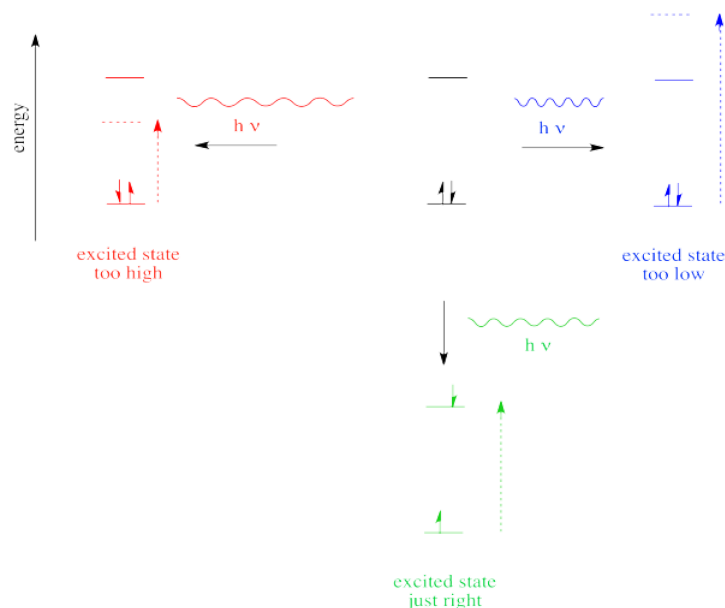


15.1: Introduction to Photochemistry

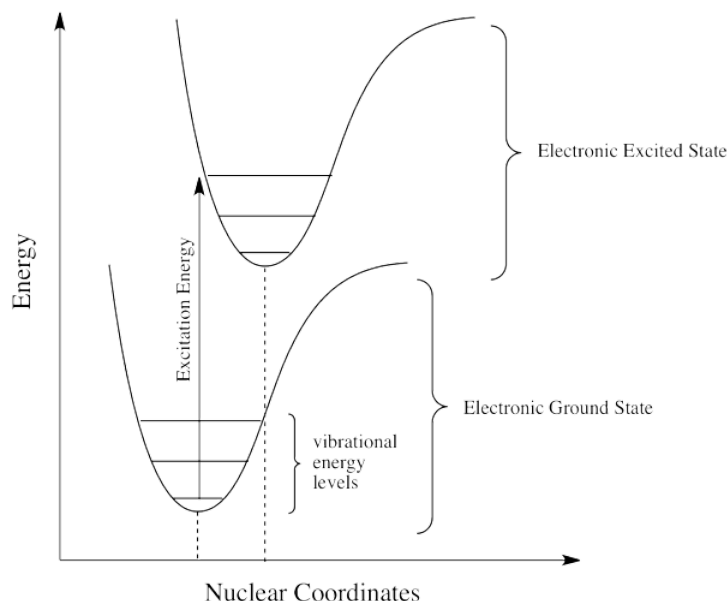
So far, we have come across one big rule of photon absorbance. In order to be absorbed, a photon's energy has to match an energy difference within the compound that is absorbing it.



In the case of visible or ultraviolet light, the energy of a photon is roughly in the region that would be appropriate to promote an electron to a higher energy level. Different wavelengths would be able to promote different electrons, depending on the energy difference between an occupied electronic energy level and an unoccupied one. Other types of electromagnetic radiation would not be able to promote an electron, but they would be coupled to other events. For example, absorption of infrared light is tied to vibrational energy levels. Microwave radiation is tied to rotational energy levels in molecules. Thus, one reason a photon may or may not be absorbed has to do with whether its energy corresponds to the available energy differences within the molecule or ion that it encounters.

Franck-Condon: Electronic and Vibrational Coupling

Photons face other limitations. One of these is a moderate variation on our main rule. It is called the Frank Condon Principle. According to this idea, when an electron is excited from its normal position, the ground state, to a higher energy level, the optimal positions of atoms in the molecule may need to shift. Because electronic motion is much faster than nuclear motion, however, any shifting of atoms needed to optimize positions as they should be in the excited state will have to wait until after the electron gets excited. In that case, when the electron lands and the atoms aren't yet in their lowest energy positions for the excited state, the molecule will find itself in an excited vibrational state as well as an excited electronic state.



That means the required energy for excitation doesn't just correspond to the difference in electronic energy levels; it is fine-tuned to reach a vibrational energy level, which is quantized as well.

- The Franck Condon Principle states that electronic transitions are vertical.
- A vertical transition is one in which none of the nuclei move while the electron journeys from one state to another.
- A vertical transition may begin in a vibrational ground state of an electronic ground state and end in a vibrational excited state of an electronic excited state.

LaPorte: Orbital Symmetry

There are other restrictions on electronic excitation. Symmetry selection rules, for instance, state that the donor orbital (from which the electron comes) and the acceptor orbital (to which the electron is promoted) must have different symmetry. The reasons for this rule are based in the mathematics of quantum mechanics. What constitutes the same symmetry vs. different symmetry is a little more complicated than we will get into here. Briefly, let's just look at one "symmetry element" and compare how two orbitals might differ with respect to that element.

If an orbital is centrosymmetric, one can imagine each point on the orbital reflecting through the very centre of the orbital to a point on the other side. At the end of the operation, the orbital appears unchanged. That means the orbital is symmetric with respect to a centre of inversion.



If we do the same thing with a sigma antibonding orbital, things turn out differently.



In the drawing, the locations of the atoms are labelled A and B, but the symmetry of the orbital itself doesn't depend on that. If we imagine sending each point on this orbital through the very centre to the other side, we arrive at a picture that looks exactly the opposite of what we started with. These two orbitals have different symmetry. A transition from one to the other is allowed by symmetry.

Problem RO2.1.

Decide whether each of the following orbitals is centrosymmetric.

- a) an s orbital b) a p orbital c) a d orbital d) a π orbital e) a π^* orbital

Problem RO2.2.

Decide whether each of the following transitions would be allowed by symmetry.

- a) $\pi \rightarrow \pi^*$ b) $p \rightarrow \pi^*$ c) $p \rightarrow \sigma^*$ d) $d \rightarrow d$

Symmetry selection rules are in reality more like "strong suggestions." They depend on the symmetry of the molecule remaining strictly static, but all kinds of distortions occur through molecular vibrations. Nevertheless, these rules influence the likelihood of a given transition. The likelihood of a transition, similarly, has an influence upon the extinction coefficient, ϵ .

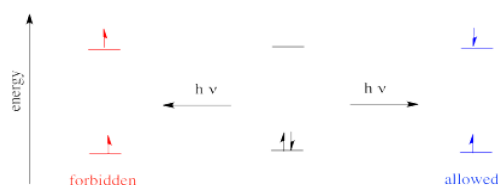
transition	ϵ , extinction coefficient
$\pi \rightarrow \pi^*$	3,000 - 25,000 $\text{M}^{-1} \text{cm}^{-1}$
$p \rightarrow \pi^*$	20 - 150 $\text{M}^{-1} \text{cm}^{-1}$
$p \rightarrow \sigma^*$	100 - 7,000
$d \rightarrow d$	5 - 400 $\text{M}^{-1} \text{cm}^{-1}$

Spin State

Let's take a quick look at one last rule about electronic emissions. This rule concerns the spin of the excited electron, or more correctly, the "spin state" of the excited species. The spin state describes the number of unpaired electrons in the molecule or ion.

number of unpaired electrons	spin state
0	singlet
1	doublet
2	triplet
3	quartet

The rule says that in an electronic transition, the spin state of the molecule must be preserved. That means if there are no unpaired electrons before the transition, then the excited species must also have no unpaired electrons. If there are two unpaired electrons before the transition, the excited state must also have two unpaired electrons.



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