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

Project title:
Highly-accurate molecular spectroscopy for atmospheric and fundamental studies

1.1. Project goals

- Development of the cavity-enhanced spectrometer with the frequency axis linked to the primary frequency standard
- High-resolution study of visible and near-infrared transitions of small molecules such as CO, O_2, H_2, CO_2 with the use of advanced theoretical line-shape models

1.2. Outline

High-quality data on molecular spectral line shapes are crucial in metrological, atmospheric, astrophysical as well as fundamental studies. Many of these applications have very strict requirements for data accuracy. The satellite-based monitoring of greenhouse gases concentration, conducted by ESA, NASA and JAXA, i.e. European, US and Japanese space agencies, already needs sub-percent accuracy of reference laboratory data [1]. Satellite measurements in the atmosphere enable studies on e.g. global warming, climate zones shifting and increasing severity of weather phenomena. Validation of the quantum electrodynamics (QED) predictions [2] and searching for the new physics beyond the Standard Model [3] require experimentally determined H_2 transition frequencies with at least 10 significant digits. In modelling of exoplanets atmospheres the completeness of global theoretical fits of line-shape parameters for more complex molecules requires inclusion of - usually very weak - transitions from higher overtones [4].

To reach project goals the state-of-the-art spectrometer enabling a high-resolution molecular line-shape study with the frequency axis linked to the primary frequency standard will be developed by the PhD student. In order to retrieve very accurate spectroscopic data three ultra-sensitive cavity-enhanced techniques will be used: well established cavity ring-down spectroscopy (CRDS) [5], cavity mode-width spectroscopy (CMWS) [6], and developed in our research group cavity mode-dispersion spectroscopy (CMDS) [7]. The last technique is based solely on the measurement of the frequency, i.e. the physical quantity currently determined the most accurately, and has the potential to become the most accurate of all absorption and dispersion spectroscopic methods [8].

On the other hand, the line-shape parameters can be provided by the theoretical ab initio calculations of collisional effects. However, only for the simplest systems, like H_2, full set of the parameters may be obtained with good accuracy. For more complex ones, such as CO and CO_2, mainly for line intensities first successful attempts have been presented with sufficient accuracy. Such calculations need to be verified with high-quality laboratory measurements, which will be done in the project within our collaboration with world-leading theoretical groups from University College London and Universite de Rennes. The feasibility of joint experimental and theoretical approach to the line intensity determination was recently verified at the promille level [9], which fulfils present requirements of the remote sensing of the Earth's atmosphere.

The precise and accurate study of molecular spectral lines requires proper description in terms of line-shape profiles [10]. The PhD student task will be the data analysis using sophisticated line-shape models including e.g. the speed dependence of collisional width and shift and Dicke narrowing. In case of molecular hydrogen, the PhD student task will also be a very accurate comparison of spectral line shapes with the theoretical predictions form the first principles of quantum mechanics. Here another goal is the determination of the line positions with sub-MHz uncertainties which will allow the tests of QED for molecules at an unprecedented level of accuracy.
Theoretically supported lists of retrieved experimentally line-shape parameters, which are needed for spectra modelling, will be incorporated into existing and new generation spectroscopic databases like the most popular HITRAN database.

1.3. Work plan

- Development of cavity enhanced spectrometer
- Measurements of molecular spectra
- Line-shape analysis of measured spectra

1.4. Literature *(max. 10 listed, as a suggestion for a PhD candidate)*

[1] C. E. Miller et al., C. R. Physique 6, 876 (2005).
[2] J. Komasa et al., Phys. Rev. A 100, 032519 (2019).
[3] W. Ubachs et al., J. Mol. Spectrosc. 320, 1 (2016).
[4] G. Li et al., Astrophys. J. Suppl. Ser. 216, 15 (2015).
[5] A. O'Keefe, D. A. G. Deacon, Rev. Sci. Instrum. 59, 2544 (1988).
[6] A. Cygan et al., Opt. Express 21, 29744 (2013).
[7] A. Cygan et al., Opt. Express 23, 14472 (2015).
[8] A. Cygan et al., Opt. Express 27, 21810 (2019).
[9] K. Bielska et al., Phys. Rev. Lett. 129, 043002 (2022).
[10] H. Tran et al., J. Quant. Spectrosc. Radiat. Transfer 129, 199 (2013).

1.5. Required initial knowledge and skills of the PhD candidate

Knowledge of optics, electronics, spectroscopy, atomic and molecular physics at the level corresponding to standard undergraduate university courses. Experience in construction of experimental optical systems and/or spectral line-shape analysis is welcome. Skills and experience in programming (Labview/Mathematica/C++/Fortran) and numerical methods will be an additional advantage. Teamwork ability and high motivation for research work. Good command of the English language.

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

Knowledge, skills and experience in development of cavity-enhanced spectrometers and high-sensitive experimental techniques (CRDS, CMWS, CMDS). Knowledge of molecular spectroscopy, spectral line-shape theories and numerical methods. Preparation for writing scientific articles and setting experimental goals. Development of skills needed in international collaboration with experimental and theoretical groups.