Name:

Quiz 10

Chemistry 3BB3; Winter 2004

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

2. **Write the formula for the Franck-Condon factor in terms of the nuclear wave functions of the initial ($\chi_{\nu i}(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots)$) and final ($\chi_{\mu f}(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots)$) states.**

3. **Sketch the potential energy surface and the absorbance spectrum observed for predissociation.**

4. **Sketch the potential energy surface and the absorbance spectrum observed for dissociation.**

Name:

5-7. For each of the following problems, denote the lineshape you expect to observe as "L" (Lorentzian) or "G" (Gaussian). When you expect the lineshape to be a hybrid of the two, use "V" (Voight). The species whose spectrum is being measured is *italicized.*

________ The spectrum of the *sodium cation*, dissolved in water.

________ The spectrum of *ozone* in the upper atmosphere (low pressure and low temperature).

________ The Haber process for the synthesis of ammonia is usually carried out at high temperature and pressure. Suppose you measure the production of *ammonia* by measuring the intensity of a characteristic absorbance of this molecule.

$$3H_2\,(\mathrm{g}) + N_2\,(\mathrm{g}) \rightleftharpoons 2NH_3\,(\mathrm{g}) \qquad \text{(Haber Process)}$$

________ In order to prevent air-born impurities from intercalating the alloys synthesized, blast furnaces often operate at high temperature (obviously) but low pressure. Suppose you monitor the presence of *sulfur dioxide* (a problematic contimant) is monitored using a characteristic emission of the molecule.

________ One can form a block of dry ice by condensing carbon dioxide. This is done most efficiently when the concentration of carbon dioxide is high (so this is high pressure, low temperature). Unfortunately, it is difficult to separate N_2 from CO_2, so there is often an appreciable nitrogen impurity in dry ice blocks, even though the partial pressure of nitrogen can be small. Suppose you monitor the amount of *nitrogen* in your equipment by measuring its spectrum.

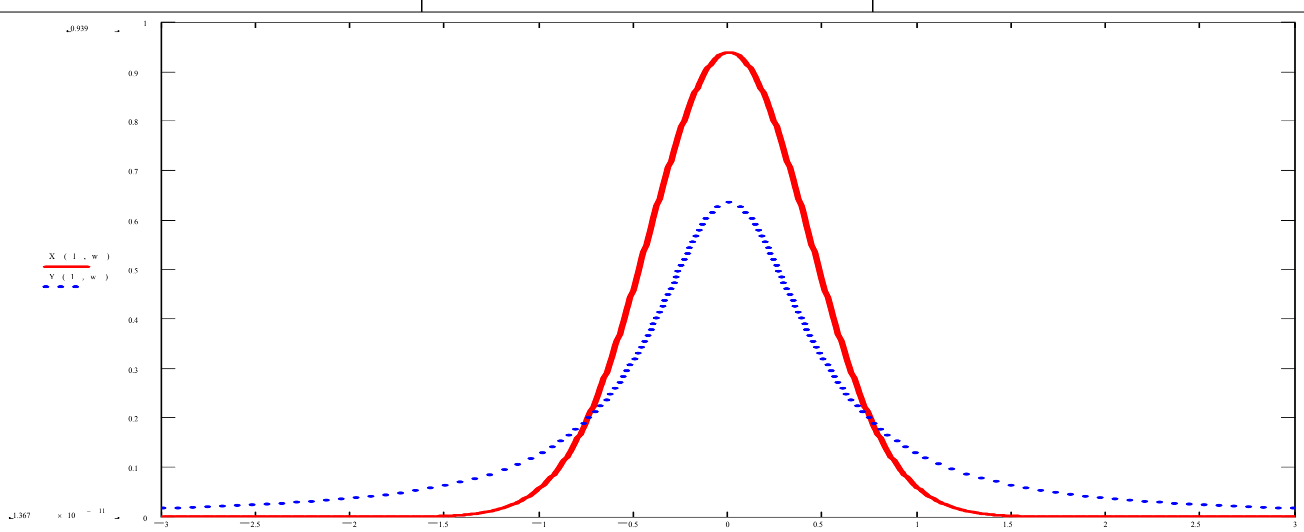
________ Consider the same system, but now we are interested in the spectrum of *carbon dioxide*.

8-10. 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) Complete the following table, writing the equation for both line shapes and denoting which line shape is associated with broadening mechanisms.

Type of Line Shape	Formula for Line Shape	Type of Broadening
		Inhomogeneous
		Homogeneous



Name:

Quiz 10

Chemistry 3BB3; Winter 2004

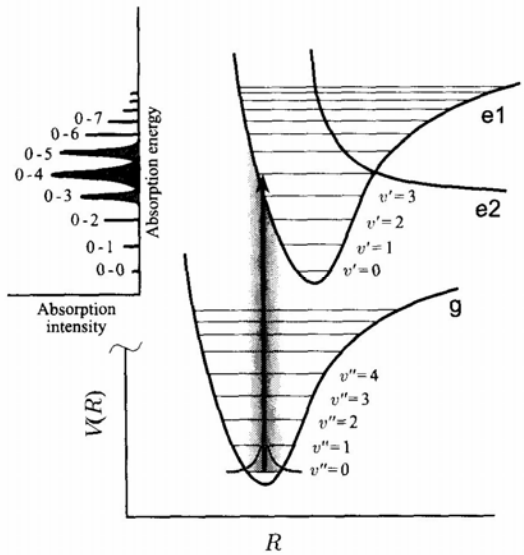
1. **Write down Fermi's golden rule for dipole transitions:**

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

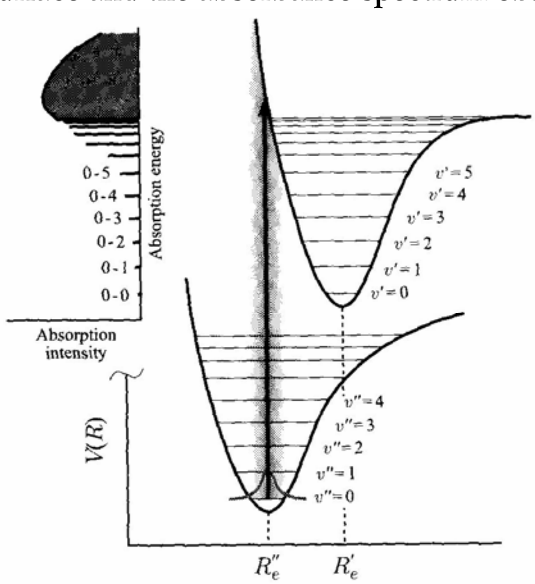
2. **Write the formula for the Franck-Condon factor in terms of the nuclear wave functions of the initial ($\chi_{\nu i}\left(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots\right)$) and final ($\chi_{\mu f}\left(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots\right)$) states.**

$$F_{\mu f,\nu i} \equiv \left|\left\langle \chi_{\mu f} \middle| \chi_{\nu i} \right\rangle\right|^2$$

3. **Sketch the potential energy surface and the absorbance spectrum observed for predissociation.**



4. **Sketch the potential energy surface and the absorbance spectrum observed for dissociation.**



Name:

5-7. For each of the following problems, denote the lineshape you expect to observe as "L" (Lorentzian) or "G" (Gaussian). When you expect the lineshape to be a hybrid of the two, use "V" (Voight). The species whose spectrum is being measured is *italicized*.

__**G**_____ The spectrum of the *sodium cation*, dissolved in water.

__**L**_____ The spectrum of *ozone* in the upper atmosphere (low pressure and low temperature).

__**V**_____ The Haber process for the synthesis of ammonia is usually carried out at high temperature and pressure. Suppose you measure the production of *ammonia* by measuring the intensity of a characteristic absorbance of this molecule.

$$3H_2\,(\mathrm{g}) + N_2\,(\mathrm{g}) \rightleftharpoons 2NH_3\,(\mathrm{g}) \qquad \text{(Haber Process)}$$

__**G**_____ In order to prevent air-born impurities from intercalating the alloys synthesized, blast furnaces often operate at high temperature (obviously) but low pressure. Suppose you monitor the presence of *sulfur dioxide* (a problematic contimant) is monitored using a characteristic emission of the molecule.

__**L**_____ One can form a block of dry ice by condensing carbon dioxide. This is done most efficiently when the concentration of carbon dioxide is high (so this is high pressure, low temperature). Unfortunately, it is difficult to separate N_2 from CO_2, so there is often an appreciable nitrogen impurity in dry ice blocks, even though the partial pressure of nitrogen can be small. Suppose you monitor the amount of *nitrogen* in your equipment by measuring its spectrum.

__**L**_____ Consider the same system, but now we are interested in the spectrum of *carbon dioxide*.

8-10. 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) Complete the following table, writing the equation for both line shapes and denoting which line shape is associated with 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