CHEM 243 – Physical Chemistry

Class Test **6 pm, Tuesday 16 September 2008**

Time Allowed: ONE hour

Instructions: Answer **ALL questions**
Total marks: 60

Useful Information:

$c = 2.998 \times 10^{10}$ cm s^{-1} $R = 8.314$ J mol^{-1} K^{-1}

$m_e = 9.109 \times 10^{-31}$ kg $e = 1.602 \times 10^{-19}$ C

$N_A = 6.022 \times 10^{-23}$ mol^{-1} amu $= 1.661 \times 10^{-27}$ kg

$h = 6.626 \times 10^{-34}$ J s $\hbar = 1.055 \times 10^{-34}$ J s

$\varepsilon_o = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-1} 0 K = –273.15 °C

M_r(H) = 1.0079 M_r(Cl) = 35.453

M_r(^{1}H) = 1.0078 M_r(^{35}Cl) = 34.969

M_r(^{2}H) = 2.0140 M_r(^{37}Cl) = 36.966

$E = h\nu$ $c = \nu\lambda$

(1) $E = \dfrac{n^2h^2}{8mL^2}$ (2) $E = \dfrac{(m_l)^2 h^2}{8\pi^2 mr^2}$

$E = h\dfrac{\hbar}{4\pi I}J(J+1)$ $I = \mu R^2$

$E = h(\nu + \frac{1}{2})\dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}}$ $\dfrac{1}{\mu} = \dfrac{1}{m_A} + \dfrac{1}{m_B}$

$E = \dfrac{-m_e e^4 Z^2}{n^2 32(\pi\varepsilon_o)^2\hbar^2}$ $\lambda = h/p$

$A = -\log_{10}\left(\dfrac{I}{I_0}\right)$ $A = \varepsilon c l$

(a) (6 marks)

For **both** equations (1) and (2) in the Information above:

(i) Describe the quantum mechanical system for which the equation holds.

(ii) Indicate the quantum number and the values that it may take.

(b) (9 marks)

Briefly describe the general components of a spectrometer and how they are assembled together so that spectroscopy may be carried out.

(c) (36 marks)

(Note: Data required for answering this question are given in Useful Information.)

For the $^{1}H^{35}Cl$ molecule, the bond length is $R = 127.4$ pm and the force constant is $k = 516$ N m^{-1}.

(i) Show that the reduced mass of this molecule is $\mu = 1.627 \times 10^{-27}$ kg.

(ii) Show that the rotational constant of this molecule is $B = 10.60$ cm^{-1}.

(iii) State the gross selection rule for rotational spectroscopy and explain that this molecule satisfies it.

(iv) Describe the microwave absorption spectrum of this molecule, explaining your answer.

(v) Show that the vibrational frequency of this molecule is $\tilde{\nu} = 2\,990$ cm^{-1}.

(vi) State the gross selection rule for vibrational spectroscopy and explain that this molecule satisfies it.

(vii) Describe the infrared absorption spectrum of this molecule, explaining your answer.

(viii) Calculate the line spacing (in cm^{-1}) of the microwave absorption spectrum of $^{1}H^{37}Cl$.

(ix) Calculate the position (in cm^{-1}) of the signal in the infrared absorption spectrum of $^{2}H^{35}Cl$.

(d) (9 marks)

Outline three experimental phenomena that classical physics could not explain, thereby leading to the development of quantum mechanics.

In each case **outline** how quantum mechanics solved the problem.