

APPLICATIONS OF SPECTROSCOPY (UV-VISIBLE SPECTROSCOPY) PART 2

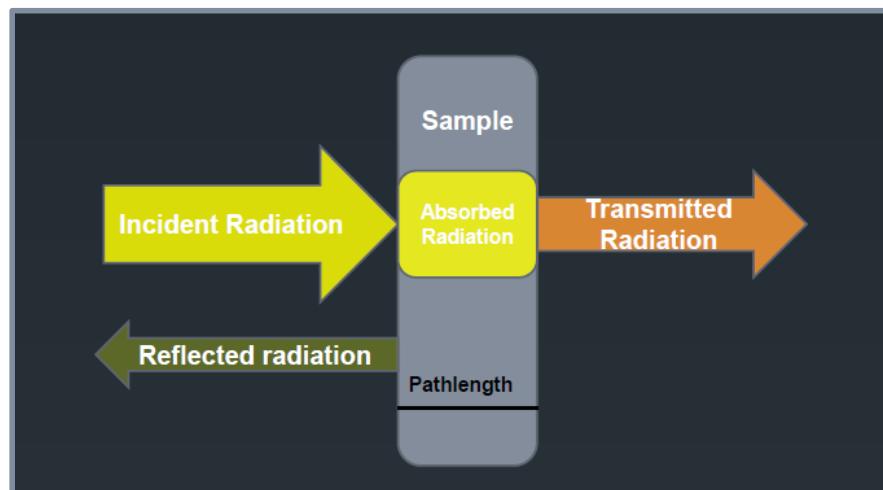
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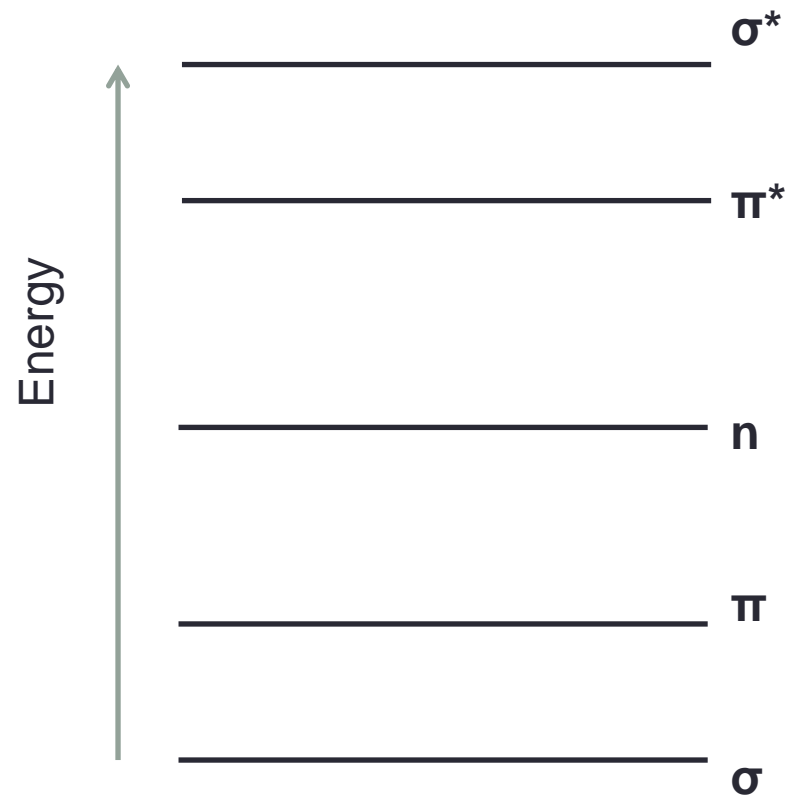
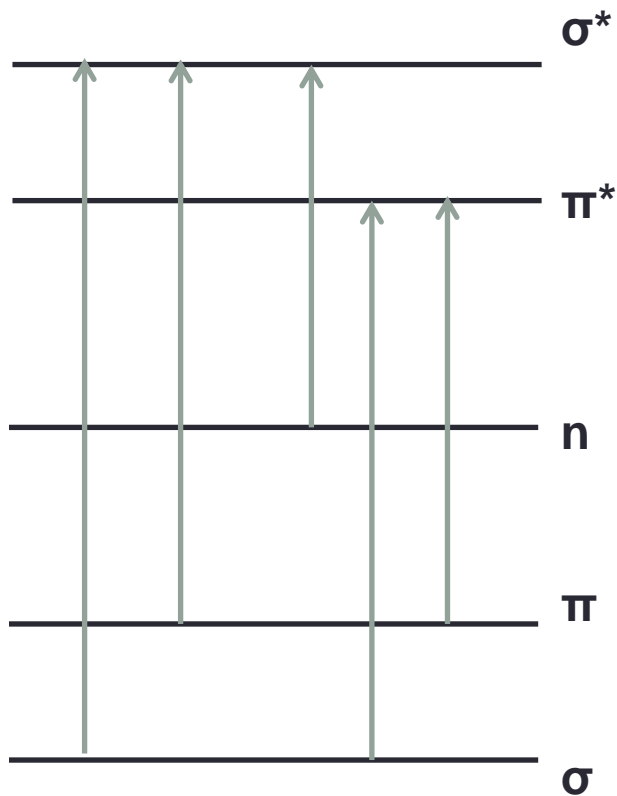
- **Most of the organic molecules are transparent in UV and visible range of radiation i.e. between 190-800 nm. This limits the application of this technique. However some molecules show absorption in this region. The result obtained can be combined with IR and NMR data to get the structural data about the organic compounds.**
- **When a radiation of UV-Visible range passes through a sample in cuvette it either absorbs or transmits the radiation. Also some part of radiation is reflected. The major importance of analysis is about the transmitted and absorbed radiation range.**



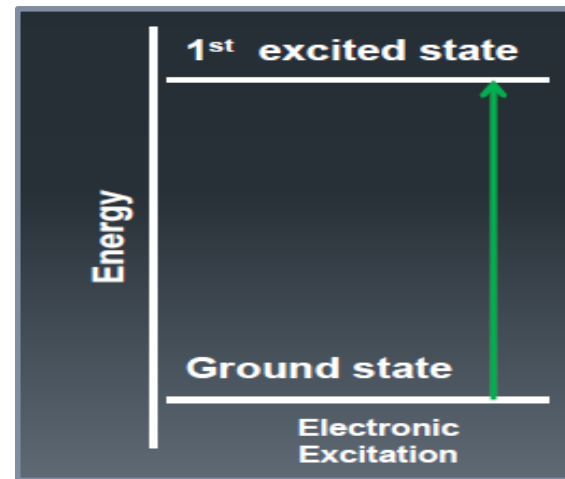
- As a result of electronic excitation the electron in molecules gets excited from low energy ground state to high energy excited state.
- The spectrum obtained is known as absorption spectrum which is plotted for the absorbance or transmittance vs. wavelength in nm.
- The transitions of electrons is between electronic energy levels. The electrons in *HIGHEST OCCUPIED MOLECULAR ORBITAL (HOMO) and LOWEST UNOCCUPIED MOLECULAR ORBITAL (LUMO)*.
- The difference between electronic energy levels mostly lie between 125 to 650 kJ/mole.
- The energy for various electronic levels can be given as

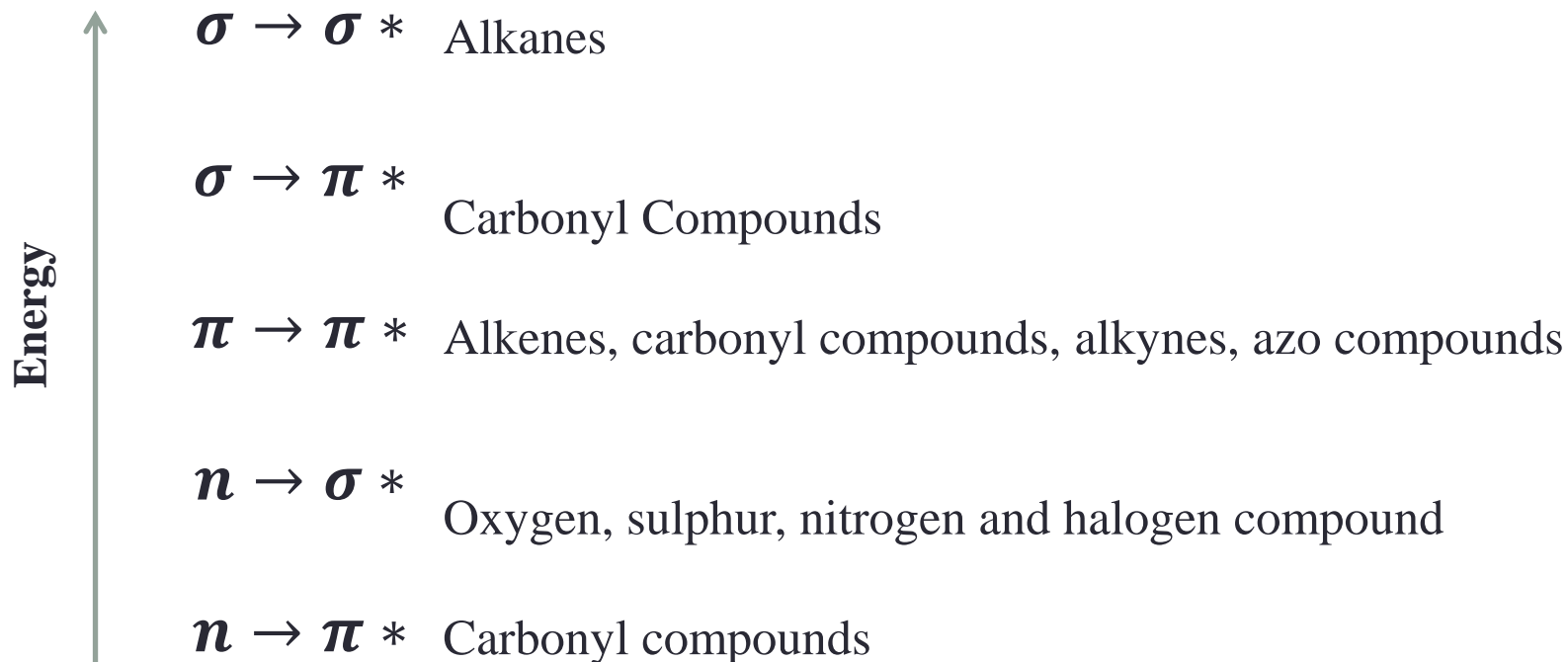
$$\sigma < \pi < n$$

The value of σ^* or π^* orbitals are higher than these and vary according to the molecular structure.



There are five types of possible transitions:

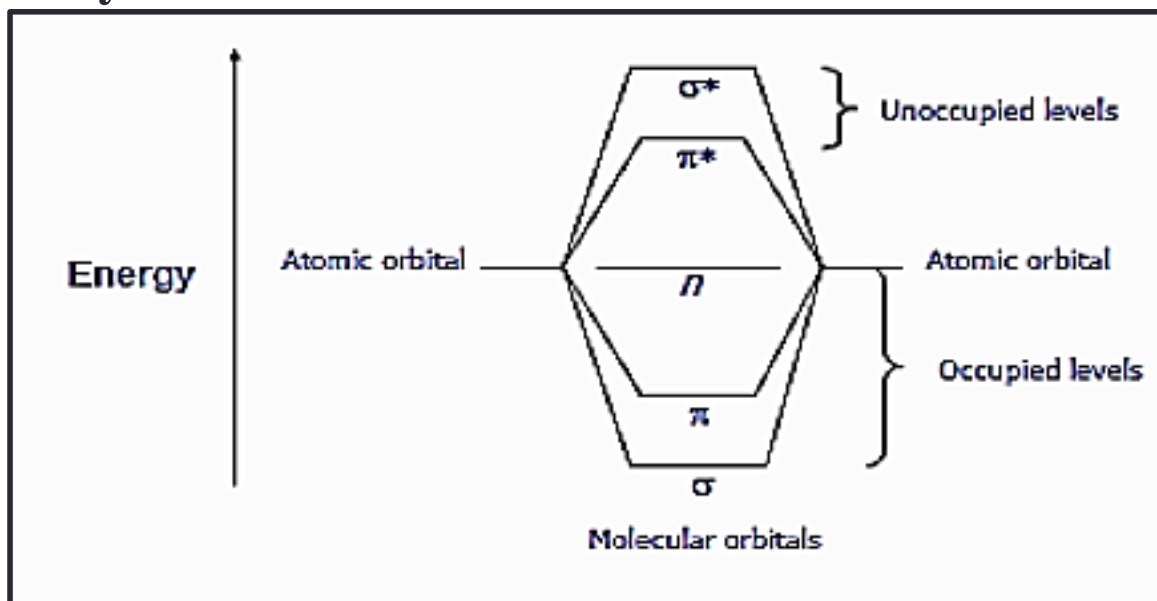




- **Transitions of lowest energy is the most important transition.**
- **However, not all transitions are possible. The transitions that are not allowed are known as “Forbidden transitions”.**
- **There are certain restrictions that have been imposed on the systems for transitions. These are called “Selection Rules.”**

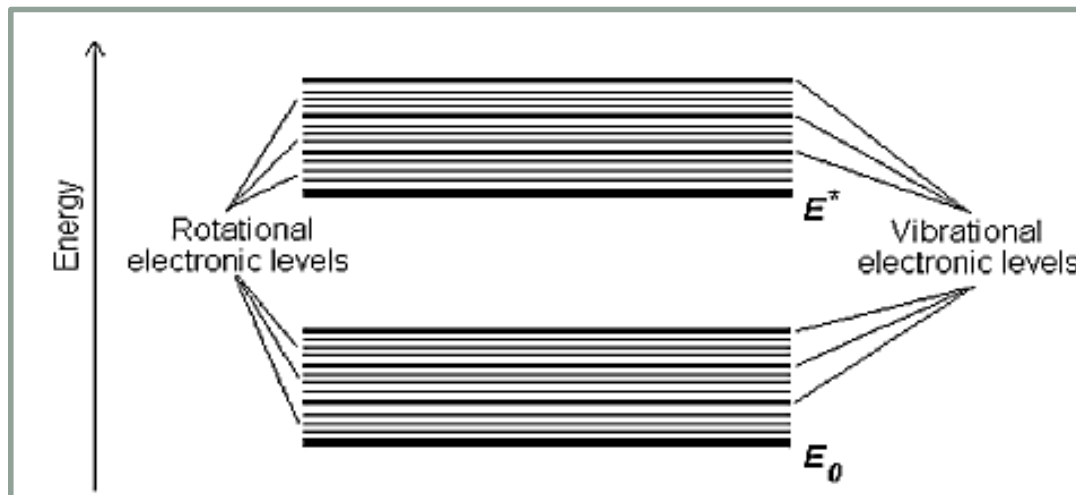
Selection Rule in UV-Vis spectroscopy

- According to first rule: The transitions that leads to the change in spin quantum number of the electrons are not allowed and are forbidden.
- The change in the energy level must be ± 1 . The $n \rightarrow \pi^*$ transition is however one such example where it is forbidden theoretically but is an observable entity.



The Origin of UV band structure

Due to the quantization of energy level the UV –vis absorption band shows a sharp spectrum in the case of atoms. Things slightly change when we talk about molecules. In case of molecules the absorption spectrum shows a range of wavelength due to the excited rotational and vibrational modes of transitions at room temperature. This molecular vibration can not be frozen even when we try at absolute zero. The rotational and vibrational are thus *superimposed* on the electronic level.



Principle of absorption spectroscopy

- The amount of radiation absorbed is directly proportional to the number of molecules that absorbs radiation. This relation has been explained in the terms of Lambert-Beer Law which is shown as

$$A = \epsilon cl = \log \frac{I_0}{I}$$

Where **A** = absorbance of the radiation by the sample

I₀ = Intensity of incident radiation

I = Intensity of light leaving the sample

c = molar concentration of the sample

ε = molar absorptivity of the sample

l = length of the sample cuvette in cm

Deviations of Lambert-Beer Law

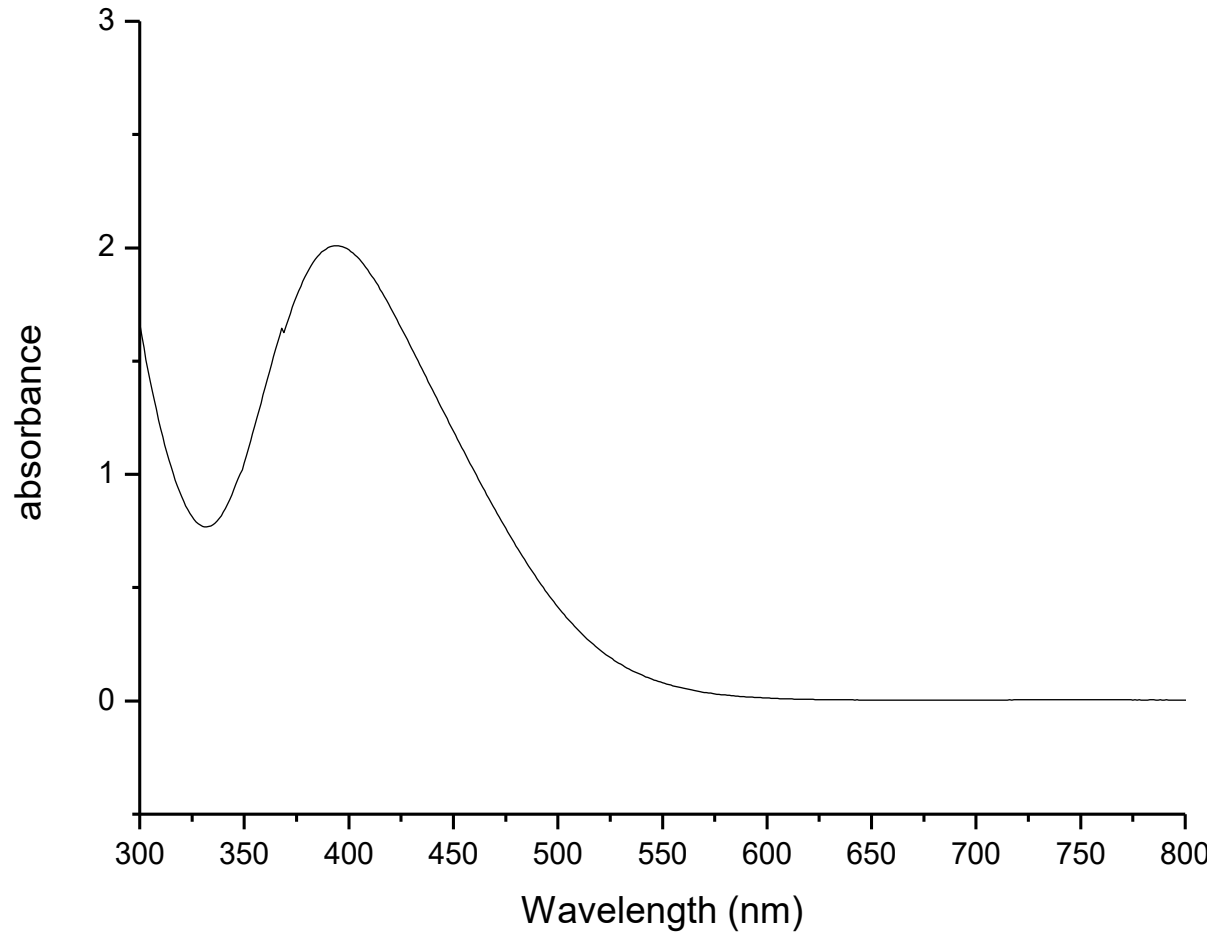
- **This law is only observed for the system having single absorbing species. In case sample consists of many species, this law does not prove that effective**
- **This law does not hold good for the systems which have solute-solvent interaction. In case of some metal complexes, the metal ion forms coordinate bonds even with the solvent molecule.**
- **The law fails miserably for very concentrated samples and holds no importance for such samples.**
- **Sometimes there exists a thermal equilibrium between HOMO and LUMO which may fail the law.**
- **Fluorescent samples also deviate from the equation.**

Instrumentation

- Three major parts of a spectrophotometer consists of **light source, a monochromator and a detector.**
- Usually light source is a deuterium lamp that emits Ultra-Violet radiation and a tungsten lamp for visible radiation.
- Monochromator is a kind of diffraction grating which spreads the beam of light into its component wavelengths. A system of slits focus the desired wavelength on the sample. The light that passes through sample after being absorbed is transmitted and is recorded by the detector.
- The detector is photomultiplier tube or photodiode.
- In double-beam instrument, the transmitted light is split into two beams: **sample and reference beam.**

A Sample of UV-Vis Spectra

The spectrum is plotted as absorbance vs wavelength (nm). The maximum wavelength of absorbance is known as λ_{max} . It relates to the molar absorptivity coefficient.



Solvents

The choice of the solvents is made on following criteria:

- **It should not absorb in the same region in which the substance spectrum lies.**
- **The effect of solvent on spectrum fine structure should be known and well established.**
- **Polarity of solvent should be taken into proper consideration.**
- **Third criteria is the ability of good solvent to influence the wavelength of ultra violet light that is absorbed either by stabilization of ground state or excited state.**

Solvent Cut off (nm)	
Water	190
Ethanol	205
Acetonitrile	190
Chloroform	240
1,4 dioxane	215
n-hexane	201
Methanol	205
Isooctane	195
Trimethylphosphate	210
Cyclohexane	195

Solvent Shift on $n \rightarrow \pi^*$ transition

Solvent	Water	Ethanol	Methanol	CHCl ₃	Hexane
λ_{max} (nm)	264.5	272	270	277	279

- In polar solvents the solute-solvent may form hydrogen bonding which may affect the fine structure.
- 95% ethanol-hexane is considered one of the most suitable solvent for spectrum studying in UV Visible spectroscopy.
- Polar solvents shift $n \rightarrow \pi^*$ type transitions to a shorter wavelength by forming hydrogen bond with ground state
- $\pi \rightarrow \pi^*$ shifts to longer wavelength in case of polar solvents.

What is a chromophore?

- **An atom or a group of atoms which determine the absorption spectrum of a species of molecule is known as chromophore.**
- **As structural changes occur in chromophore, the energy and intensity of the absorption are supposed to change accordingly.**
- **However it is difficult to determine how the energy or intensity will change. For this there are certain empirical rules that are framed on the basis of various experimental data and theoretical assumptions that relate between these two.**
- **We will discuss this in brief here.**

Alkanes, Alcohols, Ethers, Amines, Sulphur Compounds, Alkene, Alkynes, Carbonyls

- Alkanes contain single bonds and have no atoms with unshared pair of electrons. The only possible electronic transition is $\sigma \rightarrow \sigma^*$ type. These are high energy transitions and absorb UV at shorter wavelength.
- Alcohols, Ethers, Amines, Sulphur Compounds contain atoms bearing non bonding electrons, transitions of $n \rightarrow \sigma^*$ type becomes important. They are also high energy transitions but they absorb within experimentally accessible range.
- Alcohols and amines absorb in range of 175-200 nm, organic thiols absorb in between 200-220 nm. While most of them absorb below the solvent cutoff points they do not show any spectrum with the solvent.

Alkanes, Alcohols, Ethers, Amines, Sulphur Compounds, Alkene, Alkynes, Carbonyls

- In unsaturated molecules $\pi \rightarrow \pi^*$ transitions are quite possible. They are high energy but the position of the spectrum is sensitive to the presence of substitution. The alkene and alkynes absorb around 175 nm and 170 nm respectively.
- Unsaturated molecules with atoms such as Oxygen or nitrogen show transition in $n \rightarrow \pi^*$ type. They are most studied one carbonyls as they are forbidden transitions. They are highly sensitive to substitution and typically falls between 280-290 nm. Most of them are forbidden and low intensity. $\pi \rightarrow \pi^*$ in carbonyls are about 188 nm and are very high intensity.

Typical absorption of simple isolated chromophores

Class	Transition	λ_{\max} (nm)	$\log \epsilon$
R-OH	$n \rightarrow \sigma^*$	180	2.5
R-O-R	$n \rightarrow \sigma^*$	180	3.5
R-NH ₂	$n \rightarrow \sigma^*$	190	3.5
R-SH	$n \rightarrow \sigma^*$	201	3.0
Tertiary alkane	$\pi \rightarrow \pi^*$	175	3.0
Alkynes	$\pi \rightarrow \pi^*$	170	3.0
R-CN	$n \rightarrow \pi^*$	160	<1.0
R-N=N-R	$n \rightarrow \pi^*$	340	<1.0
R-NO ₂	$n \rightarrow \pi^*$	271	<1.0
R-CHO	$\pi \rightarrow \pi^*, n \rightarrow \pi^*$	190, 290	2.0, 1.0
Ketone	$\pi \rightarrow \pi^*, n \rightarrow \pi^*$	180, 280	3.0, 1.5
RCOOH	$n \rightarrow \pi^*$	205	1.5
RCOOR'	$n \rightarrow \pi^*$	205	1.5
RCONH ₂	$n \rightarrow \pi^*$	210	1.5

Text is in update.....