5.) Spectrums of hydrogen and alkali metals

1.) Introduction

One of mankind's amazing ability that we can detect a certain wavelength range of the electromagnetic radiation, namely the light, and we can process it with the most ancient and complex optical system, the eye, then we convert it into information. The exact reason why this range is important in terms of vision is left for other sciences. The "spectrum" term, which means sight in Latin, comes from Newton, who placed a prism into the path of penetrating sunlight, and thus admired the created colorful phenomenon.

Electromagnetic radiation is always present in the world, and based on the classic electrodynamics we know that the material's accelerating charges radiate and provide a spectrum of continuous distribution. Fraunhofer was the first who saw the color line image. Bunsen was one of the pioneers of the elements spectroscopic observation, and as a result of his work the spectral analysis has developed to a separate science of physics. The spectrum lines clearly characterize a chemical element, so even new elements have been discovered on the basis of lines.

The established empirical relationships between the atoms line spectra and the spectral lines have become an important touchstone of modern physics. Within the framework of classical physics the explanation of the atoms spectral lines is not possible. The semi-classical Bohr- and Bohr-Sommerfeld's model of the atom clearly describe the main features of hydrogen and approximately the spectra of alkali atoms, but a quantitative explanation of the fine structure of the spectra is only possible by means of modern quantum theory. The essence of the model is that the atomic electron states are characterized by quantum numbers, and for these conditions discrete energies are specified, respectively. The electrons of atoms in the ground state occupy the lowest energy state allowed by the Pauli principle, and at excitation the electrons jump to a higher energy state according to the selection rules. If one of the excited electrons gets into a lower power state, the corresponding difference will be radiated out as a photon what is observed spectroscopically, in such a way that equation (1) stands:

$$\Delta E = h\nu = h\frac{c}{\lambda} \quad (1)$$

in which the emitted light frequency is ν, h is the Planck constant, λ is the wavelength, and c is speed of light.

2.) Spectrum of the hydrogen atom

Hydrogen is the simplest element, it only has a proton and an electron. According to the Bohr model the electron's angular momentum is quantized, it is an integer multiple of $h/2\pi$ .Taking this condition into account and the attractive Coulomb interaction between the electron and proton, the possible energy levels are:

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2}\cdot\frac{1}{n^2} \quad (2)$$

where e is the electron charge, m_e is its mass, ϵ_0 is the vacuum permittivity, and n is the principal quantum number. Without an external field the energy of the electron is only dependent of the principal quantum number in the hydrogen atom. The

$$T_n = -\frac{E_n}{hc}$$

quantities are called *terms*. Their difference is equal to the reciprocal quantity of the wavelength of the emitted light.

Putting the (2) equation into (1) we get that

$$\frac{1}{\lambda}=\frac{m_e e^4}{8\epsilon_0^2 h^3 c}\cdot\left(\frac{1}{n^2}-\frac{1}{m^2}\right)=R_\infty\left(\frac{1}{n^2}-\frac{1}{m^2}\right) \quad (3)$$

where R_∞ Rydberg constant of a motionless atom with infinity weight, *n* and *m* are positive integers. Of course, *m* is greater than *n*. Using the (3) expression we will not get a full agreement with the spectroscopic data. This is due to the fact that the electron doesn't orbit around the proton but the joint center of the electron-proton system. According to the detailed calculations we can correct the error, if we replace the electron's mass with the reduced mass, and in this way:

$$R_H=R_\infty\cdot\left(1+\frac{m_e}{m_p}\right)^{-1}=\frac{m_e e^4}{8\epsilon_0^2 h^3 c}\cdot\left(1+\frac{m_e}{m_p}\right)^{-1} \quad (4)$$

If we consider all the transitions where *n* is fixed and *m* is greater than *n*, then the (3) modified with the (4) expression will describe one-one color line sequence. The n=2 and m is an integer bigger than 2 series is the Balmer series. J. Balmer found the hydrogen lines series in 1885 when he analyzed the spectroscopic data, thus it was named after him. The transitions of the Balmer series are in the range of visible light, the n=1 transitions, namely the Lymann series belong to the ultraviolet, the other transitions belong to the infrared range. From equation (4) we can conclude if we analyze something similar to the hydrogen, but with an electron that's orbiting around different weighted core, then in the reduced mass we need to use the new core weight instead of m_p. If a new core is a system consisting of a proton and a neutron, which is called deuterium, then the lines of deuterium will be very close to the hydrogens, and

$$\frac{\lambda_H}{\lambda_D}=\frac{1+\frac{m_e}{m_p}}{1+\frac{m_e}{m_p+m_n}} \quad (5)$$

From the wavelength ratio, making equal to the proton's mass with the neutron's, we can determine the mass ratio of the proton and the electron. Harold Urey while testing the spectrum of hydrogen found the small intensity lines near the hydrogen lines, discovering the heavy hydrogen, for which he received the chemical Nobel Prize in 1934.

3.) The spectrum of the alkali atoms

The terms of the alkali atoms show a lot of matches, but also differences with the hydrogen atom. The agreement is due to the fact that the alkali atoms have one electron on the outer shell, and the rest of the electrons form a closed inert gas shell structure. The nucleus and the loaded shells together form the nuclear core, and the outer electron is connecter to this nucleus core like an effective core. The outermost electron is the valence electron, because this takes part in the chemical bonds, but it is also called illuminating electron because the alkali atoms optical spectra are formed by exciting this electron. The difference is due to the fact that at greater distance the illuminating electron feels a central Coulomb field, but getting closer to the nucleus core it deforms it, therefore it is now a dipole which has superimposed on a Coulomb potential, or moving in a quadrupole field. In this way the degradation of the energy levels by the secondary quantum number stops, and the energy levels observed at the hydrogen will separate. In the spectrum of alkali atoms exist lines very close to each other with doublet structure. The reason for this is that the electron has its own spin and orbital angular momentum, which also have magnetic moment. The interaction of these two magnetic moments also affect the terms. In the case of hydrogen there is spin-orbit interaction, but it hardly affects the terms. Let's look at the sodium's very

characteristic yellow double lines. The 3s orbit l=0 and the 3p orbit l=1 orbit angular momentum would be equal in levels according to the Bohr model, but based on the Schrödinger equation because of the calculated orbits overlap ant there are some relativistic effects that the different orbits with l will have different energy levels. The doublet structure depends on the spin and orbital angular momentum's originating angular moment, which is called j internal quantum number. The spin can only be parallel or anti-parallel to the orbital angular moment, therefore for l=1 orbital moment there could be j=3/2 or j=1/2 value, but for l=0 where j is positive it could only be j=1=2 value. In the appendix F1, we are referring to the equation (5) when we show the term differences of alkali atoms:

$$T_{n,j} = -R_M \frac{Z^{*2}}{n^2}\left[1+\frac{\alpha Z^{*2}}{n}\cdot\left(\frac{1}{j+\frac{1}{2}}-\frac{3}{4n}\right)\right] \quad (6)$$

where R_M can be calculated by (4), if the mass of the proton will be displaced by M core mass. Z^* is the effective core charge, which means that the illuminating electron doesn't move in the field of the core shielded by the Z-1 electron, but in a field of a Z^* core with greater charge. In the state of P the value of Z^* for alkali atoms

for sodium	Z=11	Z*=3.55
for potassium	Z=19	Z*=5.96
for rubidium	Z=37	Z*=10.0
for cesium	Z=55	Z*=14.2

The shielding is strongly dependent on the atomic number. The α fine-structure constant was introduced by Sommerfeld, when he wanted to correct the Bohr model.

$$\alpha = \frac{e^2}{2\epsilon_0 hc} \approx \frac{1}{137} \quad (7)$$

The first physical interpretation in the relativistic Bohr model is the relation between the velocity of the electron moving on the first orbit and the speed of light in vacuum. For identifying the terms Russel and Sanders introduced a nomination widely used today, their description and explanation can be found in the appendix. W. Grotrian developed a graphical method for representing the spectral lines and terms, these figures greatly facilitate our orientation among the spectral lines. As an example we show on Figure 1. the hydrogen's Grotrian diagram. The wavelengths of the transitions are measured in angstroms.

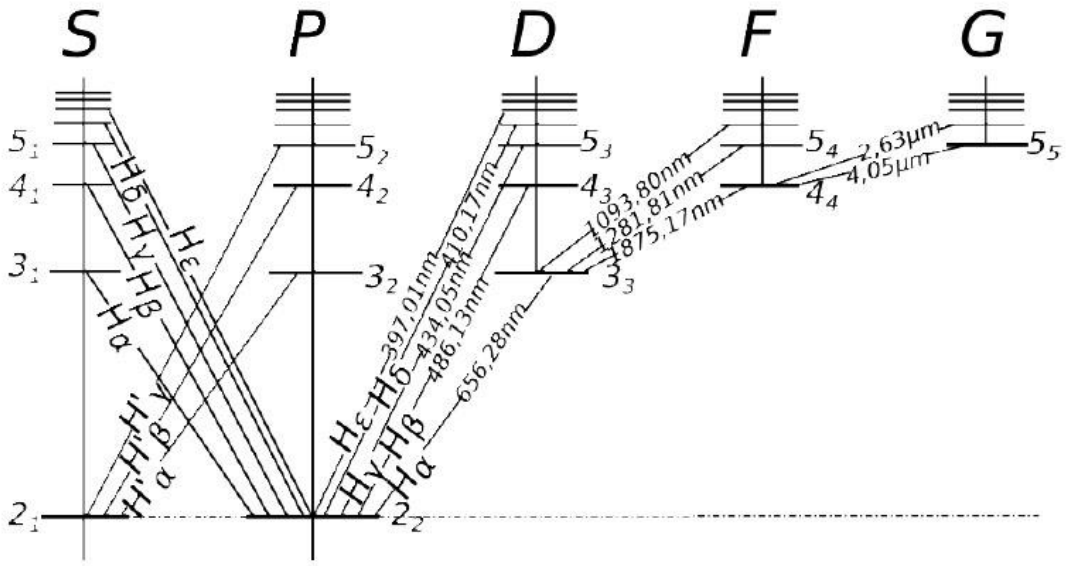

Figure 1.

4.) The operation of spectroscopes

The most important part of the equipments used for spectral analysis is the color separating element, which could be an optical grid or a prism. In our measurement we will use spectroscope with a holographic optical grid. The holographic optical grid is not only a series of light and dark lines. The profile of the lines are special, from the deflection caused by interference (diffraction) it only allows the first order to pass through, according to Figure 2. The grid is characterized by the grid constant, which is $d = 1\mu m$ in this case.

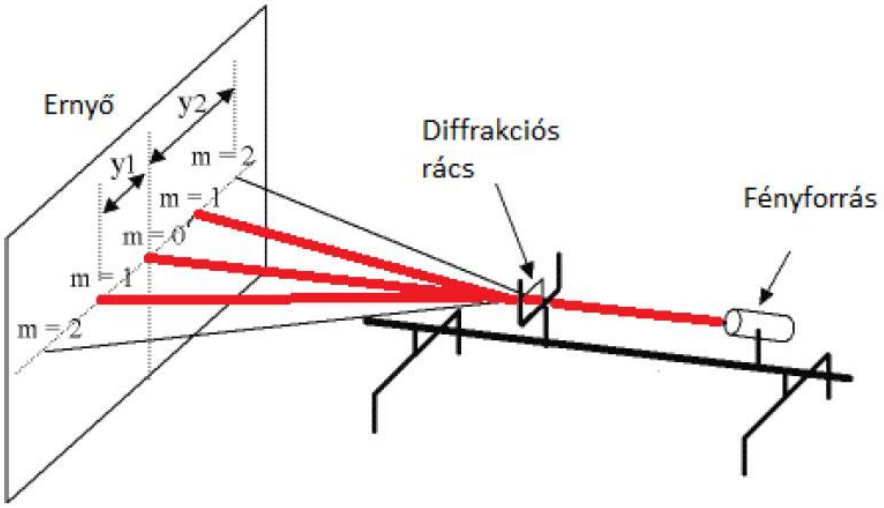

Figure 2. The diffraction image of the optical grid. At the case of holographic grid only the red paths are existing (zero and first order). Ernyő= Screen, Diffrakciós rács=diffraction grid, Fényforrás=light source.

A very important feature of the grid is the resolution, $Rs = \lambda / d\lambda$, where $d\lambda$ is the difference between the two wavelengths of neighboring two lines which are only just distinguishable from each other. The resolution can be increased with decreasing the grid constant, but we need to make sure that the grid constant is at least twice of the wavelength, which in the case of visible light is around $1\mu m$. It stands for all grids that the inevitable imaging aberrations are the smallest when the ray of light is perpendicular to the surface of the grid. The parts of the spectroscope are R slit, K collimator, through these the light gets to the prism or grit, and T is the telescope for observing the spectrum.

The spectroscope goniometer is a device which is used for very precise measurement of the deflection angle of the light created by the diffraction on the grid. For the right operation we need to create some conditions, which claim precise settings. These settings should not be made at the laboratory exercise, the spectroscope have already been set, so we ask every student not to change these settings, or if you consider changing them seriously, ask for the help of the teacher. These settings are the following: the telescope and the collimator should be aligned on an axis and they must be parallel, the normal of the subject table must be perpendicular to the telescope-collimator axis.

Figure 3. The spectroscope used in the measurement

The only setting that is needed to be done is to make the grid perpendicular to the incident beam. For this we need to find the minimal deflection angle. Let us imagine an optical grit which is not perpendicular to the incident beam (Figure 4.). It is evident that the perpendicular projection of the grit has a smaller grit constant.

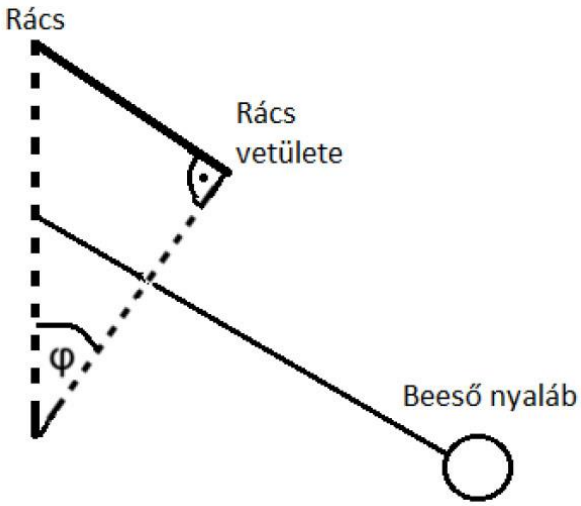

Figure 4. In the case of non-perpendicular incidence the projection of the grit's grit constant is smaller than the original constant, precisely $d_\phi = d \cdot \cos\phi$. Rács=grit, Rács vetülete=projection of the grit, Beeső nyaláb=incidence beam.

According to the diffraction law we got strengthening in the Θ directions where the given λ wavelength of the incidence beam and the grit constant *d* and some kind of *n* integer stands that

$$d \cdot \sin\Theta = n\lambda$$

It can be seen that *d* and Θ are inversely proportional to each other, and because the maximum of $\cos\phi$ is at 0, the grit is perpendicular to the incident beam when the deflection angle is minimal. The diffracted beams connected to different *n* are called *order*. In this case because we use a holographic grit, we can only see the first order.

The angle scale of the goniometer has to be zeroed first. Let's find the 0 order beam on any kind of spectral lamp, and set the angle scale to zero. For this the magnifiers will help us, which can be freely turned over the scale. Beside the 360° scale we have the help of a short Vernier scale as well. Because the whole circle is divided by half angles, the Vernier scale is divided into 30 parts. This works like a caliper, namely we can read the minute of arc value from the opposing verniers.

During the measurement on the far side of the collimator we can adjust the two slits in the vertical and horizontal directions for changing the beam's size, for example thinning it. The thinner the beam is that we work with, the smaller the light intensity, but the resolution gets better. The appropriate slit adjustments should be made by each students.

5.) Light sources used during measurements

During the measurements we use *spectral lamps*. These discharge pipes were designed for spectroscopic purposes. The spectrum of hydrogen and deuterium will be created by a special, 150 Pa pressurized Geissler pipe. In this pipe we use the positive column's light as a light source. The middle part is the capillary pipe, here the produced light intensity is greater. For the operation of the lamps 1500V high voltage is needed. The lamps are operational when the switch is turned on. The alkali metals, the mercury and cadmium spectrum are created by metal-gas lamps. Metals are not in the gas consistency on room temperature, and their atoms start to produce the necessary density gas phase during the heating up. For the operation of the lamp first the metal has to be evaporated, or at least create a high enough concentration inside it. One solution is to put some thousands of volt of startup voltage on the lamp, and when we have enough charge carriers we can increase the voltage. In practice another procedure is being widely used. During the making of the lamps near the two main electrodes they put an auxiliary electrode, which is connected to the power line through a series of resistors. The metal-gas lamps contain some kPa of low pressure noble gas. The power is connected to the lamp poles through a current-limiting ballast resistor. In this case because of the some mA startup current between the auxiliary electrodes and the main electrode the pipe starts to heat up. At the end of this process a part of the metal will evaporate, and conduction begins, the current becomes as great as amperes. Warning, each time we need to connect the chosen lamp to the power supply first, and just after this we can turn it on! Otherwise the inductive ballast which provides the current restriction could fail. The discharge pipes emit ultraviolet radiation as well. **Do not look directly into the light of the lamp, otherwise you could get conjunctivitis (pink-eye)!** In the spectrum of the lamps there are different intensity lines. Because of the operation of the human eye we should work in darkness, therefore we can detect the smaller intensity lines. The luminosity of the light can be increased by widening the slits, but then the lines will be wider, and the position measurement would be less precise.

6.) Measurement tasks

1. With the help of the Cd lamp to eliminate the mechanical errors calibrate the microscope. Measure all the lines of the Cd lamp.
2. For the lines of the Cd lamp look up the difference between the measured and the real lines from a spectral line chart, and represent it in the function of the measured lines. All further measurements will needed to be corrected. Use linear interpolation. The error of the newly measured line should be determined from the errors of the two neighboring lines used in the calibration, assuming that the error changes linearly on a small distance like this. All measured lines have to be corrected with an error like this.

3. Measure the spectral lines of the deuterium lamp. From each line of the Balmer series you have to calculate the R_H Rydberg constant and their average.
4. The proton and electron mass ratio can be determined by using equation (4). Calculate or estimate this ratio from the lines of the deuterium-hydrogen lamp.
5. Measure the lines of Na and K lamps.
6. Make qualitative examination on the spectrum of the Ne lamp. Measure the strongest lines. Identify the main differences between the alkali and the noble gas spectrum (Figure 7.). What are the reasons for this from the electron structure?
7. Identify the transitions using the supplied Grotrian diagrams (Figure 5. and 6.).
8. Determine the α fine-structure constant from the Na doublet using equation (6).

7.) Review questions

1. What are the statements of the Bohr model?
2. What energy levels are possible for hydrogen according to the Bohr model?
3. What is the Rydberg constant?
4. How can you measure the ratio of the proton and electron mass?
5. In the case of alkali atoms why the energy of the electron depends of the secondary quantum number?
6. What is the fine-structure constant?
7. What are the parts of a spectroscope?
8. What is the diffraction law in case of an optical grit?
9. How spectral lamps work?
10. What are the Grotrian diagrams?

8.) Grotrian diagrams

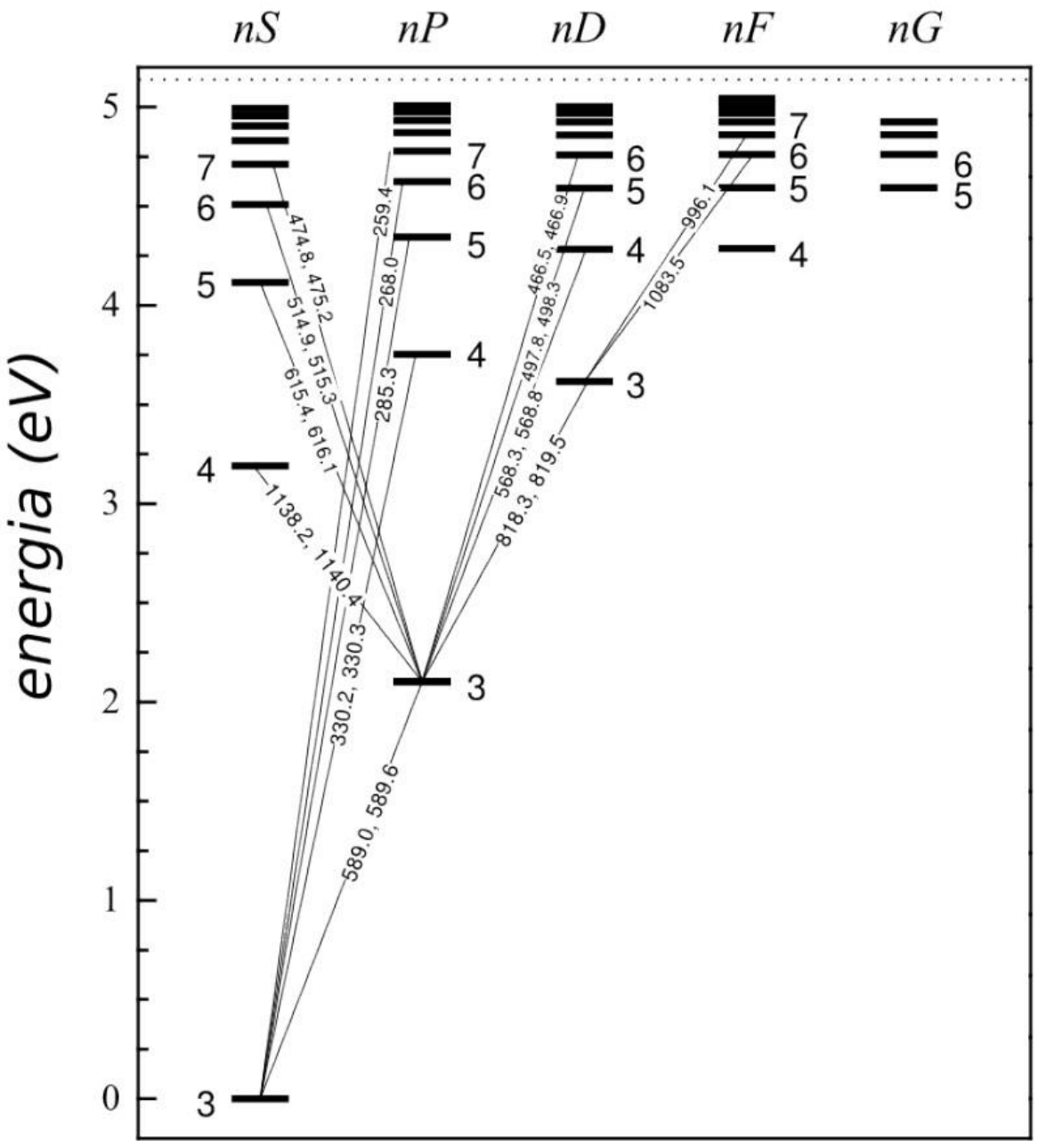

Figure 5. Na's Grotrian diagram

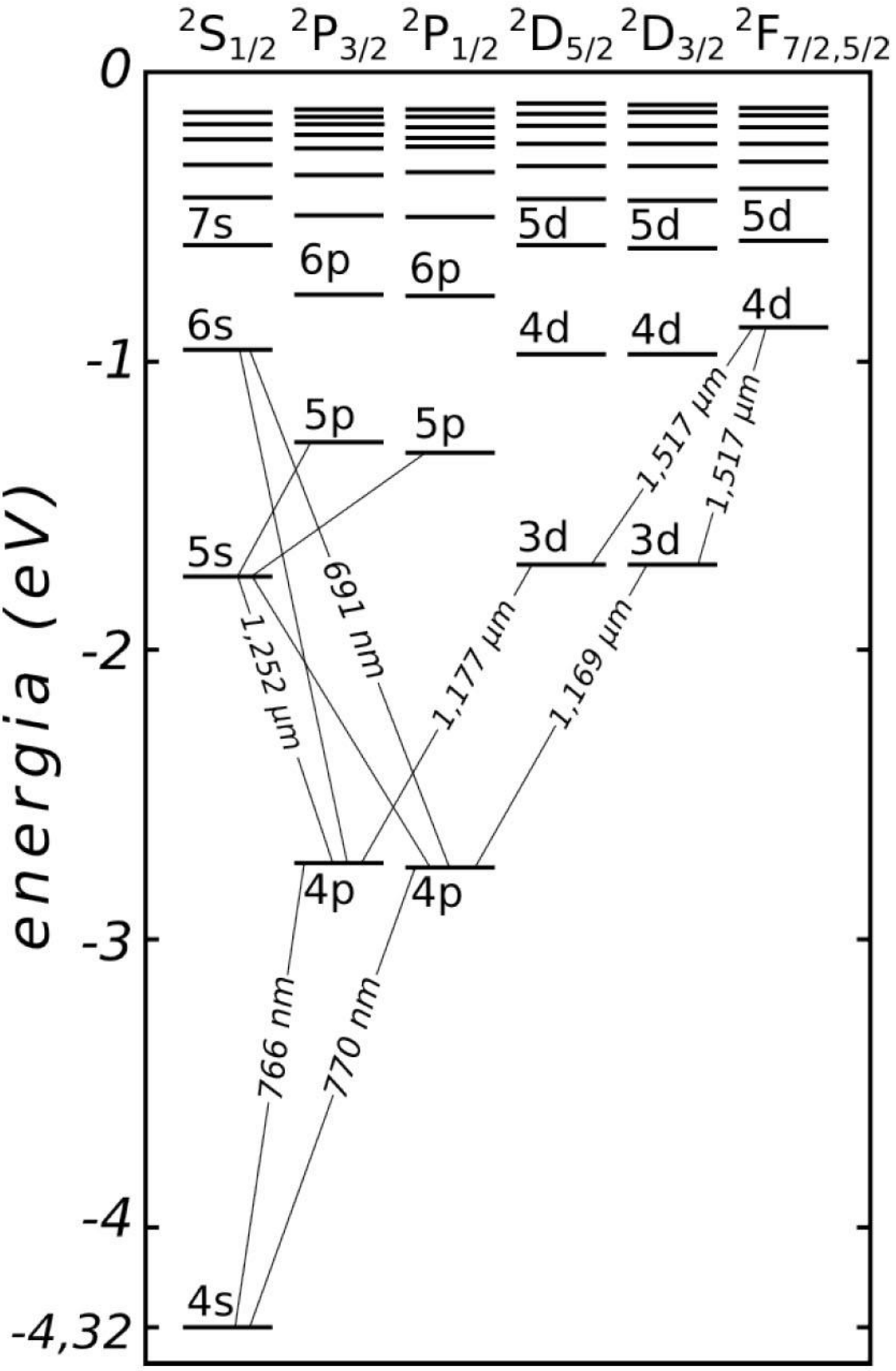

Figure 6. K's Grotrian diagram

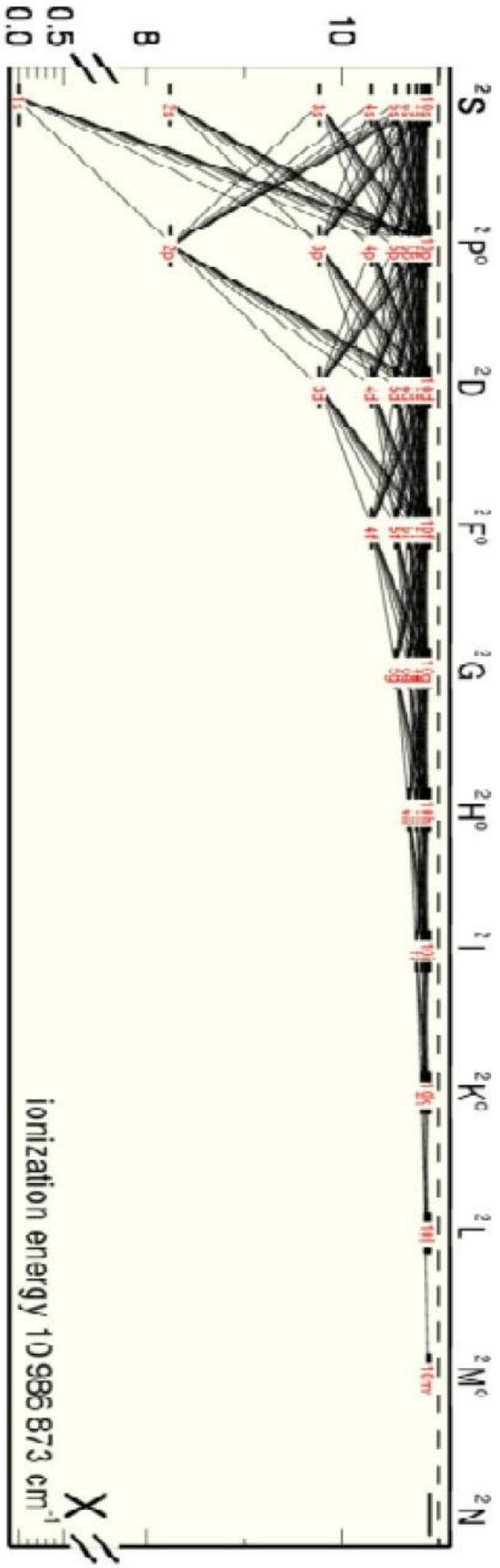

Figure 7. Ne's Grotrian diagram for possible transitions. Only for informing!