

Spectroscopy

I. The Long-Wavelength Approximation **Equation Section (Next)**

Because the wavelength of light is much larger than the size of a molecule, we can assume that the molecule only sees an oscillating dipole field. We want to quantify this result further, and see where it might fail.

The most useful spectra for chemical purposes come from UV-vis spectroscopy (where one measures the energies of valence orbitals directly), but one can also obtain interesting information by from the X-ray regime, where one excites (or ionizes) core electrons. One can use this information to find the oxidation states of atoms, for instance and, by carefully monitoring absorbance and/or fluorescence, gain some information about the valence orbitals and orbital energies.

In the UV-regime, as discussed in class and in the notes, the wavelength of the radiation is generally much larger than the size of the orbitals with which it interacts, so the long-wavelength approximation works quite well. This is less clear in the X-ray regime, when we are considering, say, the ionization of the 1s orbital in Iron (or some other “heavy atom”). The energy of the 1s orbital is well approximated by the Hydrogenic formula,

$$E \approx -\frac{Z^2}{2} \quad (1.1)$$

and the orbital shape is quite close to

$$\psi_{\mathbf{r}} = \sqrt{\frac{Z^3}{\pi}} e^{-Zr} \quad (1.2)$$

where Z is the atomic number in question. From problem I in problem set 3, we know that the average distance of an electron from the atom in a 1s orbital is given by

$$\begin{aligned} \langle r \rangle_{n,l,m} &\equiv \frac{1}{2Z} (3n^2 - l(l+1)) \\ &= \frac{3}{2Z} \end{aligned} \quad (1.3)$$

Combining what we know, then, we have that the ionization potential for a 1s-electron in an atom is approximate

$$IP \approx \frac{1}{2} Z^2 \quad (1.4)$$

and the size of the 1s-orbital is approximately.

$$R \approx \frac{3}{2Z} \quad (1.5)$$

Once the extent of an orbital is the same size as $\frac{\lambda}{2}$, then it is possible that one end of the molecule is in a strong negative field while the other end is in a strong positive field, and the long-wavelength approximation will not be valid. Indeed, the long-wavelength approximation will be questionable whenever the electric field changes more than a few percent over the extent of a molecule.

A. At about what value of Z does the long-wavelength approximate begin to break down for the excitation of the core electrons?

You may find it helpful that $1 \text{ Hartree} = 4.359 \cdot 10^{-18} \text{ Joule}$.

II. Population Inversion and the Laser **Equation Section (Next)**

This is a “classic” problem, wherein we relate what we have learned about spectroscopy to describe the populations of energy levels. This analysis actually dates all the way back to Einstein, who laid the groundwork for the discovery of the laser in 1917.

Let i denote the initial state of a system and f denote its final state; we assume the initial state has lower energy than the final state. Suppose the system is in equilibrium with an electromagnetic (=light) field, so that the number of molecules in the initial state, N_i , and the number of molecules in the final state, N_f . The rate at which molecules are excited from the initial state to the final state in the presence of light with energy density $g \hbar \omega$ should be proportional to the energy density of the light and the number of molecules in the initial state. Einstein wrote the constant of proportionality as B_{fi} , and so the excitation rate is

$$\text{rate of absorbance} = B_{fi} \cdot g \hbar \omega_{fi} N_i \quad (\text{II.1})$$

We have noted that the rate of stimulated emission is the same as the rate of absorbance. Consequently, the rate of stimulate emission will be proportional to the energy density and the number of molecules in the final state, with the same constant of proportionality, $B_{if} = B_{fi}$. Thus

$$\text{rate of stimulated emission} = B_{fi} \cdot g \hbar \omega_{fi} N_f. \quad (\text{II.2})$$

As anyone who has ever done a spectrum knows, however, a molecule is quite capable of fluorescing even in the total absence of incident radiation. This process, known as spontaneous emission of light,¹ is clearly independent of the energy density in the incident light field and is proportional to the number of molecules in the excited state. Of course, the constant of proportionality is probably different from the proportionality constant for stimulated emission, since the two processes are fundamentally different. So we write the constant of proportionality as A_{fi} and have.

$$\text{rate of spontaneous emission} = A_{fi} N_f \quad (\text{II.3})$$

A_{fi} and B_{fi} are called the Einstein rate coefficients. Clearly, both coefficients are positive. There is, obviously, no such thing as “spontaneous absorption.”

A. Derive a formula for B_{fi} from Fermi's Golden Rule.

Using Eqs. (II.1)-(II.3), we can write the rate of change for the number of atoms in the initial

$$\frac{dN_i}{dt} = -B_{fi} g \hbar \omega_{fi} N_i + B_{fi} g \hbar \omega_{fi} N_f + A_{fi} N_f \quad (\text{II.4})$$

and “final” states,

$$\frac{dN_f}{dt} = +B_{fi} g \hbar \omega_{fi} N_i - B_{fi} g \hbar \omega_{fi} N_f - A_{fi} N_f \quad (\text{II.5})$$

B. Comparing Eqs. (II.4) and (II.5), why is $N_i > N_f$.

At equilibrium, $\frac{dN_i}{dt} = \frac{dN_f}{dt} = 0$. We have, then, setting Eqs. (II.4) and (II.5) equal to one another, that

$$-B_{fi} g \hbar \omega_{fi} N_i + B_{fi} g \hbar \omega_{fi} N_f + A_{fi} N_f = B_{fi} g \hbar \omega_{fi} N_i - B_{fi} g \hbar \omega_{fi} N_f - A_{fi} N_f \quad (\text{II.6})$$

and so

$$\frac{N_f}{N_i} = \frac{B_{fi} g \hbar \omega_{fi}}{B_{fi} g \hbar \omega_{fi} + A_{fi}} \quad (\text{II.7})$$

¹ What exactly is spontaneous emission? It is a quantum effect, and if we had used a quantum theory for light the phenomenon of spontaneous emission would have fallen out of the theory very naturally. Essentially, every field has a “zeroth order” oscillation, and this is true even of the vacuum. The “vacuum oscillation” is associated with the creation and annihilation of a particle (or particles) in time, and can occur so long as the energy times the duration for which the particles exist is suitably small. More precisely, one has that $\Delta E \Delta t \approx \frac{\hbar}{2}$. So that a photon can “be created” provided it is “destroyed” again quickly enough. If the photon, however, stimulates a transition during its fleeting existence, after the “stimulating” photon has disappeared, the “stimulated” photon will still exist. Voila, “spontaneous” emission.

C. Suppose the light source is very intense, so that $B_{fi}g \hbar\omega_{fi}$ is much larger than A_{fi} . Show that

$$\frac{N_f}{N_i} \approx 1 - \frac{A_{fi}}{B_{fi}g \hbar\omega_{fi}} \quad (11.8)$$

D. Explain why, in a very intense light source, there is essentially no net absorbance of radiation. That is, why will light of frequency ω_{fi} shine “right through” a sample if it is strong enough.

We would like to find an expression for A_{fi} , but we don't want to have to do it the “right way” and consider the quantum theory of light. One way to do this is to put our system in an oven. Then, the relative populations of the final and initial states are given by the Boltzmann distribution, so

$$\frac{N_f}{N_i} = e^{-\hbar\omega_{fi}/kT} \quad (11.9)$$

where k is Boltzmann's constant and T is the absolute temperature. The other unknown in Eq. (11.7), $g \hbar\omega_{fi}$, is the intensity of the light source. However, the molecule is in an oven, so the light source is the black-body radiation from the oven's walls and, assuming these are also at temperature T (that is, our oven is perfectly insulated), we can use the black-body radiation law

$$g \hbar\omega_{fi} = \frac{2\hbar\omega_{fi}^3}{\pi c^3} \cdot \left(e^{\hbar\omega_{fi}/kT} - 1 \right)^{-1}. \quad (11.10)$$

We substitute this results into Eq. (11.7) to obtain

$$\begin{aligned} e^{-\hbar\omega_{fi}/kT} &= \frac{B_{fi} \frac{2\hbar\omega_{fi}^3}{\pi c^3} \cdot \left(e^{\hbar\omega_{fi}/kT} - 1 \right)^{-1}}{B_{fi} \frac{2\hbar\omega_{fi}^3}{\pi c^3} \cdot \left(e^{\hbar\omega_{fi}/kT} - 1 \right)^{-1} + A_{fi}} \\ e^{\hbar\omega_{fi}/kT} &= 1 + \frac{A_{fi}}{B_{fi} \frac{2\hbar\omega_{fi}^3}{\pi c^3} \cdot \left(e^{\hbar\omega_{fi}/kT} - 1 \right)^{-1}} \\ A_{fi} &= \frac{2\hbar\omega_{fi}^3}{\pi c^3} B_{fi}. \end{aligned} \quad (11.11)$$

E. The red-orange glow of hot hydrogen gas (remember the Hindenberg!) is due to the 3p-2s transition of the Hydrogen atom, $A_{fi} = 6.7 \cdot 10^7 \frac{1}{s}$. Compute $\frac{N_f}{N_i}$ and $\frac{A_{3p,2s}}{g \hbar\omega_{3p,2s}}$ at $T = 300^\circ K$, $T = 10,000^\circ K$, and $T = 100,000^\circ K$. What can you say about the relative rates of spontaneous emission, A_{fi} and stimulated emission, $B_{fi}g \hbar\omega_{fi}$ in the absence of light?

How does a laser work? As a very simple case, we consider the “green line” for the Argon ion laser. This resembles a 3-level laser system, which is the simplest (but four-level lasers are more efficient) type of laser. The Argon ion is generated by a high-voltage electric discharge, which ionizes the Argon atom and excites it to a high-energy state, which then relaxes to the $^4D_{5/2}$ state. This state then decays to the ground state $^2P_{3/2}$. However, because we have brought in a “third state” (the highly excited ion), we can achieve

population inversion. This is helped by the fact that the excited state of interest decays very slowly (this is a spin-forbidden transition), so that A_{fi} is very small.

As an example that we can actually “solve”, we might consider a three-level system like the one shown below, which (vaguely) resembles the intensity-determining features of a four-level laser like the Nd-YAG laser. In this case, the system is “pumped” with light of frequency ω_{31} , and then population inversion is achieved between the second and third states, causing a laser transition. We can write the rate coefficients as

$$\begin{aligned}\frac{dN_1}{dt} &= -g \hbar\omega_{31} B_{31}N_1 + A_{21}N_2 + A_{31}N_3 + g \hbar\omega_{31} B_{31}N_3 \\ \frac{dN_2}{dt} &= A_{32}N_3 - A_{21}N_2 \\ \frac{dN_3}{dt} &= g \hbar\omega_{31} B_{31}N_1 - A_{32}N_3 - A_{31}N_3 - g \hbar\omega_{31} B_{31}N_3\end{aligned}\tag{II.12}$$

and, as before, at equilibrium $\frac{dN_1}{dt} = \frac{dN_2}{dt} = \frac{dN_3}{dt} = 0$. From the second equation we find that

$$\frac{N_3}{N_2} = \frac{A_{21}}{A_{32}}\tag{II.13}$$

Equation (II.13) is a general result, and can be easily understood (we probably could have guessed it). Clearly, we can have a laser only if $N_3 > N_2$, and it is best if N_3 is much greater than N_2 ($N_3 \gg N_2$).

F. From Eq. (II.13), what can you say about the relative spontaneous emission rates for the “higher” and “lower” energy states in a laser?

Based on Eq. (II.13), why do laser lines usually correspond to “forbidden transitions.”

For example, if it were not for the perturbation inflicted on the Nd^{3+} ion by the $\text{Y}_3\text{Al}_5\text{O}_{12}$ lattice, the popular Nd-YAG laser transition corresponding to A_{32} is electric dipole forbidden, magnetic dipole forbidden, electric quadrupole forbidden, and magnetic quadrupole forbidden, while the transition corresponding to A_{21} is electric dipole allowed.

III. Lifetime Broadening Equation Section (Next)

Most of the effects that broaden spectral lines could be eliminated, in principle, by taking a spectrum at zero temperature and zero pressure and, in fact, high-resolution spectra are often taken under ultra-high vacuum conditions at liquid-helium temperatures. However, there is always a “homogeneous broadening” associated with spontaneous emission: there is no way to avoid the “decay time” associated with spontaneous emission, as it is an inherent property of the system.²

The rate of spontaneous decay is given by Eq. (II.3), and in order to relate this to expressions for homogeneous broadening (see the notes) we need to find the probability, P_τ that a molecule in its excited state at $t = 0$ will still be in its excited state at $t = \tau$. The rate of transition is known from Eq. (II.3), and so the probability a molecule in its excited state at time $t = \tau$ “emits” to the ground state (or, more properly, state i), is proportional to the number of molecules in the excited state (which is proportional to P_τ if the light source measuring the absorption spectrum is not very powerful), so we have

$$dP_\tau = -A_{fi}P_\tau d\tau.\tag{III.1}$$

² This is a lie. There is a weird quantum-mechanical result that says that if you constantly observe a system it can never change its state. For obvious reasons, it is called the “watched pot paradox.” But “constantly observing” a system is extremely difficult and is not done in the context of chemical spectroscopy.

A. Show that $P \tau = e^{-A_{21}\tau}$.

The natural lifetime of an excited state is defined as the time it takes for $P \tau$ to decay from $P 0 = 1$ to $P \tau = \frac{1}{e}$ in the absence of external fields. It follows from the definition and Eq. (III.1) that the lifetime of a state is

$$\tau \equiv \frac{1}{A_{21}}. \quad (\text{III.2})$$

B. Referring to the section on homogeneous broadening in the notes, show that the line shape is given by

$$I \omega \equiv \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} \frac{p_i}{8\pi} \left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 \left(\frac{A_{21}}{A_{21}^2 + \omega - \omega_{fi}}^2 - \frac{A_{21}}{A_{21}^2 + \omega + \omega_{fi}}^2 \right). \quad (\text{III.3})$$

If we assume that the initial state is the ground state ($i = 0$), that the incident light is very weak (so $p_0 \approx 1$ and $p_f \approx 0$), we find that

$$I \omega \equiv \frac{1}{8\pi} \left| \langle \Phi_f | \hat{\mu}_x | \Phi_0 \rangle \right|^2 \left(\frac{A_{f0}}{A_{f0}^2 + \omega - \omega_{f0}}^2 - \frac{A_{f0}}{A_{f0}^2 + \omega + \omega_{f0}}^2 \right). \quad (\text{III.4})$$

C. Plot Eq. (III.4), assuming that the “pre-factor” is equal to $\frac{1}{\pi}$.

The full-width at half-maximum of the spectral line you just plotted is

$$2A_{21} = \frac{2}{\tau} \quad (\text{III.5})$$

Putting the molecule in any external field at all with broaden the line further and shorten the lifetime of the excited state. The error in frequency of the excited state, then, is always greater than

$$\Delta\omega \geq 2A_{21} = \frac{2}{\tau} \quad (\text{III.6})$$

and so the energy uncertainty in the spectral line satisfies the inequality

$$\Delta E \equiv \hbar \Delta\omega \geq \hbar \frac{2}{\tau} \quad (\text{III.7})$$

$$\tau \Delta E \geq \frac{\hbar}{2}$$

Equation (III.7) is sometimes called the “energy-time” uncertainty principle but it should be clear that it is really just a manifestation of the fundamental relationship from the Fourier transform, which is usually stated

$$\Delta t \cdot \Delta\nu \geq \frac{1}{2}. \quad (\text{III.8})$$

One of the most important uses of spectral states with long lifetimes is the laser, as discussed in the previous problem. Another important use is in the measurement of time. The *definition* of a second is that the time it takes for 9192631770 periods of the oscillation associated with the hyperfine splitting in the ^{133}Cs atom. (This is the basis of the “atomic clocks” used in satellite positioning systems.)

Clearly, in order to define a “second” in this way we must know the frequency of an oscillation very accurately, and this can only be done if width of the spectral line corresponding to a transition is very, very small.

The longest lived electronic excited state we know of is the $^2F_{7/2}$ to $^2S_{1/2}$ transition for $^{172}\text{Yb}^+$, which has a characteristic wavelength of 467 nm and a lifetime of about 8.4 years. (The transition is electric *octupole* allowed.) According to Eq. (III.8), we should be able to measure the frequency of the transition with an error of only about

$$\Delta\nu \approx \frac{1}{2\tau} \quad (\text{III.9})$$

and, in practice, we can do slightly better than this.

D. Approximate the inherent uncertainty in the frequency of the $^2F_{7/2}$ to $^2S_{1/2}$ transition. What is the relative error in the frequency of the transition?

E. What is the inherent error in the period of this oscillation? How many oscillations are there (roughly) per second? What is the theoretical limit on the accuracy with which the number of oscillations per second can be measured?

F. What is the approximate error in the wave length? What is the relative error in the wavelength?

(You can compute this by computing the wavelength for $\nu + \Delta\nu$ and ν , and comparing.)

We can compare this transition to a (typical) transition in $^{172}\text{Yb}^+$. For example, the $^2P_{1/2}$ to $^2S_{1/2}$ transition has a wavelength of 369 nm and a lifetime of 8 ns .

G. Approximate the inherent uncertainty in the frequency of the $^2P_{1/2}$ to $^2S_{1/2}$ transition.

H. What is the approximate absolute error in the wave length?

Note that states with long lifetimes have “very pure” frequencies and wavelengths—they give very monochromatic light. This is yet another reason why, in designing lasers, one tends to prefer states with long lifetimes as the “initial state” for stimulated emission.

IV. Selection Rules Equation Section (Next)

When deriving selection rules, one's life is made much easier if one remembers that given any odd function of x ,³ then

$$\int_{-a}^a f(x) dx = 0 \quad (\text{IV.1})$$

A. Derive Eq. (IV.1) from the definition of an odd function.

B. For the one-electron atom, use Eq. (IV.1) to explain why

- (a) transitions from one s-orbital to another s-orbital are dipole forbidden.
- (b) transitions from one p-orbital to another p-orbital are dipole forbidden.
- (c) transitions from an s-orbital to a d-orbital are dipole forbidden.
- (d) transitions from the 1s to the 2p orbital are dipole allowed

V. Spectra of Molecules in Solution (1.4) Equation Section (Next)

Suppose we have measured the absorbance spectrum of a P-atom molecule in solution and in the gas phase. We observe two effects.

³ A function is odd if $f(-x) = -f(x)$. A function is even if $f(-x) = f(x)$.

- The absorbance maxima of the gas-phase spectra, $\omega_{f_i}^{gas}$ and solution-phase spectra $\omega_{f_i}^{sol.}$ are different. What is more, the spectral shifts show no obvious pattern, with the frequency shift due to solvation $\Delta^{sol.}\omega_{f_i} = \omega_{f_i}^{sol.} - \omega_{f_i}^{gas}$ being positive in some cases, and negative in others.
- The spectral lines in the solution phase are broader than in the gas phase. What is more, the dominant line-shape looks Gaussian, and not Lorentzian (presumably our gas-phase spectrum suffers from collisional broadening).

We want to explain these effects. The key to doing so is to note that, for any property that depends on the positions of the solvent molecules but not their momentum, the expectation value can be computed (in classical statistical thermodynamics) as⁴

$$\overline{A_i} = \frac{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d A(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N) e^{-\beta U_i^{BO}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)} d\mathbf{q}_1 \dots d\mathbf{q}_N}{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d e^{-\beta U_i^{BO}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)} d\mathbf{q}_1 \dots d\mathbf{q}_N} \quad (V.1)$$

where $\mathbf{q}_1, \dots, \mathbf{q}_N$ denote the positions of the nuclei of all N particles in the system (both solvent and solute), $U_i^{BO}(\mathbf{q}_1, \dots, \mathbf{q}_N)$ is the Born-Oppenheimer potential energy surface for the i^{th} excited state of the molecule, and describes both the solvent and the solute. $\beta = \frac{1}{kT}$, where k is Boltzmann's constant and T is the absolute temperature, and the system is confined to a cubic box with side d ($volume = d^3$). Here $A(\mathbf{q}_1, \dots, \mathbf{q}_N)$ is a property of the system, expressed as a function of the nuclear positions. For example, the average value of the Born-Oppenheimer potential is

$$\overline{U_i^{BO}} = \frac{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d U_i^{BO}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N) e^{-\beta U_i^{BO}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)} d\mathbf{q}_1 \dots d\mathbf{q}_N}{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d e^{-\beta U_i^{BO}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)} d\mathbf{q}_1 \dots d\mathbf{q}_N} \quad (V.2)$$

You might think that the average excitation energy, then, would be given by

⁴ The interpretation of this formula is rather simple. Given two states with potential energies V_1 and V_2 and identical kinetic energies, the probability of observing a system in state 1 is

$$\frac{e^{-\beta V_1}}{e^{-\beta V_1} + e^{-\beta V_2}},$$

which is just the Boltzmann-distribution law. If property A has value A_1 in state 1 and A_2 in state 2, then the average value of A is just

$$\overline{A} = A_1 p_1 + A_2 p_2,$$

where p_1 and p_2 are the probability of observing states 1 and 2, respectively. But, from above, we have that

$$\overline{A} = A_1 p_1 + A_2 p_2 = A_1 \frac{e^{-\beta V_1}}{e^{-\beta V_1} + e^{-\beta V_2}} + A_2 \frac{e^{-\beta V_2}}{e^{-\beta V_1} + e^{-\beta V_2}} = \frac{A_1 e^{-\beta V_1} + A_2 e^{-\beta V_2}}{e^{-\beta V_1} + e^{-\beta V_2}}.$$

To extend this result to more states, we merely sum over additional states in the numerator and the denominator,

$$\overline{A} = \frac{\sum_{i=1}^N A_i e^{-\beta V_i}}{\sum_{i=1}^N e^{-\beta V_i}}.$$

Now, however, we want to “sum” over all possible positions of the nuclei, which means integrating over $\mathbf{q}_1, \dots, \mathbf{q}_N$, where the integration interval is the volume of the box. This gives Eq. (V.1).

$$\overline{\Delta U_{fi}} \equiv \overline{U_f^{BO}} - \overline{U_i^{BO}}. \quad (\text{V.3})$$

This is not the case, however. If we computed the excitation energy in this fashion, we would allow the molecule and solvent to change geometry, so that the final state was as stable as possible. However, because the transition from initial to final state happens very quickly, there is no time for the molecular nuclei—much less the surrounding solvent molecules—to adjust.

A. Explain why Eq. (V.3) severely underestimates the excitation energy?

Let's order our coordinates so that the P molecular nuclei are $\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_P$. We want to know compute the average energy of the system when nucleus 1 is at \mathbf{R}_1 , nucleus 2 is at \mathbf{R}_2 , ..., and nucleus P is at \mathbf{R}_P . To compute this result, we use Bayes' theorem, which says that

Bayes' Theorem: Let $P(A, B)$ denote the probability of observing events A and event B both occurring. The probability of observing event A , given that event B has occurred, is

$$P(A|B) = \frac{P(A, B)}{P(B)} \quad (\text{V.4})$$

where $P(B)$ is the probability of observing event B (whether or not A occurs).

Most people find Bayes' theorem intuitively obvious when it is written as $P(A, B) = P(A|B) P(B)$. For example, if there is a 20% chance that you will fail the next test and a 50% chance that, if you fail the next test, you will also fail the final, then there is a 10% chance that you will fail both the next test and the final. Similarly, in the NCAA tournament, if there is a 90% that Duke will beat Colorado State and a 70% chance they will beat Creighton (my pick for round #2), then there is a 54% chance they will make the sweet sixteen. If there is a 40% chance that Duke will beat Kansas (pick for round 3) and a 20% chance that, if Duke beats Kansas, it will be able to beat Arizona, then we wind up with a 4.32% chance Duke makes the Final Four (sorry Cathy).

Using Bayes' theorem we compute

$$\begin{aligned}
& \left(\begin{array}{l} \text{Average energy of the system} \\ \text{given that the nuclei are at} \\ \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P \end{array} \right) = \left(\begin{array}{l} \text{Probability the nuclei} \\ \text{are at } \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P \\ \text{and the average energy} \\ \text{has some value} \end{array} \right) / \left(\begin{array}{l} \text{Probability the nuclei} \\ \text{are at } \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P \end{array} \right) \\
& \frac{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d U_i^{BO}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N) \prod_{k=1}^P \delta(\mathbf{q}_k - \mathbf{R}_k) e^{\beta U_i^{BO}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)} d\mathbf{q}_1 \dots d\mathbf{q}_N}{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d e^{-\beta U_i^{BO}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)} d\mathbf{q}_1 \dots d\mathbf{q}_N} \\
& \overline{U_i^{BO}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P)} = \frac{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d \prod_{k=1}^P \delta(\mathbf{q}_k - \mathbf{R}_k) e^{\beta U_i^{BO}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)} d\mathbf{q}_1 \dots d\mathbf{q}_N}{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d e^{-\beta U_i^{BO}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)} d\mathbf{q}_1 \dots d\mathbf{q}_N} \\
& = \frac{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d U_i^{BO}(\mathbf{R}_1, \dots, \mathbf{R}_P, \mathbf{q}_{P+1}, \dots, \mathbf{q}_N) e^{-\beta U_i^{BO}(\mathbf{R}_1, \dots, \mathbf{R}_P, \mathbf{q}_{P+1}, \dots, \mathbf{q}_N)} d\mathbf{q}_{P+1} \dots d\mathbf{q}_N}{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d e^{-\beta U_i^{BO}(\mathbf{R}_1, \dots, \mathbf{R}_P, \mathbf{q}_{P+1}, \dots, \mathbf{q}_N)} d\mathbf{q}_{P+1} \dots d\mathbf{q}_N} \quad (\text{V.5})
\end{aligned}$$

If we are very lucky, then $U_i^{BO}(\mathbf{q}_1, \dots, \mathbf{q}_N)$ can be written (or at least accurately approximated) as the sum of the potential-energy function for the molecule in question, $U_i^{BO}(\mathbf{q}_1, \dots, \mathbf{q}_P)$ and the potential energy surface for the remainder of the solution (including solvent, solute, etc.), $U_i^{BO}(\mathbf{q}_{P+1}, \dots, \mathbf{q}_N)$. If this is the case, then we can say that the molecular states are independent of the solute, and the spectrum will not change significantly due to solvation.

B. Follow up on the previous assertion. Specifically, substitute

$$U_i^{BO}(\mathbf{q}_1, \dots, \mathbf{q}_N) = U_i^{BO}(\mathbf{q}_1, \dots, \mathbf{q}_P) + U_i^{BO}(\mathbf{q}_{P+1}, \dots, \mathbf{q}_N) \quad (\text{V.6})$$

into Eq. (V.5) and evaluate $\overline{U_i^{BO}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P)}$.

To model the spectrum in solution, we take note that the amplitude of the absorption (ignoring the factors that characterize the source) is just

$$I(\omega) \approx \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} \left[p_i \left| \langle \Phi_f | \hat{\mu} | \Phi_i \rangle \right|^2 \cdot \mathcal{P}_{f_i}(\omega) \right] \quad (\text{V.7})$$

where $\mathcal{P}_{f_i}(\omega)$ denotes the probability that the absorption has frequency ω . We note that, in solution, it is difficult to characterize the dipole matrix element in Eq. (V.7), because quantifying the “wave function” for a subsystem is mathematically ill-defined. Our approach starts with the probability of observing the nuclei of the molecule and solvent at the positions \mathbf{R}_α when the molecule is in the i^{th} excited state,

$$P_i(\mathbf{R}_1, \dots, \mathbf{R}_N) \equiv \frac{e^{-\beta U_i^{BO}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)}}{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d e^{-\beta U_i^{BO}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)} d\mathbf{q}_1 \dots d\mathbf{q}_N} \quad (\text{V.8})$$

C. Derive Eq. (V.8). (Hint, look at Eq. (V.5).)

Next, we compute the frequency associated with the transition from state i to state f for this solvent configuration⁵

$$\omega \equiv \frac{U_f^{BO}(\mathbf{R}_1, \dots, \mathbf{R}_N) - U_i^{BO}(\mathbf{R}_1, \dots, \mathbf{R}_N)}{\hbar}. \quad (\text{V.9})$$

The probability that the transition frequency from state i to state f is ω , then, can be computed as

$$P_{if}(\omega) \equiv \iiint \dots \int \chi_\omega \frac{U_f^{BO}(\mathbf{R}_1, \dots, \mathbf{R}_N) - U_i^{BO}(\mathbf{R}_1, \dots, \mathbf{R}_N)}{\hbar} \mathcal{P}_i(\mathbf{R}_1, \dots, \mathbf{R}_N) d\mathbf{R}_1 \dots d\mathbf{R}_N \quad (\text{V.10})$$

where the characteristic function, χ_ω , is defined to be one when $\omega = \omega_0$ and zero otherwise:

$$\chi_{\omega_0}(\omega) \equiv \begin{cases} 1 & \omega_0 = \omega \\ 0 & \omega_0 \neq \omega \end{cases} \quad (\text{V.11})$$

Equation (V.11) is not quite the result we are looking for, because if the transition dipole, $\langle \Phi_f | \hat{\mu} | \Phi_i \rangle$, is small (or zero) the absorption at this frequency will be weak. To address this issue, we must recognize that the dipole matrix element is expected to depend on the positions of the molecular nuclei (cf. Eq. (91) in the notes) and a (hopefully weak, but perhaps not negligible) dependence on the arrangement of the surrounding solvent molecules,⁶ and so define the nuclear transition dipole operator as,

$$\mu_{fi}(\mathbf{R}_1, \dots, \mathbf{R}_N) = \left\langle \xi_f \left| \sum_{i=1}^N -e \cdot \frac{x_i + y_i + z_i}{3} \right| \xi_i \right\rangle_{\mathbf{r}_1 \dots \mathbf{r}_N} \approx \langle \Phi_f | \hat{\mu} | \Phi_i \rangle, \quad (\text{V.12})$$

where $\xi_f(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_N)$ and $\xi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_N)$ are the electronic wave functions in the Born-Oppenheimer approximation and the notation in Eq. (V.12) denotes that only the electronic coordinates are subject to integration. In setting $\mu_{fi}(\mathbf{R}_1, \dots, \mathbf{R}_N)$ equal to the dipole transition matrix element, $\langle \Phi_f | \hat{\mu} | \Phi_i \rangle$, we are implicitly neglecting the quantization of rotational and vibrational motion in solution, and assuming, instead, that the nuclei can be considered classical particles. (This is already implicit in the key equation, (V.1), and corrections for this approximation are most easily made at a later stage in the development. No correction is necessary when, as is often the case, the vibration fine-structure of electronic transitions is not observed in solution.)

Next, we assume that the number of molecules in excited electronic states is negligible. (So $p_i = \delta_{i0}$.) This is an excellent approximation in the absence of radiation: because the spacing of electronic states is large compared to thermal energies, very few molecules are in excited electronic states at room temperature. (At room temperature, $kT \approx .001$ Hartree. Since the thermal probability of the first excited state being occupied is almost exactly $e^{-\Delta E_{10}/kT}$, and since typical electronic excitation energies, ΔE_{10} , range from several hundredths of a Hartree up to a few Hartrees, we see that the probability of observing a molecule in an excited state is very, very small.)

The assumption that only the ground state is occupied is also accurate in the presence of the light source as long as the light source isn't strong enough to introduce appreciable population into the excited states. (This is usually true unless the light source is a laser.) Consequently, we are observing the absorbance spectrum of the ground state only, $i = 0$.

⁵ Note that we do not allow the nuclei of the molecule being probed or the surrounding solvent to rearrange during the excitation process. This circumvents the problem afflicting Eq. (V.3).

⁶ The role of the solvent molecules can be very important: they reduce the symmetry of the system and thus enable one to observe transitions that would be forbidden by symmetry in the gas phase.

Putting all these considerations together, we have

$$I_{g.s.} \omega = \sum_{f=0}^{\infty} \iiint \cdots \int |\mu_{f0}(\mathbf{R}_1, \dots, \mathbf{R}_N)|^2 \chi_{\omega} \frac{U_f^{BO}(\mathbf{R}_1, \dots, \mathbf{R}_N) - U_0^{BO}(\mathbf{R}_1, \dots, \mathbf{R}_N)}{\hbar} \mathcal{P}_0(\mathbf{R}_1, \dots, \mathbf{R}_N) d\mathbf{R}_1 \dots d\mathbf{R}_N \quad (\text{V.13})$$

We can now address the experimental observations about spectra in solutions.

D. There is inhomogeneous broadening of the spectral lines due to the different microscopic environments felt by different molecules. Because of this, this broadening mechanism is often called “site” broadening. With reference to Eq. (V.13), explain why this “site” broadening happens here, but not in the gas phase.

E. In words, characterize the types of distribution functions, $\mathcal{P}_0(\mathbf{R}_1, \dots, \mathbf{R}_N)$, that would be associated with the least site broadening.

In class, I said that inhomogeneous broadening mechanisms are associated with Gaussian lineshapes. This is not always true for site broadening, because it is possible that the different “molecular environments” are quite disparate. In particular, when suppose that, in solution the microscopic environment around the molecule is characterized with two dominant solvation patterns. Since both patterns will exist in solution, they tend to have similar energies,

$$U_0^{BO} \text{ solvation pattern 1} \approx U_0^{BO} \text{ solvation pattern 2} \quad (\text{V.14})$$

However, when we excite the molecule to the state f , it is possible that the two solvation patterns will have substantially different energies,

$$U_f^{BO} \text{ solvation pattern 1} \neq U_f^{BO} \text{ solvation pattern 2} . \quad (\text{V.15})$$

This results in “solvent splitting of spectral lines” (often manifest as a shoulder instead of a true splitting). Note that this effect is due to the fact that spectral transitions occur quickly, before molecules have a chance to relax.

F. In words, describe what one can say about the amount of solvent stabilization in the ground and excited states when the transition frequency for excitation to state f is higher in solution than it is in the gas phase? What about when the transition frequency is lower?

G. In most heteronuclear diatomic with a large dipole moment, the first excited state has a relatively small dipole moment. Do you expect the frequency of the excitation from the ground to the first excited state to be higher or lower in a polar solvent than in the gas phase?

Rigorous explanations for the fact that site broadening often induces a line-shape that is (roughly) Gaussian are usually quite sophisticated and make heavy use of “hand-waving.” Most explanations start explanation by finding the most probable geometry for the molecular coordinates, $\mathbf{R}_1, \dots, \mathbf{R}_P$. This can be obtained from Eq. (V.8). First:

H. Why does the following equation represent the probability of observing atom 1 at \mathbf{R}_1 , atom 2 at \mathbf{R}_2 , etc.?

$$P(\mathbf{R}_1, \dots, \mathbf{R}_P) = \iiint \cdots \int P(\mathbf{R}_1, \dots, \mathbf{R}_N) d\mathbf{R}_{P+1} \dots d\mathbf{R}_N \quad (\text{V.16})$$

Given $P_p \mathbf{R}_1, \dots, \mathbf{R}_p$, the most probably arrangement of the molecular nuclei is found by finding the largest value of $P_p \mathbf{R}_1, \dots, \mathbf{R}_p$. The associated positions of the molecule's nuclei, $\mathbf{R}_1^{mp}, \mathbf{R}_2^{mp}, \dots, \mathbf{R}_p^{mp}$, will be used in the following.

The simplest explanation for a Gaussian lineshape assumes that the molecular nuclei, $\mathbf{R}_1, \dots, \mathbf{R}_p$, are fixed while the remaining coordinates vary “randomly” about their equilibrium positions. The “peak” in the spectrum corresponds to the most-likely separation between the initial and final states, and can be computed from a formula similar to Eq. (V.5), namely

$$\begin{aligned} & \overline{U_{fi}^{BO}} \mathbf{R}_1^{mp}, \mathbf{R}_2^{mp}, \dots, \mathbf{R}_p^{mp} \\ &= \frac{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d \left(U_f^{BO} \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}, \mathbf{q}_{P+1}, \dots, \mathbf{q}_N \right. \\ & \quad \left. - U_i^{BO} \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}, \mathbf{q}_{P+1}, \dots, \mathbf{q}_N \right) e^{-\beta U_i^{BO} \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}, \mathbf{q}_{P+1}, \dots, \mathbf{q}_N} d\mathbf{q}_{P+1} \dots d\mathbf{q}_N}{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d e^{-\beta U_i^{BO} \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}, \mathbf{q}_{P+1}, \dots, \mathbf{q}_N} d\mathbf{q}_{P+1} \dots d\mathbf{q}_N} \quad (V.17) \end{aligned}$$

The “fluctuation” the excitation energy is just the generalization of the formula for the variance

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 \quad (V.18)$$

and so

$$\begin{aligned} & \sigma_{fi}^2 \mathbf{R}_1^{mp}, \mathbf{R}_2^{mp}, \dots, \mathbf{R}_p^{mp} \\ &= \frac{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d \left(U_f^{BO} \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}, \mathbf{q}_{P+1}, \dots, \mathbf{q}_N \right)^2 \\ & \quad \left(U_i^{BO} \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}, \mathbf{q}_{P+1}, \dots, \mathbf{q}_N \right) e^{-\beta U_i^{BO} \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}, \mathbf{q}_{P+1}, \dots, \mathbf{q}_N} d\mathbf{q}_{P+1} \dots d\mathbf{q}_N}{\int_{-d}^d \int_{-d}^d \int_{-d}^d \dots \int_{-d}^d e^{-\beta U_i^{BO} \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}, \mathbf{q}_{P+1}, \dots, \mathbf{q}_N} d\mathbf{q}_{P+1} \dots d\mathbf{q}_N} \\ & - \left(\overline{U_{fi}^{BO}} \mathbf{R}_1^{mp}, \mathbf{R}_2^{mp}, \dots, \mathbf{R}_p^{mp} \right)^2 \quad (V.19) \end{aligned}$$

Using Eq. (V.19), we model the distribution of excitation energies as:

$$E_{fi} \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}, \Delta E \approx \frac{1}{\sqrt{2\pi\sigma_{fi}^2 \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}}} e^{-\frac{1}{2} \left(\frac{\Delta E - \overline{U_{fi}^{BO}} \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}}{\sigma_{fi}^2 \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}} \right)^2}, \quad (V.20)$$

There are two cases of interest. For molecules that are not “floppy” or labile, $P_p \mathbf{R}_1, \dots, \mathbf{R}_p$ is strongly peaked near the most-probable nuclear positions and, substituting Eq. (V.20) into the formula for the absorption frequency, one finds that the absorption associated with the excitation from the initial state i to the final state, f , is proportional to

$$I_{fi} \omega \propto \frac{1}{\sqrt{2\pi\sigma_{fi}^2 \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}}} e^{-\frac{1}{2} \left(\frac{\hbar\omega - \overline{U_{fi}^{BO}} \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}}{\sigma_{fi}^2 \mathbf{R}_1^{mp}, \dots, \mathbf{R}_p^{mp}} \right)^2}, \quad (V.21)$$

When the molecule is floppy or labile, a much more complicated analysis is needed, and Gaussian line shapes are generally not observed. Coordination compounds, in particular, will have much broader

absorbance features than would be predicted by Eq. (V.21), in part because the number of ligands associated with the metal center tends to vary with respect to time (especially for labile ligands).

In all of this analysis, we have implicitly neglected vibrational structure (which is, in fact, sometimes observed) and its effects on the spectrum. Indeed, it is very rare that solvation processes consider quantum mechanical vibrational effects. Why can we get away with this? Suppose the a given molecular (or solvent) motion can be described as a harmonic oscillator with some force constant, k . The potential, then, is

$$V = \frac{1}{2} \kappa x^2 \quad (\text{V.22})$$

and, substituting into the classical expression for the probability distribution function of the harmonic oscillator, Eq. (V.8), we see that

$$P_{cl} \ x = \sqrt{\frac{\kappa}{2\pi kT}} e^{-\frac{1}{2}\kappa x^2 / k_B T}. \quad (\text{V.23})$$

This can be compared to the ground state probability distribution function for the Harmonic oscillator,

$$P_{qu} \ x = \sqrt{\frac{\sqrt{\kappa m}}{\pi \hbar}} e^{-\sqrt{\kappa m} x^2 / \hbar} \quad (\text{V.24})$$

The “spread” of these distributions can be measured with the variances, which are

$$\begin{aligned} \sigma_{cl}^2 &\equiv \frac{k_B T}{\kappa} \\ \sigma_{qu}^2 &= \frac{2\hbar}{\sqrt{\kappa m}} \end{aligned} \quad (\text{V.25})$$

This implies that the classical “variance” is larger than the zero-point quantum variance whenever

$$\begin{aligned} \sigma_{cl}^2 &\gtrsim \sigma_{qu}^2 \\ \frac{k_B T}{\kappa} &\gtrsim \frac{2\hbar}{\sqrt{\kappa m}} \\ \frac{k_B T}{2\hbar} \sqrt{\frac{m}{\kappa}} &\gtrsim 1 \\ \frac{k_B T}{2\hbar \nu} &\gtrsim 1 \end{aligned} \quad (\text{V.26})$$

I. Given a typical vibrational frequency of 10^{14} Hz, how “hot” must a system be before Eq. (V.26) is satisfied?

In general, once

$$\frac{k_B T}{2\hbar \nu} \gg 1, \quad (\text{V.27})$$

the description of our system with classical models is acceptable.

VI. Atomic Spectra **Equation Section (Next)**

Go to the library and pick up Atomic Energy Levels and Grotrian Diagrams, Volume I, by Stanley Bashkin and John O. Stoner Jr. (North Holland, New York, 1975). (It's in the reference section.) Look at the Grotrian diagrams. Pick up to four, Xerox them, and label the transitions as E1 (dipole allowed), E2 (quadrupole allowed), M1 (magnetic dipole allowed), SO (spin-orbit coupling allowed), etc.. I'll accept a label of "huh?" for truly inexplicable transitions.

Some of the Grotrian diagrams get very complicated (Vanadium and Chromium have their own dictionary-thick *volume!*), so you should keep things simple. Choose (a) closed-shell species (e.g., He, Ne, etc.) and (b) open-shell species (e.g., Li, Na, etc.). I must approve the diagram(s) you plan on doing BEFORE you do it. Also, if you do multiple diagrams you should comment on the differences. (E.g., why does the diagram for Na look a little different from that for Li? Why does the diagram for Ne^{+8} look different from that for He?)