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. 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 and searching for the new physics beyond the Standard Model require experimentally determined H_2 transition frequencies with at least 10 significant digits. In modelling of exoplanets atmospheres, including searching for extra-terrestrial life, the completeness of global theoretical fits of line-shape parameters for more complex molecules requires inclusion of - usually very weak - transitions from higher overtones.

In the project the state-of-the-art, high-resolution ultra-sensitive spectrometer based on cavity-enhanced techniques will be developed. Here variety of techniques could be used based on absorption and resonant dispersion measurement, from well-established cavity ring-down spectroscopy (CRDS) through purely frequency-based cavity mode-dispersion spectroscopy (CMDS) to recently developed in our research group heterodyne CRDS.

The details of the molecular spectra might be obtained from the theoretical ab initio calculations of collisional effects. However, only for the simplest systems, like H_2, full set of the spectral line-shape 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, which fulfills present requirements of the remote sensing in the Earth's atmosphere.

The precise and accurate study of molecular spectral lines requires proper description in terms of line-shape profiles. The data analysis should be performed using sophisticated

line-shape models including e.g. the speed dependence of collisional width and shift and Dicke narrowing. Wherever possible (mainly for H_2) the theoretical predictions from the first principles of quantum mechanics will be verified, including 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. 7 listed, as a suggestion for a PhD candidate preliminary study)*

[1] P. F. Bernath, Phil. Trans. R. Soc. A. **372**, 20130087 (2014).

[2] G. Li et al., Astrophys. J. Suppl. Ser. **216**, 15 (2015).

[3] W. Ubachs et al., J. Mol. Spectrosc. **320**, 1 (2016).

[4] A. Cygan et al., Opt. Express **27**, 21810 (2019).

[5] K. Bielska et al., Phys. Rev. Lett. **129**, 043002 (2022).

[6] L. Gianfrani et al., Riv. Nuovo Cim. **47**, 229 (2024).

[7] A. Cygan et al., Sci. Adv. **11**, eadp8556 (2025).

1.5. Required initial knowledge and skills of the PhD candidate

Knowledge of optics, electronics, 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/Python) 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 enabling work in world-leading groups devoted to various aspects of quantum physics, optics and metrology. Knowledge, skills and experience in development of cavity-enhanced spectrometers and high-sensitive spectroscopic techniques. 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.