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

Project title: High-accuracy optical spectroscopy of absolute isotope ratios in greenhouse gases

1.1. Project goals

The goal of this PhD project is to improve the accuracy of absolute isotopic ratio measurements in greenhouse gases by (i) developing new high-accuracy frequency-based optical spectroscopy methods, (ii) high-accuracy spectroscopic measurements of the line intensities of CO_2, CO and CH_4 isotopologues, which will also be used to verify high-accuracy *ab initio* line intensity calculations, and (iii) demonstrating absolute isotope ratio measurements with sub-‰ level accuracy. A database of accurate line intensities, combined with the high-accuracy optical spectroscopy methods developed in our laboratories, will help establish new optical standards for absolute isotope ratio measurements. The project will also have an impact on other fields using accurate spectroscopy, such as quantum-electrodynamic tests in simple molecular systems (such as D_2, HD), optical thermometry, and the development of new optical standards of reference gases.

1.2. Outline

Stable isotope ratio measurements are crucial for many fields of science, allowing the identification of the sample's origin and its transformation. They occupy a special place in atmospheric research and climate change monitoring, providing an effective method for detecting the sources and sinks of greenhouse gases. In this field, there are the highest requirements for interlaboratory comparability of isotope measurements, reaching the level of 0.1‰. Although commonly used mass spectrometry techniques enable measurements of relative isotope ratios with precision up to 0.01‰, the achieved combined uncertainties of the absolute isotope ratios are no better than 1–2‰ [1]. The main problems in absolute isotope ratio studies result from statistical uncertainties of the used reference absolute isotope ratios, uncertainties introduced by multi-step calibrations of mass spectrometers against metrological standards, and exhaustion of reference materials or their unstable composition over time. For example, the Vienna PeeDee Belemnite reference scale [2] used to study isotopes of the most important greenhouse gases has shown a systematic deviation of -11‰ over the past 67 years. The lack of alternative techniques for independent measurement of absolute isotope ratios has hampered further development of this field. It is now becoming obvious that the only way to make progress and ensure global consistency in stable isotope research is to enable traceability of isotope ratio measurements to the International System of Units (SI) [3]. As a result, some efforts have already been made to develop and characterize new certified reference materials. An alternative is to develop SI-traceable methods for direct measurement of absolute isotope ratios, which bypass the need for reference materials and complex calibrations against them. In the latter case, ultrasensitive optical spectroscopy techniques now show great potential, as significant progress has recently been made in their accuracy [4]. Their main advantages are simple, lowcost systems enabling in-situ monitoring, spectroscopic selectivity and possible calibration-free absolute measurements of isotopologues concentrations based on known spectral line intensities [1]. Unfortunately, the vast majority of optical isotope analyzers need calibration against reference isotope ratios because the commonly used light intensity detection systems are prone to systematic errors and the line shape analysis is usually treated in a simplified way. Our team specializes in developing dispersive optical spectroscopy methods [4,5] that rely solely on accurate frequency measurements rather than light intensity detection, so they can be also easily related to frequency standards. These methods have recently demonstrated sub-‰ accuracy in line intensity measurements of the main isotopologue CO, supported by best *ab initio* results of similar accuracy [6]. In addition, our recent improvements and planned improvements within the project in the accuracy of the cavity ring-down spectroscopy [7], a common method used in laboratory and commercial optical isotope analyzers, should contribute to improving the quality of isotope studies conducted using them.

1.3. Work plan

- Development of high-accuracy spectroscopy methods (building of necessary optical and electrical systems, implementation of heterodyne detection with the use of cw and comb-based laser systems, performing numerical calculations and simulations, writing measurement software)
- Measurements and analysis of spectra of isotopologues of greenhouse gases (control of the measurement procedure, acquisition and analysis of experimental data, preparation of the uncertainty budget, comparison of results with literature data).
- Presentation of results including publications and conference presentations
- PhD thesis preparation

1.1. Literature *(max. 7 listed, as a suggestion for a PhD candidate preliminary study)*

[1] A. J. Fleisher, et al., Nature Phys. 17, 889 (2021).

[2] A. Srivastava, R. M. Verkouteren, Anal. Bioanal. Chem. 410, 4153 (2018).

[3] G. Skrzypek, et al., Rapid Commun. Mass Spectrom. 34, e8890 (2020).

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

[5] A. Cygan et al., Opt. Express 23, 14472 (2015).

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

[7] A. Cygan et al., Science Advances 11, eadp8556 (2025).

1.2. Required initial knowledge and skills of the PhD candidate

Knowledge of optics, spectroscopy, atomic and molecular physics. Good skills and experience in numerical methods and programming (preferred Labview, Mathematica, Fortran, Python). Mathematical skills in theoretical calculations. Experience in laboratory work is desirable, especially in building and using optical laser-based systems. Independence at work is welcome. High commitment to work and excellent problem-solving skills. Written and verbal communication and presentation skills (including English). Teamwork skills.

1.3. Expected development of the PhD candidate’s knowledge and skills

Knowledge, skills, and experience in laboratory work: building electro-optical systems (especially cavity-enhanced spectrometers), techniques of phase and intensity modulation of light, techniques of laser frequency stabilization, experimental techniques of molecular spectroscopy. Good knowledge of molecular spectroscopy, theoretical skills in description of interactions of light with molecules and with optical cavity. Skills in programming and numerical methods. Experience in finding solutions, making hypotheses and formulating final conclusions. Presentation skills, including research papers and conference presentations.