

Question	Score	out of
1		6
2		4
3		5
Total		15

Name: _____

Student Number: _____

Chem 3PA3 - Fall 2013

2nd Midterm

Time: 50 min

Calculators are allowed!

No notes, books or personal paper are allowed!

Attempt all questions.

In answering the questions, show all steps of your reasoning and calculation!*This exam is worth a total of 16%, i. e. you should be scoring on average 0.3% per minute!***Potentially Useful Numbers and Formulas:** (Note the difference between h and \hbar !)

$h = 6.6261 \times 10^{-34} \text{ Js}$; $m_e = 9.1094 \times 10^{-31} \text{ kg}$; $e = 1.6022 \times 10^{-19} \text{ C}$; $c = 2.9979 \times 10^8 \text{ m/s}$;
 $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$; $k_B = 1.38066 \times 10^{-23} \text{ J/K}$; $a_0 = 5.291772 \times 10^{-9} \text{ cm}$; $l_{C=C, \text{ Benzene}} = 0.14 \text{ nm}$;
 $1 \text{ nm} = 10^{-9} \text{ m}$; $1 \text{ J} = 6.242 \times 10^{18} \text{ eV} = 5.034 \times 10^{22} \text{ cm}^{-1}$

Rigid Rotor: $B = \frac{h}{8\pi^2 c \mu r^2}$ Harmonic Oscillator: $\psi_0(x) = \sqrt{\frac{\beta^2}{\pi}} e^{-\frac{(\beta x)^2}{2}}$; $\beta^2 = \frac{\sqrt{(k m)}}{\hbar}$

$$\psi_1(x) = \sqrt{\frac{\beta^2}{2\pi}} (2\beta x) e^{-\frac{(\beta x)^2}{2}}; \beta^2 = \frac{\sqrt{(k m)}}{\hbar} \quad \psi_2(x) = \sqrt{\frac{\beta^2}{8\pi}} (4(\beta x)^2 - 2) e^{-\frac{(\beta x)^2}{2}}; \beta^2 = \frac{\sqrt{(k m)}}{\hbar}$$

$$h_{v+1} - 2zh_v + 2vh_{v-1} = 0$$

$$\int_{-\infty}^{+\infty} h_{v'} h_v e^{-z^2} dz = \begin{cases} 0 & \text{if } v' \neq v \\ \sqrt{\pi} 2^v v! & \text{if } v' = v \end{cases}$$

Potentially Useful Integrals:

$$\int_0^{\infty} e^{-cx^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{c}} \quad ; \quad \int_0^{\infty} x^2 e^{-cx^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{c^3}} \quad ; \quad \int_0^{\infty} x e^{-cx^2} dx = \frac{1}{2c} \quad ; \quad \int_0^{\infty} x^{2n+1} e^{-cx^2} dx = \frac{n!}{2c^{n+1}}$$

$$\int_0^{\infty} x^{2n} e^{-cx^2} dx = \frac{(2n-1)(2n-3)\dots(3)(1)}{2^{n+1}} \sqrt{\frac{\pi}{c^{2n+1}}} \quad ; \quad \int_{-\infty}^0 x^n e^{-cx^2} dx = (-1)^n \int_0^{\infty} x^n e^{-cx^2} dx$$

$$\int \sin^2(cx) dx = \frac{x}{2} - \frac{\sin(2cx)}{4c} \quad ; \quad \int x \sin^2(cx) dx = \frac{x^2}{4} - \frac{x \sin(2cx)}{4c} - \frac{\cos(2cx)}{8c^2}$$

$$\int x^2 \sin^2(cx) dx = \frac{x^3}{6} - \left(\frac{x^2}{4c} - \frac{1}{8c^3} \right) \sin(2cx) - \frac{x \cos(2cx)}{4c^2}$$

1) (6) Harmonic oscillator.

- (a) (1) Qualitatively, sketch the potential energy curves and energy levels for both the harmonic oscillator and a particle in a box, pointing out important features (commonalities & differences)!
- (b) (2) Write out the Hamiltonian operator and its eigenvalues for the three-dimensional harmonic oscillator using k_x , k_y , and k_z to denote the 3 force constants!
- (b) (3) For a 3D harmonic oscillator with $k_x = k_y = k_z$, find the degree of degeneracy for each of the four lowest energy levels.

2) (4) Perturbation theory.

The potential energy curve of the umbrella motion of the ammonia molecule could be approximated by adding a barrier of the shape $a \cdot e^{-bx^2}$ to the center of a regular harmonic oscillator potential, thus turning it into a double well potential. Using perturbation theory, find the first order correction to the ground state energy, if the ideal system is the harmonic oscillator and first order perturbing Hamiltonian consists of the barrier described above!

3) (5) Vibrational-rotational spectroscopy.

Assume $r_{eq} = 113.1 \text{ pm}$, $k = 1902 \text{ N/m}$ for all isotopes of CO.

(a) (2) What is ΔH^0 (in Joules) of the reaction $^{13}\text{C}^{17}\text{O} + ^{12}\text{C}^{16}\text{O} \rightarrow ^{12}\text{C}^{17}\text{O} + ^{13}\text{C}^{16}\text{O}$? Assume that all molecules are harmonic oscillators in their vibrational ground states. You only need to consider the differences in vibrational energy between the different isotopes.

(b) (3) The selection rules in Raman vibrational-rotational spectroscopy are $\Delta n = +/-1$, $\Delta J = 0, +/-2$. Assuming that the harmonic oscillator and rigid rotor models hold, derive a formula for the locations of the vibrational-rotational transitions in the O branch ($\Delta J = -2$) in terms of B_e . For $^{13}\text{C}^{17}\text{O}$, predict the positions (in cm^{-1}) of the first line each of the O and the S branch ($\Delta J = -2$ and $\Delta J = +2$ respectively).