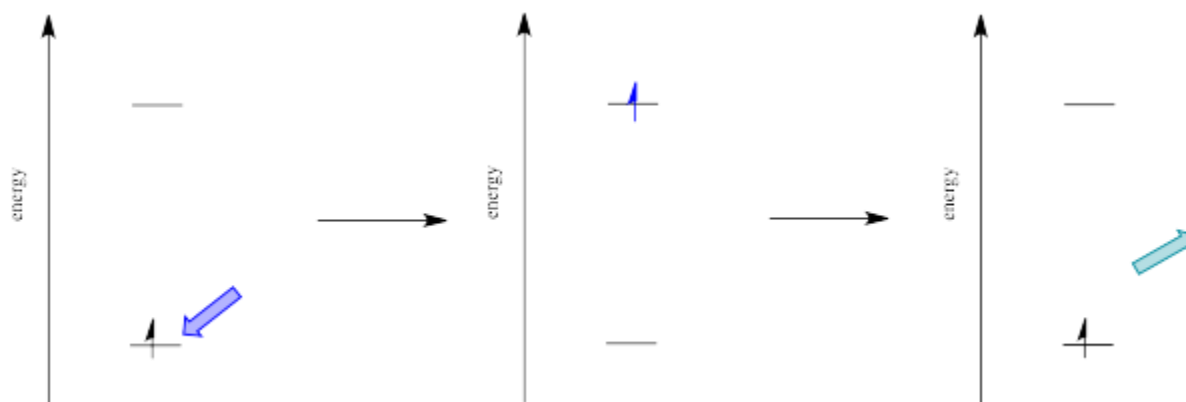


# FLUORESCENCE & PHOSPHORESCENCE

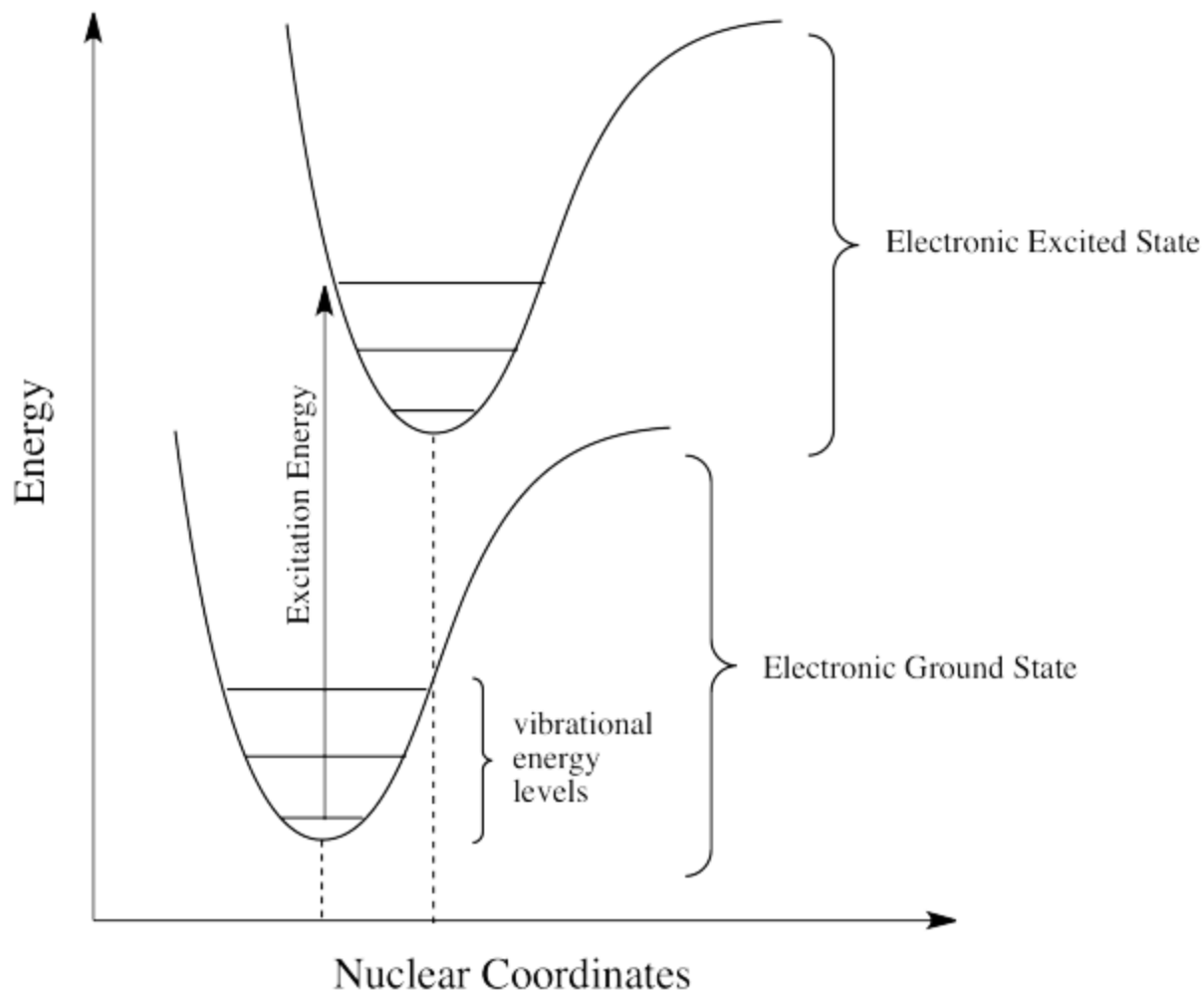
Sometimes, when an excited state species relaxes, giving off a photon, the wavelength of the photon is different from the one that initially led to excitation. When this happens, the photon is invariably red-shifted; its wavelength is longer than the initial one. This situation is called "fluorescence".



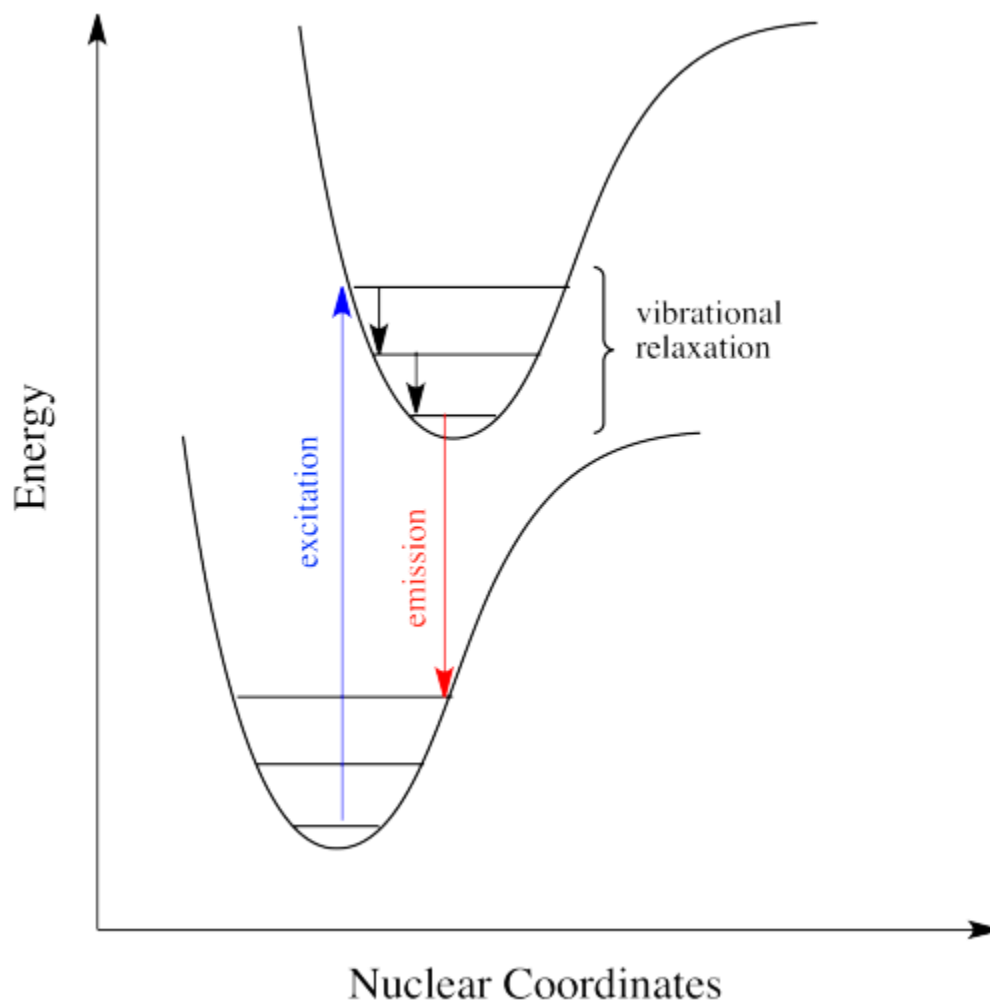
How can that be? Isn't energy quantized? How is the molecule suddenly taking a commission out of the energy the original photon brought with it?

## Relaxation and Fluorescence

This discrepancy is related to the Franck-Condon principle from the previous page. When an electron is promoted to an electronic excited state, it often ends up in an excited vibrational state as well. Thus, some of the energy put into electronic excitation is immediately passed into vibrational energy. Vibrational energy, however, doesn't just travel in photons. It can be gained or lost through molecular collisions and heat transfer.



The electron might simply drop down again immediately; a photon would be emitted of exactly the same wavelength as the one that was previously absorbed. On the other hand, if the molecule relaxes into a lower vibrational state, some of that initial energy will have been lost as heat. When the electron relaxes, the distance back to the ground state is a little shorter. The photon that is emitted will have lower energy and longer wavelength than the initial one.



Just how does a molecule undergo vibrational relaxation? Vibrational energy is the energy used to lengthen or shorten bonds, or to widen or squeeze bond angles. Given a big enough molecule, some of this vibrational energy could be transferred into bond lengths and angles further away from the electronic transition. Otherwise, if the molecule is small, it may transfer some of its energy in collisions with other molecules.

There are lots of examples of energy being transferred this way in everyday life. In a game of pool, one billiard ball can transfer its energy to another, sending it toward the pocket. Barry Bonds can transfer a considerable amount of energy through his bat into a baseball, sending it out of the park, just as Serena Williams can send a whole lot of energy whizzing back at her sister. In curling, one stone can transfer its energy to another, sending it out of the house and giving Canada the gold over Sweden.

Source: <http://employees.csbsju.edu/cschaller/Reactivity/photochem/PCfluorescence.htm>