

NORTH CAROLINA STATE UNIVERSITY

Department of Chemistry

Name _____

CH 795T

Molecular Spectroscopy

Problem Set #7

Nov. 26, 2007

Due Date: Dec. 5, 2007

1. Consider a sum-over-states picture for absorption and Raman cross sections for a metalloporphyrin (or other pi-system) that has a B band and a Q band. The energy of 0-0' transition for each band is given by E_{B0} and E_{Q0} , respectively. Let us assume that these values of $40,000 \text{ cm}^{-1}$ and $20,000 \text{ cm}^{-1}$, respectively. Assume that $\Gamma_f = 100 \text{ cm}^{-1}$.

$$\sigma = \sum_v \frac{\langle i | e\sigma | f \rangle^2 \langle 0 | v \rangle^2}{E_{fv} - E_{B0} - \hbar\omega - i\Gamma_f} + \sum_u \frac{\left(\frac{\langle r | \left(\frac{\partial H}{\partial Q} \right) | f \rangle \langle u | Q | v \rangle \langle i | e\sigma | r \rangle}{E_{f,v} - E_{r,u}} \right)^2 \langle 0 | u \rangle^2}{E_{fu} - E_{Q0} - \hbar\omega - i\Gamma_f}$$

The transition moment is

$$\langle i | e\sigma | f \rangle = 1$$

And the Herzberg-Teller coupling is

$$\frac{\langle r | \left(\frac{\partial H}{\partial Q} \right) | f \rangle \langle i | e\sigma | r \rangle}{E_{f,v} - E_{r,u}} = 0.3$$

To make this tractable we assume that the Herzberg-Teller coupling is 1/10 as big as the transition moment. We will normalize the transition moment to 1. Furthermore, we consider the fact that the Frank-Condon envelop in a sum-over-states model at zero temperature is given by the Poisson distribution. Thus, the formula becomes:

$$\sigma = \sum_v \frac{e^{-S} S^v}{v!} \left(\frac{\langle 0 | v \rangle^2}{E_{fv} - E_{B0} - \hbar\omega - i\Gamma_f} + \sum_u \frac{0.09 (\langle u | Q | v \rangle \langle 0 | u \rangle)^2}{E_{fu} - E_{Q0} - \hbar\omega - i\Gamma_f} \right)$$

Assume that the vibronic mode is 1000 cm^{-1} . Determine the shape of the absorption spectrum if S has the following values S = 0.1, 0.5, 1.0 and 2.0 by filling in the appropriate values in the tables below. Consider interactions only up to $v = 4$. Assume that $\alpha = 1$.

S (overlaps)	0.1	0.5	1.0	2.0
$\langle 0 0'\rangle$				
$\langle 0 1'\rangle$				
$\langle 0 2'\rangle$				
$\langle 0 3'\rangle$				
$\langle 0 4'\rangle$				

Coupling	Magnitude
$\langle 1' Q 0'\rangle$	
$\langle 2' Q 1'\rangle$	
$\langle 3' Q 2'\rangle$	
$\langle 4' Q 3'\rangle$	

FC	0.1	0.5	1.0	2.0
$\langle 0 0'\rangle^2$				
$\langle 0 1'\rangle^2$				
$\langle 0 2'\rangle^2$				
$\langle 0 3'\rangle^2$				
$\langle 0 4'\rangle^2$				

VB	0.1	0.5	1.0	2.0
$\langle 1' Q 0'\rangle^2 \langle 0 1'\rangle^2$				
$\langle 2' Q 1'\rangle^2 \langle 0 2'\rangle^2$				
$\langle 3' Q 2'\rangle^2 \langle 0 3'\rangle^2$				
$\langle 4' Q 3'\rangle^2 \langle 0 4'\rangle^2$				

$\langle 0' Q 1'\rangle^2 \langle 0 0'\rangle^2$				
$\langle 1' Q 2'\rangle^2 \langle 0 1'\rangle^2$				
$\langle 2' Q 3'\rangle^2 \langle 0 2'\rangle^2$				
$\langle 3' Q 4'\rangle^2 \langle 0 3'\rangle^2$				

2. Calculate the resonant Raman cross sections for the same two transitions. Use the Kramer's-Heisenberg-Dirac formula for the Raman cross section. The A-term and B-terms are:

$$\left(\alpha_{\rho\sigma} \right)_{if} = \left(\sum_v \frac{\langle i0 | e\sigma | fv \rangle \langle fv | e\rho | i1 \rangle}{E_{fv} - E_{B0} - \hbar\omega - i\Gamma_v} + \sum_u \frac{\langle i0 | e\sigma | ru \rangle \langle ru | (\partial H / \partial Q) | fv \rangle \langle v | Q | u \rangle \langle fv | e\rho | i1 \rangle}{E_{r0} - E_{n1} \over E_{fv} - E_{Q0} - \hbar\omega - i\Gamma_v} \right)^2$$

Here we will assume that the transition moments and Herberg-Teller term have the values given above:

$$\langle i | e\sigma | r \rangle \frac{\langle ru | (\partial H / \partial Q) | fv \rangle}{E_{r0} - E_{fv}} = 0.3$$

and $\langle i | e\sigma | f \rangle = \langle i | e\rho | f \rangle = 1$

$$\alpha_{if} = \left(\sum_v \frac{\langle 0 | v \rangle \langle v | 1 \rangle}{E_{fv} - E_{B0} - \hbar\omega - i\Gamma_v} + \sum_u \frac{0.3 \langle i | u \rangle \langle u | Q | v \rangle \langle v | 1 \rangle}{E_{fv} - E_{Q0} - \hbar\omega - i\Gamma_v} \right)^2$$

As above for the absorption spectrum, please fill in the Tables with the appropriate values that predict the Raman excitation profiles for the Franck-Condon active and vibronic bands. You will need to calculate the FC factors for some of the overlaps to the final $|1\rangle$ state. Use the example in Problem set 6 to do this.

S (overlaps)	0.1	0.5	1.0	2.0
$\langle 0' 1 \rangle$				
$\langle 1' 1 \rangle$				
$\langle 2' 1 \rangle$				
$\langle 3' 1 \rangle$				

FC	0.1	0.5	1.0	2.0
$\langle 0 0' \rangle \langle 0' 1 \rangle$				
$\langle 0 1' \rangle \langle 1' 1 \rangle$				
$\langle 0 2' \rangle \langle 2' 1 \rangle$				
$\langle 0 3' \rangle \langle 3' 1 \rangle$				

VB	0.1	0.5	1.0	2.0
$\langle 0 0'\rangle\langle 0' Q 1'\rangle\langle 1' 1\rangle$				
$\langle 0 1'\rangle\langle 1' Q 2'\rangle\langle 2' 1\rangle$				
$\langle 0 1'\rangle\langle 1' Q 0'\rangle\langle 0' 1\rangle$				
$\langle 0 2'\rangle\langle 2' Q 3'\rangle\langle 3' 1\rangle$				
$\langle 0 2'\rangle\langle 2' Q 1'\rangle\langle 1' 1\rangle$				
$\langle 0 3'\rangle\langle 3' Q 2'\rangle\langle 2' 1\rangle$				
$\langle 0 4'\rangle\langle 4' Q 3'\rangle\langle 3' 1\rangle$				

3. Sketch or calculate the absorption spectrum and REP for each case ($S = 0.1, 0.5, 1.0$ and 2.0). Keep in mind that there are two bands and that the vibronic coupling term is 0.3 at the amplitude level.