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Numerical Simulations of Diatomic Molecular Optical Spectra

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NUMERICAL SIMULATIONS OF DIATOMIC MOLECULAR OPTICAL SPECTRA

NUMERICKÉ SIMULACE OPTICKÝCH SPEKTER DVOUATOMOVÝCH MOLEKUL

SHORT VERSION OF PH.D. THESIS

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Neexistuje žádný kvantový svět. Existuje pouze abstraktní kvantový popis.
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1 Introduction

Molecular spectra contain much information about molecular structure. It is possible directly to compute various energetic levels of the examined molecule, determine information about the electronic structure and vibrational and rotational behavior of the molecule. In addition to these features it is possible to detect the presence of various molecules in stars, planets and comets, higher atmosphere and intercosmic space based on the interpretation of molecular spectra. Also it is possible to predict physical conditions in these objects.

And so in these days the molecular spectroscopy becomes an important branch of sciences and the study of molecular spectra is currently expanding. That is why the numerical simulations of diatomic molecular spectra are widely used in many different fields of physical and chemical sciences.

Besides the physical astronomy it is possible to use numerical simulations of optical spectra to calculate the physical and chemical properties of observed molecules from their spectra with lower resolution. Other important areas include plasma-chemical technologies (monitoring plasma-chemical processes, detecting chemical reactions in plasma, etc.), both in the laboratories and in the industry. Numerical simulations could be applied as a powerful aid to determine the plasma properties even when the experimental spectrum is not well resolved, i.e. without the well visible rotational structure, and thus they could be widely used based on low budget.

Simulated spectra simplify the analysis of the experimental spectrum. For example by using the modelling spectrum, it is easy to determine the rotational temperature, which is usually equal to the neutral gas temperature, vibrational distribution or vibrational temperature for the equilibrium or non-equilibrium plasma and also identify some molecular spectral systems which are not listed in spectral tables.

Until the present days many software programs were created. But the disadvantage of these programs or algorithms is that they are usable only for one spectral system or only for definite molecules and also the high price of their licences. One exception is the program Lifbase [1] developed for the platform MS-DOS and after adapted for the Microsoft Windows. That is why its operation is complicated. Its another disadvantage is that it is not universal and it is possible to use it only for a few spectral systems for which it is designed.

The general algorithm for numerical simulations of diatomic molecular optical spectra was developed to solve this problem. This algorithm is a part of the program Simul and it is based on the theoretical calculations and on the values of known molecular constants. The parametric database system was projected for the universal application.

For the current theme of this research this work was also supported by the Czech Ministery of Education grant No. 2004/0150. This research project enriched this work with additional knowledge and also specified its goals. With this support the development of the general algorithms could be sped up, optimalized and tested with the real, experimental optical spectra. The program Simul was enhanced with other features, such as the statistics to comparison of experimental and simulated spectra, automatic determination of plasma parameters, solution of the apparatus function based on deconvolution and also the new concept of uncertainties was included [2].

Except the program Simul there was created the other program RotSimul that is focused on simulations of polyatomic molecular rotational spectra and the effects relevant as determination of molecular constants from experimental data, moment of inertia or analyses of measured rotational spectra included the statistical functions and line fitting.

So the present state of the programs Simul and RotSimul allow their practical usage in spectroscopy laboratories and also in the education at the university level.

In the following text there are described all principles of the used methods in these two programs from the quantum theory of rotational and electronic spectra through the general bases of mathematical methods to their applications to the optical spectra.

There are also discussed the results of the numerical simulations of optical spectra, other features and possibilities of these program and the sense of their usage in laboratories and in practice.

2 Principles of numerical simulations of rotational spectra for polyatomic molecules

The main reason of the modullation of rotational spectra is to easier measure the molecular spectra and also to economize on the time of measurement and the sample. The principle of the numerical simulation is based on the theoretical calculations of the transition frequencies between the higher lower energetic states. For example the formula (1) is deduced for the symmetric prolate rotor [3].

$$\upsilon = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 + \dots \tag{1}$$

where υ is the transition frequency, B represents the rotational constant, J and K are the rotational quantum numbers (where $|K| \leq 0, 1, \dots, J$), D_J and D_{JK} are centrifugal distortion constants — they depend on the bond strength.

The equation (1) is applicable to most measurements, but sometimes it is necessary to use a different higher order correction for centrifugal stretching where H_J, H_{JK}, H_{KJ} are the sextic centrifugal constants [4].

$$\begin{gathered}\upsilon = h\left\{2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 + \right. \\ \left. + H_J(J+1)^3\left[(J+2)^2 - J^3\right] + 4H_{JK}(J+1)^3K^2 + 2H_{KJ}(J+1)K^4\right\}\end{gathered} \tag{2}$$

As the other step the absorption coefficient α_{max} is calculated according the following equation.

$$\alpha_{max} = \frac{8\pi^2 N F_m \upsilon_0^2}{3ckT\Delta\upsilon}\left(1 - \frac{h\upsilon_0}{2kT}\right)|(m|\hat{\mu}|n)|^2 \tag{3}$$

where $\Delta\upsilon$ is the half-width of line measured at its half-intensity.

If the dipole moment components are taken as a constant in the rotating bodyfixed axes and the resonant frequency is substituted by the transition frequency it is possible to calculate the maximum absorption coefficient in cm^{-1} – for example for symmetric-top rotor by

$$\alpha_{max} = X\upsilon_0^3\left(1 - \frac{0{,}024\upsilon_0}{T}\right)\left[1 - \frac{K^2}{(J+1)^2}\right]\mathrm{e}^{\left(-\frac{0{,}024J\upsilon_0}{T}\right)}\mathrm{e}^{\left(-\frac{0{,}0484(A-B)K^2}{T}\right)} \approx \tag{4}$$

$$\approx X\upsilon_0^3\left(1 - \frac{0{,}024\upsilon_0}{T}\right)\left(1 - \frac{0{,}024J\upsilon_0}{T}\right)\left[1 - \frac{K^2}{(J+1)^2}\right]\left[1 - \frac{0{,}048(A-B)K^2}{T}\right] \tag{5}$$

$$X = \frac{6{,}11 \times 10^{-4} F_m i_c \mu^2 \sigma g_I g_K \sqrt{A}}{(\Delta\upsilon)_1 T^{\frac{5}{2}}} \tag{6}$$

where magnitudes υ_0, A, B jsou v GHz, $(\Delta\upsilon)_1$ is in MHz units, $g_K = 1$ for $K = 0$ and $g_K = 2$ for $K > 0$, σ is the symmetry number, g_I is the reduced nuclear statistical weight factor and F_m is the fraction of molecules in the particular vibrational state and is calculated according to the formula (7)

$$F_m = F_\nu = \frac{d_\nu \exp(-\frac{h\Sigma_i \upsilon_i \omega_i}{kT})}{Q_\nu} \tag{7}$$

$$Q_\nu = \prod_{i=1}^{i}(1 - e^{-h\omega_i/kT})^{-d_i} \tag{8}$$

where d_ν is the number of vibrational modes,[1] ω_i is the fundamental frequency and each different frequency appears only once in cm^{-1} and d_i is the degeneracy of the fundamental vibration.

The spectral transition energy is defined precisely and every transition has its one own line. But in the reality, the line with the profile function, that is called the spectral band, is measured. The spectral band is caused by many different effects, for example by the natural line width, Doppler broadening or pressure broadening.

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[1] The number of vibrational modes d_ν is equal $3N-6$ for N-atomic non-linear molecules and $3N-5$ for linear N-atomic molecules.

3 Numerical simulations of diatomic molecular electron-vibrational-rotational spectra

3.1 Principles of the electronic spectra simulations

The first reason for creating the program Simul was to develop an universal software for electron-vibrational-rotational spectra simulations for diatomic molecules [5]. That is why it was necessary to devise the general algorithm that is independent on the spectral system. The principle of this algorithm is based on a well-known Herzberg's book [6] and Kovacs's later calculations [7].

Its first step includes the calculation of the energy levels (vibrational and rotational) of both electronic states (higher and lower) by the following equations that are valid only for $^1\Sigma \rightarrow ^1\Sigma$ transition. The values of molecular constants for each diatomic molecules are stored in this database of the program Simul that can be simply completed from the external source by the user.

$$E_{e\nu J} = T_e + hc\omega\left(\nu + \frac{1}{2}\right) - hc\omega x_e\left(\nu + \frac{1}{2}\right)^2 + hc\omega y_e\left(\nu + \frac{1}{2}\right)^3 - \ldots + F_\nu(J) \tag{9}$$

$$\begin{aligned} F_\nu(J) &= \left[B_e - \alpha\left(\nu + \frac{1}{2}\right) + \gamma\left(\nu + \frac{1}{2}\right) + \ldots\right] hcJ(J+1) - \\ &\quad - \left[D_e + \beta_e\left(\nu + \frac{1}{2}\right) + \ldots\right] hcJ(J+1)^2 + \ldots \end{aligned} \tag{10}$$

where ν and J represent the vibrational and rotational quantum numbers, the other symbols are constants; their values for many electronic states can be found in Huber's tables [8], Internet accessible databases and in many separated articles, too. Some of the constants can be calculated from the other constants, for details see [6]–[7].

In the case of the multiplet states, the rotational energy levels must be calculated separately for each of the sublevels, for example for the doublet $^2\Sigma \rightarrow ^2\Sigma$ transition the $J(J+1)$ must be replaced with $(J+1/2)(J-1/2)$ for lower doublet level or with $(J+1/2)(J+3/2)$ for the higher one. These calculations are done separately for each vibrational level of the calculated electronic transition.

The next step involves a calculation of relative populations (vibrational and rotational) at a higher electronic state in the case of emission spectra or at a lower state at absorption. The rotational relative population can be usually approximated by Boltzmann distribution (formula (11)).

$$N_J \approx \exp\left(-\frac{F_J hc}{kT_r}\right) \tag{11}$$

The expression of the vibrational distribution can be used as Boltzmannian only in cases of the equilibrium distribution according to the equation (12). The program Simul allows the manual setting of the relative populations before the calculation in the case of the disequilibrium.

$$N_\nu = N\frac{\mathrm{e}^{-\frac{E_\nu}{kT}}}{1 + \mathrm{e}^{-\frac{E_1}{kT}} + \mathrm{e}^{-\frac{E_2}{kT}} + \ldots} \tag{12}$$

The intensities of the spectral lines are calculated by the formulae discussed in the theory of the optical spectra and it is given by the following expression.

$$I^{n'\,\nu'\,J'}_{n''\,\nu''\,J''} = \mathrm{const} A_{\nu'\nu'} N_{\nu'} N_{J'} \tilde{\upsilon}^4 S_{J'\,J''} \tag{13}$$

where $A_{\nu'\nu'}$ characterises the probability of one vibrational band and in the calculation is taken as a constant setted by the user, N_ν and $N_{J'}$ are relative populations at the vibrational level ν' and the rotational level J', $\tilde{\upsilon}$ is the wave number of the spectral line and $S_{J'\,J''}$ represents the transition strength. The factors $S_{J'\,J''}$ are functions of the spectral branch and both of the rotational quantum numbers and thus they must be calculated separately. For singlet-singlet transitions there are only three branches (P, Q, R – by change of the rotational quantum number), for doublet-doublet transitions there are 12 branches, for triplet-triplet transitions there are 27 branches, etc. The other dependence of the $S_{J'J''}$ factors is the dependence on the total orbital momentum of both electronic states and on the change of this number at a dipole transition (according to rules of the transition the allowed change is 0 or 1). The expressions for $S_{J'J''}$ factor calculation can be found in [7] for all kinds of the dipole transitions.

The next step of one vibrational band simulation is the application of the spectral line profile (theoretically or experimentally obtained) on each of the electronic-vibrational-rotational line calculated by the equation (13).

Finally, the summarization of the rotational lines (with the profile, of course) over all branches is done and the final synthetic spectrum in the adjusted spectral interval is obtained by a summarisation of the entire vibrational band lying in this interval.

3.2 Problems of the electronic spectra simulations

But numerical simulations of electronic spectra are not that simple; there exist many problems that complicate the generalization of the algorithm. One of them is the effects that cause an imperfect overlap of the simulated spectrum with the experimentally obtained one – the spectra are shifted. In figure 3.1 the non-ideal overlap is the most distinctive at the higher values of the quantum rotational number, in the presented case it is at lower wavelengths. It is possible to observe the same effect in the positions of the vibrational band heads as shown in figure 3.2.

This situation reasons in the fact that the first approximation is used in the equations for the optical spectra simulation. The other reason of this effect represents the molecular constant values because they could not be known with un-limited accuracy and also their various sources indicate different values. Their influence is shown in figures 3.3, 3.4. There are two dissimilar spectra of the $B_2\Sigma^+ - X_2\Sigma^+$ system of the CN radical simulated at the same conditions but two different sources of their molecular constants were used.

Another problem is the transition probability that is given as constants;[2] this problem can be observed through the difference in the band intensities.

The profile of the rotational line represents another problem occurred in computation of the optical spectra. In figure 3.1, the rotational lines in the calculated spectrum are approximated by the Gaussian profile which is elicited from the theoretical bases.

Another group of inaccuracies can be caused by the apparatus function. It causes distortion of the experimentally obtained spectrum. To minimize its influence, it is possible to use spectrometers with high resolution or to clarify the experimental spectrum by various mathematical methods. Differences among them lie in their features, such as the stability, oscillations and physical sense. Some methods of the apparatus function solution are discussed in the section 4, page 14.

Besides the disturbing effects presented above that cause the errors in spectrum there is possible to use the simulated spectra to the experimentally obtained data analysis.

3.3 Application of the simulated electronic spectra

The simulated spectra of diatomic molecules can be used for three main determinations of the plasma parameters even in the case when the experimental spectrum is not well resolved, i.e. without the well visible rotational structure.

The first field – and probably the most frequently used – is a determination of the rotational temperature that is usually equal to the neutral gas temperature. The second field is a determination of the vibrational distribution, or the vibrational temperature in the case of the non-equilibrium or equilibrium plasma. The third, not commonly used application, is an identification of some molecular spectral systems, which are relatively rare observed and thus they are not presented in spectral tables or not all bands can be there found.

To test the developed general algorithm, the optical spectra of nitrogen was firstly chosen, and then other spectra were tested with the program Simul – for example the spectra of CN or OH radical. The results of the numerical simulations of these spectra and also their comparisons with the experimental spectra are shown in figures 3.5–3.8. According to them it is evident that the developed general algorithm was optimized and due to the problems with the accuracy of the band head positions, this program requires a specialist in optical spectroscopy of diatomic molecules.

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[2] During the development of the program Simul no literature that generalizes the transition probability calculation for all spectral systems was found. That is why the solution of the manual setting of its values was created.

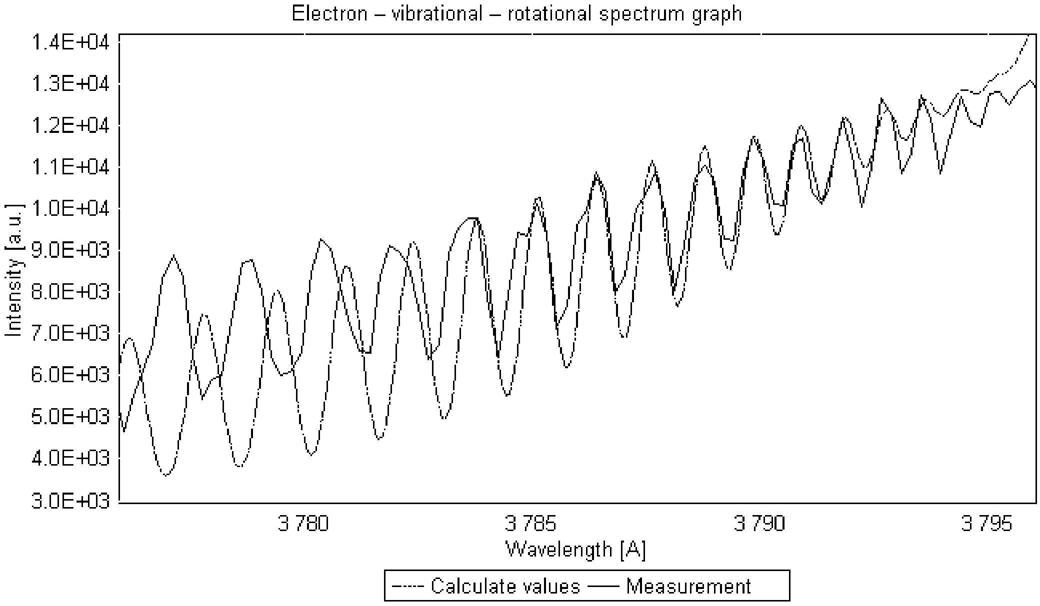

Figure 3.1: Inaccuracy of the overlap between calculated and experimentally obtained spectra. At the higher rotational quantum number (at shorter wavelengths), shifts of the rotational line positions can be clearly observed (2^{nd} positive nitrogen 0–2 band). The calculated spectrum was created by the software Simul.

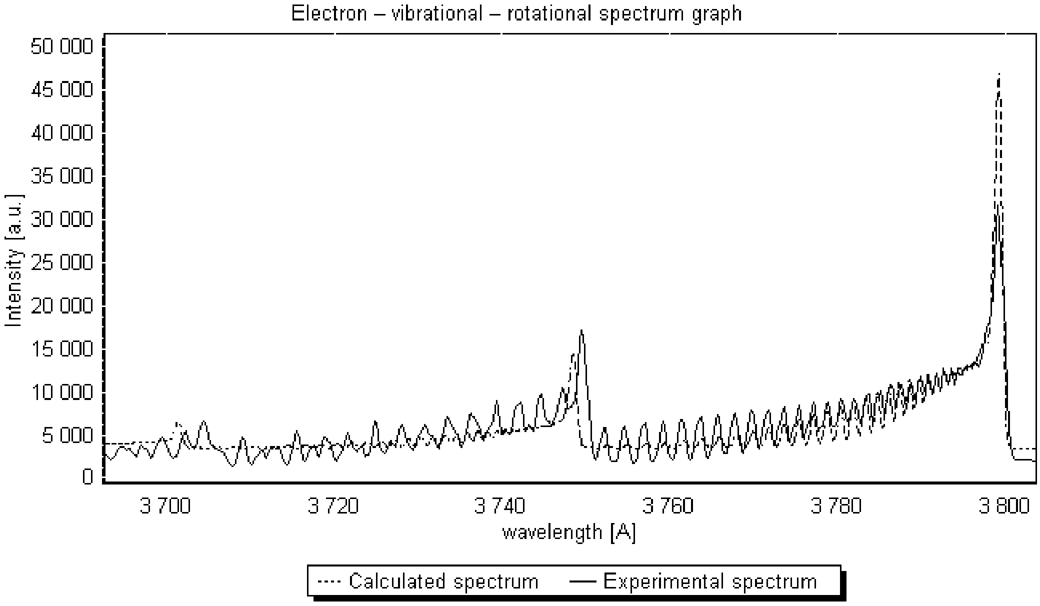

Figure 3.2: Inaccuracy of the overlap between calculated and experimentally obtained spectra. At the higher vibrational quantum number (at 3750 Å), shifts of the vibrational head position can be clearly observed (2^{nd} positive nitrogen 0–2 band). The simulated spectrum was made by the software Simul.

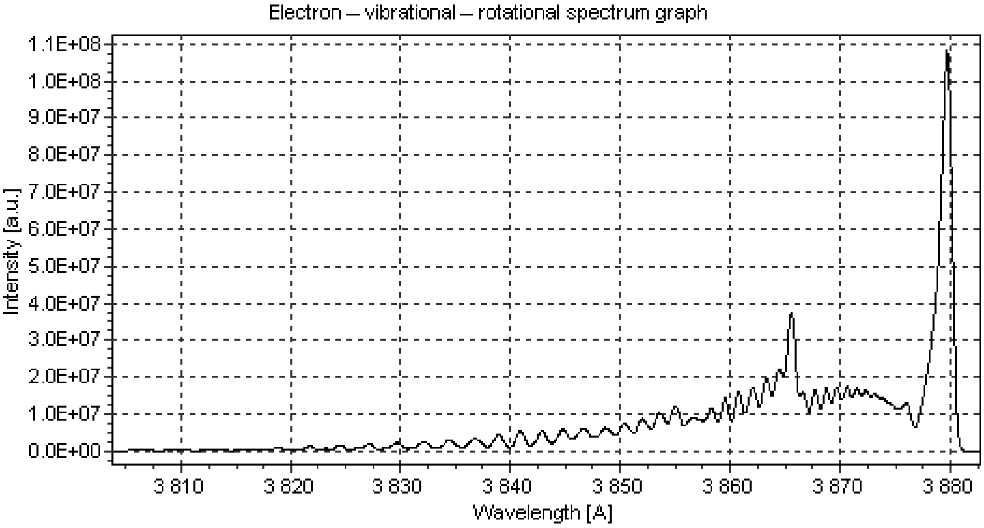

Figure 3.3: Simulated spectrum of the CN radical $B^2\Sigma^+–X^2\Sigma^+$ system with the molecular constant values that were taken from the Pearse's book [9]. This spectrum was calculated by the program Simul with the vibrational temperature at 5000 K and rotational temperature at 450 K.

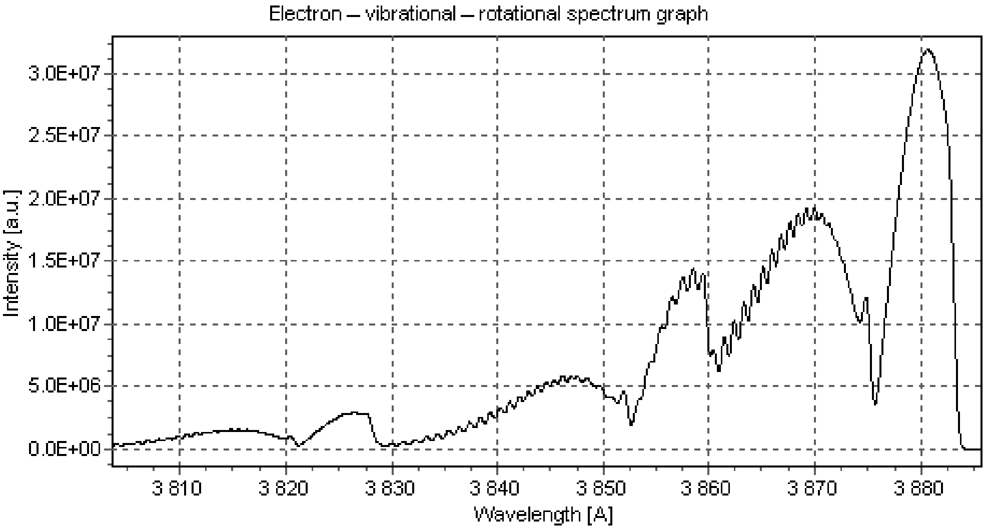

Figure 3.4: Simulated spectrum of the CN radical $B^2\Sigma^+–\ X^2\Sigma^+$ system. As the source of the molecular constant values I used the article "Photoelectron spectroscopy of CN^-, NCO^-, and NCS^-" taken from Journal of Chemical Physics [10]. The spectrum was made by the program Simul with the vibrational temperature at 5000 K and rotational temperature at 450 K.

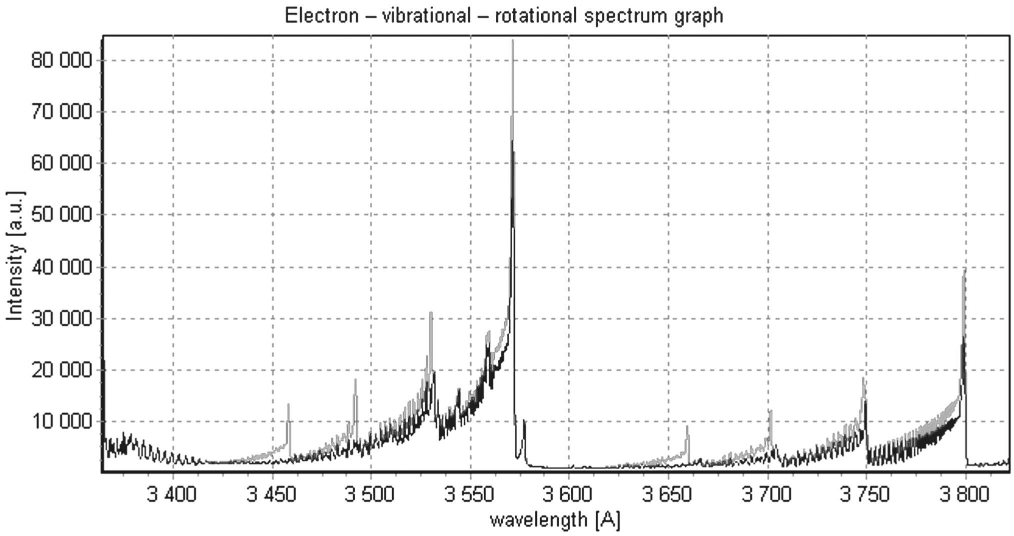

Figure 3.5: Electron-vibrational-rotational spectrum of the the nitrogen second positive system $C^3\Pi_u$–$B^3\Pi_g$ system. The black line represents the experimental spectrum and the grey line is the simulated spectrum that was calculated with the rotational temperature at 450 K and the vibrational temperature at 6500 K.

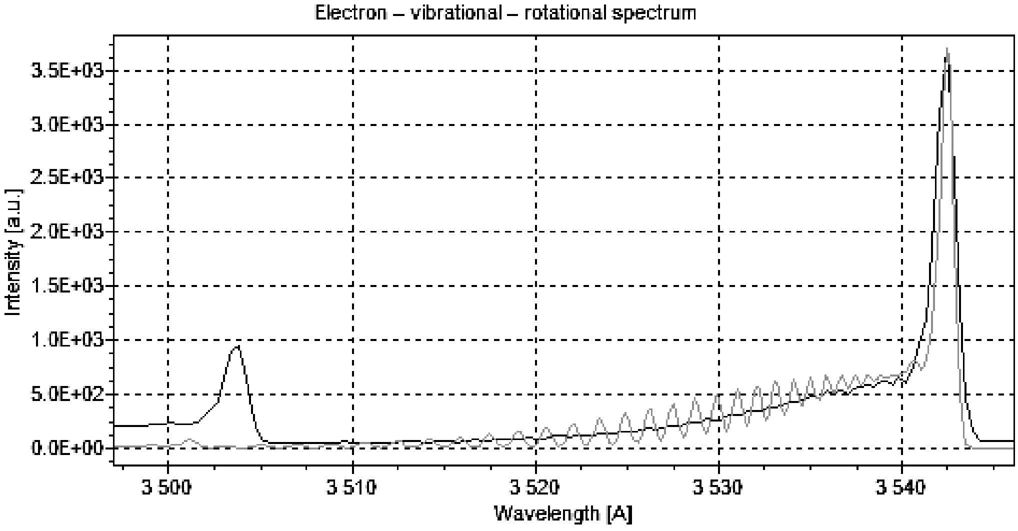

Figure 3.6: Electron-vibrational-rotational spectrum of the nitrogen second positive system $\left(C^3\Pi_u - B^3\Pi_g\right)$ (0-1 band). The black line represents the experimental spectrum and the grey line is the simulated spectrum with the resolved rotational structure. This spectrum was calculated with the rotational temperature at 450 K and the vibrational temperature at 700 K.

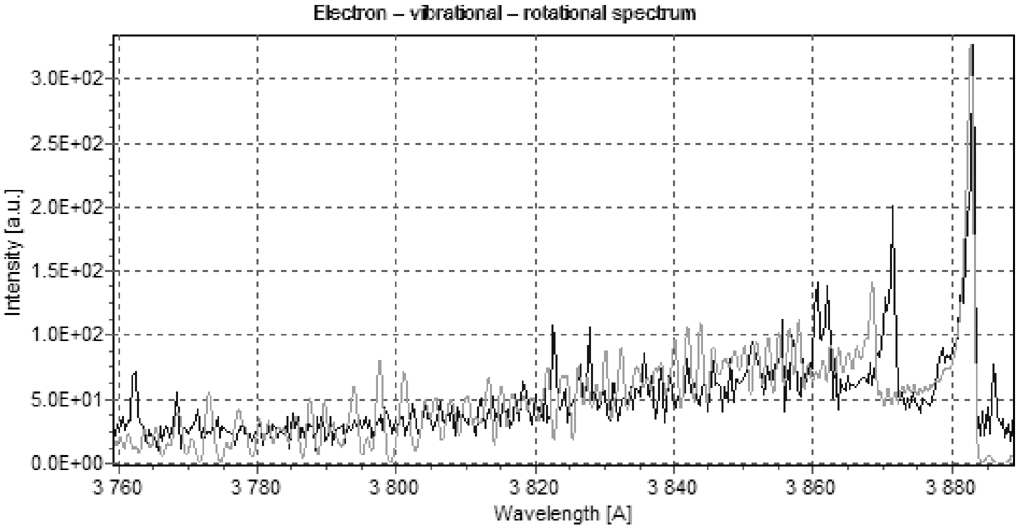

Figure 3.7: Electron-vibrational-rotational spectrum of the CN radical $B^2\Sigma^+ - X^2\Sigma^+$ system. The black line represents the experimental spectrum and the grey line is the simulated spectrum that was calculated with the rotational temperature at 2500 K and the vibrational temperature at 8000 K.

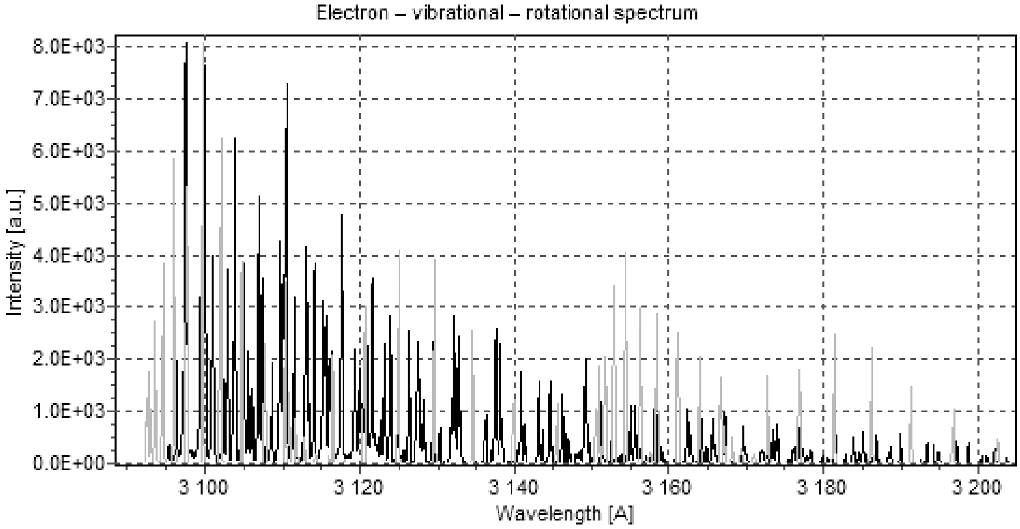

Figure 3.8: Electron-vibrational-rotational spectrum of the OH radical $A^2\Sigma^+ - X^2\Pi$ system. The black line represents the experimental spectrum and the grey line is the simulated spectrum with the rotational temperature at 600 K and the vibrational temperature at 8000 K.

4 Solution of deconvolution by Fourier transform and its application to optical spectra

The measured spectrum includes expect the measured line also the other line called the apparatus function. Its profile depends on the used apparatus, its equipments, experimental conditions and also experiences of the experimenter. For correct analysis of the measured spectrum it is needed to clear spectrum from the signal noise (apparatus function). But this procedure is not so easy. It means to solve the convolution integral (14). Mathematicians offer many arithmetic processes but most of them are without the physical sense. The solution of this problem by Fourier transform and its influence on the measured optical spectrum is discussed in the following paragraphs.

$$h(x) = \int\limits_{-\infty}^{+\infty} k(y) g(x-y)\,\mathrm{d}y \tag{14}$$

Where $h(x)$ characterises the measured spectrum, the function $k(y)$ represents the experimental spectrum without noise and the function $g(x-y)$ is the apparatus function.

4.1 Fourier transform and deconvolution

Fourier transform[3] changes one function to the other function from which features it is possible to know the information about the original function. The F-view of the function $s(t)$ is the complex function $S(\nu)$ of the real parameter defined by the integral (15) [17]. The equation (16) represents the inversion of the F-view by which it is possible to obtain the original function.

$$\mathrm{F}[s(t)] = S(\nu) = \int\limits_{-\infty}^{+\infty} s(t) e^{-2\pi i\nu t}\mathrm{d}t \tag{15}$$

$$\mathrm{F}^{-1}[S(\nu)] = s(t) = \int\limits_{-\infty}^{+\infty} S(\nu) e^{2\pi i\nu t}\mathrm{d}\nu \tag{16}$$

Fourier transform has one of the most important feature for solving the deconvolution – it converts the convolution of the original functions to the product of the views [18].

$$\mathrm{F}[(k*g)(t)] = K(\nu)G(\nu) \tag{17}$$

$$\mathrm{F}[(k(t)g(t)(t)] = K(\nu) * G(\nu) \tag{18}$$

Where the function $H(\nu)$ represents the experimental spectrum with noise, the function $K(\nu)$ is the high-resolved spectrum without noise and the $G(\nu)$ is the apparatus function [19].

To calculate the function $K(\nu)$ it is needed to know the profiles of the measured line and the shape of the apparatus function. For the shape of the apparatus function it is required small side peaks and the sharp, high and narrow main peak. This condition is realized by the triangular or trapezium profile that well-copy the shape of the apparatus function of the grating spectrometer.

The triangular profile belongs to the most common used shape of the apparatus function. Its mathematical formula is represented by the following equations.

$$g_T(t) = \begin{cases} 1 - \frac{|t|}{T} & \text{pro} \quad |t| \le T \\ 0 & \text{pro} \quad |t| > T \end{cases} \tag{19}$$

$$\mathrm{F}[g_T(t)] = T\mathrm{sinc}^2(\pi T\nu) \tag{20}$$

The trapezium shape is the other profile that can be used. But this profile has the disadvantage in the decrease in the main peak to the negative values (see the figure **??**). This feature can signify

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[3] The mathematical procedure of the Fourier transform is described in details in the many mathematical literature as [11], [12], [13], [14], [15], [16] and that's why this capitol is devoted only to the short description of its principle.

negatively in the experimental spectrum. The mathematical formula of the trapezium shape is expressed by the following equations.

$$g_T(t) = \begin{cases} 0 & \text{pro} \quad |t| \geq T \\ \frac{t+T}{T-b} & \text{pro} \quad t \in \langle -T, -b \rangle \\ 1 & \text{pro} \quad t \in \langle -b, b \rangle \\ \frac{-t+t}{T-b} & \text{pro} \quad t \in \langle b, T \rangle \end{cases} \tag{21}$$

$$\mathrm{F}[g_t(t)] = (T+b)\mathrm{sinc}\pi\nu(b+T)\mathrm{sinc}\pi\nu(b-T) \tag{22}$$

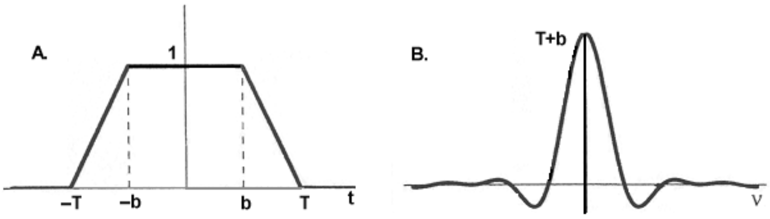

Figure 4.1: There is the shape of the trapezium function. The letter A is the function g(t) and the letter B represents the function obtained by the Fourier transform.

It is possible to use the others profiles of the apparatus functions. The difference between them is in the number of used parameters that have influence to the width and high of the main and side peaks.[4]

4.2 Application of the solution to the optical spectra

The solution of the deconvolution by the Fourier transform is very general and it can be applied in all of the sciences branches where are used the measured instruments. This section deals with the results of this solution application to the optical spectra and determination of their rotational levels.

At the figure 4.2 there is a simulated electron-vibrational-rotational spectrum with well-resoluted vibrational head but without rotational levels which are important to the determination of the rotational temperature.[5] To distinguish the rotational levels was used the triangular shape of the apparatus function with the $T = 8.5$ Å. By this method it is possible to observe three distinguished rotational level. This number of rotational levels is the minimum from which it is possible to determine the rotational temperature.

When the T parameter of this function is changed to the value 3.5 Å, the different spectrum is obtained (the figure 4.3). This spectrum has more distinguished rotational levels, the intensities of them copy the original line and it is more suitable to the rotational temperature's determination then the spectrum with the parameter $T = 8.4$ Å.

If the results of the deconvolution by Fourier transform are compared between each other, it is evidently that there is a small difference between the values of the apparatus function's parameters and a sizeable difference between the shapes of deconvolution's spectra. There is the spectrum with a lot of distinguished rotational levels and also the spectrum with the repressed rotational levels. From this is flown that the usage of Fourier transform depends on the expected results, the other analysis of the obtained spectrum and also on experiences and sense of the user.

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[4] More details about this solution and results of the others apparatus functions are described in the full version of the dissertation thesis.

[5] There are used the simulated spectra of the CN radical that well-copy the shape of the real spectrum of this molecule. The reason of the simulated spectra used is in the conveniently studying of the behaviour of the deconvolution for various shapes of the apparatus function.

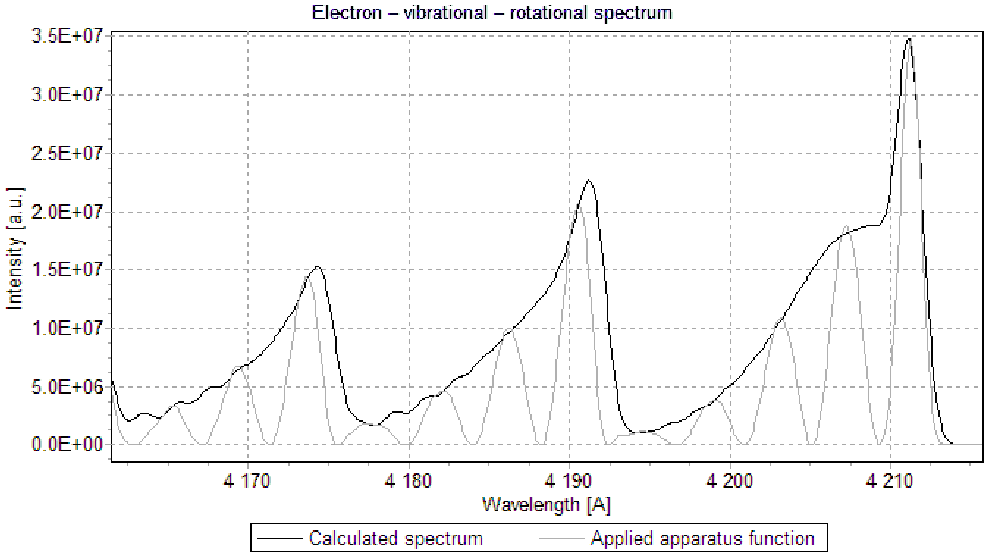

Figure 4.2: Electron-vibrational-rotational spectrum of the $B^2\sum^+ - X^2\sum^+$ system of the CN radical. The black line represents the simulated spectrum by the program Simul [5] and the grey line is the deconvolution spectrum of this line after application the triangular function with $T = 8.5\,\text{Å}$ and FT.

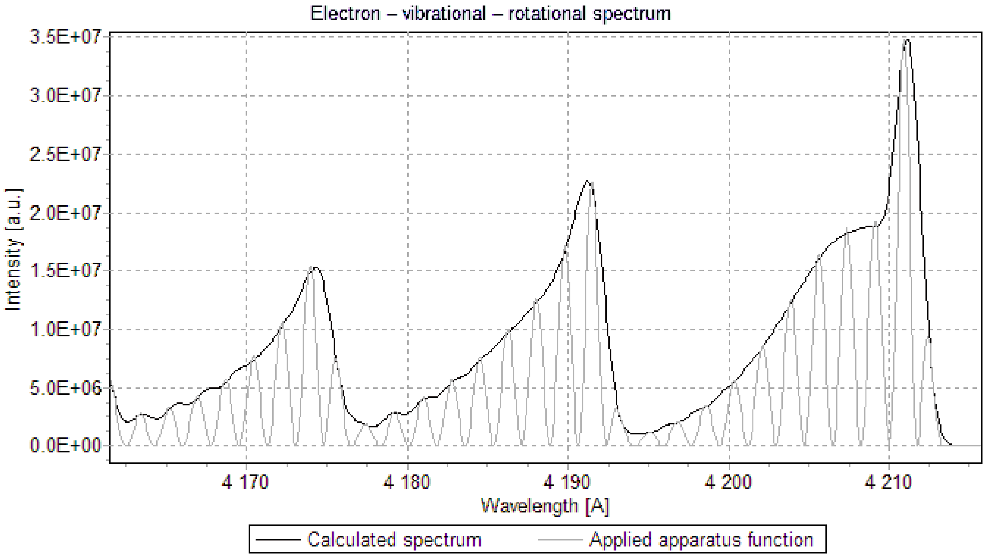

Figure 4.3: Electron-vibrational-rotational spectrum of the $B^2\sum^+ - X^2\sum^+$ system of the CN radical. The black line represents the simulated spectrum by program Simul [5] and the grey line is the deconvolution spectrum of this line after application the triangular function with $T = 3.5\,\text{Å}$ and FT.

5 Structure and features of programs Simul and RotSimul

5.1 Program Simul

The software Simul ranks among the universal software concerning the electron-vibrational-rotational spectra simulations for diatomic molecules. It has been being developed since the year 2000 applying the theoretical calculations of Herzberg [6], Kovacs [7] and Pearse [9]. At first, it was intended as the software only for electron-vibrational-rotational spectra simulation of diatomic molecules. But during the time it has been changed in the structure and its actual structure is presented in the figure 5.1.

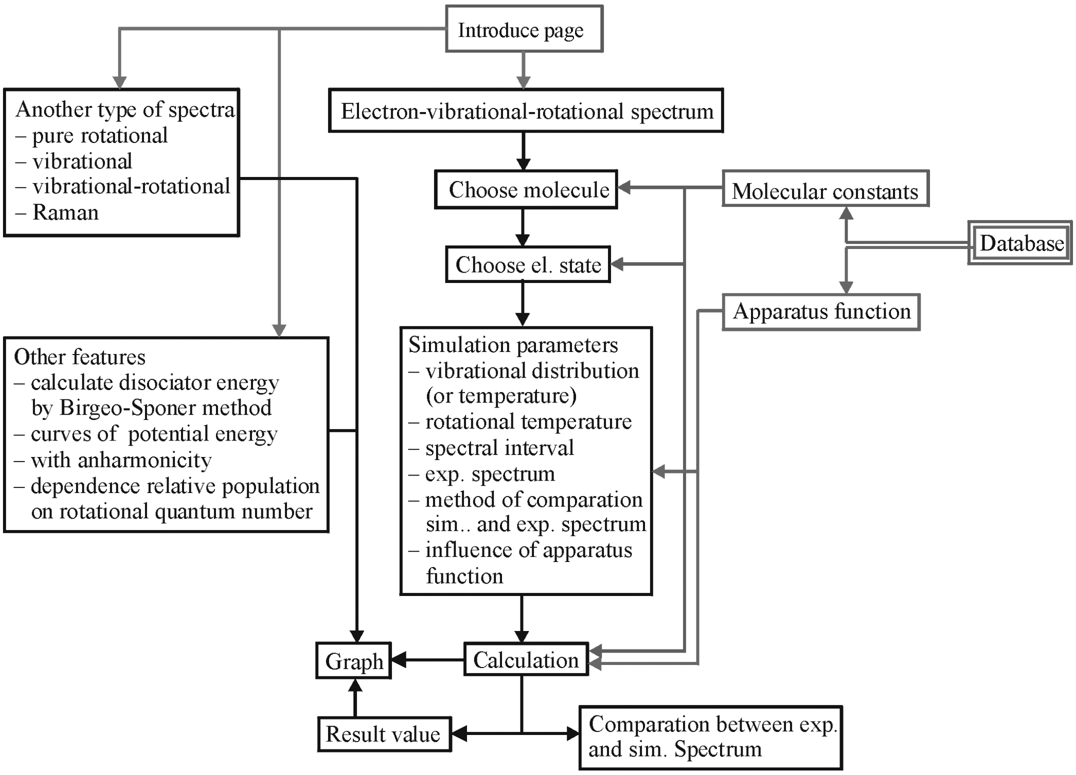

Figure 5.1: The scheme and features of the software Simul.

The schematic structure of the program Simul is shown in figure 5.1. According to the scheme of the program, Simul belongs to the universal programs whose advantages are the simple running and use and mainly its database of the molecular constants and the apparatus function you can control, complete, edit or delete yourself without any problems.

But during the developing the software has changed its structure. Nowadays it is possible to simulate electron-vibrational-rotational spectra in the equilibrium or non-equilibrium state for diatomic molecules. Beside these spectra there is also the possibility to calculate the pure rotational spectra, Raman spectra with the nuclear spin inclusion, pure vibrational spectra and simple rotational-vibrational spectra with or without anharmonicity.

As it is evident from the figure 5.1 except the optical spectra it is possible to module some graphs, for example graph of the potential energy for harmonic or anharmonic vibrator or Birgeo-Sponer diagram for disociation energy or the dependence of the relative population on the rotational number.

After the detailed studying of this program scheme it is obvious that it has also other features – for example outputs of the calculated data that can be shown in a graph as a table or saved in a file and operated with them later or in the other table processor or graphic software – for example Origin or Microsoft Excel. This software Simul offers some comparing methods with another spectra that you measure or calculate by different or this software.

5.2 Program RotSimul

The program RotSimul is the software for simulations of the rotational spectra for linear, spherical, prolate symmetric, obligate symmetric and asymmetric rotor. These simulations are based on the well-known theoretical calculations of Gordy [4]. This program contains knowledge obtained during the stage in the Laboratory of Physics of Lasers, Atomes and Molecules of the University of Technology and Sciences Lille 1 in France.

At the first this program was created only for predictions of the rotational transition frequencies of symmetric prolate rotors of observed molecules as the response to the need to econimize the time of measurement and also quantity of used samples. There was added other features during the experiences with rotational spectroscopy as calculations of the moment of inertia for linear, bent, pyramidal, planar and axial symmetric molecules and also authomatic determination of molecular constants as described in the section **??**, page **??**.

According to the figure 5.2 it is obvious that this program contains also the menu to analyse experimental spectra. It means to create the graph from experimental data and do with them the statistics as linear regression, quadratic linear regression, polynomial regression, sum of exponentials, H-spline, fit by the Gaussian curve or the numerical calculations of derivatives (first–fourth) from the selected area.

A specialist in spectroscopy appreciates the possibility of the Gaussian curve parameter determination by the non-linear least squares regression and also the rotational lines fitting by the Gaussian or Lorentzian profiles and comparison of the simulated and experimental spectum together.

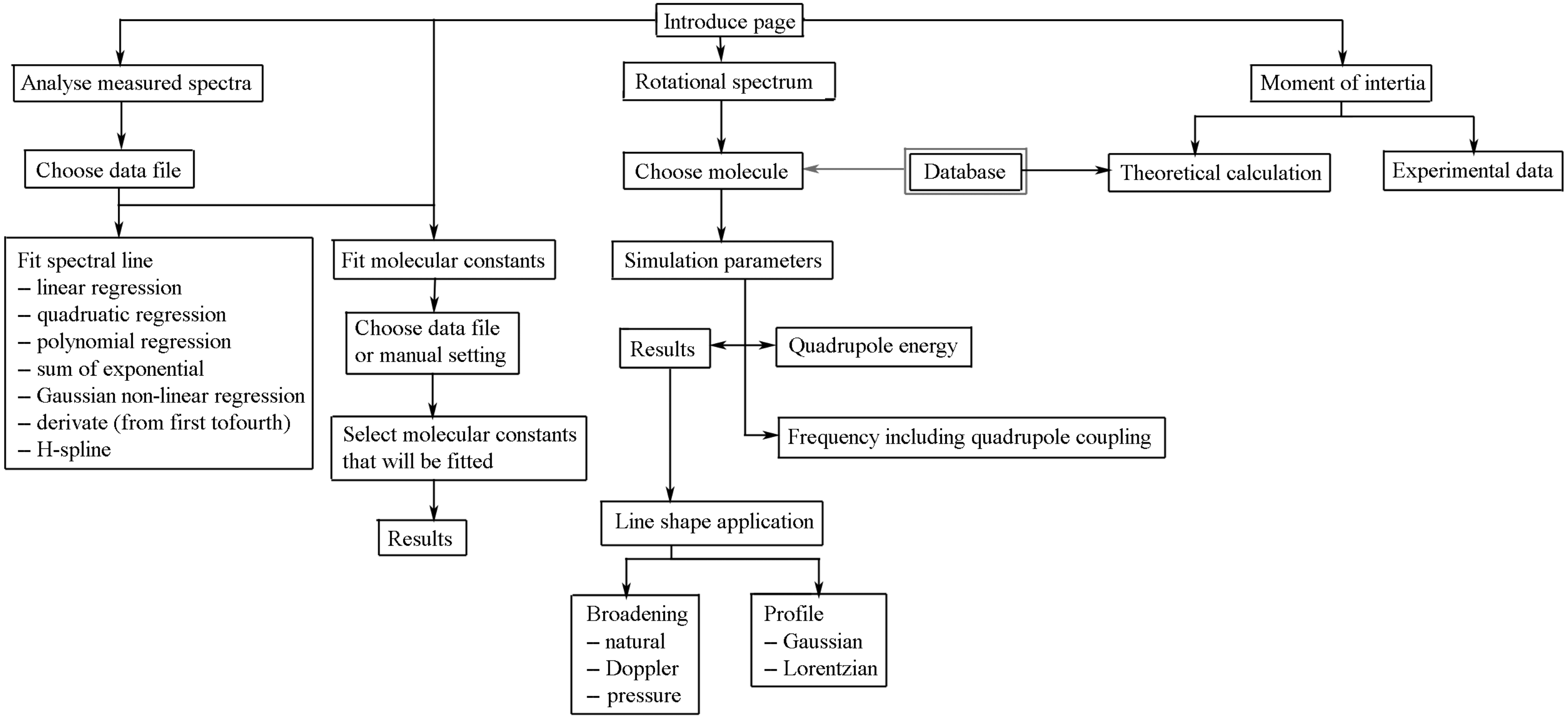

Figure 5.2: The scheme and features of the software RotSimul.

6 Conclusion

This work dealt with numerical simulations of optical spectra and subsequent problems. One of the main goals of this thesis was to create a universal program "Simul" that allows to compute electron-vibrational-rotational spectra of diatomic molecules according to the theoretical calculations. One of the reasons for its development was to make a program that will not be limited for only one spectral system but it will be universal. So the first step of this work was to suggest the general algorithm and then it was applied to the grafic platform of Simul. Its universality was solved by the general database system whose manipulating is not difficult and the user can easily control the values of molecular constants by setting, editing or deleting.

Another advantage of this program is its use in the operating system Microsoft Windows which means that its operation is very simple. The platform of this program was projected very generally and it was not a problem to change it for the system Unix. But during this work it was not necessary because all users of these programs prefered the system Microsoft Windows.

During the time of this algorithm development there were found problems not only from spectroscopy but also from the other scientific domains, such as numerical mathematics, statistics, algorithmization and also programming in the language Delphi. So to find the successful solution of the general algorithm it was necessary to study all these domains and also consult the proposed solution with specialists in spectroscopy and also in other scientific branches.

The colaborations with specialists supposed the effectiveness of the developement and also the relation with the potential users of this program who tested the beta versions and their results were compared with experimental data. That is why the non-ideal overlap between the simulated and measured spectrum was analysed by the statistics and this solution was later discussed.

For the current topic of this theme this work was also supported by the Czech Ministery of Education grant No. 2004/0150. With this support it was possible to translate the program Simul into English, write the operation manual for its operation, create its web sites where its actual version is available for free download [5] and optimized the algorithms.

It was also cooperated with both foreign laboratories such as Institute of Solution Chemistry of Russian Academy of Sciences in Russia; Vinca Institute in Belgrade in Serbia or Combustion Physics of Lund Institute of Technology in Sweden and Czech laboratories as Institute of Physical Chemistry of the Academy of Sciences of the Czech Republic; Laboratory of Plasma Physics and Plasma Sources of Faculty of Science of Masaryk University in Brno or Faculty of Mechanical Engineering of Brno University of Technology.

The cooperation with many spectroscopy laboratories had the influence on this work and enriched its goals to problems of apparatus functions. There are solved two different methods of the deconvolution solution. The first one is called the sequence method and is based on the possibility to substitute the convolution integral by the summarization of the discrete values. It was demonstrated that this method is not suitable to use in practice.

The other applied method is based on the Fourier transformation and the shape of the apparatus function. In the program Simul there were applied these apparatus functions – triangular, trapezium, rectangular, exponential, Blackman-Harris cosine or quarterwave cosine. This procedure has also the convenience in the physical application in the spectroscopy. It was established that the shape of the deconvoluted spectrum depends on the values of the apparatus function's parameters. One of the disadvantages of this method is the repression of some peaks which are needed to the other calculations and further analyses as the rotational temperature calculation.

But with the this program it is possible to simulate, except electron-vibrational-rotational spectra, also the other spectra as rotational or vibrational and possibly Raman's spectra. To other features belong the determination of the dissociation energy and calculation of the potential curves with or without influence on anharmonicity. It is possible to observe the immediate influence of the values of simulation parameteres on shapes of spectral lines. For this reason this program can be used as the modelling software during teaching the quantum chemistry or in plasma lessons because students can simulate various diatomic optical spectra with various simulation parameters and so they can examine the development of these parameters on the shape of the simulation spectrum and compare it with the real spectra.

Numerical simulations of the optical spectra have problems with the accuracy of energetic levels calculations of both electron states where the first approximation is used and also with the accuracy of molecular constants values on which the computations are based. In spite of this disadvatage the simulated spectra can be used for experimental spectra analyses.

By the spectra modelling it is possible to estimate the rotational temperature and in the case of the equilibrium plasma simulation also the vibrational temperature. During the development there were applied also others methods of rotational temperature determination as Knaus and Caye; Janin and Eyraurde or Ornstein-van Wijkov method.

This program is also possible to use for decoding experimental spectra measured with low resolution and so it allows to spread in optical spectroscopy for monitoring of plasma-chemical processes as determination of ionization degree in plasma or defined chemical reactions in plasma both in laboratories and also in industry. To the non-usual usage it is ranked the identification of some of molecular spectral bands or systems that are not presented in the spectral tables or databases.

At the same time as optimizating features of the program Simul there was made contact with the Laboratory of Physics of Lasers, Atomes and Molecules of the University of Technologies and Sciences Lille 1 in France and this cooperation led to organizing the exchange stay there. During this exchange stay the goals of this thesis were extended and so besides the program Simul the other program called RotSimul was developed.

This software is focused only on simulations of rotational spectra but not just for diatomic molecules but also for polyatomic molecules. Among the other advantages of this program are calculations of the moment of inertia both according to the theoretical calculations or from the experimental data. There was also included another algorithm that provides the determination of molecular constants from the measured spectra.

In RotSimul there were also added some statistical functions and the selected line fitting by the Gaussian curve, quadratic function, etc., and also the numerical calculations of first, second, third and fourth derivatives as the response to the need for the fast analyses of the experimental rotational spectra.

Currently, there exist two complex programs – Simul and RotSimul that were successfully presented in many international conferences and the results of development were published in international journals. These programs are possible to use in the practice in spectroscopy laboratories or in the education at the university level and they are also available for download from the web sites as freewares.

This work allowed me to get familiar with microworld in details and also with the processes that are in progress in it. During looking for solutions of the problems I could try to apply my knowledge from many domains in one area and connect them together. I could also try to lead the research project and also colaborate with many interesting people from various institutions.

But I also uncovered others possibilities that can variegate these programs for example the calculations of the vibrational transition probability or the direct determination of the vibrational temperature determination. The simulated database of spectra could be created and used for the experimental spectra identification. I believe that some other works will be picked up the threads of this one and these programs will be reached of further beneficial features both in the practice and in the teaching.

After all the time invested in the development I hope that algorithms of the both created programs are optimized, fast, effective and exact with simple operation of calculations and Simul and RotSimul are original, atractive, useful and universal softwares. Of course, some other features could be added in the future. The calculation of the vibrational transition probabilitis will be the most needed function.

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7 Curriculum Vitaeu

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Education and Academic Qualitifications

1997–2002	Ing. (MSc) of Physical and Applied Chemistry (with honours), Institute of Physical and Applied Chemistry, Faculty of Chemistry, Brno University of Technology
2000–2002	Complementary Pedagogical Study, Institute of Social Sciences, Faculty of Civil Engineering, Brno University of Technology
2002–2004	Ing. (MSc) of Quality Management (with honours), Institute of Metrology and Quality Assurance Testing, Faculty of Mechanical Engineering, Brno University of Technology
2002–2005	Ph.D., Doctoral Study of Physical Chemistry, Institute of Physical and Applied Chemistry, Faculty of Chemistry, Brno University of Technology

2003	First Aid Certificate, Czech Red Cross
2003–2004	Certificate of Security in the Electrotechnics – according the law n. 50/78Sb. in the Czech Republic, ev. n. J 28/04

Scholarships and Awards

2001	Special Award	Competition Student's Created Activities, section Materials and Technology, Faculty of Chemistry, Brno University of Technology
2001	Nomination of member	of Regional jury of the EXPO Science AMAVET
2001	3rd place	Competition Student's Created Activities, section Social Sciences, Faculty of Civil Engineering, Brno University of Technology
2002	2nd place	Competition Student's Created Activities, section Materials and Technology, Faculty of Chemistry, Brno University of Technology
2002	Nomination of member	of National jury of the EXPO Science AMAVET
2002	Prestige Award of Directeur of Faculty of Chemistry	for excellent results during studying, diploma thesis and representation of Faculty of Chemistry, Faculty of Chemistry, Brno University of Technology

Professional Experiences

1997–2000	training of PC users in the company Jan Dvořák
1997–2000	training, application of Image Processing for analysis of ultrasound's images for specialized medical surgeries at the hospital St. Anna in Brno

Pedagogical Activities

2002–2004	Laboratory of Physics I, (168h.) at FCH VUT Brno
2002–2004	Laboratory of Physics II, (168h.) at at FCH VUT Brno

Cooperating with Scientific Projects Supported by the Czech Science Foundation (GACR)

1999–2001	*Surface Activation of Synthetic Polymer Materials in Non-Isothermic Low Temperature Plasma* – project n. 104/99/0307
2003–...	*Advanced Topics in Physics and Chemistry of Plasmas* – project n. 202/03/H162

Solved Scientific Projects Supported by the Czech Ministry of Education (FRVS)

2003–2004	*Numerical Simulations of Optical Spectra and their Statistics* – Project n. 2004/1677
2003–2004	*Mutlimedial Exercisebook for Teaching Physics* – Projekt n. 2004/1662

8 Publications

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9 Souhrn

Dizertační práce se zabývá problematikou numerických simulací spekter a to jak spekter elektron-vibračně-rotačních, vibračně-rotačních či vibračních dvouatomových molekul, tak i rotačních spekter pro polyatomové molekuly. Jejím hlavním cílem je vyvinutí univerzálních algoritmů numerických simulací zmíněných spekter na základě známých molekulových konstant.

První část této práce se zabývá teoretickými podklady pro řešení výpočtu. Výklad postupuje od nejjednoduší problematiky simulací rotačních spekter pro polyatomové molekuly přes složitější numerické výpočty vibračních nebo vibračně-rotačních spekter až k základům simulací elektron-vibračně-rotačních spekter dvouatomových molekul. Kromě řešení přechodů dvouatomových molekul rozebírá i výpočty absorpčních koeficientů, intenzit a tudíž i stanovení Höhnel-Londonových faktorů či výpočtem pravděpodobnosti přechodu.

Další část této práce je orientována na základní principy matematických a numerických metod použitých pro simulaci spekter jako je convex hull, numerické derivování křivek, nelineární regrese či dekonvoluce a konvoluce.

V tomto textu jsou také popsány metody určení hodnoty disociační energie a závislosti tvaru potenciální křivky na konstantě síly vazby a dalších proměnných. Tato část se zabývá i problematikou určení profilu spektrální čáry (Gaussův či Lorentzův) a detailně rozebírá přirozené, Dopplerovo a tlakové rozšíření rotační čáry.

Tato dizertační práce se též věnuje matematickému odvození průběhu přístrojové funkce a to jak sekvenční metodou tak i pomocí Fourierovy transformace. V této části jsou uvedeny i nedostatky zmíněných metod.

Součástí práce je vytvořený program Simul, který představuje jeden z jejích hlavních cílů. Tento program umožňuje mimo simulací elektron-vibračně-rotačních spekter dvouatomových molekul a jejich porovnání s experimentálně naměřeným spektrem (v této práci byla použita experimentální spektra molekuly dusíku a radikálů OH a CN) i simulaci čistě rotačních, vibračních, vibračně-rotačních a Ramanových spekter dvouatomových molekul. Jednou z výhod tohoto programu je to, že není omezen pouze na jeden spektrální systém, což je zajištěno díky navržené databazi molekulových konstant.

Mimo uvedená spektra lze pomocí vytvořeného programu určit i hodnotu disociační energie Birgeho-Sponerovou metodou, případně grafické zobrazení potenciálových křivek bez zohlednění anharmonicity i s jejím zahrnutím do výpočtu.

Tato práce rozebírá i využití programu ve spektroskopii, jako je určení rotační teploty, a tak i teploty neutrálního plynu, jak pomocí simulací, tak i Knausovou a Cayovou metodou, Janinovou a Eyraurdovou methodou nebo Ornstein-van Wijkovovou metodou. Mimo stanovení rotační teploty lze zjistit i vibrační rozložení a u rovnovážného plazmatu vibrační teplotu. Pomocí tohoto programu lze identifikovat i molekulární systémy, které nejsou uvedeny ve spektrálních tabulkách. Díky tomuto programu je možno používat i spektrometry s malým rozlišením, což je podstatně levnější.

Další stěžejní částí této práce je vytvořený program RotSimul, který je zaměřen na simulaci rotačních spekter lineárních, sférických, symetrických a asymetrických rotátorů. Výsledky tohoto programu byly testovány na molekule H_3SiCl (symetrický rotátor).

Pomocí tohoto programu je možné i stanovit moment setrvačnosti pro linearní, lomenou, pyramidální, planární a axiálně symetrickou molekulu nebo stanovit molekulové konstanty. Součástí tohoto programu je i analýza experimentálních spekter a to pomocí lineární regrese, kvadratické regrese, polynomiální regrese, součtu exponenciálů, H-splinem, nelineární regrese Gaussovy křivky a numerických derivací (od první až po čtvrtou).

Kromě spektroskopických laboratoří lze oba programy (Simul i RotSimul) používat ve výuce kvantové chemie či diagnostiky plazmatu jako názornou pomůcku, například pro simulaci různých podmínek experimentu s rychlou odezvou.

V závěru této práce jsou shrnuty i problémy, které se mohou objevit, a také omezení při použití různých doplňkových funkcí těchto programů.