

Chemistry 416 “Spectroscopy”
Fall Semester 1997
Dr. Rainer Glaser

Second 1-Hour Examination
“UV/Vis Spectroscopy”

Monday, November 3, 1997, 8:40 - 9:30

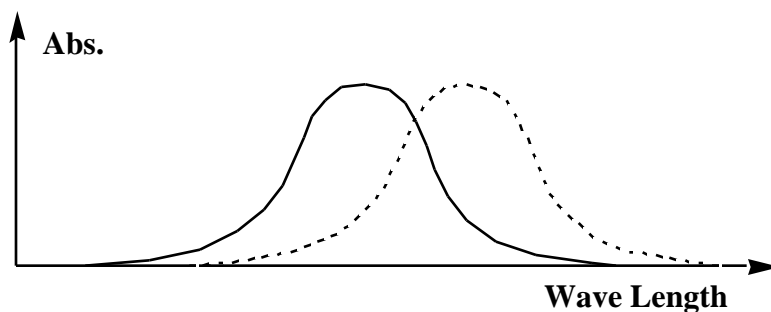
Name:
Answer Key

Question 1 (Basics)	30	
Question 2 (Combination)	28	
Question 3 (MOs & States)	20	
Question 4 (ORD)	12	
Question 5 (Octant Rule)	10	
Total	100	

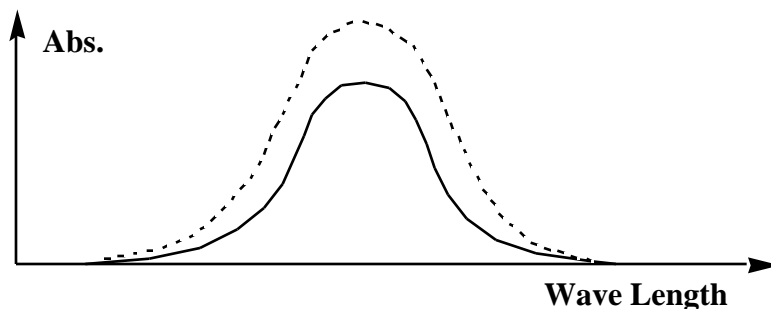
Question 1. Basics of UV/Vis Spectroscopy and Nomenclature. (30 points)

In parts (a) - (c), a UV/Vis peak is shown schematically which was recorded in solution. You should draw a second peak which satisfies the stated condition. (3 points each)

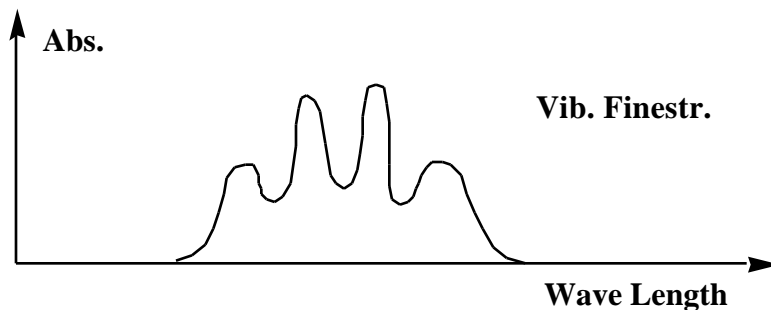
(a) Draw a peak that is shifted **bathochromically** relative to the peak shown.



(b) Draw a peak that shows **hyperchromism** relative to the peak shown.

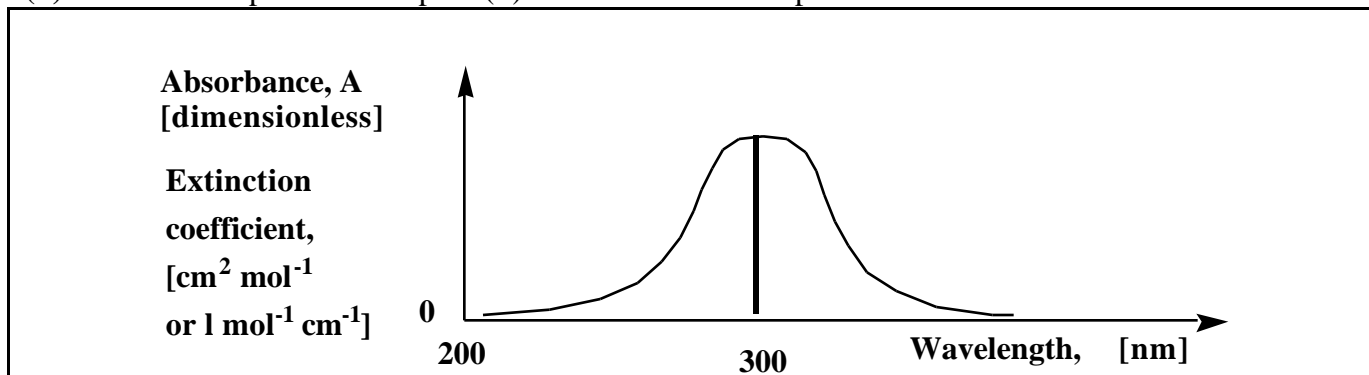


(c) Indicate expected changes to the **peak shape** if the spectrum would be recorded in the gas phase.

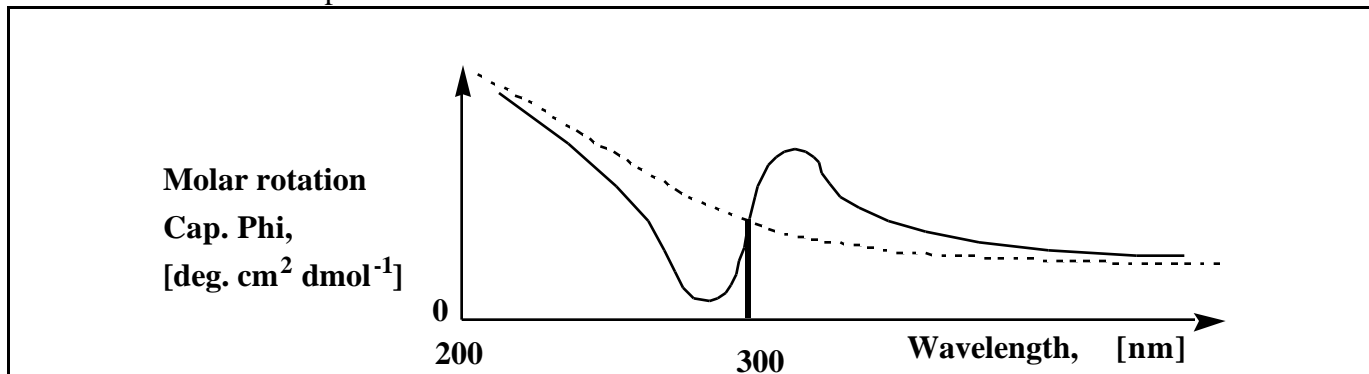


In parts (c) - (f), draw schematic spectra that match the criteria specified. In each case, the spectrum should be drawn for wavelengths of 200 - 500 nm. For each of the spectra, provide the following items: (1) Provide the name and the symbol of the axis parameter. (2) Provide the units for each axis parameter. (3) Draw a schematic spectrum. (7 points each)

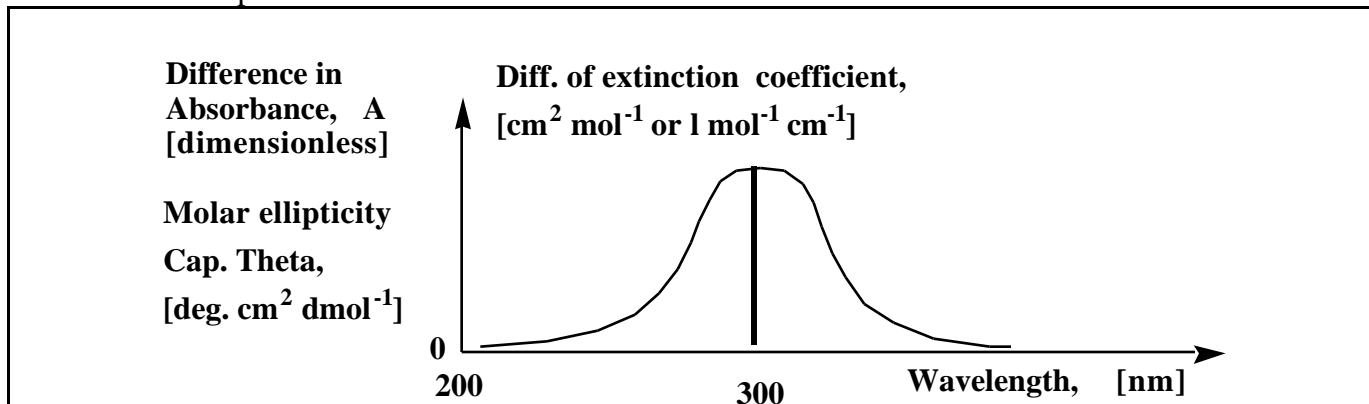
(d) The UV/Vis spectrum of a pure (+) enantiomer of a compound that absorbs at 300 nm.



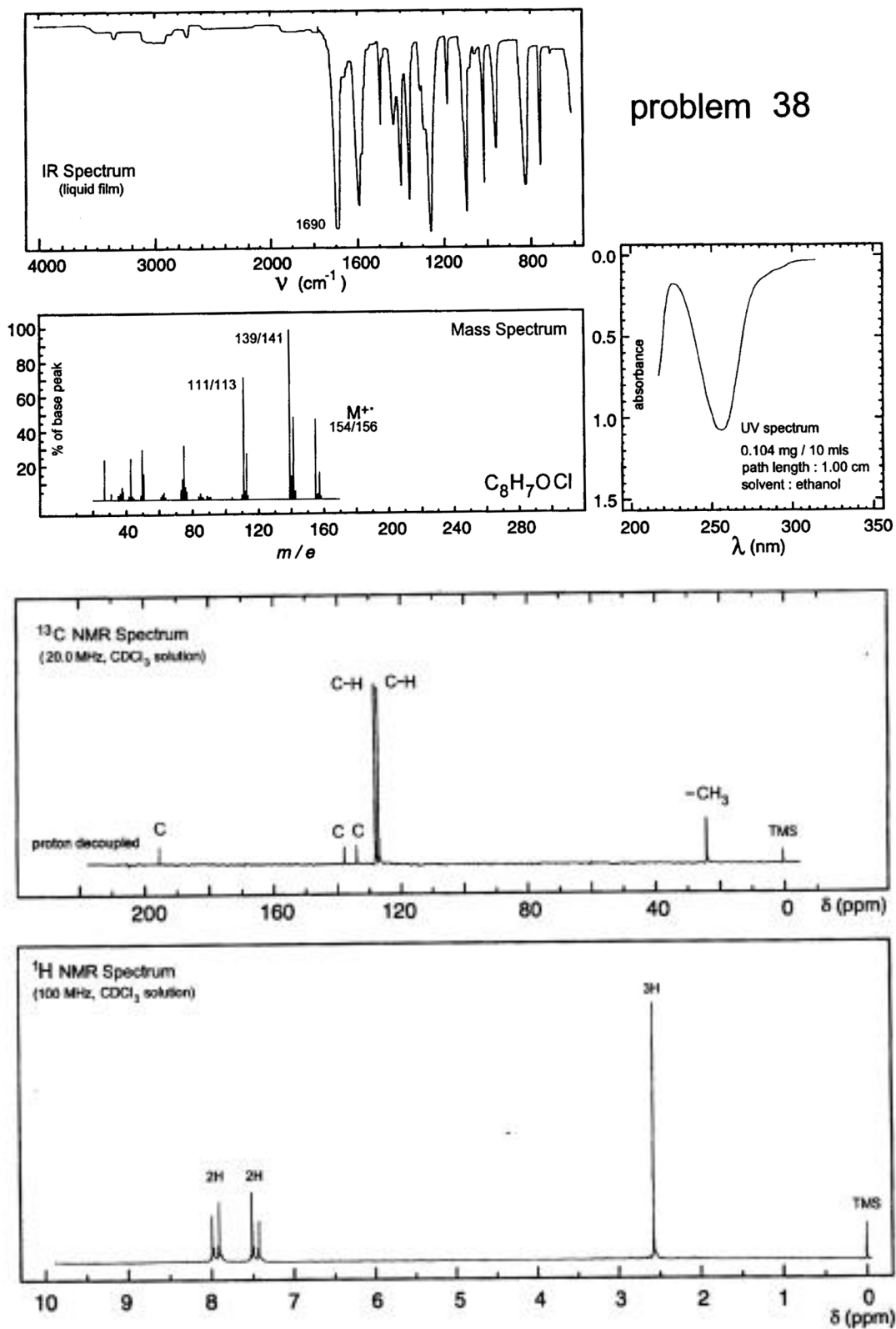
(e) The optical rotatory dispersion (ORD) spectrum of a pure (+) enantiomer of a compound that absorbs at 300 nm and shows a positive Cotton Effect.



(f) The circular dichroism (CD) spectrum of a pure (+) enantiomer of a compound that absorbs at 300 nm and shows a positive Cotton Effect.



Question 2. Combination Problem and Increment Systems. (25 points)



(a) Draw the structure and give the name of the unknown. (str. 5 p., name 2 p.)

para-chloroacetophenone. Every IUPAC compatible name is OK.

(b) What pertinent information about the unknown did you obtain from the IR spectrum?

CO in ketone, not CO in acid chloride

(c) The H-NMR spectrum contains two doublets at about 7.45 and 8 ppm. Using the increment system to predict the H-NMR chemical shifts of substituted benzenes, assign these peaks to the correct hydrogens in the structure you suggested in part (a). [Hint: You may use the tables on page H255ff in Pretsch et al.] (8 points)

H meta to Cl: $7.26 + 0.03$ (o-Cl) + 0.14 (m-COMe) = 7.43 ppm

H meta to COMe: $7.26 + -.62$ (o-COMe) - 0.02 (m-Cl) = 7.86 ppm

similar numbers with Lambert's table

(d) Use an increment system for the prediction of UV/Vis spectra to compute the absorption maximum for the compound you suggested in (a). How does the computed number compare to the measured spectrum? Provide the source for the increment system you used. (8 points)

Pretsch U40, Scott rules

246 (Ph-COR, R= alkyl) + 10 (p-Cl) = 256 nm.

Right on!

Question 4. Circular Dichroism of the Benzene Chromophore. (12 points)

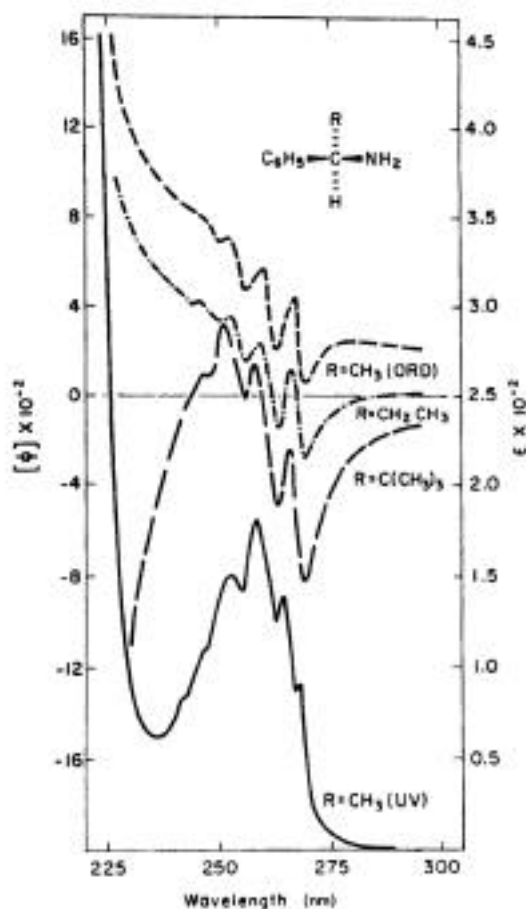


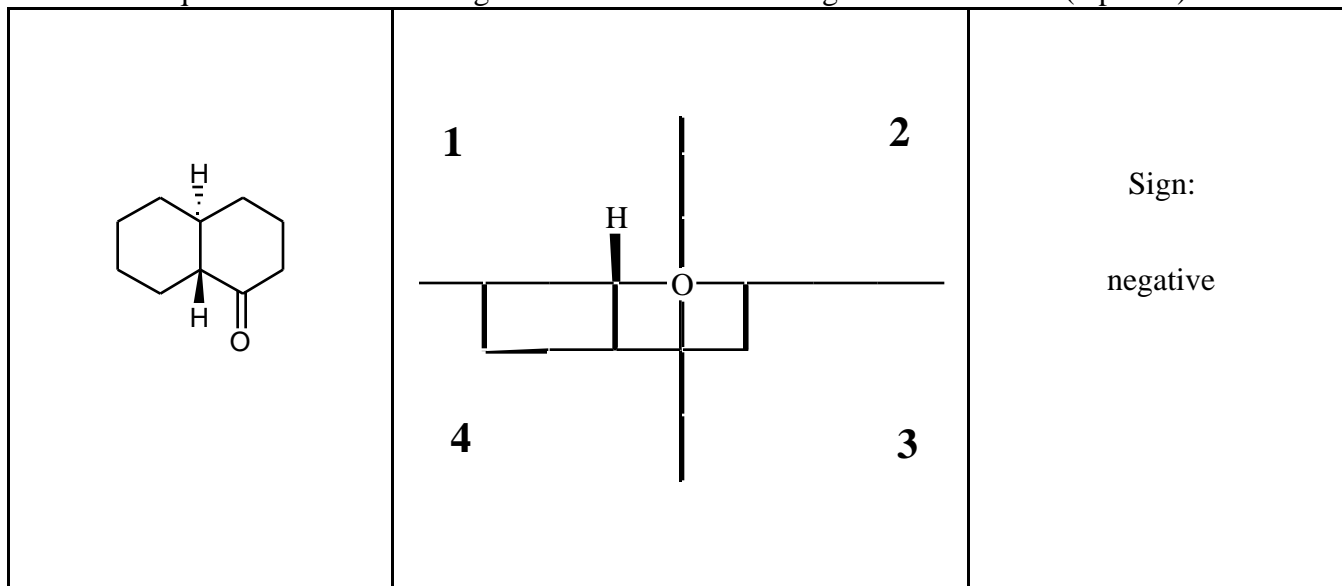
Figure 15.2 Electronic absorption spectrum (UV) of (*R*)- α -phenylethylamine [(*R*)-**1a**, $R = \text{CH}_3$] in absolute ethanol and optical rotatory dispersion (ORD) of (*R*)- α -phenylethylamine [(*R*)-**1a**, $R = \text{CH}_3$], (*R*)- α -phenyl-*n*-propylamine [(*R*)-**2a**, $R = \text{CH}_2\text{CH}_3$], and (*R*)- α -phenyl-neopentylamine [(*R*)-**3a**, $R = \text{C}(\text{CH}_3)_3$] in methanol (reprinted with permission from *Tetrahedron*, 1968, **24**, 1327–35; Copyright 1968, Pergamon Press).

These anilines with the *R* configuration display a number of _____ (positive, **negative**) Cotton effects associated with the 1L_b (give label of the band) transition that are superimposed on a strong plain background curve. While the benzene chromophore is inherently achiral, the chiral anilines show ORD spectra because the chromophore is chirally perturbed. For (*R*)- α -phenylethylamine [(*R*)-**1a**] and (*R*)- α -phenyl-*n*-propylamine [(*R*)-**2a**], the plain dispersion curves from 225 to 240 nm are positive and their rotatory powers in methanol using sodium D light are positive. Below 240 nm, the plain dispersion curve for (*R*)- α -phenyl-neopentylamine [(*R*)-**3a**] is negative. In a qualitative way it is easy to understand why the background ORD curve of (*R*)-**3a** is negative. The background curve at 225–240 nm is the sum of the long-wavelength wings for all of the Cotton effects at shorter wavelengths. Thus, the background curves in Fig. 15.2 are the sums of a number of positive and negative plain dispersion curves associated with positive and negative Cotton effects of the 1B and 1L_a (give labels of the bands) transitions in the UV region.

Question 5. Octant Rule. (10 points)

“The Chiroptical Properties of Carbonyl Compounds” D. N. Kirk *Tetrahedron* **1986**, 42, 777.

(a) In the space provided in the center, draw the projection of the ketone shown. Indicate the sign for each of the quadrants in the drawing. Determine the overall sign for the ketone. (5 points)



(b) Now consider the derivative with its Me-group in the α -position. Consider carefully whether this methyl group lies in octant 1, octant 2, octant 3, or octant 4, or in neither one of these. Explain your answer with a drawing that clearly shows the three planes that define the octants. (5 points)

