

Experiment 5

UV-Visible Spectroscopy

Effect of Solvent on λ_{max}

Question format: Choose the single best answer and circle A, B, C, or D.

Advanced Multiple-Choice Questions

1. Which electronic-transition profile is most consistent with a carbonyl chromophore?

- A. It contains only σ electrons and therefore undergoes only $\sigma \rightarrow \sigma^*$ transition.
- B. It contains π and non-bonding electrons and may undergo both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.
- C. It contains only non-bonding electrons and therefore undergoes only $n \rightarrow \sigma^*$ transition.
- D. It cannot absorb in the ultraviolet region unless an auxochrome is removed.

2. An absorption band changes from 275 nm with an absorbance of 0.84 to 248 nm with an absorbance of 0.53. Which combination correctly describes the observed changes?

- A. Bathochromic and hyperchromic effects
- B. Bathochromic and hypochromic effects
- C. Hypsochromic and hyperchromic effects
- D. Hypsochromic and hypochromic effects

3. Why does increasing solvent polarity generally cause a hypsochromic shift for an $n \rightarrow \pi^*$ transition?

- A. The π^* orbital is stabilized more strongly than the n orbital, reducing the energy gap.
- B. Hydrogen bonding stabilizes the non-bonding electrons, increasing the energy gap between n and π^* .
- C. The π orbital is destabilized while the n orbital remains unaffected.
- D. Polar solvents eliminate the non-bonding electrons from the chromophore.

4. Which explanation best accounts for the bathochromic shift of a $\pi \rightarrow \pi^*$ transition in a polar solvent?

- A. The π orbital is stabilized more than the π^* orbital.
- B. The π^* orbital is more polar and is stabilized to a greater extent than the π orbital.
- C. The solvent increases the energy difference between π and π^* .
- D. Hydrogen bonding converts the $\pi \rightarrow \pi^*$ transition into an $n \rightarrow \pi^*$ transition.

5. For an $n \rightarrow \pi^*$ transition, the absorption maximum changes from 279 nm in hexane to 270 nm in methanol and 264 nm in water. Which conclusion is most appropriate?

- A. Increasing solvent polarity produces a progressive bathochromic shift.
- B. Increasing solvent polarity produces a progressive hypsochromic shift.
- C. Solvent polarity affects intensity but not wavelength.
- D. The transition changes from $n \rightarrow \pi^*$ to $\pi \rightarrow \pi^*$ in water.

6. The provided solvent-effect data show that, from hexane to water, the $\pi \rightarrow \pi^*$ band shifts from 230 to 245 nm, whereas the $n \rightarrow \pi^*$ band shifts from 327 to 305 nm. Which statement correctly interprets these results?

- A. Both transitions undergo bathochromic shifts.
- B. Both transitions undergo hypsochromic shifts.
- C. The $\pi \rightarrow \pi^*$ transition undergoes a bathochromic shift, while the $n \rightarrow \pi^*$ transition undergoes a hypsochromic shift.
- D. The $\pi \rightarrow \pi^*$ transition undergoes a hypsochromic shift, while the $n \rightarrow \pi^*$ transition undergoes a bathochromic shift.

7. Which statement most accurately defines an auxochrome?

- A. A group that always absorbs strongly in the visible region independently of any chromophore
- B. A functional group containing non-bonding electrons that modifies the wavelength or intensity of a chromophore when attached to it
- C. A group that eliminates conjugation and always causes a hypochromic effect
- D. A saturated hydrocarbon group that acts as the primary source of ultraviolet absorption

8. Benzene, phenol, and aniline have λ_{max} values of approximately 255, 270, and 280 nm, respectively. What is the most reasonable explanation for this trend?

- A. The OH and NH₂ groups decrease conjugation and increase the transition energy.
- B. The OH and NH₂ groups act as auxochromes and modify the aromatic chromophore, shifting absorption to longer wavelengths.
- C. Benzene undergoes $n \rightarrow \pi^*$ transition, while phenol and aniline undergo only $\sigma \rightarrow \sigma^*$ transition.
- D. The increasing molecular weight alone is responsible for the wavelength increase.

9. What is the principal spectroscopic consequence of converting phenol into phenoxide ion in an alkaline medium?

- A. Reduced conjugation, blue shift, and reduced absorption intensity
- B. Increased conjugation, red shift, and increased absorption intensity
- C. Loss of the aromatic π -system with no change in λ_{max}
- D. Protonation of oxygen followed by a hypochromic effect only

10. Why does protonation of an aromatic amine in acidic medium generally produce a hypsochromic shift?

- A. Protonation increases delocalization of the nitrogen lone pair over the aromatic ring.
- B. Protonation removes the aromatic π electrons completely.
- C. Protonation disturbs conjugation between the nitrogen lone pair and the aromatic π -system.
- D. Protonation stabilizes the excited state more strongly than the ground state.

11. Which solvent-selection criterion is most appropriate for UV spectroscopic analysis?

- A. The solvent should absorb more strongly than the analyte at the analytical wavelength.
- B. The solvent should neither absorb significantly in the analyte's absorption region nor undesirably affect its spectrum.
- C. Only highly polar solvents should be used for every compound.
- D. The solvent must always produce the longest possible λ_{max} .

12. In the acetone procedure, 0.50 mL of acetone is diluted to 10.0 mL, then 1.00 mL of this solution is diluted again to 10.0 mL. What is the final acetone concentration?

- A. 0.05% v/v
- B. 0.50% v/v
- C. 5.0% v/v
- D. 10.0% v/v

13. A paracetamol stock solution is prepared by dissolving 50 mg in 50 mL. A 5.0 mL portion is diluted to 50.0 mL, followed by diluting 2.5 mL of that solution to 25.0 mL. What is the final concentration?

- A. 0.001 mg/mL
- B. 0.010 mg/mL
- C. 0.100 mg/mL
- D. 1.00 mg/mL

14. Bromophenol blue has a λ_{max} of 437 nm in HCl and 591 nm in distilled water. Relative to the acidic medium, the change observed in water is best described as:

- A. A 154 nm hypsochromic shift
- B. A 154 nm bathochromic shift
- C. A 28 nm bathochromic shift
- D. A hyperchromic effect with no wavelength change

15. During the practical experiment, why must each acetone or paracetamol solution be scanned against an appropriate blank over 200-400 nm?

- A. To eliminate instrumental and solvent contributions and determine both λ_{max} and maximum absorbance of the analyte
- B. To convert every $n \rightarrow \pi^*$ transition into a $\pi \rightarrow \pi^*$ transition
- C. To ensure that absorbance remains identical in all solvents
- D. To determine the molecular weight of the analyte directly from the spectrum

Model Answer Key

Check your responses only after completing all questions.

1. B	6. C	11. B
2. D	7. B	12. B
3. B	8. B	13. B
4. B	9. B	14. B
5. B	10. C	15. A

Calculation Check

Question 12	First dilution: $0.50/10.0 = 0.05 = 5.0\% \text{ v/v}$. Second dilution is 1:10, so final concentration = $0.50\% \text{ v/v}$. Answer: B.
Question 13	Stock = $50 \text{ mg} / 50 \text{ mL} = 1.00 \text{ mg/mL}$. After 5.0 mL to 50.0 mL: 0.100 mg/mL . After 2.5 mL to 25.0 mL: 0.010 mg/mL . Answer: B.

Core concepts assessed: chromophores, auxochromes, bathochromic and hypsochromic shifts, hyperchromic and hypochromic effects, solvent polarity, pH effects, electronic transitions, and practical dilution steps.