R E V I E W

of a dissertation for the acquisition of the educational and scientific degree "doctor" in professional direction 4.1 Physical Sciences; physics of atoms and molecules;

by defense procedure at the Faculty of Physics (FzF) of Sofia University "St. Kliment Ohridski" (SU)

The review is prepared by: Prof. Dr. Kiril Borisov Blagoev, in his capacity as a member of the scientific jury according to Order No. RD38-273 / 03.06.2024 of the Rector of Sofia University.

Dissertation topic: "Ultrafine structure of selected states in diatomic molecules"

Author of the dissertation: MSc Velizar Rosenov Stoyanov

I. General description of the presented materials

1. Data on the submitted documents

MSc Velizar Stoyanov has submitted a dissertation and an Abstract, as well as the mandatory tables for the Faculty of Physics of the SU. We have also been presented with 13 other documents - an order for enrollment in doctoral studies; order to extend the period of doctoral studies; deduction order; applicant's curriculum vitae; declaration of authorship; diploma and application for the degree "master"; protocol for the originality of the dissertation work, signed by Assoc. prof. Dr. Sn. Yordanova; statement by Assoc. prof. Dr. Sn. Yordanova in connection with a procedure to prevent plagiarism in dissertation works; certificate of passed exams. In the official documents - declaration of authorship, references for originality and absence of plagiarism, the title of the dissertation work is indicated, which is more general than the title in the dissertation work and the abstract "Investigation of the fine and surface structure of the $c^3\ \Sigma^+$ state in KRb" The documents submitted by the candidate for the defense correspond to the requirements of the ZRASRBhigh school of science and mathematics, PPZRASRB and the Regulations for the terms and conditions for acquiring scientific degrees and occupying academic positions at SU "St. Kliment Ohridski" (PURPNSZADSU).

2. Applicant data

MSc V. Stoyanov graduated from the high school of science and mathematics "Prof. Emmanuel Ivanov" in Kyustendil. Graduated with a master's degree in Phys. Fac. of SU"St. Kl. Ohridski". He worked as a technician in 2017-2018 at IBPHOTONICS. In 2020 - 2021, he worked as a physicist in NIS at SU "St. Kl. Ohridski". In 2022-2023 he is a first-level researcher in the program of SU "St. Kl. Ohridskt" young scientists and postdoctoral students. From 2023, he is a young scientist under the SU marker program for innovation and technology transfer. In 2020 V. Stoyanov is enrolled as a doctoral student in Phys. Fac. of SU "St. Kl. Ohridski" in the Department of "Optics and Spectroscopy" with supervisor Prof. A. Pashov. The term of the doctoral studies has been extended until the middle of 2024, when the dissertation has been submitted for preliminary defense and the defense procedure has started.

3. General description of the candidate's scientific achievements

The dissertation consists of 172 pages and is written in English. The material is divided into 10 chapters, of which 1 chapter is an introduction and the objectives of the dissertation work are indicated; Chapter 2 is dedicated to the area discussed in the dissertation; Chapter 9 is a conclusion and Chapter 10 is a list of the author's publications. The bibliography includes 104 scientific papers and books of other authors and is divided into articles and books. The remaining chapters - from 3 to 8 are grouped into two parts - first part "Theory" - chapter 3 to 6, and chapter 6 is devoted to the theoretical foundations of saturation spectroscopy. The second part "Experiment" includes chapters 7 and 8, and in chapter 8 the numerical calculations are considered and the obtained results are discussed. The dissertation contains 31 figures and 5 tables. The abstract is written in Bulgarian and its content corresponds to the content of the dissertation. The chapters of the Abstract are distinguished from the numbering of the chapters in the dissertation. I noticed a small number of typographical errors in the text of the thesis. I would like to draw the author's attention to the fact that the purpose of the dissertation is to obtain new data on the energy states of the studied molecules and the constants of the h.f.st., for the realization of which it is necessary to fulfill the tasks indicated at the end of the Introduction. The findings and conclusion should present the results of the research, not a summary of the work done.

V. Stoyanov's dissertation is in the field of molecular spectroscopy, finding new terms and determining their energies, finding the components of the hyperfine structure of excited states and determining the constants of the hyperfine structure of KRb^{85} and KRb^{87} molecules. The basis of these studies is the precise determination of the wavelength of the transitions from these states. The research has an experimental and theoretical nature. Such an approach is appropriate in the study of complex molecular spectra, since the combination of experimental and theoretical studies give more precise constants and on the other hand, experimental studies verify theoretical models. The work is topical. Data on the spectra of diatomic molecules are necessary for the development of astrophysical research and quantum optics.

In the introduction, a brief literature review of the available information on the spectra of the heteronuclear molecules of the alkali elements, and in particular the KRb molecule, is presented. The work is devoted to studying the fine and hyperfine structure of the c $^3\Sigma^+$ state, which is strongly related to the $B^1\Pi$ state of the KRb^{85} and KRb^{87} molecules. The theoretical part is presented in chapters 3, 4 and 5 of the dissertation. An effective Hamiltonian of a diatomic molecule is introduced. Next is a separation of the variables involving the motion of the electrons and their spin from the spin of the nucleus. The effective Hamiltonian method was chosen over the coupled channel method. The angular part of the Hamiltonian is considered as a perturbation that removes the degeneracy. The effective Hamiltonian in this case is limited to the two discussed states $B^1\Pi$ and $c^3\Sigma^+$. The effective Hamiltonian is a sum of the matrix responsible for the fine structure and the diagonal block of the Fermi matrix - contact interaction, taking into account that nucleus that has the predominant influence to form the hyperfine structure, which is the Rb one. The influence of the K nucleus is neglected. Thus, in the effective Hamiltonian there remain 11 constants responsible for the energies of the two states, their rotational constants; centrifugal corrections; fine structure; the Λ doubling constant and the Fermi-contact interaction constant. The theoretical description presented in this way leads to those expressions which are necessary in the numerical calculation of the constants in reading and the experimental results. In chapter 6, a brief theoretical basis of the experimental method of saturation spectroscopy in weak and strong field conditions and two counter-propagating beams is given.

The theoretical part of the work demonstrates the author's good knowledge of the theoretical description of the spectra of diatomic molecules.

In the dissertation, 4 experiments are carried out, all based on the interaction of laser radiation with the studied environment. These are - Laser Induced Fluorescence, Saturation Spectroscopy, Laser Filter Spectroscopy and Double Optical Resonance Saturation Laser Spectroscopy. For the source of K and Rb molecules, a heat pipe is used, where, in addition to KRb molecules, K_2 and Rb_2 molecules are also formed, which further complicates the task of correct registration and analysis of the spectra of the discussed molecules. The advantages and disadvantages of the selected source compared to the other possibility - a molecular beam in relation of the influence of the Doppler and collisional broadening of the spectral lines and the advantage of working for a considerable experimental time with a constant source of molecules have been analyzed. The natural isotopic mixtures of the studied metals were used. Experimental conditions were chosen - pressure of the buffer gas and the temperature of the metal tube and, accordingly, of the pressure of the saturated vapors of the metals, which were a compromise with regard to the intensity of the registered spectra and the Doppler and collisional broadening. Wavelength calibration is performed by a standard technique by comparison with the well-studied spectrum of the I_2 molecule and using a conofocalic interferometer and wavelength meter. The latter is used for a rough estimate of the spectral region of study. Laser diodes with an external diffraction grating are used. Spectrum scanning is performed with synchronous variation of the resonator with the grating and the laser current. Maintaining the laser and scanning frequency is done with lab-made controllers. The useful signal is extracted by lock-in detection. The laser-induced fluorescence experiment proved to be suitable for isolating some transitions to the B $^1\Pi$ state. The spectrum is analyzed with a Fourier spectrometer. The experiment with two laser beams from one laser source propagating in opposite directions and with the application of a filter in front of the recording diode allows to simplify the recorded spectrum and eliminate the Doppler broadening. This experiment is used to identify the transitions from the perturbation region of the two states. The spectra obtained by saturation spectroscopy with two beams - pump and probe, taking into account the collision, Doppler and broadening from the passage of molecules through the excitation zone are too complex and from the presence of lines from other molecules of the studied elements and the spectroscopy of induced fluorescence and absorption with filtering allows to identify and examine the sought transitions. The experimental results on registration of h.f.st. of transitions from the c $^3\Sigma^+$ state were recorded by double optical resonance saturation spectroscopy. Here, a second laser is applied, with the pump laser at a fixed frequency tuned to the frequency of a known transition thus marking the ground state, and the frequency of the probe laser scanned in the region where transitions to the common ground state are expected to be recorded.

Using the four experimental techniques, 130 transitions of $^{39}K^{85}Rb$ and 118 transitions of ^{39}K ^{87}Rb were identified. Energies were determined by considering well-known ground state energies. Most of the registered transitions are for the *B* state. 86 terms of the ^{39}K ^{85}Rb molecule have been determined, of which 6 belong to *c* terms. For this molecule, no splitting of the h.f.st. spectral lines is observed, but only their broadening due to the presence of unseparated, close-lying h.f.st. components. 82 terms of the $^{39}K^{87}Rb$ molecule have been determined, of which 4 belong to the *c* terms. Registered h.f.st. on 6 lines of 4 components each.

The experiments were carried out with high-tech equipment, including both factory and laboratory-made components. The obtained experimental data on the fine and hyperfine structure of the investigated states and the theoretical data obtained from the nonlinear fit, in my opinion, agree very well, taking into account the complexity of the experimental and theoretical tasks. The theoretical assumption that the nucleus of Rb plays a major role in the formation of the hyper fine structure is confirmed. For the ^{39}K ^{85}Rb molecule, the components of the hyper fine structure could not be experimentally separated and a broadening of the spectral lines was recorded. Deconvolution of the broadened spectral lines with 6 components of the h.f.st. was performed. The contributions of various parameters leading to the type of observed spectral lines were analyzed. The experiment and theoretical calculations have been performed at a high level and the maximum has been obtained with these experimental apparatuses and theoretical approximations

I have two questions - how is the error formed when determining the constants from (1) the experimentally recorded spectra (2) from the theoretically obtained spectra.

As far as I can consider, a significant part of the theoretical and experimental research was performed by author. The scientific publications included in the dissertation meet the minimum national requirements (according to Art. 2b, paras. 2 and 3 of the RSARB) and, accordingly, the additional requirements of the SU "St. Kliment Ohridski" for acquiring the educational and scientific degree "doctor" in the relevant scientific field and professional direction. There is no proven plagiarism in the submitted dissertation and abstract. The author is very well acquainted with the available on the topic literature.

4. Content analysis of the applicant's scientific and scientific-applied achievements contained in the materials for participation in the competition.

Based on the above, it can be concluded that the candidate's scientific contributions have the character of: obtaining new data on the spectra of diatomic molecules of the alkaline elements and enriching existing knowledge. According to the SCOPUS system, there are no citations to the author's works, so far.

5. Critical notes and recommendations I have essentially no critical remarks.

6. I have no personal impressions of the candidate

7. Conclusion

After having familiarized myself with the presented dissertation work, Abstract and other materials, I believe that the conducted research is of a high scientific level. Based on the analysis of their significance and the scientific contributions contained in them, I confirm that the scientific achievements meet the requirements of the ZARSRB and the Regulations for its application and the relevant Regulations of SU

"St. Kliment Ohridski" for acquiring the educational and scientific degree "doctor". In particular, the candidate satisfies the minimum national requirements in the professional direction and no plagiarism has been found in the dissertation, abstract and scientific works submitted for the competition. I give my positive assessment of the dissertation work.

II. GENERAL CONCLUSION

Based on the above, I strongly recommend to the scientific jury to award the educational and scientific degree "doctor" in a professional direction. 4.1 Physical sciences; physics of atoms and molecules to MSc Velizar Rosenov Stoyanov.

25.08.2024 Prepared the review:

prof. Kiril Blagoev