Name:

Quiz 4

Chemistry 3BB3; Winter 2003

There are 110 points possible, so you can think of the last question as a "bonus".

1. **You put a molecule in the presence of light. The light travels in the z-direction and the magnetic field oscillates in the y-direction. The electric field vector oscillates in the**
   (a) x-direction.
   (b) y-direction
   (c) z-direction

2. **Which of the following are valid relationships for light/photons? Here c is the speed of light, h is Planck's constant, and $\hbar \equiv \frac{h}{2\pi}$.**

   (a) wave number $= \dfrac{2\pi}{\text{wavelength}}$

   (b) wavelength $= \dfrac{\text{Energy}}{h \cdot c}$

   (c) momentum $\cdot$ wavelength $= h$

   (d) Energy $= h \cdot (\text{frequency})$

   (e) angular frequency $= c \cdot \text{wavelength}$

   (f) wavelength $\cdot$ frequency $= c$

   (g) angular frequency $= c \cdot \dfrac{1}{\text{wave number}}$

3. **In the long wavelength approximation, we argued that the field a small molecule in the presence of UV-visible radiation experienced was to a good approximation**
   (a) A magnetic moment, or "dipole", that oscillates in time.
   (b) A magnetic "dipole" that changes periodically over the spatial extent of the molecule.
   (c) An electric dipole that oscillates in time.
   (d) An electric dipole that changes periodically over the spatial extent of the molecule.
   (e) A constant electric field.
   (f) A positive electric field whose magnitude oscillates in time, but its direction does not.

4. **Write down the time-dependent Schrödinger Equation.**

5. **Suppose Ψ_k is the eigenfunction for a stationary state. We can write the time-dependent eigenfunction as**
$$\Psi_k\left(r_1,\ldots,r_N;t\right) \equiv \Phi_k\left(r_1,\ldots,r_N\right) \cdot \chi(t)$$
   where $\Phi_k\left(r_1,\ldots r_N\right)$ is an eigenfunction of the time-independent Schrödinger equation,
$$\hat{H}\Phi_k\left(r_1,\ldots,r_N\right) = E_k\Phi_k\left(r_1,\ldots,r_N\right)$$
   What is $\chi(t)$?

$$\chi(t) =$$

Name:

6. **When one mixes two a solution of potassium thiocyanate and Iron(III) chloride, one observes a blood-red color due to Iron(III) isothiocyanate species. The absorption is due to an electronic transition from the ground state, with energy $E_{g.s.}$, to a low-lying excited state, with energy $E_{exc.}$.**

   (a) Write an expression for the frequency (or angular frequency) of the absorbed radiation?

   (b) About what wavelength do you expect the absorbed light to have?

The following scenario should be referred to in problems 7-9:
A molecule is in its ground state at time $t = 0$. A light source whose frequency has been tuned to induce a transition to the first excited state is turned on at $t = 0$. According to time-dependent perturbation theory, we can approximate the wave function of the system as

$$\Psi(\tau, t) = c_0(t)\Psi_0(\tau, t) + c_1(t)\Psi_1(\tau, t)$$

where $\Psi_0(\tau, t)$ is the ground-state wave function and $\Psi_1(\tau, t)$ is the wave function for the first excited state. (Here τ denotes the electronic and nuclear coordinates.)

7. **For short times, $t > 0$, the coefficient of the first-excited state wave function, $c_1(t)$,**

   (a) is independent of t.

   (b) is proportional to t.

   (c) is proportion to t^2.

   (d) is proportional to $\frac{1}{t}$.

   (e) is proportional to $\cos(\omega t)$, where ω is the angular frequency of the light source.

8. **Which of the following are true statements about the rate of excitation, W_{10}, for a broad bandwidth source within the long-wavelength approximation. In what follows, $g(\hbar\omega_{10})$ is the energy density of the light source at the transition frequency, the amplitude of the light's electric and magnetic fields are proportional to V, t is the time for which the molecule has been exposed to the light source, and**

$$\left\langle \Phi_1 \left| \hat{\mu}_x \right| \Phi_0 \right\rangle = \left\langle \Phi_1 \left| \sum_{i=1}^{N} -ex_i + \sum_{\alpha=1}^{M} eX_\alpha \right| \Phi_0 \right\rangle$$
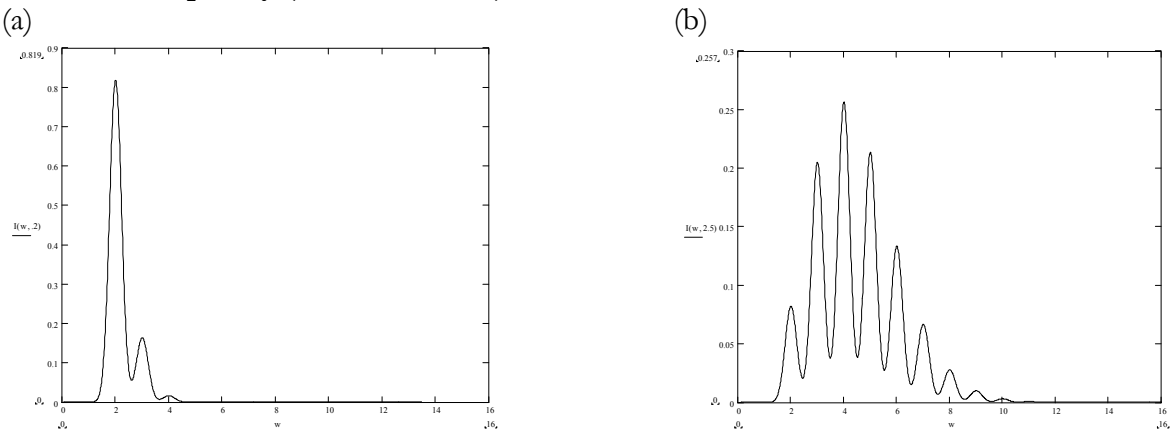
   denotes the transition dipole.

   (a) As $t \to \infty$, the rate of excitation, W_{10}, and the rate of stimulated emission, W_{01}, become equal.

   (b) The rate of excitation is proportional to the amplitude of the light's fields, V.

   (c) The rate of excitation is inversely proportional to V.

   (d) The rate of excitation is proportional to V^2.

   (e) The rate of excitation is proportional to the energy-density of the light at the excitation frequency, $g(\hbar\omega_{10})$.

   (f) The rate of excitation is inversely proportional to $g(\hbar\omega_{10})$.

   (g) The rate of excitation is proportional to $\left(g(\hbar\omega_{10})\right)^2$.

   (h) The rate of excitation is proportional to $\mathrm{sinc}\left(g(\hbar\omega_{10})\right)$.

   (i) The rate of excitation is proportional to the magnitude of the transition dipole, $\left|\left\langle \Phi_1 \left| \hat{\mu}_x \right| \Phi_0 \right\rangle\right|$.

   (j) The rate of excitation is inversely proportional to $\left|\left\langle \Phi_1 \left| \hat{\mu}_x \right| \Phi_0 \right\rangle\right|$.

   (k) The rate of excitation is proportional to $\left|\left\langle \Phi_1 \left| \hat{\mu}_x \right| \Phi_0 \right\rangle\right|^2$.

9. If $\left\langle \Phi_1 \left| \hat{\mu}_x \right| \Phi_0 \right\rangle = 0$, we say that the transition from the ground to first-excited state is:

    (a) electric dipole allowed.   (c) magnetic dipole allowed.

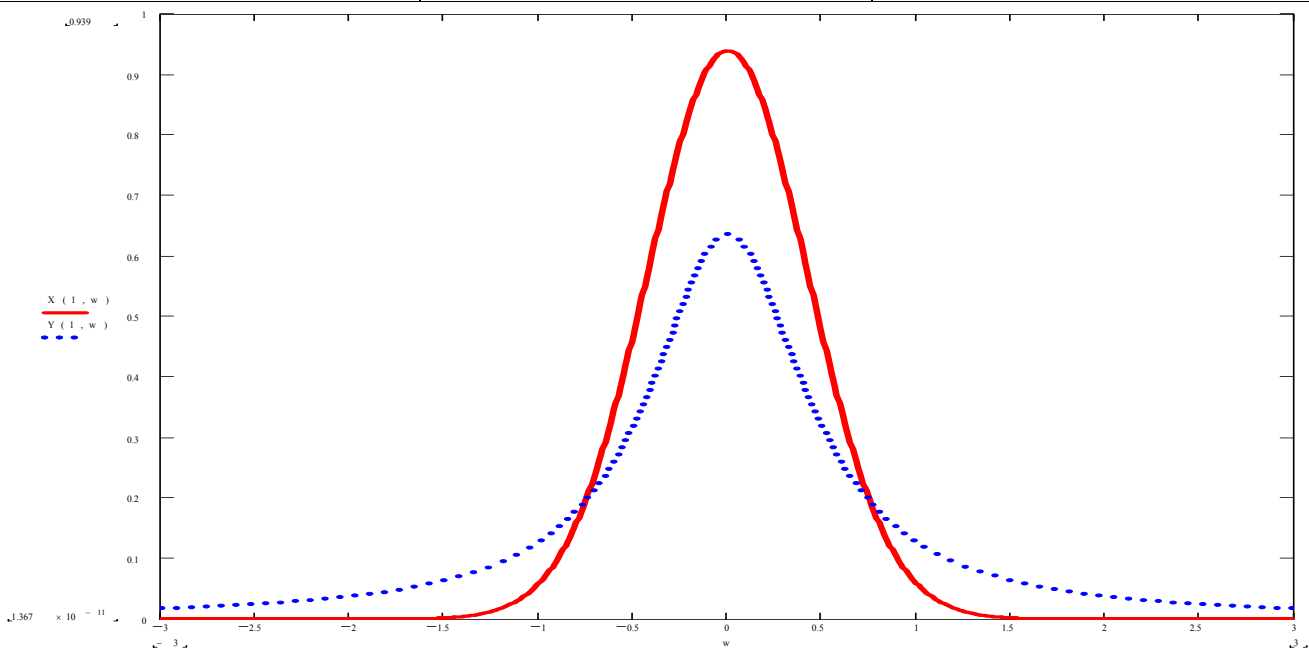   (b) electric dipole forbidden.   (d) magnetic dipole forbidden

10. The first excited state of N_2 is characterized by the excitation of an electron from a bonding to a non-bonding orbital. The absorption spectrum associated with this transition would be expected to most strongly resemble which of the following plots of intensity (vertical axis) versus frequency (horizontal axis).

(a)

(b)

11. The following plot includes both a Lorentzian and a Gaussian line shape.

    (i) Clearly label the Gaussian line shape and the Lorentzian line shape.

    (ii) The following table has the equation for both line shapes. Complete the table by (1) labeling each formula correctly and (2) denoting which line shape is associated with homogeneous broadening mechanisms and which line shape is associated with inhomogeneous broadening mechanisms

Type of Line Shape	Formula for Line Shape	Type of Broadening
	$\dfrac{\frac{\Gamma}{2\pi}}{\left(\frac{\Gamma}{2}\right)^2 + \left(\omega - \omega_0\right)^2}$	
	$\frac{2}{\Gamma}\sqrt{\frac{\ln(2)}{\pi}}e^{-4\ln(2)\left(\frac{\omega - \omega_0}{\Gamma}\right)^2}$	

Name:

Key for Quiz 4

Chemistry 3BB3; Winter 2003

There are 110 points possible, so you can think of the last question as a "bonus".

1. **You put a molecule in the presence of light. The light travels in the z-direction and the magnetic field oscillates in the y-direction. The electric field vector oscillates in the**

   (a) x**-direction.**   (b) y-direction   (c) z-direction

2. **Which of the following are valid relationships for light/photons? Here c is the speed of light, h is Planck's constant, and $\hbar \equiv \frac{h}{2\pi}$.**

   (a) wave number $= \dfrac{2\pi}{\text{wavelength}}$

   (b) wavelength $= \dfrac{\text{Energy}}{h \cdot c}$

   (c) momentum $\cdot$ wavelength $= h$

   (d) Energy $= h \cdot (\text{frequency})$

   (e) angular frequency $= c \cdot \text{wavelength}$

   (f) wavelength $\cdot$ frequency $= c$

   (g) angular frequency $= \dfrac{c}{\text{wave number}}$

3. **In the long wavelength approximation, we argued that the field a small molecule in the presence of UV-visible radiation experienced was to a good approximation**
   (a) A magnetic moment, or "dipole", that oscillates in time.
   (b) A magnetic "dipole" that changes periodically over the spatial extent of the molecule.
   (c) An electric dipole that oscillates in time.
   (d) An electric dipole that changes periodically over the spatial extent of the molecule.
   (e) A constant electric field.
   (f) A positive electric field whose magnitude oscillates in time, but its direction does not.

4. **Write down the time-dependent Schrödinger Equation.**
$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

5. **Suppose Ψ_k is the eigenfunction for a stationary state. We can write the time-dependent eigenfunction as**
$$\Psi_k\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N;t\right) \equiv \Phi_k\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N\right)\cdot\chi(t)$$

   where $\Phi_k\left(\boldsymbol{r}_1,\ldots \boldsymbol{r}_N\right)$ is an eigenfunction of the time-independent Schrödinger equation,
$$\hat{H}\Phi_k\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N\right) = E_k\Phi_k\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N\right)$$

   What is $\chi(t)$?

$$\chi(t) = e^{-iE_k t/\hbar}$$

6. When one mixes two a solution of potassium thiocyanate and Iron(III) chloride, one observes a blood-red color due to Iron(III) isothiocyanate species. The absorption is due to an electronic transition from the ground state, with energy $E_{g.s.}$, to a low-lying excited state, with energy $E_{exc.}$.

   (a) Write an expression for the frequency (or angular frequency) of the absorbed radiation?

   $$\omega_{transition} = \frac{E_{exc.} - E_{g.s.}}{\hbar} \qquad \text{OR} \qquad \nu_{trans} = \frac{E_{exc.} - E_{g.s.}}{h}$$

   (b) About what wavelength do you expect the absorbed light to have?

   If we observe a red color, then the blue light must be absorbed. This gives an absorbance in the lower wavelength range of the visible spectrum—about 450 nm or so is reasonable.

The following scenario should be referred to in problems 7-9:

A molecule is in its ground state at time $t = 0$. A light source whose frequency has been tuned to induce a transition to the first excited state is turned on at $t = 0$. According to time-dependent perturbation theory, we can approximate the wave function of the system as

$$\Psi(\tau, t) = c_0(t)\Psi_0(\tau, t) + c_1(t)\Psi_1(\tau, t)$$

where $\Psi_0(\tau, t)$ is the ground-state wave function and $\Psi_1(\tau, t)$ is the wave function for the first excited state. (Here τ denotes the dependence on the electronic and nuclear coordinates.)

7. For short times, $t > 0$, the coefficient of the first-excited state wave function, $c_1(t)$,

   (a) is independent of t.

   (d) is proportional to $\frac{1}{t}$.

   (b) is proportional to t.

   (e) is proportional to $\cos(\omega t)$, where ω is the angular frequency of the light source.

   (c) is proportion to t^2.

8. Which of the following are true statements about the rate of excitation, W_{10}, for a broad bandwidth source within the long-wavelength approximation. In what follows, $g(\hbar\omega_{10})$ is the energy density of the light source at the transition frequency, the amplitude of the light's electric and magnetic fields are proportional to V, t is the time for which the molecule has been exposed to the light source, and

   $$\left\langle \Phi_1 \left| \hat{\mu}_x \right| \Phi_0 \right\rangle = \left\langle \Phi_1 \left| \sum_{i=1}^{N} -ex_i + \sum_{\alpha=1}^{M} eX_\alpha \right| \Phi_0 \right\rangle$$

   denotes the transition dipole.

   (a) As $t \to \infty$, the rate of excitation, W_{10}, and the rate of stimulated emission, W_{01}, become equal.

   (b) The rate of excitation is proportional to the amplitude of the light's fields, V.

   (c) The rate of excitation is inversely proportional to V.

   (d) The rate of excitation is proportional to V^2.

   (e) The rate of excitation is proportional to the energy-density of the light at the excitation frequency, $g(\hbar\omega_{10})$.

   (f) The rate of excitation is inversely proportional to $g(\hbar\omega_{10})$.

   (g) The rate of excitation is proportional to $\left(g(\hbar\omega_{10})\right)^2$.

   (h) The rate of excitation is proportional to $\text{sinc}\left(g(\hbar\omega_{10})\right)$.

   (i) The rate of excitation is proportional to the magnitude of the transition dipole, $\left|\left\langle \Phi_1 \left| \hat{\mu}_x \right| \Phi_0 \right\rangle\right|$.

   (j) The rate of excitation is inversely proportional to $\left|\left\langle \Phi_1 \left| \hat{\mu}_x \right| \Phi_0 \right\rangle\right|$.

   (k) The rate of excitation is proportional to $\left|\left\langle \Phi_1 \left| \hat{\mu}_x \right| \Phi_0 \right\rangle\right|^2$.
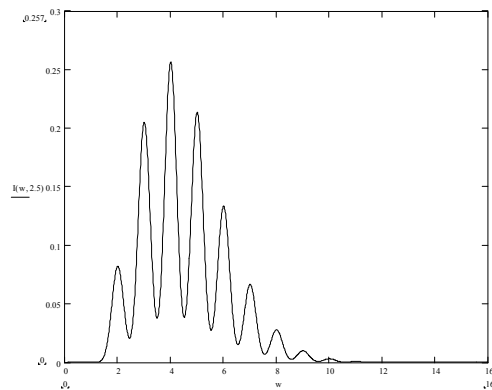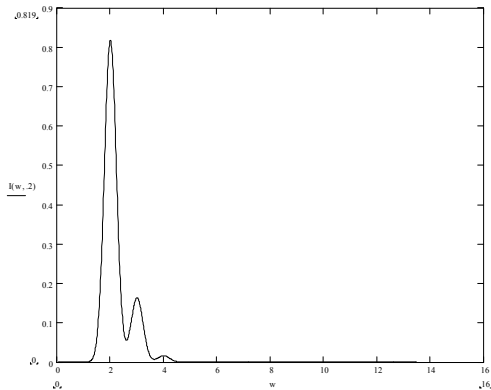
9. If $\left\langle \Phi_1 \left| \hat{\mu}_x \right| \Phi_0 \right\rangle = 0$, we say that the transition from the ground to first-excited state is:

(a) electric dipole allowed.   (c) magnetic dipole allowed.

(b) electric dipole forbidden.   (d) magnetic dipole forbidden

10. The first excited state of N_2 is characterized by the excitation of an electron from a bonding to a non-bonding orbital. The absorption spectrum associated with this transition would be expected to most strongly resemble which of the following plots of intensity (vertical axis) versus frequency (horizontal axis).
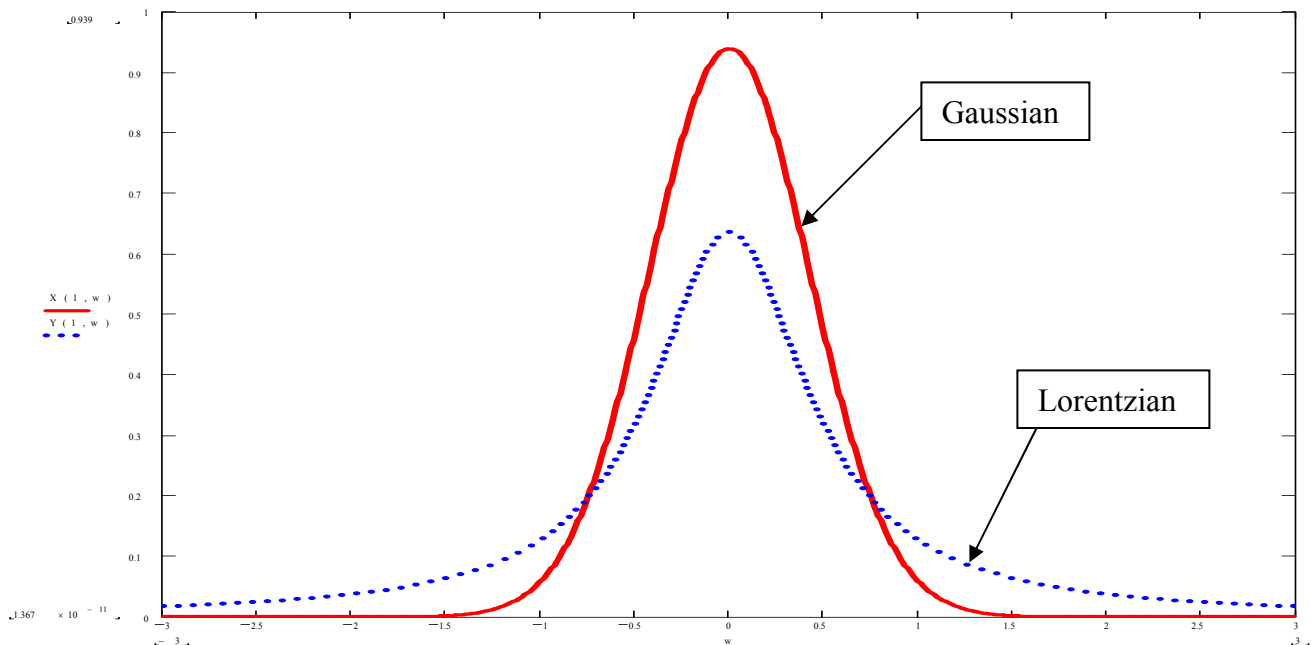
(a) would be appropriate if the bond length did not change very much.   **(b)** (appropriate when the bond length changes significantly).

11. The following plot includes both a Lorentzian and a Gaussian line shape.
   (i) Clearly label the Gaussian line shape and the Lorentzian line shape.
   (ii) The following table has the equation for both line shapes. Complete the table by (1) labeling each formula correctly and (2) denoting which line shape is associated with homogeneous broadening mechanisms and which line shape is associated with inhomogeneous broadening mechanisms

Type of Line Shape	Formula for Line Shape	Type of Broadening
Lorentzian	$$\dfrac{\frac{\Gamma}{2\pi}}{\left(\frac{\Gamma}{2}\right)^2 + \left(\omega - \omega_0\right)^2}$$	homogeneous
Gaussian	$$\frac{2}{\Gamma}\sqrt{\frac{\ln(2)}{\pi}}e^{-4\ln(2)\left[\frac{\omega-\omega_0}{\Gamma}\right]^2}$$	inhomogeneous

The solid curve is the Gaussian.