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

Project title: Cavity-enhanced two-dimensional spectroscopy with optical frequency combs

1.3. Project goals

- Develop a new approach for studying ultrafast dynamics with optical cavities and frequency combs.
- Obtain new and decisive experimental data on molecular optical coherence diffusion in the gas phase (the Dicke effect).
- Explore applications of this new technique, such as characterization of complex gas mixtures.

1.4. Outline

Time-resolved nonlinear spectroscopy techniques, such as transient absorption spectroscopy and 2D spectroscopy, are routinely used to study ultrafast dynamics [1]. Owing to the limited sensitivity of these techniques, they are most commonly applied to optically thick samples, such as solid and liquid solutions. Using frequency comb lasers and optical cavities one can perform ultrafast optical spectroscopy with high sensitivity, enabling work in dilute gas-phase molecules and clusters. In a recent example, cavity-enhanced transient absorption spectroscopy was used to explain excited-state intramolecular proton transfer in salicylideneaniline and to explain differences between solution-phase optical measurements and gas-phase photoelectron measurements of this system [2]. These results and advances in generation of high-power optical frequency combs in the mid infrared provide a way to perform cavity-enhanced 2D infrared (CE-2DIR) spectroscopy [3].

CE-2DIR spectroscopy will enable tracking of the evolving couplings between molecular vibrational modes and intramolecular degrees of freedom. 2DIR spectroscopy can also be combined with the high resolution of Fourier-transform spectroscopy to enable measurements of the shapes of individual resonances within a single vibrational mode. While collisional damping/dephasing and their correlations with translational motion are most commonly observed in linear spectroscopy, 2DIR spectroscopy will shine a new light on the problem. 2DIR spectroscopy separates inhomogenous from homogenous broadening, which will allow us to decouple various line-shape effects.

1.5. Work plan

Tasks performed in collaboration with other group members: undergraduate students, postdoctoral researcher, supervisors.

- Build a master oscillator and dual difference-frequency generator setups with tunable offset frequencies.
- Prepare measurement setup: pulse delay stabilization, comb-cavity higher-order mode locking, building 2D Fourier-transform spectrometer, etc.
- Measure high-resolution 2DIR CO-Ar line shapes. Perform *ab initio* calculations and compare with experimental data.
- Explore other applications of CE-2DIR spectroscopy as time permits. Write thesis.

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

1. P. Hamm and M. Zanni, Concepts and methods of 2D infrared spectroscopy, 1st ed. Cambridge: Cambridge University Press, 2011.

2. M. C. Silfies, A. Mehmood, G. Kowzan, E. G. Hohenstein, B. G. Levine, and T. K. Allison, The Journal of Chemical Physics, 159, 104304, 2023, doi: 10.1063/5.0161238.

3. T. K. Allison, Journal of Physics B, 50, 044004, 2017, doi: 10.1088/1361-6455/50/4/044004.
4. G. Kowzan and T. K. Allison, J. Phys. Chem. Lett., 13, 11650–11654, 2022, doi: 10.1021/acs.jpclett.2c03331.
5. G. Kowzan and T. K. Allison, Phys. Rev. A, 106, 042819, 2022, doi: 10.1103/PhysRevA.106.042819.
6. G. Kowzan et al., Physical Review A, 102, 012821, 2020, doi: 10.1103/physreva.102.012821.

1.7. Required initial knowledge and skills of the PhD candidate

The candidate is expected to have knowledge and skills of a Master's in physics or technical physics.

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

The candidate will develop knowledge and skills in ultrafast optics, nonlinear optics and spectroscopy, laser stabilization, nonequilibrium statistical mechanics. The candidate will learn practical skills in designing and building optomechanical setups, fiber lasers and fiber amplifiers, vacuum systems and high-finesse optical cavities, experiment control and automation, data acquisition systems, signal processing, data analysis and visualization. The candidate will learn to disseminate their results and communicate science to various audiences.