

Optical emission spectroscopy of plasma

Optical spectroscopy (mainly the emission spectroscopy) is one of the fundamental plasma diagnostic methods. It is universal for various plasma kinds (low and high pressure without temperature limits) and it has no influence on the studied object (this fact is fully valid for emission spectroscopy, however, some influence exists in absorption spectroscopy but it can be neglected). Spectroscopic measurements partially allow determination of the plasma composition and also the information about temperature and energy distribution can be easily obtained.

Plasma temperature can be calculated from spectral lines broadening. To measure the broadening, the spectrometer with a very high resolution (better than 0.01 nm) is needed. The temperature calculation is not easy procedure and it requires high mathematics and data processing such as apparatus function, line deconvolution, numeric simulation, etc. Thus it is not included in this laboratory work. Details about these calculations can be found in many references.

The molecular spectroscopy of plasma is degraded mainly to the spectra of diatomic molecules. The high resolution allowing measuring of fine (or hyper fine) structure in electron-vibrational-rotational bands is necessary. Determination of plasma composition from the molecular spectra is not easy because molecular bands are spread in the wide range of wavelengths and various bands overlap each other and also they are overlapped by various atomic lines. Further not all the diatomic spectra can be found in the spectral tables and common spectral tables do not include the detail information about band shape. Due to these facts the plasma composition is better to measure by some other methods like mass spectrometry, gas chromatography, etc. Therefore the molecular spectroscopy is used for the temperature determination and for the calculation of the excitation energies nowadays. These tasks are subject of this practical work as well.

Rotational temperature determination

The rotational temperature corresponds to the distribution of the molecular rotational states. The rotational temperature is nearly equal to the neutral gas temperature because the rotational states redistribution (estimation of the Boltzmann distribution of rotational states) is very fast (in order of ps). An example of the rotational spectrum with high resolution for different temperatures is given in Fig. 1.

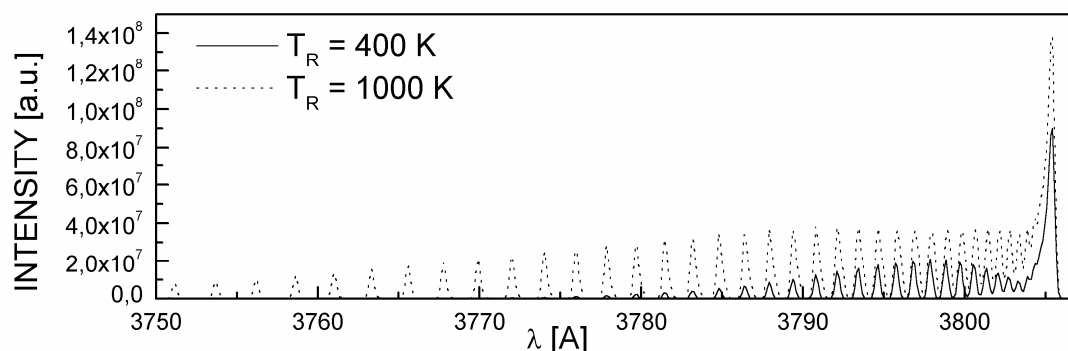


Fig. 1: High resolved spectrum of 0-2 band of nitrogen second positive system for different temperatures.

Number of molecules excited into separate rotational states of the same vibrational level in given electronic state can be calculated by Boltzmann distribution function

$$N(J) \sim e^{-\frac{E_R(J)}{k_B T_R}} \quad (1)$$

The observed spectral transitions are electron-vibrational-rotational and thus the final spectral line intensity is given by the overlap of electronic, vibrational and rotational state functions. The line intensity using the first order approximation of rotational energy can be given as

$$I_{n'',v'',J''}^{n',v',J'} = C \cdot |R_{el.}^{n',n''}|^2 \cdot |R_{vibr.}^{v',v''}|^2 \cdot S_{J',J''} \cdot e^{-\frac{B'J(J+1)}{k_B T_R}} \quad (2)$$

where C is the same constant for all rotational lines in one spectral branch at given temperature, T_R is rotational temperature. The expressions in absolute values correspond to the electron and vibrational state functions overlaps and they are constant for selected vibrational-rotational band. The $S_{J',J''}$ constant includes rotational state degeneration and spin-orbit coupling in the given state. $S_{J',J''}=J'+1$ for the R-branch of singlet transition without change of orbital momentum (the most simple case). The equation given above can be rewritten as

$$\ln \frac{I_{n'',v'',J''}^{n',v',J'}}{J'+1} = -\frac{B'J'(J'+1)}{k_B T_R} + const \quad (3)$$

It can be seen that we plot logarithm at the left side as a function of $J(J+1)$ we obtain linear dependence (so called *pyrometric straight line*) and from its slope K , the rotational temperature can be calculated by formula

$$T_R = -\frac{hcB'_v}{Kk_B} \quad (4)$$

The rotational constant B' is putted in m^{-1} units.

The calculation is more complicated if the transition is not singlet. There are two possibilities. If the multiplet lines are close each other the singlet expression can be applied. The other way is based on the fact $\sum_{J'} S_{J,J''} = 2J' + 1$. Therefore

$$\ln \sum \frac{I_{n'',v'',J''}^{n',v',J'}}{2J'+1} = -\frac{hcF_{J'}}{k_B T_R} + const \quad (5)$$

The rotational temperature can be also calculated from separate multiplet components but the very high resolution spectrum must be used and also it is necessary to have all $S_{J,J''}$ factors. This procedure is not common in practice.

Estimation of vibrational distribution and vibrational temperature

Number of molecules excited into given vibrational state (characterized by vibrational quantum number v) is proportional by Boltzmann law to $e^{-\frac{E_v}{k_B T}}$ where E_v is vibrational energy. The total number of excited molecules in this state is given by the expression

$$N_v = N \cdot \frac{e^{-\frac{E_v}{k_B T}}}{1 + e^{-\frac{E_1}{k_B T}} + e^{-\frac{E_2}{k_B T}} + \dots} \quad (6)$$

Intensity of vibrational band is subsequently given as

$$I_{v',v''} = const \cdot v^4 A(v'v'') e^{-\frac{E_v}{k_B T}} \quad (7)$$

where v' is vibrational quantum number of upper state, v'' is vibrational quantum number of lower state, $A(v'v'')$ is transition probability (can be found in tables and corresponds to the electron-vibration state functions overlap) and ν is wavenumber (mainly wavenumber of the band head). Examples of equilibrium and non-equilibrium distributions are given in Fig. 2.

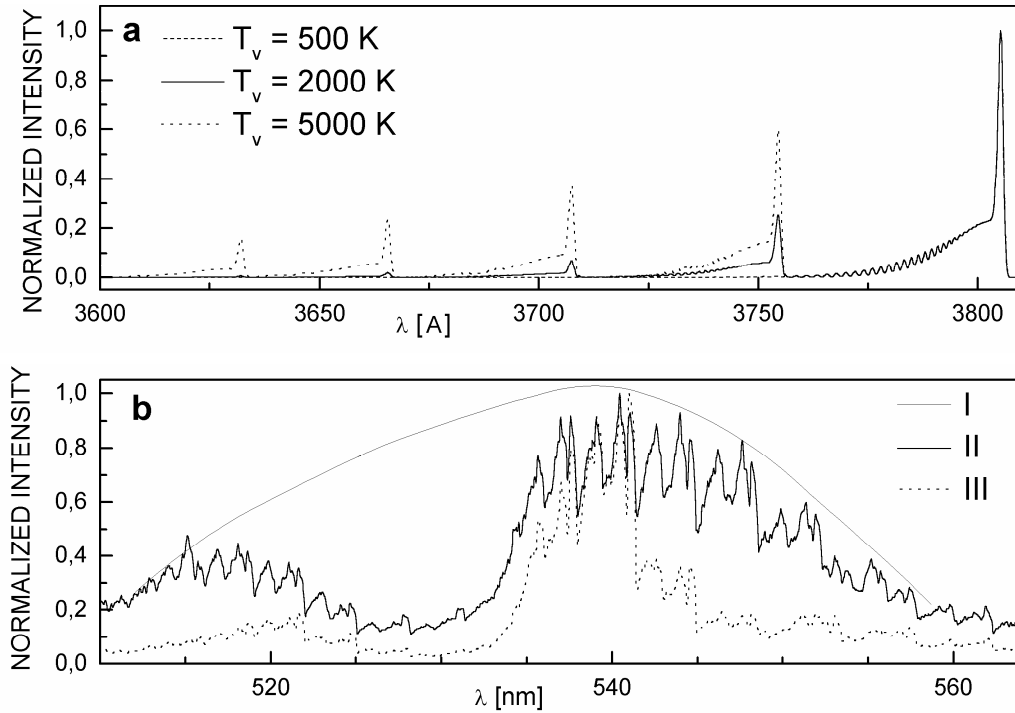


Fig. 2: Spectra corresponding to the equilibrium vibrational distribution for different temperatures (a – nitrogen second positive system - $N_2(C^3\Pi_u) \rightarrow (B^3\Pi_g)$) and non-equilibrium vibrational distribution (b – nitrogen first positive system - $N_2(B^3\Pi_g) \rightarrow (A^3\Sigma_u^+)$): I – intensities corresponding to the equilibrium; II – distribution influenced by predissociation; III – distribution influenced by recombination.

The expression for vibrational band intensity shows that plot of $\ln \frac{I_{v'v''}}{\nu^4 A(v'v'')}$ as a function of E'_v

should be linear if the distribution is equilibrial. The vibrational temperature can be calculated from the slope of this straight line.

The band intensity is a sum of intensities of all rotational lines of this band. The calculation of this integral value is not easy because the bands overlap with the others. In many cases, the intensity can be represented by the intensity of band head (if band head exists). It is a good possibility but it can be valid only if the band head is composed of the same or nearly the same number of rotational lines. This can be assumed within one sequence in the spectrum (the sequence is the group of bands with the same difference of vibrational quantum number). Some bands have more complicated structure with more band heads. In that case it is necessary to use the same band heads.

Vibrational temperature is usually higher than rotational and lower than the electron temperature in non-isothermic plasma. The vibrational temperature is influenced by the ionization degree, electron temperature, pressure and temperature of neutral gas and also by kinetic processes mainly during the post discharge. Thus the vibrational temperature interpretation could be very complicated.

Optical spectrometer

Spectrometers used for plasma diagnostics are in principle similar as UV-VIS spectrometers used in chemistry. The main difference is its much higher spectral resolution (better than 0.01 nm) and in the case of emission spectrometry, there is not any lamp inside the spectrometer.

The gratings with density higher than 300 gr/mm are used for the overview spectra. The gratings with density up to 1200 gr/mm are manufactured by ruling, higher densities (up to 7200 gr/mm) are made holographically. Optical prisms are used in older spectrometers, only. The adjustable slits are installed at the entrance of spectrometer. CCD (matrix or linear) or photomultipliers and photodiodes are used as detectors. All these elements give the final spectrometer resolution and they have also influence on the spectral record quality. Modern spectrometers are fully controlled by computer and thus the spectroscopy is a very user friendly technique.

Tasks

1. Record the spectrum of discharge lamp emitted from electrode regions and in the middle. Use spectral range of 300 – 800 nm with grating of 1200 gr/mm. Identify the nitrogen spectral bands and calculate vibrational temperatures from nitrogen 1st and 2nd positive and 1st negative system.
2. Calculate the rotational temperature using the partially resolved rotational structure of 0-2 band of nitrogen 2nd positive system (grating 1200 gr/mm, wavelength range 373 – 382 nm).
3. Remeasure the task 2 using the 3600 gr/mm grating; the hyperfine structure of the band will be well visible. Try to measure the input slit width influence on the spectrum resolution.

Appendix

Table 1: Vibration energies of selected nitrogen states in units of 10^{-20} J.

Level	N ₂ (B ³ Π _g)	N ₂ (C ³ Π _u)	N ₂ ⁺ (B ² Σ _u ⁺)
0	120.1473	179.0903	52.9705
1	123.5342	183.0680	57.6814
2	126.8642	186.9551	62.2877
3	130.1369	190.7255	66.7782
4	133.3523	194.3276	71.1396
5	136.5102		75.3559
6	139.6109		79.4090
7	142.6548		83.2782
8	145.6423		86.9407
9	148.5741		
10	151.4512		
11	154.2746		
12	157.0455		
13	159.7652		
14	162.4354		
15	165.0577		
16	167.6342		
17	170.1667		
18	172.6577		
19	175.1095		
20	177.5246		
21	179.9060		
22	182.2564		

Table 2: Band head wavelengths (upper number in nm) and transition probabilities (bottom number in s^{-1}) for the nitrogen second positive system $\text{N}_2(\text{C } ^3\Pi_u) \rightarrow (\text{B } ^3\Pi_g)$.

ν''	ν'	0	1	2	3	4	5	6	7	8	9	10
0		337.0	357.6	380.4	405.8	434.3	465.5	503.2	545.2	593.8	650.7	718.1
		1.31 E07	8.84 E06	3.56 E06	1.10 E06	2.92 E05	6.98 E04	1.55 E04	3.29 E03	6.74 E02	1.34 E02	2.59 E01
1		315.8	333.8	353.6	375.4	399.7	426.8	457.3	491.7	530.9	575.9	628.1
		1.19 E07	5.87 E06	5.54 E06	4.93 E06	2.43 E06	8.98 E05	2.78 E05	7.68 E04	1.95 E04	4.68 E03	1.07 E03
2		297.6	313.5	330.9	349.9	370.9	394.2	420.0	448.9	481.3	518.0	559.9
		397 E06	1.01 E07	7.99 E06	7.11 E06	4.04 E06	3.14 E06	1.57 E06	6.14 E05	2.06 E05	6.19 E04	1.72 E04
3		281.8	296.1	311.5	328.4	346.8	367.1	389.4	414.0	441.5	472.2	506.7
		5.28 E05	7.30 E06	5.94 E06	5.85 E06	4.15 E06	3.00 E06	2.35 E06	2.01 E06	9.76 E05	3.91 E05	1.37 E05
4		268.4	281.2	295.2	310.2	326.6	344.5	364.1	385.6	409.3	435.5	464.8
		1.38 E04	1.30 E05	9.03 E05	3.02 E06	3.71 E06	3.24 E06	2.62 E06	2.33 E06	2.09 E06	1.23 E06	5.78 E05

Table 3: Band head wavelengths (upper number in nm) and transition probabilities (bottom number in s^{-1}) for the nitrogen first positive system $\text{N}_2(\text{B } ^3\Pi_g) \rightarrow (\text{A } ^3\Sigma_u^+)$.

[illegible]

Table 4: Band head wavelengths (upper number in nm) and transition probabilities (bottom number in s^{-1}) for the nitrogen first negative system $N_2^+ (B^2\Sigma_u^+) \rightarrow (X^2\Sigma_g^+)$.

				0 - 0	391.2 1.14 E07	0 - 1	427.5 3.71 E06	0 - 2	470.6 7.84 E05
		1 - 0	358.0 5.76 E06	1 - 1	388.2 4.03 E06	1 - 2	423.4 4.28 E06	1 - 3	464.9 1.57 E06
2 - 0	330.5 9.02 E05	2 - 1	356.1 7.88 E06	2 - 2	385.5 2.27 E06	2 - 3	419.7 3.47 E06	2 - 4	459.7 3.47 E06
3 - 1	329.6 2.08 E06	3 - 2	354.6 8.09 E06	3 - 3	383.3 3.77 E06	3 - 4	416.5 2.32 E06	3 - 5	455.2 2.13 E06
4 - 2	329.0 1.19 E06	4 - 3	353.6 7.46 E06	4 - 4	381.6 1.91 E06	4 - 5	413.9 1.31 E06	4 - 6	451.4 1.93 E06
5 - 3	328.9 4.09 E06	5 - 4	353.0 6.63 E06	5 - 5	380.5 8.38 E05	5 - 6	412.0 6.07 E05	5 - 7	448.5 1.56 E06
6 - 4	329.3 4.72 E06	6 - 5	353.1 5.90 E06	6 - 6	380.1 8.01 E05	6 - 7	410.9 6.01 E05	6 - 8	446.6 1.15 E06
7 - 5	330.4 5.04 E06	7 - 6	353.9 5.42 E06	7 - 7	380.5 9.44 E05	7 - 8	410.9 4.64 E05	7 - 9	445.8 7.68 E05

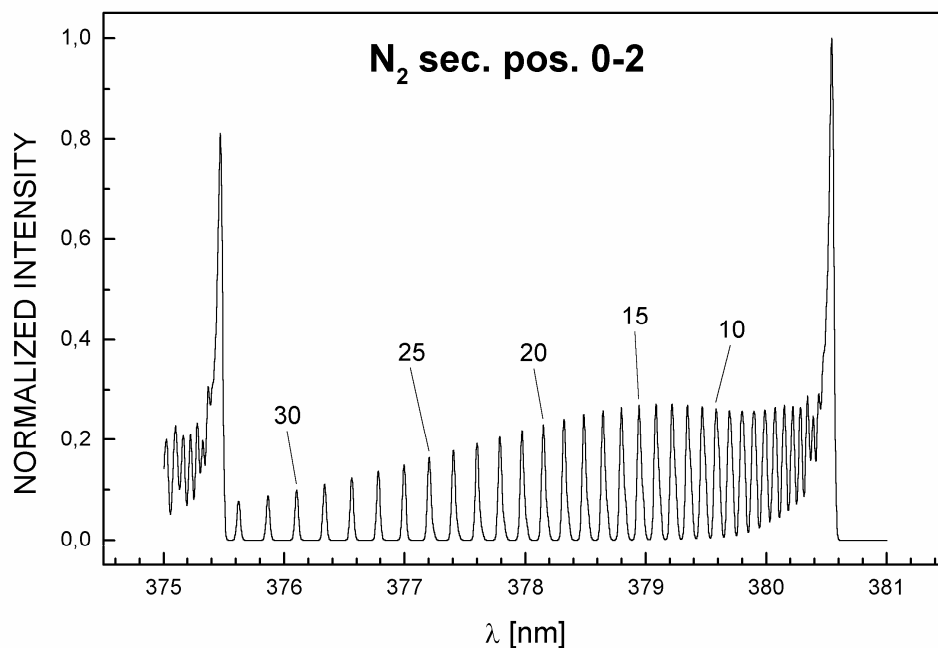


Fig. 4: Rotational structure of nitrogen second positive 0-2 band $N_2 (C^3\Pi_u) \rightarrow (B^3\Pi_g)$; numbers are rotational numbers in upper state of this transition.

Important constants

Boltzmann constant $k_B = 1.380662 \cdot 10^{-23} \text{ JK}^{-1}$,

Planck constant $h = 6.24176 \cdot 10^{-34} \text{ Js}$,

Light velocity in vacuum $c = 2.997924580 \cdot 10^8 \text{ ms}^{-1}$,

Rotational constant of $N_2 (C^3\Pi_u, v = 0) B_v = 1.81491 \text{ cm}^{-1} = 3.60529 \cdot 10^{-23} \text{ J}$,

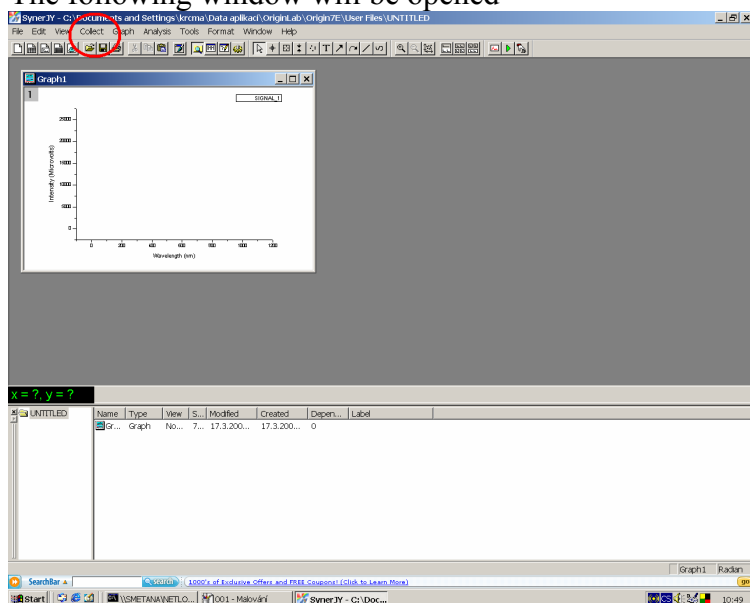
$1 \text{ cm}^{-1} = 1.98648 \cdot 10^{-23} \text{ J}$.

References

- [1] Herzberg G.: *Molecular Spectra and Molecular Structure, Vol. I: Spectra of Diatomic Molecules*, D. Van Nostrand Co., New York 1950.
- [2] Kovacs I.: *Rotational Structure in the Spectra of Diatomic Molecules*, Akademiai Kiado, Budapest 1969.
- [3] Pearse R. W. B., Gaydon A. G.: *The Identification of Molecular Spectra*, John Wiley, London 1976.

Spectrometer Jobin Yvon TRIAX 550 with software SynerJY – operating manual

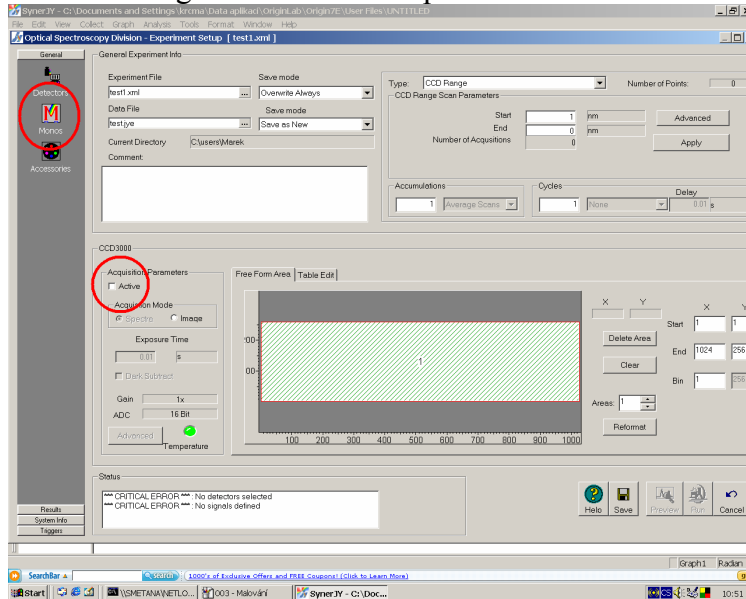
1. Switch on the SPECTRUM ONE controller of CCD (switch is at back side)
2. Switch on the spectrometer – switch is on the cable
3. Switch on PC
4. Log in to net
5. Open „Ovládací panely“ in „Start“ menu. Change the setting of numbers in „Místní nastavení“ – instead of comma give point and after that, close this window.
6. Start the SynerJY software
7. The following window will be opened



Choose „Collect“ (marked by red circle in picture) and subsequently choose „Experiment setup“

8. In the next window click „OK“ and the initialization of spectrometer starts. If the spectrometer was fully switched off before your measurement this initialization could take about 2 minutes

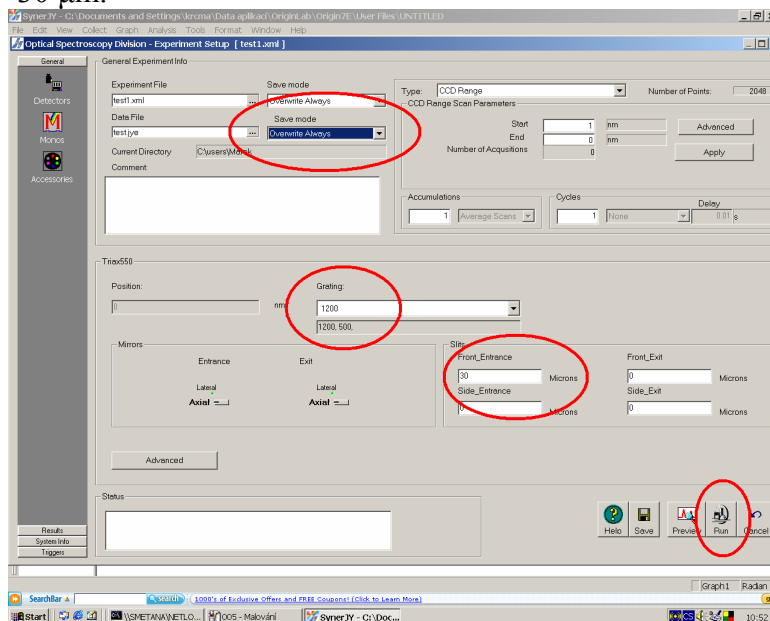
9. The following window will be opened after the successful initialization.



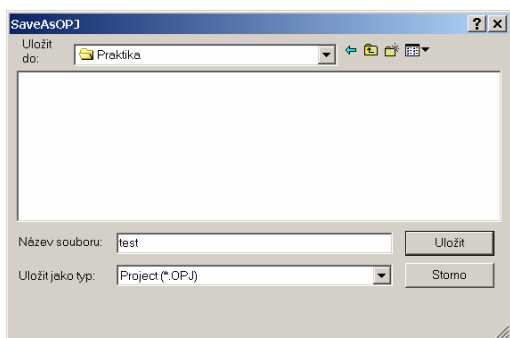
Activate the CCD detector if it is not activated – click on the marked square.

Change the detector window to the mono window (at the top left)

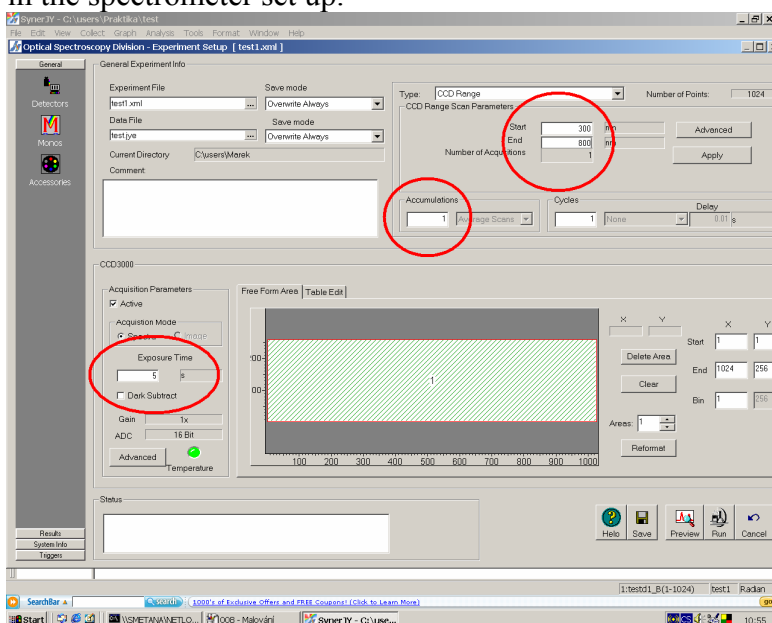
10. Change the grating to 1200 gr/mm and set the entrance slit, the best choice is about 10 – 30 μm .



Change the „Save mode” (at the top) to Overwrite always” and start the first measurement (bottom right). This measurement is necessary for the grating change only. When spectrum is recorded the window „File exist“ will be open – choose „No“. The normal saving window will be open. On the drive „C:\USER\PRAKTIKA\”, create your own directory and save the file. Use this directory during the whole work.



11. Repeat the step 7 (initialization by step 8 is omitted) and go to the „Detector“ at the top left in the spectrometer set up.

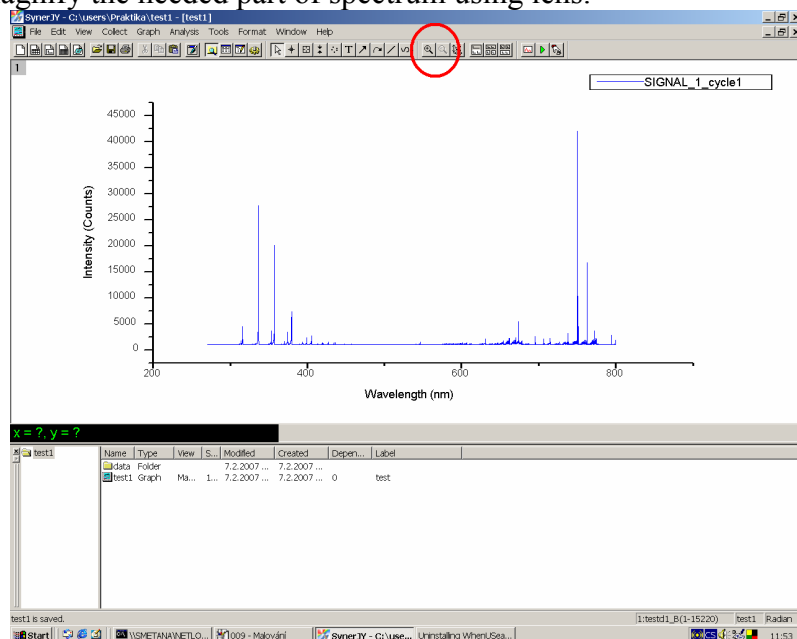


Get appropriate integration time (it should be between 0.1 and 1 second) and the spectral range. Get the number of averaging scans in „Accumulations“ and in our case it should be stored at 1.

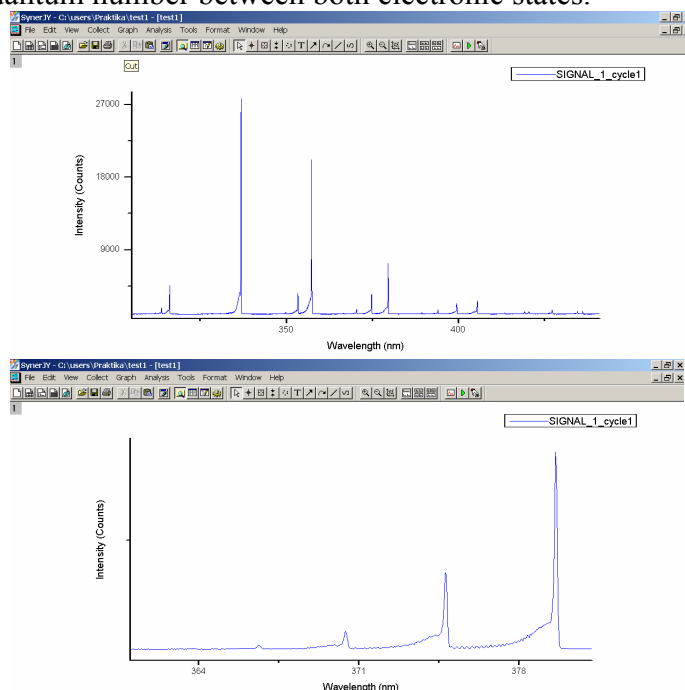
12. Ask teacher for the discharge lamp switching.
13. Put the optical cable to the light source in given position.
14. Record the spectrum (press „Run“ button).
15. The spectrum scan is shown at monitor.
16. Save the measured spectrum in your directory.
17. Measure the next spectrum by the same procedure since the step 11.
18. The task 3 needs another grating. Change it in the window described in step 10. The error warning about mono position will be shown probably, say „OK“.
19. Switch off the PC, spectrometer and CCD controller after the measuring.
20. All problems and unexpected actions say immediately to teacher.

Data processing

1. Magnify the needed part of spectrum using lens.

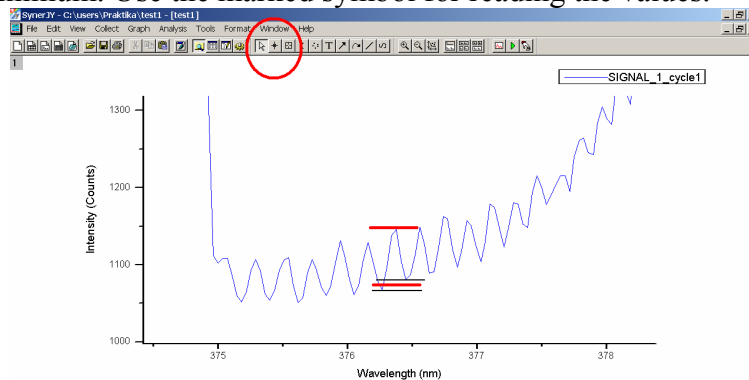


2. The molecular spectrum of nitrogen second positive system is shown below. There are more similar structures in the spectrum that correspond to given vibrational-rotational bands of the same electronic transition (the same spectral system). The spectral system can be divided into the sequences (second figure) that are characterized by the same difference of vibrational quantum number between both electronic states.

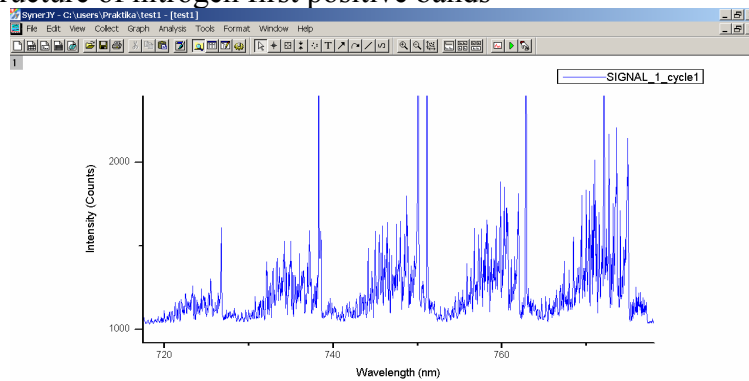


3. Band intensity is the sum of all rotational lines in band (i.e. area under the spectrum) in the reality but it should be replaced by the band head intensity if this head is formed by the same (or nearly the same) number of rotational lines. This is usually valid within one sequence. Read both the band head maximum and minimum because is no background subtraction there.

4. Intensities of rotational lines can be also estimated as their maximum and minimum but due to the overlapping of rotational lines the minima from both sides must be included as average minimum. Use the marked symbol for reading the values.



5. Calculate vibrational and rotational temperatures from the measured intensities and calculate their uncertainties.
6. Structure of nitrogen first positive bands



7. Besides the molecular bands, the atomic lines can be seen in the spectrum. The atomic lines are usually displaced within about 5-7 points of spectrum (see below). Sometimes the CCD detector makes sometimes also false points, too, but they are like singularities within max. 2 points.

