

## Problem Set PS05

ISSUED: 2/10/99 Due: 2/17/00

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Name \_\_\_\_\_

**Instructions.** Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

### Mathematical Exercises

1. Evaluate the Fourier transform of  $f(t) = \Theta(t)e^{-\alpha t}$  by hand. Check your result using MATHEMATICA. Sketch a plot of both  $f(t)$  and  $\tilde{f}(\omega)$ .
2. Evaluate the Fourier transform of  $f(t) = e^{-\alpha|t|}$  by hand. Check your result using MATHEMATICA. Sketch a plot of both  $f(t)$  and  $\tilde{f}(\omega)$ .

### Exercises

3. A Raman spectrum of a molecular liquid is shown below. Based on hot band profile determine the temperature at which the spectrum was taken.
4. A high resolution ro-vibrational spectrum of a diatomic gas sample is shown below. Based on the P and R branches determine the temperature at which the spectrum was taken. Assume a perfect rigid rotor.
5. Sketch on graph paper the P and R branches for the ro-vibrational spectrum of  $N_2$  ( $\omega_e = 2359\text{cm}^{-1}$   $B_e = 2.0\text{cm}^{-1}$  and  $\alpha_e = 0.017\text{cm}^{-1}$ ).
6. We saw that for a vibration to be IR allowed the dipole must change during the vibration. In more mathematical terms, a transition is IR allowed if

$$\left| \int_{\text{space}} \psi_{\text{final}}^* \vec{x} \psi_{\text{initial}} d\Omega \right|^2 \neq 0.$$

It is IR forbidden if the above integral is equal to zero. For a one dimensional Harmonic oscillator this reduces to

$$\left| \int_{-\infty}^{\infty} \psi_{\text{final}}^* x \psi_{\text{initial}} dx \right|^2 \neq 0.$$

Convince yourself by means of a few examples that  $\Delta n = \pm 1$  is a selection rule for the harmonic oscillator. That is, show

$$\left| \int_{-\infty}^{\infty} \psi_{\text{final}}^* x \psi_{\text{initial}} dx \right|^2 = 0$$

when the final and initial states differ by more than one vibrational quanta.

7. Vibronic transitions can be expressed mathematically as

$$\left| \int_{\text{all ele space}} \int_{\text{all vib space}} \psi_{e,\text{final}}^* \psi_{v,\text{final}}^* \vec{x}_e \psi_{e,\text{initial}} \psi_{v,\text{initial}} d\Omega_e d\Omega_v \right|^2$$

$$\left| \int_{\text{all ele space}} \psi_{v,\text{final}}^* \psi_{v,\text{initial}} d\Omega_v \right|^2 \left| \int_{\text{all vib space}} \psi_{e,\text{final}}^* \vec{x}_e \psi_{e,\text{initial}} d\Omega_e \right|^2.$$

The electronic factor,

$$\left| \int_{\text{all vib space}} \psi_{e,\text{final}}^* \vec{x}_e \psi_{e,\text{initial}} d\Omega_e \right|^2,$$

is some constant which depends on the two electronic levels involved. The vibrational factor,

$$\left| \int_{\text{all ele space}} \psi_{v,\text{final}}^* \psi_{v,\text{initial}} d\Omega_v \right|^2,$$

is called the *Franck–Condon factor* and it determines the strength of the initial vibrational to final vibrational transition. The Franck–Condon factors depend on both the shift in the equilibrium position and the change in force constant in going from the one electronic state to the next. Assume the initial and final electronic states can be modelled with harmonic potentials. Also assume that the force constant for each state is the same. Use MATHEMATICA to calculate a few Franck–Condon factors when the equilibrium positions are the same. Now try some when the equilibrium positions are not the same.

### Conceptual Problems

8. An active area of research these days involves the theoretical and experimental investigation of spectral line broadening mechanisms in liquid phase spectroscopy. These studies provide much useful information including a deepening of our understanding of how molecules interact with their environment. There are two classes of line broadening mechanisms i) homogeneous and ii) inhomogeneous. These mechanisms are distinguished according to their time scales. Homogeneous broadening mechanisms are processes which occur much faster than the speed of the instrument making the measurement. Conversely Inhomogeneous mechanisms occur on a time scale much slower than the instrument making the measurement. In pure homogeneous process all the molecules that contribute to the observed signal rapidly sample many local environments. This broadens the contribution of each individual molecule. That is the signal arising from each molecule is itself broad and is very much like the signal from any other molecule. In the pure inhomogeneous case, each molecule is “frozen” in its own local environment. Therefore although the signal from any one molecule is rather narrow, the observed signal is the sum of the signals from all the molecules each of which has a slightly different central frequency. Thus the observed spectral line is broad. In real systems both mechanisms are at work, however many times one of the mechanisms dominate.

- (a) Based on the above discussion and your chemical intuition, how do think the relative contribution of homogeneous and inhomogeneous broadening goes with temperature.

- (b) Based on the above discussion and your chemical intuition, how do think the relative contribution of homogeneous and inhomogeneous broadening goes with viscosity.
- (c) A dye is embedded in plastic, which mechanism would you suspect contributes most the broadening
- (d) In a regular Raman experiment one of the strong vibrational line of liquid pyridine is about  $1\text{cm}^{-1}$  broad. In a SERS (surface enhanced Raman scattering) experiment the Raman signal is enormously enhanced when pyridine adsorbs to a rough silver surface. All one sees in the SERS spectrum is the signal coming from the adsorbed pyridine molecules. The same line as seen in the regular Raman experiment is now about  $10\text{cm}^{-1}$  broad. What does this say about the kinetics of the adsorption process. That is, when a pyridine molecule sticks to the surface does it come off right a way and get replaced by a new pyridine or does it stay adsorbed for longer period of time?
- (e) Try to draw a picture that illustrates the difference between homogeneous and inhomogeneous broadening.

9. What is the Stokes shift?

10. Sketch the ground and first excited electronic energy levels for the following cases

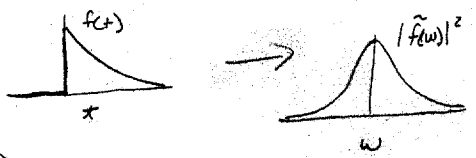
Force Constant	Equilibrium Position
$k_{\text{ground}} > k_{\text{excited}}$	$R_{eq,\text{ground}} = R_{eq,\text{excited}}$
$k_{\text{ground}} > k_{\text{excited}}$	$R_{eq,\text{ground}} < R_{eq,\text{excited}}$
$k_{\text{ground}} < k_{\text{excited}}$	$R_{eq,\text{ground}} < R_{eq,\text{excited}}$
$k_{\text{ground}} > 0, k_{\text{excited}} = 0$	--

11. Does the following data for oxygen make sense? Explain

Electronic level	$R_{eq}$	$B_e$
ground	$1.208\text{\AA}$	$1.46\text{cm}^{-1}$
first excited	$1.216\text{\AA}$	$1.43\text{cm}^{-1}$
second excited	$1.604\text{\AA}$	$0.82\text{cm}^{-1}$

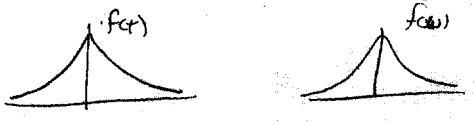
①  $\tilde{f}(\omega) = \int_{-\infty}^{\infty} \Theta(x) e^{-\alpha x} e^{i\omega x} dx = \int_0^{\infty} e^{(-\alpha+i\omega)x} dx$

$f(x) = \frac{1}{-\alpha+i\omega} e^{(-\alpha+i\omega)x} \Big|_0^{\infty} = \frac{1}{\alpha-i\omega}$



②  $\tilde{f}(\omega) = \int_{-\infty}^{\infty} e^{-\alpha|x|} e^{i\omega x} dx = \int_{-\infty}^0 e^{(\alpha+i\omega)x} dx + \int_0^{\infty} e^{(-\alpha+i\omega)x} dx$

$\tilde{f}(\omega) = \frac{1}{\alpha+i\omega} + \frac{1}{\alpha-i\omega} = \frac{2\alpha}{\alpha^2 + \omega^2}$  ← This type of function is called a Lorentzian



③ For Morse Oscillator  $\Delta E = h\omega - 2h\nu x_e(n+1)$   
 From graph  $2h\nu x_e = 10 \text{ cm}^{-1}$ ,  $h\nu = 1010 \text{ cm}^{-1}$   
 so  $\Delta E_{0 \rightarrow 1} = 1000 \text{ cm}^{-1}$   
 $\Delta E_{1 \rightarrow 2} = 990 \text{ cm}^{-1}$   
 $\Delta E_{2 \rightarrow 3} = 980 \text{ cm}^{-1}$

$\frac{n_1}{n_0} = e^{-\Delta E_{0 \rightarrow 1} / kT} \Rightarrow \frac{0.37}{1.0} = 0.37 = e^{-1000 \text{ cm}^{-1} / kT}$

$\ln(0.37) = -9800 \text{ cm}^{-1} / kT \Rightarrow kT = 9800 \text{ cm}^{-1} / \ln(1/0.37)$

so  $kT = 1005 \text{ cm}^{-1} \Rightarrow T = 1449 \text{ K}$

Should verify with other lines

④

skip this one

⑤ your graph

7 of 3

⑥ your work on Mathematics

⑦ your work on Mathematics

⑧ (a) As  $T \uparrow$  homogeneous broadening tends to dominate the broadening

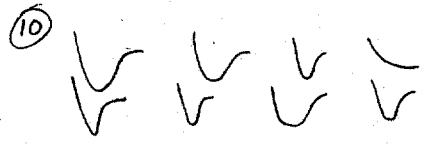
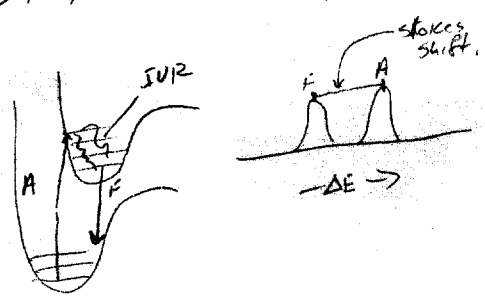
(b) As  $\eta \uparrow$  inhomogeneous broadening tends to dominate the broadening

(c) inhomogeneous broadening

(d) skip this question - not enough info

(e) homogeneous inhomogeneous:

⑨



⑩ yes  
 $I \uparrow$  Bec