

QMS Problem set 3 (due 4.2.2021)

Warm-up: (Each warm-up is connected to one of the problems (first warm-up to first problem etc.))

W1: Answer problem E7E.1(b) (2 points)

E7E.1(b) Calculate the zero-point energy of a harmonic oscillator consisting of a particle of mass 5.16×10^{-26} kg and force constant 285 N m^{-1} .

W2: Answer problem E11C.8(a) (2 points)

E11C.8(a) Infrared absorption by $^1\text{H}^{127}\text{I}$ gives rise to an R branch from $v = 0$. What is the wavenumber of the line originating from the rotational state with $J = 2$?

Hint: Use data from Table 11C.1.

W3: Answer problem P11C.5 (4 points)

P11C.5 The $^1\text{H}^{35}\text{Cl}$ molecule is quite well described by the Morse potential energy with $hc\bar{D}_e = 5.33 \text{ eV}$, $\bar{\nu} = 2989.7 \text{ cm}^{-1}$, and $x_e \bar{\nu} = 52.05 \text{ cm}^{-1}$.

Assuming that the potential is unchanged on deuteration, predict the dissociation energies ($hc\bar{D}_e$, in electronvolts) of (a) $^1\text{H}^{35}\text{Cl}$, (b) $^2\text{H}^{35}\text{Cl}$.

Problems:

P1: Answer P7E.9 (5 points)

P7E.9 A function of the form $e^{-g x^2}$ is a solution of the Schrödinger equation for the harmonic oscillator (eqn 7E.2), provided that g is chosen correctly. In this problem you will find the correct form of g . (a) Start by substituting $\psi = e^{-g x^2}$ into the left-hand side of eqn 7E.2 and evaluating the second derivative. (b) You will find that in general the resulting expression is not of the form constant $\times \psi$, implying that ψ is not a solution to the equation. However, by choosing the value of g such that the terms in x^2 cancel one another, a solution is obtained. Find the required form of g and hence the corresponding energy. (c) Confirm that the function so obtained is indeed the ground state of the harmonic oscillator, as quoted in eqn 7E.7, and that it has the energy expected from eqn 7E.3.

P2: Answer P11C.17 (6 points)

P11C.17 At low resolution, the strongest absorption band in the infrared absorption spectrum of $^{12}\text{C}^{16}\text{O}$ is centred at 2150 cm^{-1} . Upon closer examination at higher resolution, this band is observed to be split into two sets of closely spaced peaks, one on each side of the centre of the spectrum at 2143.26 cm^{-1} . The separation between the peaks immediately to the right and left of the centre is 7.655 cm^{-1} . Make the harmonic oscillator and rigid rotor approximations and calculate from these data: (a) the vibrational wavenumber of a CO molecule, (b) its molar zero-point vibrational energy, (c) the force constant of the CO bond, (d) the rotational constant \bar{B} , and (e) the bond length of CO.

P3: Answer P11C.6 (5 points)

P11C.6 The Morse potential energy (eqn. 11C_7) is very useful as a simple representation of the actual molecular potential energy. When $^{85}\text{Rb}^1\text{H}$ was studied, it was found that $\bar{\nu} = 936.8\text{ cm}^{-1}$ and $x_e \bar{\nu} = 14.15\text{ cm}^{-1}$. Plot the potential energy curve from 50 pm to 800 pm around $R_e = 236.7\text{ pm}$. Then go on to explore how the rotation of a molecule may weaken its bond by allowing for the kinetic energy of rotation of a molecule and plotting $V^* = V + hc \bar{B} J(J+1)$ with \bar{B} . Plot these curves on the same diagram for $J = 40, 80,$ and 100 , and observe how the dissociation energy is affected by the rotation. *Hints:* Taking $\bar{B} = 3.020\text{ cm}^{-1}$ as the equilibrium bond length will greatly simplify the calculation. The mass of ^{85}Rb is $84.9118 m_u$.