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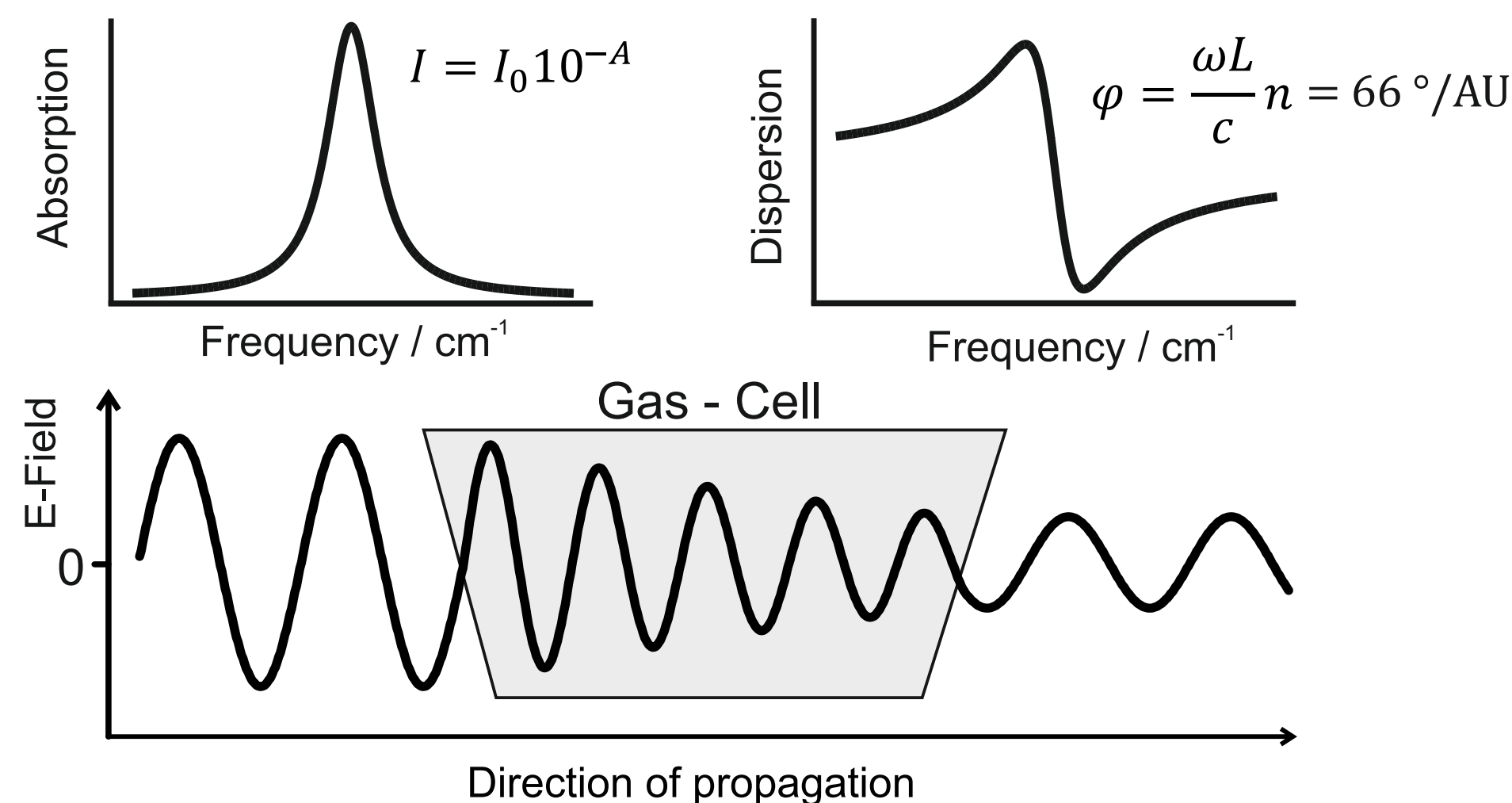
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1)

## DISPERSION SPECTROSCOPY

### Dispersion and Absorption

A sample's absorption - and refractive index spectrum are interrelated through Kramers-Kronig relation. Therefore, both share the same level of information, and both are useful probes for qualitative and quantitative chemical analysis. Qualitative spectroscopic information is especially rich in the mid-Infrared spectral region where the fundamental (and most intense) vibrational transitions of most molecules are found.



### Dispersion - vs. Absorption Spectroscopy

Spectroscopic trace gas analysis is mostly based on (Laser -) absorption spectroscopy. New techniques of laser based dispersion spectroscopy were developed and applied to trace gas analysis recently.[1,2] Since they measure light's phase, they are immune to intensity fluctuations at the detector. Also, the recorded phase scales linearly (rather than exponentially) with concentration. This holds the potential of complementing absorption based sensing in applications suffering from strongly fluctuating intensities, such as stand off detection or sensing in the presence of particles.

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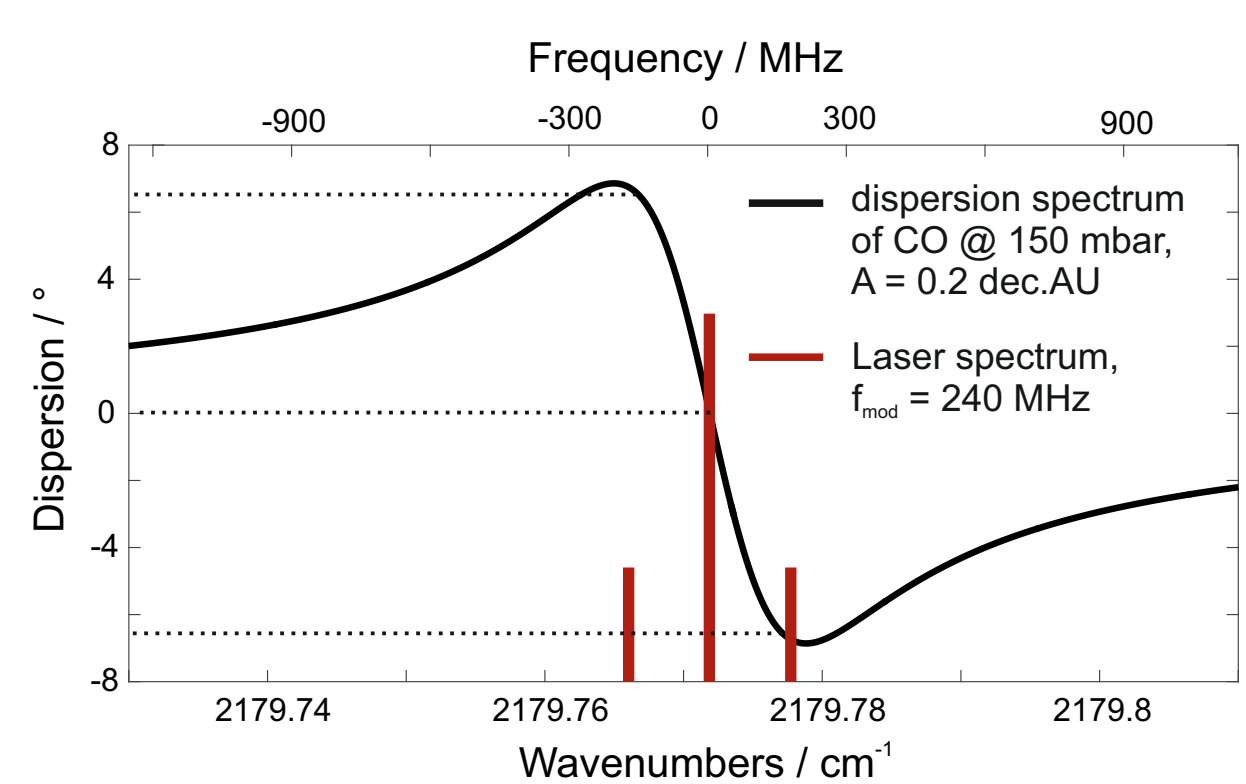
## HETERODYNE PHASE SENSITIVE DISPERSION SPECTROSCOPY

### Principles of HPSDS

HPSDS senses molecular dispersion using radio frequency amplitude modulated (RF-AM) lasers. In the laser's emitted spectrum this yields two sidebands shifted from the center frequency by the modulation frequency  $f_{\text{mod}}$ .

In proximity of a ro-vibrational resonance, the three spectral components experience differing refractive indices, yielding phase shifts between the individual lines. The difference between these phase shifts is the phase of the beating signal (the modulated signal) at a fast photo detector. This is the same principle used in laser range finding.

The phase shift at the molecular resonance frequency scales linearly with refractive index and hence concentration. The phase shift is maximized by choosing  $f_{\text{mod}} = 0.59 \text{ FWHM}$ . For CO, FWHM  $\sim 3.4 \text{ GHz/atm}$ .



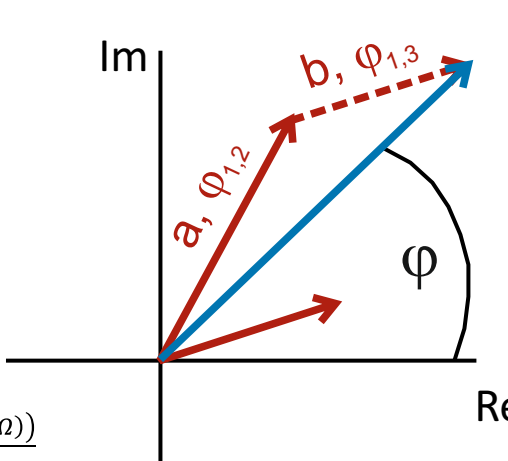
$$\varphi = \text{atan} \left( \frac{a \sin(\varphi_{12}) - b \sin(\varphi_{13})}{a \cos(\varphi_{12}) + b \cos(\varphi_{13})} \right)$$

$$\varphi_{12} = \frac{\omega_0 L}{c} (n(\omega_0) - n(\omega_0 - \Omega))$$

$$\varphi_{13} = \frac{\omega_0 L}{c} (n(\omega_0 + \Omega) - n(\omega_0))$$

$$a = 10 \frac{(A(\omega_0) + A(\omega_0 - \Omega))}{2}, \quad b = 10 \frac{(A(\omega_0) + A(\omega_0 + \Omega))}{2}$$

$$\varphi = \frac{\omega_0 L}{2c} (n(\omega_0 + \Omega) - n(\omega_0 - \Omega)) \quad \text{for } a = b, \text{ i.e. } \omega_0 = \omega_{\text{center}}$$



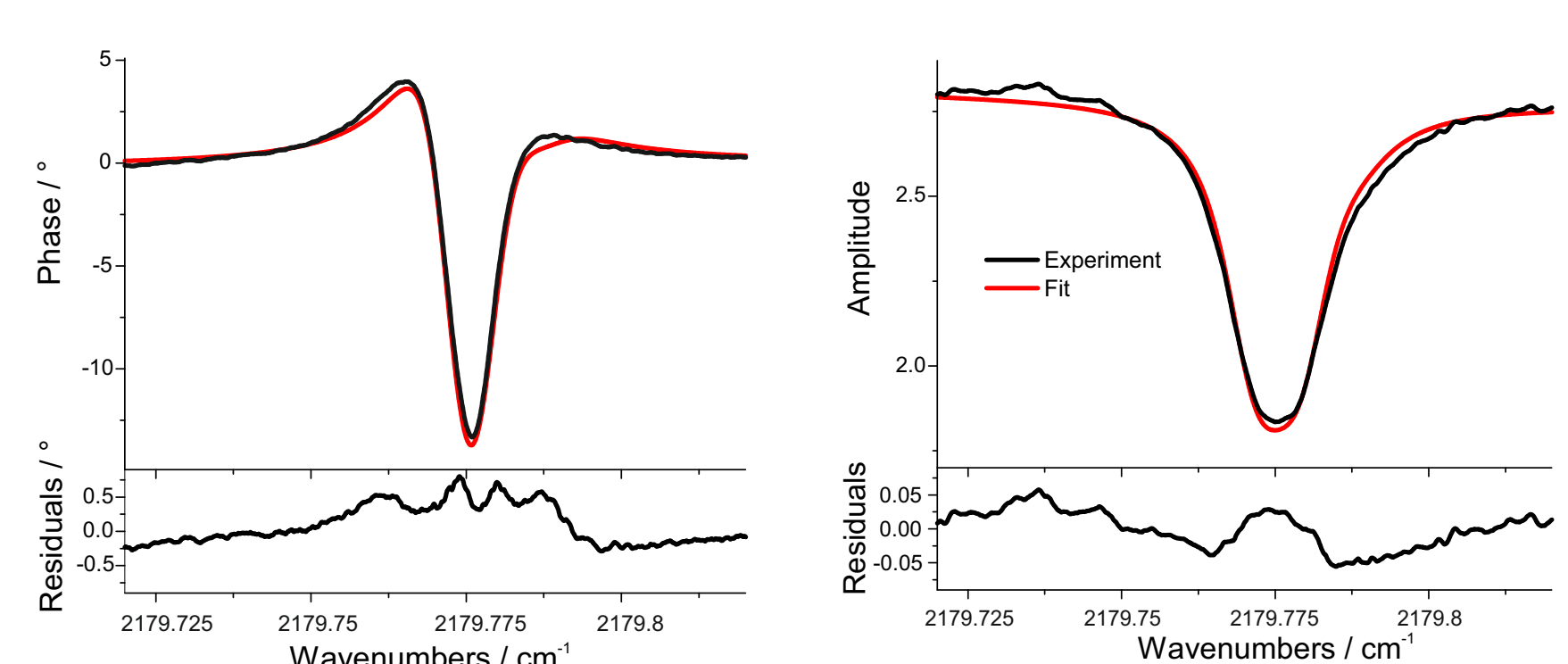
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## MODELLING OF HPSDS

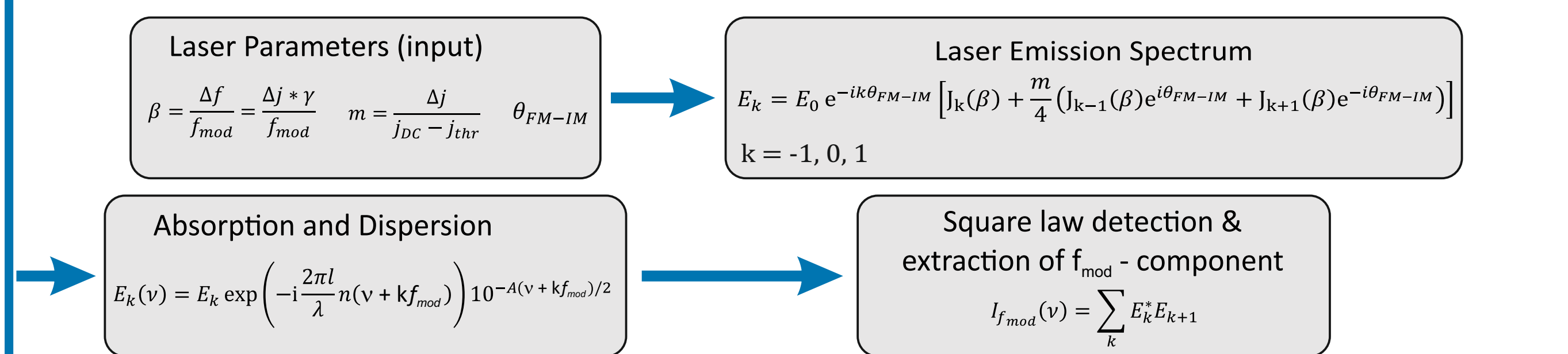
### Dispersion and Absorption

Using a model described in [3] implemented in Matlab, HPSDS spectra can be simulated and fitted. This allows for the retrieval of molecular concentrations without the need of calibration.

Moreover, the model includes residual frequency modulation that accompanies amplitude modulation in directly modulated semiconductor lasers. This is essential for concentration retrieval from experimental spectra via fitting.



$\Delta f$  ... Amplitude of Frequency Modulation  
 $\Delta j$  ... Amplitude of Current Modulation  
 $\gamma$  ... Current Tuning coefficient ( $\gamma = \gamma(f_{\text{mod}})$ )  
 $f_{\text{mod}}$  ... Modulation Frequency  
 $j_{\text{DC}}$  ... Laser bias current  
 $j_{\text{thr}}$  ... Laser threshold current  
 $\theta_{\text{FM-IM}}$  ... FM-IM Phase shift  
 $E_k$  ... k-th spectral line, centered at  $\nu + k f_{\text{mod}}$   
 $J_k$  ... k-th order Bessel Function of first kind  
 $l$  ... Path length through sample  
 $A$  ... Absorption  
 $n$  ... Refractive index  
 $\nu$  ... Laser center frequency  
 $I_{\text{mod}}$  ... Complex amplitude of modulation signal



3)

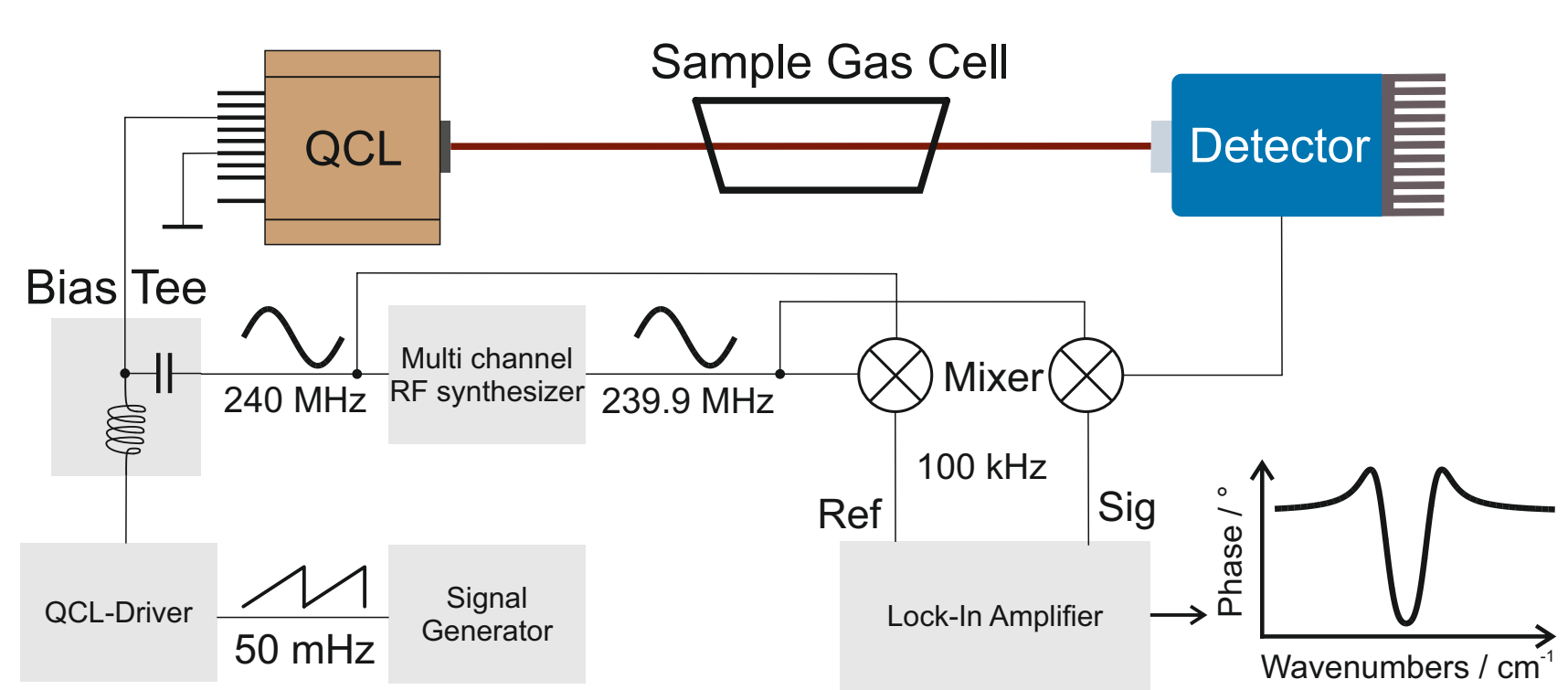
## SETUP

### General layout

Since RF electrooptic amplitude modulators are not available in the Mid-IR, we employ direct current modulation. The bias current and RF modulation current from a four channel RF synthesizer are combined in a bias tee and applied to the DFB-Quantum Cascade Laser (QCL). After passing the gas cell, the modulated radiation is detected on a fast photovoltaic detector. The phase of the detected RF modulation signal is analyzed after down-mixing to  $\sim 100 \text{ kHz}$  in a Lock-In amplifier. Spectra are recorded by slowly ramping the bias current.

### Details

Sample: CO in N<sub>2</sub> at 150 mbar  
Gas Cell: home built, 10 cm  
DFB-QCL: AdTech HHL @ 2179.7 cm<sup>-1</sup>  
RF-synthesizer: Holzworth HS 9004a  
Detector: VIGO PVMI-4TE with FIP preamplifier  
Lock-In: ZIMFLI



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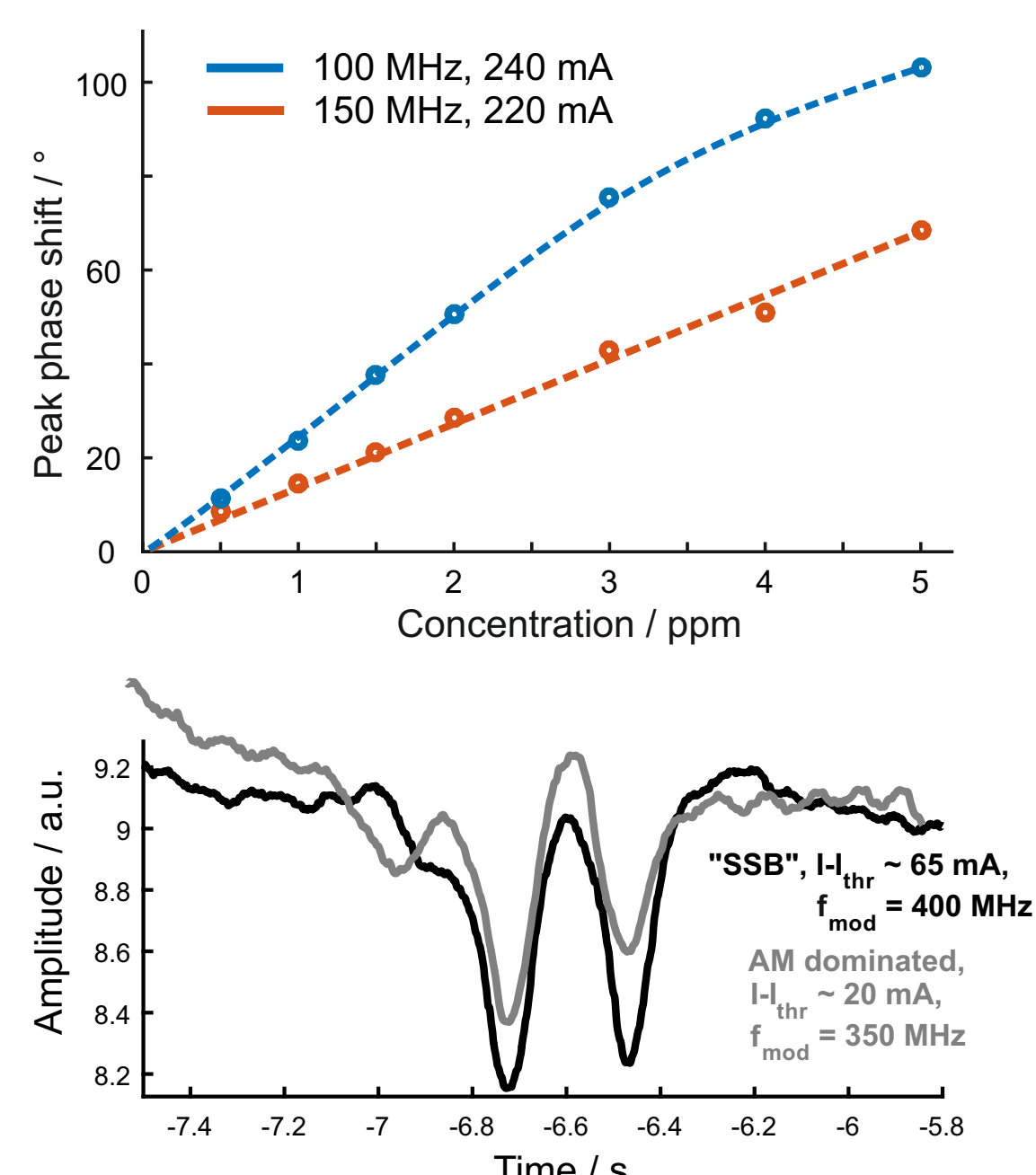
## INFLUENCE OF LASER SETPOINT

### Amplitude - and Frequency response to direct current modulation

Direct current modulation leads to amplitude- and frequency modulation (FM). Only the phase from pure amplitude (AM) - or single sideband (SSB) modulation scale linearly with molecular dispersion.

To suppress FM, the modulation frequency and bias current must be adjusted. A small bias current and high modulation frequencies favor AM.

In DFB-QCLs conditions exist for which one sideband is strongly suppressed, yielding a spectrum similar to SSB modulation.[3] This can be seen directly in the amplitude of the recorded modulation signal if the modulation frequency exceeds the FWHM of the molecular resonance.

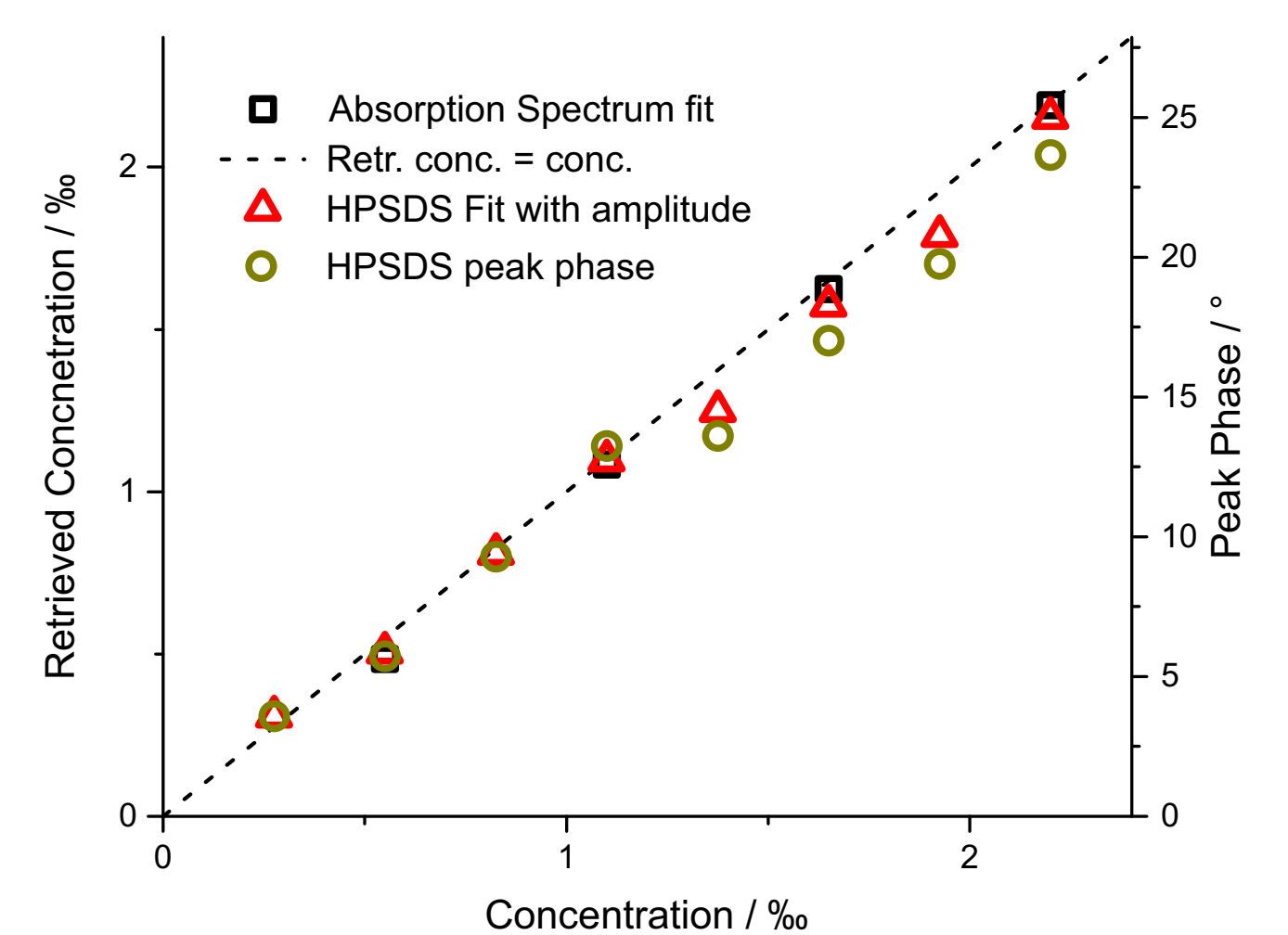


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## CALIBRATION FOR CO IN N<sub>2</sub>

### Experimental

Using a home built gas mixing unit, samples of CO in N<sub>2</sub> with concentrations from 0.3% to 2.2% were prepared. HPSDS spectra were recorded and analyzed by means of peak phase shift and fitting of a Voigt profile to the full complex HPSDS spectrum (amplitude and phase). For a comparison, absorption spectra were recorded without current modulation using an optical chopper and fitted using a Voigt profile to retrieve CO concentration.



### Results

The retrieved concentrations from fitting of absorption and HPSDS spectra agree well, while the peak phase yielded an underestimation for higher concentrations if a linear correlation is assumed. The linear range of the HPSDS peak phase strongly depends on the magnitude of frequency modulation resulting from direct current modulation.[4]

## REFERENCES

- [1] G. Wysocki and D. Weidmann, Opt. Express 18, 26123 (2010).
- [2] P. Martín-Mateos and P. Acedo, Opt. Express 22, 15143 (2014).
- [3] A. Hangauer, G. Spinner, M. Nikodem, and G. Wysocki, Opt. Express 22, 23439 (2014).
- [4] Martín-Mateos, P., Hayden, J., Acedo, P., & Lendl, B. (2017). Analytical Chemistry, 89(11), 5916–5922.

## REFERENCES

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