

الاجابة النموذجية لامتحان كيمياء طيفية (1)

312ك

(ورقة امتحانية كاملة)

الفرقة : الثالثة

الشعبة : الكيمياء

التاريخ : الأربعاء 2013 / 5 / 29

الممتحن : د/ محمد عبد الرحمن موسى ابو ريا

قسم : الكيمياء

كلية : العلوم

Model Answer

1 – a) Define each of the following terms:

i. Auxochrome.

ii. K band.

iii. Fermi resonance band.

iv. Hyperchromic shift.

Answer

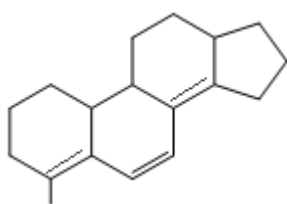
Auxochrome: A group which extends the conjugation of a chromophore by sharing of nonbonding electrons. They themselves fail to produce the colour; but when present along with the chromophores shift the absorption to longer wavelength.

K band: A band originate as a result of the possible transition in a compound containing a conjugated system in UV spectra.

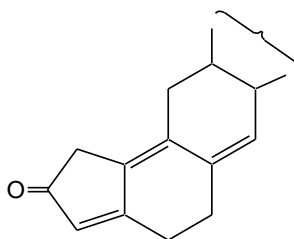
Fermi resonance band: A Fermi resonance is the shifting of the energies and intensities of absorption bands in an infrared or Raman spectrum, it occurs between normal and overtone modes, if they are nearly coincident in energy leads to two effects. First, the high energy mode shifts to high energy and the low energy mode shifts to still lower energy. Second, the weaker mode gains intensity.

Hyperchromic effect: An increase in absorption intensity.

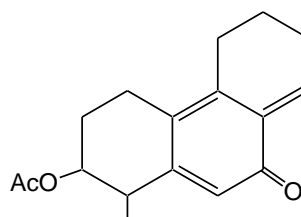
b) Calculate λ_{\max} of the following compounds:



(i)



(ii)

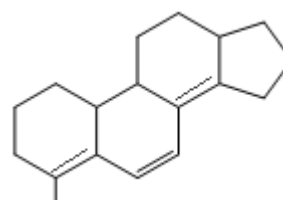


(iii)

Answer

i)

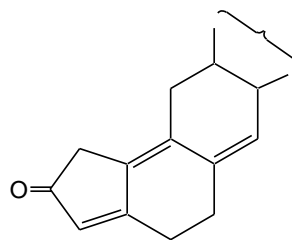
Parent heteroannular	215 nm
Extending conjugation	30 nm
Exocyclic double bond	3×5 nm
Ring residues	5×5 nm
	<hr/>
	285 nm



ii)

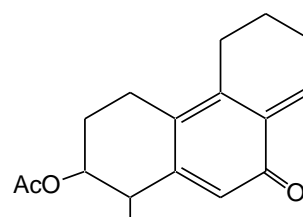
α, β unsaturated cyclopentanone	202 nm
Extending conjugation	2×30 nm
Exocyclic double bond	4×5 nm
β -ring residue	12 nm
γ -ring residue	18 nm
δ -ring residue	18 nm
higher ring residue	2×18 nm

366 nm



α, β unsaturated ketone	215 nm
Extending conjugation	2×30 nm
Exocyclic double bond	4×5 nm
Homoannular diene	39 nm
β -ring residue	12 nm
γ -ring residue	18 nm
δ -ring residue	18 nm
higher ring residue	18 nm

400 nm



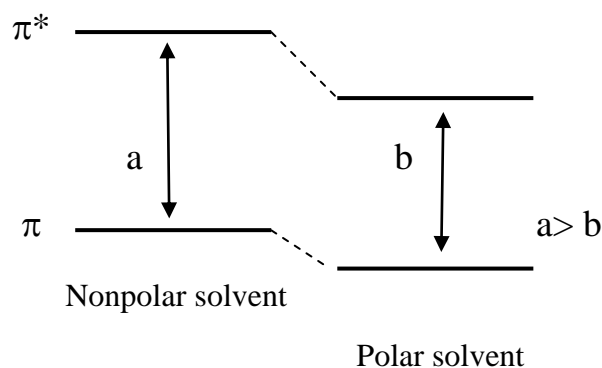
2- a) What are the solvent effects on the electronic transition in UV spectroscopy?

Answer

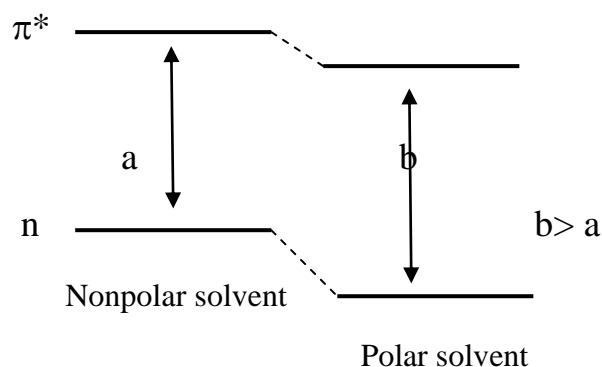
Solvent effects on organic reactivity and on absorption spectra have been studied for more than a century. It is well known that the photo-physical behavior of a dissolved dye depends on the nature of its environment, i.e. the intensity, shape, and maximum absorption wavelength of the absorption band of dye in solution depends strongly on the solvent-solute interactions and solvent nature.

Polar solvents "blur" vibrational features more than nonpolar. Polar solvents more likely to shift absorption maxima Shifts of λ_{\max} with solvent polarity.

$\pi \rightarrow \pi^*$ bathochromic/red shift. The absorption band moves to longer wavelength by increasing the polarity of the solvent. The dipole interactions with the solvent molecules lower the energy of excited state more than that of ground state.



$n \rightarrow \pi^*$ hypsochromic/blue shift. The absorption band moves to shorter wavelength by increasing the polarity of the solvent. The hydrogen bond with solvent molecules takes place to lesser extent with the carbonyl group in the excited state.

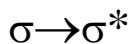


b) What are the types of electronic transitions in the following compounds:



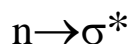
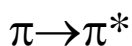
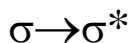
Answer

The types of electronic transitions in $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ are:



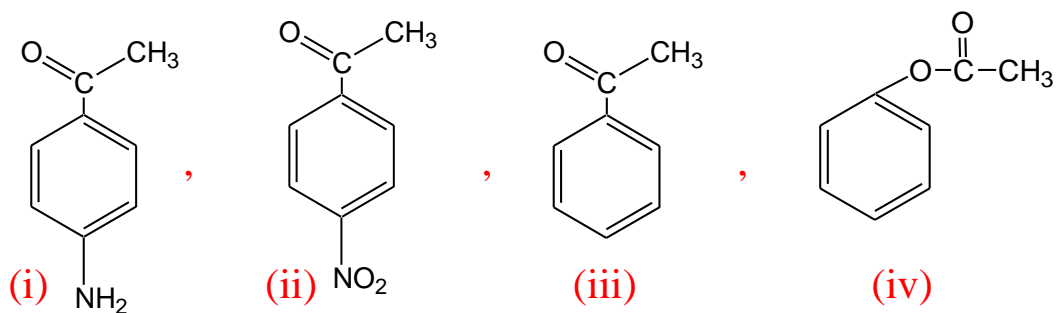
and $\pi \rightarrow \pi^*$

The types of electronic transitions in $\text{CH}_2=\text{CH}-\text{CHO}$ are:

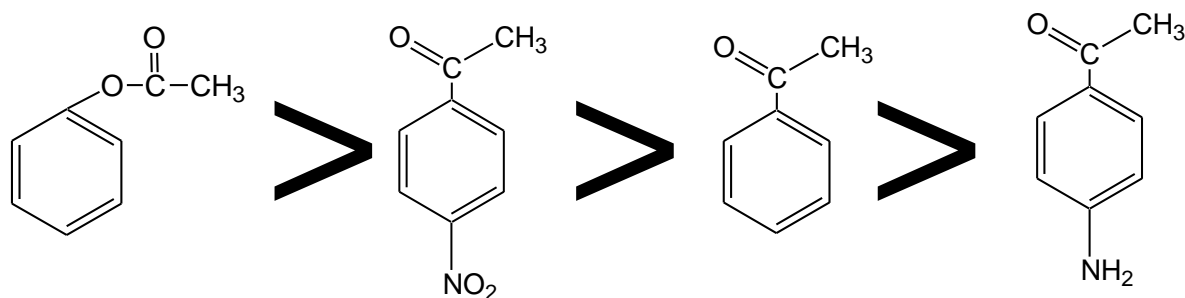


and $n \rightarrow \pi^*$

c) Arrange the following compounds according to decreasing the wavenumber of C=O:



Answer



In compound (iv) the oxygen withdrawing electrons by inductive effect so increase the double bond character and shift to higher wave number.

In compound (ii) the NITRO group withdrawing electrons by mesomeric effect but less than compound (iv) and increase the double bond character and shift to higher wave number.

compound (i) the amino group is donating group so it decrease the double bond character and shift to lower wave number.

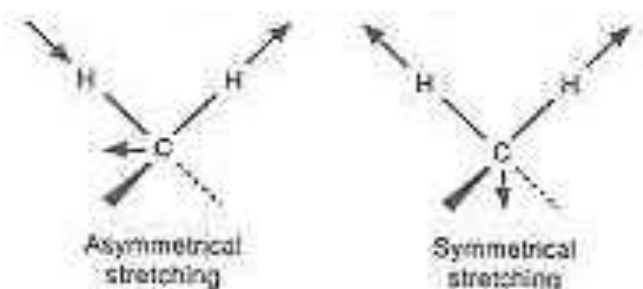
3- a) What are the types of molecular vibration?

Answer

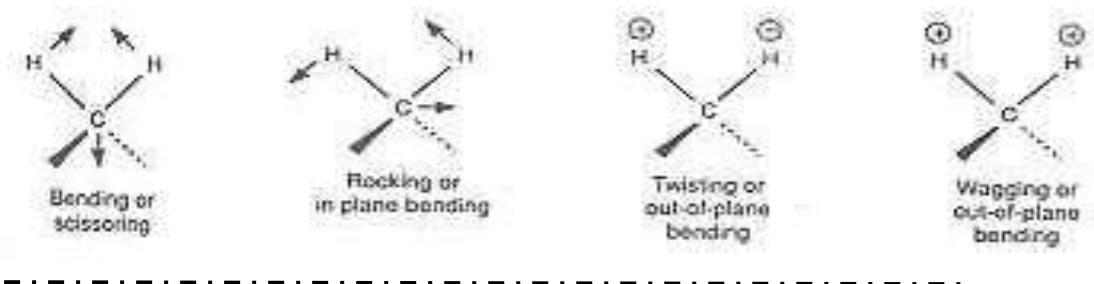
A molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion. The frequency of the periodic motion is known as a vibration frequency.

It can be divided into two types:

1- Stretching: a change in the length of a bond, such as C-H or C-C.



2- Bending: a change in the angle between two bonds, such as the HCH angle in a methylene group.



b) How will you differentiate between the following pairs of compounds using IR spectra?

i) $\text{CH}_3\text{CH}_2\text{CHO}$, $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$

ii) o-hydroxy benzoic acid, m-hydroxy benzoic acid.

iii) $\text{CH}_3\text{CH}_2\text{CN}$, $\text{CH}_3\text{CH}_2\text{NH}_2$

iv) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{OH}$

Answer

i) $\text{CH}_3\text{CH}_2\text{CHO}$, $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$

The propanal gives characteristic bands at : $1720-1740\text{ cm}^{-1}$ due to $\nu\text{ C=O}$ str.

The 2-propen-1-ol give characteristic bands at : $3300-3600\text{ cm}^{-1}$ due to $\nu\text{ O-H}$ str.

16505 cm^{-1} due to $\nu\text{ C=C}$ str.

ii) o-hydroxy benzoic acid, m-hydroxy benzoic acid.

Both show similar broad band at $3000-2500\text{ cm}^{-1}$ due to $\nu\text{ O-H}$ str.

But in o-hydroxy benzoic acid the intramolecular hydrogen bond takes place and shift to lower wave number and didn't affect by concentration.

iii) $\text{CH}_3\text{CH}_2\text{CN}$, $\text{CH}_3\text{CH}_2\text{NH}_2$

$\text{CH}_3\text{CH}_2\text{CN}$ gives characteristic bands at : 2250 cm^{-1} due to $\nu\text{ CN}$ str.

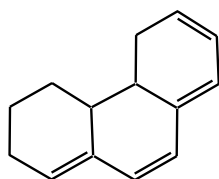
The ethyl amine gives characteristic bands at : $3250-3500\text{ cm}^{-1}$ due to $\nu\text{ N-H}$ str.

iv) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{OH}$

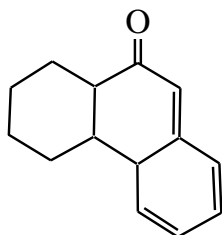
v) The benzyl amine gives characteristic bands at : $3250-3500\text{ cm}^{-1}$ due to $\nu\text{ N-H}$ str.,
at : $1600-1500, 1460\text{ cm}^{-1}$ due to $\nu\text{ C=C}$ str. Of benzene ring and bands at : $3100-3050\text{ cm}^{-1}$ due to $\nu\text{ =C-H}$ str.

$\text{CH}_3\text{CH}_2\text{OH}$ gives characteristic bands at : $3300-3600\text{ cm}^{-1}$ due to $\nu\text{ O-H}$ str. and bands at : $2720-2900\text{ cm}^{-1}$ due to $\nu\text{ -C-H}$ str.

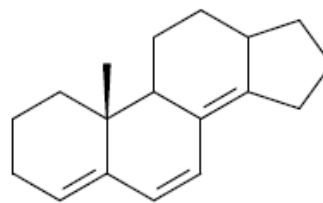
4-a) Calculate λ_{\max} of the following compounds:



(i)



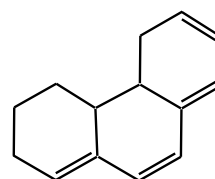
(ii)



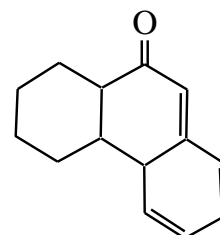
(iii)

Answer

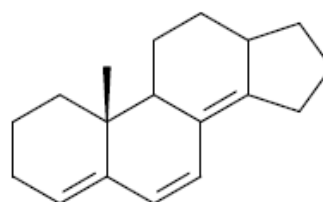
Parent homoannular	253 nm
Extending conjugation	2× 30 nm
Exocyclic double bond	2×5 nm
Ring residues	4×5 nm
	<u>343 nm</u>



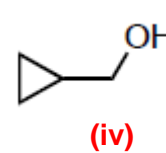
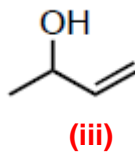
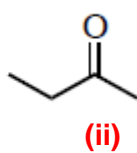
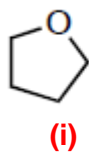
α, β unsaturated ketone	215 nm
Extending conjugation	2× 30 nm
Exocyclic double bond	5 nm
Homoannular diene	39 nm
β -ring residue	12 nm
higher ring residue	18 nm
	<u>349 nm</u>



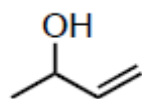
Parent heteroannular	215 nm
Extending conjugation	30 nm
Exocyclic double bond	3×5 nm
Ring residues	5×5 nm
	<u>285 nm</u>



b) Which of the following compounds gives an IR spectrum with a peak at 3300 cm^{-1} and at 1640 cm^{-1} ? (4 Marks)



Answer



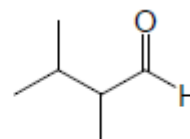
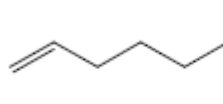
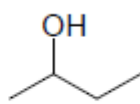
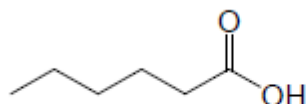
Compounds (iii) gives an IR spectrum with a peak at 3300 cm^{-1} and at 1640 cm^{-1}

c) Briefly explain why a C=O bond stretch occurs at 1750 cm^{-1} and a C-O stretch occurs at 1100 cm^{-1} . (4 Marks)

Answer

The double bond in the C=O is a stronger bond, so it vibrates at a higher frequency (higher energy) than the single bond.

5- Match the following compounds that are listed below with corresponding Infrared spectra that are displayed on the following. (Illustrate your choice)



Answer

