1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)

Project title:

Cavity enhanced spectroscopy of the molecular oxygen

1.1. Project goals

This project is aimed to an investigation of the molecular oxygen spectrum. The use of spectroscopic techniques utilizing high finesse optical cavity will allow for accurate determination of the spectral parameters of weak molecular transitions. As a result the collection of very accurate data for line positions, intensities and other line shape parameters will be developed, which can be used for the fundamental research and applications. Such data would be valuable for compilation of new generation spectroscopic databases and for improving molecular constants.

1.2. Outline

The knowledge of accurate spectroscopic parameters is very important in the remote sensing for high-accuracy measurements of atmospheric greenhouse gases (GHG) such as CO_2, CH_4, N_2O and others. It is equally important to know the spectroscopic parameters for oxygen molecule, since oxygen lines are often used as a reference for intensity calibration of atmospheric spectra recorded by ground-based or satellite instruments due to the uniform mixing of oxygen throughout the atmosphere. For instance, Total Carbon Column Observing Network (TCCON) is a worldwide network of ground-based Fourier Transform Spectrometers which record direct solar spectra in the near-infrared to measure GHGs. Airmass column calibration in the TCCON is obtained exclusively from the spectra of the 7885 cm^{-1} oxygen band. TCCON data are essential for validating satellite observation and carbon cycle modeling. Both validations require accuracy of 0.3% on TCCON GHGs column retrievals. However, the current accuracy is only around 1-2% and additional aircraft calibration is required to realize the 0.3% accuracy. A significant part of the uncertainties related to TCCON retrieval is associated with available accuracy of spectral line data of O_2. Data available in the HITRAN database, which is the main database for atmospheric purposes, mostly come from calculations and present large uncertainties. Also, laboratory data are mainly limited to center frequencies and intensity factors, resulting from the analysis of FTIR spectra by means of the Voigt line-shape model.

Experimental data will be collected using the frequency-stabilized cavity ring-down spectrometer (FS-CRDS) linked to the optical frequency comb which is currently one of the most sensitive and widely recognized methods for trace gas detection and precise measurements of weak absorption spectra. Two other techniques in the high finesse cavities, i.e. CMWS (cavity mode-width spectroscopy) and CMDS (cavity mode-dispersion spectroscopy), which are complementary to CRDS, has been developed in our laboratory recently. CMWS is based on the measurement of the cavity mode width, while CMDS relies on measurement of the cavity mode shift due to sample dispersion.

An important part of this project is the data analysis which employs multispectrum fitting technique, that is the simultaneous fitting of spectra acquired in a range of parameters such as pressure and/or temperature. To fit high quality experimental data the advanced line-shape models taking into account speed-dependent and Dicke-narrowing effects as well as correlations between velocity-changing and dephasing collisions will be used.

1.3. Work plan

Introduction to cavity ring-down spectroscopy and other cavity enhanced methods
Methodology of the multispectrum data analysis and interpretation.
Experimental study of oxygen spectra.
Data analysis using advanced line-shape models to provide a set of high accuracy spectroscopic data.

1.4. Literature

A. Cygan et al. *Precise cavity enhanced absorption spectroscopy*, Journal of Physics Conference Series Volume: 548, Article Number: 012015 (2014).

J. Tennyson, et al., *Recommended isolated-line profile for representing high-resolution spectroscopic transition* (IUPAC Technical Report). Pure Appl Chem 86, 1931-43 (2014).

J. Domysławska, et al, *Line-shape analysis for high J R-branch transitions of the oxygen B band,* J. Quant. Spectrosc. Radiat. Transf. **242,** 106789 (2020).

1.5. Required initial knowledge and skills of the PhD candidate

- MSc in physics, chemistry or related field ,
- knowledge of optics, atomic and molecular physics, laser spectroscopy, electronics and numerical methods at the level equivalent to basic university courses,
- programming skills in at least one programming language ,
- good command of English language,
- motivation for research work and teamwork skills.

1.6. Expected development of the PhD candidate's knowledge and skills

PhD student will learn the advanced high sensitivity and high resolution experimental technique using the state-of-the art instrumentation together with advance theory for atomic and molecular interactions and theory of spectral line shapes. Also the extensive knowledge of LabView programming and data analysis at advanced level will be the outcome.