GASERA

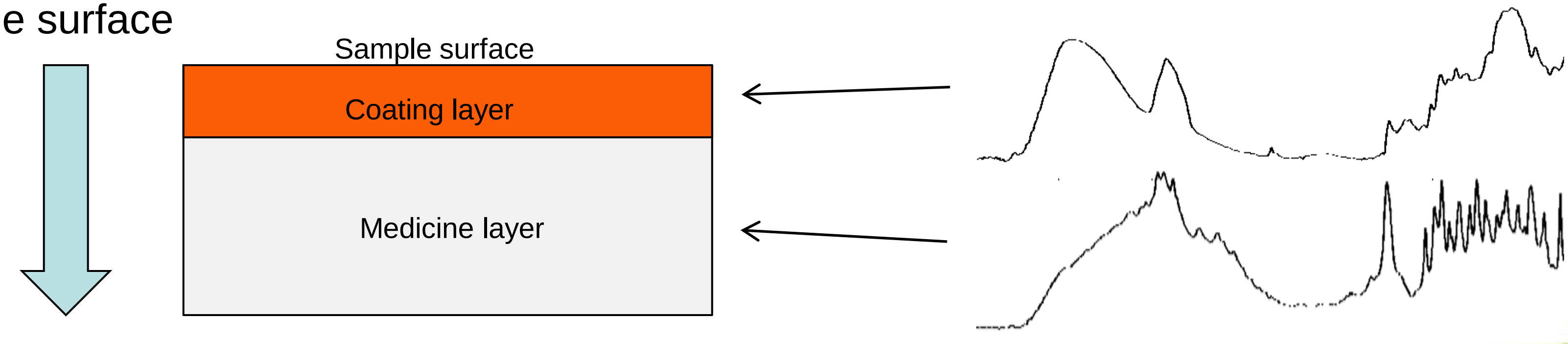
Depth Profiling with Photoacoustic Spectroscopy

Technical note 11th May 2010

Introduction

Sample:
coated tablet

- Depth varying information can be obtained with photoacoustic spectroscopy.
- Depth scale is selected by varying the mirror velocity or modulation frequency in the FTIR interferometer and phase of the spectra.
- It is possible to vary depth from range of below 1 µm to few hundreds of micrometers.
- Spectra from different depth ranges can be measured.
- Depth of different layer interfaces can be determined.
- Distance between different layers can be determined with higher resolution by using the phase data.
- Spectra from two different layers can be separated from each other.



Depth from
the surface

Layered sample

Sample surface

Coating layer

Medicine layer

Spectrum of the layer

Introduction to depth varying measurements with PAS

What can be done?	Continuous scan	Step scan	Comments
Spectrum can be measured starting from the surface to variable depth in the sample.	Depth range from 0 – 0.1 µm to 0 - 100 µm	Depth range from 0 - 1 µm to 0 - 500 µm	Straightforward measurement is performed by varying mirror velocity or modulation frequency.
Thickness of different layers can be determined by varying the mirror velocity	Signal from different depths is received by selecting absorption lines at different wavenumbers at different mirror velocities.	Signal from different depths is received by changing modulation frequency.	Depth resolution is determined by the thermal diffusion length (0.1 – 100 µm)
Distance between two layers can be calculated.	Adjacent absorption lines allow determination of relative phase and depth of two materials.	Intensity of any absorption line allows the determination of relative phase and distance between different layers.	Depth resolution can be order of magnitude better than only by varying the mirror velocity (0.01 – 3 µm).
Spectra from two different layers can be separated and the material in the layers identified.	Material at each layer is identified according to certain peaks. The processed spectrum contains data from several layers.	The spectra from the top or bottom layer can be minimized for spectral search of the other layer spectrum. The processed spectrum contains data only from a single layer.	Step-scan allows the separation of the whole spectrum by using the phase of the signal.
Relative depths of several layers can be calculated.	If there happens to be adjacent absorption lines, the relative depth of more than two components can be determined	Relative depths of several layers can be determined by calculating the phase difference between signals from components at different layers.	Step-scan has good depth resolution, whilst with the continuous scan the resolution depends on the distance of absorption lines.

Photoacoustic signal generation from different depths

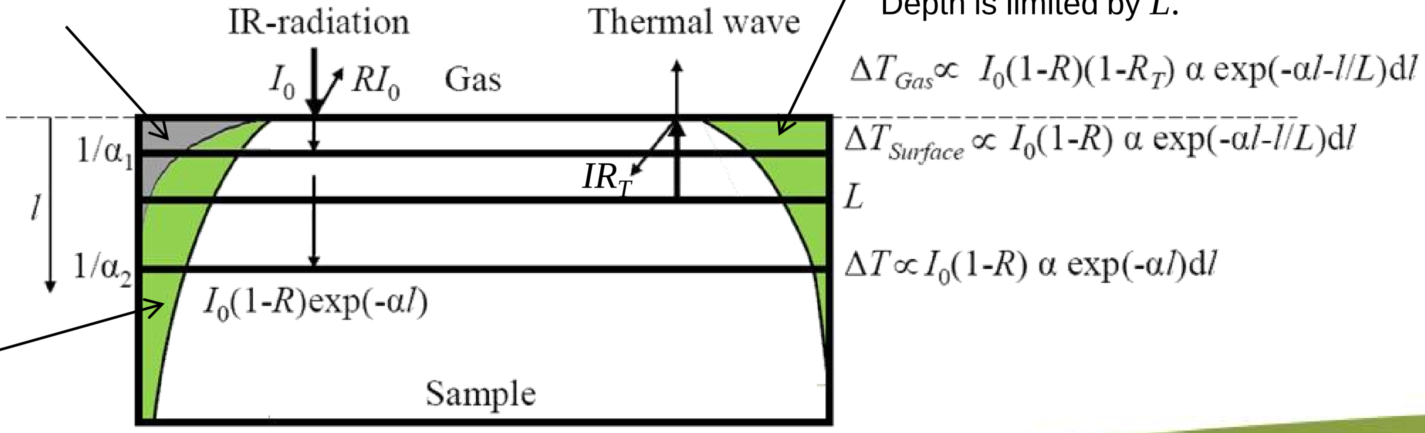
- Part of the IR-radiation I_0 is reflected. Amount of the reflection RI_0 depends from the sample surface reflectance R.
- Rest of the radiation $I_0(1-R)$ is absorbed to the sample according to Beer's law $I_0(1-R)\exp(-\alpha l)$ depending on the depth l and absorption coefficient $\alpha(\nu)$ at different wavelengths ν.
- If the sample is thin, part of the radiation might transmit the sample and hit another surface. In thicker samples the radiation just penetrates deeper to the sample.
- If the sample is a strong absorber, the sampling depth is determined by the absorption coefficient, $l = 1/\alpha$.
- If the sample is transparent, thermal diffusivity length L determines the sampling depth.
- The temperature rise ΔT_{Gas} in a gas layer on the sample surface is induced by the heat energy arising from different depths depending on the absorption coefficient and thermal diffusion length of the sample.

Thermal diffusion length limits the sampling depth with optically transparent samples.

Depth is limited by L.

Light intensity decay in a strong absorbing sample.

Depth is limited by $1/\alpha$



Light intensity decay in a transparent sample, $\alpha_2 << \alpha_1$

Units of photoacoustic sensing and FTIR

$$\nu = \frac{f}{c_{OPD}} = \frac{f}{\lambda_{laser} f_{laser}} = \nu_{laser} \frac{f}{f_{laser}}$$

$$L = \sqrt{\frac{2K}{\omega \rho c_p}} = \sqrt{\frac{D}{\pi f}}$$

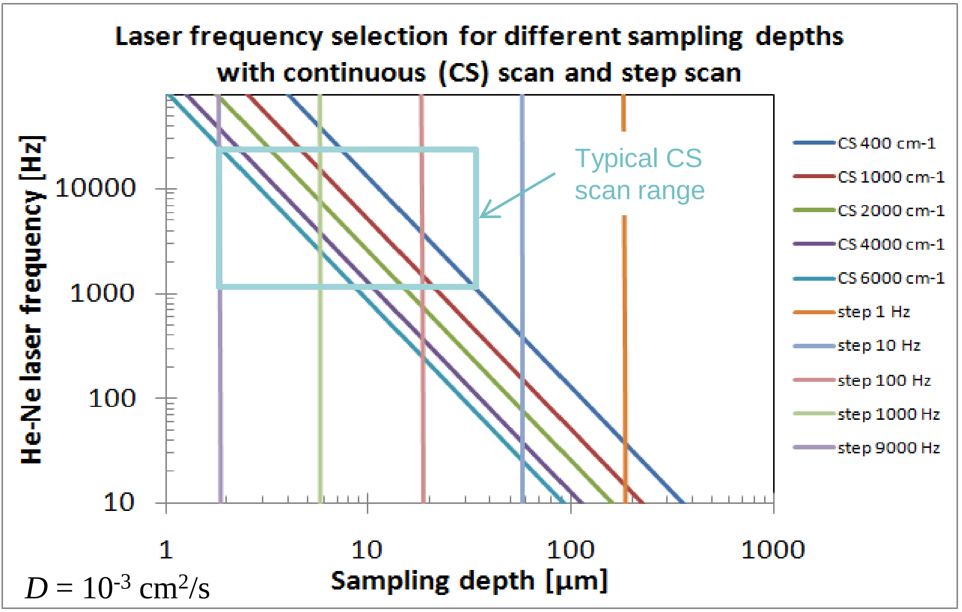
$$L_{\max} = 2\pi L$$

Modulation frequency [Hz]	Depth resolution [µm / °]	Sampling depth L [µm]	Maximum depth $2\pi L$ [µm]
1	3.1	178	1121
10	0.98	56.4	354
40	0.49	28.2	177
100	0.31	17.8	112
400	0.16	8.92	56.0
1000	0.10	5.64	35.4
4000	0.05	2.82	17.7
10000	0.03	1.78	11.2
20000	0.02	1.26	7.9
80000	0.01	0.63	4.0

$D = 10^{-3}\ \mathrm{cm^2/s}$

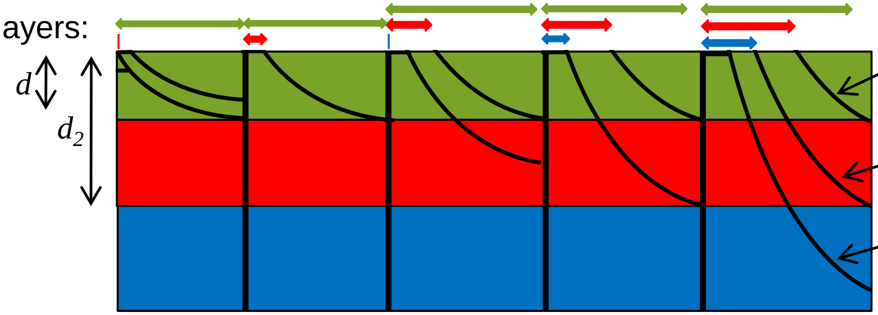
- Optical path difference (OPD) velocity c_{OPD} determines on how the wavenumber (ν) converts to an acoustic frequency f. The unit of OPD velocity is [cm/s]. It is often given as laser frequency f_{laser} [Hz], which means the acoustic frequency that the laser wavelength λ_{laser} is sensed. The best signal is below the first cantilever resonance frequency. The resonance is usually between 800 Hz – 1500 Hz.
- Sampling depth is determined by the thermal diffusivity length L, which can be varied by OPD velocity. It depends on modulation frequency and sample thermal diffusivity D. Thermal diffusivity can be expressed also by thermal conductivity K, density ρ and specific heat capacity c_p of the sample, and the angular frequency of the intensity modulation $\omega = 2\pi f$.
- Sampling depth resolution tells how deep slice does one degree in phase corresponds with different OPD velocities.
- Maximum sampling depth from where thermal wave can travel to the surface is $2\pi L$. However, the amplitude from the maximum depth has decayed by factor 0.00187.
- Minimum sampling depth can be reduced by factor 3, if linearization is used. It is possible to get sampling depths corresponding to laser frequency of 80kHz and OPD velocity of 5 cm/s.
- OPD velocity is controlled by the mirror velocity. E.g. in Michelson interferometer the OPD velocity is twice the mirror velocity.

Variable depth from the surface by changing mirror velocity or modulation frequency



$D = 10^{-3}$ cm^2/s

- By changing mirror velocity and selecting absorption lines from different wavenumbers information from different depths can be achieved.
- By using high mirror velocity and high modulation frequencies only the surface layer is sampled.
- Signal from deeper layers start to occur when modulation frequency is decreased.
- Signal from depth L is decayed to 1/e-part.



Photoacoustic signal intensity from different layers:

1st layer ⟷

2nd layer ⟷

3rd layer ⟷

Thermal decay from the 1st interface

Thermal decay from the 2nd interface

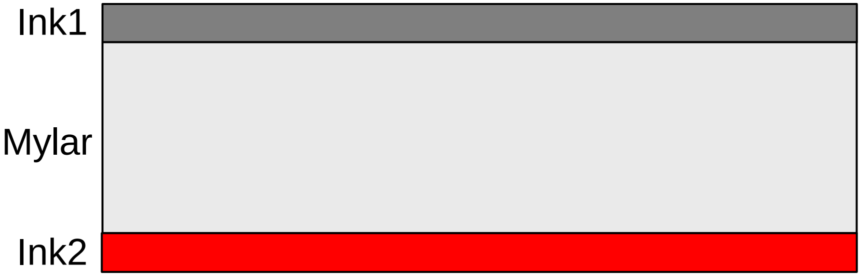
Thermal decay from the 3rd layer

Thermal diffusion length:	$L < d$,	$L = d$,	$d_1 < L < d_2$,	$L = d_2$,	$L > d_2$,
He-Ne Laser frequency:	*10 kHz*	*7.5 kHz*	*2.5 kHz*	*1.6 kHz*	*1.0 kHz*

Thickness of the ink layer– an example measurement

- An example measurement was done with a Mylar membrane covered by a thin layer of ink on both sides.
- The ink layer thickness was estimated by using PA301 and continuous scan interferometer (Bruker Tensor 27).

Sample cross-section

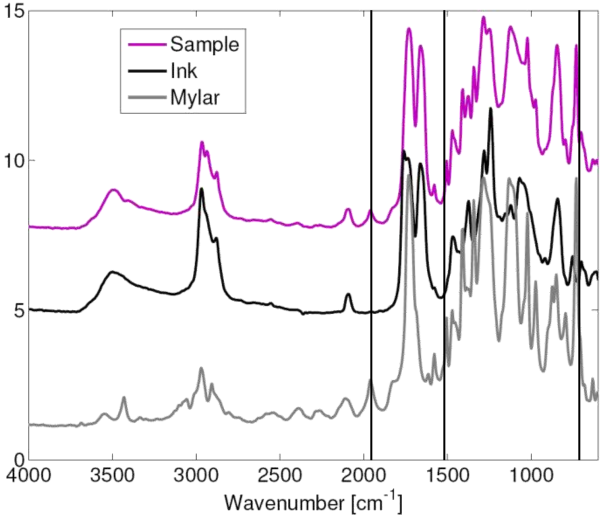


Ink1 on aluminum

Mylar

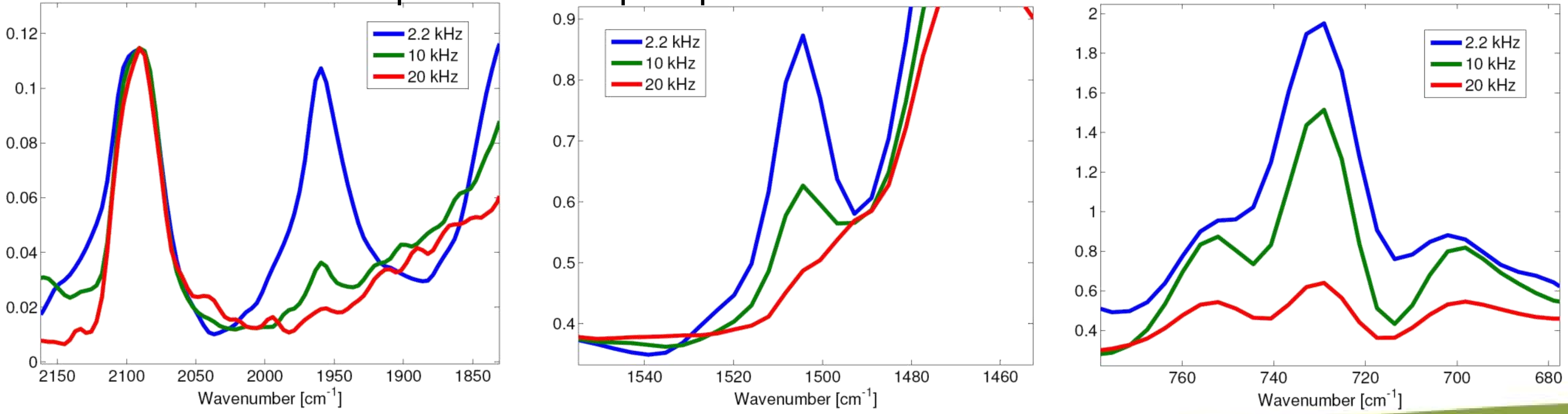
Ink1 on Mylar and Ink2 below Mylar

Thickness of the ink layer



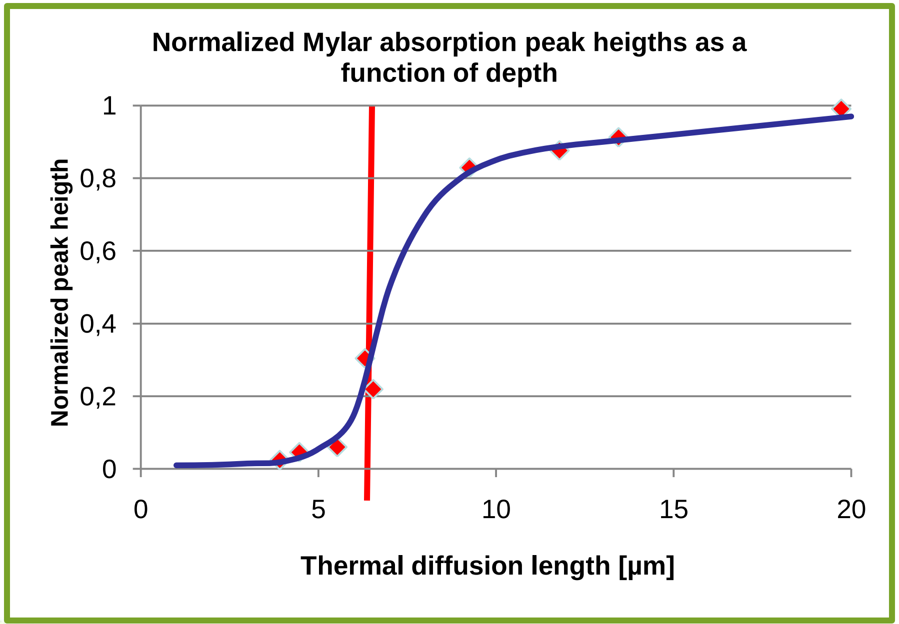
- Mylar has characteristic absorption lines e.g. at 730 cm^{-1}, 1505 cm^{-1}, and 1960 cm^{-1}.
- The sample spectra measured with different mirror velocities were normalized by using a characteristic absorption line of Ink1 at 1660 cm^{-1} and 2090 cm^{-1}.
- It can be seen that Mylar peaks rise with slower mirror velocities and much faster with high wavenumbers than low.

Selected peaks of sample spectrum with different mirror velocities



Thickness of the ink layer

Peak wavenumber	Laser frequency	Peak frequency	Thermal diffusion length	Peak heigth	Normalized peak heigth
cm^{-1}	Hz	Hz	µm		
730	2200	97	19.7	20.8	1
730	10000	443	9.2	17.4	0.83
730	20000	886	6.5	4.6	0.22
1505	2200	210	13.4	1.2	0.91
1505	10000	953	6.3	0.4	0.30
1505	20000	1905	4.5	0.06	0.046
1960	2200	273	11.8	0.73	0.88
1960	10000	1241	5.5	0.05	0.06
1960	20000	2481	3.9	0.02	0.024



- Thermal diffusion length can be calculated and it is different for each modulation frequency.
- By following 3 absorption lines with 3 different mirror velocities, 9 different depths are received by using continuous scan.
- The absorption peak heights were normalized to 1.
- When normalized absorption line intensities are plotted as a function of thermal diffusion length, the thickness of the first layer can be estimated.
- In this example the ink thickness on Mylar membrane was approximately 7 µm.
- The same could be done for the second layer, if slow enough mirror velocities are available in the spectrometer.
- This kind of analyses can be done either by using continuous scan or step-scan.

Continuous scan interferometry – projection spectrum and relative depth

Interferogram

$$I(x)=\int_{-\infty}^{\infty}E(\nu)e^{-i2\pi\nu x}d\nu$$

Amplitude spectrum

$$E(\nu)=\int_{-\infty}^{\infty}I(x)e^{-i2\pi\nu x}dx,\quad E(-\nu)=E^{*}(\nu)$$

Power spectrum

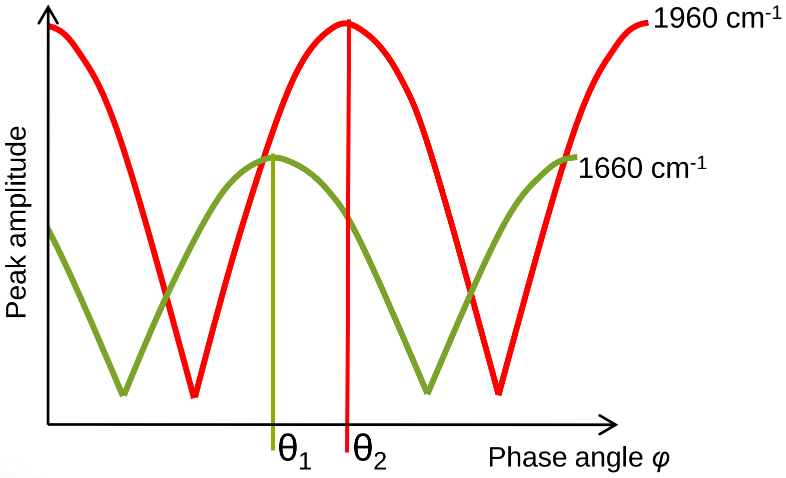
$$\left|E(\nu)\right|=\sqrt{\mathrm{Re}\{E(\nu)\}^{2}+\mathrm{Im}\{E(\nu)\}^{2}}$$

Phase spectrum

$$\theta(\nu)=\tan^{-1}\left(\frac{\mathrm{Im}\{E(\nu)\}}{\mathrm{Re}\{E(\nu)\}}\right)$$

Projection spectrum

$$\begin{aligned}E(\nu,\varphi)&=\mathrm{Re}\{E(\nu)\}\cdot\cos\varphi+\mathrm{Im}\{E(\nu)\}\cdot\sin\varphi\\&=\left|E(\nu)\right|\cdot\cos(\varphi-\theta(\nu))\end{aligned}$$

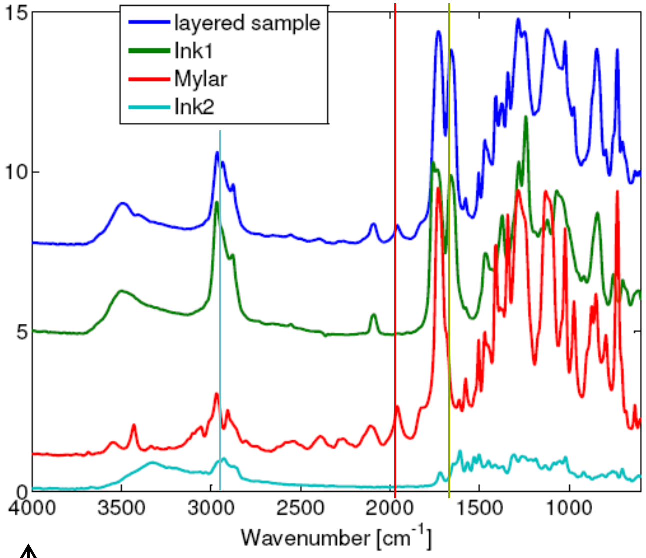


- With continuous scan one will get an interferogram, which has the phase of the photoacoustic signal.
- The phase spectrum can be calculated from the imaginary and real parts of the Fourier transform of the interferogram.
- Further the projection of the spectrum to the selected phase angle can be calculated from the real and imaginary parts of the spectrum or using the phase spectrum.
- Each wavenumber in the spectrum represents different frequency and so the absorption lines whose intensity is followed should be close to each other ($\nu_1\approx\nu_2\rightarrow L_1\approx L_2$) .

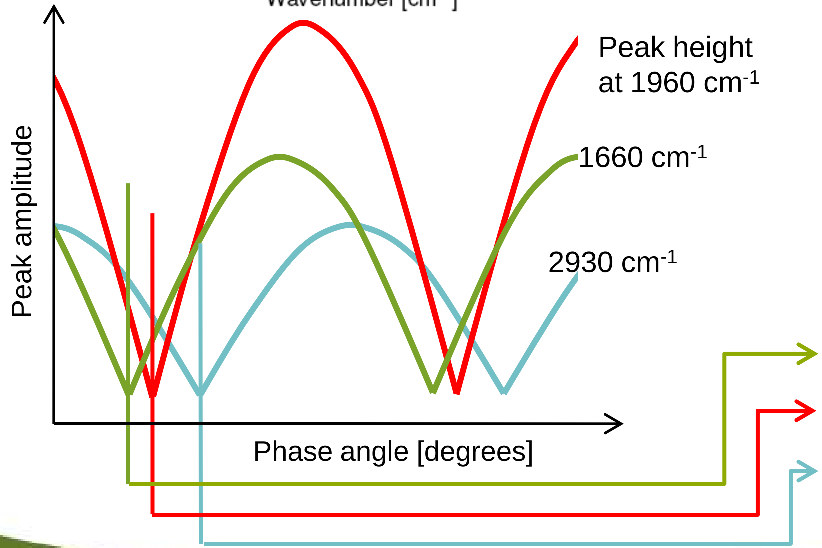
Relative depth

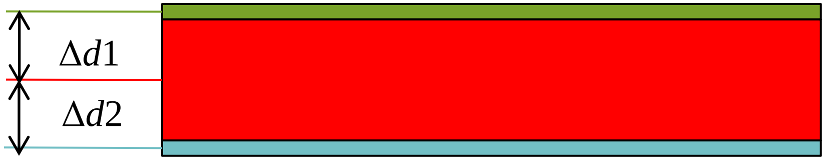
$$\begin{aligned}\Delta d&=\frac{2\pi}{360^{\circ}}\left(L_2\Delta\theta_2-L_1\Delta\theta_1\right)\\&=\frac{2\sqrt{\pi D}}{360^{\circ}}\left[\frac{\theta_2}{\sqrt{f_2}}-\frac{\theta_1}{\sqrt{f_1}}+\left(\frac{\theta_0}{\sqrt{f_1}}-\frac{\theta_0}{\sqrt{f_2}}\right)\right]\\&\overset{f_1\approx f_2}{\approx}\frac{2\pi}{360^{\circ}}\sqrt{\frac{D}{\pi f_{avg12}}}\cdot(\theta_2-\theta_1)\end{aligned}$$

Calculation of the relative depth of different components using step-scan



- Relative depth of different components can be determined by calculating the projection spectrum at different phases of the signal.
- When the absorption peak heights corresponding to each component are plotted against the phase angle, it can be observed that they follow the absolute value of a sine curve.
- The peaks have to be selected already for the known wavenumbers or grouped by the phase difference if they are unknown.
- By varying the modulation frequency, the depth scale and resolution can be varied
- By determining the phase difference of these curves the relative depth of each component can be calculated.



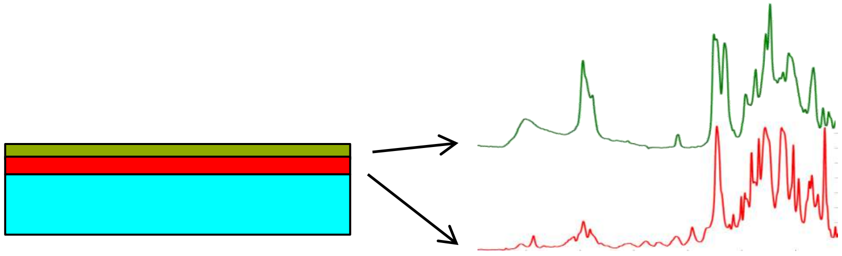


$\theta_1 = 15^\circ$

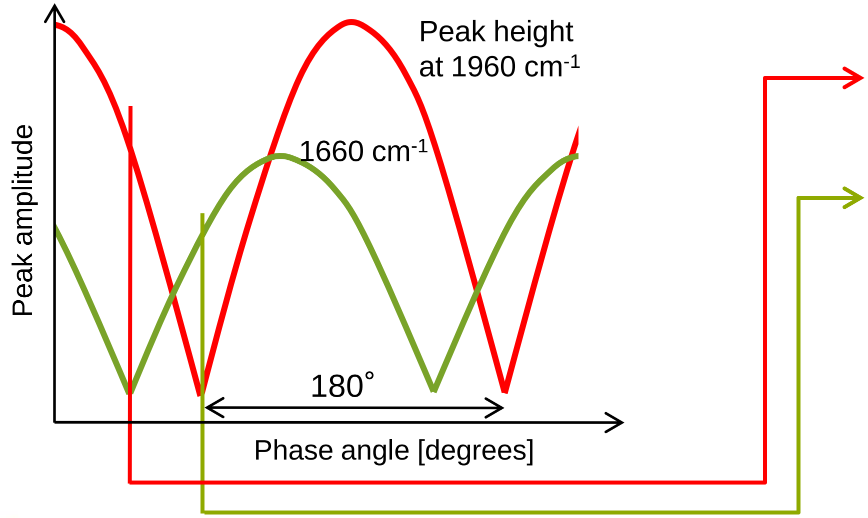
$\theta_2 = 55^\circ \;\rightarrow\; \Delta d1 = 2\pi L(\theta_2 - \theta_1)/360^\circ = 9\ \mu\text{m}.$

$\theta_3 = 95^\circ \;\rightarrow\; \Delta d2 = 2\pi L(\theta_3 - \theta_2)/360^\circ = 9\ \mu\text{m}$

Measuring spectra of different components at different depths using step-scan



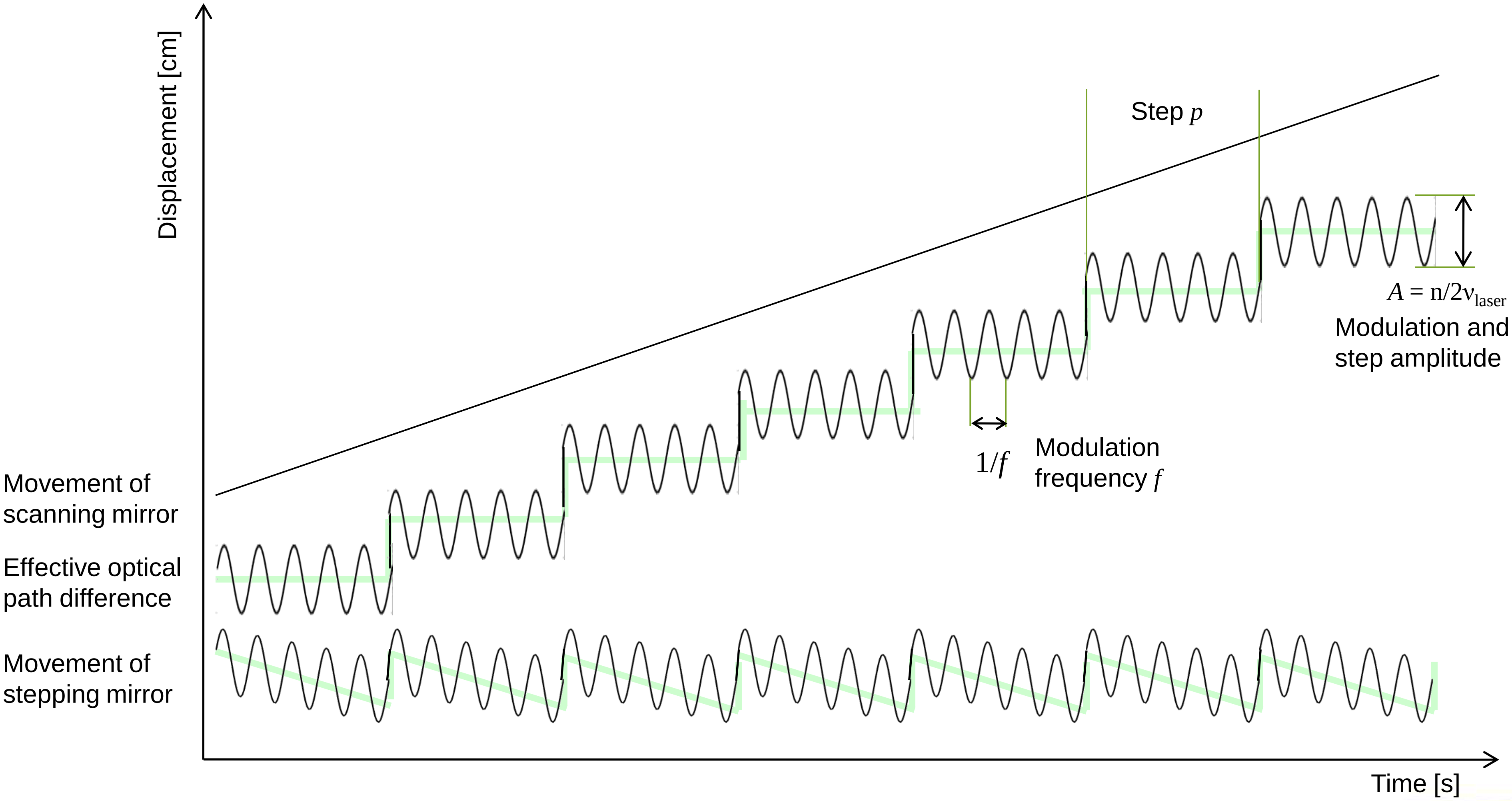
- If the components at different layers are unknown, it is possible to eliminate the spectrum of one layer at the time in order to make the spectrum of other layers visible.
- The separated spectra can then be used for identification of the material in a certain layer.



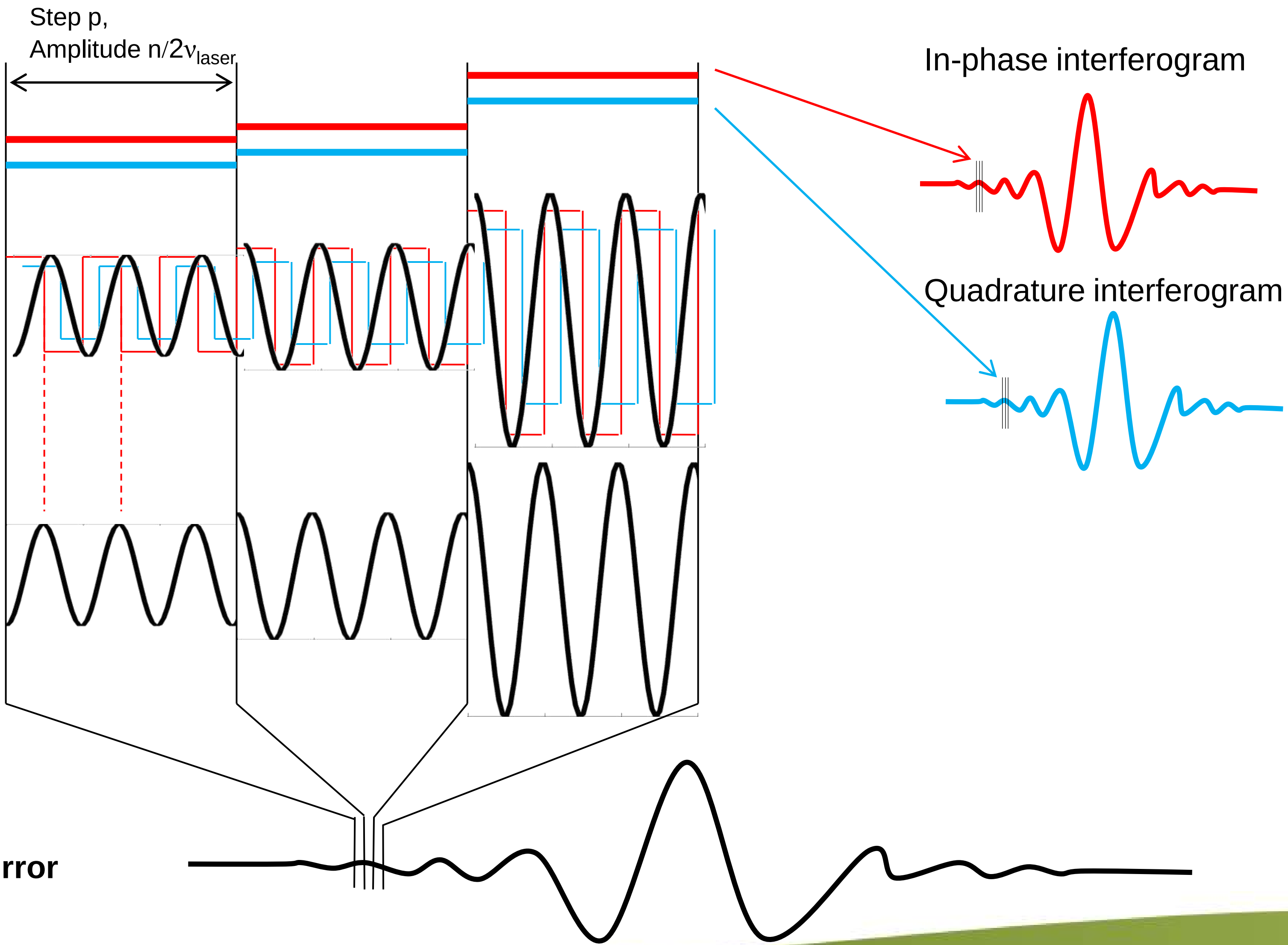
θ = 95˚ - The projection to this phase minimizes the Ink1 spectrum.

θ = 135˚ - The projection to this phase minimizes the Mylar spectrum.

Mirror movements in step-scan interferometry



Phase data in step-scan interferometry



4. PA-signal intensity of each step
In phase.
quadrature

3. PA-signal with phase delay.
In phase.
quadrant phase

2. Light intensity modulation due stepping mirror movement

1. Light intensity at different scanning mirror positions

Step-scan interferometry – calculation of the projection spectrum

1. Light power at different stepping mirror positions $P(x) = 2\int_0^\infty E(v)\cos(2\pi vx)dv$

2. Light power due vibrating mirror at different steps $\Delta P(x) = -2\int_0^\infty E(v)\sin(2\pi vx)dv \times \delta\sin(ft)$

3. PA-signal with phase delay. $\Delta I(x) = -2\cdot C\int_0^\infty E(v)\sin(2\pi vx)dv \times \delta\sin(ft+\varepsilon)$

4. PA-signal magnitude of each step.

$$M_0(p) = M(p)\cos(\theta(p))$$
$$M_{90}(p) = M(p)\sin(\theta(p))$$

5. In-phase interferogram and quadrature interferogram

$$M_0(p) \xrightarrow{x=avg(p)} I_0(x)$$
$$M_{90}(p) \rightarrow I_{90}(x)$$

6. Projection interferogram to phase *φ* $I_\varphi(x) = I_0(x)\cos\varphi + I_{90}(x)\sin\varphi$

7. In-phase and quadrature spectra

$$I_0(x) \xrightarrow{FT} S_0(v)$$
$$I_{90}(x) \rightarrow S_{90}(v)$$

8. Power spectrum $S(v) = (S_0(v)^2 + S_{90}(v)^2)^{½}$

9. Phase spectrum $\theta(v) = \tan^{-1}\left(\frac{S_{90}(v)}{S_0(v)}\right)$

10. Projection spectrum $S(\varphi,v) = (S_R(\varphi,v)^2 + S_I(\varphi,v)^2)^{½} / S_B(v),\quad I_\varphi(x) \xrightarrow{FT} \left\{\begin{array}{l} S_R(\varphi,v) \\ S_I(\varphi,v) \end{array}\right.$

11. Relative depth

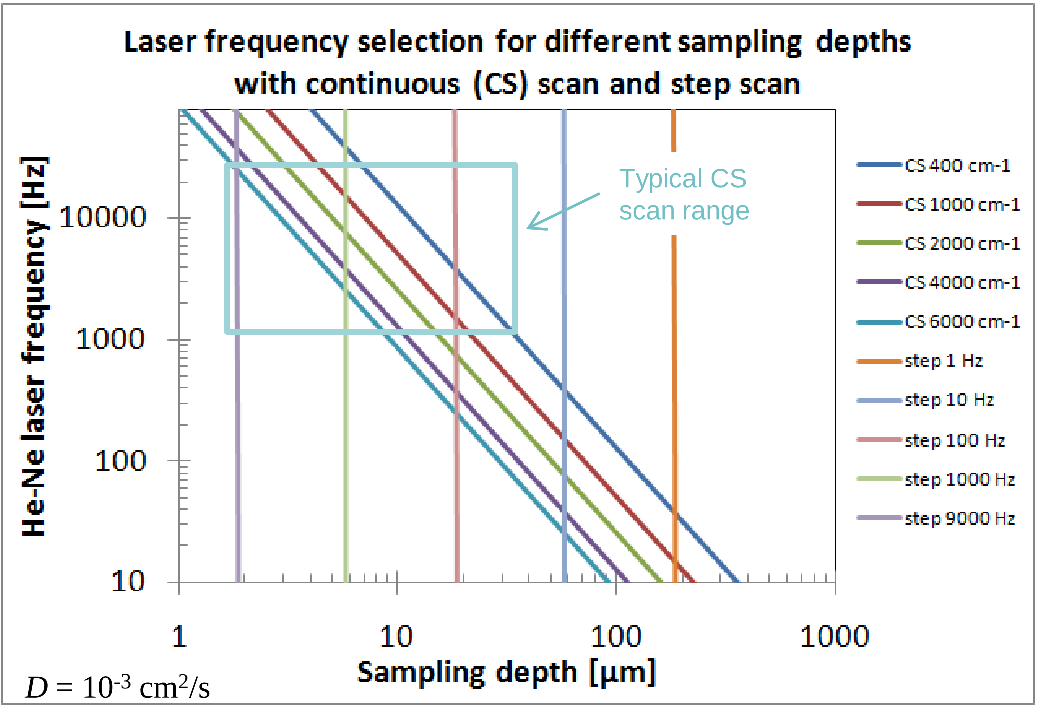
$$\Delta d = 2\pi L(\theta_2 - \theta_1)/360^\circ$$

Linearization of the photoacoustic spectrum

- The primary motivation for linearization is in reducing the saturation of high absorbing lines.
- Linearization also makes the sampling depth 3 times shallower than if only pure magnitude spectra were used.
- Commercial spectroscopic software such as Win-IR and Omnic contain integrated linearization function.
- The linearization is performed by:
    - Measuring single beam spectra of the sample and glassy carbon reference.
    - The interferograms are then shifted to have equal centerburst retardation , if necessary.
    - Both interferograms are Fourier transformed to have sample real S_R and imaginary S_I spectra, and reference real R_R and imaginary R_I spectra.
    - Finally the linearized spectrum can be calculated from the following equation.

$$S_l = \frac{\left(S_R^2 + S_I^2\right)}{\sqrt{2}\left(S_I R_R - S_R R_I\right)}$$

Comparison of continuous and step-scan interferometry



- Range of mirror velocities
  - In continuous scan interferometers the He-Ne laser frequency in a typical interferometer could range from ~ 2.5 kHz to 100 kHz. However SNR is not high enough for practical measurements above 20 – 30 kHz. Some continuous scan interferometers are capable of mirror velocitiess below 1 kHz.
  - Linearization makes sampling depth 3 times shorter with any mirror velocity making practical depth correspond to laser frequency of 80 kHz (1-5µm, $D = 10^{-3}\ \mathrm{cm^2/s}$)
  - Linearization requires phase matching with glassy carbon reference sample.
  - With step-scan the range is much higher starting from 1 Hz to 9 kHz. High frequencies are achieved using higher harmonic frequencies of square wave modulation, even 9th harmonics is used. The signal strength is reduced according to1/f-law towards higher harmonic frequencies.
- Depth vs. spectrum wavenumbers
  - In continuous scan the measurement depth is different for each wavenumber while in step scan it is constant.
- Calculation of phase differences
  - The calculation of phase spectra allows the determination of relative depth of several different layers with the resolution of 60 times higher than the measurement depth is – so this way also layer thicknesses well below 1 µm can be studied.
  - In continuous scan the absorption lines used for calculation of phase difference should be close to each other.