

INFREERED SPECTROSCOPY

PRESENTATION IS MADE BY STUDENT GROUP 33339/1
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CONTENT

1. Theory
2. Instrumentation
3. Fourier transform IR spectrometers(FTIR)
4. Measurement techniques
5. Mid-infrared (MIR)
6. Near-infrared (NIR)

THEORY

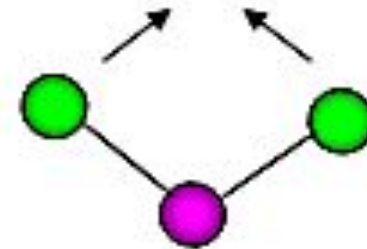
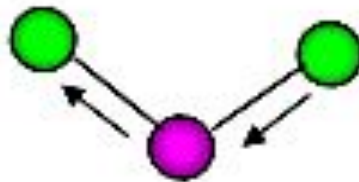
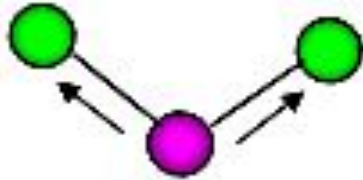
- measurement of IR radiation absorbed by or reflected from a sample
- absorption of IR radiation is related to the changes of vibrational or rotational energy states of molecules
- applications:
 - analysis of gaseous, liquid or solid samples
 - identification of compounds
 - quantitative analysis
- information deduced from IR spectrum:
 - functional groups of molecules, constitution of molecules
 - interaction among molecules

VIBRATIONAL TRANSITIONS

- Fundamental (normal):
change of vibrational quantum number $\Delta v = 1$
high probability \rightarrow high values of ϵ
- Overtones:
the difference of vibrational quantum number $\Delta v = 2; 3 \dots$
lower probability \rightarrow low values of ϵ
- Combination:
simultaneous change of two or more vibrational numbers for a polyatomic molecule

TYPES OF VIBRATION

- **Stretching:** the length of chemical bond (the inter-nuclear distance) is changed
 - symmetric
 - anti-symmetric
- **Bending:** the valence angle is changed
 - symmetric and anti-symmetric vibrations
 - vibrations in plane and vibrations out of plane



symmetric stretch anti-symmetric stretch scissoring bend

WHICH SUBSTANCES GIVE A SIGNAL IN IR SPECTRUM?

YES

- ✓ Molecules that contain polar bonds
- ✓ Molecules composed of atoms of different elements
- ✓ Organic compounds and inorganic compounds (H₂O, CO₂, NO₂, HCl, salts...)

NO

- ❖ Pure chemical elements in molecular or crystal state
- ❖ Ar, O₂, O₃, N₂, Cl₂, S₈, silicon, graphite, diamond...

IR signal of a molecule is proportional to square of the change of dipole moment that occurs during vibrational motion of the molecule.

SPECTRAL REGIONS AND CORRESPONDING ANALYTICAL TECHNIQUES

	λ (μm)	
Near infrared region (near infrared spectroscopy, NIR)	0.8 – 2.5	12 500 – 4 000
Mid infrared region (mid infrared spectroscopy, Mid IR, MIR)	2.5 – 25	4 000 – 400
Far infrared region far infrared spectroscopy, FIR)	25 – 1000	400 – 10

MIR – normal vibrational transitions

NIR – overtones

FIR – normal vibrations of weak bonds and bonds of heavy atoms

INSTRUMENTATION FOR IR SPECTROSCOPY

MAIN COMPONENTS OF AN INSTRUMENT

radiation source

measuring (and reference) cell

wavelength selector

detector (transducer)

TYPES OF INSTRUMENTS

simple instruments with a filter

classical instruments with a monochromator

instruments based on an interferometer (FTIR)

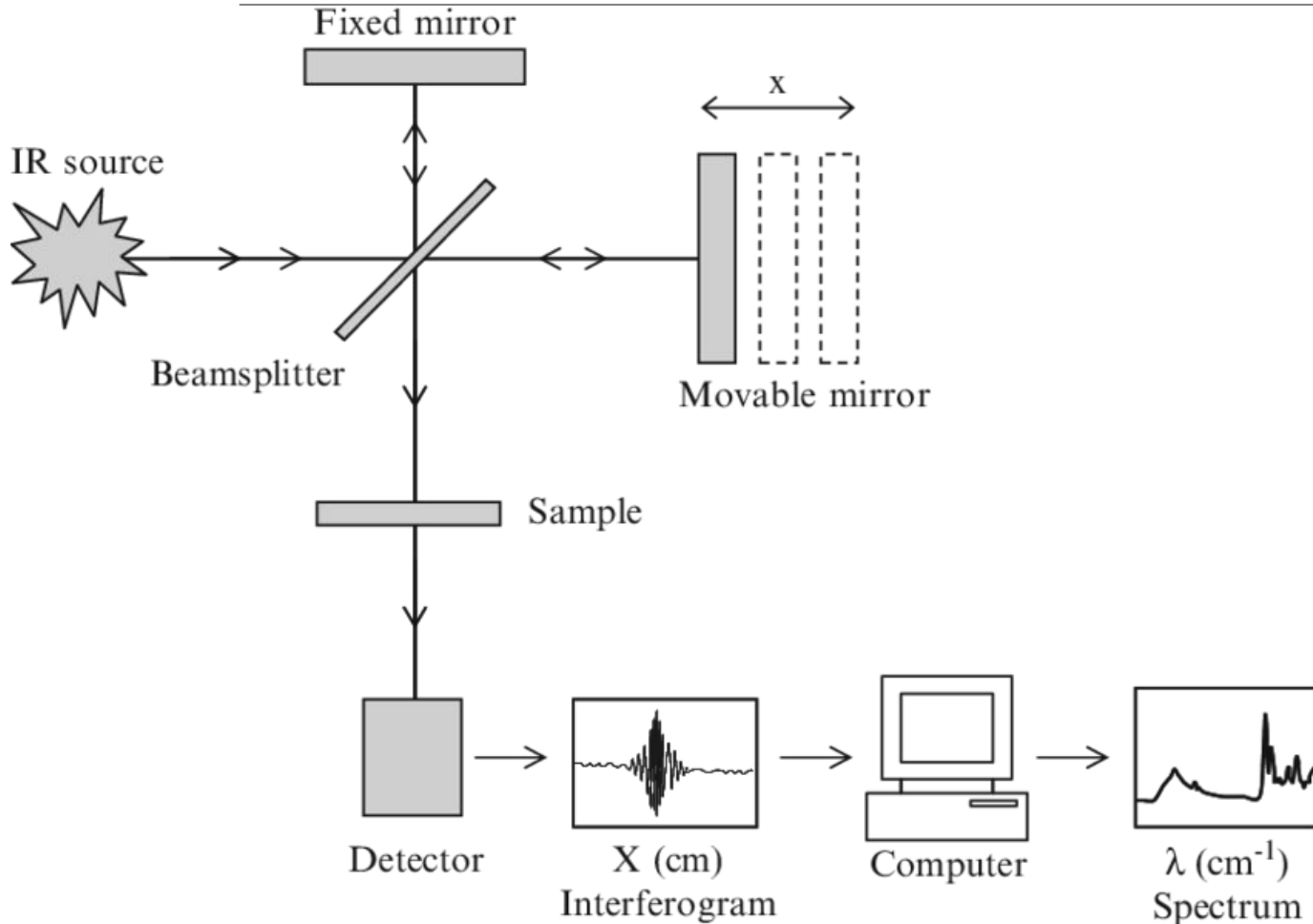
SOURCES OF IR RADIATION

- For NIR: tungsten lamp
- For MIR:
 - Globar = electrically heated (1100 °C) silicon carbide rod
 - it gives maximum intensity at $\lambda = 2 \mu\text{m}$; at lower temp. – shift of maximum to a longer wavelength (600 °C $\rightarrow \lambda_{\text{max}} = 3,5 \mu\text{m}$)
 - lasers CO₂, PbS – $\lambda_{\text{max}} = 9\text{--}11 \mu\text{m}$

TRANSDUCERS OF IR RADIATION

- Pyroelectric triglycine sulphate detectors
 - work at the normal temperature
- Photoconductive detectors MCT (HgTe/CdTe)
 - work at the temp. of liquid nitrogen (-196 °C)
 - high sensitivity
 - fast response
 - are used for MIR and FIR
- Germanium bolometers
 - are used for FIR
 - work at the temp. of liquid helium (-271,7 °C)

FOURIER TRANSFORM IR SPECTROMETERS (FTIR)



ADVANTAGES OF FTIR

- Dispersion elements are not necessary \rightarrow more energy enters the sample
- Fast spectrum recording ($< 1\text{s}$)
- High resolution (up to 0.01 cm^{-1})

MEASUREMENT TECHNIQUES IN IR SPECTROSCOPY

1. TRANSMISSION TECHNIQUE

the measurement of transmittance, absorbance $T = I/I_0$; $A_\lambda = \log_{10}(\frac{1}{T})$

2. REFLECTION TECHNIQUE

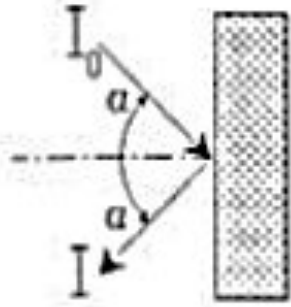
the measurement of the radiation reflected from sample reflectance $R = I/I_0$;
optical density $OD = \log_{10}(\frac{1}{R}) = -\log_{10}(R)$

3. ATR TECHNIQUE

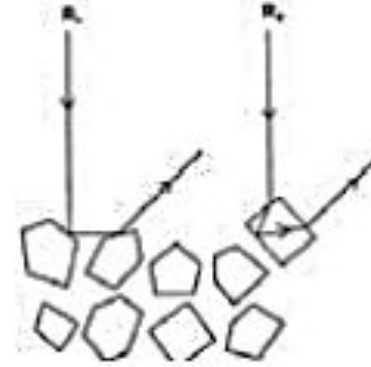
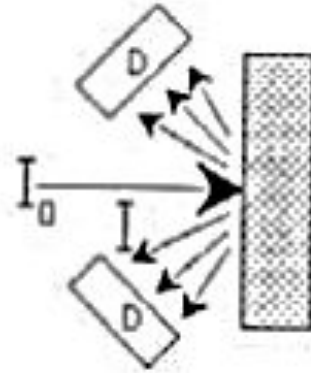
attenuated total reflectance, or internal reflectance

Reflection techniques

Specular reflection:

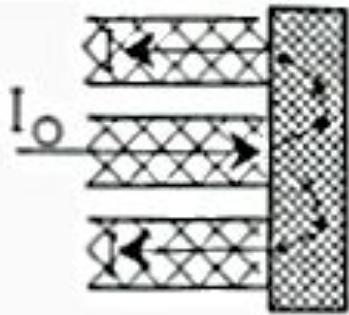


Diffusion reflection:



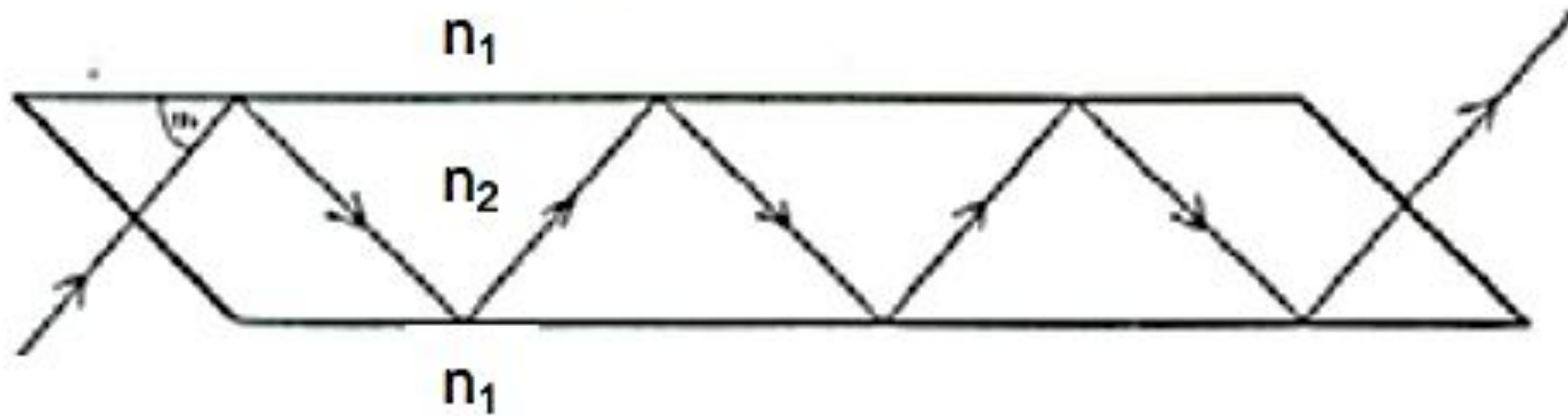
common technique
in NIR for solid
powdered samples

Special arrangement:



measurement of interreflectance – the use of optical cables


ATR technique



ADVANTAGES OF ATR

- ❑ Simple preparation of sample before measurement
- ❑ Non-transparent samples can be analyzed

REQUIREMENTS FOR A SAMPLE AND A CRYSTAL

- ❑ Good adherence of the sample to the crystal
 - ❑ Mechanical strength of the crystal (when the sample is pressed against the crystal)
 - ❑ Inertness of the crystal against samples
 - ❑ Removal of sample residue from the crystal using various solvents
- 

MID-INFRARED SPECTROSCOPY (Mid IR)

Mid IR region is divided into two sub-regions:

- Region of characteristic vibrations of functional groups
2.5–8 μm (4000–1250 cm^{-1})
contains the characteristic bands of individual bonds and functional groups that correspond mainly to stretching vibrations
- Fingerprint region
8–25 μm (1250–400 cm^{-1})
contains the bands corresponding mainly to bending vibrations
the spectrum in this region characterizes each molecule as an integral whole

Steps of identification process

1. Searching for functional groups on the basis of characteristic vibrations (using tables)
2. Confrontation with the results of other tests
 - elementary analysis of the compound
→ stoichiometric formula of the compound
 - determination of molecular mass (from mass spectrum)
→ molecular formula of the compound → calculation of unsaturation index
3. Drawing of all possible structures that correspond to the presence of groups, molecular formula and unsaturation index
4. Comparison of the measured IR spectrum with the spectra of the suggested compounds found in an atlas or a database of spectra
→ identification
5. Verification of identity using other spectral methods (MS, NMR)

NEAR INFRARED SPECTROSCOPY (NIR)

- NIR region: 800 to 2500 nm or 12 500 to 4 000 cm^{-1}
- NIR spectra contain less intensive signals
 - combination bands
 - overtone bands the change of vibration quantum number Δv is 2; 3; 4...;
if the fundamental vibration occurs at the wavelength of λ_0 ,
the first overtone appears at $\lambda_1 \approx \lambda_0/2$,
the second at $\lambda_2 \approx \lambda_0/3$,
the third at $\lambda_3 \approx \lambda_0/4$, etc., the strength of signal gradually decreases
- NIR spectra are measured by
 - transmission technique
 - diffusion-reflection technique
 - ATR technique

Making determinations of ... in food analysis

□ WATER

□ FAT

□ PROTEINS

□ CARBOHYDRATES

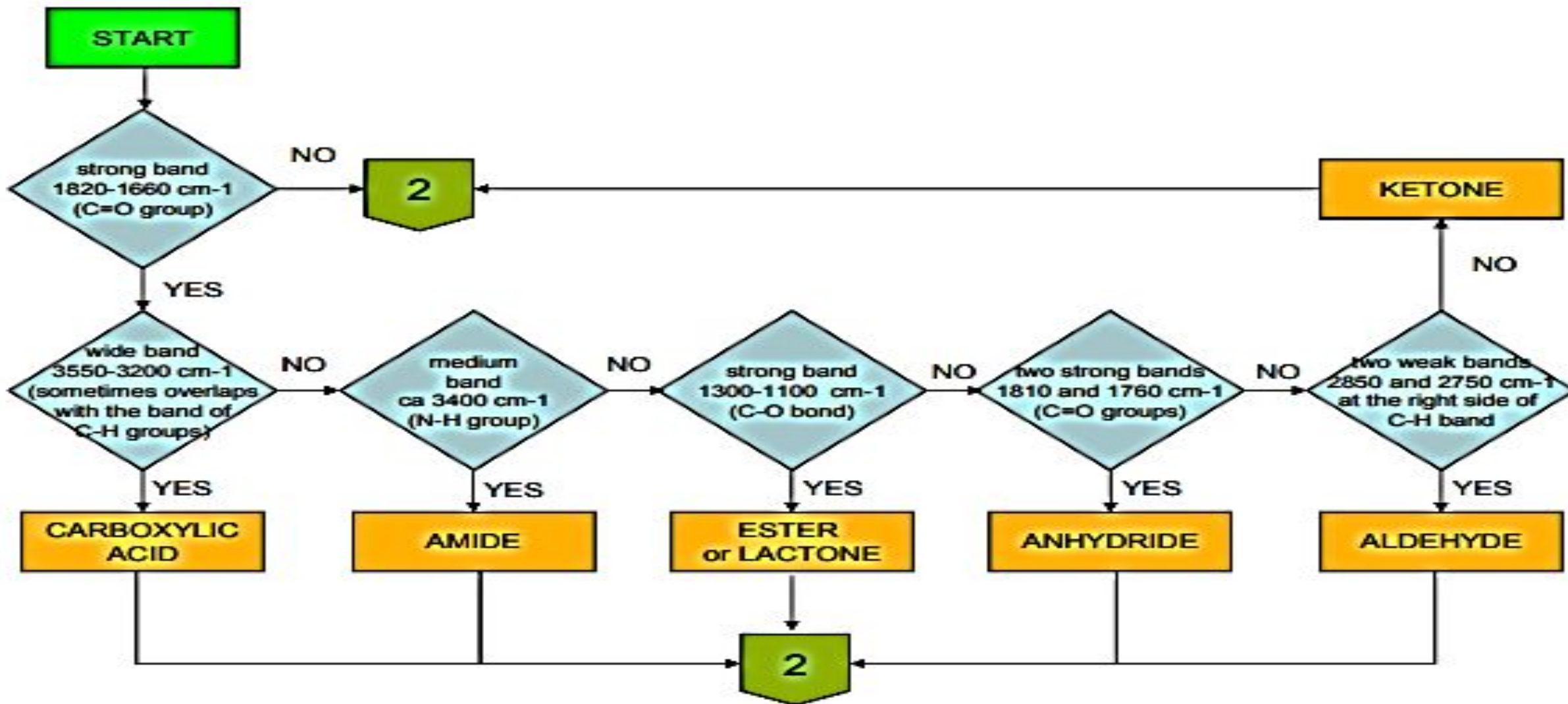
□ SUGARS

□ ALCOHOLS

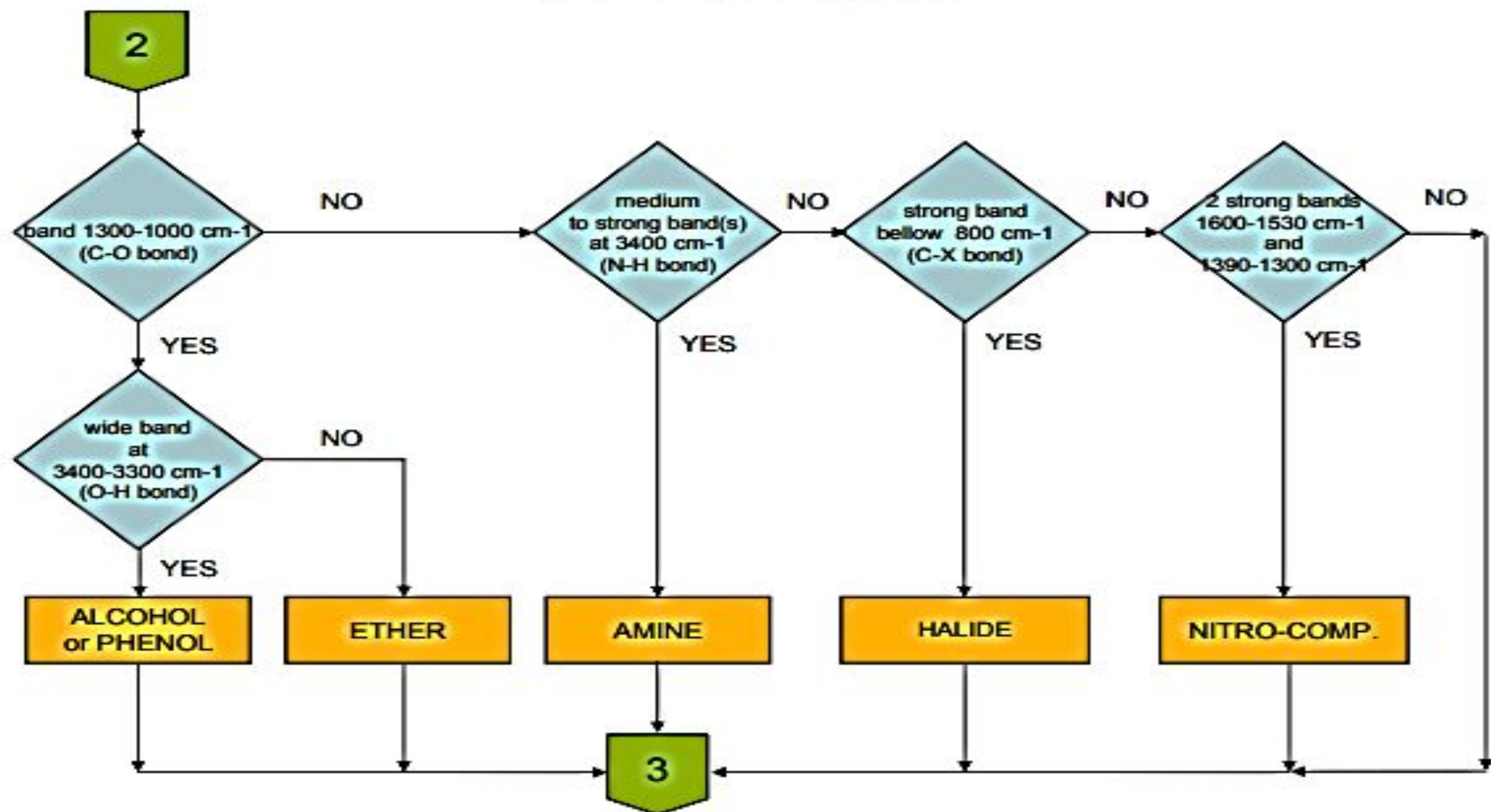
ATTACHMENTS

Look on IR spectrum: identification of functional groups

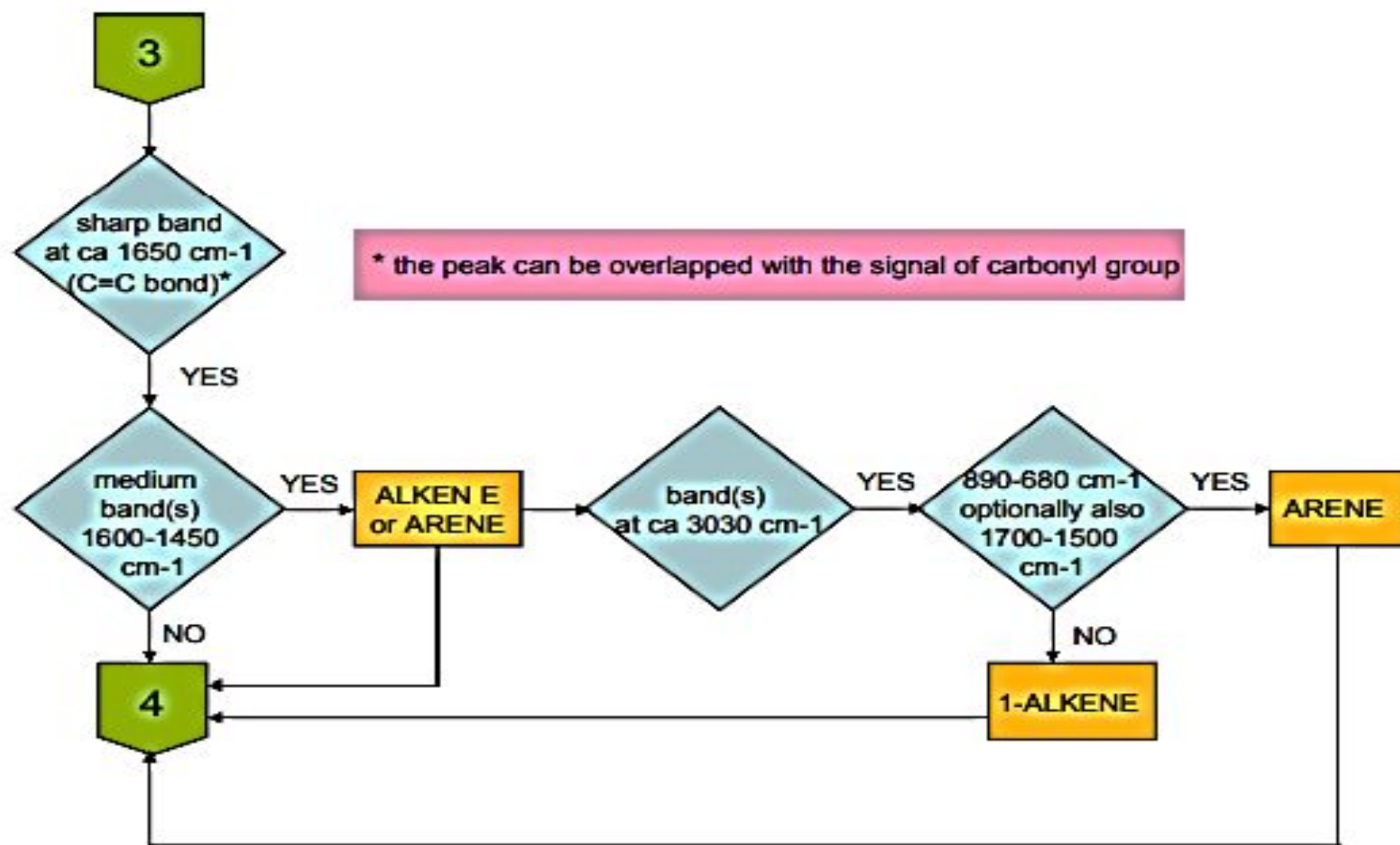
1. carbonyl groups



Look on IR spectrum: identification of functional groups
2. other functional groups

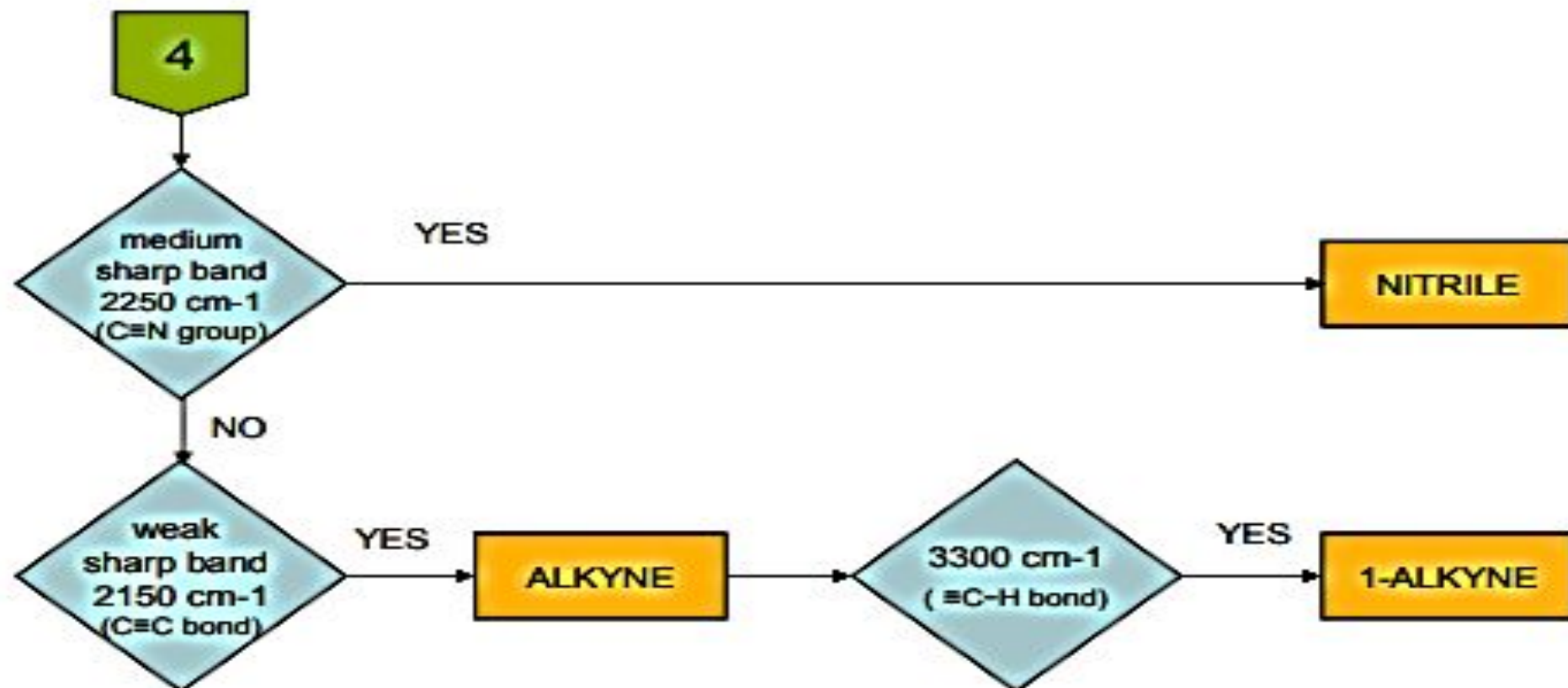


Look on IR spectrum: identification of functional groups
3. double bond and aromatic ring



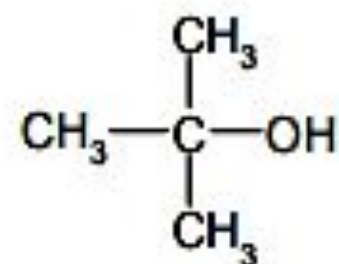
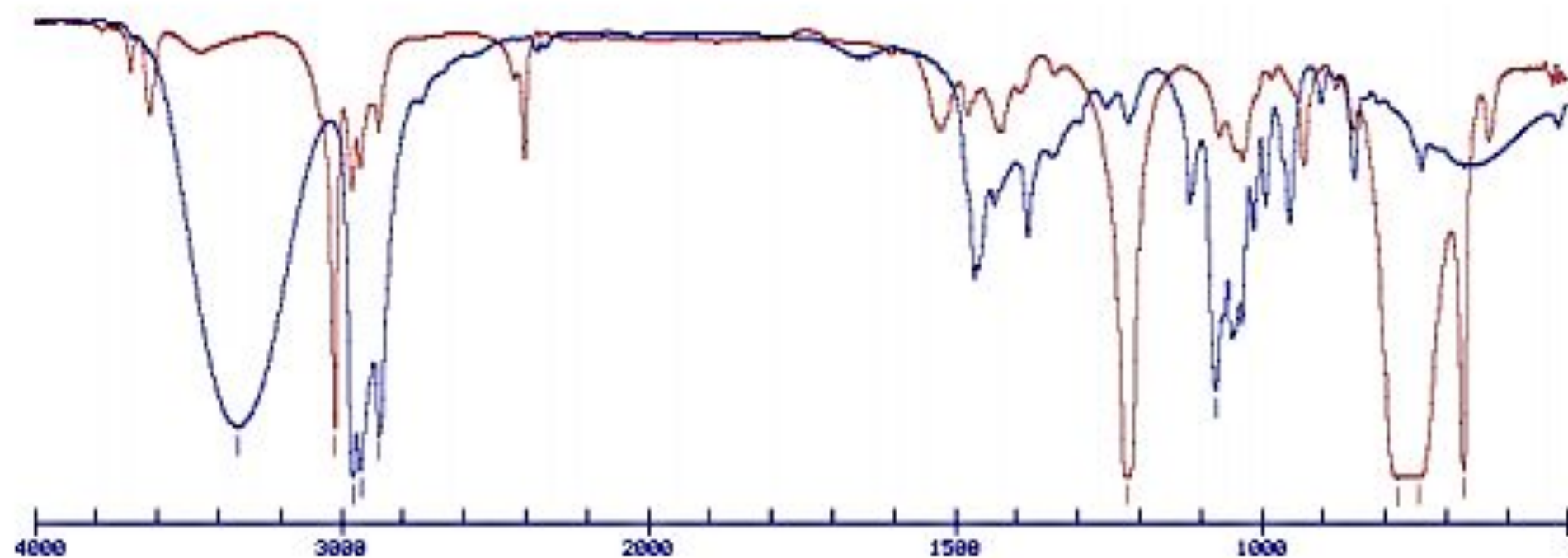
Look on IR spectrum: identification of functional groups

4. triple bond



If the spectrum does not contain any of above mentioned bands, the compound is probably a saturated hydrocarbon. Spectra of these hydrocarbons are simple and contain :

- strong band at ca 2900 cm⁻¹ (C-H stretching),
- medium and sharp band at ca 1470 cm⁻¹ (CH₂ bending),
- weak sharp band at ca 1400±50 cm⁻¹ (CH₃ bending),
- optionally a band at 720 cm⁻¹ (signal of longer hydrocarbon chains)



pure tert. butanol

diluted solution of tert. butanol in CHCl_3

THANK YOU FOR YOUR
ATTENTION!
