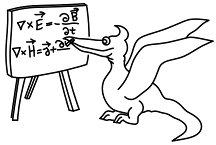

Serial: Optical Spectroscopy of Molecules

This is a machine-assisted translation of a czech serial. If any questions or problems arise, please, send an e-mail to fykos@fykos.org

Dear readers, allow me to welcome you to the second installment of our series on experimental methods in physics. Today, we will continue to explore spectroscopic techniques; however, unlike the previous part, we will move somewhat lower in the electromagnetic spectrum—focusing mainly on the visible region, that is, methods of optical spectroscopy. We will reach the very boundary between physics and chemistry. Everything will be explained in a way that allows enthusiastic high school students like you to understand at least the basic principles behind several commonly used experimental methods—and above all, to grasp the significance of such experiments.

Theory without experiment would be like a body without a soul. You can learn about all the techniques mentioned here in far greater detail during university studies or from the vast number of available resources. I do not believe that a deeper understanding would be achieved by burdening the reader with rigorous mathematics or advanced quantum mechanics. However, for those interested, additional explanatory notes will be provided. Let us begin.

Introduction to the Basics of Chemical Bonding

A molecule consists of two or more atoms connected by a chemical bond, within which a certain amount of energy is stored. But what exactly is a chemical bond? As mentioned in the previous part, every atom has a nucleus surrounded by an electron cloud composed of layers (shells) labeled according to the *principal quantum number* n. The electrons farthest from the nucleus are the most reactive. The outermost shell is called the valence shell, and by the number of valence electrons, we can classify an atom within the periodic table—distinguishing, for example, alkali metals from halogens.

But that is not all. Each shell (beyond the first) is divided into subshells, called orbitals, described by the *azimuthal quantum number* l, which takes values from 0 to $n-1$. The shape of orbitals can be precisely calculated (you may know from chemistry the basic types: s ($l=0$), p ($l=1$), d ($l=2$), f, and hypothetically further). This was a major success of quantum theory.

Quantum mechanics further tells us that the intuitive picture of electrons as *charged spheres* cannot work for several reasons. An electron is always somewhat *spread out* in space. Therefore, we move to a description in terms of orbitals—regions of space where an electron can be found with some probability. Each orbital can contain at most two electrons with opposite spins, often represented by boxes with arrows pointing up and down.

Higher orbitals are degenerate—e.g., the p orbital is actually threefold and accommodates six electrons, d is fivefold with ten electrons, etc. However, degeneracy holds only in the absence of a magnetic field. When a magnetic field is applied, orbitals interact with it differently, so degeneracy is *lifted* and the orbitals can be distinguished by the *magnetic quantum number* m, which ranges from $-l$ to $+l$. The complete description of all electrons in an atom is called the electron configuration, which for iron is shown in Figure 1.

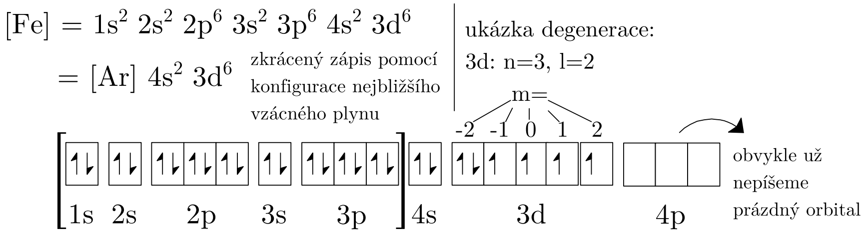

Figure 1: Schematic representation of orbitals and electron configuration of an atom.

The first quantum mechanical description of the chemical bond, published in 1927 by W. H. Heiti and F. W. London, considered only the overlap of atomic orbitals. However, it could not explain the properties of molecules formed from heavier atoms. Today, we know that the original atomic orbitals actually vanish, giving rise to new, *molecular orbitals* with different behavior and energy levels. This understanding comes from the study of wave function combinations (functions that describe electron distributions). To distinguish molecular orbitals from atomic ones, we denote them by Greek letters (as in chemical bonds): σ, π, (δ, etc.). Orbitals with lower energy than the atomic ones are called *bonding*, and those with higher energy are *antibonding*. A graphical representation of this concept is shown in Figure 2.

There are exceptions to this rule. If an atomic orbital has no spatially or energetically suitable counterpart, its shape and energy remain nearly unchanged. Such orbitals are called *nonbonding* and are denoted as n or by the symbol of the original orbital. [1]

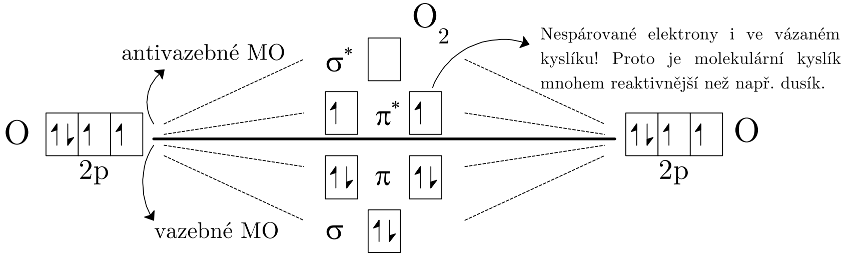

Figure 2: Formation of molecular orbitals in O_2 by combination of atomic orbitals.

An important concept is bond polarity, with two extreme cases: a nonpolar bond and a highly polar (ionic) bond. We will return to this later.

The Molecule as an Oscillator... Almost

Let us now explain the formation of a bond in a diatomic molecule. When we bring two atoms close together, their electron clouds repel each other, since electrons experience a repulsive elec-

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[1] Examples include p orbitals in oxygen in a water molecule, or in fluorine in hydrogen fluoride (HF). Nonbonding orbitals commonly occur when atoms with very different electronic structures form bonds.

trostatic Coulomb interaction. At the same time, however, the electrons are strongly attracted to the nuclei by that same interaction. The behavior of this potential energy can be described, for example, by the Lennard-Jones potential, which is, however, rather complicated to compute (the resulting equations are not analytically solvable).

An elegant way to deal with such complex equations is to find similar, yet simpler ones. With both eyes metaphorically closed, we shall therefore assume that the potential has an approximately parabolic shape—that is, that it is harmonic. This yields a much simpler expression, one that resembles the equation of a harmonic oscillator—in fact, it is a disguised oscillator. Regardless of this approximation, the result is that there exists a certain distance at which the energy reaches its minimum value. The atoms stabilize at the distance where the orbitals overlap "just right", forming a so-called covalent bond, in which electrons are shared between both atoms. In this way, a more energetically favorable bound state can arise—that is, a molecule.

The simplest mechanical model of a molecule is a dumbbell, where the atoms act as masses and the chemical bond as a rod. This *rigid rotator* allows us to describe molecular rotations. In reality, however, the bond is not perfectly rigid—its length oscillates around the equilibrium position. You can already see where the oscillator will come in handy. Molecular vibrations can thus be described as a vibrating spring. The analogy is apt, since the bond is stretched both during rotation and vibration.

For the moment of inertia of a molecule with atomic masses m_1, m_2, the following holds:

$$I = m' R^2 ,$$

where m' is the so-called reduced mass, given by

$$m' = \frac{m_1 m_2}{m_1 + m_2} .$$

The oscillator is then described by the force equation

$$F = k(r - r_0) ,$$

where r_0 is the equilibrium distance and k is the spring constant (stiffness). The total energy of the molecule is therefore the sum of its rotational and vibrational energies:

$$E = \frac{1}{2} I\,\omega^2 + \frac{1}{2} k (r - r_0)^2 .$$

As the size of the molecule increases, the number of possible oscillations (more precisely, degrees of freedom) between atoms grows faster than the number of rotational modes. For a reasonably large molecule, rotational energies thus become negligible compared to vibrational ones, and in most experimental methods, vibrational energy levels are the more significant. (So far, we have only approximated the diatomic case.)

For the vibration frequency of a given pair of atoms, we have:

$$\omega = \sqrt{\frac{k}{m'}} , \quad \text{or} \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m'}} .$$

We have just stated that vibrations stretch and compress bonds. This necessarily implies that molecular orbitals are not rigid either. An important consequence of this is the appearance of fine shifts in energy levels, which we are capable of measuring and interpreting.

From the standpoint of quantum mechanics, the oscillator cannot vibrate arbitrarily. Its vibrations are quantized and satisfy

$$E = \left(n + \frac{1}{2}\right) h\nu,$$

where h is Planck's constant and n is the vibrational quantum number (not to be confused with the principal quantum number n—unfortunately, there are only so many letters). Because of the uncertainty principle, position and momentum cannot be known simultaneously with absolute precision. Consequently, the energy of the oscillator does not rest at zero, as one might intuitively expect, but is shifted by a constant term known as the *zero-point energy*.

If we depict the situation described, we obtain Figure 3.

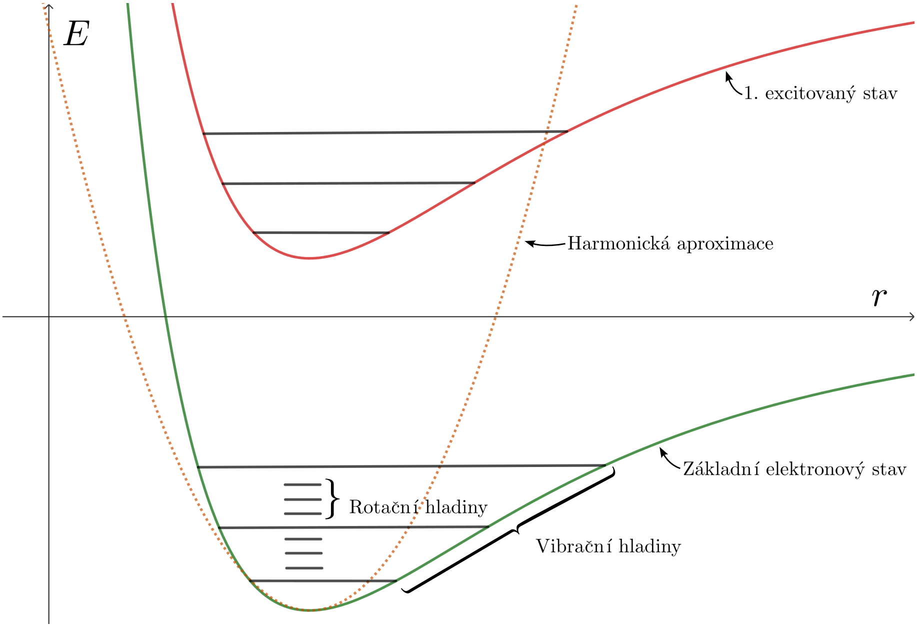

Figure 3: Representation of molecular energy levels. Comparison of the Lennard-Jones and harmonic potentials.

The Molecule as a Vibrating Dipole

When a covalent bond is formed between two different atoms, the electrons are not attracted to both with equal strength. As a result, positive and negative partial charges are distributed across the molecule. In extreme cases, such as when a salt molecule dissolves in water, the molecule can dissociate completely into a sodium cation (with a positive unit charge) and a chloride anion (with a negative unit charge). However, we are primarily interested in situations where the molecule remains intact.

An electric dipole is a structure that appears electrically neutral from afar (it has no net charge) but possesses positively and negatively charged poles. The dipole moment is defined as a vector quantity:

$$\mathbf{p} = q\mathbf{r}.$$

Each polar bond therefore contributes its own dipole moment. However, the mere presence of polar bonds does not necessarily mean that the entire molecule behaves as a dipole. The vector sum of all dipoles must also be nonzero. For example, carbon dioxide is not a dipole, because its two bond contributions point in opposite directions and cancel each other out, while water *is* a dipole due to its nonlinear geometry.

When bond vibrations occur, the dipole moment of the molecule changes. From electrodynamics, we know that an oscillating dipole (in this case, the molecule) emits electromagnetic radiation. Conversely, incoming radiation (light) can induce a dipole moment by ”nudging” one of the bonds. These are two interconnected phenomena.

But must the emitted light have the same wavelength as the incident light? The answer is no—but we shall leave the explanation for a little later. Let us now make a short detour into optics.

Optical Radiation

The word optics originates from the Greek *οψς* — *opsis* — meaning sight or view. In a narrower sense, optics was the science of light, or what we now describe as the visible region of electromagnetic radiation. However, both optics and the term optical radiation are now understood in a broader sense, which we will adopt here, to include the infrared and ultraviolet regions as well. These frequencies or wavelengths are of the same order as visible radiation, and we therefore use lenses and other optical components to manipulate them. Typically, this range spans from 100 nm to 1 mm, corresponding to photon energies from 1 meV up to 10 eV.

Absorption of energies on the order of fractions of an eV usually manifests only as heating of the sample. It involves molecular rotations and vibrations that dissipate as heat. At energies on the order of eV, however, electrons are excited to higher orbitals, allowing certain chemical reactions to occur. For instance, the very fact that you can see this text is a consequence of chemical and subsequent electrical processes in your eyes. In plants, irradiation of chlorophyll by visible light triggers a cascade of chemical reactions collectively known as photosynthesis.

At about 5 eV, the photon energy becomes high enough to eject valence electrons (those in the outermost shell) from atoms. Such radiation is termed ionizing and induces chemical reactions directly, potentially damaging living organisms. This category includes part of the UV spectrum, as well as X-rays and gamma rays. The importance of X-ray radiation for spectroscopy was discussed in the previous installment. Let us now examine a few basic methods of optical spectroscopy that you may encounter in research.

Electronic Spectroscopy

A brief clarification: the term *electronic* differs from *electron* in the context of chemical physics because it does not imply that electrons must be removed from atoms, as in X-ray methods. Rather, it refers to relatively energetic processes involving electron transitions between different energy levels—excitations typically on the order of a few eV.

UV/Vis Absorption Spectroscopy

As the name suggests, this spectroscopy relies on the fact that every substance absorbs part of the incident radiation, described by the Lambert–Beer law:

$$I = I_0 10^{-\varepsilon c l}$$

Absorption (and thus attenuation of the signal) is exponentially dependent on the sample path length l, the concentration of the absorbing substance c, and the molar absorption coefficient ε, which is typically strongly wavelength-dependent. If it were not, the entire world would appear gray.

This spectroscopic method involves electronic excitation and de-excitation between molecular orbitals (e.g., $\sigma - \sigma^*$ or $\pi - \pi^*$), corresponding to energy differences within the UV/Vis range (wavelengths 200–800 nm). Aromatic hydrocarbons (those containing benzene rings, for example) are particularly well-measured, as they strongly absorb in the near-UV region. In the visible range, most substances absorb at least part of the spectrum—just look around: most objects are colored. Thus, UV/Vis spectroscopy is a very universal and simple method, though its universality comes at the cost of lower precision. By itself, it provides information about electronic excitations within a molecule but cannot determine molecular structure.

There are exceptions—transparent substances such as water or saturated hydrocarbons are entirely transparent to UV/Vis (except for far-UV below 200 nm) and are thus suitable as solvents but cannot themselves be measured.

Fluorescence Spectroscopy

After absorption of radiation, emission of light may also occur. Typically, the emitted light has a longer wavelength due to internal relaxation processes within the material, involving molecular vibrations. When a photon excites an electron, it transitions to a higher orbital and a higher vibrational level. The vibrational energy can be dissipated internally (as heat), so the emitted photon corresponds to the energy difference between molecular orbitals only, resulting in an energy loss. This shift is known as the Stokes shift.

Emission can occur within picoseconds—fluorescence, which is the focus here—or within fractions of a second to hours—phosphorescence, known from glow-in-the-dark materials. The mechanisms are fundamentally different: phosphorescence involves trapping of energy in states from which emission is quantum-mechanically unlikely, hence the long duration. Fluorescence can be observed in many contexts, as shown in Figure 4.

Fluorescence measurements often complement UV/Vis absorption (if the substance exhibits fluorescence). They are widely used in the study of cellular membranes containing lipids and other biomolecules. For example, protein fluorescence depends on conformation (spatial arrangement), making it indispensable in biophysics of living systems.

Vibrational Spectroscopy

The following two methods share the purpose of studying molecular motion and identification. They probe lower-energy processes and are conventionally plotted as intensity versus wavenumber (cm^{-1}). The spectra depend entirely on the chemical structure of the substance and any solvent present. Vibrational frequencies extend up to about $4\,000\,\mathrm{cm}^{-1}$, typically divided into regions below and above $1\,500\,\mathrm{cm}^{-1}$. The lower region, known as the *fingerprint region*, contains

Figure 4: Extremely strong fluorescence of a disodium fluorescein solution under violet laser illumination. The original beam is visible only in reflected light. Weak fluorescence of textile in transmitted light is caused by optical brighteners in laundry detergent.

deformation vibrations (changes in bond angles). The higher region corresponds to characteristic stretching vibrations of chemical functional groups. The boundary is not sharp and depends on the specific molecule and bond types (single, double, etc.).

Infrared Spectroscopy

This is an absorption spectroscopy method but operates on a different principle than UV/Vis. Infrared radiation lacks the energy to excite electrons; its energy, however, is comparable to molecular vibrations. When the wavelength *matches* a molecular vibration, the dipole moment changes. Thus, the fundamental condition for an IR-active vibration is a change in the dipole moment of the molecule. The IR spectrum therefore reveals vibrations that involve redistribution of charge.

Most modern spectrometers use FTIR (Fourier-transform infrared) technology. The instrument contains a heated rod (globar) or another broadband IR source. The light passes through an optical setup based on the Michelson interferometer shown in Figure 5, where one mirror moves. The varying optical path produces interference patterns; by Fourier transformation, path differences are converted to frequency (wavenumber).

Raman Spectroscopy

Unlike the previously discussed absorption-based methods, Raman spectroscopy is a scattering method. You are familiar with light scattering from nearly any medium, even air. The classical type, responsible for the blue color of the sky, is called Rayleigh scattering. In this elastic process, the light retains its wavelength. In contrast, inelastic scattering (energy non-conserving) occurs when a photon interacts with a vibrating molecule, transferring part of its energy. The scattered photon thus has a different frequency. Remarkably, this frequency shift is independent of the excitation wavelength—any light source can be used, and only the frequency shift is measured. This is the essence of Raman scattering, whose theory is more complex.[2]

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[2] A rigorous explanation requires quantum perturbation theory, which we will spare the reader. Future physicists and chemists will encounter it in due time.

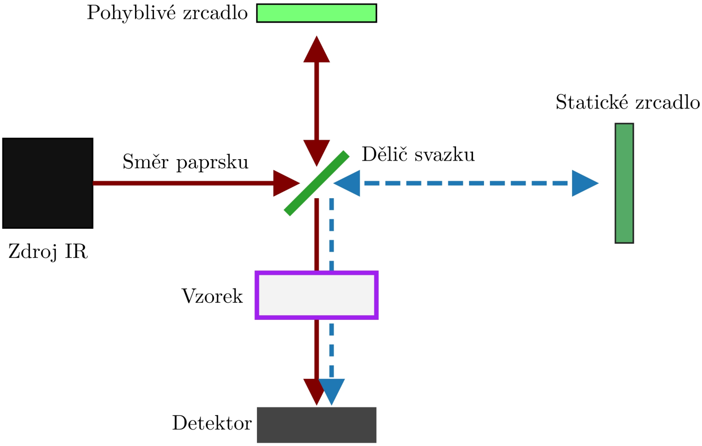

Figure 5: Schematic of an FT infrared spectrometer utilizing interference.

Raman spectrometers exist in various configurations, such as the right-angle setup in Figure 6. Instruments differ in whether they collect reflected or transmitted scattered light. Because inelastic scattering is many orders of magnitude weaker than elastic scattering, strong filtering of Rayleigh-scattered light is essential.

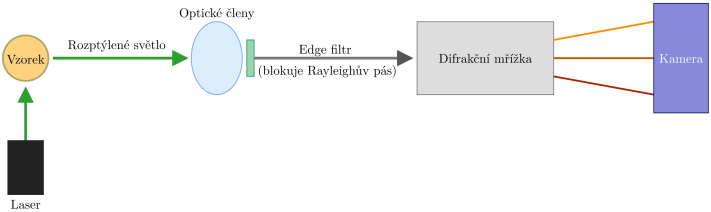

Figure 6: Schematic of a Raman spectrometer with right-angle configuration.

From a quantum-mechanical viewpoint, in addition to the real electronic and vibrational energy levels (recall the molecular oscillator), there exist virtual levels. Due to the uncertainty principle, a very short interaction time implies a large energy uncertainty. A photon may thus temporarily excite a molecule to a virtual state, followed by relaxation to an excited vibrational state—effectively transferring a small portion of energy from the photon to the molecule. With a few approximations, this can also be described classically: the dependence of the dipole moment on the local electric field is characterized by the *polarizability* α, generally a tensor quantity varying in space. In simplified form:

$$\mathbf{p} = \alpha \mathbf{E}.$$

The vibration can be expressed harmonically as

$$Q = Q_0 \cos(\omega_{\mathrm{vib}} t + \delta),$$

and α may be written as a static part α_0 and a dynamic part depending on Q. The electric field of the incident light is

$$E = E_0 \cos(\omega t),$$

and using trigonometric identities, we obtain:

$$p = \alpha_0 E_0 \cos(\omega t) + \frac{1}{2} \frac{\partial \alpha}{\partial Q} Q_0 \cos((\omega \pm \omega_{\mathrm{vib}})t \pm \delta),$$

where the first term represents Rayleigh scattering and the second Raman scattering. The plus and minus signs correspond to Stokes and anti-Stokes shifts, respectively (Figure 7). At normal temperatures, the Stokes process dominates.

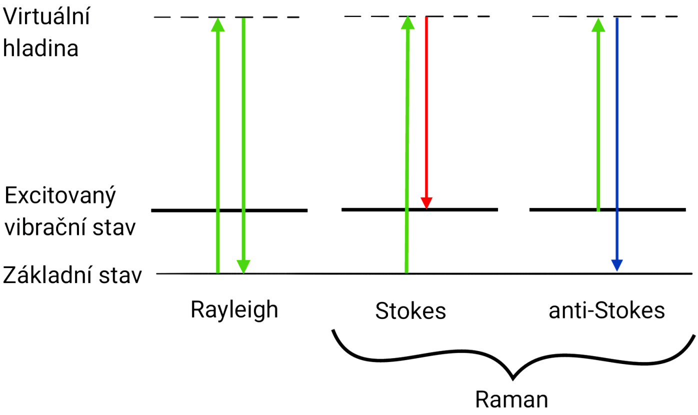

Figure 7: Energy exchange in photon scattering on a molecule.

Polarizability depends on molecular orbital shapes and electron density. When part of a molecule “expands” or “contracts”, local polarizability changes. Overlaps between molecular orbitals—particularly between the highest occupied and lowest unoccupied orbitals (HOMO/LUMO, see Figure 8)—play a crucial role. Such vibrations are Raman-active. Often, a vibration visible in Raman spectroscopy is invisible in IR spectroscopy and vice versa, though this is not a strict rule.

Interpreting spectra of complex molecules is a challenging task, requiring deep understanding of molecular behavior in various environments and reactions. In one of the problems, you will act as a young scientist and assign vibrational modes to the observed bands in the spectrum of the oxonium cation (H_3O^+). This cation has a pyramidal shape and four normal vibrational modes (two of them degenerate). Although degeneracy is unimportant for the task, the shapes of these vibrations are crucial. An illustration of the oxonium vibrational modes is shown in Figure 9.

Appendix: Chiral-Sensitive Spectroscopy

The methods discussed so far are not primarily intended to distinguish the chirality of the measured sample. Chirality is a molecular property in which two so-called enantiomers exist—

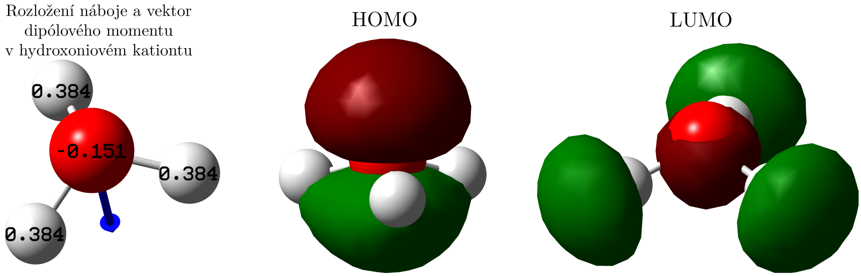

Figure 8: Charge distribution, dipole moment, and molecular orbitals of the oxonium cation.

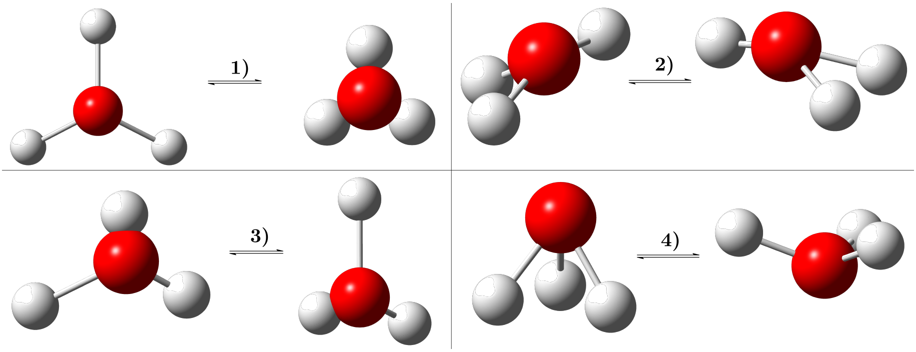

Figure 9: Oxonium kation vibration modes.

mirror images of each other, as illustrated in Figure 10. In simplified terms, chiral organic compounds are those that contain at least one carbon atom bonded to four different substituents. Although their atomic and electronic structures are identical, their chemical behavior may differ significantly.

Levodopa (a synthetic amino acid, see the figure) releases dopamine during metabolism and thus helps alleviate the symptoms of Parkinson's disease, whereas dextrodopa has no biological effect because the human body cannot metabolize D-amino acids (all naturally occurring amino acids are L-enantiomers). The prefixes *levo-* (left) and *dextro-* (right) indicate the direction in which a substance rotates the plane of polarized light in solution. In other cases, one of the enantiomers may even be toxic.

Among the chiral-sensitive methods are, for example, vibrational circular dichroism (VCD), derived from infrared spectroscopy, and Raman optical activity (ROA), derived from standard Raman spectroscopy. In both cases, the sample is illuminated with circularly polarized light. The recorded spectrum represents the difference between measurements using left- and right-circularly polarized light. From such spectra, it is possible to determine which molecular groups are optically active (so-called chiral centers).

If the spectra for both polarizations are identical, it indicates that the molecule is achiral or that a racemic mixture is being measured (i.e., the sample contains both enantiomers in equal

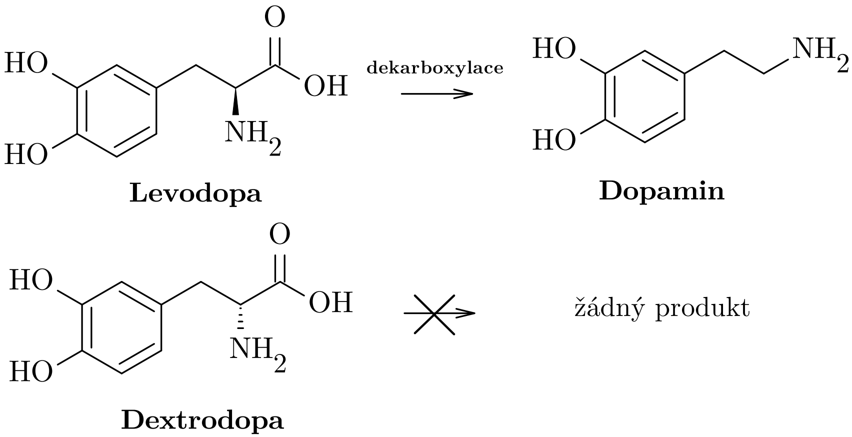

Figure 10: Enantiomers of L- and D-dopa. The dashed bond indicates a direction below the molecular plane, while the solid bond indicates a direction above the plane.

proportions). The isolation or synthesis of a single enantiomer can be challenging and generally requires stereoselective chemical synthesis methods, typically involving the addition of chiral reagents to the reaction mixture.

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