

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 22: Molecular spectroscopy

References

1. Levine, *Physical Chemistry*, Chapter 20, 23.11

Key Concepts

- The conductivity of a semiconductor is typically small at room temperature and may not reach meaningful levels until temperatures of about 900 K. In order to alter the band structure of a semiconductor, dopants are typically added to create an extrinsic semiconductor. There are two types of dopants that can be added:
 - n-type: add a species that has one extra electron as compared to the host lattice (i.e. adding P to Si).
 - * n-type dopants create donor levels in the band gap near the bottom of the conduction band.
 - * This provides extra electrons to the conduction band leading to an increase in the concentration of electrons .
 - p-type: add a species that has one less electron as compared to the host lattice (i.e. adding B to Si).
 - * p-type dopants create acceptor levels in the band gap near the top of the valence band.
 - * This provides extra empty electron states easily accessible to electrons in the top of the valence band. This produces holes in the valence band .
- Spectroscopy of atoms only involved electronic transitions from one electronic state to another. Vibrational and rotational energy states do not exist in atoms.
- Electronic spectroscopy becomes more complex when molecules are considered. In addition to electronic states, molecules can have additional vibrational and rotational energy states.
 - Vibrational states are separated by smaller energies as compared to electronic states. These transitions fall into the IR region of the spectrum.
 - Rotational states are spaced at even smaller energies, usually in the microwave region of the spectrum.
- When looking at a UV/Vis spectrum of a molecule, there is finer structure due to the additional transitions (vibrational states) in between the larger electronic transition. This is why atomic spectrum contain sharp lines while the spectrum of a diatomic molecule would have several peaks spaced close together, which are a result of these additional transitions. A large polyatomic molecule has broad peaks (as we see in the lab) due to the overlap of many of these fine structure peaks.
- Several different kinds of transitions are possible in molecular spectroscopy:
 1. Radiative transitions: this is what we have considered so far. The transition between energy states results in either the absorption or emission of a photon. In the visible part of the spectrum this is what gives substances their color. Color substances appear colored due to the absorption of the complementary color of light. For example, chlorophyll appears green because it absorbs in the red. These types of transitions are the source of fluorescence.
 2. Non-radiative transitions: these typically occur between adjacent vibrational states through some dissipative process that does not result in the emission of a photon. Energy is dissipated through some sort of motion or collision.

3. Transition between “forbidden” electron states: this type of transition occurs infrequently and involves a transition between spin states, i.e. from the singlet to triplet state. From our approximations, these transitions are not “allowed”, which just means the probability is low. However, they do happen and are slow to decay back to the ground state. It is these types of transition that result in phosphorescence.