

Name: \_\_\_\_\_  
Student Number: \_\_\_\_\_  
Tutorial: \_\_\_\_\_

## **PHYSICS 294 – QUANTUM AND THERMAL PHYSICS**

### **QUIZ 2**

Feb. 28, 2023  
Duration: 20 min

| No.    | Maximum | Marks |
|--------|---------|-------|
| 1.     | 5       |       |
| 2.     | 10      |       |
| 3.     | 10      |       |
| Total: |         | /25   |

**Answer all questions on the question paper using a pen in the space provided. Write legibly!**

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**No aids allowed except for a non-programmed calculator and equation sheet provided**

1. (5 pts)

a) (1pt) The bond angle for molecules with  $sp^3d^2$  hybridization is:  $90^\circ$

b) (2pts) Define an ionic bond and give an example.

An ionic bond is where an electron is completely localized on the more electronegative atom in a bonded pair of atoms. This effect leaves a positive charge on one atom and net negative charge on complementary bonded atom. NaCl is just one example.

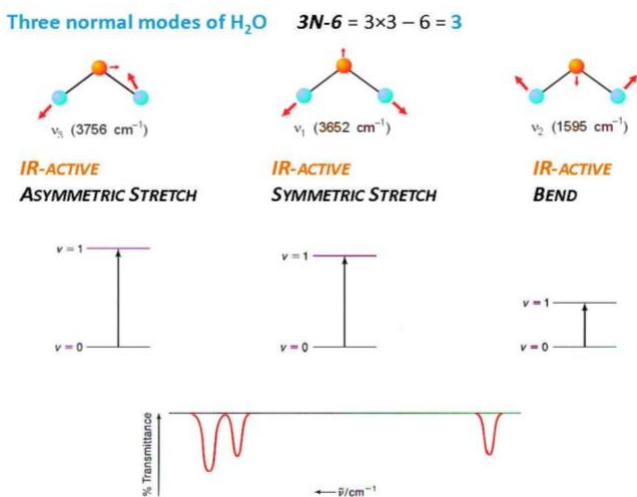
c) (2pts) What is the selection rule for the absorption of light with respect to symmetry? Briefly explain.

The transition between two electronic or vibrational states must involve a change in symmetry. The overall product must be a odd function (so the  $\langle \mu \rangle \neq 0$ ). (1pt)

This condition ensures that there is a net dipole moment that allows the E field to transfer to energy from the light to the molecular frame. (1pt). Either a bond dipole (vibrations) or transition dipole moment (electronic transitions) are involved in enabling coupling of the E field to the atomic motions (vibrations) or change in electron distribution.

2. (10 pts) It is often neglected that water is the dominant greenhouse gas. As a percentage of the atmosphere it can be up to 4% compared to approximately 0.04% for  $CO_2$ .

a) (5pts) Draw the vibrational normal modes of water and label which are IR active.



Number of vibrational modes 2pts

Specific motions 2 pts

All IR active 1 pt

b) (5pts) What would the effect of deuteration be on the IR spectrum of water (i.e, replacing H with deuterium (proton + neutron),  $\text{H}_2\text{O} \rightarrow \text{D}_2\text{O}$ ? Give the relation for calculating the resonant frequency and explain if deuteration would lead to absorption at longer or shorter wavelengths in the Infrared region of the solar spectrum.

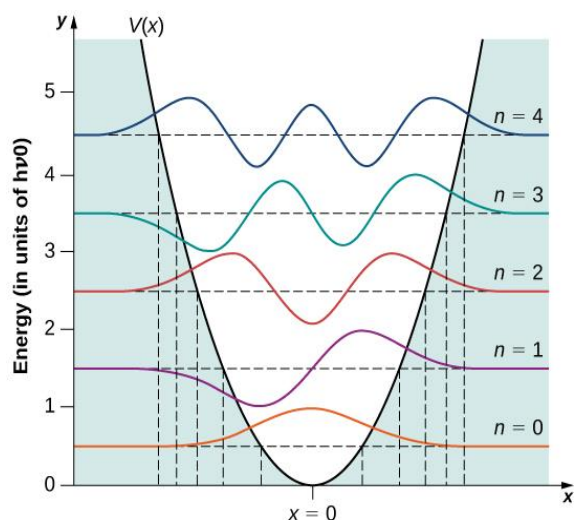
The effect of deuteration would be to lower the frequency of the resonant vibrational IR active modes due to the larger mass. The bond strength is determined by the atomic number of the element ( $Z_{\text{eff}}$ ) and this is unchanged, so larger mass with same bond strength = lower frequency (3pts)

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu_{AB}}}$$

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$$

These are the relevant relations, considering localized motions between O and H (D) atoms. Larger mass, larger reduced mass, the lower the frequency and longer the wavelength (2pts)

3. (10 pts) Draw the wavefunctions for the Quantum Harmonic Oscillator on the harmonic potential shown below. Be sure to label energy levels with respect to quantum number n and show the energy difference between levels – for the first 5 energy levels.



The  $n=0$  to  $n=4$  wavefunctions should be shown as above (5pts). Tunneling region should be shown as amplitude beyond classic turning points (2 pts). Equally spaced energy levels separated by  $h\nu$  (with  $n=0$  at  $\frac{1}{2} h\nu$ ) 3 pts..-1 pt if  $n=0$  is not shown as  $\frac{1}{2} h\nu$

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## **PHYSICS 294 – QUANTUM AND THERMAL PHYSICS**

### **QUIZ 2**

March 2, 2023  
Duration: 20 min

| No.    | Maximum | Marks |
|--------|---------|-------|
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| 2.     | 10      |       |
| 3.     | 10      |       |
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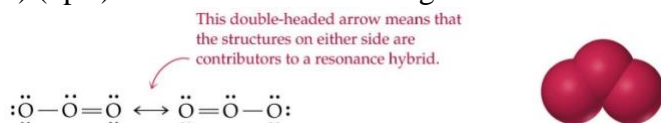
**No aids allowed except for a non-programmed calculator and equation sheet provided**

1. (5 pts)

a) (1pt) The bond angle for molecules with  $sp^3$  hybridization (without lone pairs of electrons) is:  $109.5^\circ$

b) (2pts) Which of the following molecules are IR active? (a)  $N_2$ , (b)  $HBr$ , (c)  $CH_4$  (d)  $Xe$ , (e)  $H_2O_2$ .  $HBr$ ,  $H_2O_2$ .

c) (2pts) Draw the structure and give the number of normal vibrational modes of ozone,  $O_3$ .



The key point is that  $O_3$  is not linear with drawing (1pt) and therefore has  $3N-6$  vibrational modes like water or 3 vibrational modes (1pt)

2. (10 pts) The fundamental frequency of vibration for  $D^{35}Cl$  is  $\nu = 6.24 \times 10^{13} \text{ sec}^{-1}$ .

(a) (5pts) Write down the expression to calculate the force constant,  $k$ , for the  $D^{35}Cl$  bond explicating giving the mass and resonant frequency. You don't need to evaluate it.

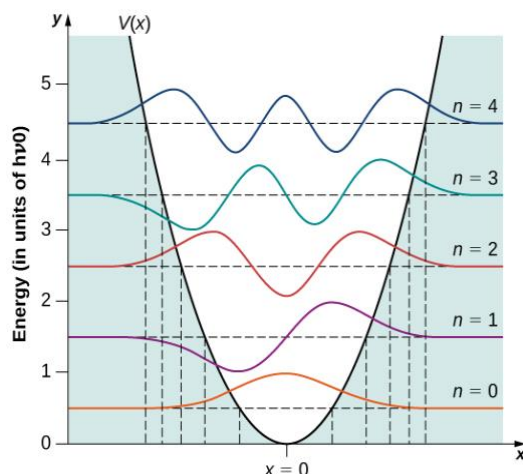
From equation sheet:  $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu_{AB}}}$ ; such that  $k = 4\pi^2 \mu_{AB} \nu^2$ ; where  $\mu_{AB} = m_D m_{Cl} / (m_D + m_{Cl})$  and  $\nu = 6.24 \times 10^{13} \text{ s}^{-1}$ .

3pts for identifying correct relation, and 2 pts for correctly identifying reduce mass ( $D = 2 \text{ amu}$  and  $Cl$  has  $35 \text{ amu}$ )

(b) (5pts) Would the frequency be higher or lower for  $HCl$  relative to  $DCl$ ? Brief explanation.

With the above expression, the key concept is that the bond strength depends only on the electron distribution about the nuclei and if the number of protons do not change the bond energy must be the same (3pts). Give the inverse relation with reduced mass the lower reduced mass for  $HCl$  will give a higher resonant frequency (2pts)

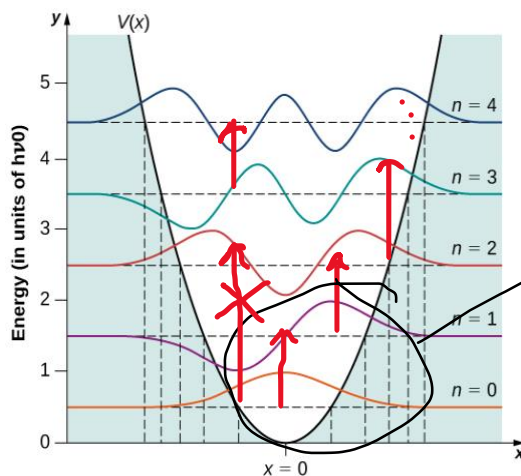
3. (10 pts) The potential for a quantum harmonic oscillator is shown below.



a) (5pts) Draw the harmonic oscillator wavefunctions for the first 5 vibrational energy levels using the above figure. Be sure to show explicitly the difference in energy between levels.

As above. Showing  $n=0$  to  $n=4$  equally spaced by energy  $h\nu$  (3pts), amplitude outside classic turning points re: tunneling (1pt), zero point energy  $E_0 = \frac{1}{2} h\nu$  for  $n=0$  (1pt).

b) (5pts) Assuming this potential represents HCl, draw vertical arrows in the above figure showing the allowed, IR active transitions, from the lowest vibrational energy level. (Hint think about symmetry relations for selection rules.) Provide a brief explanation for the symmetry dependence.



Only need to show the  $n=0$  to  $n=1$  transition as allowed re: population is primarily in  $n=0$ . However, you do need to explain difference in symmetry and relationship to this difference in motion leading to a dipole moment to couple to the E field....allowing transfer of energy/photon to the molecular frame/motions.

There should be one arrow from  $n=0$  to  $n=1$ , or any other level with  $\Delta n=1$  (2pts). This condition ensures there is difference in mass distribution/probability that leads to dipole moment that can couple to the field. This selection rule explicitly defines vibration levels with different symmetries (3pts). Note, it would nice to show that  $\Delta n = 2, 4, 6 \dots$  involve the same symmetry and therefore do not lead to a net charge displacement or dipole moment in describing stable allowed vibrational motions of the atoms relative to one another. (By extension for a purely harmonic oscillator  $\Delta n = 1, 3, 5 \dots$  would all involve levels with a change in symmetry and would be IR active...no penalty for these higher level considerations.) Normally just the lowest level is shown as it is the only level that has any appreciable population.

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## **PHYSICS 294 – QUANTUM AND THERMAL PHYSICS**

### **QUIZ 2**

March 1, 2023  
Duration: 20 min

| No.    | Maximum | Marks |
|--------|---------|-------|
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1. (5 pts)

a) (1pt) The bond angle for molecules with sp hybridization is:  $180^\circ$

b) (2pts) What is the bond order of  $F_2$  and  $F_2^+$ ? **1 and 1.5 respectively**

c) (2pts) Is the vibrational mode of  $F_2$  or  $F_2^+$  IR active? Briefly explain.

Neither. For  $F_2$  there is no dipole moment, completely equal (1pt). For  $F_2^+$  one could argue there is a dipole moment with + on one F atom and neutral on the other but the electron is removed from a  $\pi^*$  MO which has equal probability distribution for the electrons (or hole in this case).

2. (10 pts) Despite He being the most inert element, there are weak van der Waals forces, which account for the formation of a dimer. The potential energy of the helium dimer ( $He_2$ ) bound by such force is given by,  $V = \frac{B}{r^{13}} - \frac{C}{r^6}$

Where  $B = 9.29 \times 10^4 \text{ kJ } \text{\AA}^{13} (\text{mol dimer})^{-1}$  and  $C = 97.7 \text{ kJ } \text{\AA}^6 (\text{mol dimer})^{-1}$

(a) (5pts) Explain briefly van der Waals or Dispersion forces.

Van der Waals forces arise from instantaneous fluctuations in electron density that create corresponding fluctuation dipole moments (2pts). This instantaneous dipole moment in one atom induces a dipole in a neighbouring atom (2pts). There is a net attractive force that scales at  $1/r^6$  corresponding to a dipole-dipole interaction (1pt). Some discretion if distance dependence not mentioned.

(b) (5pts) Show or describe how you would determine the equilibrium distance between the He atoms with the above relation without evaluating it (set the problem up).

Take the first derivative with respect to  $r$  and set equal to 0 (3pts). Explicitly from problem set:

(a) The equilibrium distance,  $r_e$ , can be calculated by setting  $\frac{dV}{dr} = 0$ .

$$\begin{aligned}\frac{dV}{dr} &= -\frac{13B}{r^{14}} + \frac{6C}{r^7} \\ -\frac{13B}{r_e^{14}} + \frac{6C}{r_e^7} &= 0\end{aligned}$$

$$r_e = \left(\frac{13B}{6C}\right)^{1/7} = \left\{ \frac{13 [9.29 \times 10^4 \text{ kJ } \text{\AA}^{13} (\text{mol dimer})^{-1}]}{6 [97.7 \text{ kJ } \text{\AA}^6 (\text{mol dimer})^{-1}]} \right\}^{1/7} = 2.975 \text{ \AA} = 2.98 \text{ \AA}$$

Only need to show up to the 3<sup>rd</sup> line (2pts)

3. (10 pts) The different processes involved in the absorption and emission of light is shown below

- a) (5pts) Briefly explain the selection rules for absorption and emission. Discuss symmetry requirements (re: expectation value for the transition dipole moment) and spin considerations.

The selection rules are that  $\Delta S = 0$ , no change in electron spin (1pt), and there must be a change in symmetry between the levels undergoing a light induced transition (3pts). The symmetry requirements reflects that this condition is needed to generate a transition dipole moment via the light induced change in electron distribution to enable the transfer of energy from the light to the molecular frame with respect to the change in electron distribution. Mathematically  $\langle \mu \rangle \neq 0$  iff there is a change in symmetry between the two electronic states involved in the absorption of a photon (1pt). The relation:

$\mu_{mn} = \int \psi_n \mu \psi_m d\tau$  was given in the equation sheet...and should be used in responding to this question or covered in the way the question was answered. Basically  $\mu$  is an odd function and for this integral to be nonvanishing requires the product  $\psi_n \psi_m$  to be an odd function for the overall expectation value to give an even function, nonzero integral. Again, this relation ensures there is a change in charge distribution that is nonuniform and leads to transition dipole moment.

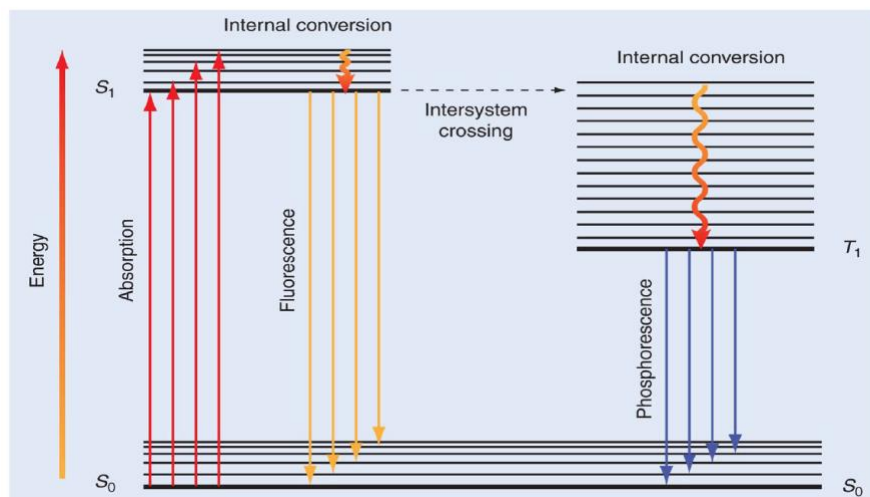
- b) (2pts) The wavy lines in the above figure represent what process? Brief explanation.

The wavy lines represent vibrational relaxation from higher vibrational levels to lower vibrational levels that conserve energy (2pts). In the excited state the density of vibration levels is so high that all vibronic excitations relax on 100 femtosecond timescale to the lowest vibration level to emit (or relax by internal conversion to the lower electronic level). (As an aside: This intramolecular vibrational energy distribution occurs on 100 fs time scales and is faster than any other process. This effect leads to Kasha's rule that all emission occurs from lowest  $v=0$  level of all fluorescent (spin allowed) and phosphorescent (slower spin forbidden) states.

- c) (3pts) Phosphorescence is a spin forbidden process. Explain why the energy for emission from  $T_1$  is lower than fluorescence from the level labelled  $S_1$ ?

The  $T_1$  level is lower in energy due to Hund's rule (2pts). In principle  $S_1$  and  $T_1$  only differ in the electron spin.  $S_1$  has both electrons in the singly occupied ground and excited states paired; whereas they are parallel for the  $T_1$  or triplet state. Hund's rule is lower in energy as the paired electrons now have more spatially distinct electron

distributions, less e-e repulsion (In higher level courses you will see how this condition requires the spatial part of the wavefunction to be antisymmetric to electron exchange, requiring 2 different spatially related orbitals. This lowers e-e repulsion. The spin function must be symmetric to exchange by definition for two identical spin states). Hund's rule only applies to electronic levels that are degenerate, as in this case. (1pt)



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## **PHYSICS 294 – QUANTUM AND THERMAL PHYSICS**

### **QUIZ 2**

Feb. 27, 2023  
Duration: 20 min

| No.    | Maximum | Marks |
|--------|---------|-------|
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1. (5 pts)

a) (1pt) The bond angle for molecules with  $sp^2$  hybridization is:  $120^\circ$

b) (2pts) Briefly define a hydrogen (H) bond and which elements form H bonds.

A hydrogen bond specifically involves the formation of a bond with electrostatic attraction between H and more electron negative atoms. (1pt) The H atom takes on positive character relative to a partial negative charge on the more electronegative element. (either underlined explanation works). There is some degree of electron sharing between H and other elements in the process that goes beyond an electrostatic or dipole-dipole bond.

Only O, N, F are considered H bond formers (1pt) due to their propensity and larger electronegativity compared to H.

c) (2pts) What are the selection rules for the absorption of light with respect to spin? Briefly explain.

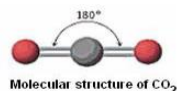
$$\Delta S = 0 \text{ (1pt)}$$

The electromagnetic field is well off resonance to have magnetic fields on resonance to flip or change the electron spin states. (1pt)

2. (10 pts) There is a major problem with  $CO_2$  as a greenhouse gas in the combustion of fossil fuels.

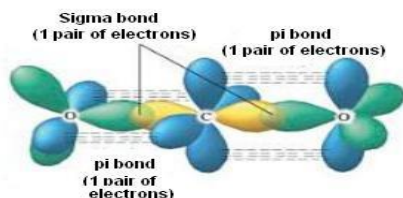
a) (5pts) Draw the structure of  $CO_2$  showing bond order.

$O=C=O$  linear (2 pts)



Some indication of octet rule

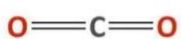
C is  $sp$  hybridized with drawing showing  $sp$  orbital overlap with O p orbitals to a  $\sigma$  bond and C p orbitals overlap with O p orbitals to form a  $\pi$  bonds (2pts either in words or in figure as below)



Bond order of C and O atoms is 2 (1pt)

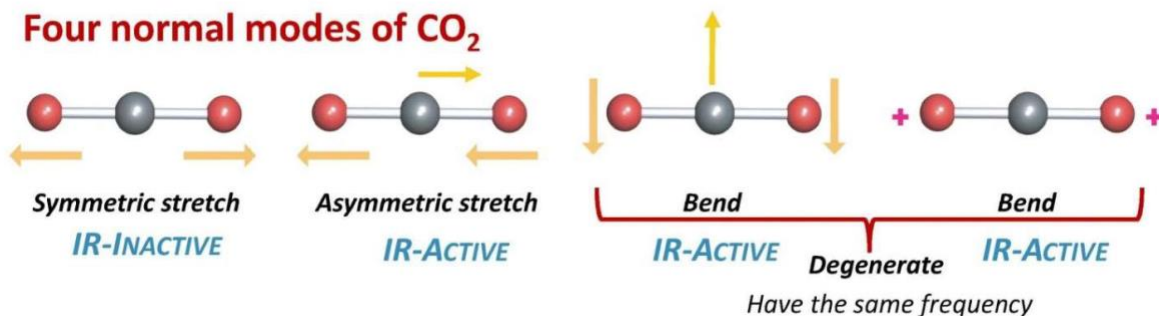
b) (5pts) Draw the normal vibrational modes of CO<sub>2</sub> and label which motions are IR active and involved in absorbing IR and Greenhouse Gas Effect.

A Linear molecule of  $N$  atoms can vibrate in  $3N-5$  modes.



$$3N-5 = 3 \times 3 - 5 = 4$$

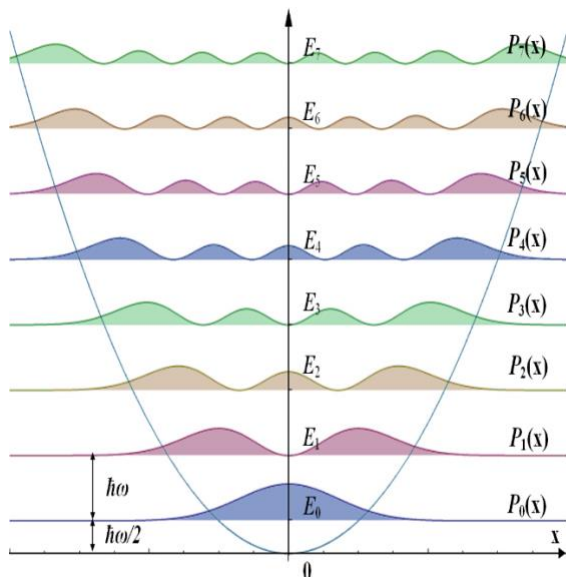
### Four normal modes of CO<sub>2</sub>



Identifying 4 vibrational modes (1pt)

Drawing the 4 modes and showing symmetric is IR inactive (4pts)

3. (10 pts) Draw the probability distributions for the Quantum Harmonic Oscillator on the harmonic potential shown below. Be sure to label energy levels with respect to quantum number  $n$  and show the energy difference between levels – for the first 5 energy levels.



As above superimposed on provided potential, for  $n=0, 1, 2, 3, 4$ , showing probability outside classic turning points, i.e., tunneling probability (5pts). The levels should be equally spaced with separation  $h\nu$  (4pts) and zero point energy of  $\frac{1}{2} h\nu$  (1pt).