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

Project title: Precise and accurate spectroscopy of weak molecular transitions

1.1. Project goals

- Development of the cavity-enhanced spectrometer with the frequency axis linked to the primary frequency standard
- High-resolution molecular line-shape study of near-infrared transitions of CO and HD
- Comparison of experimentally retrieved line-shape parameters with the results of ab initio calculations

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 already needs sub-percent accuracy of reference laboratory data [1]. In case of molecular hydrogen the validation of comprehensive sets of theoretical line-shape parameters [2] or of the quantum electrodynamics (QED) predictions about the transitions frequencies [3] requires experimental values determined with at least 0.1% level accuracy or 10 meaningful digits, respectively. 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 address these problems in this PhD project a joint experimental and theoretical study is planned.

To reach this goal from experimental point of view the state-of-the-art spectrometer to enable a high-resolution molecular line-shape study with the frequency axis linked to the primary frequency standard will be developed. 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 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 accurate, and has the potential to become the most accurate of all absorption and dispersion spectroscopic methods.

In case of the molecular target, carbon monoxide, the comparison of measured line intensities with the results of ab initio calculations performed by our partners from the theoretical molecular spectroscopy group at University College London will be done. The precise and accurate study of CO spectral lines, which will be done for the first time, requires proper description in terms of line-shape profiles [8]. The PhD student task will be the data analysis of these transitions using a sophisticated line-shape model including e.g. the speed dependence of collisional width and shift and Dicke narrowing. Moreover, other line-shape parameters, like line position or collisional width and shift, will be provided to support environmental and atmospheric research.

In case of the second target, molecular hydrogen, spectral line shapes are strongly influenced by the collisional effects which makes them untypical and difficult to be modelled. Here the PhD student task will be a very accurate comparison of spectral line shapes with the theoretical predictions form the first principles of quantum mechanics. The quantum scattering calculations based on highly accurate potential energy surface will be done together with recognized theoretical group from Universite de Rennes. 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.

Retrieved, experimentally supported theoretical list of 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

- Construction of cavity enhanced spectrometer
- Measurements of CO and HD spectra
- Line-shape analysis of CO and HD spectra

1.4. Literature

[1] C. E. Miller et al., C. R. Physique **6**, 876 (2005).

[2] K. Stankiewicz et al., J. Quant. Spectrosc. Radiat. Transfer **254**, 107194 (2020).

[3] J. Komasa et al., Phys. Rev. A **100**, 032519 (2019).

[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] H. Tran et al., J. Quant. Spectrosc. Radiat. Transfer **129**, 199 (2013).

1.5. Required initial knowledge and skills of the PhD candidate

Good knowledge of optics, electronics, spectroscopy, atomic and molecular physics. 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. 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 construction of cavity-enhanced spectrometer and high-sensitive experimental techniques (CRDS, CMWS, CMDS). Knowledge of molecular spectroscopy, spectral line-shape theories and numerical methods.