

**NORTH CAROLINA STATE UNIVERSITY**

Department of Chemistry

Name \_\_\_\_\_

CH 795T

Molecular Spectroscopy

Problem Set #6

Nov. 5, 2007

Due Date: Nov. 16, 2007

This problem set concerns the calculation of absorption and Raman spectra using TIMETHERM. We will explore the absorption spectrum and Raman excitation profile (REP) for model systems.

The basic system is a molecule with a single vibrational mode of  $1000\text{ cm}^{-1}$ . This could be a diatomic (e.g.  $\text{F}_2$ ).

1. Using a Lorentzian broadening of  $\Gamma = 50\text{ cm}^{-1}$ , a mode frequency of  $\omega = 1000\text{ cm}^{-1}$  and a temperature of 300 K calculate the absorption spectrum (ABS) and REP for the following cases  
 $S = 0.1, S = 0.5, S = 1.0, S = 2.0$ 
  - A. Plot both the ABS and REP for each value of the electron-phonon coupling constant.
  - B. Why does the REP differ in shape from ABS?
2. Using a mode frequency of  $1000\text{ cm}^{-1}$ ,  $S = 1.0$ , and a temperature of 300 K calculate the value of the ABS and REP for the following values of the Lorentzian broadening.  $\Gamma = 100\text{ cm}^{-1}, \Gamma = 200\text{ cm}^{-1}, \Gamma = 500\text{ cm}^{-1}, \Gamma = 1000\text{ cm}^{-1}$ ,
  - A. Plot the ABS and REP.
  - B. To understand what is occurring plot  $\langle f|i(t)\rangle$  for each of these cases.
  - C. Describe the effect of increasing  $\Gamma$  on the time-correlation function and on the spectra.
3. Perform two-mode calculations using the following parameters.
  - I. System 1  
 $\omega_1 = 1000\text{ cm}^{-1}, S_1 = 0.5$   
 $\omega_2 = 500\text{ cm}^{-1}, S_2 = 2.0$
  - II. System 2  
 $\omega_1 = 1000\text{ cm}^{-1}, S_1 = 0.5$   
 $\omega_2 = 100\text{ cm}^{-1}, S_2 = 10.0$
  - III. System 3  
 $\omega_1 = 1000\text{ cm}^{-1}, S_1 = 0.5$   
 $\omega_2 = 30\text{ cm}^{-1}, S_2 = 33$
  - A. What is the sum  $\lambda = S_1\omega_1 + S_2\omega_2$  in each case?
  - B. What is the effect of including a low frequency mode in each case?