

Assignment 12

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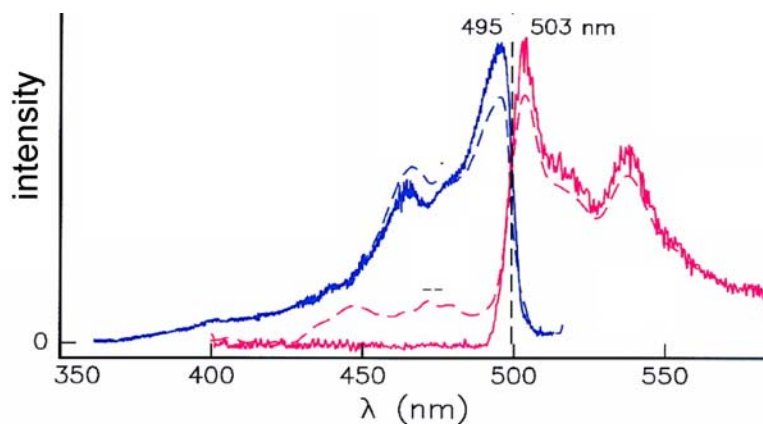
Physics G731

Fall 2007

Due Wednesday, Dec. 5.

Vibronic structure of fluorescent proteins. The figure below shows absorption and emission spectra of a fluorescent protein as blue and red traces, respectively.

- (a) From the data in the figure, estimate the energy difference (in cm^{-1}) between the minima of the ground and excited state energy surfaces.
- (b) Estimate the frequency (in cm^{-1}) of one vibrational mode that is coupled to the electronic transition.
- (b) Estimate the (dimensionless) coupling strength S of this vibrational mode to the electronic transition, assuming that both absorption and emission occur from the lowest vibrational level.



Spectral moment analysis. Although electronic line shapes can be quite complex, you can evaluate some general spectral properties starting from the fundamental expression

$$\sigma(\bar{\nu}) = 4\pi^2\alpha\bar{\nu} \left| \hat{e} \cdot \vec{R}_{fi} \right|^2 \mathcal{L}(\bar{\nu} - \bar{\nu}_{fi})$$

for the absorption cross section.

- (a) Consider all transitions from initial states $|i\rangle = |g\rangle |\chi_i\rangle$ on the ground state energy surface to final states $|f\rangle = |e\rangle |\chi_f\rangle$ on an excited energy surface. Derive the general form

$$\sigma(\bar{\nu}) = 4\pi^2\alpha\bar{\nu} \left| \hat{e} \cdot \vec{R}_{eg} \right|^2 \mathcal{S}(\bar{\nu})$$

for the absorption cross section of a vibronically broadened electronic transition in the Condon approximation (which neglects the dependence of the transition dipole $\vec{R}_{eg} = \langle e | \sum_j z_j \vec{r}_j | g \rangle$ on nuclear displacements). The overlaps of the initial and final vibrational states $|\chi_i\rangle$ and $|\chi_f\rangle$, at energies E_i and E_f , respectively, control the shape of the asymmetric vibronic function

$$\mathcal{S}(\bar{\nu}) = \sum_{if} p_i |\langle \chi_f | \chi_i \rangle|^2 \mathcal{L}(\bar{\nu} - \bar{\nu}_{fi}),$$

by determining the relative contributions of normalized lineshapes $\mathcal{L}(\bar{\nu} - \bar{\nu}_{fi})$ centered at $\bar{\nu}_{fi} = (E_f - E_i)/hc$. Next, you will explore how the absorption spectrum changes with temperature by examining the moments

$$\Sigma_n = \int_0^\infty \bar{\nu}^n \frac{\sigma(\bar{\nu})}{\bar{\nu}} d\bar{\nu}$$

of the function $\sigma(\bar{\nu})/\bar{\nu}$.

- (b) Use closure ($\sum_f |\chi_f\rangle \langle \chi_f| = 1$) and normalization of $\mathcal{L}(\bar{\nu})$ ($\int_0^\infty \mathcal{L}(\bar{\nu}) d\bar{\nu} = 1$) to show that the zeroth moment Σ_0 is independent of the initial state occupation probabilities p_i (assumed to be normalized, $\sum_i p_i = 1$), and thus does not vary with temperature. Average over the orientation of the molecular transition dipole \vec{R}_{eg} with respect to the polarization vector \hat{e} to show that

$$\bar{\Sigma}_0 = \left\langle \int_0^\infty \frac{\sigma(\bar{\nu})}{\bar{\nu}} d\bar{\nu} \right\rangle = \frac{4}{3} \pi^2 \alpha R_{eg}^2$$

has a constant value proportional to the square of R_{eg} .

(c) Express the first moment

$$\Sigma_1 = \Sigma_0 \left(\frac{1}{hc} \right)^n \langle (V_e - V_g) \rangle_T$$

in terms of the thermally averaged expectation value

$$\langle \cdots \rangle_T = \sum_i p_i \langle \chi_i | \cdots | \chi_i \rangle$$

of the difference potential $V_e - V_g$ evaluated on the *ground state* surface. The fact that the vibrational states are eigenstates of the nuclear Hamiltonian will allow you to make the useful substitutions

$$E_i |\chi_i\rangle = (T_n + V_g) |\chi_i\rangle$$

and

$$E_f |\chi_f\rangle = (T_n + V_e) |\chi_f\rangle,$$

where the kinetic energy operator $T_n = -\frac{1}{2}\hbar^2 \sum_\alpha \partial^2 / \partial Q_\alpha^2$ has the same form on both surfaces. You will need to assume that the line shape function is symmetric ($\mathcal{L}(\bar{\nu}) = \mathcal{L}(-\bar{\nu})$), so that $\int \bar{\nu} \mathcal{L}(\bar{\nu} - E/hc) d\bar{\nu} = E/hc$.

To evaluate the first moment explicitly, you will make the harmonic approximation and further assume linear coupling, so that the minimum of the excited state potential surface

$$V_e = E_0 + \sum_\alpha \frac{1}{2} \omega_\alpha^2 (Q_\alpha - \Delta_\alpha)^2$$

is displaced horizontally (by Δ_α) as well as vertically (by $E_0 = hc\bar{\nu}_0$) with respect to the ground state potential surface

$$V_g = \sum_\alpha \frac{1}{2} \omega_\alpha^2 Q_\alpha^2,$$

but the frequencies and normal modes are identical on both surfaces. For simplicity, express the horizontal shift

$$\Delta_\alpha = S_\alpha^{1/2} \sqrt{\frac{2\hbar}{\omega_\alpha}}$$

along mode α in terms of the dimensionless electron-nuclear coupling strength S_α .

(d) Under these conditions, show that the first moment

$$\Sigma_1 = \Sigma_0 \left(\bar{\nu}_0 + \sum_{\alpha} S_{\alpha} \bar{\nu}_{\alpha} \right)$$

has a temperature-independent value determined by the vibrational frequencies and coupling strengths. Further, show that the centroid $\langle \bar{\nu} \rangle = \Sigma_1 / \Sigma_0$ of the absorption spectrum yields the vertical excitation energy from the minimum of the ground state surface ($\{Q_{\alpha} = 0\}$), which is larger than the separation $\bar{\nu}_0$ between the minima of the two surfaces.

(e) Show that the second moment

$$\Sigma_2 = \Sigma_0 \left[\left(\frac{\Sigma_1}{\Sigma_0} \right)^2 + \sum_{\alpha} (2\bar{n}_{\alpha} + 1) S_{\alpha} \bar{\nu}_{\alpha}^2 + \bar{\Gamma}^2 \right]$$

does depend on temperature through the thermal occupation factors

$$\bar{n}_{\alpha} = \frac{\sum_{\alpha} n_{\alpha} \exp(-n_{\alpha} hc \bar{\nu}_{\alpha} / k_B T)}{\sum_{\alpha} \exp(-n_{\alpha} hc \bar{\nu}_{\alpha} / k_B T)}$$

leading to an overall mean squared linewidth

$$\langle \Delta \bar{\nu}^2 \rangle = \langle \bar{\nu}^2 \rangle_T - \langle \bar{\nu} \rangle^2 = \frac{\Sigma_2}{\Sigma_0} - \left(\frac{\Sigma_1}{\Sigma_0} \right)^2 = \sum_{\alpha} S_{\alpha} \bar{\nu}_{\alpha}^2 \coth \left(\frac{hc \bar{\nu}_{\alpha}}{2k_B T} \right) + \bar{\Gamma}^2.$$

Here, $\bar{\Gamma}^2 = \int \bar{\nu}^2 \mathcal{L}(\bar{\nu}) d\bar{\nu}$ is the mean squared linewidth of an individual transition, which you will assume to be constant (in fact, it may vary slightly because of shorter lifetimes for higher-lying vibrational states).