Name_____ Student #_____

Quiz 12
CHEM 3PA3; Fall 2018

This quiz has 5 problems worth 20 points each. There are 10 bonus points….

1. The infrared spectrum of $^{1}H^{35}Cl$ consists of an intense line at 2886 cm^{-1}. **What is the location of an analogous intense line in the spectrum of $^{2}D^{37}Cl$?** Please put your answer in the blank below for easy grading.

_____ cm^{-1}

2. The equation for transition rates from an initial to a final state according to Fermi's Golden Rule is listed below.

$$W_{fi} = \frac{2\pi V^2 \left[g\left(\hbar\omega_{fi}\right) + g\left(\hbar\omega_{if}\right) \right]}{\hbar} \left| \left\langle \Phi_f \left| \mu_x \right| \Phi_i \right\rangle \right|^2$$

Explain the meaning/importance of each term in this expression.

3. What are the three main approximations that are used to derive Fermi's Golden Rule?

Bonus (10 pts) One of the observed absorption lines in the spectrum of the Scandium atom ($[\mathrm{Ar}]4s^2 3d^1$) corresponds to excitation of an electron from the *3d* orbital to the *5s* orbital. **Which of the following approximations is inadequate to explain this process?**
(a) long-wavelength approximation. (b) weak-field approximation. (c) long-time approximation.

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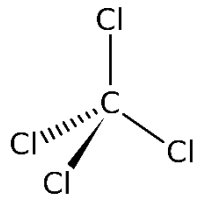
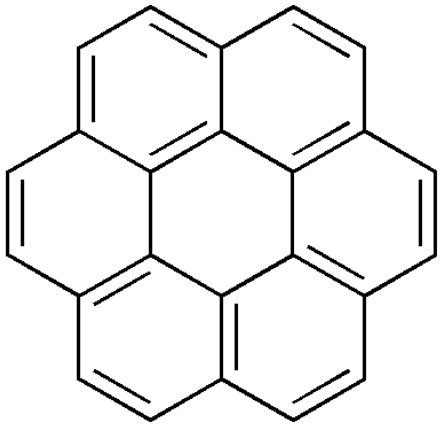
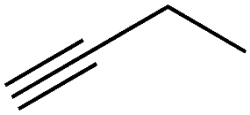
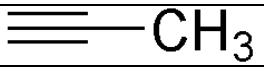
4. Fill in the first column of the following table, labelling the following molecules as:

O oblate symmetric top
P prolate symmetric top
S spherical top
A asymmetric top

Type of "top"	Name of Molecule	Structure of Molecule
	Carbon tetrachloride	
	Coronene	
	1-butyne	
	propyne	

5. Match the following systems to the energy level diagrams on the next two pages. Each line indicates an energy level, and the number in parenthesis next to the line indicates the degeneracy of that level. That is, the positions of the lines give the relative energies of the ground state (the first line) and a few excited states, and the number in parenthesis indicates the number of states with that energy.

_____ **One-Electron Atom**

_____ **One-Dimensional Harmonic Oscillator**

_____ **One-Dimensional Particle in a Box with Infinite Sides**

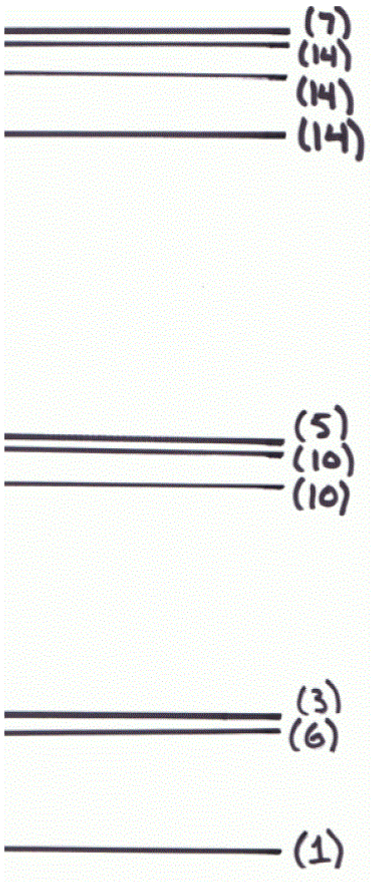
_____ **Rigid Rotation of a Spherical Top Molecule**

_____ **Rigid Rotation of a Oblate Symmetric Top Molecule**

_____ **Rigid Rotation of a Prolate Symmetric Top Molecule**

Name_____ Student #_____

A



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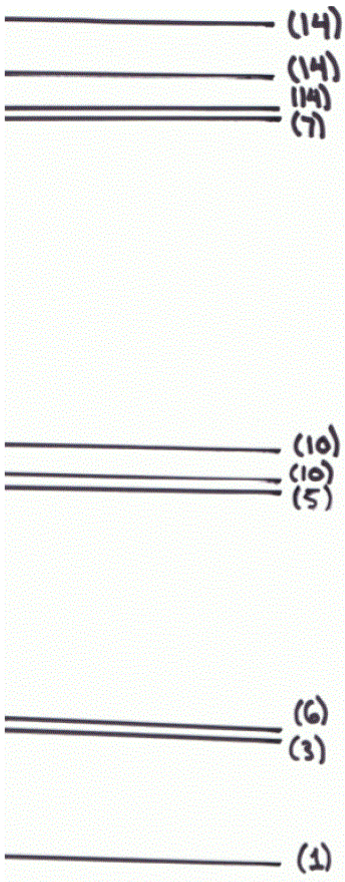

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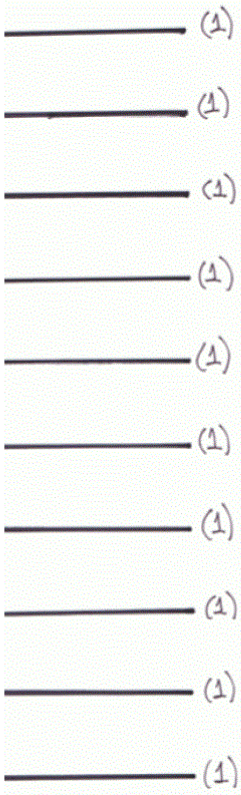

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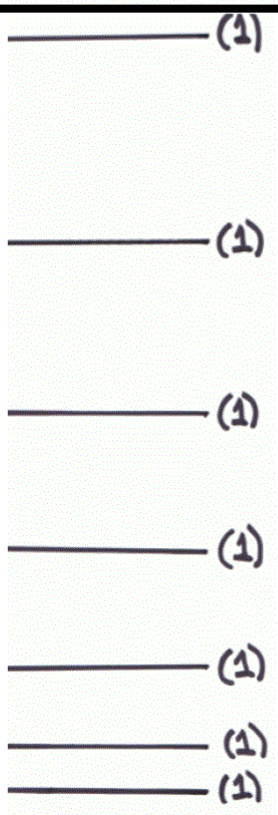

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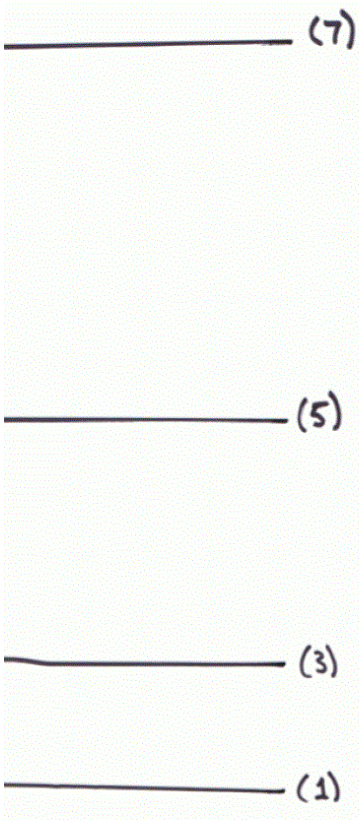

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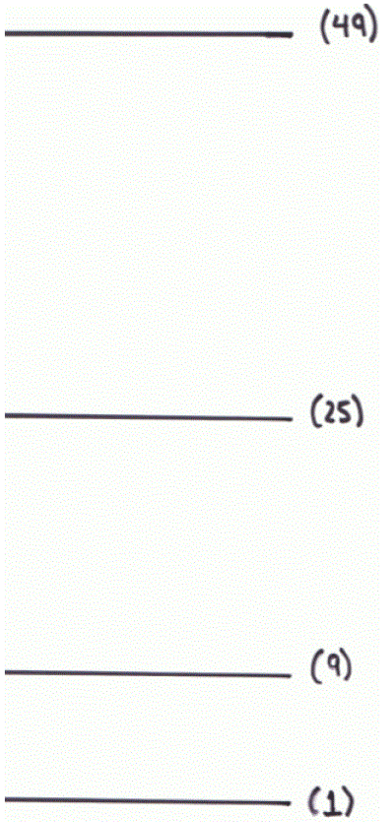

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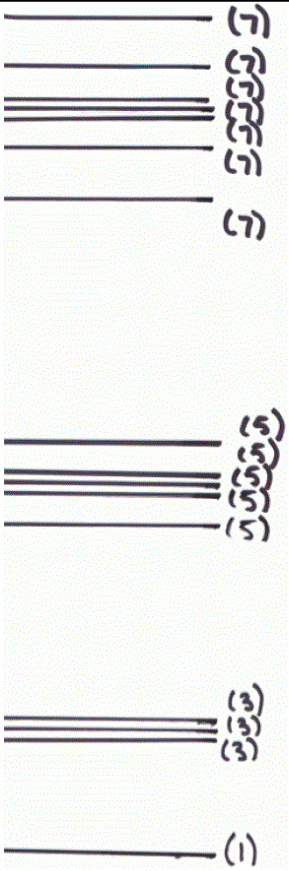

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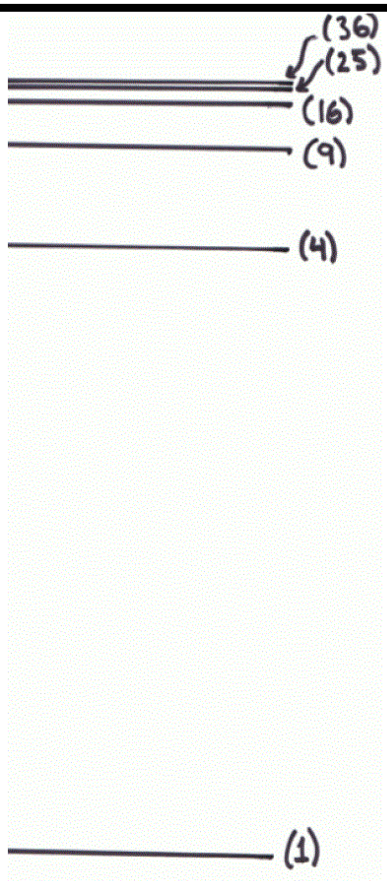

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Quiz 12
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__2066_____ cm^{-1}

There are several different ways to compute this. The easiest, I think, is to realize that the transition frequency is

$$h\nu = \frac{hc}{\lambda} = hc\bar{\nu} = \hbar\omega = \hbar\sqrt{\frac{k}{\mu}}$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

and that the force constant is the same for both $^{1}H^{35}Cl$ and $^{2}D^{37}Cl$. So

$$\frac{\bar{\nu}_{^{1}H^{35}Cl}}{\bar{\nu}_{^{2}D^{37}Cl}} = \sqrt{\frac{\mu_{^{2}D^{37}Cl}}{\mu_{^{1}H^{35}Cl}}}$$

$$\bar{\nu}_{^{2}D^{37}Cl} = \bar{\nu}_{^{1}H^{35}Cl}\cdot\sqrt{\frac{\mu_{^{1}H^{35}Cl}}{\mu_{^{2}D^{37}Cl}}} = \left(2886\ cm^{-1}\right)\sqrt{\frac{\frac{1\cdot 35}{1+35}}{\frac{2\cdot 37}{2+37}}} = \left(2886\ cm^{-1}\right)\sqrt{\frac{35\cdot 39}{36\cdot 74}} = 2066\ cm^{-1}$$

2. The equation for transition rates from an initial to a final state according to Fermi's Golden Rule is listed below.

$$W_{fi} = \frac{2\pi V^2\left[g\left(\hbar\omega_{fi}\right)+g\left(\hbar\omega_{if}\right)\right]}{\hbar}\left|\left\langle\Phi_f\left|\mu_x\right|\Phi_i\right\rangle\right|^2$$

Explain the meaning/importance of each term in this expression.

The V is the amplitude of the electric field, or the intensity of the radiation. The stronger the field the higher the rate of transitions. The fact $g\left(\hbar\omega_{fi}\right)$ and $g\left(\hbar\omega_{if}\right)$ enter the expression symmetrically means that absorption of radiation by a lower-energy state to form a higher-energy state and stimulated emission of radiation from a higher-energy state to a lower-energy state occur at the same rate. The term $g\left(\hbar\omega_{fi}\right)$ is the density-of-states of photons with energy $\hbar\omega_{fi}$. If the photons do not have the correct energy to perform the transition, then no transition occurs (in the weak-field approximation).

Finally, $\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2$ provides dipole (E1) selection rules: if the final state isn't such that a oscillating dipole field can induces transitions from the initial state, then no transition occurs.

3. What are the three main approximations that are used to derive Fermi's Golden Rule?

long wavelength approximation; weak field approximation; long time approximation.

Bonus (10 pts) One of the observed absorption lines in the spectrum of the Scandium atom ($[Ar]4s^2 3d^1$) corresponds to excitation of an electron from the *3d* orbital to the *5s* orbital. **Which of the following approximations is inadequate to explain this process?**

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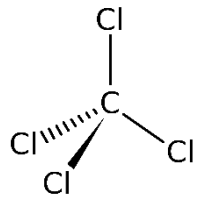
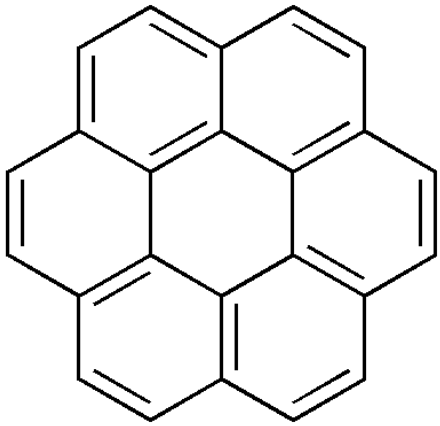
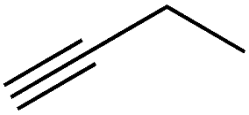
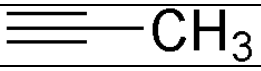
S	**Carbon tetrachloride**	
O	**Coronene**	
A	**1-butyne**	
P	**propyne**	

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_D____One-Dimensional Particle in a Box with Infinite Sides

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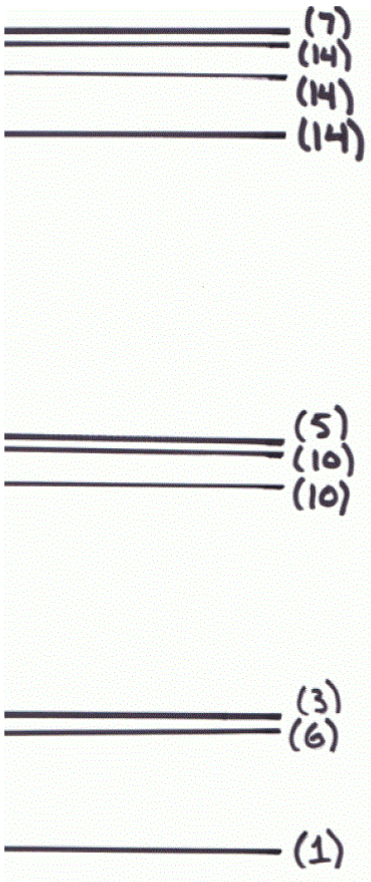

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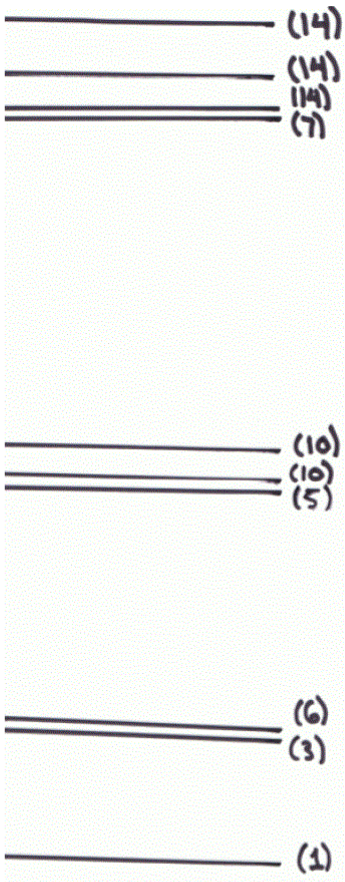

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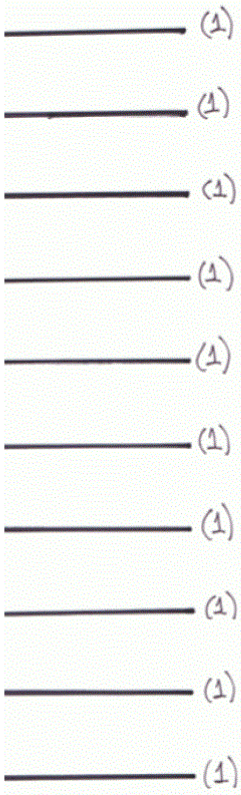

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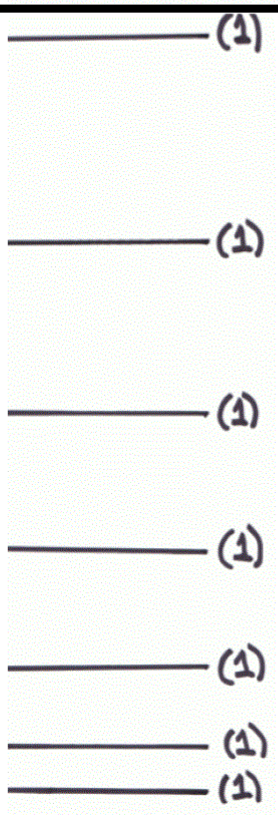

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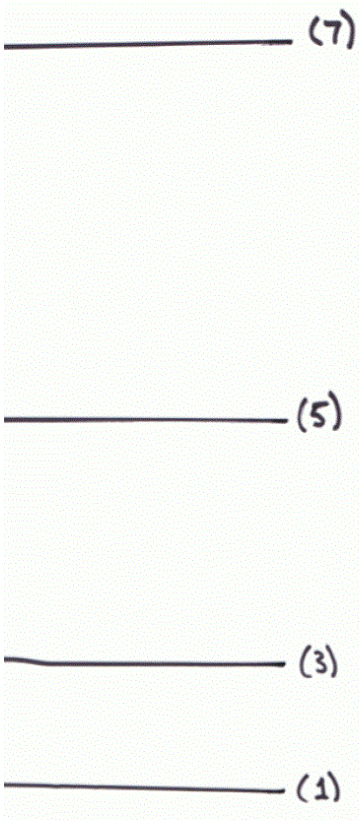

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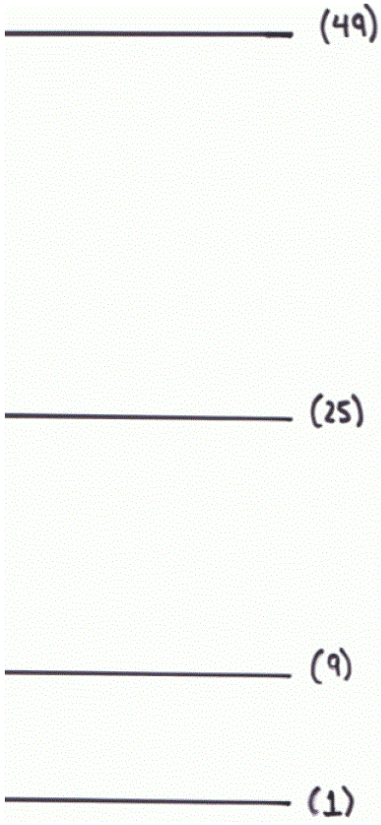

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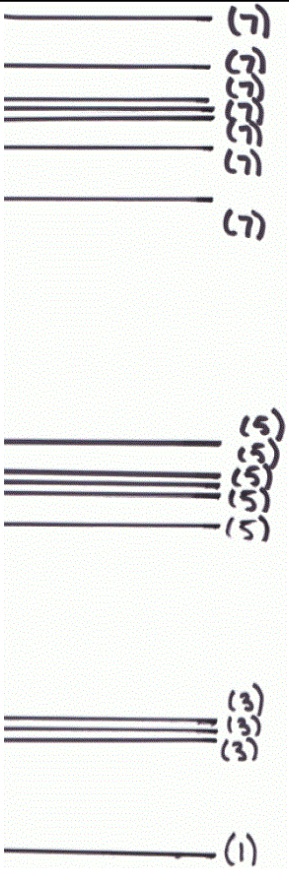

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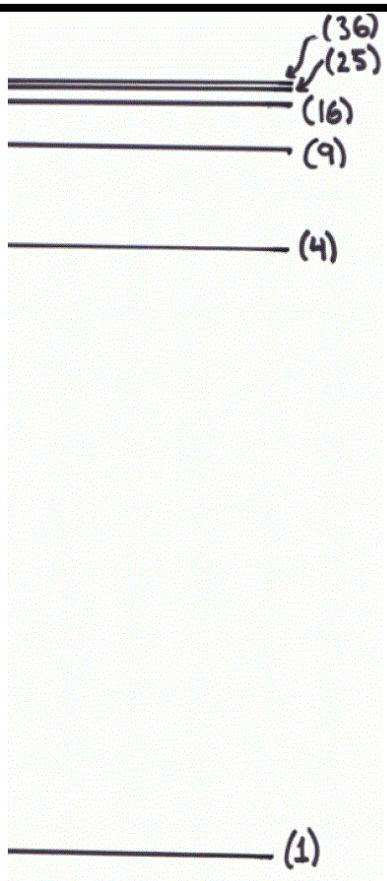

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