Review of the PhD dissertation
of Mr. Aleksandr Andreevich Balashov
entitled *High-resolution spectroscopy of the 6th overtone band of carbon monoxide*

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The PhD dissertation of Mr. Aleksandr Andreevich Balashov entitled *„High-resolution spectroscopy of the 6th overtone band of carbon monoxide"* has been written under the supervision of Dr hab. Katarzyna Bielska and under the co-supervision of Prof. dr hab. Daniel Lisak. The dissertation is a result of the scientific research conducted by Mr. Balashov in the Department of Atomic, Molecular and Optical Physics in the Institute of Physics of the Nicolaus Copernicus University in Torun, Poland. The research goal was to study experimentally the 6th overtone band of carbon monoxide (CO) near 690 nm that has never been investigated before. The research was further motivated by the fact that CO is one of the most important trace gases in the Earth's atmosphere and it is the second most abundant molecule in space. Moreover, CO commonly serves as a benchmark molecule for a high-accuracy absorption line intensity study and for testing the most advanced *ab initio* calculations of its molecular properties, and it has been revealed, that further improvement in the calculations requires also experimental studies of the 6th overtone band of CO. In the submitted dissertation Author presented line intensities measured with high accuracy which, consequently, motivated new *ab initio* calculations performer by Author collaborators from the University College London, UK (group of prof. Oleg Polyansky).

In its structure, the PhD dissertation of Mr. Balashov consists of: very useful list of notations and abbreviations used throughout the text, abstract (in English and in Polish), table of contents, introduction, five chapters (1-5), four appendices (A.1-A.4), list of Author's publications (including that comprising the dissertation published in The Journal of Chemical Physics) and bibliography containing of 109 records.

Allow me now go through the dissertation chapter by chapter.

In the introduction Author presents a detailed motivation for the experimental investigation of the 6th overtone band of CO. The motivation is juxtaposed with a very general overview of the perspective of remote sensing of gases in the context of composition of Earth's atmosphere, composition of interstellar media and molecular clouds, monitoring of greenhouse gases and climate change. The overview is supported by a number of well-chosen references. Moreover, the Author argues that the experimental studies of CO have to be confronted with a physically justified theoretical model that allows to calculate potential energy curves (PEC), dipole moment curves (DMC) and, ultimately, spectra that have been recorded. In case of CO, the experiment-to-theory comparison has its own history adequately illustrated by Author with appropriate bibliography and comparison with studies of a simple molecule such as H_2. The introduction concludes with the goal of the dissertation which is the first measurement of (7-0) overtone transitions in CO which is highly sensitive to small

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changes in PEC and/or DMC posing excellent object to above-mentioned experiment-to-theory confrontation.

Chapter one is devoted to the chosen measurement technique which should assure not only measurement of very weak transitions (for CO 6th overtone it is $1\text{-}5\cdot10^{-30}$ cm/molecule) but also to provide quantitative information on their intensities and line-shape parameters. In this context Author describes two techniques: the cavity ring-down spectroscopy (CRDS) which can be employed to register line intensities as low as $1.5\cdot10^{-31}$ cm/molecule, and the cavity mode width spectroscopy (CMWS) which is less sensitive to low absorption than the CRDS but has a wider dynamic range of absorption measurement and was used by Author in a testing phase (for estimation of the nonlinearity of the detection system).

In chapter two experimental setup is presented. Its main components are: the absorption cell with an elaborated system of maintaining and controlling a given temperature, a system of controlling length of the absorption cell, and frequency-controlled optical setup. Here, Author describes frequency measurements and tests of the ring-down time measurements. Author emphasizes the fact that the CRDS setup was modified to accommodate measurements of extremely weak transitions by decreasing the noise level and improving the sensitivity of the detection. During the experiment, precise and reliable measurement of the optical frequency across the 6th overtone band spectrum of CO was secured with an optical beat note between frequency of the probe laser and the optical frequency comb. The frequency measurement was referenced to Coordinated Universal Time that was transmitted to the laboratory from the Space Research Centre of Astro-Geodynamic Observatory of the Polish Academy of Sciences in Borówiec. Author describes carefully performed extensive tests of the optical setup, including probe laser beam extinction ratio by AOM, beat note between the probe laser and the comb stability observations and linearity of the detection system.

Chapter three is devoted to analysis of the experimental spectra consisting of losses in the cavity caused by absorption in gas and self-losses constituting a base-line. The process includes analyses of: the line profile, the experimental data and the apparatus function. Here, Author describes and examines a variety of ways of describing spectral line profiles recorded that allow to include an influence of different description parameters such as collisional (e.g., phase-changing collisions) and Doppler (e.g., speed-dependent effects) broadenings, pressure broadening, line mixing and temperature dependence. Author lists Lorentzian, Gaussian, Voight, speed-dependent Voigt profiles, Dickie narrowing, Galatry, Nelkin-Ghatak, and Hartmann-Tran profiles, and evaluates them as possible ways to describe line profiles of the measured transitions. Moreover, Author states that to retrieve values of spectroscopic parameters a multi-dimensional optimization has to be used while the line profile has to be chosen with respect to the experimental conditions, the data signal-to-noise ratio and the condition that ratio of the collisional (Γ_0) and Doppler (Γ_D) widths has to span from $\Gamma_0/\Gamma_D << 1$ to $\Gamma_0/\Gamma_D >>1$.

In chapter four measurements and results are presented and discussed. Results of the first measurements of (7-0) absorption band of main CO isotopologue (which one?) is presented with detail. Fifteen rotational lines in the band were chosen in such a way that they cover a broad range of J'' (mostly belonging to P-branch) and that they omit strong spectral transitions of H_2O and oxygen (O or O_2?; it is not clear here; it is partly clarified later). The measurements were performed for several pressures of the gas in the absorption cell. Pressure-broadened lines belonging to R-branch were not included in the measurements and analysis. As the measured spectrum is very weak, Author took a great care to correctly determine the spectra baseline representing losses that are not related to absorption in the gas. To represent the line profile, a speed-dependent Voigt profile with quadratic approximation of speed dependence was chosen as it provided the best results as far as reliability of the determined line-shape parameters are concerned. The line profiles are supplemented with a very detailed uncertainty budget for P10 line-profile parameters as an example, which proves reliability of the obtained results. Finally, in Tables 4.2 and 4.3 Author collects line-shape parameters obtained for all measured lines. Author compares own results with those available in HITRAN2020 database (semiempirical calculation of Li et al. (Ref. [50]), and with those of theoretical study performed by Medvedev and Ushakov (Ref. [104]) and obtained in group of prof. Oleg Polyansky (Ref. [106]) proving an increasing consistency of experiment-to-theory relation.

Finally, chapter five presents conclusions. Here, Author, in a concise way, summarizes the work performed and the results obtained and analysed emphasizing that, among others:

- the CRDS spectrometer has been adequately modified to work in a visible range (687-707 nm) and to achieve requested sensitivity and active temperature stabilization in order to measure for the first time the very weak 6^{th} overtone band in CO;
- the rotational lines of 6^{th} overtone band of CO have been recorded near 690 nm;
- the line profiles were analysed beyond the Voigt profile approximation;
- the reliability and the uncertainty estimation of the determined line parameters has been increased;
- the speed-dependence effects have been observed and analysed for the first time for such a weak transition;
- the high-accuracy experimental results inspired new *ab initio* calculations that are part of a model that would give a possibility of predicting line intensities of all bands of a given molecule.

Concluding chapter five, Author specifies which parts of the whole endeavour have been made with his participation convincing of his dominant role in the project.

After this overview of the dissertation several questions, doubts and necessity for clarification arose.

- It is my feeling that in abstract as well as in introduction Author does not sufficiently argued why the experimental studies of the 6^{th} overtone band of CO had not been done before in spite of the fact that it is located in a spectroscopically “convenient” spectral region (near 690 nm); please clarify.

- In introduction (page 15) there is a definition of υ and J quantum numbers that are assigned to the lower and upper level of the vibrational and rotational transitions, respectively; it is my impression that υ'' and υ' were defined for the upper and lower levels, respectively while J'' and J' were defined the other way around, for the lower and upper levels, respectively; please explain and/or clarify.
- In Chapter 4 (page 47) there is nothing mentioned on the isotopic composition of carbon monoxide and isotopologue of which spectrum was recorded except a statement that it was the main carbon monoxide isotopologue; please clarify.
- In Chapter 4 (page 47) Author mentioned strong oxygen lines that can interfere with the (7-0) band of CO recorded in the experiment; is it atomic oxygen (O) or molecular oxygen (O_2) that is mentioned there?; please clarify.

Below, I made several remarks (also critical ones) concerning the editorial work and the way how the dissertation was presented.

Certain remarks with respect to bibliography:

- in Ref. [26], in the title, name of planet Mars should start with a capital letter M;
- in Ref. [29], names of authors should be written as “Wang C. and Sahay P.”;
- in Ref. [45], in the title, the name of the database should be written with capital letters HITRAN;
- in Refs. [59] and [61], an initial of Śliwczyński is missing, should be “Śliwczyński Ł.”;
- in Ref. [62], according to the adopted convention all first names should be written with initials only;
- in Ref. [96], in the title, carbon monoxide symbol should be written with capital letters CO;
- in Ref. [98], in the title, the wavelength units should be “μm” not “m”;

Some remarks with respect to terminology and nomenclature:

- page 17: according to Ref. [45], “value of the transition” should be replaced with “value of the intensity”;
- page 34: “spectrum of the gas” is somewhat inaccurate, as it is later referred to molecules only: “spectrum…of allowed transitions of the molecules”;
- page 62: in Fig. 4.8 and in the figure caption “Medvedev et al.” should be replaced by “Medvedev and Ushakov”.

General remark with respect to the dissertation as a whole. Despite of the above critical minor remarks, the dissertation of Mr. Balashov has been written very carefully with attention to detail as far as the content as well as figures and tables are concerned. The content, despite it is written not in Author’s mother tongue, is understandable for the Reviewer who’s English is not mother tongue as well. Figures and tables have been prepared and edited with great care being very good illustration of the dissertation content.

Summarizing, I believe the PhD dissertation of Mr. Aleksandr Andreevich Balashov entitled „*High-resolution spectroscopy of the 6th overtone band of carbon monoxide*” presents a high scientific value, taking into account the scientific problem posed, the method of its solution, the experimental work performed and the results achieved. The dissertation is a significant contribution to the development of spectroscopic research of carbon monoxide also from the theoretical side, and it fills gaps in databases of spectroscopic constants.

The minor critical remarks presented above, listed out of the Reviewer’s obligation, do not diminish my very good assessment of the PhD dissertation. Hereby, I confirm that PhD dissertation of Mr. Aleksandr Andreevich Balashov entitled „*High-resolution spectroscopy of the 6th overtone band of carbon monoxide*” fulfils requirements of *The Law on Higher Education and Science* of July 20, 2018 on academic degrees and academic titles and on degrees and titles in the field of art (Article 187, item 1 and 2), and, therefore, I apply for an admission of Mr. Aleksandr Andreevich Balashov for further stages of the defence of his PhD dissertation.

Podpisany elektronicznie przez
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Kraków, September 6, 2023