Conventional FTIR spectroscopy of molecular vibrations in Fabry-Pérot cavities

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Abstract

Infrared radiation is absorbed by molecules when the frequency of the radiation matches dipole-allowed vibrational transitions of the molecule. In this summer program, experiments are carried out to study strong coupling of molecular vibrations (organic solvents: isopropanol; ethanol and mainly CS2) to Fabry- Perot cavity modes. Moreover, it is investigated how the length of the resonator modulates the absorption features of the molecule. Conventional Fourier-transform infrared (FTIR) spectroscopy is used to characterize the molecule-cavity system.

1 Introduction

1.1 Fourier-transform infrared spectroscopy (FTIR)

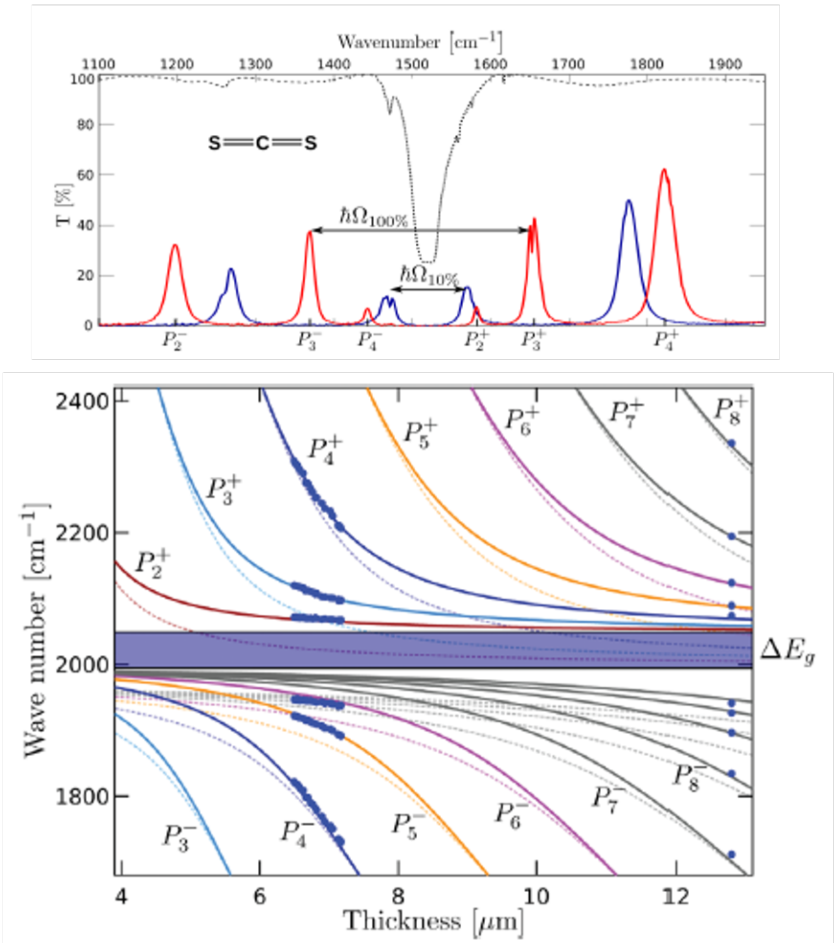
FTIR stands for Fourier Transform Infrared Spectroscopy. It is an optical device to detect infrared spectroscopy. When a broad band infrared radiation is inputted to a sample, radiation of some frequency range will be absorbed by the sample, and some will transmit though the sample. For every different material, a unique infrared spectrum will be generated. This infrared spectrum demonstrates the molecular absorption and transmission, making FTIR an useful device to identify unknown material and determine the purity of a sample.

1.2 Fabry Perot cavity

A Fabry-Perot cavity is an optical cavity that is consisted by a set of mirrors, commonly two plane mirrors with a higher reflection rate and a lower transmission rate. It has very high sensitivity and maximizes response of an optical system due to constructive interference under resonance condition. When the distance of the two mirrors (cavity length) is exactly an integer number of the half wavelength of the input laser, the cavity reaches resonance condition and constructive interference happens inside the cavity. [1]

1.3 Strong coupling

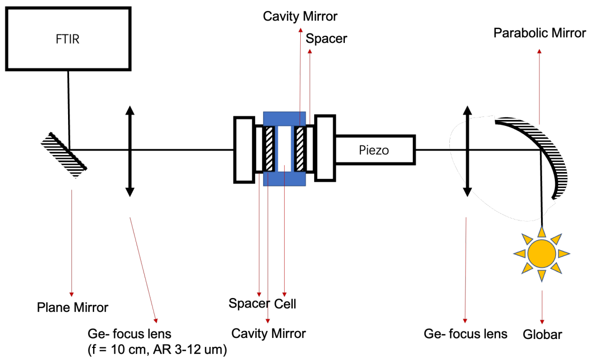
The concept of dressing quantum states with light originates from the quantum optics community [2,3], but has also been applied to more complex solid-state and molecular systems. Recently, hybridizing vibrational transition and modes of an optical resonator has found exciting applications in controlling chemical reactions [4]. Such systems typically consist of a low quality Fabry-Pérot resonator with a length of only a few microns to match a strong dipole-allowed vibrational transition in the mid-infrared.

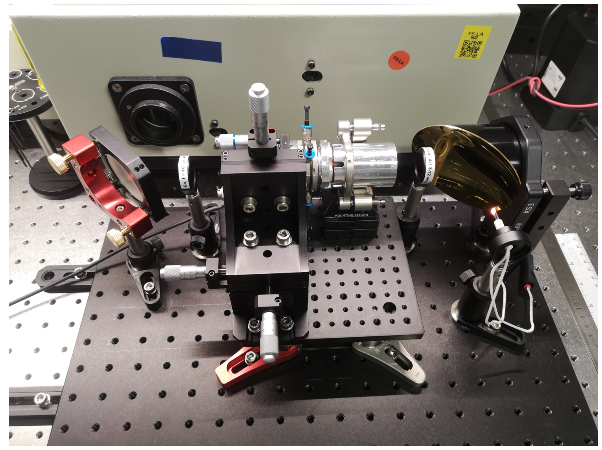


George et al. Phys. Rev. Lett. 117,153601 (2016)

When the transmission of a such a cavity is measured, the optical resonance splits up into two polaritonic modes which are separated in the spectrum by the so-called Rabi-frequency (Figure 1 [5]). This frequency essentially depends on the dipole strength of the vibrational transition and the concentration of the molecules in the cavity [4]. The coupling between the light mode and the molecular transition is called strong when the Rabi splitting is larger than both the width of the vibrational transition and the width of the optical mode. While the former one depends on the choice of the molecule, the latter one is determined by the mirror reflectance and the cavity length.

2 Set up





In this experiment, set up as shown in figure 2 and figure 3 is used to measure the transmission spectrum of the molecule- cavity system. A globar is used as broadband light source. Then light is collimated by a parabolic mirror to irradiate the cavity. Two germanium lenses on two sides of the cavity are used to focus the light into the cavity. In the end, light is guided to FTIR spectrometer by a plane mirror.

2.1 Molecule

CS_2 is used as the molecule inside the cavity because it has a very strong absorption band in IR range around $1500\,\mathrm{cm}^{-1}$. Although being slightly toxic and smelling unpleasant, it is commonly material in infrared spectroscopy and has shown ultrastrong coupling behavior [George2016].

Other organic solvents are also used to fill the cell in order to test certain characteristics of the whole set up.

2.2 Cavity

Figure 1 roughly shows the set-up of the cavity. Cavity mirrors are connected to the metal frame through a 4 mm and a 5 mm thick spacer in order to realise a micrometer scale distance between the two mirrors mechanically. Larger holes are drilled in the center of the spacers so that light is not blocked by the spacers.

One of the cavity mirrors is glued on a piezo, whose length can be adjusted by applying electric voltage, thus enabling cavity length tunability.

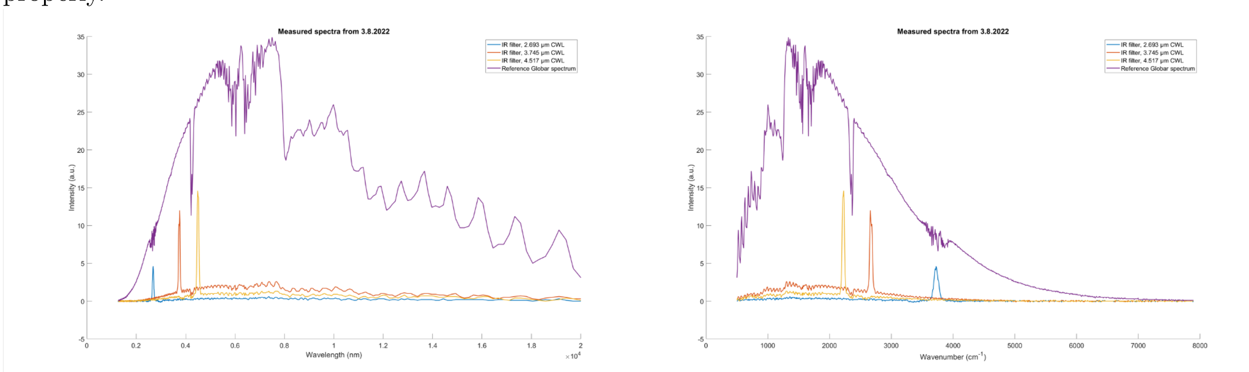
The most important part is that the two cavity mirrors are parallel to each other and have only a very micron-scale distance. They are put inside the cell with two O- rings to seal the cell better. Two CaF2 substrates sputter-coated with 10 nm Au80Pd20 are used as the cavity mirrors in the experiments. 20 percent Pd is mixed with gold to reduce scattering effect of the mirrors.

Crystal bond is used as adhesive, so that the set up is able to be reused easily by fixing different mirrors as cavity mirrors. Under a temperature of around 120 °C, it is convenient to be applied or removed.

3 Measurements and results

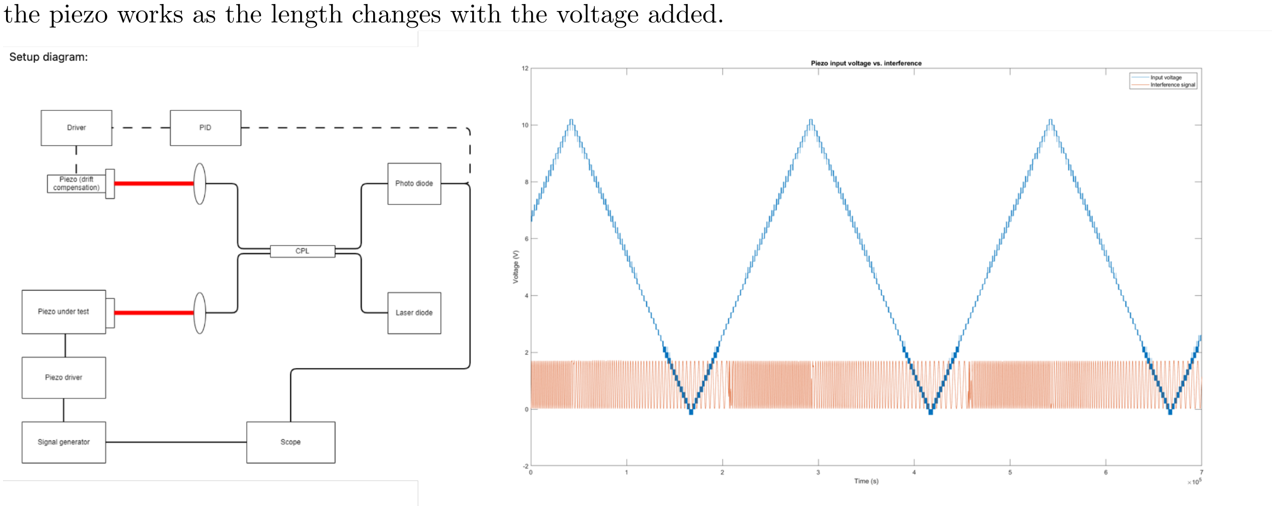
3.1 FTIR tested with IR filters

In order to test the FTIR device, IR filters are put respectively between globar and FTIR. Results are shown in Figure 4. The transmission Spectrum of the three IR filter (2.693 µm; 3.745 µm; 4.517µm) shows transmission peak right at the wavelength of the filters, which indicates that the FTIR functions properly.



3.2 Piezo tested with interferometer

The piezo glued on the metal element is tested with an interferometer shown in Figure 5. A sliver mirror is attached to the piezo and couples the light back to the detector. By tuning the voltage applied to the piezo driver, a changing signal on the interferometer is observed, which indicates that the piezo works as the length changes with the voltage added.

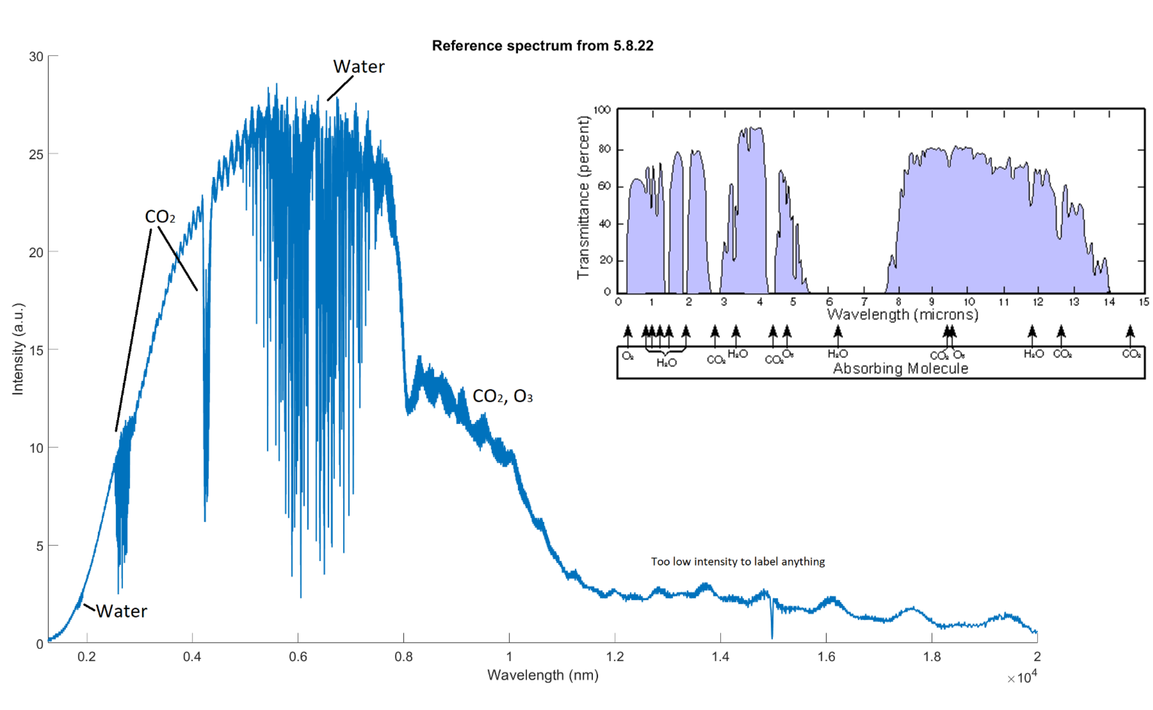


Piezo traveling with varying input voltage is measured to the piezo driver on the setup used for measuring fast piezo bandwidths. A signal generator with low frequency is used to get a 0-10 V output range.

Going up with the voltage, some kind of delay occurs, while going down starts immediately and stops later after the voltage already goes up again. The piezo seems to travel the same way though, in case of the full 0-10 V the controller can do. 42 fringes are observed. after multiplying the number of fringes and wavelength of the laser (1030 nm), 43.26 um is calculated as the largest adjustment length, which is less than 60 um as is expected.

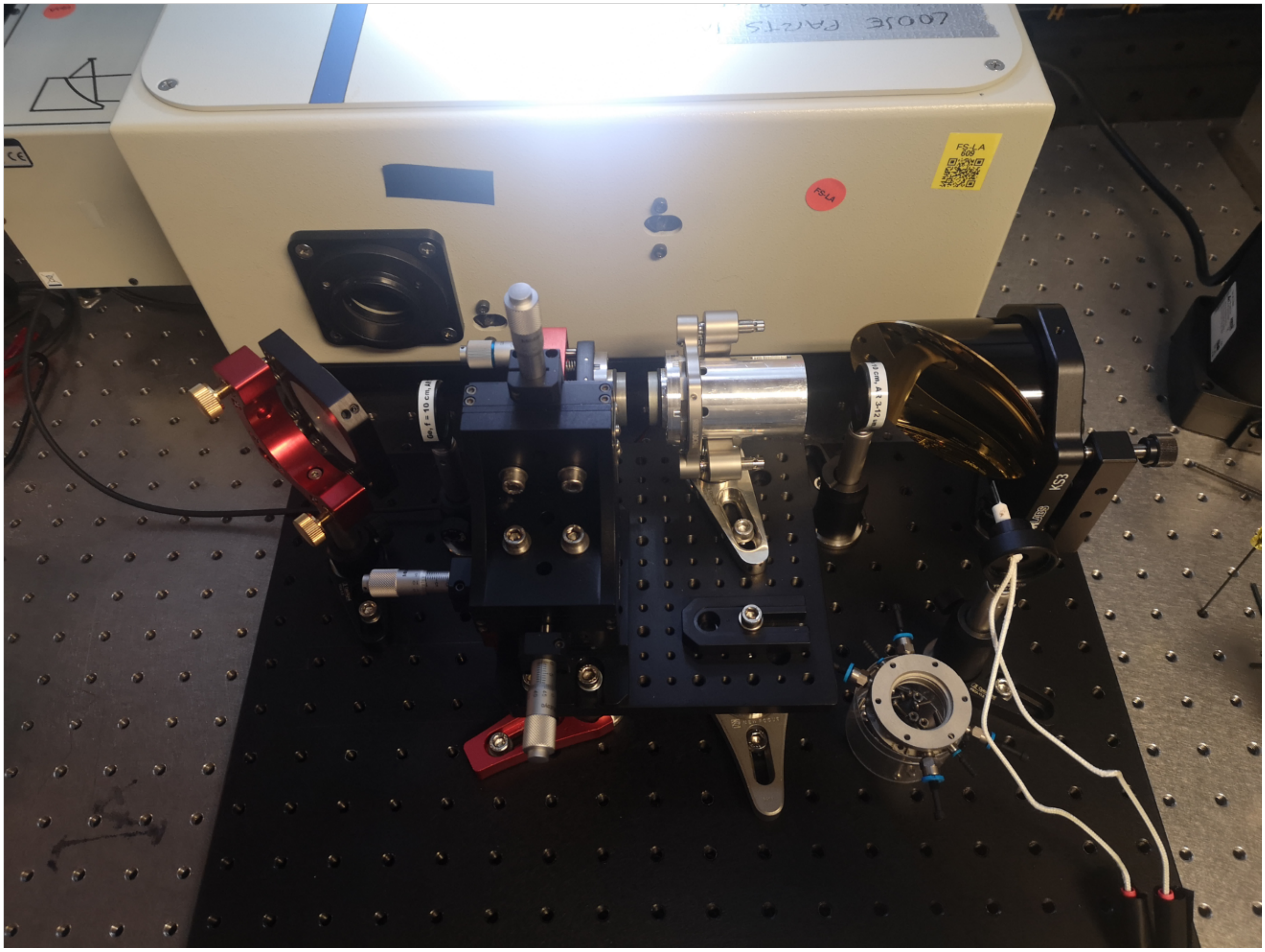
3.3 Main absorption features labeling

A FTIR spectrum of the light emitted by the globar was taken as a reference spectrum. It exhibited typical atmospheric absorption features as shown in Figure 6. [6]



3.4 Tunability testing with uncoated grmanium mirror

After careful alignment, two 6 mm thick germanium substrates are well paralleled with a very small distance in between (Figure 7).



Fringes are observed in the spectrum. The Fourier transform of spectrum data directly reveals the etalon spacing as shown in Figure 8.

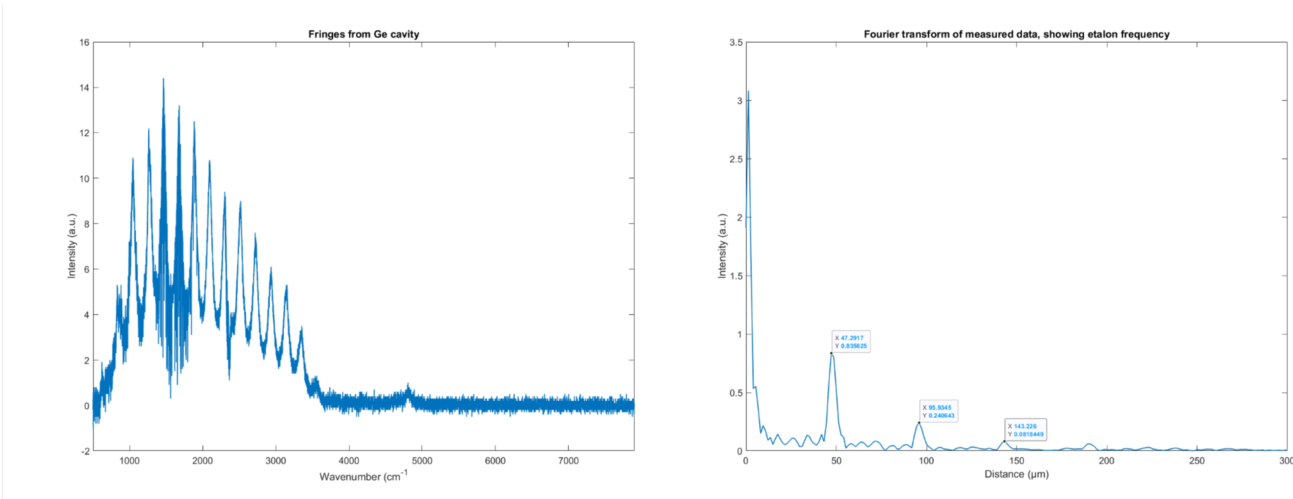
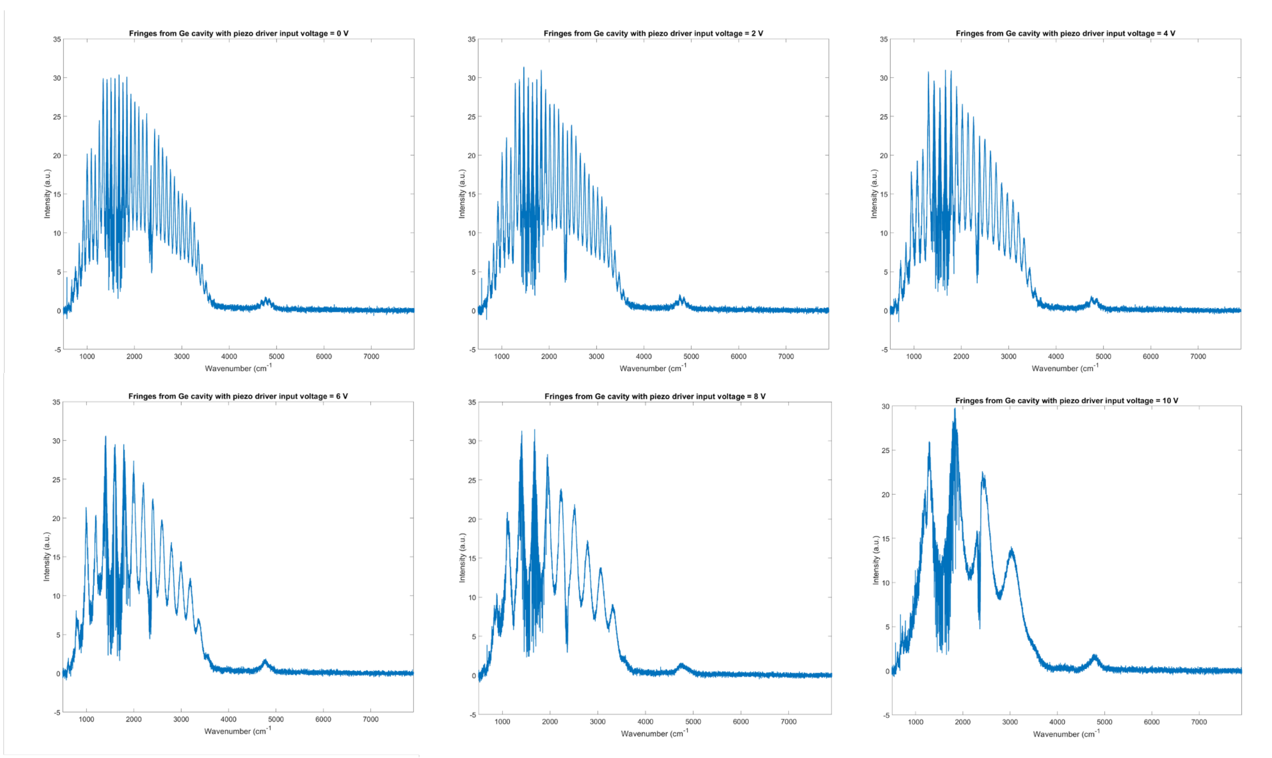
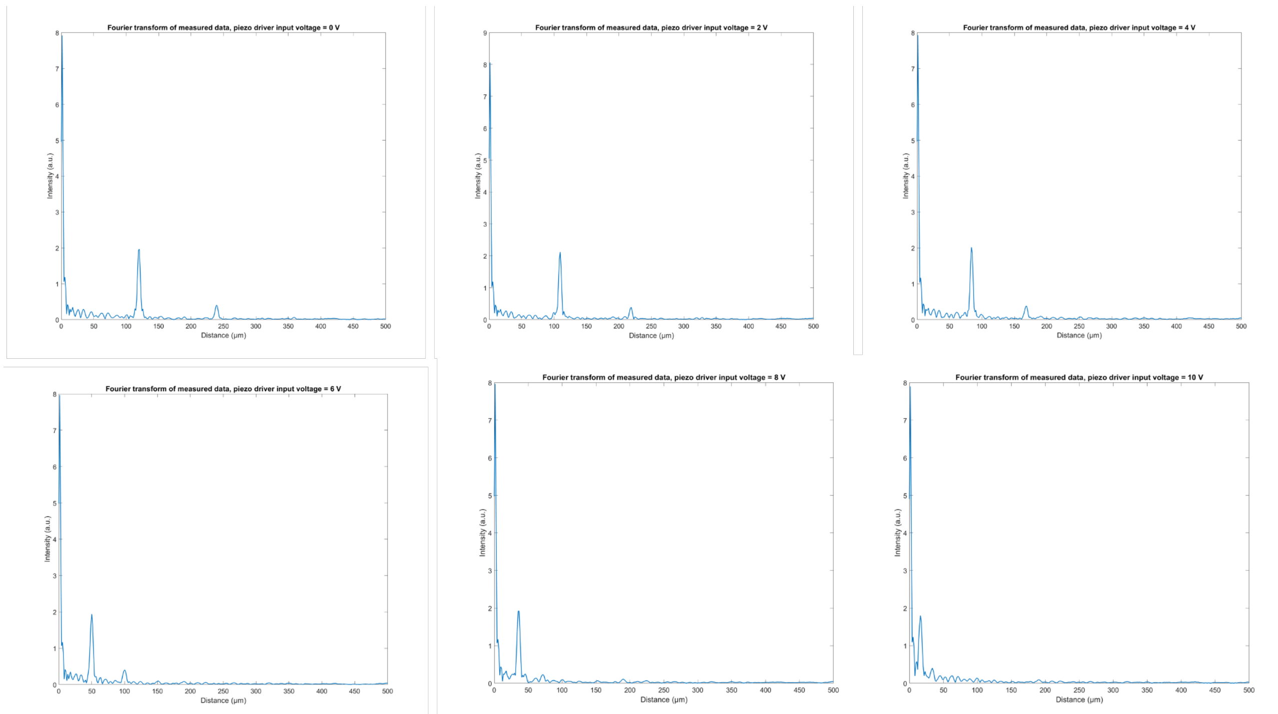
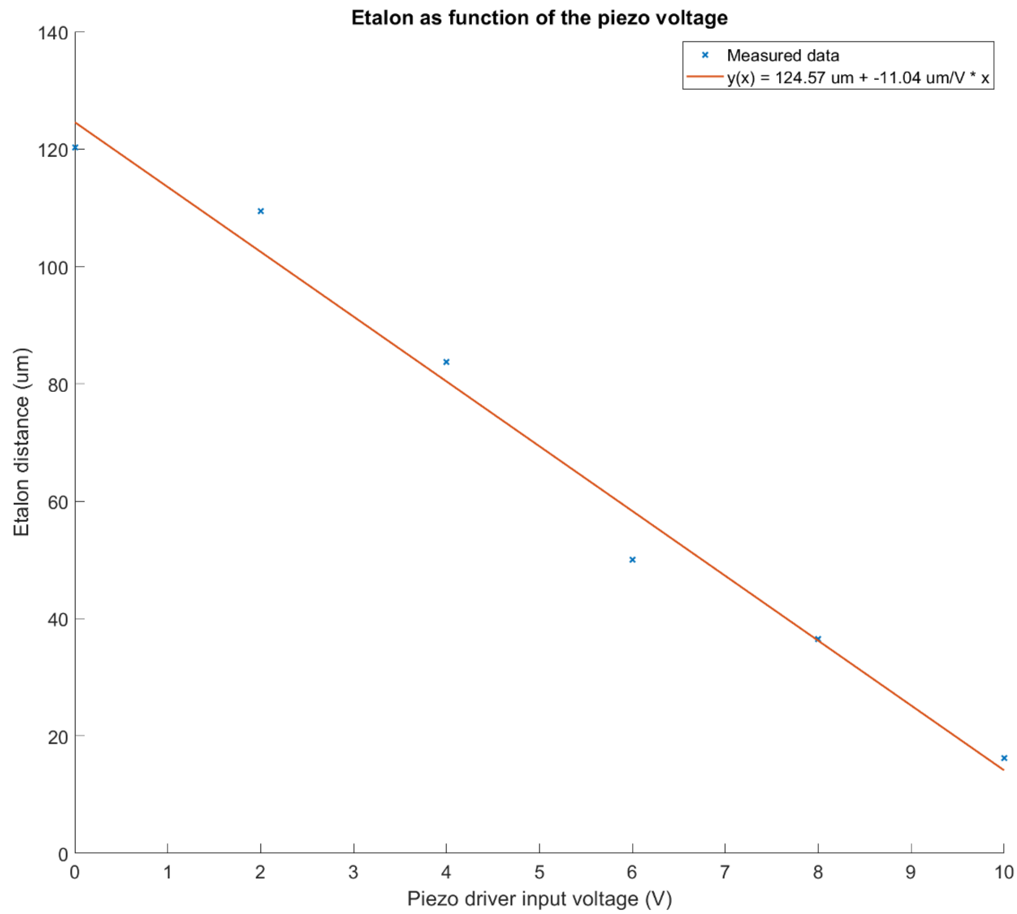


Figure 9 and figure 10 demonstrate cavity tuning with the piezo. The piezo is moved by different input voltages, as set via the potentiometer on the driver, while the fringe spacings are captured. (Figure 9). As shown in figure 10, the etalon distances are measured via FFT (using peakfinder on the first peak > 0 in the FFT). A linear curve to see how much the piezo tunes the cavity is fitted. Spectras at 0-10 V piezo driver input voltages (*100 for the actual piezo voltage) in 2 V steps are measured. Measured spectra shown in figure 9.





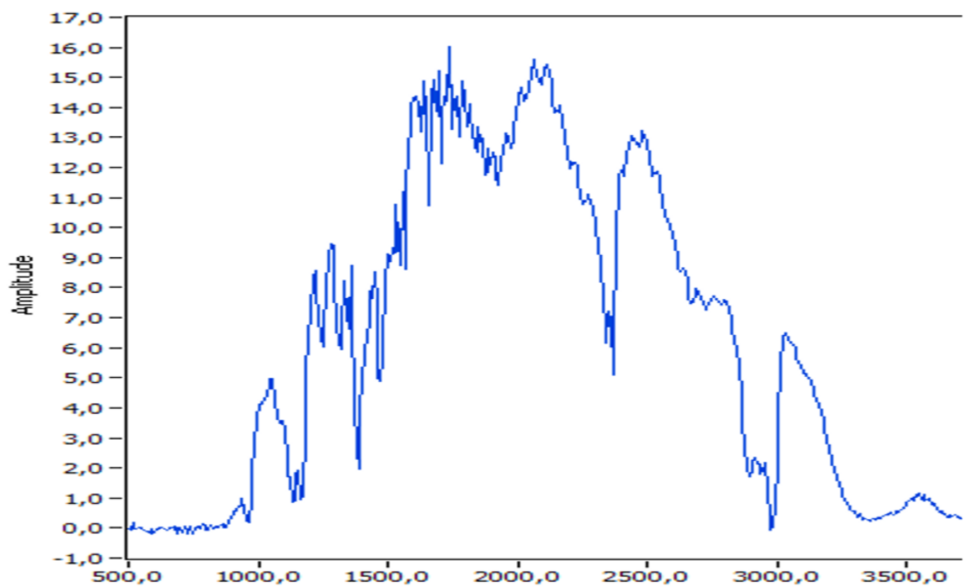
Using the "peakfinder" algorithm, the position of this first peak is measured and is plotted as a function of the piezo driver input voltage. A linear function to them are later fitted. (Figure 11)

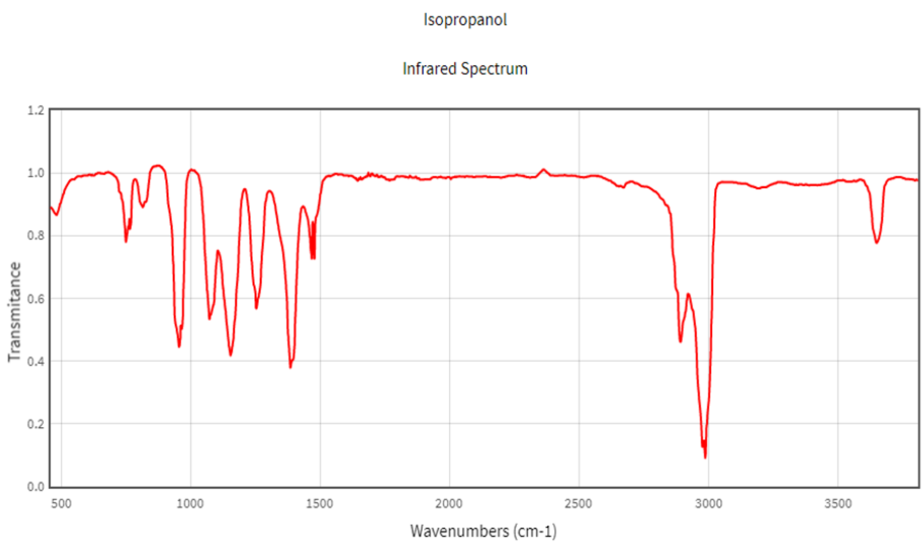


Here, the input voltage changes the etalons length by around 11 µm/V, which corresponds to an actual piezo extension of around 5.5 µm/100 V (in actual piezo voltage). For the full range, it extends around 55.2 µm going from 0 to 1000 V, which is closer to the 60 µm from the piezos datasheet (PI_Datenblatt_P-010xxH-P-025xxH.pdf) than the 43 µm which were measured interferometrically.

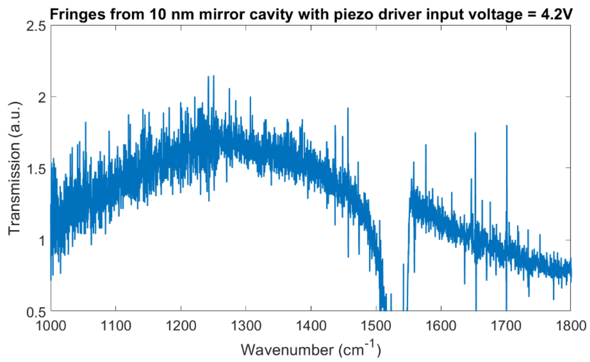
3.5 Transmission spectrum of Fabry-Pérot resonator with organic solvents (isopropanol; ethanol; CS_2)

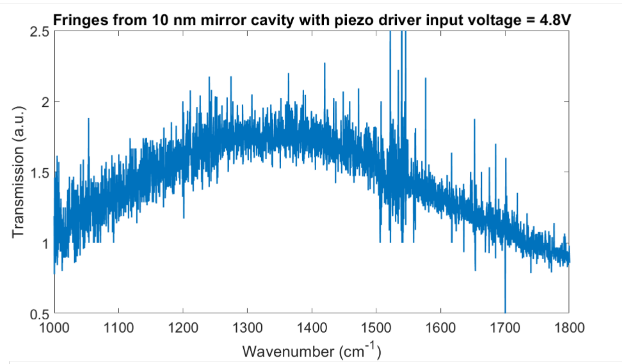
Spectra are measured of an aligned cavity with different organic solvents inside the cell. Figure 12 shows spectra of isopropanol under 10 Voltage input on the piezo. In comparison with the transmission spectrum found in the NIST webbase (Figure 12 [7]), the absorption peaks mach quite well as seen in figure 12 and figure 13.

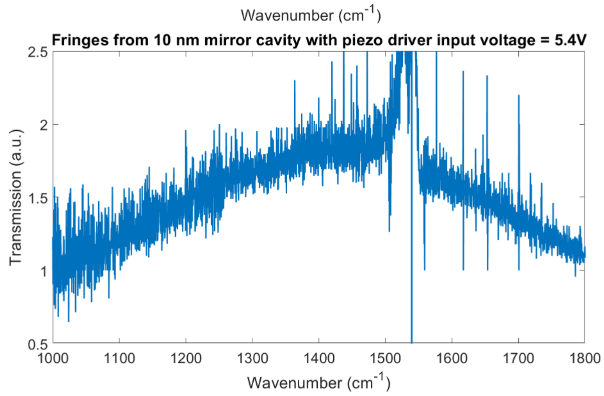


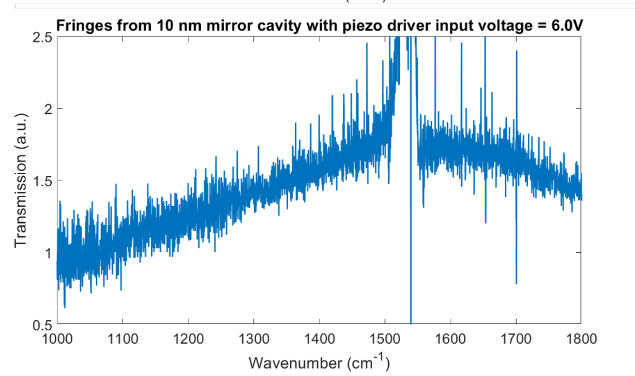


Measurements of an empty cell and with CS2 injected into the cell are also carried out. Unfortunately, the spectra measured for the empty cavity has a bad resolution. Therefore, spectra with CS2 inside under 10 V input are used as reference to determine transmission. This results in positive and negative absorption of CS2 (because CS2 also absorbs in the reference case). Figure 14 shows transmission spectrum under 4 different voltage inputs. It is very apparent that the cavity is tunable but the strong coupling regime could not be reached because of the huge optical mode linewidth.


Fringes from 10 nm mirror cavity with piezo driver input voltage = 4.2V
Transmission (a.u.)
Wavenumber (cm^{-1})


Fringes from 10 nm mirror cavity with piezo driver input voltage = 4.8V
Transmission (a.u.)
Wavenumber (cm^{-1})


Fringes from 10 nm mirror cavity with piezo driver input voltage = 5.4V
Transmission (a.u.)
Wavenumber (cm^{-1})


Fringes from 10 nm mirror cavity with piezo driver input voltage = 6.0V
Transmission (a.u.)
Wavenumber (cm^{-1})

4 Problems and Improvement

4.1 FTIR- MIR LAB

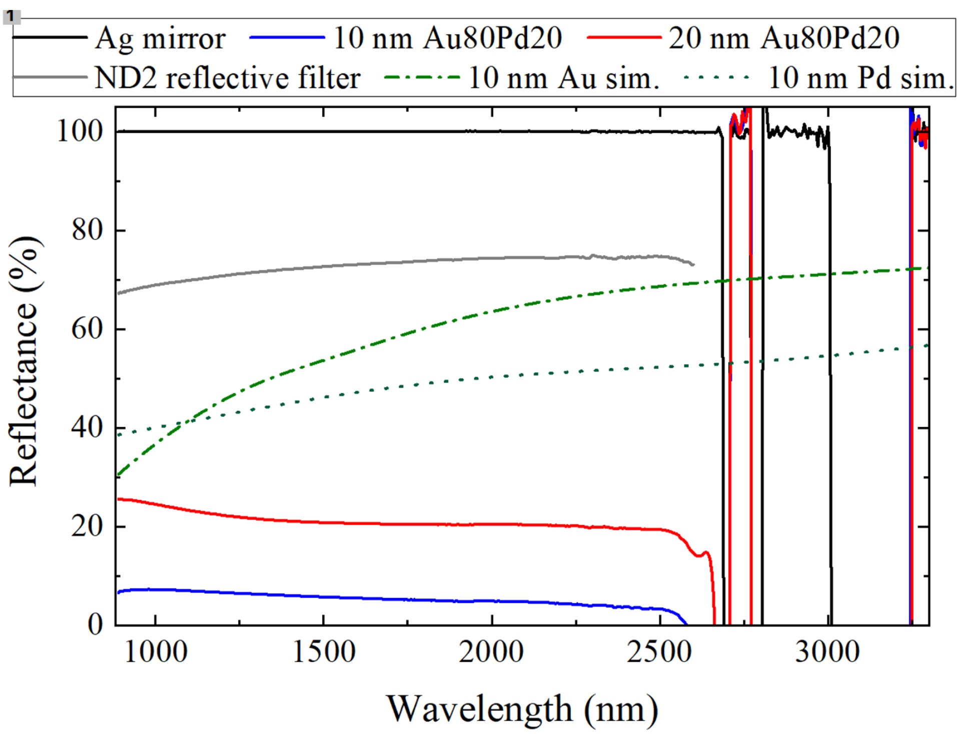
The FTIR spectrometer is used with the software MIR LAB, where a wavelength shift is always found in the result spectrum. The problem was solved by applying a half of the wavelength of He-Ne Laser (reference laser in FTIR) in the configuration.

4.2 Set up

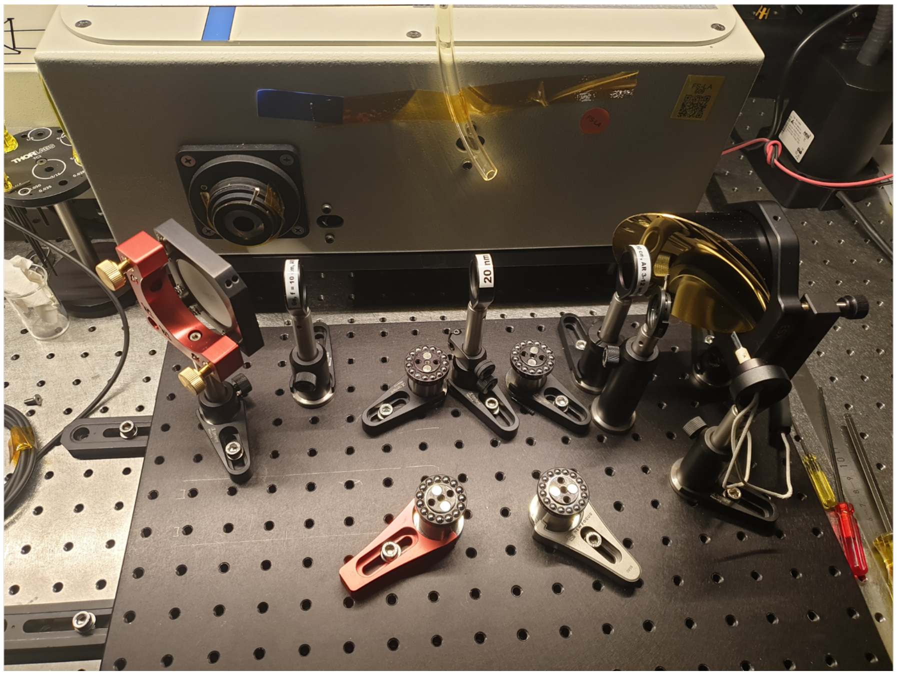
The cavity- cell set up is the first generation designed, making it quite difficult to assemble and align. Liquid vaporizing is another annoying issue for this set up although 2 O- rings are applied on both mirror sides. But the cell can always be refilled.

4.3 Reflectivity

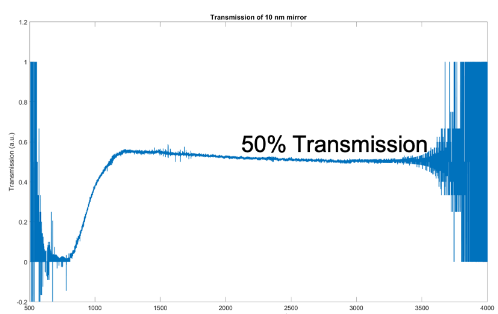
In the final set up, the mirrors (10 nm coating) seem to exhibit too low reflectivity according to the reflectivity measured with a spectrophotometer, see figure 15. This results in a broad transmission range and no clear peaks could be located in the cavity measurements.



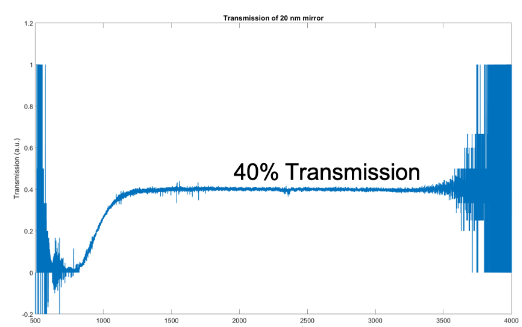
Transmission is also measured in the setup where two mirrors with coating thickness of 10 nm and 20 nm being put respectively into the focus of the two lenses where the cavity would sit (Figure 16)



The transmission measurments are shown in figure 17



10nm Coating Au80Pd20



20nm Coating Au80Pd20

Above 1000 cm^{-1}, the 10 nm mirror has around 50 percent transmission with slight decrease towards higher frequencies. The 20 nm coating shows around 40 percent transmission with flat response. Below 1000 cm^{-1}, the CaF2 absorbs the light.

5 Summary and Outlook

Optic experiments require patience and accuracy. Much time was spent by sheer alignment of the optic system. In this summer program, we managed to fix the problem of FTIR device and found a useful procedure to realise a good assembly and alignment of the cavity-cell set up. Finally, we are able to demonstrate the tunability of the resonator with our data.

The biggest problem we have for this experiment is the low reflectivity of the cavity mirrors. Better metallic mirrors with FTIR are suggested to be used in the new attempt. We already have 20 nm thickness Au80Pd20 coating mirrors sputtered but still would need higher reflectivity and a small redidual transmission. Another option are dielectric mirrors and the MIR comb as light source (for smaller spot sizes in the cell).

6 Acknowledgement

I wish to express my sincere gratitude to Dominic Laumer for the guidence and fun lab work through out the program.

I sincerely thank Marcus Seidel for the supervising and idea for problems we confront in our experiment.

I also thank Ingmar Hartl for helping me get involved in the FSLA group and the guidance and suggestions that are offered.

And finally a warm thank you to all the personal who organize this summer program and the summer school students who participate the program, for this fun and fulfilled summer.

7 Reference

[1] Optical Cavity Inference Techniques for Low Noise Interferometry Jorge Ramirez Advised by Craig Cahillane, Anchal Gupta, and Professor Rana X. Adhikari

[2] C. Cohen-Tannoudji and S. Reynaud, J. Phys. B: Atom. Mol. Phys. 10 345 (1977) *NOTE: the best reference would be probably the famous quantum mechanics book by Nobel laurate Cohen-Tannoudji, but I don't have the book myself

[3] J. Dalibard and C. Cohen-Tannoudji, J. Opt. Soc. Am. B 2, 1707-1720 (1985)

[4] Nagarajan et al., JACS 143, 16877 (2021)

[5] J. George et al. Phys. Rev. Lett. 117,153601 (2016)

[6] https://en.wikipedia.org/wiki/Transmittance#/media/File:Atmosfaerisk_spredning.png

[7] Isopropyl Alcohol (nist.gov)