We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Organic Compounds FT-IR Spectroscopy

Adina Elena Segneanu, Ioan Gozescu[*],
Anamaria Dabici, Paula Sfirloaga and Zoltan Szabadai
National Institute for Research and Development in Electrochemistry and
Condensed Matter, Timisoara (INCEMC-Timisoara)
Romania

1. Introduction

General spectral range of electromagnetic radiation with a wavelength greater than 750 nm (i.e. with the number of wavelength below 13000 cm^{-1}) bears the name of the domain infrared (IR). In this field samples absorb electromagnetic radiation due to transitions of vibration of the structure of molecules, molecular transitions in vibrations crystalline network (if the sample is in the solid state of aggregation) or due to transitions of molecular rotation. Subdomain of spectral wavelengths between 2500 - 50000 nm (respectively the wave numbers 4000 to 200 cm^{-1}) bears the name of the *middle infrared domain.*

From the point of view of analytical control of medicinal products, this domain is the most used. At the base of absorption is being generated electromagnetic radiation in this area spectral transitions are the vibrations of individual molecules or of crystalline network (if the sample examined is solid). Show effects such transitions caused by the vibrations of individual molecules provides information about molecular structure of the sample examined, and show effects such crystalline network to identify a particular forms of crystallization of the substance of interest.

The most frequent use of the absorption spectrophototometry in the middle infrared field lies in the identification of substances through molecular vibration. The wavelength (i.e, the wave numbers) of the of the absorption band are characteristic chemical identity of the substance in question. The intensity of the absorption bands allows quantitative analysis of the samples but, unlike in the ultraviolet and visible, in the infrared field diffuse radiation is much more refreshing, and for this reason quantitative determination infrared, are affected by notable errors.

From the standpoint of analytical use, the spectra of molecular vibration is enjoying increased popularity in comparison to the study of the crystal latice's vibrations. A molecule may be considered to be a vibrator with more than one degree of freedom, able to execute more modes of vibration. In each mode of vibration every atom in the molecule oscillates about their own position of equilibrium. Such oscillations have different amplitudes for

---

[*] Corresponding Author

different atoms of the molecule, but at a certain mode of vibration, each atom in the molecule oscillates with the same frequency. In other words, the frequency of oscillations of the atoms in molecule is characteristic of a particular mode of oscillation of the molecule.

A molecule composed of N atoms has several possible modes of oscillation. In each mode of oscillation (in principle) all the atoms of molecule perform periodic shifts around level position with a frequency of oscillation mode which is a feature of the assembly. Because each of the N atoms can run periodic shifts in 3 perpendicular directions each other, the assembly of N atoms can have 3N ways of motion. But, those displacements that correspond to moving molecule as a whole (not deform the geometry of the molecule) and movements, which correspond to entire molecules rotation about an axis (also without deforming the molecule's geometry), do not represent actual oscillation (associated with actual deformation of the molecule).

These displacements (3 in number) and rotations around the three orthogonal axis (also 3 in number) are eliminated of the total number of atomic movements possible. Therefore, a molecule is, in general, (3N - 6) distinct modes of oscillation and in each of these (3N - 6) modes of oscillation each atom oscillates with frequencies characteristic individual modes of vibration. A special case represents molecules whose structures are linear, because in these cases the inertia of the molecule, in relation to the axis flush by molecule, it is practically zero. For this reason, in the case of a linear molecules consisting of N atoms, the number of modes of vibration is 3N - 5.

2. The vibration of a diatomic molecule

For an understanding of the vibrations of a polyatomic molecule, should be first a preliminary analysis of the oscillations of a molecule composed of two atoms linked by covalent binding. Such a molecule, with N= 2 atoms, shows N = 3x2 - 5 = 1 modes of vibration. The steering as defined by the covalent binding of the two atoms is the only special steering, it is ordinary to accept that atoms will move (in a periodic motion) after direction of the covalent connection. Assembly oscillation may be considered in relation to several systems of reference. It may choose as origin of the system of reference the center of gravity of the diatomic assembly.

In this case the both atoms perform periodic shifts in relation to this reference point. The mathematical analysis of oscillations is advantageous to place the reference origin in one of atoms. In this case, however, in the place of mass m_A and m_B of the atoms of the molecule A-B are used *reduced mass* (noted with μ) of the assembly dimolecule. Reduced mass is calculated from the **mA** and **mB** of atoms of the dimolecule assembly in accordance with following relationship.

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B} \tag{1}$$

Rigorous deduction of the relationship (1) can be found in literature on the subject. During the oscillation, the kinetic energy, E_c, and potential energy E_p of the assembly are varying, periodically. If the system does not radiate energy to environment, or do not accept energy

from the environment, then the amount of E_c and E_p remains constant during oscillation. Potential energy is dependent on the single variable of the diatomic system (namely, the deviation of the **Δr** inter-atomic distance to **r**0) which is variable in time. Potential energy dependence of the **Δr** (i.e. lengthening the deformation of the diatomic molecule) is expressed, in the harmonic approximation, of the relationship (2).

$$E_p = \frac{1}{2} \cdot k \cdot \Delta r^2 = \frac{1}{2} \cdot k \cdot (r - r_0)^2 \qquad (2)$$

In the relationship (2) the coefficient 'k' is *constant of force*, size that characterises the strength of inter-atomic connection in the molecule. On the basis of expression (2) the potential energy of the diatomic assembly, using the mechanics in this quantum mechanics, may deduct quantified values ('allowed') of diatomic oscillator.

These values of energy 'allowed' shall be calculated on the basis of the expression (3) by substituting for the number of quantum vibration (**n**vib) integers numbers (0, 1, 2, . .

$$E_{vib}(n_{vib}) = E_c + E_p = h \cdot v_0 \cdot \left(n_{vib} + \frac{1}{2} \right) \qquad (3)$$

The expression (3) shows that the energy E_{vib} (the sume of the kinetic energy E_c and potential energy E_p) has a state of vibration allowed to diatomic system depends on the number of vibration quantum n_{vib}.

The lower value of energy (in the fundamental vibration's state diatomic system) is obtained by replacing **n**vib= 0 in the relationship (3). In the relationship (3) h is the size Planck constant. (6,626075 x 10^{-34} Js). If diatomic molecule fundamental changes from the vibration (**n**vib = 0) in the state of vibration excited immediately above (**n**vib = 1), then change of energy **ΔE**vib**(0→1)** is expressed by the relationship (4).

$$\Delta E_{vib}(0 \to 1) = h.v0 \qquad (4)$$

This value to change the vibration energy determines how often (or the number of wavelength) at which diatomic molecule shows preferential absorption of radiation.

In principle, diatomic molecule can pass from the fundamental (**n**vib = 0) in a excited state (for example, corresponding **n**vib = 2) but, those quantum transitions in which the number is changing more than one establishment are prohibited by the rules of selection.

Rigorous justification of the rules of selection is treated in detail in literature on the subject.

Preferred frequency (**v**$_0$), the favorite number of wave **n**vib = 0 to which a small diatomic molecule absorbs radiation (hence to which generates a strip of absorption) as the transition (0→1), is expressed quantitatively the relationship (5)

$$v_0 = \frac{1}{2 \cdot \pi} \cdot \sqrt{\frac{k}{\mu}} \quad ; \quad \tilde{v}_0 = \frac{1}{2 \cdot \pi \cdot c} \cdot \sqrt{\frac{k}{\mu}} \qquad (5)$$

In the relationship (5) 'C' is the speed of propagation of electromagnetic radiation in a vacuum. At the harmonic approximation, the dependency $\Delta\mathbf{r}$ is sinusoidal. But in the case of molecules, the potential energy is dependent on the momentary deflection $\Delta\mathbf{r}$ of the system in a manner more complicated, so the approximation describes successfully the harmonic oscillations limited to a diatomic molecules. As a result of difficulties with mathematical order but the description of molecular oscillations, especially in the case poliatomice molecules, it accepts harmonic approximation."

$$E_p = D_e \cdot \left[1 - e^{-\beta \cdot (r-r_0)} \right]^2 \tag{6}$$

Figure 1 represents the dependency of potential energy E_p of a diatomic molecules to the momentary distance (r) in a approximately more faithful than the harmonic (based on parabolic dependence). In a more or less accurate in the description diatomic vibration of molecules, energy dependence potential (E_p) by the distance inter atomic (r) is described by a function of type Morse (6) in place of a relationship of type (2).
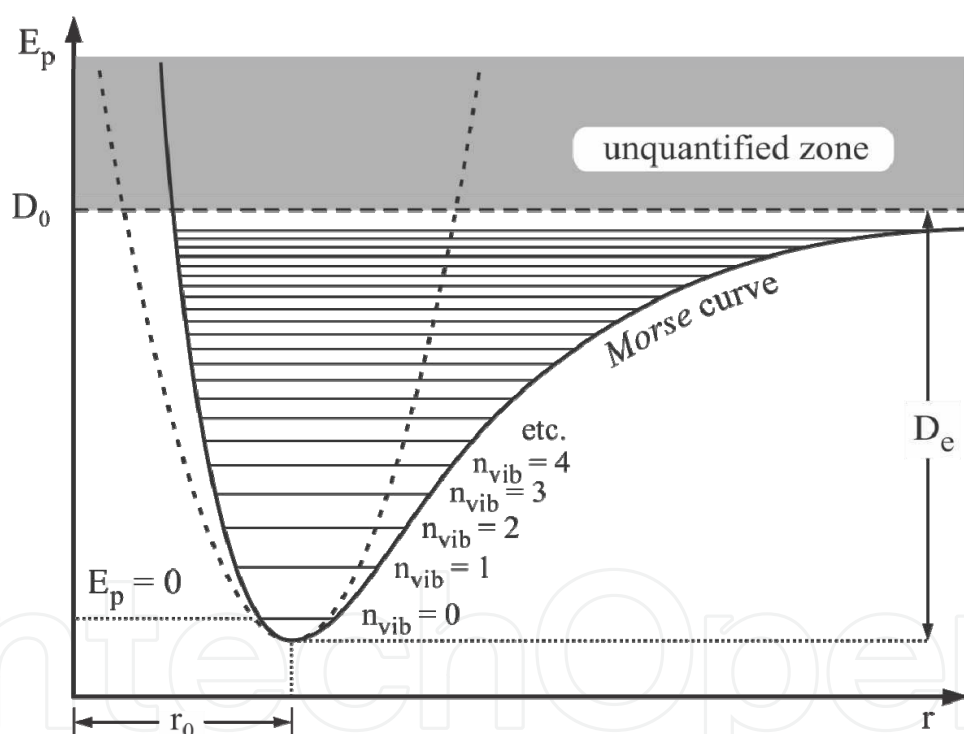

Fig. 1. Dependency of potential energy Ep of a diatomic molecule to the momentary distance

In the function (6.) the coefficient β depends on the mass reduced (μ) of the assembly diatomic, in accordance with relationship (7).

$$\beta = v_0 \cdot \sqrt{2 \cdot \pi^2 \cdot \mu \cdot D_e} \tag{7}$$

Continuous curve in figure 1 graphically represents the function (6). Morse function curve is compared with the curve corresponding harmonic approximation (parable with the interrupted curve).

The horizontal lines, arranged on the inside of the cavity Morse curve, shows the values allowed (quantifiable) of the energy of vibration of the assembly diatomic. Advanced to a deformation of the length of connection inter atomic, the energy potential of deformation tends toward a limit value (D_0) over which the energy of deformation of the assembly shall cease to be quantified.

In an approximation more accurate, 'anharmonic', in the phenomenon of vibration, the amounts permitted of the energy of oscillation are expressed a relationship similar to (3), with the difference that the anarmonic approximation. Status of vibration energy depends on the binomial n_{vib} quantum number after an expression of the degree 2 in relation:.

$$E_{vib}(n_{vib}) = E_c + E_p = h \cdot v_0 \cdot \left(n_{vib} + \frac{1}{2} \right) - h \cdot v_0 \cdot x \cdot \left(n_{vib} + \frac{1}{2} \right)^2$$

$$v_0 = \frac{1}{2 \cdot \pi} \cdot \sqrt{\frac{k}{\mu}}$$

(8)

The coefficient 'x' in the relationship (8) characterized quantitatively anarmonicity of molecule diatomic vibration, i.e. the drift behavior system from the model of harmonic vibration.

3. Potential energy dependence of the inter atomic distance of a diatomic molecule in Morse potential energy approximation

In inharmonic approximation of the vibration of diatomic molecules of the selection rule, relating to the variation in n_{vib} allowed for the quantum number, it is not so strict as in the case described harmonics. The model does not exclude the possibility inharmonic transitions between the status of vibration to which variation $n$vib quantum number to be 2,3 , etc. , in practice IR spectrophotometry.

Transitions associated with variations in higher than the unit are called harmonics of the upper fundamental transition (i.e., the transition that starts at the same lower status, but for which $\Delta n_{vib} = 1$).

The appearance of the absorption bands assigned to upper harmonics inherent in spectra are observed frequently in IR (especially in the case polyatomic molecules), but as a rule occur with intensities that are smaller than corresponding fundamental bands.

Strips of the upper harmonics associated with fundamental tape appear at frequencies (or wave numbers) which are approximately multiples whole frequency (or the wave-number) fundamental.

Another practical consequence of the inharmonicity of vibration of molecules is the rise of the inter-combination bands in the IR absorption spectra.

These bands of absorptions are observed at frequencies equal to the sum or the difference between two frequencies or fundamental frequency of a fundamental and a harmonic one. By cause of bands of combination appear various normal modes of oscillation of the molecule. The high harmonics and the bands of combination in IR absorption spectra cause considerably complications in their interpretation.

4. Vibration of polyatomic molecules

In the case the vibration diatomic molecules atoms can oscillate just in the direction of connection covalent) binding atoms. In the case of molecules consisting of several atoms (N atoms) the description of the assembly oscillations, even in harmonic approximation, is significantly more complicated. In principle, each atom in the structure molecule can execute, independently of the other atoms of the same molecule, the three-way oscillation linear independent (after three axes orthogonal coordinate attached each of atoms).

Therefore, the N atoms can run periodic shifts after 3N directions. In other words, a polyatomic molecule, consisting of N atoms, has 3N degrees of freedom of movement of constituent atoms. From this number, not all directions of movement of individual atoms correspond to deformations of real three-dimensional structure of the molecule, as oscillations in which each constituent atom is moving at the same time in the same direction, with the same amplitude and phase. They are equivalent to move whole molecules (translation molecule) without deforming them.

Also, movements that the N atoms can be synchronized in such a way that the assembly rotation movements correspond to atomic molecule as a whole, without causing structural deformation. Whereas entire molecule can be translated into 3 directions linear independent of each other and can rotate around a three axis-oriented perpendicular to each other. Of the total number of 3N directions of movement are deleted atomic 6 shifts (that is 6 degrees of freedom) in order to obtain the number (3N - 6) for detailed rules for the movement of atoms, therefore the same number of modes of oscillation actual molecular structure. .

It must be remembered, however that if molecule is not free, but is linked to a structure with crystalline comparable forces with those which act between atoms of molecule, then moving molecule as a whole from its position of equilibrium means a deformation, But, in this case is not of the molecule, instead of the structure supra molecular (crystalline lattice) in which molecule is a constituent.

In the particular case of a molecules polyatomic (with N atoms) having structure linear (all the atoms constituents are willing co-linear), the number of actual oscillation of the molecule is equal to (3N - 5). In this case is deleted of the total number of 3N possible directions of displacement 3. Degrees of freedom correlated with translation no deformation of the entire molecule and only 2 degrees of freedom corresponding to rotation molecule around two mutually orthogonal axis and perpendicular to the longitudinal axis of the molecule.

The explanation lies in the fact that in this case of the inertia of the molecule to the third axis of rotation (the flush to the longitudinal axis of the molecule) is vertical, so that rotation around this axis is virtually builds up kinetic energy.

At each of the (3N - 6) (i.e. (3N - 5)) possible ways of real oscillation, in principle each of constituents of atoms vibrating molecule running around their own positions of equilibrium. But in a particular mode of oscillation, individual atoms oscillate after other directions and with other amplitudes, but with the same frequency (feature mode of vibration in question). Directions and the amplitudes individual travel, and the frequency (common) of oscillation are characteristic mode of vibration.

The vibrating atoms in a molecule polyatomic can be described as a function of internal coordinates instead of cartesian coordinates. Such are eliminated those movements which correspond translations to atoms and rotation molecule without deformation. Internal coordinates of a molecules polyatomic can be defined in different ways. How to define the most frequently involves the covalent connection between pairs of atoms connect (l_{ab} for atoms a and b), Angles between connections covalent) binding centered on an atom common (α_{abc} for atoms a and c bound by common atom (b) and diedral angles θ_{abcd} (the angle of the plans P and R containing three connections between four **atoms covalent) binding) (Figure 2).**
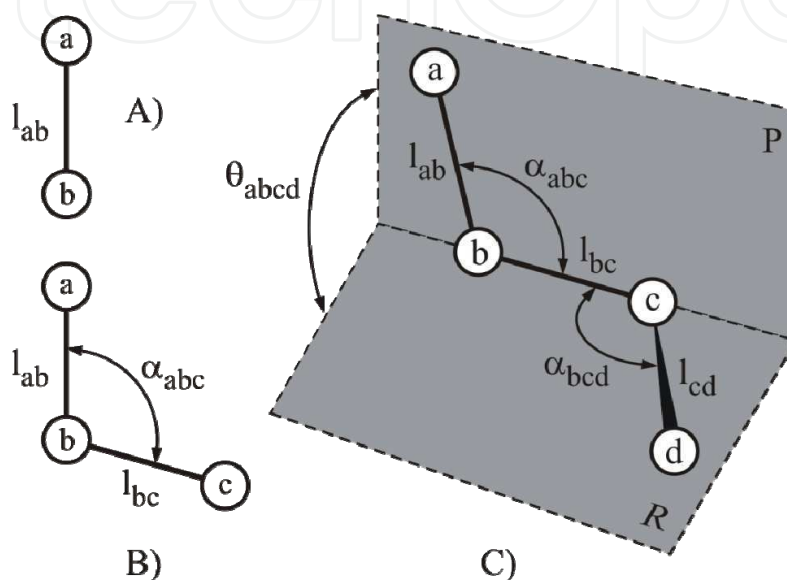

Fig. 2. Define Internal coordinates l , α and θ

Each vibration mode of the molecule can be described as a time-dependent periodic variation of all the internal coordinates. For a specific molecular structure, consisting of N atoms, the whole structure runs ((3N-6) or (3N-5)) modes of preferential oscillations, involving in (3N-6) (or (3N-5)) ways the internal coordinates of the molecule. These "preferential" types of oscillations represent the normal oscillations of the molecule. In each normal type of oscillation, all the internal coordinates of the molecule oscillate at a common frequency (in principle), specific for that type of oscillation.

In each normal mode of oscillation, the internal coordinates are involved in varying degrees. For a normal oscillation is characteristic of the internal coordinate of the molecule (e.g., a covalent bond length) is more involved than the others, then it may be said (with some tolerance) that normally oscillation that the respective oscillation type is characteristic for the respective internal coordinate (e.g., the length of the covalent bond).

Figure 3 represents the fine vibration structure of the fundamental electronic state and of the first excited electronic states, for the case of a hypothetical triatomic molecule. This type of molecule has 3·3-6=3 normal vibration modes. Oscillation modes are also represented in Figure 3, indicating the direction and the direction of the relative shift of the individual atoms in one of the half period of oscillation. Each electronic state consists in a number of vibration states characterized by the vibration quantum numbers $\mathbf{n_{vib}}$. For each normal way

of vibration (indicated by "1", "2" and "3" in Figure 3), the vibrations in the electronic states may be differently arranged. In other words, for different normal types of vibrations, the fundamental electronic state is differently "split" in substrates of vibration. In practice, the most probable vibrational transition occurs between the vibration states corresponding to the quantum numbers $n_{vib}=0$ and $n_{vib}=1$ for each normal vibration (transitions represented in Figure 3 by bold arrows). There is only a diminished probability to also occur, for every type of normal vibration, transitions between the vibration states corresponding to the quantum numbers $n_{vib}=0$ and $n_{vib}=2$ (transitions depicted in Figure 3 by dashed arrows). This kind of transition at a normal vibration type generates its first superior harmonic.
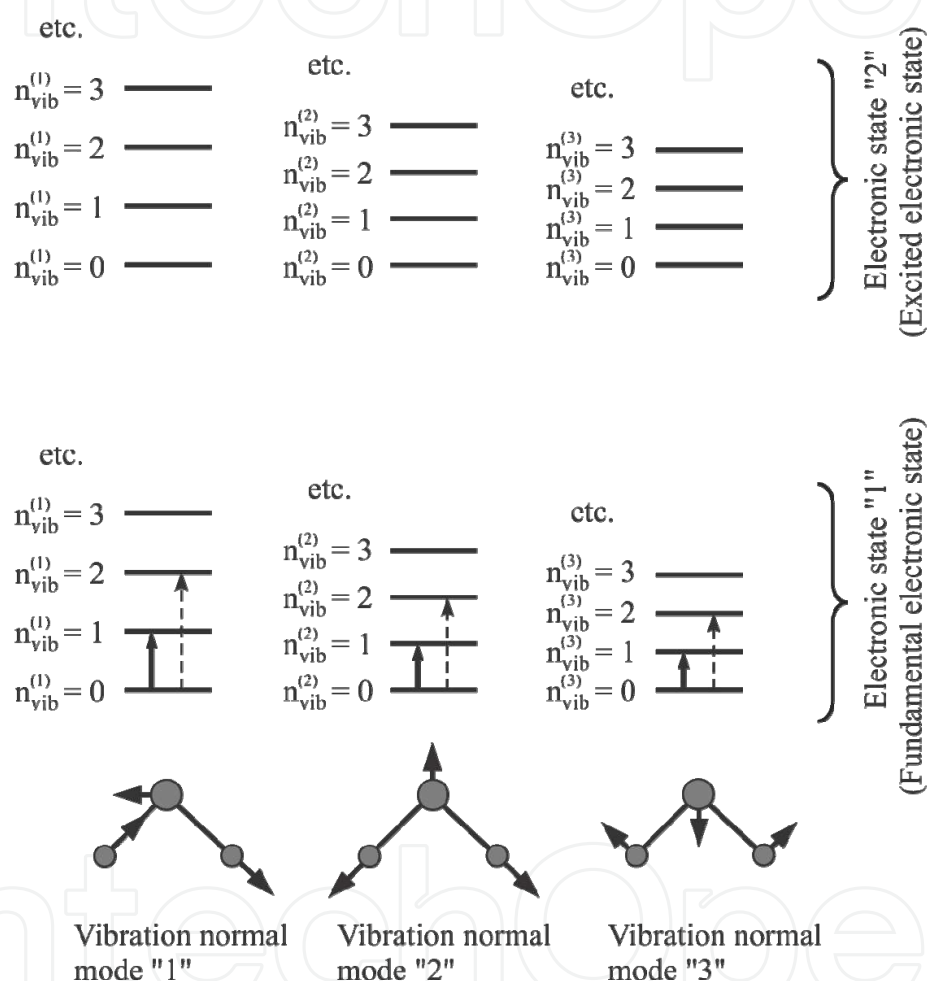

Fig. 3. Fine vibration structure of the fundamental and first excited electronic states

The transition between the vibrational states is initiated by the absorption of radiation with proper frequency (or wave number). The transition is visualized, in principle, by the appearance of the absorption band in the absorption spectrum of the analyzed substance. The incident radiation on the sample. Probability that is able produce transitions between the vibrational states of the fundamental electronic state), is located in the infrared (IR) domain. In principle, the IR absorption spectrum of a molecule contains a number of absorption bands that is equal to the normal modes of vibration of the molecule in question. Thus, in the case illustrated in Figure 3, the molecule would present the first absorption band corresponding to the normal mode of vibration no. "1" at the highest value of the wave

number (the energy gap is maximum), the second absorption band corresponding to the normal mode of vibration no. "2", at an intermediate wave number (the energy gap is intermediate) and the third absorption band corresponding to the normal mode of vibration no."3", at the lowest value number of the wave number (the energy gap is the smallest). The superior indices of the vibration quantum numbers that are present in Figure 3 $\left(n_{vib}^1, n_{vib}^2, n_{vib}^3\right)$ refers to the serial number of the respective normal vibration mode. The above made statement made, that each normal vibration type generates an absorption band in the IR spectrum of the analyzed substance, is true only in principle. It is common that not all the normal vibration types of a molecule (3N-5 or 3N-6, for an N atoms molecule) to present absorbtion bands.

If the covalent bonds in a molecule (or a molecular fragment) have comparable force constants or the masses of the atoms involved in the covalent bonds are close, then those atoms are involved, to some extent, in all possible normal modes of vibration of the molecule (or molecular fragment). In these situations, the individual internal coordinates (bond lengths or individual angles) do not independently vibrate; their vibrations are coupled, generating the appropriate number (N) of normal vibrations.

If one of the atoms linked by a covalent bond has a much smaller mass than the other atom (for example, the C-H, N-H, O-H, S, H, P-H bonds), the reduced mass of the ensemble of bound atoms is almost equal to the mass of the lighter atom and in this case the oscillation of the bond length is quasi-independent from the oscillation of the rest of the molecule. It may be said, in this case, that the absorption band associated with the normal mode of vibration affects the covalent bond, and it is characteristic of the presence of that chemical bond in the molecule structure.

On the other hand, if two atoms in a molecule are connected by a significantly stronger covalent bond then the other covalent bonds of the molecule (e.g., the isolated double or triple bond, as in one of the cases: >C=C<, >C=O, >C=N-, -N=N-, -C-C-), than the vibration of the respective bond can be also considered quasi-independent from the oscillation of the rest of the molecule. In this case, we can say that in one of the normal modes of vibration of the molecule practically occurs only the elongation oscillation of that bond, so the optical absorption band, generated in the IR spectrum by the normal mode of vibration, is characteristic for the presence of that covalent bond

Often, a group of atoms (or even a functional group) have their "own" normal ways of vibrations, quasi-independent of the rest of the molecule vibrations. In these situations, the normal "own" modes of the group of atoms is manifested in the IR absorption spectrum as a corresponding number of "group characteristic bands". An example is the characteristic band of the amidic functional group.

5. Practical aspects of infrared spectrophotometric analysis

The IR absorption spectrum is the graphical representation of a measure of energy depending on a measure of wave of the involved radiation. IR practice has established the use of the wave number (reciprocal of the wave length and proportional to the frequency of the radiation) and of the percentage transmission (T%) or absorbance (A), as related to the energy of the radiation.

There are significant differences between the UV-Vis and IR absorption spectra. IR spectra, even those of samples in condensed states, are generally characterized by a large number of well defined, sharp bands, with easily localizable positions. Therefore, IR spectra are useful for the fast, non-destructive identification of the chemical substances, and it is extremely unlikely that two substances that are chemically different to have, accidentally, identical IR spectra. Instead, the quantitative determinations in the IR spectral range are more difficult because diffuse radiation in the IR spectrophotometers is greater than in the UV-Vis spectrophotometer, so the error sources affect the results of quantitative determinations more than in the UV or Vis range.

Another difference between the two spectral areas consists in the transparency (and usability) of auxiliary materials (glass, optics, etc.). Spectra of liquid samples are recorded using similar cells to those used in UV-Vis spectrophotometry, except that glass walls are made of specific transparent materials (NaCl, KBr, KCl, ZnSe, As_2S_3, KRS-5, and others). The thickness of the sample in IR spectrophotometry are usually much smaller (0.05 mm – 1 mm) than those found in the UV-Vis absorption spectrophotometry (1 – 10 mm).

The IR absorption spectra can be recorded for solid, liquid or gaseous samples. The most common presentation state of samples in drug control is solid state. Commonly practiced method for obtaining IR spectra of substances or mixtures of pharmaceutical interest in solid form, consists in incorporate them into a solid, microcrystalline medium (for exemple potassium bromide). This method of sample preparation is called "inclusion in the tablet (or pill) of potassium bromide." To achieve such a compressed is triturated a small amount medium (1-2 mg) of solid interest with 200-250 mg of potassium bromide microcrystalline. Potassium bromide used for this purpose must be high purity (purity "for spectroscopy") and dried before use for several hours at 180 ° C. The triturating of solid mixture containing the substance of interest and potassium bromide, is running in agate mortar medium (glass or porcelain mortar is not appropriate). After the grain sufficiently fine, solid mixture is placed in a special mold will compress high pressure medium (about 10 ton-force) with a hydraulic press. Before applying pressure, air is removed from the stencil to prevent inclusion of air microbubbles in solid mass during pressing, that may produce microfissure in mass tablet at the end pressure . During pressing, the potassium bromide microcrystalline are sinterising forming a solid transparent, optically homogeneous. A compressed pellet carried out in ideal conditions is transparent without opaque area. In the spectral range 4000 - 300 cm^{-1} potassium bromide shows very good transparency, which is why this mode is used preferentially for sample preparation. Whereas, the included technique of sample in a potassium bromide matrix keeps crystallization form of the sample solid, the IR spectrum obtained by compression in potassium bromide is dependent from the crystallization of the sample. For substances that shows polymorphic, the IR absorption spectrum of solid samples , included in compressed potassium br An essential difference between the UV-Vis spectra registration procedure and the IR field is that in the UV-Vis domain, the solvents absorbtion is insignificant, so their absorption can be compensate, in the case of IR domain all used solvents presents its own band absorption, sometimes even more powerful, that in these areas of the spectrum of energy received by the detector is too small to differentiate the strong absorption of the solvent from the sample absorption that exceeding only in small extent the solvent absorbtion. For this reason, in the IR absorption spectra of the solutions are frequently areas where the IR radiation detector is inactive, and the signal recorded in these areas is irrelevant. To view

the sample spectrum in these areas, is repeat the recording spectrum in another solvent that is transparent.omide, allows the identify the crystallization form of the interest substance. Another technical detail is related by the fact that in IR absorption domain the solvents presents absorption bands, sometimes quite strong. Some IR spectrophotometers operating in double beam mode (similar to the double beam spectrophotometers used in the spectral UV-Vis). In the case of UV-Vis spectrophotometers is introduced, in the right reference optical path, a vat filled with pure solvent, and the right of the second optical path is introduced a vat of the same thickness, filled with solution (solvent and solute). The electronics parts of the spectrophotometer compare the absorbances of vats located in the two optical paths and subtract the absorbance of the solvent, located in the reference route, from solution absorbances located in the route of sample. Because the interest substances absorbance is marked in UV-Vis, and the absorbance of solvent is insignificant, the difference between the absorbances associated with two optical route is almost always positive.

In IR domain, where the absorbances of dissolved substances are comparable with those of solvents. It is easily understood that if a certain place in the spectrum (the number of wavelengths $\tilde{v}$) the solvent has a strong absorption band (molar absorptivity large solvent $\varepsilon_0(\tilde{v})$ and the solute does not absorb significantly at that wavenumbers ($\varepsilon(\tilde{v})$ small), then, the same layer thickness "d", the absorbance values measured in the two opticalroute ($A_{ref}(\tilde{v})$ for route reference and $A(\tilde{v})$ for solution route), are expressed by the relations (9).

$$A_{ref}(\tilde{v}) = d \cdot \varepsilon_0(\tilde{v}) \cdot C_0$$
$$A(\tilde{v}) = d \cdot \varepsilon_0(\tilde{v}) \cdot C_0^* + d \cdot \varepsilon_0(\tilde{v}) \cdot C \qquad (9)$$

In the (9) relation, C_0 şi C_0^* represents molar concentration of pure solvent in the two cells (placed in reference route and in the sample route respectively), and C is the molar concentration of solute in the cells placed in the route sample. It is obvious that $C_0^* < C_0$ because in the sample cells is in addition to solvent, a quantity of solution. The signal recorded by spectrometry, $\Delta A(\tilde{v})$, to the number of wave $(\tilde{v})$, is the difference between the both absorbance of relationship (9)

$$\Delta A(\tilde{v}) = A(\tilde{v}) - A_{ref}(\tilde{v}) = d \cdot [\cdot \varepsilon 0(\tilde{v}) \cdot C_0^* - C_0) + \varepsilon(\tilde{v}) \cdot C] \qquad (10)$$

The first term in the right side of the parenthesis right above relationship is negative, because $C_0^* < C_0$. If $\varepsilon_0(\tilde{v})$.is significantly higher than $\varepsilon(\tilde{v})$, then it can happen that $\Delta A(\tilde{v})$ to have a negative value for the number of wave $\tilde{v}$. Obviously, such a negative value of absorbance is an artifact, without spectrophotometric real significance. To overcome this problem, manifested in solutions recording spectra, are used in the reference route a cell with variable thickness. The solution is placed in a cell of fixed thickness"d^*", lower than thickness"d", in the reference route. The absorbances $A_{ref}^*(\tilde{v})$ and $A(\tilde{v})$, and the difference of absorbances, $\Delta A^*(\tilde{v})$, associated with the two optical route, the new working conditions, are given by the relations (11).

$$A_{ref}^*(\tilde{v}) = d^* \cdot \varepsilon_0(\tilde{v}) \cdot C_0$$
$$A(\tilde{v}) = d \cdot \varepsilon_0(\tilde{v}) \cdot C_0^* + d \cdot \varepsilon(\tilde{v}) \cdot C \qquad (11)$$

If we choose suitable variable thickness of the cell in the reference route, the expression

$$\Delta A^*(\tilde{v}) = A(\tilde{v}) - A^*ref(\tilde{v} \sim) = \varepsilon_0(\tilde{v}) \cdot (d \cdot C^*0 - d^* \cdot C0) + d \cdot \varepsilon(\tilde{v}) \cdot C$$

If we choose suitable variable thickness of the cell in the reference route, the expression $(d.C^*_0 - d^*.C_0)$ is null for any value of wavenumber (as the expression does not depend on the number of wavelengths), so the choice of suitable thickness d^* resolve the problem reported for the entire spectrum. In this case the absorbance of the solute depends on its concentration, according to the relation BLB.

$$\Delta A^*(\tilde{v}) = A(\tilde{v}) - A_{ref}(\tilde{v}) = d \cdot \varepsilon(\tilde{v}) \cdot C \tag{12}$$

Because IR absorption spectra are generated by transitions between vibrational states of sample molecules and the frequency of normal modes vibration depends (in addition to the force constants associated with deformations of the molecule) of the masses of atoms, it is expected that the replacement of atoms in molecular structure sample with different isotopes of the respective atoms (isotopic marking of the molecule) to induce dramatic changes of the IR absorption spectrum of the sample.

By isotopic marking in the known positions of molecule and by confronting these changes with changes in IR absorption band positions, significant conclusions can be drawn on whether the different atoms are involved in the normal modes of vibration of the molecule. If an atom of molecule is replaced by its heavier isotope, then IR absorption bands is moving to lower wavenumbers. The most significant movement is found in these absorption bands corresponding to normal vibration modes which involves mostly the replaced atom with heavier isotope.

The biggest relative change in mass of an atom by isotopic substitution is made for replacement of the hydrogen atom (isotope 1H) with deuterium (2H isotope). It follows that by sample deuterating, the IR absorption bands associated with chemical bonds in which one of the atom is hydrogen, suffer very significant movement toward smaller wave numbers.

Isotopic displacement of absorption bands is useful and for choice of suitable solvent in those cases where the IR absorption spectrum should be recorded in solution. Because of own absorption, some solvent (eg chloroform, $HCCl_3$) can not be used except in those domain where this is sufficiently transparent. The spectral regions in which the chosen solvent substantially absorbed are not used. But if using deuterated solvent (e.g. deuterocloroform, $DCCl_3$), this have unusable areas at other wavenumbers. Original solvent (undeuterated) and deuterated solvent presents identical dissolution properties, but are complementary with respect to transparency in the IR spectral range.

6. Aspects of construction and specific features of operating mode for Fourier transform spectrophotometers (FTIR)

Old design spectrophotometers work similar with those for UV-Vis domain, i.e. are composed of radiation source, monochromator designed to select a desired wavelength radiation, the sample chamber and the radiation detector. In IR domain, diffuse radiation presents more serious problems then in ultraviolet and visible domain. Thus, in IR domain,

the ratio of useful signal and noise is more disadvantageous. The new concept of Fourier transform IR spectrophotometers meant an important step in achieving spectra with high quality even for difficult samples where the spectrophotometers with traditional construction proved to be powerless.

Construction scheme and specific features of operating mode for a Fourier Transform Infrared Spectrophotometer (FTIR – "F*ourier* **T**ransform **I**nfra**R**ed") are presented in Figure 4. It is noted that the optical assembly has no monochromator, which is replaced by a Michelson interferometer type. The polychromatic radiation from **LS** (light source) source is transmitted through concave mirror **M₁** (mirror 1) and radiation divider **BS₂** (beam splitter 2) to sample **S** (sample). After crossing the sample, the radiation reach the radiation divider **BS₁** (beam splitter 1) that divides the flow of radiation in two tracks: one for the mirrors **M₂** (mirror 2) and another for the mirrors **M₃** (mirror 3). Mirrors **M₂** and **M₃** turn back the radiation to the radiation divider **BS₁**. Reaching its surface, radiations which had different routes, merge and produce a interference phenomena. The only constructive element moving while recording the spectrum is the set of **M₃** mirrors. If the mirrors **M₃** are in position **A**, the optical path difference, corresponding to the two optical paths is null, thus the radiations which turn back on the surface of the radiation divider produces an interference maximum. By translation of **M₃** mirrors, optical path difference δ between the two routes is changed progressive.
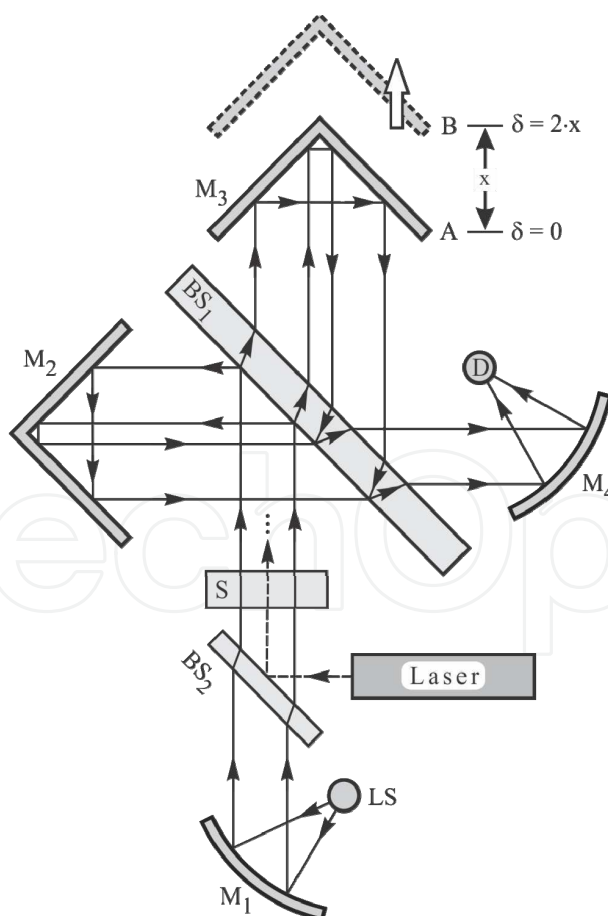

Fig. 4 Construction and operating scheme for Fourier Transform Infrared Spectrophotometer

It can be shown that the detector **D**, which measures the intensity of interference as a function of **M₃** mirrors position (so depending on the optical path difference δ between the two routes) records an interferogram which depends on inverse Fourier transform of emission spectrum of the source **LS** and on inverse Fourier transform of transparency (transmission) spectrum of the sample **S** (sample). After Fourier transform of detector **D** signal and some additional mathematical operations on detector signal the transmission (or optional absorption spectrum) spectrum of the sample **S** in known form is obtained.

Figure 4 shows the typical interferogram recorded by the detector (representing the light flux, which reached the detector, as a function of the optical path difference δ associated with **BS₁ – M₂ – BS₁** and **BS₁ – M₂ – BS₁**).

To know the exact positions of absorption maxima in the IR spectrum of the sample, the position of mirrors **M₃** must be known exactly commensurable with the radiation wavelength in each moment of this whole movement. Therefore, together with the radiation of source **LS**, it is sent another radiation, this time the radiation is monochromatic, coming from a laser emitting in the visible (usually red radiation) or near infrared (often with a wavelength of 1064 nm) range. The interferogram produced by monochromatic laser radiation is practically a sinusoidal function. This sinusoidal signal, also noted by the detector **D**, is superimposed on the signal generated by the sample. By tracking the interference maximum and minimum (sinusoidal type) of the laser radiation, it can be indicated the current location of the mirrors **M₃**, in each moment of the recording operation, with an accuracy comparable to the wavelength of laser radiation.
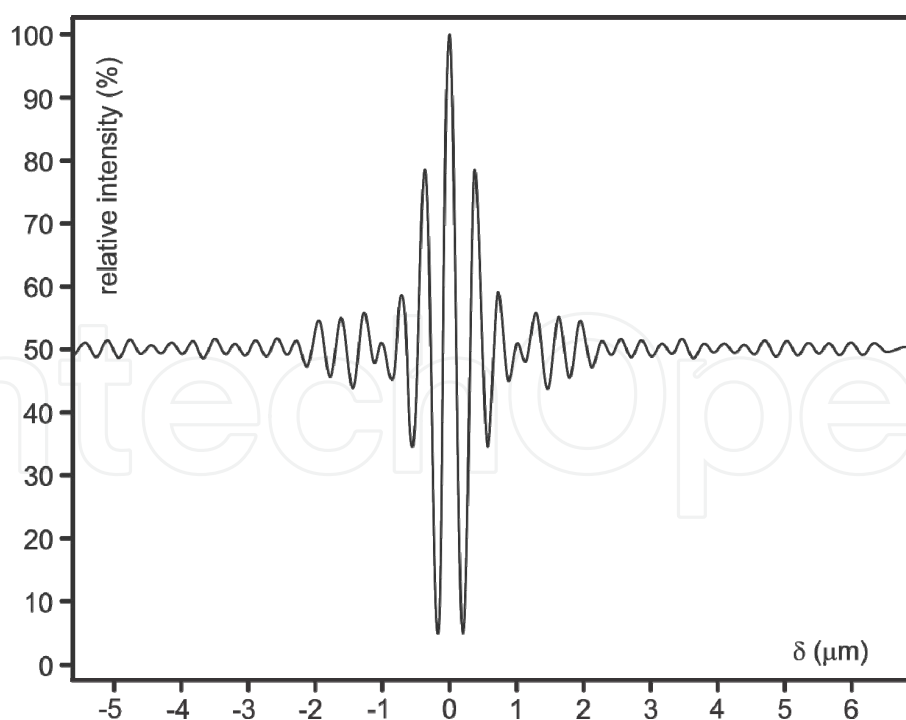

Fig. 5. The typical interferogram recorded by the detector

Recording of an IR spectrum of a sample based on Fourier Transform method has many advantages:

a. using a spectral interferometer ensures the achievement of a resolution much higher than that offered by spectrophotometers with dispersion or a high signal / noise for a given resolution;

b. lack of slits in the optical assembly of the Fourier transform spectrophotometers removes a series of disadvantages related to the fact that for spectrophotometers with dispersion the optical image of the input slit is deformed due to dispersive optical element (prism or diffractive optical network);

c. the signal / noise ratio achieved in Fourier transform spectrophotometers it is more advantageous with several magnitude orders compared with dispersion spectrophotometers;

d. because of the signal / noise ratio advantage, recording of an interferogram (a single displacement of mirrors M_3 from position corresponding to $\delta = 0$ to a position with a extreme δ value) can be achieved in a very short time (less one second) reason why, within a reasonable time, interferogram recording operation can be repeated for several times, followed by the mediation of the obtained signals.

The last aspect is particularly important for difficult samples, which absorb infrared radiation in a very advanced position. For these samples, a single interferogram recording, with all the inherent advantages of Fourier multiplexing technique, signal / noise ratio is often unsatisfactory. In these cases, overlapping a larger number of records (the number can be N), followed by calculating the arithmetic average of the records, significantly improves the signal / noise ratio. In theory errors can be demonstrated that the overlap (acquisition) of N records, followed by mediation of the obtained interferogram, the signal / noise ratio is improved by a factor equal to $\sqrt{N}$ in comparison with a single record case. Thus, and in IR spectra (obtained by the Fourier transform of the interferogram) the signal / noise ratio is improved by acquisition of spectra.

The electrical signal of the detector is digitized with an appropriate electronic interface and data (pairs of wavenumber values vs. absorbance or wavenumbers vs. transmission percentage) are stored in a file created by a computer. The stored data can be later processed in different ways. Thus, you can add or subtract algebraic different spectra, can make corrections of baseline, can reduce noise by techniques different than acquisition (e.g. "signal smoothing") or it can be presented the absorbance derived as a function of scanned size (wavenumber). Derivation of the original spectrum as a function of wavenumer often surprises some details of the IR spectrum which are harder to observe in its original form (absorbance vs. wavenumber).

7. Organic compounds

Elucidation of the molecular structure is especially important in organic chemistry. An analytical method for the identification of functional groups from organic compounds uses one of the most physical properties of a chemical compound: the infrared absorption spectrum. Compared with other physical properties: melting point, refractive index, or specific gravity which offer only a single point of comparison with other substances, the IR spectrum of a specific compound, gives a multitude of important information (position of bands, band intensity). The intensity is indicative of the number of a particular group contributing to absorption.

It is well known that molecules absorb a unique set of IR light frequencies, because the frequency of vibration involved depends on the masses of atoms involved, the nature of the bonds and the geometry of the molecule. A molecule absorbs only those frequencies of IR light that match vibrations that cause a change in the dipole moment of the molecule. Each organic molecule, with the exception of enantiomers, has a unique infrared spectrum. This is because symmetric structures and identical groups at each end of one bond will not absorb in the IR range. The spectrum has two regions. The *fingerprint* region is unique for a molecule and the *functional group* region is similar for molecules with the same functional groups.

The entire spectral pattern is unique for a given compound. The bands that appear depend on the types of bonds and the structure of the molecule.

In a complicated molecule many fundamental vibrations are possible, but not all are observed movements which do not change the dipole moment for the molecule or the those which are so much alike that they coalesce into one band.

IR is usually preferred when a combination of qualitative and quantitative analysis is required. It is often used to follow the course of organic reactions allowing the researcher to characterize the products as the reaction proceeds.

For the analysis, the samples can be liquids, solids, or gases. The only molecules transparent to IR radiation under ordinary conditions are monatomic and homonuclear molecules such as Ne, He, O_2, N_2, and H_2. One limitation of IR spectroscopy is that the solvent water is a very strong absorber and attacks NaCl sample cells.

Computerized spectra data bases and digitized spectra are widely used today especially in research, chemistry, medicine, criminology, etc

8. Interpretation of spectra

Identification of a molecular structure from the IR spectrum can be realized using information from correlation tables and absorbances from the functional group region of the spectrum and comparison of the obtained spectrum with those of known compounds or obtain a known sample of a suspected material.

A preliminary examination of a spectrum use requires the examination of two important spectrum areas: functional group region (**4000-1300 cm^{-1}**) and the **909-650** cm^{-1} region. The characteristic stretching frequencies for important functional groups such as OH, NH, and C=O occur in this portion of the spectrum. The absence of absorption in the assigned ranges for the various functional groups can usually be used as evidence for the absence of such groups from the molecule. The absence of absorption in the **1850-1540** cm^{-1} region excludes a structure containing a carbonyl group.

Strong skeletal bands for aromatics and heteroaromatics fall in the **1600-1300** cm^{-1} region of the spectrum. These skeletal bands arise from the stretching of the carbon-carbon bonds in the ring structure. The lack of strong absorption bands in the **909-650** cm^{-1} region generally indicates a aliphatic structure. Aromatic and heteroaromatic compounds display strong out-of-plane C-H bending and ring bending absorption bands in this region. The intermediate portion of the spectrum, **1300-909** cm^{-1} is usually correspond to the fingerprint region. The

absorption pattern in this region is complex, with bands originating in interacting vibrational modes. Absorption in this intermediate region is probably unique for every molecular species. For example, in the cases of hydrocarbons, organic compounds classified as saturated or unsaturated based on the absence or presence of multiple bonds, the energy of the infrared light absorbed by a C-H bond depends on the hybridization of the hybrid orbital, in the order of $sp^3 > sp^2 > sp$. The sp^3-hybridized C-H bonds in saturated hydrocarbons absorb in the 2850-3000 cm^{-1} region. The sp^2-hybridized C-H bonds from alkenes absorbs at **3080** cm^{-1}. A sp-hybridized C-H bond in a molecule, alkyne absorbs infrared at 3320 cm^{-1}. Another classification of hydrocarbons can be made based on absorptions due to the carbon-carbon bond. Carbon-carbon bond strength increases in the order of single>double>triple. Saturated hydrocarbons all contain carbon-carbon single bonds that absorb in the 800-1000 cm^{-1} region. But, unsaturated hydrocarbons also contain carbon-carbon single bonds that absorb in this same region. So, this interval can not be considered as fingerprint region because most organic compounds have carbon-carbon single bonds.

The alkanes give an IR spectrum with relatively few bands because there are only CH bonds that can stretch or bend.

The next table present the characteristic group frequencies of organic molecules.

Class	Group	Wavenumber (cm^{-1})
Hydrocarbons		
Alkane	C-H	2850-3000
	C-C	800-1000
Aromatic	C-H	3000-3100
	C=C	1450-1600
Alkene	C-H	3080-3140
	C=C	1630-1670
Alkyne	C-H	3300-3320
	C-C	2100-2140
Oxygen Compounds		
Alcohol	O-H	3300-3600
	C-O	1050-1200
Ether	C-O	1070-1150
Aldehyde	C=O	1720-1740
	C-H	2700 -2900
Carboxylic Acids	C=O	1700-1725
	O-H	2500-3300
	C-O	1100-1300
Ester	C=O	1735-1750
	C-O	1000-1300 (2 bands)
Ketone	C=O	1700-1725
Acyl halides	C=O	1785-1815
Anhydrides	C=O	1750;1820 (2 bands)
	O-C	1040-1100
Amides	C=O	1630-1695

Class	Group	Wavenumber (cm⁻¹)
	N-H	1500-1560
Isocyanates,Isothiocyanates, Diimides, Azides, Ketenes	-N=C=O, -N=C=S -N=C=N-, -N₃, C=C=O	2100-2270
Nitrogen compounds		
Amines	N-H	3300-3500
	C-N	1000-1250
	NH₂	1550-1650
	NH₂ & N-H	660-900
Nitriles	C≡N	2240-2260
Oxidized Nitrogen Functions		
Oxime **(=NOH)**	O-H	3550-3600
	C=N	1665± 15
	N-O	945± 15
Amine oxide (N-O)	aliphatic	960± 20
	aromatic	1250± 50
N=O	nitroso	1550± 50
	nitro	1530± 20;1350± 30
Alkyl bromide	C-H	667
Sulfur compounds		
Thiols	S-H	2550-2600
Esters	S-OR	700-900
Disulfide	S-S	500-540
Thiocarbonyl	C=S	1050-1200
Sulfoxide	S=O	1030-1060
Sulfone	S=O	1325± 25; 1140± 20
Sulfonic acid	S=O	1345
Sulfonyl chloride	S=O	1365± 5;1180± 10
Sulfate	S=O	1350-1450
Phosphorous compunds		
Phosphine	P-H	2280-2440 950-1250
Phosphonic acid	(O=)PO-H	2550-2700
Esters	P-OR	900-1050
Phosphine oxide	P=O	1100-1200
Phosphonate	P=O	1230-1260
Phosphate	P=O	1100-1200
Phosphoramide	P=O	1200-1275
Silicon compounds		
Silane	Si-H	2100-2360
	Si-OR	1000-1110
	Si-CH₃	1250± 10

Table 1. Schematic representation of the Infrared Group Frequencies classification

9. References

E.O. Brigham: "The Fast Fourier Transform", Prentice-Hall, Inc., 1974

P.L. Polavarapu: "Vibrational Spectra: Principles and Applications with Emphasis on Optical Activity", Elsevier Science B.V. 1998;

Y. Wang, R. Tsenkova, M. Amari, F. Terada, T. Hayashi, A. Abe, Y. Ozaki: 'Potential of Two-Dimensional Correlation Spectroscopy in Analysis of NIR Spectra of Biological Fluids. I. Two-Dimensional Correlation Analysis of Protein and Fat Concentration-Dependent Spectral Variations of Milk", Analusis Magazine, 1998:26, M64-M69

R.N. Bracewell: "The Fourier Transform and Its Applications", McGraw Hill, 2000

D. Baurecht, U.P. Fringeli: "Quantitative Modulated Excitation Fourier Transform Infrared Spectroscopy", Review of Scientific Instruments, 2001:72, 3782-3792

M-J. Paquet, M. Laviolette, M. Pézolet, M. Auger: "Two-Dimensional Infrared Correlation Spectroscopy Study of the Aggregation of Cytochrome C in the Presence of Dimyristoilphosphatidylglycerol", Biophysical Journal, 2001:81, 305-312

Y. Kauppinen, J. Partanen: "Fourier Transforms in Spectroscopy", Wiley-VCH Verlag Gmbh, 2001

J.M. Chalmers, P.R. Griffiths (Editors): "Handbook of Vibrational Spectroscopy. Theory and Instrumentation", John Wiley & Sons Ltd., 2002

M. Cho: "Two-Dimensional Optical Spectroscopy", CRC Press, 2009

P.W. Atkins, Physical Chemistry. 2nd Ed. San Francisco: W.H. Freeman and Company, 1982. Discussion of vibrational spectra from a quantum mechanical view.

B.W. Cook, K. Jones. A Programmed Introduction to Infrared Spectroscopy. New York: Heyden & Son Inc., 1972. Excellent resource for the beginning spectroscopist.

R. T. Morrison, R. N. Boyd. Organic Chemistry. 5th Ed. Boston: Allyn and Bacon, Inc., 1987. Provides a brief description of spectroscopy. Includes relevant IR spectra for each family of organic compounds.

R. L., Shriner, R. C., Fuson, D. Y., Curtin, T. C. Morrill. The Systematic Identification of Organic Compounds. 6th Ed. New York: Wiley, 1980. Contains a brief section on IR spectroscopy. Mainly a text for identification of compounds by chemical tests.

R. M., Silverstein, G. C., Bassler, T. C. Morrill. Spectrometric Identification of Organic Compounds. 4th Ed. New York: Wiley, 1981. Description of mass spectrometry, IR spectrometry, 1H NMR spectrometry, 13C spectrometry, and UV spectrometry.

A. Lee Smith,. Applied Infrared Spectroscopy: Fundamentals, Techniques, and Analytical Problem-Solving. New York: Wiley, 1979. Comprehensive treatment of IR spectroscopy. Includes history, instrumentation, sampling techniques, qualitative and quantitative applications.

G. Socrates, Infrared Characteristic Group Frequencies. 2nd Ed. Chichester: Wiley, 1994. A comprehensive reference of correlation tables.

A.Streitweiser, Jr., C. H. Heathcock. Introduction to Organic Chemistry. 2nd Ed. New York: Macmillan Publishing Co., Inc., 1981. Introductory organic text with a section on IR spectroscopy. Includes spectroscopic information as each family is presented.
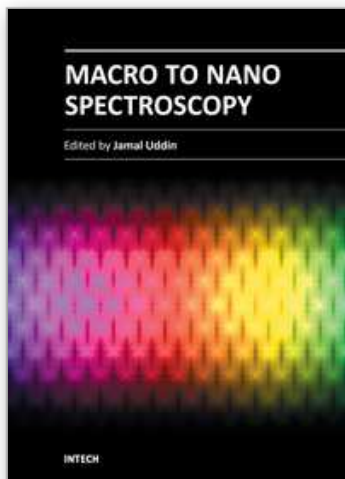
Macro To Nano Spectroscopy

Edited by Dr. Jamal Uddin

In the last few decades, Spectroscopy and its application dramatically diverted science in the direction of brand new era. This book reports on recent progress in spectroscopic technologies, theory and applications of advanced spectroscopy. In this book, we (INTECH publisher, editor and authors) have invested a lot of effort to include 20 most advanced spectroscopy chapters. We would like to invite all spectroscopy scientists to read and share the knowledge and contents of this book. The textbook is written by international scientists with expertise in Chemistry, Biochemistry, Physics, Biology and Nanotechnology many of which are active in research. We hope that the textbook will enhance the knowledge of scientists in the complexities of some spectroscopic approaches; it will stimulate both professionals and students to dedicate part of their future research in understanding relevant mechanisms and applications of chemistry, physics and material sciences.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Adina Elena Segneanu, Ioan Gozescu, Anamaria Dabici, Paula Sfirloaga and Zoltan Szabadai (2012). Organic Compounds FT-IR Spectroscopy, Macro To Nano Spectroscopy, Dr. Jamal Uddin (Ed.), ISBN: 978-953-51-0664-7, InTech, Available from: http://www.intechopen.com/books/macro-to-nano-spectroscopy/organic-compounds-ft-ir-spectroscopy

INTECH
open science | open minds