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Review of the PhD thesis entitled:

„High-resolution spectroscopy of the 6th overtone band of carbon monoxide"

by

ALEKSANDR ANDREEVICH BALASHOV

The review of the doctoral dissertation by Aleksandr Andreevich Balashov is being issued on a basis of the letter of 28th June 2023 by a Chairman of the Physical Sciences Discipline Board of Nicolaus Copernicus University in Toruń, prof. dr hab. Irenenusz Grabowski.

The dissertation was conducted under a supervision of dr hab. Katarzyna Bielska and was co-supervised by prof. dr hab. Daniel Lisak at the Nicolaus Copernicus University in Toruń, at the Faculty of Physics, Astronomy and Informatics, Institute of Physics, at the Department of Atomic, Molecular and Optical Physics.

The work by Aleksandr Balashov was devoted to an experimental study of the 6th overtone band of carbon monoxide near 690 nm. For the first time overtone transitions of (7-0) band were measured with intensities below $2 \cdot 10^{-29}$ cm/molecule. The high accuracy of the measured line intensities inspired new *ab initio* calculations, performed by collaborators from

UCL in UK, in order to develop a global model of CO absorption that would predict line intensities of all the bands within experimental uncertainty.

The manuscript was written in English on 88 pages. There are 15 figures and 4 tables included. The dissertation begins with Acknowledgements followed by Abstracts (both in English and Polish), a Table of contents, Notations and Abbreviations and Introduction.

In the Introduction the Author describes the most significant and current applications of molecular spectroscopy like remote sensing of gases, a deeper understanding of intermolecular interaction processes or developing new theoretical models. In the next paragraphs of the Introduction the Author focuses on the importance and applications of the carbon monoxide molecule. The spectroscopic notation for the vibrational bands and rotational transitions of the CO molecule is also presented in the Introduction. Since the rotational distributions of intensities in the high vibrational overtones are very sensitive to changes of potential energy curve (PEC) as well as to dipole moment curve (DMC), the experimental study of 6^{th} overtone of CO is essential to model CO absorption properly, and a theoretical model needs to be verified by the highest possible overtone measurement.

The subsequent chapter of the dissertation is Chapter 1, in which a measurement technique is introduced. The technique used for measurement of the 6^{th} overtone of CO was the CRDS (the Cavity Ring-Down Spectroscopy), which is the one of the most popular techniques of absorption determination with an optical cavity. The CMWS (Cavity Mode Width Spectroscopy) technique was used only in a testing phase to estimate the nonlinearity of the detection system.

In Chapter 2 the Author presents experimental setup that was used in his work. The description of the experimental setup starts with the details concerning absorption cell. It is followed by optical setup explanation and the way of the frequency measurement. At the end of this chapter the Author describes how the ring-down time measurements were tested.

In Chapter 3 of the dissertation experimental data analysis is conducted. Different approaches of line profile are discussed, i.e. the Voigt profile (VP), the speed-dependent Voigt profile with quadratic approximation of speed dependence (qSDVP), the Galatry profile (GP), the Nelkin-Ghatak profile (NGP), the speed-dependent Nelkin-Ghatak profile with quadratic approximation (qSDNGP), the Hartmann-Tran profile (HTP). The profiles used in the work were the limiting cases of HTP, i.e. VP, qSDVP, qSDNGP. The final analysis of experimental data was done using qSDVP, since this method turned out to be the most reliable of parameters which determined the line shape. In order to reduce the effect of correlations between line-shape parameters, a multispectrum fitting approach was used. Two approaches for multispectrum fitting are discussed. In the approach called the individual line area approach, the line areas are fitted as individual parameters for a given pressure. In the second one, line area pressure dependency is assumed to be a linear function with zero-crossing at zero pressure.

Chapter 4 presents the results of the measurements of (7-0) absorption band of carbon monoxide. In total 14 lines were measured using a CO sample of high purity. The temperature of CO was stabilized at 296.000(35) K. Each line was measured at five different pressures. The final analysis of experimental data was conducted using qSDVP and linear and individual approaches of multispectral analysis, after a comparison between three profiles, qSDVP, VP and qSDNG, has been made. Baseline aspects along with detailed uncertainty discussion have been extensively presented. The final values of line-shape parameters (line position, intensity, collisional broadening, shifting coefficients and speed-dependent parameters) for all the measured lines were obtained from qSDVP fitting with linear dependence of line intensity on the pressure. The comparison of experimental results with data available in HITRAN2020 database was presented. In collaboration with the group of Dr. Oleg Polyansky from UCL, new *ab initio* theoretical calculations have been conducted in order to develop a global model for intensity predictions within experimental uncertainty.

In Chapter 5 the Author concludes his most significant results of the dissertation thesis. One of them was a construction of an appropriate CRDS spectrometer, since to measure the sixth overtone of CO, such a spectrometer had to be rebuilt to achieve sensitivity of $1.1\cdot10^{-9}$ $cm^{-1}/s^{1/2}$. In order to stabilize the temperature, the system was improved, so the temperature could be under control. Moreover, the Author conducted the analysis of the non-linearity of the detection system and the optimization of the recording parameters. For the first time rotational-vibrational transitions of the sixth overtone of CO were registered in the visible range near 690 nm. 14 lines were measured with high accuracy of intensities. New *ab initio* calculations were carried out in order to develop a global model for line intensities predictions within experimental uncertainty for all the bands of a given molecule. In comparison to other works, the results of these calculations turned out to be very good. The shape of the lines were analyzed using an approach beyond the Voigt profile approximation. The reliability of the determined line parameters was increased. The parameters of self-broadening and pressure shift were determined with a relative uncertainty of about 5% and are consistent with the corresponding lines of lower-order overtones. For the first time speed-dependence effects were observed and studied for such weak lines. In addition to the achievements mentioned above, the Author claims that he obtained more scientific results, which are listed in the dissertation work and which have been already published or are being prepared for publications.

At this point it is worth mentioning that Aleksandr Balashov is a co-author of six papers (the seventh publication is in preparation in *Spectrochimica Acta A*). All of them are listed in the *Journal Citation Reports* (JCR) with high values of Impact Factor (IF). Four of those papers have been published in *Journal of Quantitative Spectroscopy and Radiative Transfer*, whereas other two have been published in *IEEE Transactions on Terahertz Science and Technology* and *Journal of Chemical Physics*.

At the end of the dissertation work there are Appendices, List of Publications and Bibliography. The bibliography section consists of 109 references.

Summarizing, the doctoral work of Aleksandr Balashov is well written, the objective stated. The experiment was properly thought out, prepared and conducted. The required elements of the spectrometer were reconstructed and improved. The measurement results were clearly presented and the aim of the work was achieved. Moreover, in my opinion, the results are very interesting and needed.

A reviewer's duty is also to point out some inaccuracies, typographical errors, incorrect wording etc. The work of Aleksandr Balashov was edited carefully and, apart from some minor errors – mainly typos, no major shortcomings have been noticed. Nevertheless, I would like to indicate some unclear points and ask some cognitive questions.

1) In my opinion the aim of the PhD thesis could be more emphasized by putting it into a separate chapter "The aim of work", for instance. Of course, the objective of the work was presented in the last paragraph of the Introduction, but it would be more clear and visible, I believe, if were put into an especially devoted chapter.
2) In Figure 4.1 line R1 is mislabeled, it should be R0 instead of R1, and then there are three lines in blue, which are also mislabeled (should be R1-R3 instead of R2-R4).
3) It was stated by the Author that there were 14 lines measured and studied in total, whereas in Figure 4.1 there are 15 lines altogether, including a line R22. The line R22 seems to be part of the further analysis as the determined line-shape parameters for the line R22 are presented in Tables 4.2 and 4.3. On page 63, the Author states that that line was omitted from the comparison with HITRAN2020 database for the sake of visual clarity. In my opinion, the parameters values of that line seem reasonable.
4) The Author described the use of the PEC and *ab initio* DMC in theoretical calculations that would provide predictions for intensities within experimental uncertainty and for all the bands of a molecule. It was said that initial results were very bad and after the so called "bad points" had been removed, the experimental line intensities were well reproduced. In which region did the interpolated dipole moments differ from the *ab initio* values? Was there only one such a region or more? How many "bad points" were removed? What would be the reason for such discrepancies? I would be grateful, if the Author could develop a little bit on the way the problem had been solved.

Concluding, I would like to express my very positive opinion about the PhD thesis of Aleksandr Balashov. Considering valuable results of the work, good mastery of the research technique, herein it can be concluded that the doctoral dissertation meets all the conditions specified in Article 187 of Act of July 20, 2018 "Law of Higher Education and Science"

(Journal of Law of 2021 of item 478, as amended) and thus I believe that it fully deserves to be admitted to further steps of the PhD procedure.

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