

Examination in Elementary Spectroscopy

Date: 16/01/2009

Duration: 1h

Place: Amphi Ourisson

Number of pages: 6

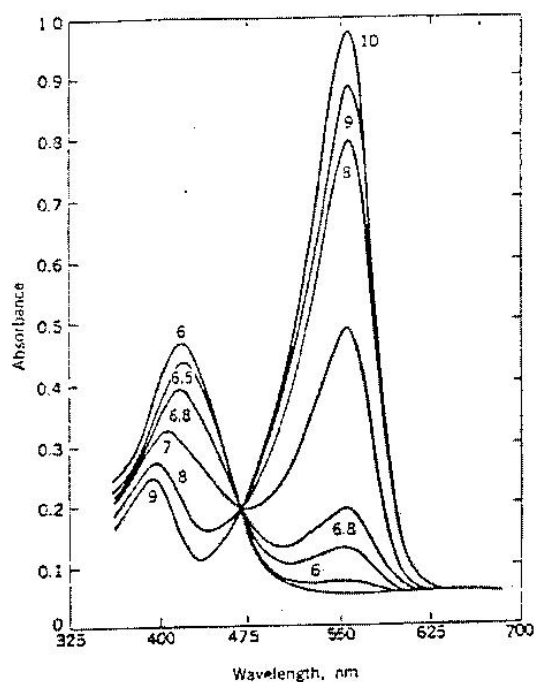
Remarks:

- Write your anonymous student number on each document leaf you hand back.
- Before starting to solve the problems, read the whole exam carefully.
- The questions do not need to be answered in a sequence.
- The number of points is given by the values \boxed{n} in the boxes.
- All documents are allowed. The use of a pocket calculator is allowed following the official note 86.228 from 28/07/1986. The exchange of pocket calculators and any documents between the candidates is strictly prohibited.

1 VIS/UV Spectroscopy

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Phenol red, a sulfonephthalein, is a powerful indicator used in acid-basic equilibria. At moderate pH values, the protonated (P_p) and unprotonated (P_u) forms of this molecule are at equilibrium. The following figure (adapted from G. W. Ewing, *Instrumental Methods of Analysis*, McGraw-Hill, New York, 1985) shows the UV-vis absorption spectrum of mixtures containing the species P_p and P_u , at different pH values, and conditions such that the total concentration c_0 of phenol red is kept constant.



For pH values lower than 6, only the protonated species is present in the mixture.

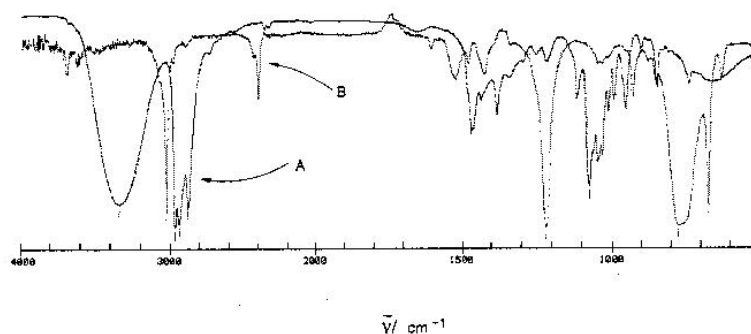
- What are the wavelengths at the absorption maxima of the P_p and P_u species, respectively? Give the corresponding transition energies in eV.
- What are the radiation colors observed, at the corresponding absorption maxima?
- Let ℓ be the optical path length, c_p the concentration of species P_p and c_u that of species P_u . Give the analytical expression for the absorbance as a function of the concentrations of the involved species at a general wave length.
- At the wave length 475 nm, the absorbance is pH-independent. This point is called the isosbestic point. Show that the molar absorption coefficients ϵ_p and ϵ_u are equal, at the isosbestic point.
- Given that the total phenol red concentration is $c_0 = 0.1$ mmol/L and that the optical path length is $\ell = 10$ cm, calculate the molar absorption coefficient at the isosbestic point.

2 IR Spectroscopy

4

Chloroform (CHCl_3) and butanol ($\text{C}_4\text{H}_{10}\text{O}$) are non-linear molecules. For each of them, give the number of vibrational modes. For chloroform, describe the different vibrational modes. What are the expected spectral ranges of the vibrational fundamentals?

The following figure superimposes the IR spectrum of chloroform and butanol. Assign spectra A and B by pointing out the occurrence of characteristic group vibrations. Concentrate at the peaks above 2000 cm^{-1} and assign all of them to characteristic group vibrations.



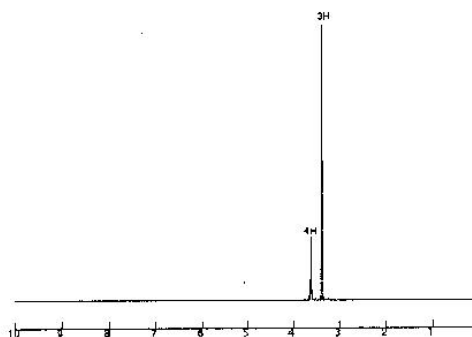
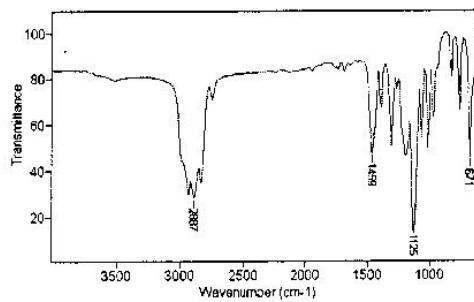
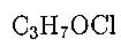
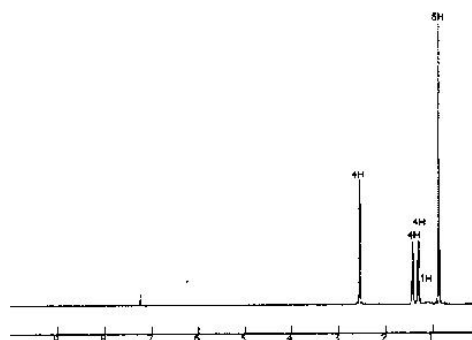
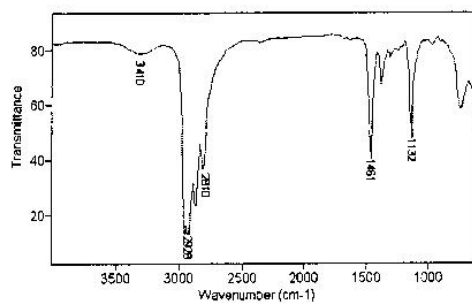
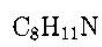
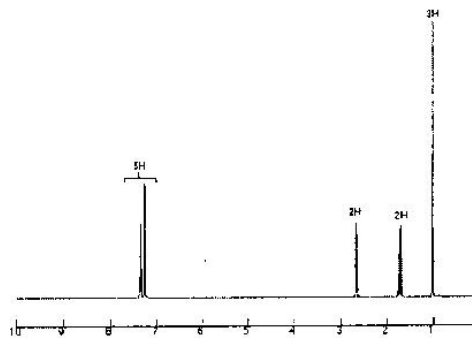
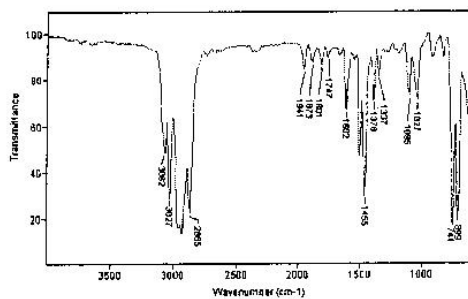
3 IR and NMR Spectroscopy

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For the following molecules, draw the tentative molecular structure based on the corresponding IR and NMR spectra. For each molecule, write one sentence containing the justification of your decision.

IR spectrum

NMR spectrum

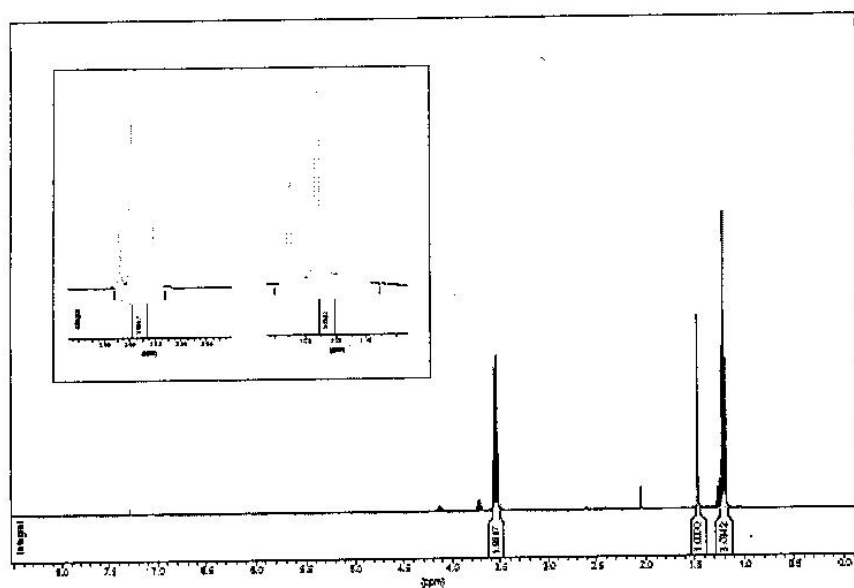


4 NMR Spectroscopy

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Predict the respective proton and carbon nmr spectra for cyclopentane. Justify your proposals (1point).

Given below are the proton and carbon spectra of an unknown compound of the molecular formula $C_8H_{18}O_3$. Identify the compound's constitution and draw its molecular structure. Hint for the 1H nmr: the coupling constants for the two multiplets at 1.21 and 3.55 ppm are 7.2 Hz each, and the respective relative integrations are 3:1:2 starting from 0 ppm (5 points).



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90.1152
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