Name:

# Quiz 7

## Chemistry 3BB3; Winter 2005

**1,2. Write down Fermi's golden rule for dipole transitions. Underline and/or label the term that is associated with the "selection rules" for allowed vs. forbidden transitions.**

**3. Which of the following transitions will be most intense:**

(a) The ${}^1D_2 \rightarrow {}^3P_0$ associated with the $[\mathrm{Xe}]6s^2 4f^{10} 5d^{10} 6p^1 6d^1$ to $[\mathrm{Xe}]6s^2 4f^{10} 5d^{10} 6p^2$ configuration of Lead (Pb, atomic number 82).

(b) The ${}^1D_2 \rightarrow {}^3P_1$ associated with the $[\mathrm{Xe}]6s^2 4f^{10} 5d^{10} 6p^1 6d^1$ to $[\mathrm{Xe}]6s^2 4f^{10} 5d^{10} 6p^2$ configuration of Lead (Pb, atomic number 82).

(c) The ${}^1D_2 \rightarrow {}^3P_0$ associated with the $[\mathrm{He}]2s^2 2p^1 3d^1$ to $[\mathrm{He}]2s^2 2p^2$ configuration of Carbon (C, atomic number 6).

(d) The ${}^1D_2 \rightarrow {}^3P_1$ associated with the $[\mathrm{He}]2s^2 2p^1 3d^1$ to $[\mathrm{He}]2s^2 2p^2$ configuration of Carbon (C, atomic number 6).

**4. You are trying to observe a transition at 408 nm but, unfortunately, the only light source in your underequipped laboratory is a laser operating at 423 nm. Your laser can operate in "continuous" mode (under which it emits a constant beam of light) or "pulsed" mode, in which it emits short "bursts" of light (the typical burst has a duration of a few femtoseconds (about $10^{-15}$ s), though the world record for the shortest pulse is right now at 650 attoseconds ($6.50 \cdot 10^{-16}\ s$).) To observe the transition at 408 nm, should you operate the laser in "continous" or "pulsed" mode?**[1]

(a) continuous.

(b) pulsed.

**5. Some people believe that the key to making better superconductors is to study systems with large amounts of vibronic coupling. Some recent work along these lines has focused on Silver Halides. If you were trying to maximize the possible vibronic coupling in this family of compounds, you would investigate primarily:**

(a) Silver Fluorides.

(b) Silver Chlorides.

**6. All other things being equal, electric quadrupole-allowed (but electric dipole-forbidden) transitions will be most intense when:**

(a) the difference in energy between the ground and excited states is large.

(b) the difference in energy between the ground and excited states is small.

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[1] In real life, one can often simulate a "pulsed" system by putting a rapidly rotating "chopper" in the laser beam. This set-up uses a rotating wheel with slits placed at various places to intermittently allow and block the laser beam.

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**7. There has been a lot of recent interest in nonlinear optical materials that double the frequency of incident light. Such materials absorb light with frequency $\omega$ but emit light with frequency $2\omega$. This effect is most likely to be observed when**

(a) the incident light has high intensity.

(b) the incident light has low intensity.

**8-10. The ground state term symbol of the Carbon atom ($1s^2 2s^2 2p^2$ electron configuration) is $^3P_0$. The excited-state term symbols of the $1s^2 2s^2 2p^1 3d^1$ electron configuration are $^3P, ^3D, ^3F, ^1P, ^1D, ^1F$. For each of the transitions mark why the transition is forbidden by putting an "x" *all* the appropriate boxes. If the transition is allowed, indicate this in the appropriate place.**

| | | **Allowed?** | **If Forbidden, Which Rule(s) are Violated?** | | |
|---|---|---|---|---|---|
| initial state | final state | | Electric Dipole Selection Rule on $L$ (orbital angular momentum) | Electric Dipole Selection Rule on $J$ (total angular moment) | Selection Rule on $S$ (spin angular momentum) |
| $^3P_1$ | $^3P_0$ | | | | |
| $^3P_2$ | $^3P_0$ | | | | |
| $^3D_1$ | $^3P_0$ | | | | |
| $^3D_3$ | $^3P_0$ | | | | |
| $^3F_2$ | $^3P_0$ | | | | |
| $^1P_1$ | $^3P_0$ | | | | |

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# Quiz 7 (Key)

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**1,2. Write down Fermi's golden rule for dipole transitions. Underline and/or label the term that is associated with the "selection rules" for allowed vs. forbidden transitions.**

$$W_{fi} = \frac{2\pi V^2 \left( g\left(\hbar\omega_{fi}\right) + g\left(-\hbar\omega_{fi}\right)\right)}{\hbar} \underline{\underline{\left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2}}$$

**3. Which of the following transitions will be most intense:**

(a) The $^1D_2 \rightarrow {}^3P_0$ associated with the $[\mathrm{Xe}]6s^2 4f^{10} 5d^{10} 6p^1 6d^1$ to $[\mathrm{Xe}]6s^2 4f^{10} 5d^{10} 6p^2$ configuration of Lead (Pb, atomic number 82).

**(b) The $^1D_2 \rightarrow {}^3P_1$ associated with the $[\mathrm{Xe}]6s^2 4f^{10} 5d^{10} 6p^1 6d^1$ to $[\mathrm{Xe}]6s^2 4f^{10} 5d^{10} 6p^2$ configuration of Lead (Pb, atomic number 82).**

(c) The $^1D_2 \rightarrow {}^3P_0$ associated with the $[\mathrm{He}]2s^2 2p^1 3d^1$ to $[\mathrm{He}]2s^2 2p^2$ configuration of Carbon (C, atomic number 6).

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| | | **Allowed?** | **If Forbidden, Which Rule(s) are Violated?** | | |
|---|---|---|---|---|---|
| initial state | final state | | Electric Dipole Selection Rule on $L$ (orbital angular momentum) | Electric Dipole Selection Rule on $J$ (total angular moment) | Selection Rule on $S$ (spin angular momentum) |
| $^3P_1$ | $^3P_0$ | **yes** | | | |
| $^3P_2$ | $^3P_0$ | | | **x** | |
| $^3D_1$ | $^3P_0$ | **yes** | | | |
| $^3D_3$ | $^3P_0$ | | | **x** | |
| $^3F_2$ | $^3P_0$ | | **x** | **x** | |
| $^1P_1$ | $^3P_0$ | | | | **x** |