

15.5: Spectroscopy

Spectroscopy is the most common method of characterizing chemical and biological compounds. While the absorption of light can be attributed to dynamics such as electronic (visible), vibrational (infrared), or rotational (microwave) excitation, one must apply quantum mechanics connect a spectrum to molecular physical properties. We are especially concerned with what makes an atom or molecule absorb light at all! As shown here, such information necessitates knowledge of the ground and excited state wavefunctions of a molecule's Hamiltonian as solved by the Schrödinger equation.

One of the central tenets of quantum mechanics is that all observables have associated operators. Absorption of light is (mostly) due to the interaction of the photon's electric field with the dipole moment of an atom or molecule. To absorb light there must be a change in the dipole moment, which is defined from classical electromechanics as $\vec{\mu} = q_1 q_2 \vec{r}$. Here, q_1 and q_2 are the charges (for hydrogen, and electron and proton) and \vec{r} is the distance between. The quantum mechanical analog is the dipole operator, which for the hydrogen atom is:

$$\hat{\mu} = -e^2 \cdot \hat{r}$$

We can calculate the expectation value of the dipole operator as it applied to a transition across energy states:

$$\langle \hat{\mu} \rangle = -e \cdot \langle \psi_i \rangle = \int \int \int \psi_f^*(r, \theta, \phi) \cdot r \cdot \psi_i(r, \theta, \phi) \cdot \partial r \cdot \sin(\theta) \partial \theta \cdot \partial \phi$$

This expression isn't quite the same as our previous examples of expectation values because different states are to the right and left of the operator. Here, ψ_i is the initial state of the atom or molecule; most likely this is the ground state. The "go-to" state is ψ_f , which must have a higher energy such that the difference in energy from the excited to the ground state matches the energy of the light absorbed:

$$\lambda = \frac{hc}{\Delta E}$$

The transition dipole moment $\langle \hat{\mu} \rangle$, sometimes called the difference dipole moment, is related to the strength of the absorption. A large $\langle \hat{\mu} \rangle$ means that the atom or molecule has a large Beer's Law (ϵ) constant, although it should be noted that the absolute strength of the transition dipole moment is not very quantitative. Mostly, $\langle \hat{\mu} \rangle$ tells us whether absorption of light occurs or not. If $\langle \hat{\mu} \rangle = 0$ then we say that the excited state is "optically silent". Otherwise, $\langle \hat{\mu} \rangle > 0$ means that the transition between ground and excited states can occur through light absorption. We can also determine what molecular properties and dynamics allow for a non-zero $\langle \hat{\mu} \rangle$; these are called selection rules.

The fact that light is polarized is an important detail when calculating the transition dipole moment. As shown in Figure 15.7, the oscillation of the photon's electric field must be represented in the dipole operator. To demonstrate we study the case of x-polarized light impinging on the 1s ground state of a hydrogen atom. To describe this correctly the dipole operator must align in the x direction, requiring a modification of the dipole operator as:

$$\hat{\mu} = -e^2 \cdot \hat{x}$$

Since atoms are round and we are working in spherical coordinates, we have to substitute the x coordinate in the spherical form as: $\hat{\mu} = -e^2 \cdot r \cdot \sin(\theta) \cos(\phi)$. Inserting this into the expression for calculating difference dipole moment yields:

$$\langle \hat{\mu} \rangle = \int_0^\infty \psi_f^*(r) \cdot r \cdot \psi_i(r) \cdot 4\pi r^2 \partial r \cdot \int_0^\pi \psi_f^*(\theta) \psi_i(\theta) \cdot \sin^2(\theta) \cdot \partial \theta \cdot \int_0^{2\pi} \psi_f^*(\phi) \psi_i(\phi) \cdot \cos(\phi) \cdot \partial \phi$$

An interesting fact of this expression is that, while we think of the radial component as being overwhelmingly important, here it isn't so. The radial integral is non-zero for any combination of initial and final states, yet, we know from experiment that hydrogen is selective as to what transitions are optically allowed. In fact, the difference dipole moment is dependent on the angular integrals, as $\langle \hat{\mu} \rangle \neq 0$ if and only if the change in angular momentum quantum number from the ground to excited state is $\Delta l = \pm 1$. This spectroscopic selection rule is consistent with the fact that a photon has an angular momentum of $l = 1$, which conserves angular momentum upon absorption of light. Thus, the ground 1s state of hydrogen can only transition to a 2p state (x, y or z) depending on the polarization of light. Likewise if a hydrogen atom is in an excited 2p state it can transition only to the 3s or one of the 3d states. There are also selection rules about Δm_l depending on the light polarization and the initial and final states. Last, the process of

fluorescence is analogous to absorption in reverse, where a drop from an excited state to the ground state creates a photon. The same $\Delta l = \pm 1$ selection rule applies.

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