SPECTROSCOPY: PROBING MOLECULES WITH LIGHT

In practice, even for systems that are very complex and poorly characterized, we would like to be able to probe molecules and find out as much about the system as we can so that we can understand reactivity, structure, bonding, etc. One of the most powerful tools for interrogating molecules is spectroscopy. Here, we tickle the system with electromagnetic radiation (i.e. light) and see how the molecules respond. The motivation for this is that different molecules respond to light in different ways. Thus, if we are creative in the ways that we probe the system with light, we can hope to find a unique spectral fingerprint that will differentiate one molecule from all other possibilities. In order to understand how spectroscopy works, we need to answer the question: how do electromagnetic waves interact with matter?

The Dipole Approximation

An electromagnetic wave of wavelength λ, produces an electric field, $\mathbf{E}(\mathbf{r},t)$, and a magnetic field, $\mathbf{B}(\mathbf{r},t)$, of the form:

$$\mathbf{E}(\mathbf{r},t)=\mathbf{E}_0\cos(\mathbf{k}\cdot\mathbf{r} - \omega t) \qquad \mathbf{B}(\mathbf{r},t)=\mathbf{B}_0\cos(\mathbf{k}\cdot\mathbf{r} - \omega t)$$

Where $\omega=2\pi\nu$ is the angular frequency of the wave, the wavevector $\mathbf{k}$ has a magnitude $2\pi/\lambda$ and $\mathbf{k}$ (the direction the wave propagates) is perpendicular to $\mathbf{E}_0$ and $\mathbf{B}_0$. Further, the electric and magnetic fields are related:

$$\mathbf{E}_0\cdot\mathbf{B}_0=0 \qquad\qquad |\mathbf{E}_0|=c|\mathbf{B}_0|$$

Thus, the electric and magnetic fields are orthogonal and the magnetic field is a factor of c (the speed of light, which is 1/137 in atomic units) smaller than the electric field. Thus we obtain a picture like the one at right, where the electric and magnetic fields oscillate transverse to the direction of propagation.

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Now, in chemistry we typically deal with the part of the spectrum from ultraviolet ($\lambda\approx100\ nm$) to radio waves ($\lambda\approx10\ m$)[1]. Meanwhile, a typical molecule

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[1] There are a few examples of spectroscopic measurements in the X-Ray region. In these cases, the wavelength can be very small and the dipole approximation is not valid.

is about 1 nm in size. Let us assume that the molecule is sitting at the origin. Then, in the 1 nm^3 volume occupied by the molecule we have:

$$\mathbf{k \cdot r} \approx |\mathbf{k}| \ |\mathbf{r}| \approx 2\pi/(100 \text{ nm}) \ \times 1 \text{ nm} = .06$$

Where we have assumed UV radiation (longer wavelengths would lead to even smaller values for $\mathbf{k \cdot r}$). Thus, $\mathbf{k \cdot r}$ is a small number and we can expand the electric and magnetic fields in a power series in $\mathbf{k \cdot r}$:

$$\mathbf{E}(\mathbf{r},t) \approx \mathbf{E_0} \ [\cos(\mathbf{k \cdot 0}-\omega t)+O(\mathbf{k \cdot r})] \approx \mathbf{E_0} \cos(\omega t)$$
$$\mathbf{B}(\mathbf{r},t) \approx \mathbf{B_0} \ [\cos(\mathbf{k \cdot 0}-\omega t)+O(\mathbf{k \cdot r})] \approx \mathbf{B_0} \cos(\omega t)$$

Where we are neglecting terms of order at most a few percent. Thus, in most chemical situations, we can think of light as applying two time dependent fields: **an oscillating, uniform electric field (top) and a uniform, oscillating magnetic field (bottom)**. This approximation is called the Dipole approximation – specifically when applied to the electric (magnetic) field it is called the electric (magnetic) dipole approximation. If we were to retain the next term in the expansion, we would have what is called the quadrupole approximation. The only time it is advisable to go to higher orders in the expansion is if the dipole contribution is exactly zero as happens, for example, due to symmetry in some cases. In this situation, even though the quadrupole (**k·r**) contributions may be small, they are certainly large compared to zero and would need to be computed.

The Interaction Hamiltonian
How do these oscillating electric and magnetic fields couple to the molecule? Well, for a system interacting with a uniform electric field $\mathbf{E}(t)$ the interaction energy is

$$\hat{H}_E\left(t\right) = -\hat{\boldsymbol{\mu}} \cdot \mathbf{E}(t) = -e \ \hat{\mathbf{r}} \cdot \mathbf{E}(t)$$

where $\boldsymbol{\mu}$ is the **electric dipole moment** of the system. Thus, uniform electric fields interact with molecular dipole moments.

Similarly, the magnetic field couples to the magnetic dipole moment, **m**. Magnetic moments arise from circulating currents and are therefore proportional to angular momentum – larger angular momentum means higher circulating currents and larger magnetic moments. If we assume that all the angular momentum in our system comes from the *intrinsic spin angular momentum*, $\mathbf{I}=(I_x, I_y, I_z)$, then the magnetic moment is strictly proportional to **I**. For example, for a particle with charge q and mass m then

$$\hat{H}_B\left(t\right) = -\hat{\mathbf{m}} \cdot \mathbf{B}(t) = -\frac{q \ g}{2m} \hat{\mathbf{I}} \cdot \mathbf{B}(t)$$

where g is a phenomenological factor (creatively called the "g-factor") that takes into account the internal structure of the particle containing the intrinsic spin – for an electron g_e=2.0023, while for a proton g_p=5.5857.

So now suppose that we have a molecule we are interested in, and it has a Hamiltonian, $\hat{H}_0$, when the field is off. Then, when the field is on, the Hamiltonian will be

$$\hat{H}(t) = \hat{H}_0 + \hat{H}_E(t) + \hat{H}_B(t)$$

Actually, in most cases, the simultaneous effects of electric and magnetic fields are not important and we will consider one or the other:

$$\hat{H}(t) \equiv \hat{H}_0 + \hat{H}_1(t) \qquad \hat{H}_1(t) \equiv \hat{H}_E(t) \quad \text{or} \quad \hat{H}_B(t).$$

Thus, **in the presence of light, a molecule feels a time-dependent Hamiltonian**. This situation is quite different with what we have discussed so far. Previously, our Hamiltonian has been time independent and our job has simply reduced to finding the eigenstates of $\hat{H}$. Now, we have a Hamiltonian that varies with time, meaning that the energy eigenvalues and eigenstates of $\hat{H}$ also change with time. What can we say that is meaningful about a system that is constantly changing?

Time Dependent Eigenstates

As it turns out, the best way to think about this problem is to think about the eigenstates of $\hat{H}_0$. When the field is off, each of these eigenstates evolves by just getting a phase factor:

$$\hat{H}_0 \phi_n(t) = E_n \phi_n(t) \qquad \Rightarrow \qquad \phi_n(t) = e^{-iE_n t/\hbar} \phi_n(0)$$

Thus, things like the probability density do not change because multiplying by the complex conjugate wipes out the phase factor:

$$\left| \phi_n(t) \right|^2 = \left\{ e^{-iE_n t/\hbar} \phi_n(0) \right\} * e^{-iE_n t/\hbar} \phi_n(0) = e^{iE_n t/\hbar} \phi_n(0) * e^{-iE_n t/\hbar} \phi_n(0) = \left| \phi_n(0) \right|^2$$

Thus, when considering measurable quantities (which always involve complex conjugates) the eigenstates of the Hamiltonian appear not to change with time. However, **when the field is on the eigenstates will change with time**. In particular, we will be interested in the rate at which the field induces transitions between an initial eigenstate ϕ_i and a final state ϕ_f.

To work out these rates, we first work out the time dependence of some arbitrary state, $\psi(t)$. We can expand $\psi(t)$ as a linear combination of the eigenstates:

$$\psi(t) = \sum_n c_n(t)\phi_n(t)$$

where $c_n(t)$ are the coefficients to be determined. Next, we plug this into the TDSE:

$$i\hbar\dot{\psi}(t) = \hat{H}\psi(t)$$

$$\Rightarrow i\hbar\frac{\partial}{\partial t}\sum_n c_n(t)\phi_n(t) = \hat{H}\sum_n c_n(t)\phi_n(t)$$

$$\Rightarrow i\hbar\sum_n \dot{c}_n(t)\phi_n(t) + c_n(t)\dot{\phi}_n(t) = \sum_n c_n(t)\left(\hat{H}_0 + \hat{H}_1(t)\right)\phi_n(t)$$

$$\Rightarrow i\hbar\sum_n \dot{c}_n(t)\phi_n(t) - \frac{iE_n}{\hbar}c_n(t)\phi_n(t) = \sum_n c_n(t)\left(E_n + \hat{H}_1(t)\right)\phi_n(t)$$

$$\Rightarrow i\hbar\sum_n \dot{c}_n(t)\phi_n(t) + \sum_n \cancel{E}_n c_n(t)\phi_n(t) = \sum_n c_n(t)\left(\cancel{E}_n + \hat{H}_1(t)\right)\phi_n(t)$$

$$\Rightarrow i\hbar\sum_n \dot{c}_n(t)\phi_n(t) = \sum_n c_n(t)\hat{H}_1(t)\phi_n(t)$$

Next, we multiply both sides by the final state we are interested in ($\phi_f{}^*$) and then integrate over all space. On the left hand side, we get:

$$i\hbar\int\phi_f^*(t)\sum_n \dot{c}_n(t)\phi_n(t)d\tau = i\hbar\sum_n \dot{c}_n(t)\int\phi_f^*(t)\phi_n(t)d\tau = i\hbar\dot{c}_f(t)$$

$$\delta_{nf}$$

Meanwhile, on the right we get:

$$\int\phi_f^*(t)\sum_n c_n(t)\hat{H}_1(t)\phi_n(t)d\tau = \sum_n c_n(t)\int\phi_f^*(t)\hat{H}_1(t)\phi_n(t)d\tau$$

Combining terms gives:

$$\Rightarrow i\hbar\dot{c}_f(t) = \sum_n \int\phi_f^*(t)\hat{H}_1(t)\phi_n(t)d\tau\, c_n(t) \qquad \textbf{Eq. 1}$$

Up to this point, we haven't used the form of H_1 at all. We note that we can re-write the light-matter interaction as:

$$\hat{H}_1(t) = \hat{V}\cos(\omega t)$$

where, for electric fields $\hat{V} \equiv -e\hat{\mathbf{r}}\cdot\mathbf{E}_0$ and for magnetic fields $\hat{V} \equiv -\dfrac{q\,g}{2m}\hat{\mathbf{I}}\cdot\mathbf{B}$.

In either case, we can re-write the cosine in terms of complex exponentials:

$$\hat{H}_1(t) = \hat{V}\tfrac{1}{2}\left(e^{i\omega t} + e^{-i\omega t}\right)$$

Plugging this into Eq.1 above gives:

$$i\hbar\dot{c}_f(t) = \sum_n \int \phi_f^*(t) \tfrac{1}{2}\hat{V}\left(e^{i\omega t} + e^{-i\omega t}\right)\phi_n(t)\,d\tau\ c_n(t)$$

$$= \sum_n \int \phi_f^*(0)e^{iE_f t/\hbar} \tfrac{1}{2}\hat{V}\left(e^{i\omega t} + e^{-i\omega t}\right)e^{-iE_n t/\hbar}\phi_n(0)\,d\tau\ c_n(t)$$

$$= \underbrace{\sum_n \int \phi_f^*(0)\tfrac{1}{2}\hat{V}\phi_n(0)\,d\tau}\ \left(e^{-i(E_n - E_f - \hbar\omega)t/\hbar} + e^{-i(E_n - E_f + \hbar\omega)t/\hbar}\right)c_n(t)$$

$$= \sum_n \qquad \tfrac{1}{2}V_{fn} \qquad\qquad \left(e^{-i(E_n - E_f - \hbar\omega)t/\hbar} + e^{-i(E_n - E_f + \hbar\omega)t/\hbar}\right)c_n(t)$$

Tickling the Molecule With Light

To this point we haven't made any approximations to the time evolution. We now make some assumptions that allow us to focus on one particular i→f transition. We make two physical assumptions:

1) The molecule starts in a particular eigenstate, ϕ_i, at t=0. This sets the initial conditions for our coefficients: only the coefficient of state i can be non-zero initially:

$$c_n(0) = 0 \qquad \text{if}\ \ n \neq i \qquad c_i(0) = 1$$

It is easy to verify that this choice gives the desired initial state:
$$\psi(0) = \sum_n c_n(0)\phi_n(0) = 0 + 0 + ...1\cdot\phi_i(0) + 0.... = \phi_i(0)$$

2) The interaction only has a small effect on the dynamics. This is certainly an approximation, and it will not always be true. We can guarantee its validity in one limit: if we reduce the intensity of our light source sufficiently, we will reduce the strength of the electric and magnetic fields to the point where the influence of the light is small. As we turn up the intensity, there may be additional effects that will come into play, and we will come back to this possibility later on. However, if we take this assumption at face value, we can assume on the right hand side that the coefficient, c_n, of a state other than ϕ_i will be much smaller than c_i for all times:

$$c_n(t) = c_i(t) \qquad \text{if}\ \ n \neq i \qquad c_i(t) \approx 1$$

Where, in the second equality we have noted that if all the other coefficients are tiny, c_i must be approximately 1 if we want our state to stay normalized.

These two assumptions lead to an equation for the coefficients of the form:

$$i\hbar\dot{c}_f(t) = \sum_n \tfrac{1}{2}V_{fn}\left(e^{-i\left(E_n-E_f-\hbar\omega\right)t/\hbar} + e^{-i\left(E_n-E_f+\hbar\omega\right)t/\hbar}\right)c_n(t)$$

$$\Rightarrow i\hbar\dot{c}_f(t) = \tfrac{1}{2}V_{fi}\left(e^{-i\left(E_i-E_f-\hbar\omega\right)t/\hbar} + e^{-i\left(E_i-E_f+\hbar\omega\right)t/\hbar}\right)c_i(t)$$

$$= \tfrac{1}{2}V_{fi}\left(e^{-i\left(E_i-E_f-\hbar\omega\right)t/\hbar} + e^{-i\left(E_i-E_f+\hbar\omega\right)t/\hbar}\right)$$

Now we can integrate this new equation to obtain $c_f(t)$:

$$i\hbar c_f(T) = \tfrac{1}{2}V_{fi}\int_0^T\left(e^{-i\left(E_i-E_f-\hbar\omega\right)t/\hbar} + e^{-i\left(E_i-E_f+\hbar\omega\right)t/\hbar}\right)dt$$

$$\Rightarrow c_f(T) = \frac{V_{fi}}{2i\hbar}\int_0^T\left(e^{-i\left(E_i-E_f-\hbar\omega\right)t/\hbar} + e^{-i\left(E_i-E_f+\hbar\omega\right)t/\hbar}\right)dt \qquad \textbf{Eq. 2}$$

Now, this formula for $c_f(T)$ is only approximate, because of assumption 2). If we wanted to improve our result for, we could plug our approximate final expression (Eq. 2) back in on the RHS of Eq. 1 and then integrate the equation again. This would lead to a better approximate solution for $c_f(t)$. Most importantly, while our approximate solution is linear the interaction matrix element, V_{fi}, after plugging the result back in, we would get terms that were quadratic in V_{fi}. By assumption 2) above, these quadratic terms will be much smaller than the linear ones we have retained above and so we feel safe in neglecting them. For these reasons, assumption 2) is known as the **linear response approximation**.

We now make the final rearrangement: we recall that we are interested in the probability of finding the system in the state f. This is given by $\left|c_f(T)\right|^2$:

$$P_{fi}(T) \equiv \left|c_f(T)\right|^2 = \frac{\left|V_{fi}\right|^2}{4\hbar^2}\left|\int_0^T\left(e^{-i\left(E_i-E_f-\hbar\omega\right)t/\hbar} + e^{-i\left(E_i-E_f+\hbar\omega\right)t/\hbar}\right)dt\right|^2$$

where the subscript "fi" reminds us that this is the probability of ending up in the final state f given that we started in the state i.

Fermi's Golden Rule

Now, usually our experiments take a long time from the point of view of electromagnetic waves. In a single second a light wave will oscillate trillions of times. Thus, our observations are likely to correspond to the long-time limit of the above expression:

$$P_{fi} = \frac{\left|V_{fi}\right|^2}{4\hbar^2} \lim_{T \to \infty} \left| \int_0^T \left(e^{-i\left(E_i - E_f - \hbar\omega\right)t/\hbar} + e^{-i\left(E_i - E_f + \hbar\omega\right)t/\hbar} \right) dt \right|^2$$

and in fact, we are usually not interested in probabilities, but rates, which are probabilities per unit time:

$$W_{fi} = \frac{\left|V_{fi}\right|^2}{4\hbar^2} \lim_{T \to \infty} \frac{1}{T} \left| \int_0^T \left(e^{-i\left(E_i - E_f - \hbar\omega\right)t/\hbar} + e^{-i\left(E_i - E_f + \hbar\omega\right)t/\hbar} \right) dt \right|^2$$

This integral looks very difficult. However, it is easy to work out with pictures because it is almost always zero. Note that both the real and imaginary parts of the integrand oscillate. Thus, we will be computing the integral of something that looks like:
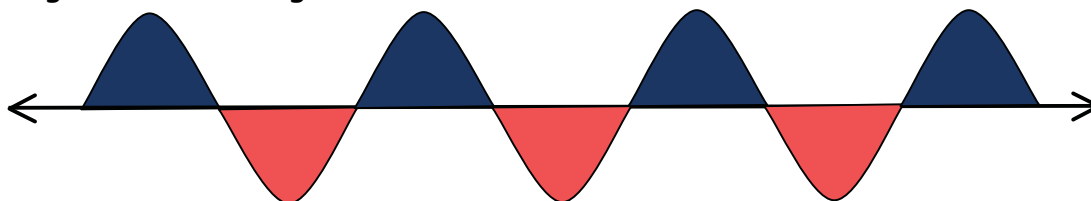
Thus, as long as the integrand oscillates, the **positive** regions will cancel out the **negative** ones and the integral will be zero. There only two situations where the integrand is not oscillatory: $E_i - E_f - \hbar\omega = 0$ (in which case the first term is unity) and $E_i - E_f + \hbar\omega = 0$ (in which case the second term is unity). We can therefore write

$$\boxed{W_{fi} \propto \frac{\left|V_{fi}\right|^2}{4\hbar^2}\left[\delta\left(E_i - E_f - \hbar\omega\right) + \delta\left(E_i - E_f + \hbar\omega\right)\right]}$$

where $\delta(x)$ is a function that is defined to be non-zero only when $x=0$. This result is called **Fermi's golden rule**. It gives us a way of predicting the rate of *any* i→f transition in *any molecule* induced by an electromagnetic field of *arbitrary frequency* coming from *any direction*. This formula – as well as generalizations that relax the electric dipole and linear response approximations – is probably the single most important relationship in terms of how chemists think about spectroscopy, and so we will dwell a bit on the interpretation of the various terms.

On the one hand, the probability of an i→f transition is proportional to

$$\left|V_{fi}\right|^2 = \left|\int \phi_f * \hat{V} \phi_i \, d\tau\right|^2$$

Thus, **if the integral of the interaction operator $\hat{V}$ between the initial and final states is zero, then the transition never happens.** This is called a **selection rule**, and a transition that does not occur because of a selection rule is said to be **forbidden**. For example, in the case of the electric field,

$$\left|V_{fi}\right|^2 = \left|\int \phi_f * \hat{\mu} \cdot \mathbf{E}_0 \phi_i \, d\tau\right|^2 = \left|\mathbf{E}_0 \cdot \int \phi_f * \hat{\mu} \phi_i \, d\tau\right|^2 \equiv \left|\mathbf{E}_0 \cdot \mu_{fi}\right|^2$$

Thus, for molecules interacting with electric fields, the transition i→f is forbidden unless the matrix element of the dipole operator between i&f is nonzero. This type of matrix element is often called a transition dipole for this reason – when the transition dipole is very large, the transition is very likely. Meanwhile, in the case of a magnetic field,

$$\left|V_{fi}\right|^2 = \left|\int \phi_f * \hat{\mathbf{m}} \cdot \mathbf{E}_0 \phi_i \, d\tau\right|^2 = \left|\frac{q\,g}{2m}\mathbf{B}_0 \cdot \int \phi_f * \hat{\mathbf{I}} \phi_i \, d\tau\right|^2 \equiv \left|\frac{q\,g}{2m}\mathbf{B}_0 \cdot \mathbf{I}_{fi}\right|^2$$

Thus, a magnetic field can only induce an i→f transition if the matrix element of one of the spin angular momentum operators is non-zero between the initial and final states. Selection rules of this type are extremely important in determining which transitions will and will not appear in our spectra.

The second thing we note about Fermi's Golden Rule is that it enforces energy conservation. We note that the energy carried by a photon is $\hbar\omega$. The δ-function portion is only non-zero if

$E_i - E_f = -\hbar\omega$ (second term) or

$E_i - E_f = \hbar\omega$ (first term). Thus, **the transition only occurs if the energy difference between the two states exactly matches the energy of the photon we are sending in.** This is depicted in the picture at right above. The way these terms are interpreted are as follows: in the first case, the light increases the energy in the system by exactly one photon worth of energy. Here, we think of a photon being *absorbed* by the molecule and exciting the system. In the second case, the light reduces the energy of

E_f _____ E_i _____

$\hbar\omega$ $\hbar\omega$

E_i _____ E_f _____

$E_f - E_i = \hbar\omega$ $E_f - E_i = \hbar\omega$
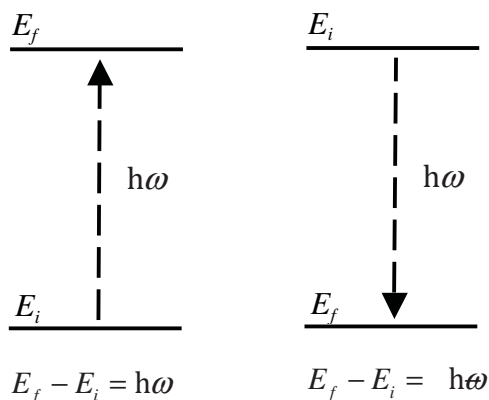
the system by exactly one photon worth of energy. Here, we think of the molecule *emitting* a photon and relaxing to a lower energy state. The fact that photon emission by a molecule can be induced by light is called stimulated emission, and is the principle on which lasers are built: basically, when you shine light on an excited molecule, you get more photons out than you put in.

In order to make much more progress with spectroscopy, we have to consider some specific choices of the molecular Hamiltonian, $\hat{H}_0$, which we do in the next several lectures. Depending on the system at hand the energy conservation and selection rules give different spectral signatures that ultimately allow us to interpret the spectra of real molecules and to characterize their physical properties.

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