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

Project title: Collision-induced quantum effects in spectra of atmospheric molecules

1.1. Project goals

Research of the Earth's atmosphere and climate changes sets new challenging requirements for knowledge of fundamental quantum interactions between molecules and light in the presence of molecular collisions. In atmospheric gas pressure and temperature conditions, well-defined optical frequencies corresponding to transitions between quantum states of molecules are strongly affected by molecular collisions, which complicate the interpretation of absorption spectra observed by satellite or ground-based instruments, but also provide additional information on observed system. In particular, lines broaden and shift their central frequencies. Moreover, the shape of their spectra changes, and the collision-induced changes of energy states involved in optical transitions can modify line intensities distribution in the molecular band. These fundamental quantum effects must be understood and described accurately for molecular systems of interest to exploit modern satellite- and ground-based optical systems for global monitoring of the Earth's atmosphere developed by space agencies worldwide (NASA, ESA, JAXA). The ability to remotely detect sources and sinks of major greenhouse gases at global and local scales requires promille accuracy of absolute line intensities and a complete model of collisional spectra. Together, they enable accurate retrieval of concentrations of particular molecules from multi-species atmospheric spectra. The current state-of-the-art reference data are often an order of magnitude less accurate. In these applications, basic research quantifying molecular collisions' role in forming spectral line shapes at various physical conditions is crucial for interpreting measurements from ground- and satellite-based spectrometers. Similar or even higher accuracies are needed for the realization of optical gas amount, concentration, and temperature standards, which, after the recent SI redefinition, allows greater flexibility in linking fundamental constants to measurable quantities and developing new optical standards.

1.2. Outline

The project will focus on laboratory measurements of line intensities, spectral line shapes, and their temperature dependences for CO_2 and N_2O bands near 1.6 µm. A challenging task is achieving uncertainties of line intensities at the promille level and determining the magnitude of the speed- and temperature dependencies of collisional line shapes. The cavity mode dispersion spectroscopy (CMDS), developed in our laboratory, enables a high dynamic range with immunity to the nonlinearity of the detection system and direct reference of both axes of the spectrum to atomic frequency standard. In this project, we aim to combine our continuous-laser approach's outstanding accuracy with the broadband nature of a frequency-comb-based spectrometer. We will develop a unique spectrometer based on heterodyne cavity ring-down spectroscopy (DC-CRDS) with broadband optical frequency comb as a frequency reference. This approach will provide a parallel measurement of absorption and dispersion spectral lines for cross-comparison and minimization of the spectra uncertainty. The resulting datasets will serve to improve the remote sensing in the atmosphere, validation of ab initio calculations of line intensities and collisional line shapes, and testing applications in optical gas metrology. The tasks will involve collaboration with several groups worldwide and participation in the externally funded research projects.

1.3. Work plan

- Adaptation and testing of CRDS/CMDS spectrometer
- Spectral line shape fitting software development
- Measurement of greenhouse gases molecular spectra
- Spectral data analysis to retrieve line parameters and uncertainties
- Comparison of results with literature and requirements of various applications
- Presentation of the results, including papers and conference presentations
- PhD thesis preparation

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

- D. A. Long, A. Cygan, R. D. van Zee, M. Okumura, C. E. Miller, D. Lisak, J. T. Hodges, "Frequency-stabilized cavity ring-down spectroscopy", Chem. Phys. Lett. 536, 1 – 8 (2012)
- J.-M. Hartmann, H. Tran, R. Armante, C. Boulet, A. Campargue, F. Forget, L. Gianfrani, I. Gordon, S. Guerlet, M. Gustafsson, J. T. Hodges, S. Kassi, D. Lisak, F. Thibault, G. C. Toon, Recent advances in collisional effects on spectra of molecular gases and their practical consequences, J. Quant. Spectrosc. Radiat. T. 213, 178-227 (2018).
- Cygan, P. Wcisło, S. Wójtewicz, G. Kowzan, M. Zaborowski, D. Charczun, K. Bielska, R. S. Trawiński, R. Ciuryło, P. Masłowski, D. Lisak, *High-accuracy and wide dynamic range frequency-based dispersion spectroscopy in an optical cavity*, Opt. Express **27**, 21810-21821 (2019).
- D. Lisak, D. Charczun, A. Nishiyama, T. Voumard, T. Wildi, G. Kowzan, V. Brasch, T. Herr, A. J. Fleisher, J. T. Hodges, R. Ciuryło, A. Cygan, P. Masłowski, *Dual-comb cavity ring-down spectroscopy*, Sci. Rep. **12**, 2377 (2022).
- K. Bielska, A. A. Kyuberis, Z. D. Reed, G. Li, A. Cygan, R. Ciuryło, E. M. Adkins, L. Lodi, N. F. Zobov, V. Ebert, D. Lisak, J. T. Hodges, J. Tennyson, and O. L. Polyansky, *Subpromille measurements and calculations of CO (3–0) overtone line intensities*, Phys. Rev. Lett. **129**, 043002 (2022).
- Cygan, S. Wójtewicz, H. Jóźwiak, G. Kowzan, N. Stolarczyk, K. Bielska, P. Wcisło, R. Ciuryło, D. Lisak, *Dispersive heterodyne cavity ring-down spectroscopy exploiting eigenmode frequencies for high-fidelity measurements*, Science Advances **11**, eadp8556 (2025).
- W. Demtroder, "Laser Spectroscopy", Springer 2008, DOI: 10.1007/978-3-540-73418-5

1.5. 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.

1.6. 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.