{\lambda}$, of a spectrometer which can just resolve the rotational spectra of $Na^{23}Cl^{35}$ and $Na^{23}Cl^{37}$ assuming R_0 to be the same for both molecules. (b) Would this spectrometer also resolve the vibrational spectra of the two molecules, assuming the force constants are the same?

ANS：

12-19、Calculate the difference in dissociation energies of H_2 and D_2 from the value $4395.2cm^{-1}$ for the reciprocal wavelength equivalent to the fundamental vibration of an H_2 molecule.

ANS：

12-20、The zero-point vibrational energy for H_2 is 0.265eV. Compare the vibrational energy levels of H_2, D_2, and HD numerically for the low-lying states.

ANS： $D_2 : 0.375eV$， $HD : 0.460eV$

12-21、From the fact the lowest electronic excited state in O_2 and N_2 molecules is over 3eV above the ground state, explain why air is transparent in the visible.

ANS：

12-22、In the vibrational Raman spectrum of HF are adjacent Raman lines of wavelength 2670Å and 3430Å. (a) What is the fundamental vibrational frequency of the molecule? (b) What is the equivalent force constant for HF ?

ANS：(a) $2.49\times10^{14}Hz$ (b) $3650nt/m$

12-23、A ruby laser ($\lambda = 6943\overset{0}{A}$) is used to excite the Raman spectrum of N_2. (a) What are the wavelengths of the lines which result from the lowest energy allowed transitions in the pure rotational spectrum of N_2? (b) What is the ratio of the intensities of the lines of part (a) at room temperature? (c) What are the wavelength of the lines which result from the allowed transitions to and from the ground state vibrational level? (d) What is the ratio of the intensities of lines of part (c) at room temperature? (e) How do the answers to parts (a) and (c) change if the laser is used to excite the Raman spectrum of diatomic molecules with nonidentical nuclei having the same rotational inertia and force constant as N_2?

ANS：

12-24、The energy-level diagram for the rotational levels in each of the two lowest vibrational states of the electronic ground state is given in Figure 12-15 for a diatomic molecule. Find the energies of the transitions that give rise to the allowed spectral lines in the infrared and Raman spectra, (a) for molecules containing two identical $i=0$ nuclei, (b) for molecules containing two identical $i=\frac{1}{2}$ nuclei, and (c) for molecules containing two nonidentical nuclei.

ANS：

12-25、Calculate the relative intensities at room temperature for the lines found in parts (a) and (b) of Problem 24.

ANS：(a) 2.91 (b) 2.88

12-26、Using the information in Figure 12-15, (a) calculate the rotational inertia, or moment of inertia, of the molecule in each vibrational level, and (b) calculate the zero-point energy.

ANS：

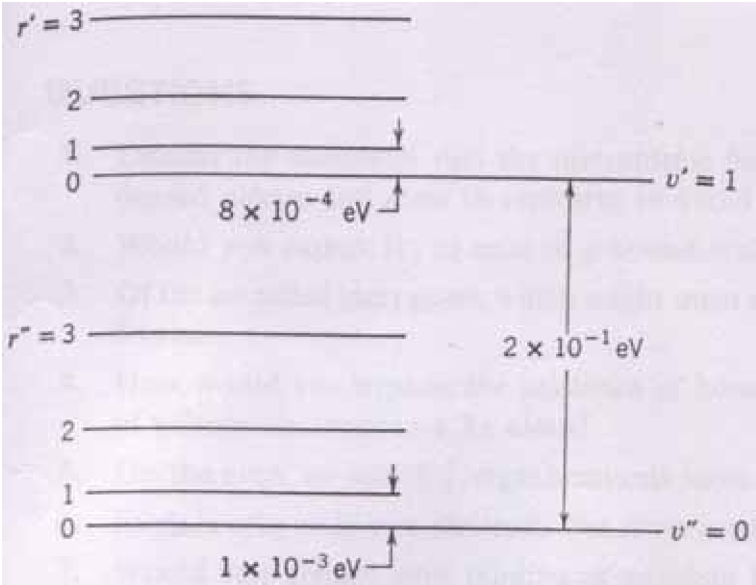

Figure 12-15 Energy levels considered in Problem 24, 25, and 26.

ANS：(a) $8.7\times10^{-47}\,kg-m^2$， $6.9\times10^{-47}\,kg-m^2$ (b) $0.1eV$

12-27、(a) How many rotational degrees of freedom do you expect in a polyatomic molecule? Translational degrees? If the molecule has N atoms ($N>2$) there should be $3N-6$ vibrational degrees of freedom, i.e., independent models of vibration. Explain. (b) How many vibrational degrees of freedom are there in an H_2O molecule? A CH_4 molecule?

ANS：

12-28、Consider the relative intensities of the spectra of H_2 and D_2 to determine which Raman rotation spectrum will yield lines alternating in intensity and having a relative intensity of $\frac{1}{2}$.

ANS：

12-29、Band spectrum measurements of diatomic molecules containing ^{35}Cl nuclei yield an alternating intensity ratio of 3/5. What is the spin of the ^{35}Cl nucleus?

ANS：$\frac{3}{2}$
