

## 2.13: Assignment of Bands Based on Solvent Effects

Spectra of organic molecules containing  $n$  and  $\pi$  electrons can frequently be assigned based on their solvent effects.

### Solvation

Solvents that do not itself absorb in the region under investigation are the most suitable for UV-visible spectroscopy. Most commonly used solvents are 95% EtOH, H<sub>2</sub>O and hexane. Often, both the intensity ( $\epsilon$ ) and  $\lambda_{max}$  shift with the change of the polarity of the solvent. While all solutes species interact with the surrounding solvent molecules to affect the electronic energies of the electronic state, charged and dipolar molecules interact especially strongly often resulting in pronounced spectral shifts.

#### Definition: Spectroscopic Changes

- **Bathochromic shift:** shift to longer  $\lambda$ , also called **red shift**.
- **Hypsochromic shift:** shift to shorter  $\lambda$ , also called **blue shift**.
- **Hyperchromism:** increase in  $\epsilon$  of a band.
- **Hypochromism:** decrease in  $\epsilon$  of a band.

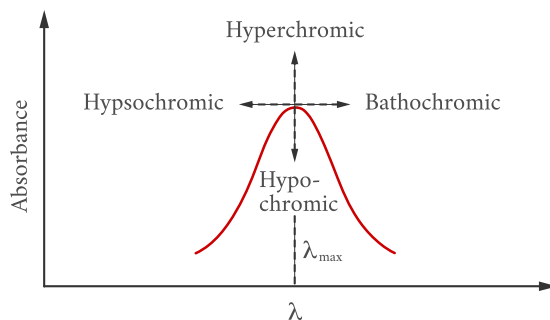


Figure 2.13.1: Terminology of Shifts in an absorption Band. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

The strength and nature of these interactions influence many properties of the solute including reaction rates. **Solvation** is the process of reorganizing solvent and solute molecules into solvation complexes and involves bond formation, hydrogen bonding, and van der Waals forces.

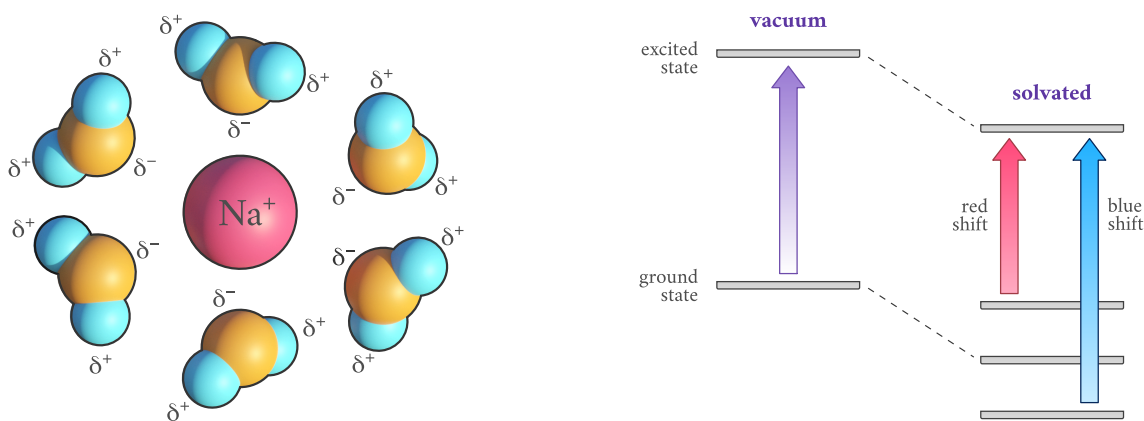


Figure 2.13.1: A sodium ion solvated by water molecules. (CC BY-NC 4.0; Ümit Kaya via LibreTexts) (left) Schematic illustration of energy level diagrams of the solute for understanding how its electronic states are changed due to the solvent effect. The vertical excitation energies required for transitions from ground to excited states are indicated with arrows. The dashed lines indicate the situation in which the excited state has the same electron distribution as the ground state. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

For compounds having  $n$ ,  $\pi$ , and  $\pi^*$  orbitals (e.g. formaldehyde), we can observe  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions. The absorption wavelength  $n \rightarrow \pi^*$  is typically longer than that of  $\pi \rightarrow \pi^*$  since the energy gap of  $n \rightarrow \pi^*$  is smaller than  $\pi \rightarrow \pi^*$ . Different types of transition are affected differently with changes in polarity.

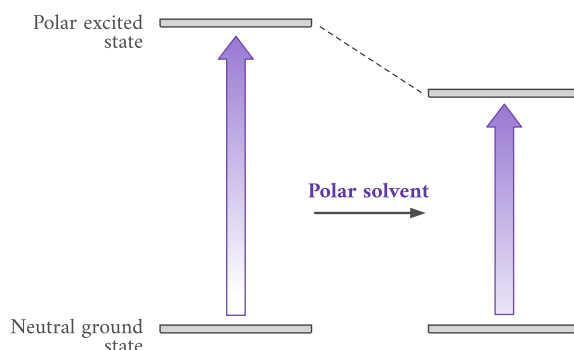
### $\sigma \rightarrow \sigma^*$ Transitions (Negligible Shifts)

Molecules showing this type of transition are non-polar since  $\sigma$  MOs are non-polar in nature. Therefore, changing the polarity of solvents has negligible effect on this transition. By increasing polarity of the solvent, compounds like hydrocarbons do not experience any appreciable shift. Thus, value of absorption maximum for non-polar compound is same in ethanol (polar) and hexane (non-polar).

### $\pi \rightarrow \pi^*$ Transitions (Bathochromic Shifts)

In case of  $\pi \rightarrow \pi^*$  transitions, the excited states are more polar than the ground state and the dipole-dipole interactions with solvent molecules lower the energy of the excited state more than that of the ground state. Therefore a polar solvent decreases the energy of  $\pi \rightarrow \pi^*$  transition and absorption maximum appears ~10-20 nm red shifted in going from hexane to ethanol solvent.

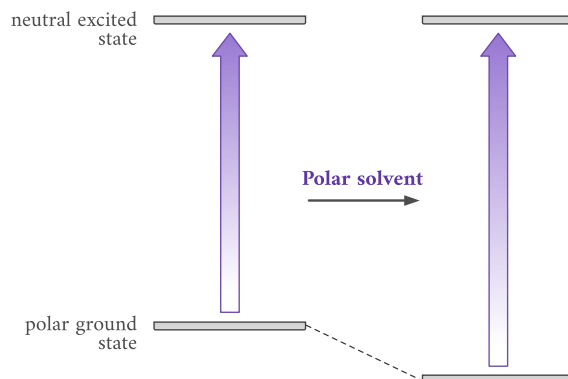
For this type of transition,  $\lambda_{max}$  value shifts to **longer wavelength** with increasing polarity solvents. If the excited state is polar, but the ground state is neutral, polar solvent will primarily interact with the excited state to stabilize it (decrease its absolute energy). Hence, absorption shifts to **longer wavelength**.



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### $n \rightarrow \sigma^*$ Transitions (Hypsochromic Shifts)

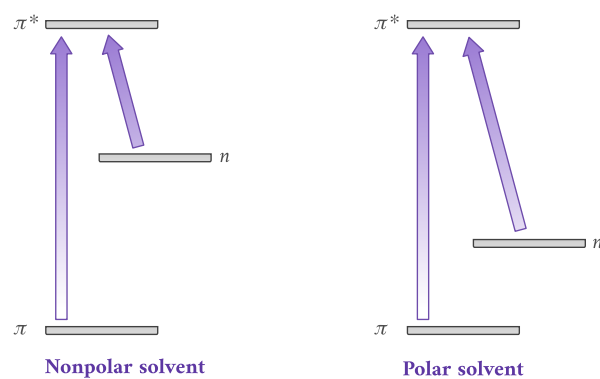
If excited state is neutral and ground states are polar. Polar solvents will preferentially solvate the ground state to lower its energy. Hence, absorption shifts to **shorter wavelength** with increasing polarity of the solvent.



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### $n \rightarrow \pi^*$ Transitions (Hypsochromic Shifts)

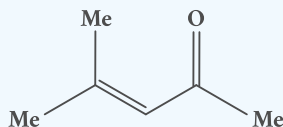
Similar to  $n \rightarrow \sigma^*$  transitions, the value of  $\lambda_{max}$  shifts to **shorter wavelength** for this transition.



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#### ✓ Example 2.13.1

Influence of solvent on the UV bands ( $\lambda_{max}$ ) of the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions of 4-methylpent-3-en-2-one is tabulate below.



Solvent	$\pi \rightarrow \pi^*$ (nm)	$n \rightarrow \pi^*$ (nm)
n-hexane	230	327

Solvent	$\pi \rightarrow \pi^*$ (nm)	$n \rightarrow \pi^*$ (nm)
ether	230	326
ethanol	237	315
water	245	305

Note that the  $\pi \rightarrow \pi^*$  increases wavelength (decreased excitation energy) and the  $n \rightarrow \pi^*$  decreases wavelength (increases excitation energy).

## Summary

In a polar solvent, the absorption of  $n \rightarrow \pi^*$  will shift to shorter wavelengths, while the  $\pi \rightarrow \pi^*$  will weakly (or not at all) shift to longer wavelengths because the polar solvent stabilizes these three orbitals in different extent,  $n > \pi^* > \pi$ , since  $\pi^*$  orbitals are more polar than  $\pi$  orbital as polar solvent stabilizes polar substances more (see [J. Chem. Phys. 121, 8435 \(2004\); doi:10.1063/1.1804957](#)). Thus, as solvent polarity increases:

- $\pi \rightarrow \pi^*$  band shifts to longer  $\lambda_{max}$
- $n \rightarrow \sigma^*$  band shifts to shorter  $\lambda_{max}$
- $n \rightarrow \pi^*$  band shifts to shorter  $\lambda_{max}$

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