الإجابة النموذجية لامتحان الكيمياء العضوية الطيفية (١)

٣١٢ ك

(ورقة امتحانية كاملة)

الفرقة : الرابعة

الشعبة : كيمياء

التاريخ : السبت ١٤ / ١ / ٢٠١٧

الممتحن : د/ محمد عبد الرحمن موسى ابو ريا

قسم : الكيمياء

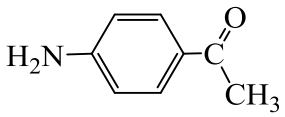
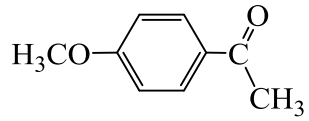
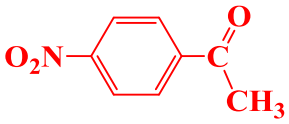
كلية : العلوم

I- Choose the correct answer:

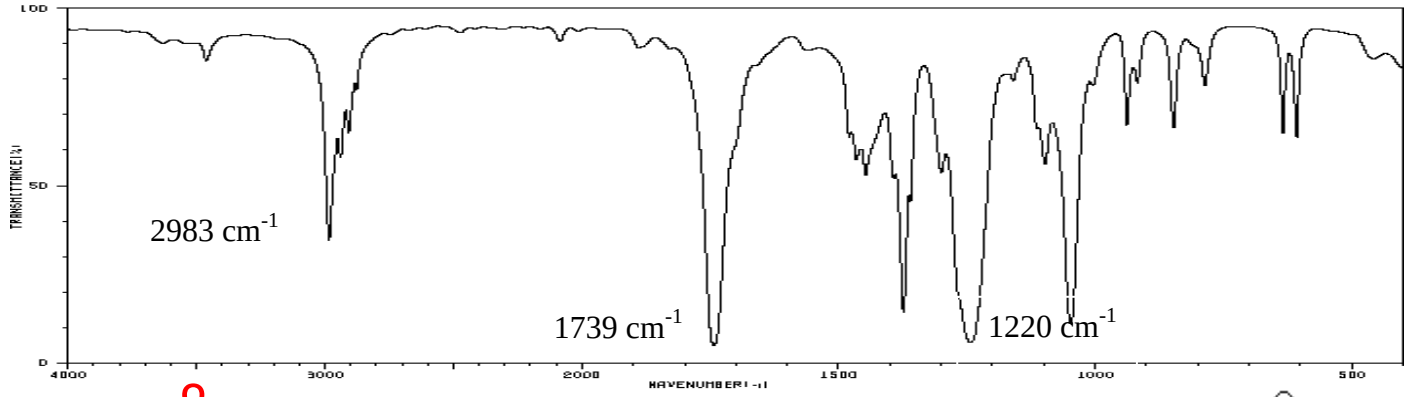
1) Which compound would be expected to show intense IR absorption at 3300 cm^{-1}?

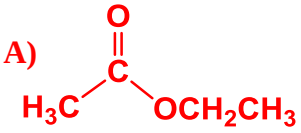
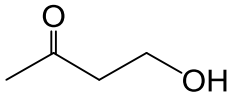
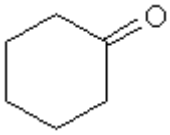
A) but-1-ene B) $H_3C-C\equiv C-CH_3$ **C)** **$H_3C-C\equiv C-H$**

2) Which of the following has a C=O stretch that occurs at the highest stretching frequency?

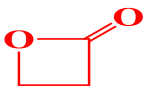
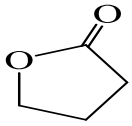
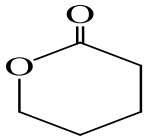
A)  B)  **C)** 

٣) Which of the following compounds match with the following IR spectrum:



A)  B)  C) 

4) Which compound would be expected to show highest stretching frequency of carbonyl group?

A)  B)  C) 

5) Which has a lower characteristic stretching frequency:

A) C-O bond B) C=O bond C) $C\equiv N$ bond

6) The vibration frequency of O-H of intermolecular bond……. by dilution.

A) increase B) decrease C) not changed

7) The region of the IR spectrum which contains the most complex vibrations (600-1400 cm^{-1}) is called the……. region of the spectrum.

A) near IR **B) fingerprint** C) stretching

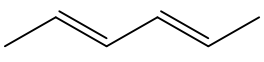
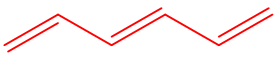
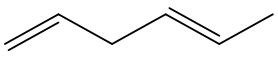
8) In order for a vibration mode to be observable in the IR, the vibration must change the…… of the molecule.

A) type of bonds B) frequency **C) dipole moment**

9) You look at an IR spectrum and see a collection of bands at 2800-2950 cm^{-1} you can conclude the molecule contains

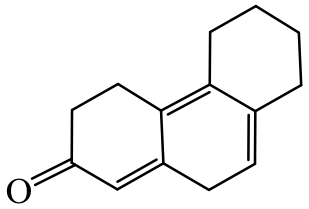
A) oxygen **B) aliphatic C-H bonds.** C) C=O bond.

10) Which of the following compounds exhibits the highest wavelength in its UV spectrum.

A)  **B)**  C) 

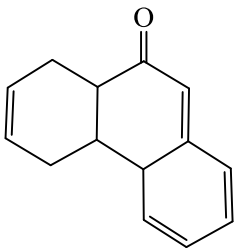
II- *a)* Calculate the λ_{max} for each of the following compounds: (12 Marks)

α,β-unsaturate ketones	215
Homoannular diene	39
Extended double bond	2 x 30
Exocyclic double bond	4 x 5
Ring residue and alkyl substituted	
β-Substituent	1 x 12
γ-Substitutent	1 x 18
δ- Substitutent	1 x 18
higher than δ	2 x 18
λmax (calc.)	418 nm



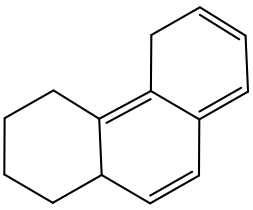
(I)

α,β-unsaturate ketones	215
Homoannular diene	39
Extended double bond	2 x 30
Exocyclic double bond	1 x 5
Ring residue and alkyl substituted	
β-Substituent	1 x 12
higher than δ	1 x 18
λmax (calc.)	349 nm



(II)

Homo annular diene	253 nm
Extended double bond	2 x 30 nm
Exocyclic double bond	3 x 5 nm
Ring residue and alkyl substituted	5 x 5 nm
λmax (calc.)	353 nm



(III)

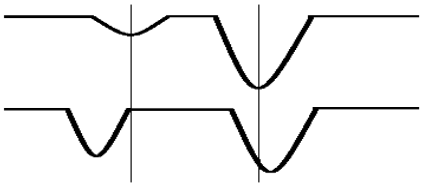
***b)* Define each of the following:**

i- Chromophores: functional groups that give electronic transitions.

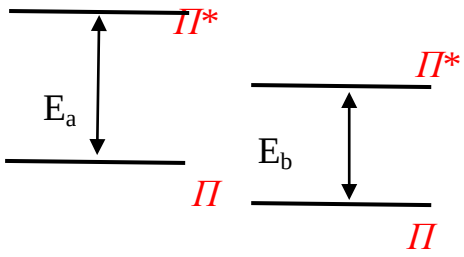
ii- Overtone Bands: Overtone bands in an infrared spectrum are analogous and are multiples of the fundamental absorption frequency (2 υ′)

iii- Bathochromic shift: shift to longer wave length λ, also called red shift.

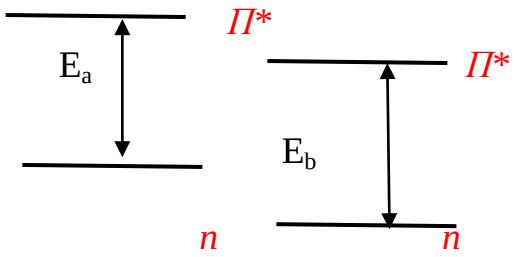
iv- Fermi Resonance: The Fermi resonance effect usually leads to two bands appearing close together when only one is expected. When an overtone or a combination band has the same frequency as, or a similar frequency to, a fundamental, two bands appear, split either side of the expected value and are of about equal intensity.



III- a) Explain the effect of polar solvents on *n* → *Π and *Π* → *Π** transition.**



In polar solvent



In polar solvent

The *Π** orbitals are more stabilized by polar solvents by forming hydrogen bond so the bond shifted to longer wave length ($E_a > E_b$) Bathochromic shift.

The *n* orbitals for unshared electrons are more stabilized by polar solvents the bond shifted to shorter wave length ($E_b > E_a$) Hypsochromic shift.

b) How can you distinguish between the following pairs of compounds (using spectroscopic methods)?

i- *p*-Aminoacetophenone & *p*-nitroacetophenone:

By using IR spectra the p-nitroacetophenone the C=O stretch occurs at the highest stretching frequency than p-Aminoacetophenone because it has withdrawing group which increase the vibration frequency.

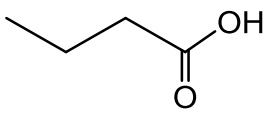
ii- Propionic acid & *2*-propanol:

By using IR spectra propionic acid gives broad band from 2500 to 3400 cm^{-1} for OH of acid and gives also intense beak at 1720 cm^{-1} for carbonyl group.

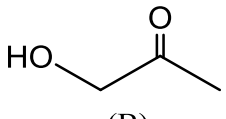
iii- Toluene & methyl cyclohexane.

By using UV spectra toluene show high wave length.

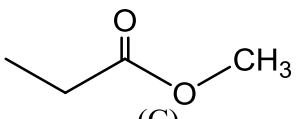
c) Match the following compounds with their IR spectrum. Give your reasoning and evidence from the spectrum itself for each match



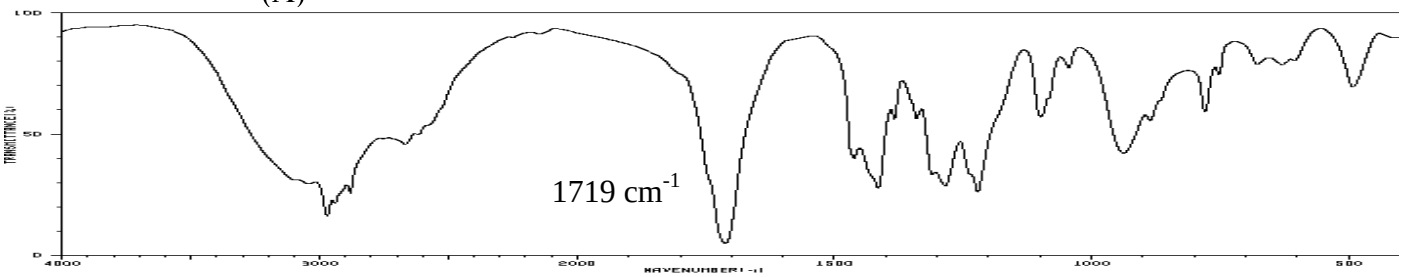
(A)

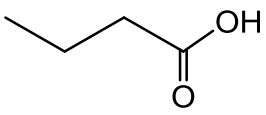


(B)



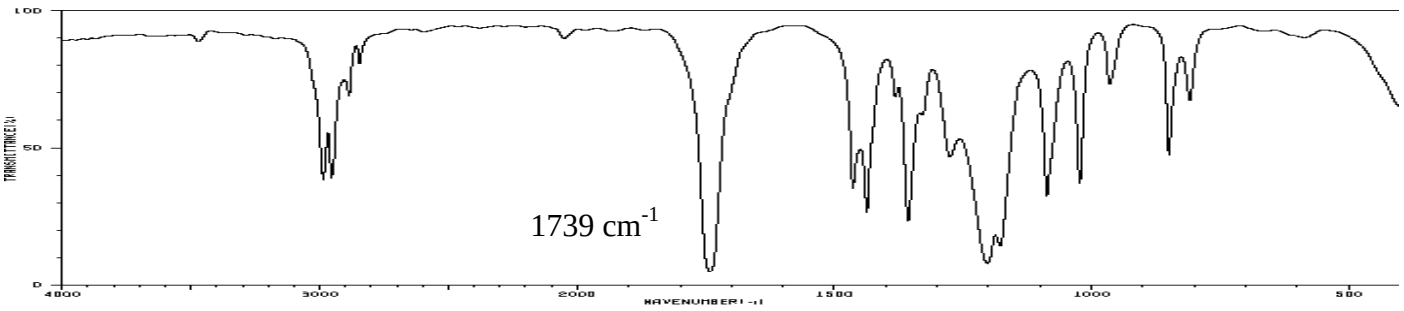
(C)

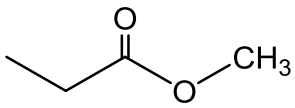




(A)

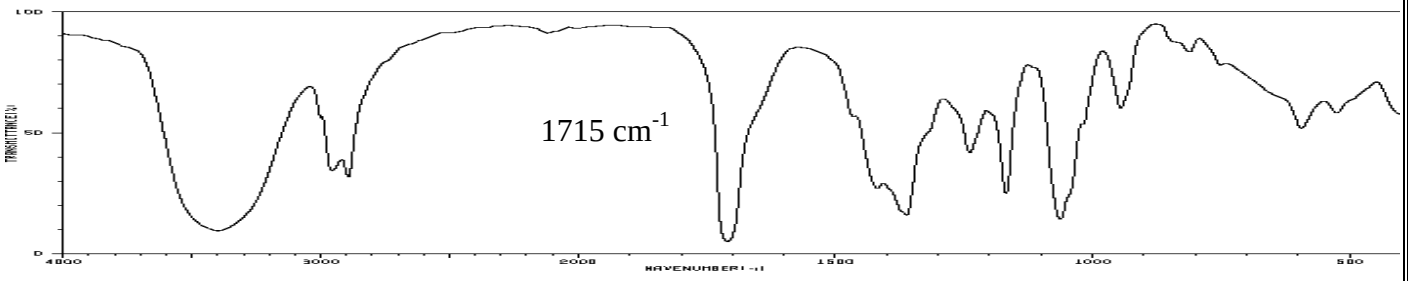
Because it shows broad band for OH of carboxylic group, also it shows also intense beak at 1720 cm^{-1} for carbonyl group.

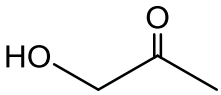




(C)

Because it shows intense beak at 1739 cm^{-1} for carbonyl group of ester.



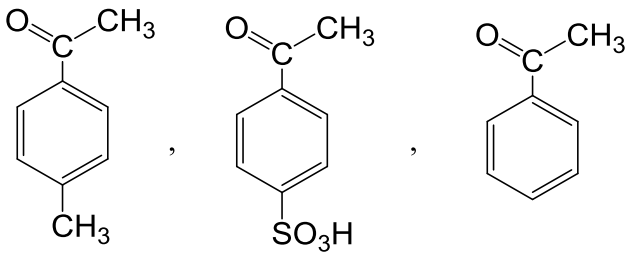


(B)

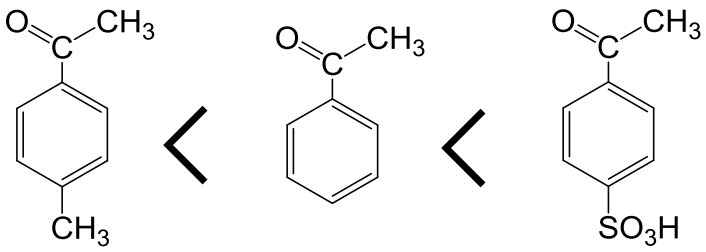
It shows both bands of OH at 3400 cm^{-1} and 1715 cm^{-1} for carbonyl group

IV- a) Arrange the following compounds according to increasing the wavenumber of C=O (Give your reasons):

i-

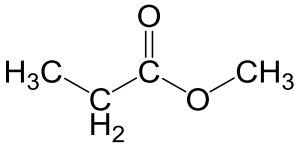
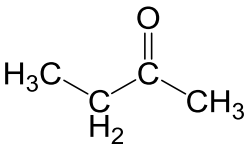
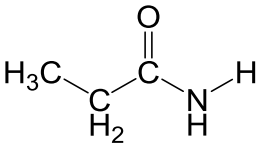


answer

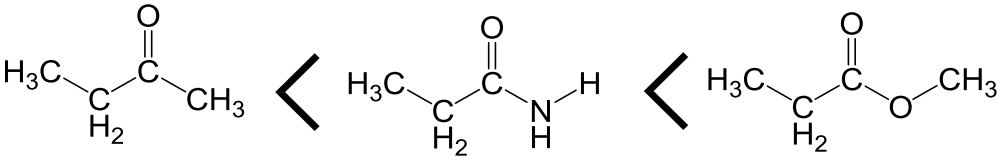


The electron donating groups -CH_3 decrease the double bond and therefore decrease the vibration frequency and vice versa the withdrawing group SO_3H increase the double bond and therefore increase the vibration frequency.

ii-

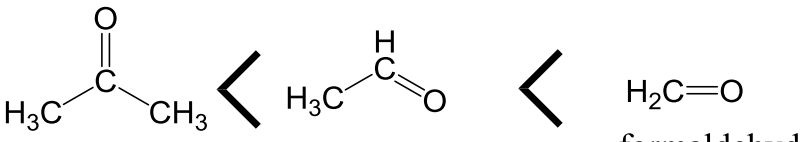
answer



Both nitrogen and oxygen have -I effect and withdraw electrons and increase the double bond character so increase the wave number, hence the oxygen is more electronegative than nitrogen so it will be more electron withdrawing than nitrogen and increase wave number.

iii- Acetaldehyde, Formaldehyde, Acetone.

answer



The electron donating groups -CH_3 decrease the double bond and therefore decrease the vibration frequency acetone have two methyl group so it will decrease the wave number than acetaldehyde which have only one methyl group and both will less than formaldehyde which have no methyl groups.

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

i- $CH_3CH=CH-CH_3$

answer

Type of transition is: $\sigma \longrightarrow \sigma^*$ **and** $\Pi \longrightarrow \Pi^*$

ii- $CH_2=CH-CHO$

answer

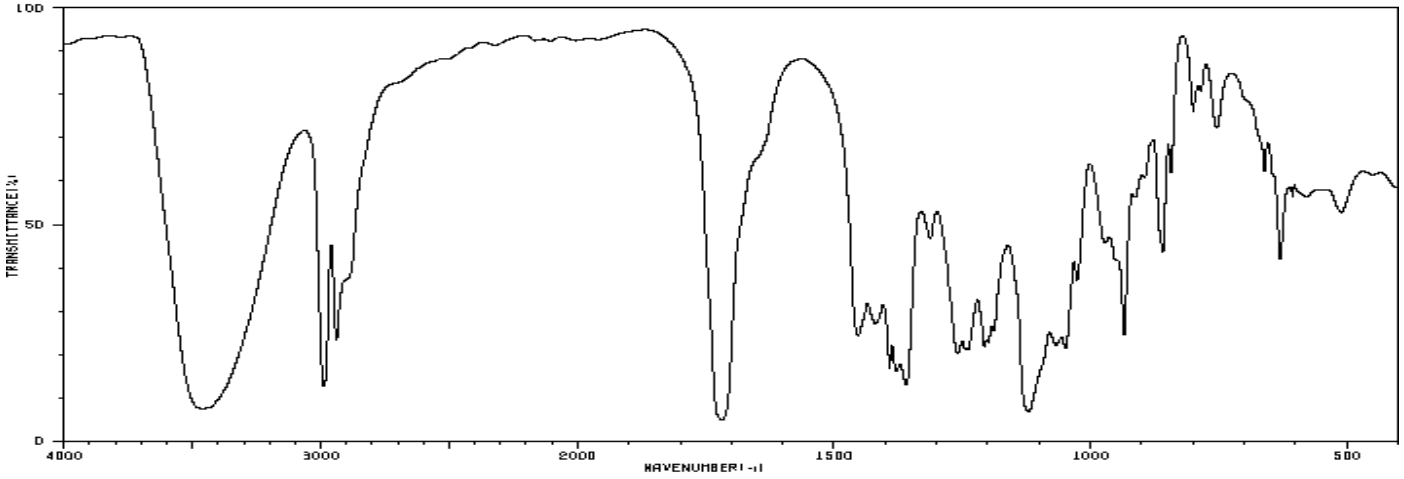
Type of transition is: $\sigma \longrightarrow \sigma^*$, $\Pi \longrightarrow \Pi^*$, $n \longrightarrow \sigma^*$ *and* $n \longrightarrow \Pi^*$

iii- $CH_3CH_2CH_2CH_3$

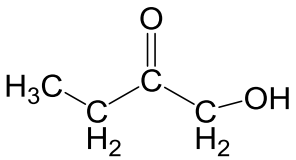
answer

Type of transition is: $\sigma \longrightarrow \sigma^*$ **only**.

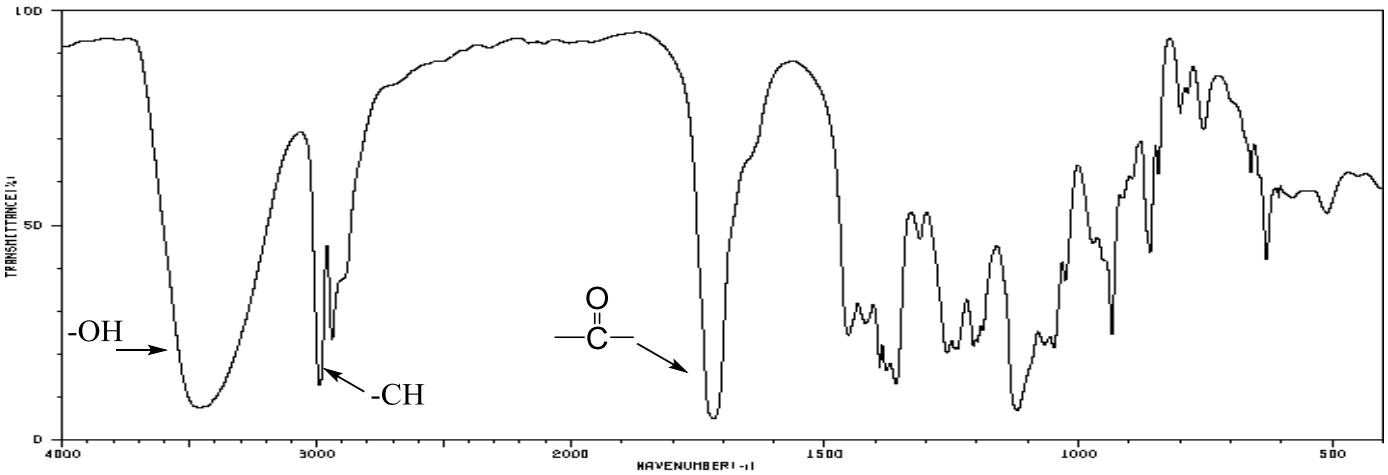
c) The IR below is for $C_4H_8O_2$. Identify and label three (3) peaks only in the spectrum that are consistent with the molecular formula given.



answer



This is the possible structure while the spectra show three important beaks such as at 3400 cm^{-1} corresponding to hydroxyl group and its not broad so it's not acidic OH group. Also it show band at 1720 cm^{-1} which corresponding to carbonyl group and band at 2980 cm^{-1} which is corresponding to -CH aliphatic.



With my best wishes,

MOHAMED ABO-RIYA