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Review of the PhD Thesis

Author:	**Aleksandr Andreevich Balashov**
Affiliation:	Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń
Title:	**High-resolution spectroscopy of the 6th overtone band of carbon monoxide**
Supervisor	dr. hab. Katarzyna Bielska, prof. UMK
Co-supervisor:	prof. dr. hab. Daniel Lisak

Introduction

The reviewed dissertation was written by Aleksandr Balashov within his work at the Institute of Physics of the Nicolaus Copernicus University in Toruń. The main scope of the thesis is related to the **first measurements** of the absorption spectrum of the weak 6th overtone of the CO molecule in the visible wavelength region (ca. 690-700 nm) using CRDS (cavity ring-down spectroscopy) technique. Further spectrum analyses, done by the author, included studies of the line profiles with determination of the highly accurate line-shape parameters.

Assessment

The thesis is written in English. The main part is 71 pages long and is divided into seven main parts: two unnumbered chapters i.e., Abstract/Streszczenie and Introduction as well as five numbered chapters (from CHAPTER 1 to CHAPTER 5). The dissertation is also supplemented with the List of abbreviations, List of the author publications, Appendices and Bibliography. The whole thesis is well organized. The layout and the order of the chapters are appropriate and the dissertation itself constitutes a logical and closed whole.

The dissertation consists of **one main published article** (p. 69, no 1. A. Balashov et al. *J. Chem. Phys.* **158**, 234306 (2023)) and six other papers, two of which (3, 6) refer to the similar topics and methodology. The above-mentioned article (1) was carried out in cooperation with foreign research institutions PTB (Physikalisch-Technische Bundesanstalt), University of Groningen and UCL (University College London). All publications included in the PhD thesis were published (or are prepared for publication) in highly impacted refereed scientific journals (e.g., *J. Chem. Phys., J. Quant. Spectrosc. Radiat. Transfer*).

In Introduction, the author has described the application of the high-accuracy molecular spectroscopy of small molecules in study and exploring Earth's and cosmic

environment. This section contains also clearly formulated the goals of his work and defined the tasks necessary to fulfil them.

In Chapter 1 we can find the physical and mathematical principles about using two similar techniques i.e. CRDS and CMWS (cavity mode width spectroscopy) for determination the value of the absorption coefficient α. Because currently expected absorption is low, the CRDS technique has been chosen for future experiment with 7-0 band of CO.

Chapter 2 describes the experimental procedures and technical details dealing with conducted measurements. Some of the experimental issues should be stressed as important for the final accuracy of the determined line positions and line-shape parameters. They are the procedure of the thermal stabilization inside the cavity (**with uncertainty of 35 mK**) and cavity length stabilization using Nd:YAG reference laser (1064 nm, long-term frequency stability better than 5 kHz) and piezo transducer for changing the cavity length. The applied double-pass configuration with precise f_{AOM} frequency modulation reduced the measurement step below FSR – about 50 MHz near the line center. Moreover, the probe laser frequency has been accurately determined from an optical beat note "observed" between used ECDL (external cavity diode laser) and OFC (optical frequency comb). Author also described the using of the highly stabilized a 10 Hz RF signal transmitted from Astro-Geodynamic Observatory for system frequency synchronization.

Chapter 3 brings three subsections and starts with crucial and detailed studies on the line profile functions. From the simplest VP (Voight profile) through the speed dependent profiles (qSDVP and qSDNGP) up to the Hartman-Tran profile (HTP) that considers correlation between molecular state-changing and molecule velocity-changing collisions. Section 3.1. ends with discussion about the pressure and temperature dependence of the line parameters. I must admit that all considerations are efficiently described, which is for sure the result of long-time experience of the "Toruń group" in experimental and theoretical study on spectral line-shape profiles. Next two subsections are devoted to the method of experimental data analysis using a multispectrum fitting procedure and to modelling of the baseline, respectively.

Chapter 4 describes the conducted measurements and obtained results. I will use this description for summary of some **important result**s achieved by the author:

- in total 14 lines of the 7-0 band of CO were studied **for the first time** as recorded by CRDS technique at five pressure values (depend on the line intensity) at highly stabilized temperature about 296 K;
- the qSDVP was used for analysis of the experimental data (on the basis conducted tests) and to provide a wide set of line-shape parameters among them speed dependent a_w and a_s parameters have been obtained **for the first time** for such weak transition;
- the Voight profile (VP) line parameters were also obtained for all observed lines and presented for comparison in Table 4.3 (p. 59);

- the comparison of the present experimental results with those obtained or extrapolated from HITRAN2020 database have shown that **quite large differences** for the absolute values of the line intensity S (Figure 4.7. a));
- the current laboratory data were used by cooperators from UCL (group of dr O. Polyansky) to careful study of the DMC for ground state of CO and to **new interpolation**, that gives the reproduction of the line intensities for 7-0 band within one standard deviation.

In Chapter 5, the author has summarized the main achievements of the thesis.

Remarks

I have a few minor remarks:

- p. 15: notation dealing with the upper and lower vibrational levels incorporated within transition under consideration, v' is usually and commonly used for the upper state and v'' for lower one;
- p. 17: "The predicted values of the transitions from 6th overtone of CO were ranging from…", what is mean "The predicted values of the transitions…"?;
- p. 47, Figure 4.1: the R-branch lines start from $R0$ or $R1$?, is there any extra line between $R1$ and $R4$?;
- p. 59, caption of the Table 4.3; is there a special reason for new unit for the line intensity S?;
- some editorial remarks
  - p. 47: corored; p. 48: usind HITRAN2020; p. 69: O2; p. 70: Co-ar;…
- p. 69, I think that author's articles should be cited in the whole dissertation by numbers form 1-6, not by "new" numbers e.g. [106] for main work A. Balashov et al. *J. Chem. Phys.* **158**, 234306 (2023).

Issues to discuss

I have two questions/suggestions for discussion:

- In Table 4.1. (p. 56) we can find that main contribution to the parameters standard uncertainty has baseline model uncertainty. Are there methods for decreasing of this impact?
- On pp. 61/62 author appointed out that the present high-accuracy measurements of the 7-0 band line intensities have motivated the new *ab initio* calculations. I think that during public defence those issues should be discuss more detailed. Especially comparison between experimental and calculated line intensities (see Fig. 5 in A. Balashov et al. *J. Chem. Phys.* **158**, 234306 (2023))

Summary and recommendation

I have to say that I was a little surprised after first look on the list of the articles (article to be exact) that comprising presented dissertation. However, after detailed review of the whole

dissertation and main work (*J. Chem. Phys.* **158**, 234306 (2023)) **I have no doubt that Mr Aleksandr Balashov has presented important and valuable experimental results dealing with high-accurate absorption spectroscopy (CRDS) of the 7-0 band, that supported state of the art *ab initio* calculations for the CO molecule**. I am impressed with the amount of work, both experimental and computational, done in the dissertation.

Mr A. Balashov has gained a broad understanding of vide aspects of the field under consideration and has mastered the typically employed theoretical methods very well. The goals formulated by the author in Introduction have been fulfilled. **The reviewed thesis proves that Mr A. Balashov has the ability to perform independent research work.**

Therefore, **I declare that the PhD thesis of Mr Aleksand Balashov meets all formal** (art. 187, p. 1 and 2, Act of 20 July 2018, Journal of Laws 2018, items 1668) **and customary requirements for the doctoral dissertations, and I am applying for admission of Mr Aleksandr Balashov to the further stages of the PhD procedure.**