# Ultraviolet (UV) and Visible (VIS) spectroscopies

ver. 20191201

### Interaction of materials with UV and VIS light

The **ultraviolet and visible light excites the electrons** of the materials, but in the meanwhile in most cases **vibrational and rotational motion are also excited**.

Atoms have the simplest spectra, because nor vibration, neither rotation is possible. However, their spectra can be still quite complex.



The emission spectrum of nitrogen atoms shows distinct bands throughout the visible range. The blue lines in the above were brightened for greater visibility in the image.

http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/modpic/nitrogenfull.jpg

### Interaction of materials with UV and VIS light

The simplest atomic spectum: the spectrum of hydrogen atom.



https://www.thoughtco.com/thmb/FbYbPAfoOunuPGmnGaX5eGt6uJU=/768x0/filters:no\_upscale():max\_bytes(150000):strip\_icc()/GettyImages-1096547948-35b3799817ca4b2fa06888893ef4a348.jpg

### Physics of the absorbtion / emission

The energy of photons must be equal to the energy difference of two energy levels (**Planck relation**):

$$\Delta E = h\nu$$

For atoms only electrons are excited, therefore we have to consider the atomic orbitals energies only.

#### According to the **Bohr's atomic model**:

- The electron is able to revolve in certain stable orbitals (called stationary orbitals) around the nucleus without radiating any energy.
- Each stationary orbital has its own discrete distance and energy.
- Electrons can only gain and lose energy by jumping from one allowed orbital to another, absorbing or emitting electromagnetic radiation with a frequency determined by the energy difference of the levels according to the Planck relation.



Niels Bohr Born: 7 October 1885 Died: 18 November 1962 Danish physicist

### Appereance of the visible lines in the spectrum of H atoms

Three lines appear in the visible range, all correspond to electron transfer to the second orbital. The Bohr's model is accurate for the hydrogen atom.



## Calculation of the wavelength and energy of a transition

According to the **Rydberg equation** the wavenumber of the emitted photon can be calculated using a simple formula:  $\tilde{\nu} = R \cdot \left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right)$ , where  $n_l$  and  $n_h$  are the quantum numbers of the lower and higher energy states, respectively and R is the Rydberg constant ( $R = 1.09737 \cdot 10^7 \text{ m}^{-1}$ ).

**Problem:** Calculate the wavelength and energy of the emission which correspond to the transiotion from the 5th orbital to the 3rd one!

$$\begin{split} \tilde{\nu} &= R \cdot \left(\frac{1}{n_{l}^{2}} - \frac{1}{n_{h}^{2}}\right) = 1.09737 \cdot 10^{7} \text{ m}^{-1} \cdot \left(\frac{1}{3^{2}} - \frac{1}{5^{2}}\right) = 7.80352 \cdot 10^{5} \text{ m}^{-1} \\ \lambda &= \frac{1}{\tilde{\nu}} = 1.28147 \cdot 10^{-6} \text{ m} = 1281.47 \text{ nm} \\ E &= h \cdot \nu = h \cdot c_{0} \cdot \tilde{\nu} = 6.62607004 \cdot 10^{-34} \frac{\text{m}^{2}\text{kg}}{\text{s}} \cdot 2.998 \cdot 10^{8} \frac{\text{m}}{\text{s}} \cdot 7.80352 \cdot 10^{5} \text{ m}^{-1} = 1.55017 \cdot 10^{-19} \frac{\text{m}^{2}\text{kg}}{\text{s}^{2}} = 1.55017 \cdot 10^{-19} \text{ J} \end{split}$$

### Beyond the Bohr's atomic model The quantummechanical atomic model

Schrödinger handled the electrons as waves and described their location with **wave functions** and gave only probabilities instead of stationary orbitals. Mathematically, the wave functions are solutions of an eigenvalue problem with given boundary conditions.

The electrons are not moving in the atoms, but exist like standing waves.



Standing waves is 2D.



Erwin Rudolf Josef Alexander Schrödinger Born: 12 August 1887 Died: 4 January 1961 Austrian physicist

https://www.physicsclassroom.com/getmedia/a784f965-be0e-48a6-a849-329ca2df6b5d/H1t6?width=500&height=343

### The quantum numbers

The wave function solutions are characterized by small integer numbers, with the quantum numbers:

- Principal quantum number (n): determines the average distance and energy of the electron
- Azimutal quantum number (I): determines th orbital angular momentum, describes the shape of the orbital
- Magnetic quantum number (m): describes the behaviour of the orbital in magnetic field (Zeeman effect)

The Bohr's model fails for multielectron atoms since does not take into account the electronelectron interactions.



### The Zeeman effect

In magnetic field the spectral lines are splitted to severeal component.

The effect if proportional to the strength of the magnetic field, therefore we can use it to measure its magnitude, e.g. in the stars/Sun.





Pieter Zeeman Born: 25 May 1865 Died: 9 October 1943 Dutch physicist

Zeeman splitting of the 5s level of  $\frac{87}{\text{Rb}}$ , including fine structure and hyperfine structure splitting. Here F = J + I, where I is the nuclear spin (for 87Rb,  $I = \frac{3}{2}$ ).

### The shape of atomic orbitals

1s atomic orbital (n = 1, l = 0, m = 0)



2s atomic orbital (n = 2, l = 0, m = 0)



3s atomic orbital (n = 3, l = 0, m = 0)



 $3p_z$  atomic orbital (n = 3, l = 1, m = 0)



 $2p_z$  atomic orbital (n = 2, l = 1, m = 0)



http://www.dartmouth.edu/~genchem/0102/spring/6winn/H.html

### **Specialities in molecule spectroscopy** The Born-Oppenheimer approximation

Despite the atom spectroscopy in molecule spectroscopy the vibration and rotation motions should be considered, too. Fortunately, the characteristic energies are quite different:  $\Delta E_{\rm electronic} \approx 10^3 \cdot \Delta E_{\rm vibration} \approx 10^6 \cdot \Delta E_{\rm rotation}$ 

And they can be treated separately according to the Born-Oppenheimer approximation.

As a consequence the total energy if a molecule can be calculated as a sum independent terms:  $E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}}$ 

**Born-Oppenheimer approximation**: the motion of atomic nuclei and electrons can be treated separately.



Max Born Born: 11 December 1882 Died: 5 January 1970 German physicist



J. Rober Oppenheimer Born: 22 April 1904 Died: 18 February 1967 Americal physicist

### The Born-Oppenheimer approximation

- **Born-Oppenheimer approximation**: the motion of atomic nuclei and electrons can be treated separately.
- Reasoning: the mass of electrons and nuclei are in the order of  $\sim 10^{-26}$  kg  $10^{-27}$  kg, the mass of electron is  $\sim 10^{-30}$  kg. This 3-4 magnitude difference leads to the same magnitude difference in their movement speed. In other words: electrons can follow the movement of nuclei immediately.
- When vibration or rotation excitation happens (motion of nuclei) the electron cloud immediately forms the corresponding wavelength.
- When electron excitation happens the nuclei can not follow immediately the changed electron state, therefore the vibrational and rotational states also change.

### The Born-Oppenheimer approximation

Excitation from electronic ground state  $(E_0)$  and vibrational ground state  $(\nu'' = 0)$  to electronic excited state  $(E_1)$ leads to a nuclei location which is not a groud state one, but an excited  $(\nu' = 2)$ .

If photon is emitted from the excited electronic state  $(E_1)$ and vibrational ground state  $(\nu' = 0)$  to electronic ground state  $(E_0)$  leads to a nuclei location which is not a groud state one, but an excited  $(\nu'' = 2)$ .

This elucidates the superposition of the rotational, vibrational and electronic spectra.

If emission happens the energy of the emmitted photon can be lower than the absorbed one if **vibration relaxation** had happened before emission, too.



### Orbitals in the molecules

- Similar to the atomic orbitals the electrons can be described in the molecules with molecular orbitals. The simplest model for the determination of these molecular orbitals is the **Linear Combination of Atomic Orbitals to Molecular Orbitals (LCAO-MO)**.
- The wave functions of atomic orbitals are combined any molecule orbitals are formed. Each combination can be done with + and sign, therefore **one bonding orbital** and

one antibonding orbital are formed.

Sigma bonds are symmetrical with respect to rotation about the bond axis.





https://ch301.cm.utexas.edu/svg/s-sigma-formation.svg

https://ch301.cm.utexas.edu/svg/s-antisigma-formation.svg

### Orbitals in the molecules

Sigma bonds are symmetrical with respect to rotation about the bond axis.

Not only s atomic orbitals, but p orbitals can form sigma bonds.



 $https://opentextbc.ca/chemistry/wp-content/uploads/sites/150/2016/05/CNX\_Chem\_08\_04\_pMOsigma.jpg$ 

All antibonding orbitals have a nodal plane perpendicular to the bond axis.

### Orbitals in the molecules

Pi bonds are NOT symmetrical with respect to rotation about the bond axis.



https://opentextbc.ca/chemistry/wp-content/uploads/sites/150/2016/05/CNX\_Chem\_08\_04\_pMOpi.jpg

The Pi bonds have a nodal plane through the nuclei regardless if it is a bonding or antibonding orbital.

### Chromophores

There are molecular structures which causes visible light absorption, called **chromophores**. Typically delocalized (conjugated) Pi bonds are chromophores.

![](_page_16_Figure_2.jpeg)

In the human eye, the molecule retinal is a conjugated chromophore. Retinal begins in an 11-cis-retinal conformation, which, upon capturing a photon γ (light) of the correct wavelength, straightens out into an all-trans-retinal conformation. This conformation change pushes against an opsin protein in the retina, which triggers a chemical signaling cascade which can result in perception of light or images by the human brain.

### HOMO – LUMO states

#### HOMO: Highest Occupied Molecular Orbital LUMO: Lowest Unoccupied Molecular Orbital

wavelength (rm)

![](_page_17_Figure_2.jpeg)

#### UV spectrum of butadiene

https://www.utsc.utoronto.ca/webapps/chemistryonline/production/uv/uv\_images/UV\_fig4.png

### Fluorescence

**Fluorescence** is the emission of light by a substance that has absorbed light or other electromagnetic radiation and **the emitted light typically has a longer wavelength**, and **therefore lower energy**, than the absorbed radiation.

The emission happens immediately after the absorption and when the absorption is stopped the fluorescence vanqueshes in a very short time.

> Fluorescent minerals emit visible light when exposed to ultraviolet light.

![](_page_18_Picture_4.jpeg)

 $https://upload.wikimedia.org/wikipedia/commons/thumb/1/12/Fluorescent\_minerals\_hg.jpg/330 px-Fluorescent\_minerals\_hg.jpg/330 px-Fluorescent\_minerals\_minerals\_minerals\_hg.jpg/330 px-Fluorescent\_minerals\_hg.jpg/330 px-Fluorescent\_minerals\_hg.jpg/330 px-Fluoresc$ 

### Phosphorescence

**Phosphorescence is similar to fluorescence** (the emission of light by a substance that has absorbed light or other electromagnetic radiation and **the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation**), but

the emission happens not immediately after the absorption but with some delay (even in the order of hudred seconds), therefore phosphorescence can last for a long time.

**CORE Glow**<sup>™</sup> luminescent products are engineered with proprietary luminescent material and synthetic resins. When exposed to daylight or a light source, the phosphorescent material becomes excited and will maintain an afterglow, initially very radiant, then slowly dissipating as dawn arrives.

![](_page_19_Picture_4.jpeg)

https://www.coregravel.ca/site/assets/files/1027/core-glow-driveway.jpg

### Fluorescence and phosphorescence

![](_page_20_Figure_1.jpeg)

Time domain of fluorescence and phophorescence

https://lh6.googleusercontent.com/\_Vkl1GfD64eHYL1HXaYOFijvfPZsxsMIHnNdDF8D2qyPC12j9obRtQZ 8hFJiXMLJ-KT6hnsN8-p4LEQILHct9YytCvYm1vRNO7MACmkWVbXnAv5XNXpzH2nn-RyVjWU307Q42tj4

### Fluorescence and phosphorescence

A more detailed explanation using Jablonski energy diagram.

It illustrates the transitions between electronic states of a molecule for the quantum mechanical processes of fluorescence and phosphorescence.

Waved lines mark non-radiative transitions. IC means internal conversion. ISC means intersystem crossing. (Figure of diploma thesis of Steve Pawlizak, 2009.)

For more details visit: https://www.edinst.com/blog/jablonski-diagram/

![](_page_21_Figure_5.jpeg)

http://home.uni-leipzig.de/pwm/web/img/intro\_fluorescence\_1.png

### Selection rules for electron excitation spectroscopies

The selection rules are quite complicated in this case.

Spin selection rule: Changes in spin multiplicity are forbidden.

Electrons in molecular orbitals are paired, according to Pauli exclusion principle. When an electron absorbs enough energy it will be excited to a higher energy state; but will keep the orientation of its spin.

![](_page_22_Figure_4.jpeg)

Laporte selection rule: there must be a change in the symmetry of the complex.

### Chemiluminescence

Certain chemical reactions yield products in excited electronic states. Decay of these excited states may then produce emission of light, a process called **chemiluminescence**.

Fireflies and many deep-sea fish show chemiluminescence. This is the working principle of the glow sticks.

In a sense, chemiluminescence is the reverse of a photochemical reaction.

![](_page_23_Picture_4.jpeg)

A chemiluminescent reaction in an Erlenmeyer flask

https://upload.wikimedia.org/wikipedia/commons/thumb/1/ 17/Chemoluminescent\_reaction.jpg/330px-Chemoluminescent\_reaction.jpg

![](_page_24_Figure_0.jpeg)

### Photolysis

**Photolysis** or **photodissociation** is the process when a chemical bond is broken after the absorption of light.

This happens due to a **repulsive excited electronic state** (a)

or

due to having enough **energy**, **above the bonding energy** in the excited state (b).

For a polyatomic molecule with enough vibrational energy to break a bond, dissociation may take a while to occur. There are many vibrational modes, and it requires time for vibrational energy to flow into the bond to be broken.

![](_page_25_Figure_6.jpeg)

(*a*)

![](_page_25_Figure_7.jpeg)

(b) Levine: Physical Chemistry 6<sup>th</sup> Edition Fig. 20.51

### Main parts of an UV/VIS spectrophotometer

- Light source
- Wavelength selector
- Sample holder
- Detector

### Light sources

Incandescent lamps: produce light as a result of a high temperature of a hot body.

This is either a glowing solid filament or a glowing gas.

**In tungsten lamp** (or other materials like NickelChrome or carbon) electric current is going through the filament causing the wire to heat up and glow. (VIS)

In gas discharge lamp an electric discharge takes place and a current starts to flow through the vapor in the lamp; this causes the gas to heat up and it turns into a plasma (atoms lose a electron and the vapor becomes ionized). The plasma conducts the electric current, heats up and starts emitting light.

**Deuterium lamp** (UV) and **high pressure mercury lamp** (UV/VIS) are widely used gas discharge lamps in spectrometry.

![](_page_27_Picture_6.jpeg)

https://static.independent.co.uk/s3fspublic/thumbnails/image/2016/01/11/17/15-light-bulb-rex.jpg?w968h681

![](_page_27_Figure_8.jpeg)

### Wavelength selectors Reflective grating

A diffraction grating a kind of diffractive optics exploits the phenomenon of wavelength selection. It contains a periodic structure, which causes spatially varying optical amplitude and/or phase changes. Most common are **reflection gratings**, where a reflecting surface has a **periodic surface relief leading to positiondependent phase changes**.

![](_page_28_Picture_2.jpeg)

The white-light output of a high-power supercontinuum source is spatially dispersed by a diffraction grating in order to demonstrate the spectral content. The beam path has been made visible with a fog machine. https://www.rp-photonics.com/img/supercontinuum\_grating.jpg

### Wavelength selectors Prism

**Different wavelengths have different refraction indices** and therefore a prism can be used to disperse the light.

A prism is a usually **triangular shaped piece of glass or quarts** that splits the light in its optical components.

![](_page_29_Picture_3.jpeg)

A plastic prism https://upload.wikimedia.org/wikipedia/commons/thumb/c/cd/Prismside-fs\_PNr%C2%B00117.jpg/255px-Prism-side-fs\_PNr%C2%B00117.jpg

![](_page_29_Picture_5.jpeg)

Dispersion of white light by prism Ali FakihAli Fakih: Diamond: Optical Properties and Coloration (Thesis 2015)

### The Czerny-Turner monochromator

Czerny-Turner monochromator is a common complex apparatus for the wavelength selection.

- (A) broad-band illumination source; (B) entrance slit; (C) curved collimator mirror;
- (D) diffraction grating; (E) curved collector mirror; (F) exit slit; (G) light leaving slit
- At the exit slit, the colors of the light are spread out, each color ( $\lambda$ ) arrives at a separate point in the exit-slit plane. The entrance slit has finite in width, therefore the light leaving the exit slit contains the entire image of the entrance slit of the selected color plus parts of the entrance slit images of nearby colors.
- Instead of diffraction grating prism can be used in the same way.

![](_page_30_Figure_6.jpeg)

https://commons.wikimedia.org/wiki/File:Czerny-turner.png

### The Paschen-Runge polychromator

- H. A. Rowland discovered at the end of the 19th century that a dispersion grating attached to a concave, mirrored surface disperses the incident light according to wavelength and focuses the image of the entrance slit. If one mounts the grating and the entrance slit on a circle, all wavelengths appear on this circle without needing any further optical elements (Rowland circle).
- Friedrich Paschen and Carl Runge used Rowland's work and at the beginning of the 20<sup>th</sup> century developed today's popular polychromator spectrometer mounting (Paschen-Runge configuration)

![](_page_31_Figure_3.jpeg)

Paschen-Runge polychromator with photomultipliers https://www.cfi.lu.lv/fileadmin/\_processed\_/b/4/csm\_Seminars1\_19.10.2016\_6364c7be05.jpg

### **Detectors** Photomultiplier tube

The most common type of detector in a UV-Vis spectrophotometer is a photomultiplier tube (PMT). It consists of a **photocathode** which releases an electron when a photon reaches the material (the **photoelectric effect**). **The multiplication effect is created by placing a series of electrodes to amplify the signal.** The first electron released from the photocathode by a photon is accelerated by an electric field of around the 1000 Volts.

Due to the increased kinetic energy caused by the electric field the electron can release more electrons when it hits the first dynode. The process of acceleration and release of more electrons by the following dynode is repeated for several times, causing a **cascade of electrons** which causes an **electric signal at the anode**. The intensity of that electric signal is a measure for the intensity of the light at the detector.

![](_page_32_Figure_3.jpeg)

Schematic figure of a photomultiplier tube https://static1.olympus-lifescience.com/data/olympusmicro/primer/ digitalimaging/concepts/images/photomultiplier.jpg?rev=630F

### **Detectors** Photodiode array

A photodiode array (PDA) consists of a row of photodiodes (in general 256, 512, 1024, or 2048 elements) which can record a full spectrum at once.
PDA elements release an electron when a photon reaches the material (photoelectric effect).

Photodiodes require more electrical charge than CCD, but can measure higher light intensity without saturation and has lower noise.

Interesting reading: Advantages of Photodiode Array by Hun Choi (SCINCO. Co. Ltd.) http://www.hwe.oita-u.ac.jp/kiki/ronnbunn/paper\_choi.pdf

![](_page_33_Picture_4.jpeg)

Hamamatsu S4111-46Q, a 46 element Si photodiode array for UV to NIR https://www.hamamatsu.com/blobs/1328783928634?blobheadername1= content-

disposition&blobheadervalue1=inline%3Bfilename%3D1328482676618.jpg &ssbinary=true

### Detectors Charge coupled device

The basic sensors of the charge coupled device (CCD) are p-doped metal-oxide semiconductor capacitors, which converts the incoming photons into electron charges at the semiconductor-oxide interface. This charge is read by the CCD.

CCD requires less electrical charge than photodiode arrays, but can measure lower light intensity without saturation and has higher noise.

![](_page_34_Picture_3.jpeg)

Hamamatsu CCD sensor https://img.directindustry.com/images\_di/photo-mg/13622-3737995.jpg