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:

|		
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)
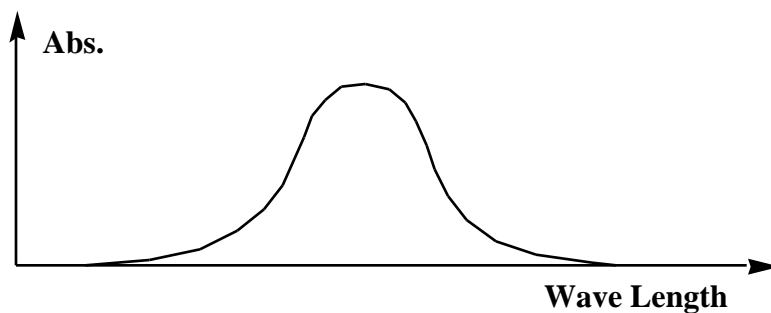
(a) Draw a peak that is shifted **bathochromically** relative to the peak shown.
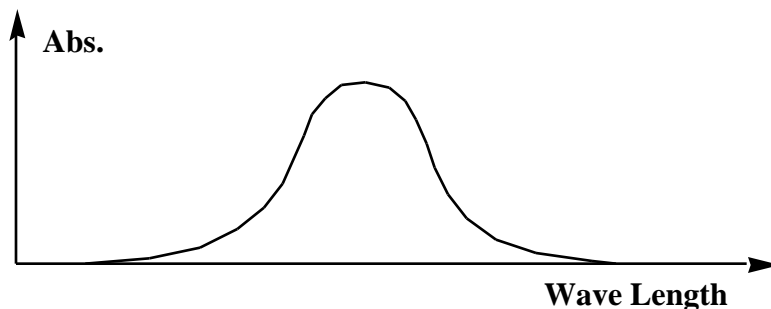
**(b)** Draw a peak that shows **hyperchromism** relative to the peak shown.
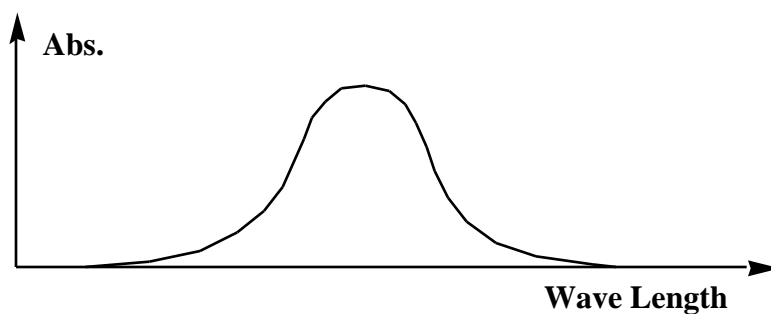
(c) Indicate expected changes to the **peak shape** if the spectrum would be recorded in the gas phase.

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)
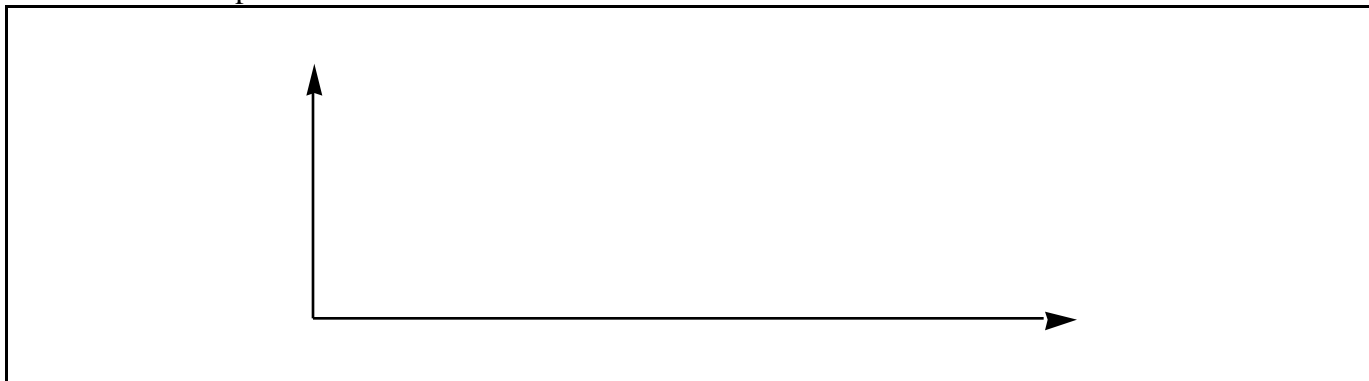
(d) The UV/Vis spectrum of a pure (+) enantiomer of a compound that absorbs at 300 nm.
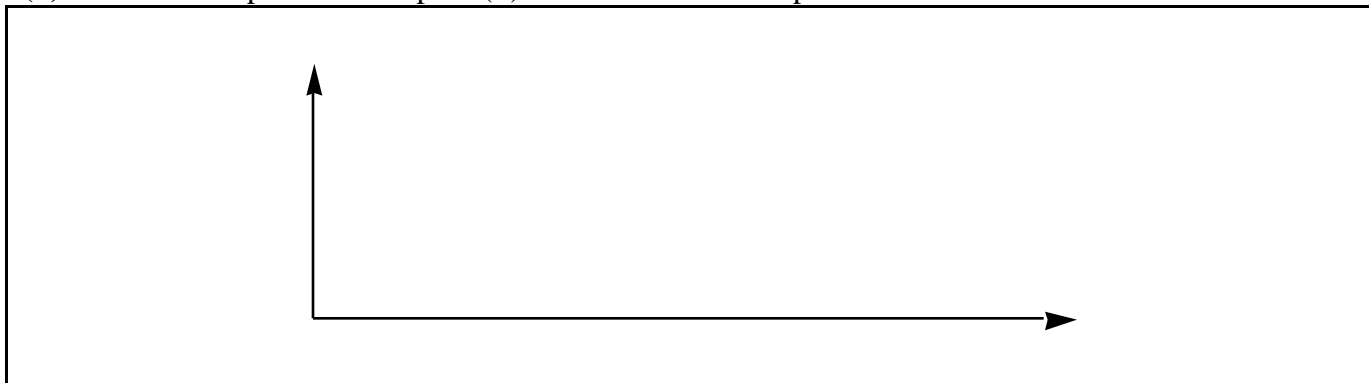
(e) The optical rotatory dispersion (ORD) spectrum of a pure (+) enantiomer of a compound that absorbs at 300 nm and shows a positive Cotton Effect.
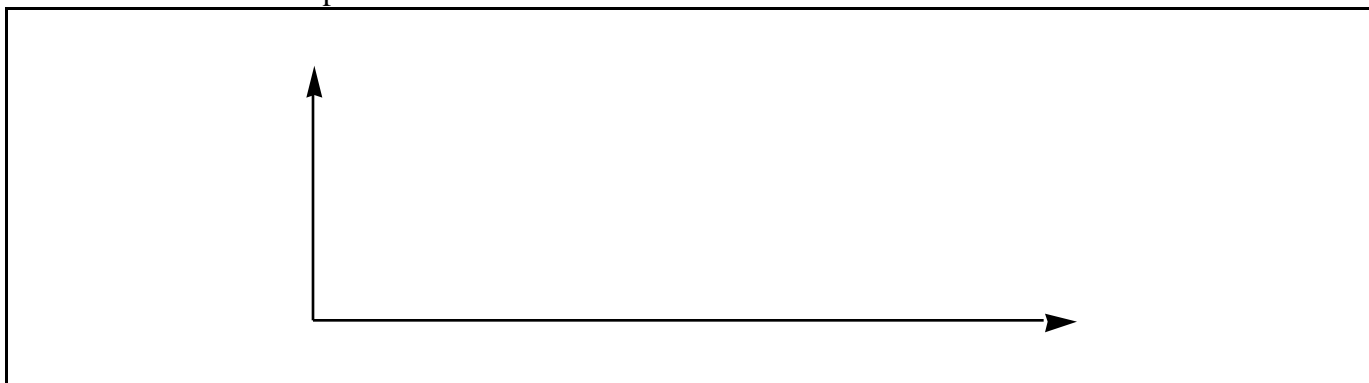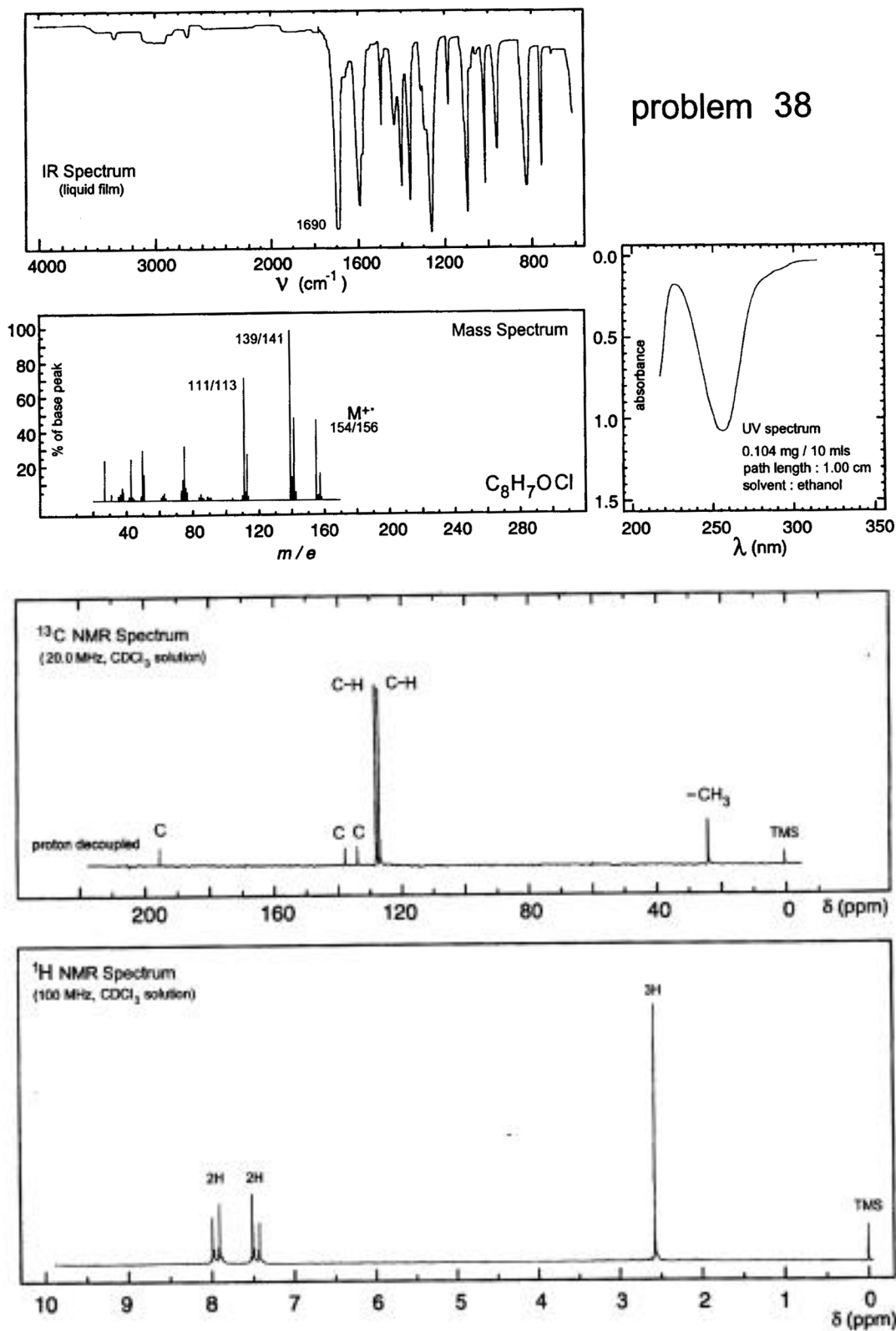
(f) The circular dichroism (CD) spectrum of a pure (+) enantiomer of a compound that absorbs at 300 nm and shows a positive Cotton Effect.

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

problem 38

IR Spectrum (liquid film)
1690
ν (cm⁻¹)

Mass Spectrum
139/141
111/113
M⁺˙
154/156
C_8H_7OCl
% of base peak
m / e

UV spectrum
0.104 mg / 10 mls
path length : 1.00 cm
solvent : ethanol
absorbance
λ (nm)

¹³C NMR Spectrum
(20.0 MHz, CDCl₃ solution)
C-H   C-H
=CH₃
C   C C   TMS
proton decoupled
δ (ppm)

¹H NMR Spectrum
(100 MHz, CDCl₃ solution)
3H
2H 2H
TMS
δ (ppm)

(a) Draw the structure and give the name of the unknown.

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

(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.]

(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.

Question 3. Molecular Orbitals and Electronic States. (20 points)

**(a)** Draw the 4 π-MOs of butadiene. Indicate the phase (sign) of each AO and show all nodes (if any).

Most bonding MO	HOMO
LUMO	Least bonding MO

(b) Draw a MO level diagram for the specified states of butadiene.

Ground State S_0	Lowest Excited Singlet State, S_1	Second Excited Singlet State, S_2	Lowest Triplet State, T_1

(c) Draw a diagram that shows the relative energies of the states S_0, S_1, S_2 and T_1. Connect the states involved in absorption, intersystem crossing, fluorescence and phosphorescence.

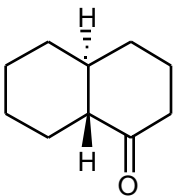**Question 4. Circular Dichroism of the Benzene Chromophore.** (12 points)
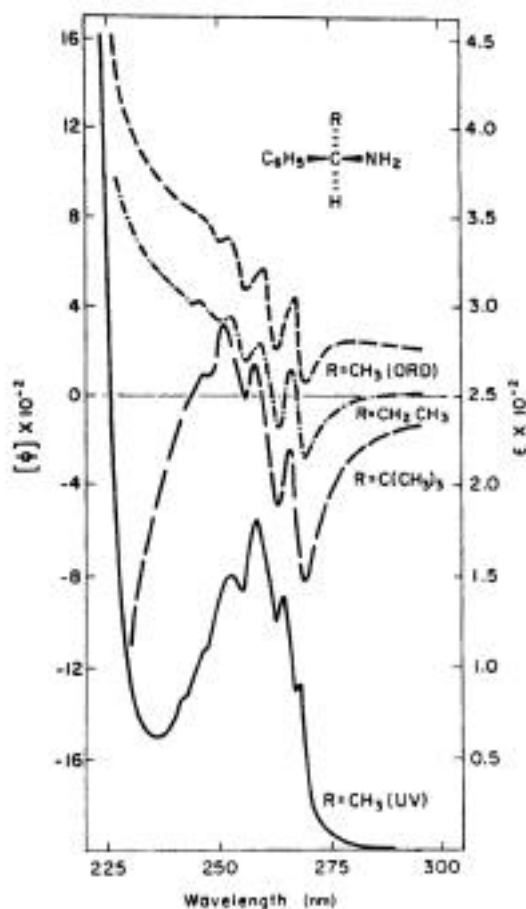
Figure 15.2 Electronic absorption spectrum (UV) of (R)-α-phenylethylamine [(R)-1a, R = CH₃] in absolute ethanol and optical rotatory dispersion (ORD) of (R)-α-phenylethylamine [(R)-1a, R = CH₃], (R)-α-phenyl-n-propylamine [(R)-2a, R = CH₂CH₃], and (R)-α-phenyl-neopentylamine [(R)-3a, R = C(CH₃)₃)] in 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 _____ (give label of the band) transition that are superimposed on a strong plain background curve. While the benzene chromophore is inherently _____, the chiral anilines show ORD spectra because the chromophore is _____. For (*R*)- -phenylethylamine [(*R*)-**1a**] and (*R*)- -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*)- -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 _____ and _____ (give labels of the bands) transitions in the UV region.

— 7 —

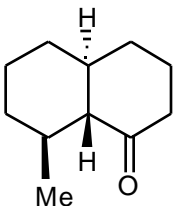**Question 5. Octant Rule.** (10 points)

"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)

	1 2	Sign:
	────────┼────────	
	4 3	

(b) Now consider the derivative with its Me-group in the '-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)

Explain: