CORK INSTITUTE OF TECHNOLOGY
INSTITIÚID TEICNEOLAÍOCHTA CHORCAÍ

Semester 2 Examinations 2009/10

Module Title: Advanced Spectroscopy

Module Code: CHEA8002

School: Science

Programme Title: **Bachelor of Science in Analytical Chemistry with Quality Assurance**

Programme Code: SACQA_8_Y4

External Examiner(s): **Dr. C. Lennon**
Internal Examiner(s): **Dr. R. Hourihane**

Instructions: **Attempt all Three Questions.**

Duration: 2 Hours

Sitting: Summer 2010

Requirements for this examination: Maths Tables

Note to Candidates: Please check the Programme Title and the Module Title to ensure that you have received the correct examination paper.
If in doubt please contact an Invigilator.

Q1. Molecular fluorescence and phosphorescence processes are known collectively as luminescence spectroscopic methods, one of the oldest analytical techniques still in use today. The two processes are related in that excitation is caused by absorption of photons of light, however, the energy transitions responsible for fluorescence do not involve a change in electron spin.

(i) Describe the background theory of luminescence spectroscopy.

(ii) Identify and discuss structural characteristics required by sample molecules analysed by these methods.

(iii) Detail the qualitative and quantitative applications of each technique as well as any the sample handling requirements associated with the methods**.** (28 marks)

Q2. Attempt **Three** of the following

(i) Apply the <u>Russel Saunders coupling approximation</u>, and deduce the term symbols and number of energy levels associated with a pair of ground state electrons p and d. Write a note explaining for the underlined term.

(ii) All spectral lines are subject to broadening. Natural line broadening is an example of one type.

(a) Write an informative note on natural line broadening.

(b) Name the other types of broadening

(c) Calculate the line width of a typical electronic excited state with $\tau \cong 10^4$ps

(iii) State the assumptions made by the Born-Oppenheimer approximation.(1927) Outline, briefly the contribution it made to interpretation of molecular spectra in terms of energy and wavefunction.

(iv) Describe in detail the operation of Laser atomisation sources. List three types of laser, outline their properties and principle uses.

(v) In addition to Chemical shift, (δ), and coupling constant, (J), the appearance of a proton nuclear magnetic resonance spectrum, (H^1NMR), depends on

(a) chemical equivalence of nuclei

(b) magnetic equivalence of nuclei …/

(c) number of coupled nuclei in a spin system

(d) the relative magnitudes of the frequency interval, (ΔVab, Hz), between coupled nuclei and their associated coupling constant, (Jab, Hz).

Write a **brief** note explaining each of the features listed (a) to (d).

(36 marks)

Q3. Attempt **Three** of the following

(i) Use the accompanying spectral data to deduce the structural formula of the unknown liquid sample, C_8H_7OCl . Explain briefly your interpretations of the various spectral features.

(ii) The key component of a Fourier Transform Infra red spectrometer, (FTIR), is the Miclelson interferometer. Outline its operation and justify its necessary inclusion in an FTIR instrument. Interferometric spectrometers offer many advantages over their dispersive counterparts, identify and explain briefly, **three** such advantages.

(iii) Background correction is essential in Atomic Absorption Spectroscopy, (AAS). Identify and describe at least **four** methods by which background correction may be achieved. Which of the methods described is most effective for high backgrounds?

(iv) Describe briefly the Raman scattering effect, (RS). List **three** advantages it offers over Infra red ,(IR), spectroscopy. There are a number of Raman-related spectroscopy's, for example Resonance Raman scattering, (RR), or Surface enhanced Raman scattering spectroscopy, (SERS) or Non-linear Raman spectroscopy, (NLRS), write a brief account of any **one** of the three listed techniques.

(v) Near infrared, (NIR), spectroscopy is fast becoming a routine tool for analysis. Discuss NIR under the following headings

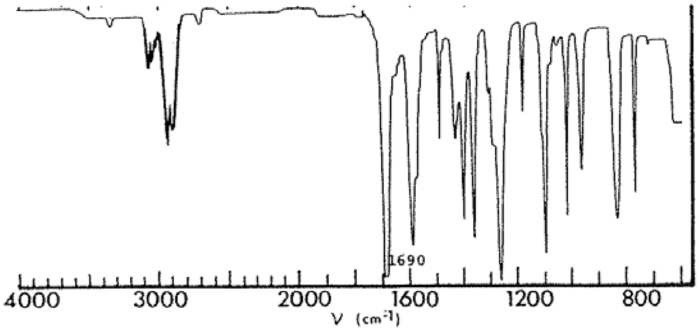
(a) spectral region and spectrum appearance

(b) bands observed and typical spectral units

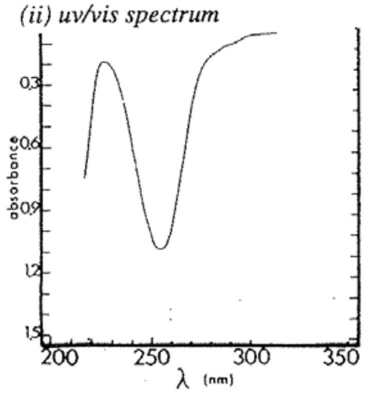
(c) NIR applications (36 marks)

Question 3(i) Liquid sample, molecular formula C_8H_7OCl

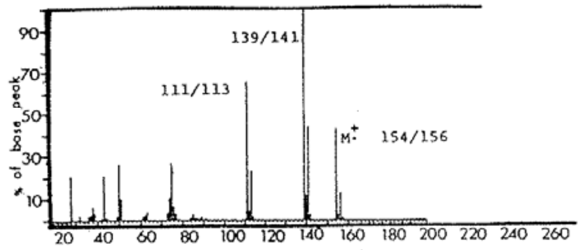
(i) infrared spectrum (liquid film)



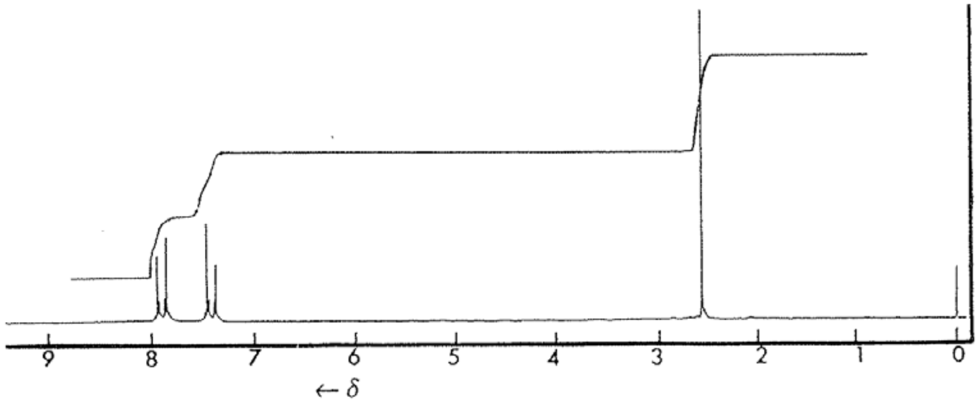
(ii) uv/vis spectrum



(iii) mass spectrum



(iv) ^1H NMR spectrum (100 MHz, $CDCl_3$)



(v) ^{13}C NMR spectrum (20 MHz, $CDCl_3$); the upper trace is the off-resonance decoupled spectrum

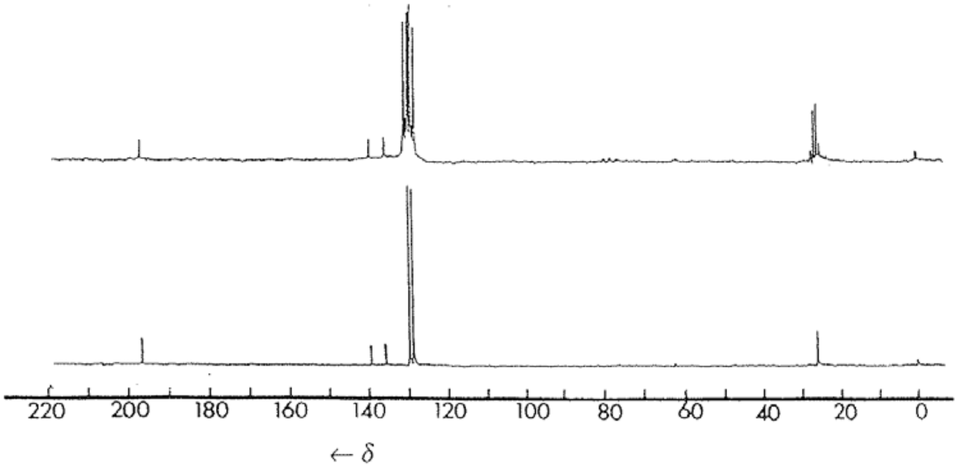
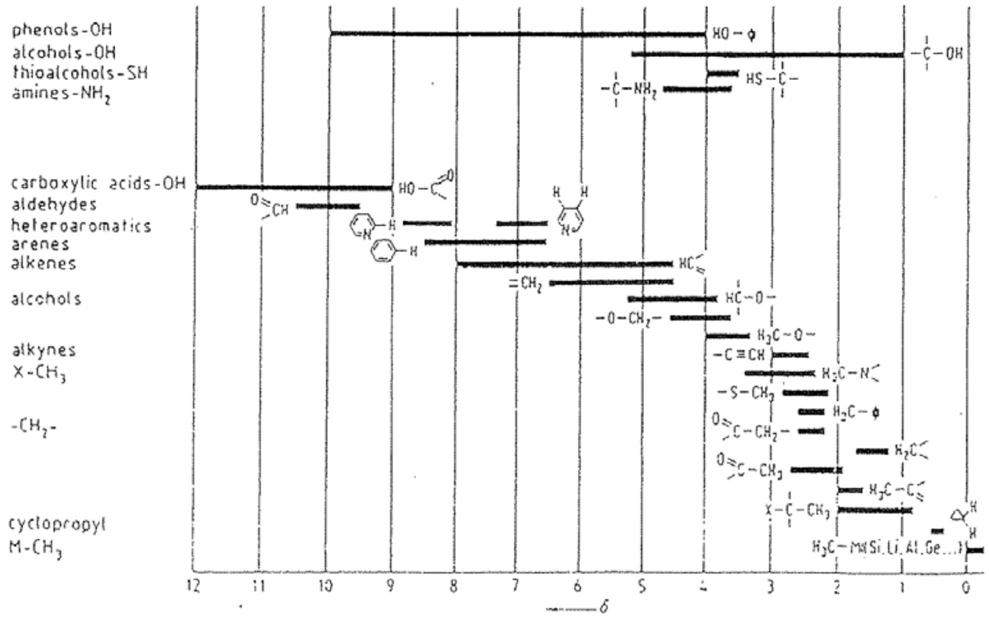


Table of infrared group frequencies

Bond	Compound type	Range/cm^{-1}	Intensity
C-H	alkanes	2850-2970	strong
	alkenes	3010-3095	medium
	alkynes	3300	strong
	arenes	3010-3100	medium
O-H	alcohols/phenols	3590-3650	variable
	H-bonded alcohols	3100-3200	variable
	carboxylic acids	3500-3550	medium
	H-bonded carb. acids	2500-3300	broad
N-H	amines, amides	3300-3500	medium
C=C	alkenes	1610-1680	variable
	arenes	1450-1600	variable
C≡C	alkynes	2100-2260	variable
C-N	amines	1180-1360	strong
C≡N	nitriles	2210-2280	strong
C-O	alcohols, ethers, esters, carboxylic acids	1050-1300	strong
C=O	aldehydes	1720-1740	strong
	ketones	1685-1725	strong
	carboxylic acids	1700-1725	strong
	esters	1735-1750	strong
	amides	1630-1690	strong
	acid chlorides	1785-1815	strong
	acid anhydrides	1740-1850 *(two bands)*	strong

^{1}H NMR chemical shifts



13C NMR chemical shifts