Name:

Quiz 9

Chemistry 3BB3; Winter 2004

1. Write down Fermi's golden rule for dipole transitions:

2. The sinc function is defined as

$$\mathrm{sinc}(x) =$$

3. In general, what is the relationship between the frequency of absorbed radiation and the difference in energy between the initial and final states?

4. Let i and f denote two different electronic states of a diatomic molecule. Let R_i and R_f denote the bond lengths of state i and state f. Let k_i and k_f denote the force constants associated with state i and state f. Transitions between the ground vibrational state, $\nu_i = 0$, of state i and the ground vibration state, $\nu_f = 0$ of state f will be most likely to occur when

(a) $R_i < R_f; k_i < k_f$ (d) $R_i \approx R_f; k_i < k_f$ (g) $R_i > R_f; k_i < k_f$

(b) $R_i < R_f; k_i \approx k_f$ (e) $R_i \approx R_f; k_i \approx k_f$ (h) $R_i > R_f; k_i \approx k_f$

(c) $R_i < R_f; k_i > k_f$ (f) $R_i \approx R_f; k_i > k_f$ (i) $R_i > R_f; k_i > k_f$

5,6. For each of the following statements, indicate whether the result follows from the weak-field approximation (W), long-time approximation (T), Long-Wavelength approximation (L), or the Condon approximation (C). (Select all that apply).

_____ Perturbation theory can be used to describe the interaction of radiation with a molecule.

_____ Nonlinear optical effects are not very important.

_____ Vibronic coupling is not very important.

_____ Electric dipole transitions are much more intense that electric quadrupole transitions.

_____ In the absence of broadening, the absorption spectrum of a molecule is a collection of delta-function peaks.

_____ Light can be absorbed not only at the usual excitation frequency, ω_{if}, but also at $\frac{1}{n}\omega_{if}$, where *n* is an integer.

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7-10. For each of the following transitions, say whether the transition is dipole forbidden or allowed. Extra points if you say what sort of transition *would* be allowed (when it is dipole forbidden). (If the transition is formally dipole allowed but quite weak, you might denote this also.)

_____ The ^3P to ^1S transition in the Silicon atom.

_____ ^3S to ^3S transitions.

_____ Transitions from the $1s^1 2p^1$ (^3P) state of Helium to the $1s^1 3p^1$ (^3P) state of Helium.

_____ Transitions from the $1s^1 2p^1$ (^3P) state of Helium to the $2s^1 3p^1$ (^3P) state of Helium.

_____ Electronic excitation from a σ_g (bonding) to a π_g (antibonding) orbital.

_____ Electronic excitation from a σ (bonding) to a π (antibonding) orbital in a heteronuclear diatomic.

_____ Electronic excitation from a π_u^+ to a π_u^- orbital.

_____ Electronic excitation from a π_u^+ to a δ_g^- orbital.

Name:

Quiz 10 Key

Chemistry 3BB3; Winter 2004

1. Write down Fermi's golden rule for dipole transitions:

$$W_{fi} = \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)}{\hbar}\left|\left\langle \Psi_f \left|\hat{\mu}\right| \Psi_i \right\rangle\right|^2$$

(Here $\hat{\mu}$ is the dipole moment operator).

2. The sinc function is defined as

$$\mathrm{sinc}\,(x) = \frac{\sin(\mathrm{x})}{x}$$

3. In general, what is the relationship between the frequency of absorbed radiation and the difference in energy between the initial and final states?

$$\nu_{fi} = \frac{E_f - E_i}{h}$$

4. Let i and f denote two different electronic states of a diatomic molecule. Let R_i and R_f denote the bond lengths of state i and state f. Let k_i and k_f denote the force constants associated with state i and state f. Transitions between the ground vibrational state, $\nu_i = 0$, of state i and the ground vibration state, $\nu_f = 0$ of state f will be most likely to occur when

(a) $R_i < R_f; k_i < k_f$ (d) $R_i \approx R_f; k_i < k_f$ (g) $R_i > R_f; k_i < k_f$

(b) $R_i < R_f; k_i \approx k_f$ **(e)** $R_i \approx R_f; k_i \approx k_f$ (h) $R_i > R_f; k_i \approx k_f$

(c) $R_i < R_f; k_i > k_f$ (f) $R_i \approx R_f; k_i > k_f$ (i) $R_i > R_f; k_i > k_f$

5,6. For each of the following statements, indicate whether the result follows from the weak-field approximation (W), long-time approximation (T), Long-Wavelength approximation (L), or the Condon approximation (C). (Select all that apply).

___W____ Perturbation theory can be used to describe the interaction of radiation with a molecule.

___W____ Nonlinear optical effects are not very important.

___C____ Vibronic coupling is not very important.

___L____ Electric dipole transitions are much more intense that electric quadrupole transitions.

___T____ In the absence of broadening, the absorption spectrum of a molecule is a collection of delta-function peaks.

_(none; in the weak-field approximation these transitions are forbidden)__ Light can be absorbed not only at the usual excitation frequency, ω_{if}, but also at $\frac{1}{n}\omega_{if}$, where n is an integer.

Name:

7-10. For each of the following transitions, say whether the transition is dipole forbidden or allowed. Extra points if you say what sort of transition *would* be allowed (when it is dipole forbidden). (If the transition is formally dipole allowed but quite weak, you might denote this also.)

_forbidden_____ The ^3P to ^1S transition in the Silicon atom.

_forbidden_____ ^3S to ^3S transitions.

_allowed_____ Transitions from the $1s^1 2p^1$ (^3P) state of Helium to the $1s^1 3p^1$ (^3P) state of Helium.

_forbidden_____ Transitions from the $1s^1 2p^1$ (^3P) state of Helium to the $2s^1 3p^1$ (^3P) state of Helium.

__forbidden_____ Electronic excitation from a σ_g (bonding) to a π_g (antibonding) orbital.

__allowed_____ Electronic excitation from a σ (bonding) to a π (antibonding) orbital in a heteronuclear diatomic.

__forbidden_____ Electronic excitation from a π_u^+ to a π_u^- orbital.

__allowed_____ Electronic excitation from a π_u^+ to a δ_g^- orbital.