PMA50

User Manual

I 24316

5th edition 2014, publication date May 2014

This manual is the original documentation for the PMA50 module.

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1 Introduction

1.1 General safety information

Read carefully all instructions and safety notes in this manual before installing and putting the PMA50 module into operation. Keep this manual for future reference available at any time.
Always observe the instructions and safety notes given in this manual. Failure to do so can lead to severe personal injuries and/or property damage. Non-observance of the instructions and safety notes also violates the intended use of the PMA50 module. (See section 1.4.) It is the operator's duty to plan and implement all necessary safety measures and to supervise their observance. Moreover, the operator must ensure that the analysis system the PMA50 module is in proper condition and fully functioning. A safe and trouble-free operation of the PMA50 module is ensured only if all components of the analysis system are installed and operated as well as maintained and repaired according to the procedures described in this manual and in compliance with all relevant safety standards and regulation. the PMA50 module should be operated only by authorized personnel which is trained in operating the PMA50 module and which is familiar with the relevant safety instructions. Do never remove or deactivate any supporting safety systems during operation. Objects and/or material not required for the operation should be kept outside the operating area of the analysis system the PMA50 module.

1.2 Classification of the safety notes

Depending on the degree of hazard, important safety notes are classified in this manual by signal words as follows:

DANGER

➢ Indicates a hazardous situation which, if not avoided, will result in death or serious (possibly irreversible) injury and major property damage.

WARNING

➢ Indicates a hazardous situation which, if not avoided, could result in death or serious (possibly irreversible) injury and major property damage.

CAUTION

➢ Indicates a hazardous situation which, if not avoided, may result in minor or moderate (reversible) injury and minor property damage.

NOTE

➢ Hazard, which could result in material damage if the appropriate safety instructions are not observed.

1.3 Overview of possible types of hazard

1.3.1 Possible hazards during operation, maintenance and repair

Hazards that can possibly occur during operating, maintaining and repairing the PMA50 module are indicated by the appropriate warning symbols. The following warning symbols indicate different dangerous situations which may be caused by an improper use of the PMA50 module:

Warning symbol	Definition
	**General hazard:** This warning symbol indicates general hazard. Observe the safety instructions and follow the precautions described in the manual to avoid personal injury and/or property damage.
	**Danger of frostbite:** This warning symbol indicates cryogenic liquids (e.g. liquid nitrogen) required to operate the PMA50 module (e.g. cooling the detector). Exposure to these liquids causes frostbite effects. Handle the liquids with utmost care. Observe the safety instructions for handling cryogenic liquids.
	**Harmful substance:** This warning symbol indicates harmful substances (e.g. detector window material BaF_2) required to operate the PMA50 module. Eye and skin contact as well as swallowing and inhaling harmful material can cause serious health problems. Handle harmful substances with utmost care. Observe the safety instructions for the harmful substance in question.
	**Toxic substance:** This warning symbol indicates toxic substances (e.g. polarizer material KRS-5) required to operate the PMA50 module. Eye and skin contact as well as swallowing and inhaling can cause death or serious health problems. Handle toxic substances with utmost care. Observe the safety instructions for the toxic substance in question.

1.3.2 Possible hazardous sample materials

There can also be hazards caused by the sample material. Depending on the type of hazardous substances you work with, you have to observe specific substance-relevant safety instructions. Affix the corresponding warning label on the appropriate position at the PMA50 module. The label must be well legible and permanently discernible. The following list contains some examples of hazardous substances:

Symbol	Definition
	**Infectious material** This warning symbol indicates the possible existence of biologically dangerous and infectious material. When working with this kind of material always observe the prevailing laboratory safety regulations and take necessary precautions and disinfection measures (e.g. wearing protective clothing, masks, gloves etc.). Non-observance may cause severe personal injury or even death. For information on how to use, dilute and efficiently apply disinfectants, refer to the *Laboratory Biosafety Manual: 2004 by WHO - World Health Organization*.
	**Radioactive material** This warning symbol indicates the possible existence of radioactivity. When working with radioactive material always observe the safety regulations and take necessary protective measures. Wear protective clothing, e.g. masks and gloves. Non-observance may cause severe personal injury or even death.
	**Corrosive substances** This warning symbol indicates the possible existence of corrosive substances. When working with corrosive substances always observe the laboratory safety regulations, and take protective measures (e.g. wear protective masks and gloves). Non-observance may cause severe personal injury or even death.

Waste disposal

Dispose all waste produced (chemicals, infectious and radioactively contaminated substances etc.) according to the prevailing laboratory regulations. Detergents and cleaning agents must be disposed according to the special waste regulations.

1.4 Intended use

The PMA50 module is designed for polarization-modulated, spectroscopic measurements (VCD and PM-IRRAS). It is suited for the following kinds of sample: solids and liquids.

The PMA50 module is approved for the use in a laboratory under the ambient conditions specified in appendix A.

The intended use includes also the compliance with the relevant standards and regulations, especially:

- national and local safety regulations
- national and local accident prevention regulations
- generally recognized technical regulations

The intended use also includes the strict observance of all instructions given in this manual, namely:

- safety instructions
- installation instructions,
- operation instructions
- repair and maintenance instructions

⚠ WARNING

Health hazard because of unintended use of the PMA50 module

Non-observance of the following safety instruction could result in serious injury (possibly irreversible skin and/or eye injuries).

➢ Do not take any action that violates the intended use. The operational safety of the PMA50 module is ensured only if it is used as intended.

1.5 Service contact data

In case you have questions about safety, installation and/or operation of the PMA50 module or you need technical assistance in case of a hardware and/or software problem, you can contact the Bruker service as follows:

- Service hotline hardware: +49 (0) 72 43 504-2020
- Service hotline software: +49 (0) 7243 504-2030
- Fax: +49 (0) 72 43 504-2100
- E-mail: service@brukeroptics.com
- Internet: www.brukeroptics.com

2 General

2.1 General information

The PMA50 module is a polarization modulation accessory for FT-IR spectrometers of the TENSOR and VERTEX series. It is designed for PM-IRRAS, VCD and other types of polarization modulation experiments.

The PMA50 module allows for both the study of circular dichroism (e.g. VCD spectroscopy) and the study of linear dichroism (e.g. PM-IRRAS). An integrated photoelastic modulator modulates the polarization as required for the measurement technique in question. All optical and electronic components are optimized for polarization modulation.

The PMA50 module allows for a fast and easy switching between the PM-IRRAS configuration and the VCD configuration.

2.2 Instrumental setup

The PMA50 module is an accessory which is coupled to the right side of a FT-IR spectrometer of the TENSOR and VERTEX series.

Figure 2.1: PMA50 module coupled to a VERTEX70 spectrometer

2.3 Technical features

The data acquisition is based on a free running delta-sigma, dual-channel A/D converter with 24-bit dynamic range. The A/D converter is integrated into the detector preamplifier electronics. The DigiTect technology ensures a signal transmission free from interferences and guarantees the highest signal-to-noise ratio. In addition, the preamplifier has an analog input and an analog output so that the analog detector signal and the input of an analog signal can be extracted, as required for PM-IRRAS measurements, for example. Another required detector feature is the dual channel acquisition mode for the simultaneous acquisition of the IR signal and the reference signal of the PEM.

The detector is mounted on an arcuate rail to allow for a user-adjustable angle of incidence (incidence angle range: between 70° and 90°). This technical feature is of special relevance for PM-IRRAS measurements.

The PMA50 module is equipped with photoelastic modulator (PEM) which modulates the polarization as required for the measurement technique in question. Depending on the applied frequency (standard frequency: 42 kHz or double standard frequency: 84 kHz), the wave plate of the optical head acts either as a half-wave plate or a quarter-wave plate. For VCD measurements, the vibrating optical element of the PEM acts as a quarter-wave plate producing light which oscillates between left and right circular polarized light. For PM-IRRAS measurements, the vibrating optical element of the PEM acts as a half-wave plate producing p-polarized and s-polarized light alternately.

2.4 Purge ability

The sample compartment and the optics of the PMA50 module are purgeable. Purging the PMA50 module with dry air or nitrogen gas reduces the content of unwanted atmospheric interferents (e.g. water vapor and carbon dioxide) inside the PMA50 module significantly. Residual absorption by these atmospheric gases can lead to a significant high noise level and may mask in the IR spectrum weak spectral features of the sample. Purging is the most common method of reducing the water vapor content inside the analyzing instrument.

2.5 Measurement techniques

The PMA50 module is especially designed for the following spectroscopic measurement techniques:

- VCD spectroscopy (vibrational circular dichroism)
- PM-IRRAS (polarization modulation infrared reflection-absorption spectroscopy)

2.5.1 VCD spectroscopy

VCD (Vibrational Circular Dichroism) is a spectroscopic measurement technique which detects the difference in absorption of right and left circularly polarized IR radiation $\Delta A = A_L - A_R$ passing through optically active compounds.

Typical fields of application of VCD spectroscopy are the determination of:

- secondary structure of proteins and peptides
- purity of enantiomers
- absolute structure of enantiomers

☞ For more detailed background information about this spectroscopic measurement technique, refer to the glossary in appendix D.

2.5.2 PM-IRRAS

PM-IRRAS is a spectroscopic measurement technique for the analysis of adsorbed matter or very thin layers on reflecting surfaces (mostly metal substrates). It is a combination of PM (Polarization modulation) and IRRAS (Infrared reflection absorption spectroscopy).

PM-IRRAS takes advantage of the fact that the adsorbate or the thin layer on the reflecting metallic substrate interacts mainly with p-polarized light at a large angle of incidence, but almost not with s-polarized light. For this purpose, the polarization of the light needs to be modulated in such a way that the sample is exposed alternately to p-polarized and s-polarized light.

In surface science, PM-IRRAS is a widely used measurement technique. Typical fields of application are the analysis of:

- coatings and ultra thin layers
- organic (sub-) monolayers on a reflective (metal) surface
- corrosion processes
- molecules adsorbed from the gas phase
- catalytic reactions
- adsorbate-modified electrode / electrolyte interfaces

☞ For more detailed background information about this spectroscopic measurement technique, refer to the glossary in appendix D.

General 2

3 Installation

3.1 General information

Installation and initial start-up of the PMA50 module are done by the Bruker service. The operating company has to provide an installation site that meets the site requirements described in section 3.5.

The installation of the PMA50 module includes the following works:

- coupling the PMA50 module to an FT-IR spectrometer (Note: This installation work is done exclusively by the Bruker service!)
- connecting the PMA50 module to the PEM controller and to the FT-IR spectrometer
- connecting the PMA50 module to a purge gas supply line

☞ **For information about the installation of the FT-IR spectrometer and the PEM controller, refer to the respective user manuals.**

3.2 Delivery scope

The delivered items are divided into standard components and optional components. So the actual delivery scope depends on the customer's order.

Standard components:	The standard delivery scope includes the following items: • PMA50 module (including the user manual) • Photoelastic modulator: The delivery scope of the photoelastic modulator includes the following components: electronic head and optical head of the PEM, PEM controller, cables (power cord and head-to-controller cable with DE9 connectors) and user manual. • Linear polarizer mounted in a rotatable holder • Lens mounted on the lens-detector-unit • MCT detector with BaF_2 window • Detector cable (cable with the DB25 connectors) • Standard sample holder
Optional components:	The delivery scope can also include following optional components: • Special sample holder for PM-IRRAS measurements • Accessory kit for VCD measurement This kit includes the following components: calibration crystal (CdS-wave plate), polarizer mounted in a rotatable holder, VCD standard (KBr pellet mounted in a pellet holder), one optical low path filter (standard: < 1800cm^{-1}) and the software package OPUS/VCD. • Liquid cell(s) • Pellet holder • Heatable sample holder • Purge option S316/V (Note: This option includes the required hoses and an air flow regulator.)

3.3 Inspecting the packaging

After having received the PMA50 module, inspect the packaging for damages.

⚠ CAUTION

Possible damage to the delivered PMA50 module because of transport damage

Non-observance of the following safety instructions could result in injury.

- ➢ Inspect the packaging for damages. If there are signs of damage contact shipping company.
- ➢ A PMA50 module delivered in a damaged packaging might be damaged as well. Therefore, in this case do not put the module into operation. Risk of injury! Contact Bruker instead. (See section 1.5.)

3.4 Transporting the PMA50 module

Due to its weight (ca. 35 kg) and dimensions, the PMA50 module has to be carried by two persons. For transporting the PMA50 module over a long distance, it is recommended to use a wheeled table, for example.

⚠ CAUTION

Injury and/or PMA50 module damage due to an inadequate method of transport

Non-observance of the following safety instructions could result in injury.

- ➢ For short-distance transport, the PMA50 module can be carried by two persons. But pay attention to the module weight (ca. 35 kg).
- ➢ For long-distance transport, put the PMA50 module on a wheeled table or use a fork lifter, for example. To avoid damages, transporting the PMA50 module in original packing is recommended.

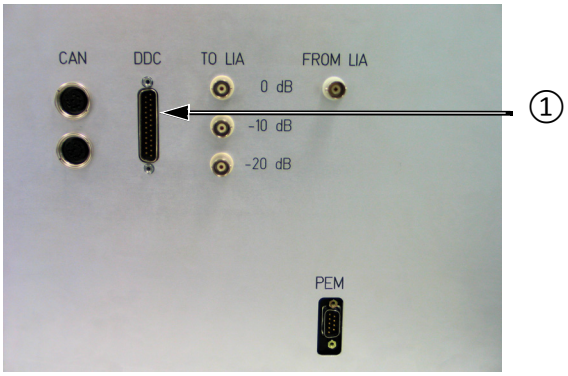
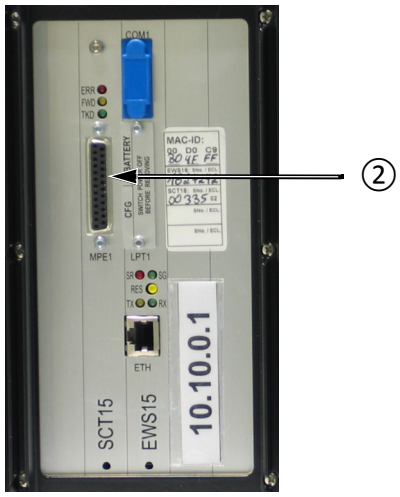
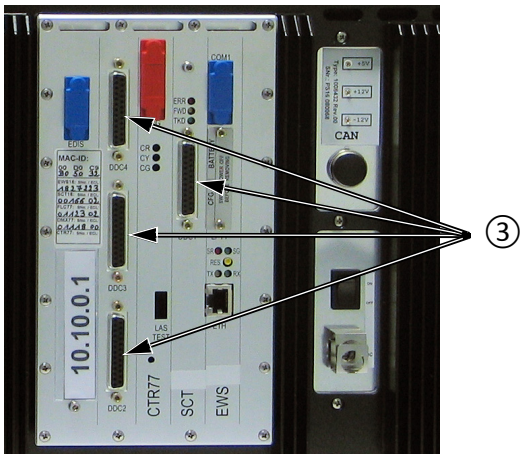
3.5 Site requirements

The operating company has to provide an installation site that meets the following site requirements:

Space requirements:	• PMA50 dimensions: 69cm x 48cm x 29cm (width x depth x height) ☞ For the exact dimensions refer to appendix C. • At the rear side, the spectrometer requires a clearance of at least 25cm (10“). • Make sure that the installation site is dimensioned for the PMA50 module **and** the FT-IR spectrometer to which it is to be coupled. ☞ For information about the spectrometer dimensions, refer to the user manual of the spectrometer in question. • The PMA50 module has to be placed on a stable and horizontal base which is rated for the weight of the PMA50 module (ca. 35 kg) **and** the weight of the FT-IR spectrometer to which it is to be coupled. ☞ For information about the spectrometer weight refer to the user manual of the spectrometer in question.
Environmental conditions:	• Ambient temperature range: 18°C - 35°C (64°F to 95°C) • Ambient temperature variations: max. 1°C/h and max. 2°C/day (Temperature variations can impair the results of long-term measurements.) • Humidity (non-condensing): ≤ 80% (relative humidity) • Installation site: in a closed room, max. 2000m above sea level • The PMA50 module should not be installed near vibration sources (e.g. ventilation hoods, air conditioners, motors elevators) or in rooms with intense floor vibrations. **Important: The PEM is extremely sensitive to shock! Risk of damage due to shock!**
Purge gas supply requirements:	• dry air or nitrogen gas (dew point < -40°C corresponds to a degree of dryness of 128ppm humidity) • oil-free and dust-free • max. pressure: 2 bar (29 psi) • Recommended purge gas flow rate: 200 liters/hour. • Purge gas flow rate should not exceed 500 liters/hour. Note: The local purge gas supply line needs to be dimensioned for a PVC hose having an outer diameter of 6mm.

3.6 Connecting the PMA50 module to the FT-IR spectrometer

With the cable connection between PMA50 module and FT-IR spectrometer, the digital detector connection is realized. Use the cable with the DB25 connectors.

Electronics unit connector panel of the PMA50 module 	male DDC connector ① at the rear side of the PMA50 module
Electronics unit connector panel of a spectrometer of the TENSOR series  **Electronics unit connector panel of a spectrometer of the VERTEX series** 	Depending on the series of the spectrometer to which the PMA50 module is coupled, connect the cable to the MPE1 socket ② at the rear side of a TENSOR spectrometer and a DDC socket ③ at the rear side of a VERTEX spectrometer, respectively. ➢ In case of a VERTEX spectrometer, there are four DDC sockets (DDC1 ... DDC4). Connect the cable to one of the four sockets. Note: The DDC4 socket cannot be used if a detector is connected to the DDC4 socket inside the spectrometer. In this case, the socket is covered with a cap.

3.7 Connecting the PMA50 module to the PEM controller

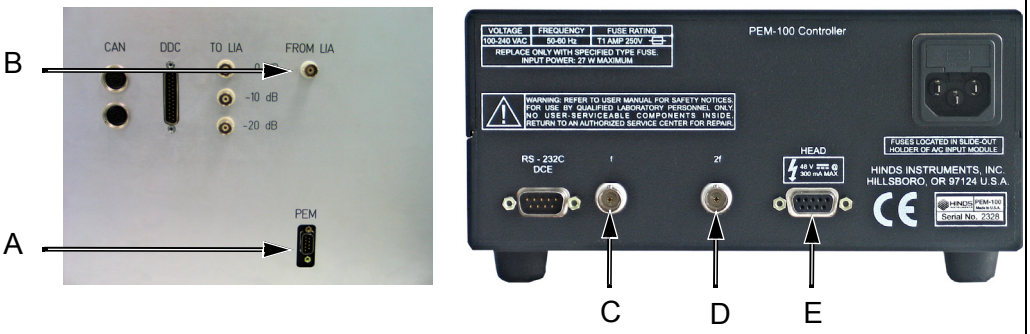


Figure 3.1: PMA50 module and PEM controller - Relevant connection sockets

Fig. 3.1	Connector name
A	PEM (male DE9 connector) Note: It is the connector of the electronic head of the PEM.
B	FROM LIA
C	f This female BNC connector provides TTL output of the PEM, first harmonic frequency (42 kHz).
D	2f This female BNC connector provides TTL output of the PEM, second harmonic frequency (84 kHz).
E	HEAD (female DE9 connector)

NOTE

To avoid damage to the electronic head of the PEM, observe the following instructions:

➢ Make sure that the **PEM controller is switched off** before you connect the PMA50 module to the PEM controller.

➢ In case you switch between VCD and PM-IRRAS, first switch off the PEM controller before you change the cable connection at the rear side of the PEM controller.

➢ Connect the cable with the DE9 plugs to the PEM connector (A in fig. 3.1) and the HEAD connector (E in fig. 3.1).

➢ **For VCD experiments only:** Connect the cable with the BNC plugs to the FROM LIA connector (B in fig. 3.1) and the connector labelled *f* (C in fig. 3.1).

☞ Note: With this cable connection, the optical element of the PEM is stressed mechanically with a frequency of 42 kHz. In this case, the optical element acts as a quarter-wave plate.

➢ **For PM-IRRAS experiments only:** Connect the cable with the BNC plugs to the FROM LIA connector (B in fig. 3.1) and the connector labelled *2f* (D in fig. 3.1).

☞ Note: With this cable connection, the optical element of the PEM is stressed mechanically with a frequency of 84kHz. In this case, the optical element acts as a half-wave plate.

3.8 Connecting PMA50 to a purge gas supply line

3.8.1 General information

The PMA50 module has two purge gas inlets; one for purging the sample compartment and the other for purging the optical bench (interferometer and detector compartment). The purge gas inlets and the purge gas outlet are at the PMA50 module rear side.

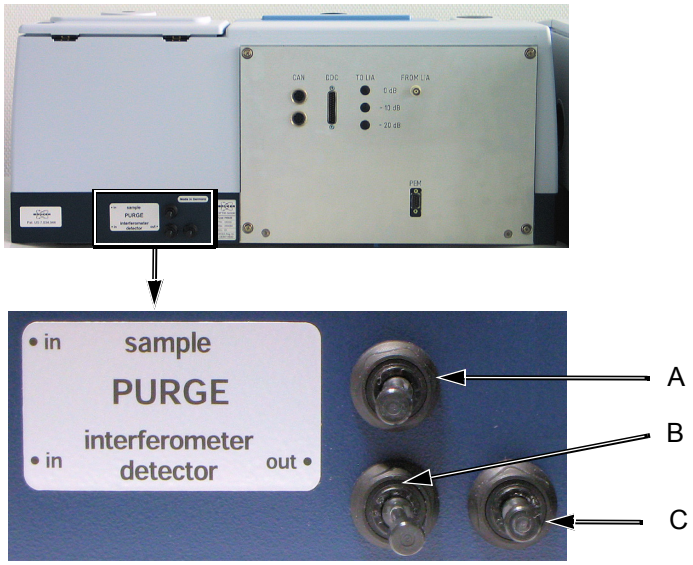


Figure 3.2: Location of the purge gas inlets and outlet (PMA50 module rear side)

Figure 3.2	Purge gas inlet / outlet for ...
A	Purge gas inlet for sample compartment (Figure 3.2 shows the purge gas inlet with installed plug.)
B	Purge gas inlet for optical bench (Figure 3.2 shows the purge gas inlet with installed plug.)
C	Purge gas outlet for the optical bench (Figure 3.2 shows the purge gas outlet with installed plug.)

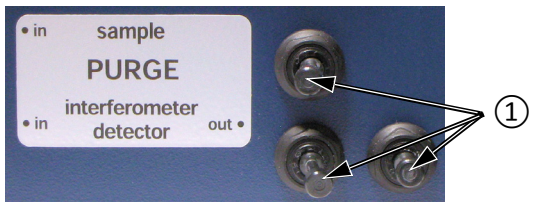
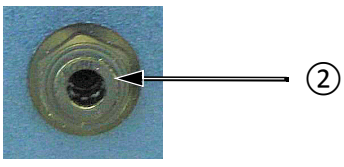
3.8.2 Purge gas supply requirements

The purge gas supply has to meet the following requirements:

- dry air or nitrogen gas (dew point < -40°C corresponds to a degree of dryness of 128ppm humidity)
- oil-free and dust-free
- max. pressure: 2 bar (29 psi)
- Controllable flow rate (Note: When the spectrometer is purged continuously the recommended flow rate is 200 liters/hour. Make sure that the flow rate does not exceed 500 liters/hour.)

3.8.3 Procedure

i The required hoses are not included in the standard delivery scope. Normally, it is the operating company's duty to provide the hoses of the required length (PVC hose, outer diameter: 6mm). Make sure that the hose is rated for the indicated operating pressure. Only in case the purge option S316/V has been ordered, the required hoses including an air flow regulator are included in the delivery scope of the spectrometer.

1	  	Remove the plugs ① from the purge gas inlets and the purge gas outlet. **Note:** When you intend to purge the optical bench, do not forget to remove the plug of the purge gas outlet as well. Otherwise, overpressure will build up inside the spectrometer during purging. This may lead to PMA50 module damage. To remove a plug, press the lock ring ② inwards and pull out the plug. **Note:** All inlet ports have such a lock ring. The lock ring prevents the hose from being pulled out unintentionally.
2		Insert the hoses into the purge gas inlets.
3	Connect the other end of the hose to the local purge gas supply line.	

Depending on whether you want to purge either only the sample compartment or only the optical bench (i.e. interferometer compartment and detector compartment) or both compartments, there are two variants for connecting the hose.

For purging EITHER the sample compartment OR the optical bench

This variant requires a stiff PVC hose with an outer diameter of 6mm.

Remove the plug from the purge gas inlet of either the sample compartment (A in fig. 3.2) or the optical bench (B in fig. 3.2) and insert the hose in the purge gas inlet.

Connect the other end of the hose to the local purge gas supply line.

For purging BOTH the sample compartment AND the optical bench

This variant requires a stiff PVC hose (T-shaped) with an outer diameter of 6mm.

Connect the main end of the T-shaped hose to the local purge gas supply line.

Remove the plugs from both purge gas inlets at the spectrometer rear side (A and B in fig. 3.2) and insert the other two ends of hose in the purge gas inlets.

4 Overview

This chapter provides an overview of all user-relevant components of the PMA50 module.

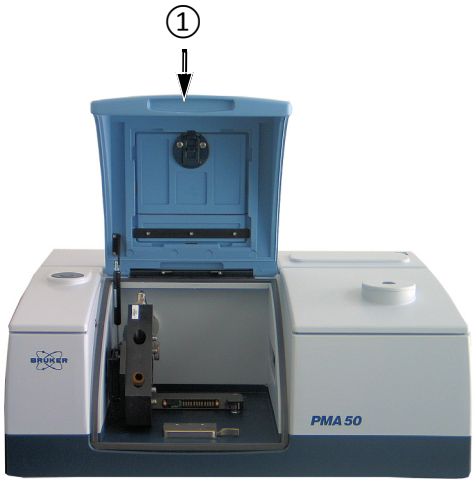
4.1 PMA50 module compartments

Figure 4.1: PMA50 module (Top view)

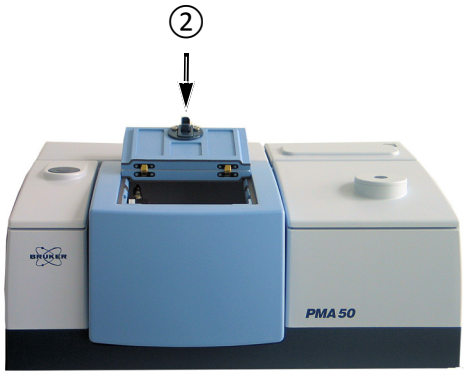
Fig. 4.1	Compartments
A	Electronics compartment
B	Mirror compartment In this compartment, the IR beam coming from the FT-IR spectrometer is coupled into the PMA50 module.
C	STATUS, HUMIDITY and LASER LED display **Important:** This LED display is **not** in use. For information regarding status, humidity and laser, see the corresponding LED display at the FT-IR spectrometer to which the PMA50 module is coupled.
D	Detector compartment
E	Sample compartment

4.2 Sample compartment

The sample compartment can be accessed from the front side as well as from the top side of the PMA50 module. You can either turn the whole sample compartment cover upwards or open only the top lid using the handle.

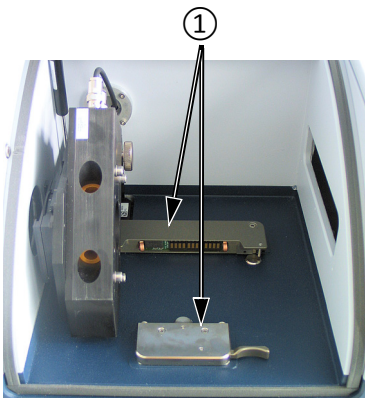


For installing the sample holder in the sample compartment or removing it, the whole sample compartment cover ① needs to turned upwards.



For loading / unloading the standard sample holder, for example, it is sufficient to turn only the top lid ② of the sample compartment cover backwards.

The sample compartment dimensions are 25cm (w) x 27cm (d) x 16cm (h).



The sample compartment is equipped with a QuickLock locking mechanism ① which allows for an exact and reproducible positioning of the sample holder in the sample compartment.

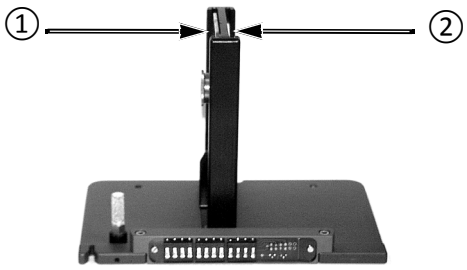
For detailed information about how to lock / unlock the sample holder in the PMA50 sample compartment, see section 5.9.

4.3 Sample holder

For each type of experiment - VCD and PM-IRRAS, there is a dedicated sample holder.

Both types of sample holder are mounted on a QuickLock baseplate. For information about how to lock / unlock the sample holder in the sample compartment of the PMA50 module, refer to section 5.9

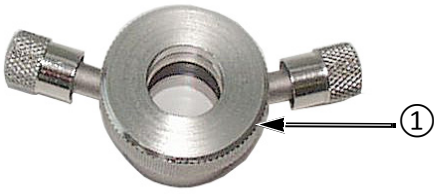
4.3.1 Sample holder and liquid cells for VCD

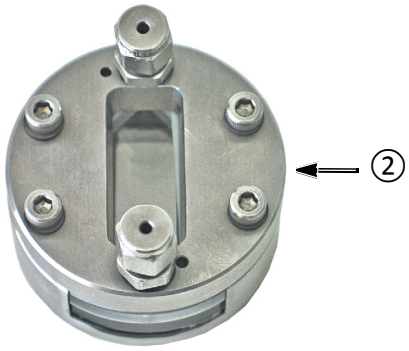


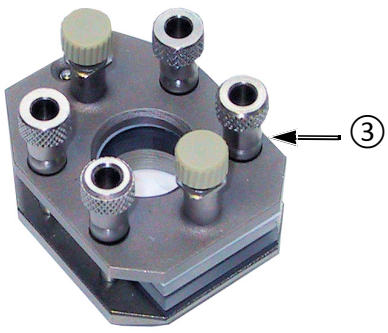
Sample holder

For VCD measurements, the standard sample holder is used.

The sample holder has two slide rails (① and ②) for inserting the pellet holder, the liquid cell attached at a magnetic holder plate, the calibration plate and the polarizer.







Liquid cells

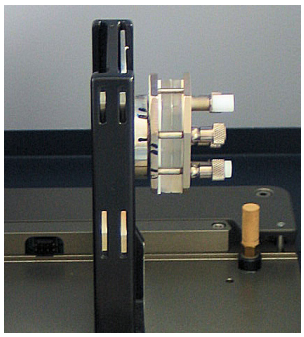
For liquid samples, the following liquid cells are available:

① - A140 - demountable liquid cell, vacuum tight (Note: This liquid cell is suitable for small amounts of volatile liquids. The usage of this liquid cell requires the magnetic holder plate A140-H.)

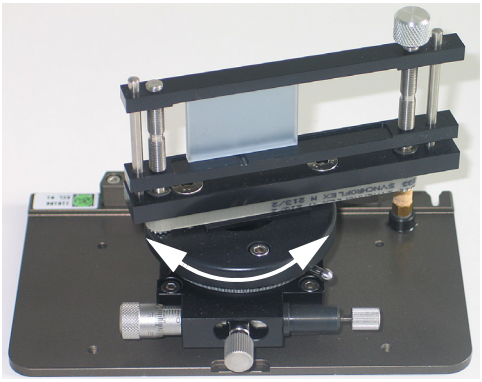
② A141D17 - demountable liquid cell, flow-through version (Note: With this liquid, the temperature of the sample can be controlled. The temperature control requires additional components.) For measurements at room temperature, the holder A141-H is required. For heating the sample, the cell holder A141-HH is required.

③ A145 - demountable liquid cell (Note: The usage of this liquid cell requires the magnetic holder plate A140-H.)

➢ For detailed information about the above listed liquid cells, refer to the attached user instructions.

	In case of the liquid cells A140 and A145, attach the liquid cell at the magnetic holder plate (A140-H) and insert it in the right slide rail of the sample holder.
	**Pellet holder** For solid samples in form of a KBr pellet, a pellet holder is available. Put the KBr pellet in the pellet holder and insert the pellet holder in a slide rail of the sample holder.
	**Heatable sample holder** For controlling the temperature of the KBr pellet, an optional heatable sample holder (A599) is available. With this sample holder, the sample can be heated up to 180°C. Note: The heatable sample holder can be inserted in a slide rail of the standard sample holder.

4.3.2 Sample holder for PM-IRRAS



For PM-IRRAS experiments, there is a dedicated sample holder with a rotatable sample clamping device (i.e. rotatable around its vertical axis).

The rotatable sample clamping device allows for adjusting the sample position in such a way that the light beam impinges on the detector element and that there is sufficient signal intensity. (Note: For PM-IRRAS, a large angle of incidence is required. This angle is set by the user by changing the detector position. See section 5.7.6.)

The clamping device of the holder is dimensioned for samples up to 33mm x 75mm.

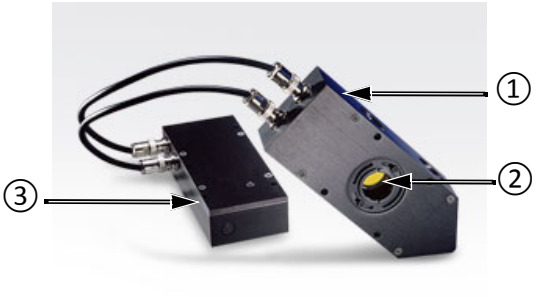
☞ For detailed information about how clamp the sample into the holder and how to position the sample, refer to section 5.7.6.

4.4 Photoelastic modulator (PEM) and controller

General information

The photoelastic modulator (PEM) changes the polarization state of the light beam at a fixed frequency. The principle of operation is based on the photoeleastic effect, in which a mechanically stressed birefringent material (i.e. the optical head of the PEM) exhibits birefringence proportional to the resulting strain. The birefringent material is bonded to a piezoelectric transducer. Both the optical element and the transducer are tuned to the same frequency. When the transducer-optical element assembly is connected to a drive circuit, it oscillates and produces a time-varying birefringence. In doing so, the optical element of the PEM acts as a "dynamic waveplate" and converts linear polarized light into light which oscillates between left and right circular polarized light or which oscillates between s-polarized and p-polarized light, depending on the applied frequency.

The antireflection coating of the PEM increases the throughput of light through the modulator in order to reduce interference effects and the fraction of light which passes through the modulator at a unwanted peak retardation.

	**Photoelastic modulator (PEM)** The PEM consists of: ① optical head ② optical element (material: ZnSe) ③ electronic head
	**PEM controller** Its primary function is to control the peak retardation of the PEM optical head. It does this by providing a DC voltage signal to the electronic head which determines the transducers vibration amplitude and thus the strain amplitude in the optical element. A current feedback loop from the electronic head enables the controller to maintain stable peak retardation levels. Using the PEM controller, the user can control the peak retardation and wavelength settings of the modulator head set.

For detailed information about the photoelastic modulator and its controller, refer to the User manual of the PEM-100 Photoelastic Modulator.

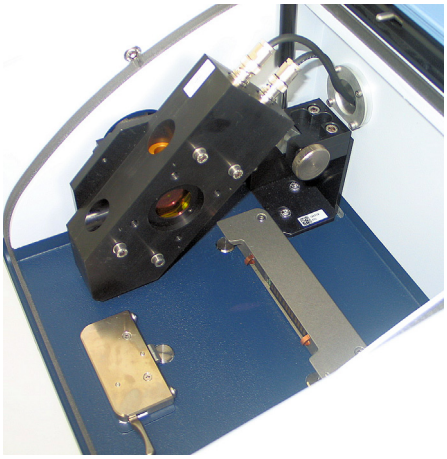


Figure 4.2: Photoelastic modulator installed in the PMA50 module

Handling instruction

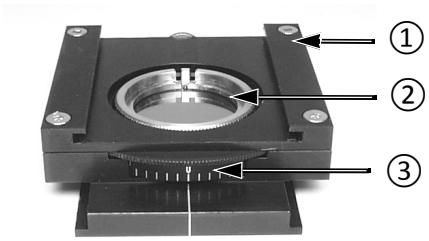
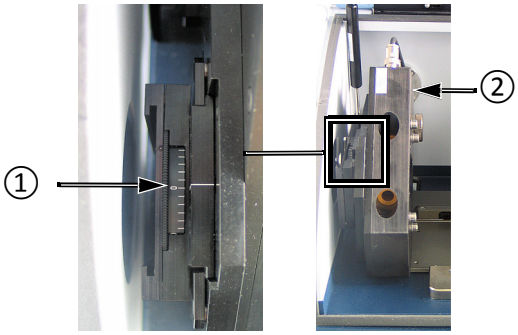
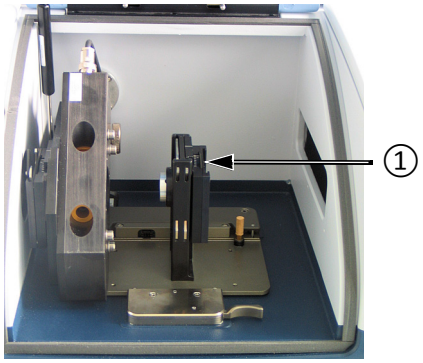
NOTE

- ➢ The photoelastic modulator is extremely shock-sensitive. Do not expose the PEM to shocks. Otherwise the PEM can be damaged irreversibly.
- ➢ Do not switch on the PEM controller until the optical head and the electronic head are interconnected. Otherwise the PEM can be damaged irreversibly.
- ➢ Before putting the PEM into operation, read carefully the PEM user manual.
- ➢ Do not try to remove or reinstall the PEM. If the PEM needs to be removed or installed, contact the Bruker service. See section 1.5.
- ➢ Do not touch the optical element as this will irreversibly damage the optical element.

4.5 Polarizer and polarizer holders

General information

For both spectroscopic measurement techniques - VCD and PM-IRRAS - a linear polarizer is required.

	The polarizer ② is integrated into a holder ①. The polarizer can be rotated manually. The angle scale ③ indicates the polarizer orientation. Rotating the polarizer changes the polarization of the light passing though the polarizer.
	The polarizer ① is inserted in the slide rail at the left side of the PEM ②.
	For VCD calibration measurements, a second polarizer ① of the same type is required. This polarizer is inserted in the right slide rail of standard sample holder.

☞ For the specifications of the polarizer, see section A.3.

Safety notes

The polarizer material is KRS-5. KRS-5 is very toxic. During normal operation, this material does not pose any health hazard. If, however, the polarizer should break because of mechanical impact, be extremely careful.

⚠ WARNING

Health hazard because of improper handling of broken toxic polarizer material

Non-observance of the following safety instructions could result in death or serious injury.

- ➢ Avoid generating dust of broken polarizer material. This material is toxic if swallowed or inhaled.
- ➢ Also avoid skin and eye contact.
- ➢ Dispose the harmful or toxic material according to the laboratory regulations and the national regulations.

Handling instruction

NOTE

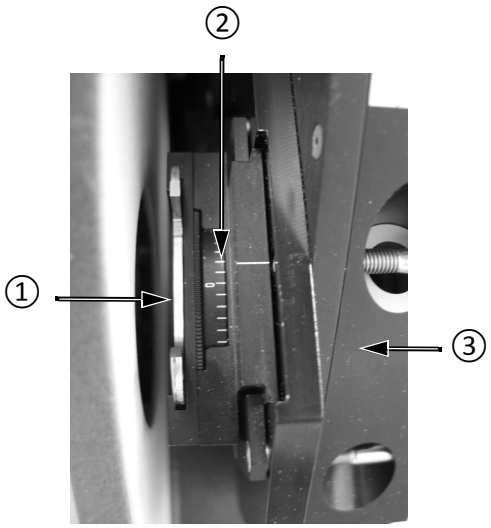
- ➢ Do not touch the surface of the polarizer. This will damage the polarizer irreversibly.

4.6 Optical low-pass filter

General information

For VCD measurements, an optical low-pass filter can be used. Optical low-pass filters with the following cutoff frequencies are available: low-pass filter < 1,828 cm^{-1} and low-pass filter < 3860cm^{-1}.

With an optical low-pass filter, a larger aperture can be used. A larger aperture increases the amount of light which in turn improves the S/N ratio.



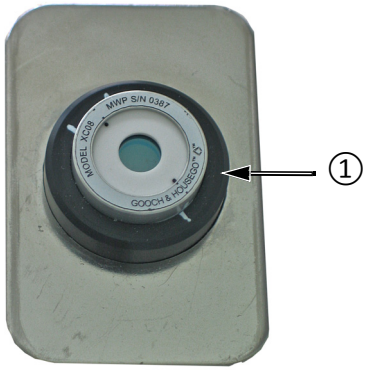
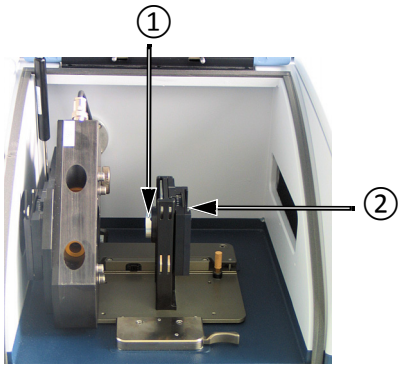
The optical low-pass filter ① has to be inserted in the slide rail at the left side of the PEM ③ and before the polarizer ② from viewpoint of the beam path.

Handling instruction

NOTE

➢ Do not touch the surface of the optical filter. This will damage the optical filter irreversibly.

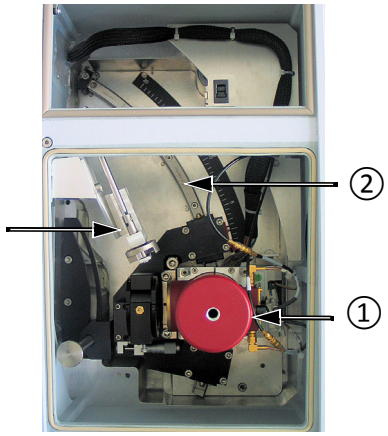
4.7 Multiple wavelength plate

	The multiple wavelength plate ① (material: CdS) is only used for calibration measurements in VCD spectroscopy. It is the calibration sample.
	The multiple wavelength plate ① has to be inserted in the left slide rail of the sample holder. Note: In the right slide rail of the sample holder, the second polarizer ② has to be inserted.

4.8 Detector

General information

The available detectors are equipped with an integrated amplifier and an A/D converter which converts the analog signal from the detector directly into a digital signal. This so called DigiTect technology allows for an interference-free signal transmission and ensures a high signal-to-noise-ratio. In addition, the detector preamplifier allows for the extraction of the analog detector signal and the input of an analog signal as required for VCD and PM-IRRAS measurements.



The detector ① is mounted on an arcuate rail ② to allow for a user-adjustable angle of incidence (incidence angle range: between 70° and 90°). See section 5.7.6.

☞ **Important:** This feature is of relevance for PM-IRRAS measurements only. For VCD measurements, the angle position of the detector has always to be 0°.

Available detectors

The standard detector for the PMA50 module is the MCT detector with BaF_2 window. This detector is well-suited for both spectroscopic measurement techniques - VCD and PM-IRRAS.

The photovoltaic MCT detector with BaF_2 window and MCT detector with ZnSe window are less sensitive than the standard detector. For this reason, they can be used for PM-IRRAS measurements, but not for VCD measurements.

Detector	Spectral range (cm^{-1})	Sensitivity	Cooling method
MCT narrow band, with BaF_2 window (Standard detector for PMA50) **HARMFUL!**	12,000 - 850	D^*:>$4x10^{10}$cm $Hz^{1/2}$ W^{-1}	Liquid N_2 cooled
Photovoltaic MCT, with BaF_2 window **HARMFUL!**	12,000 - 850	D^*:>$3x10^{10}$cm $Hz^{1/2}$ W^{-1}	Liquid N_2 cooled
MCT mid band, with ZnSe window **Toxic!**	12,000 - 600	D^*:>$2x10^{10}$cm $Hz^{1/2}$ W^{-1}	Liquid N_2 cooled

The detectors are equipped with windows of which the material is harmful or toxic. During normal operation, these materials do not pose any health hazard. However, should such a detector window break because of mechanical impact, be extremely careful.

⚠ WARNING

Health hazard because of improper handling of broken harmful or toxic detector window material

Non-observance of the following safety instructions could result in death or serious injury.

- ➢ Avoid generating dust of broken detector window material. This material is harmful or toxic if swallowed or inhaled.
- ➢ Also avoid skin and eye contact.
- ➢ Dispose the harmful or toxic material according to the laboratory regulations and the national regulations.

4.9 Electronics

The detector electronics is equipped with an integrated preamplifier and an A/D converter which converts the detected analog signals directly into digital signals. In addition, the preamplifier has an analog input and an analog output so that the analog detector signal and the input of an analog signal can be extracted, as required for PM-IRRAS measurements, for example. Another required detector feature is the dual channel acquisition mode for the simultaneous acquisition of the IR signal and the reference signal of the PEM.

For further signal processing, the spectrometer electronics is equipped with a digital high-pass filter and two digital low-pass filters.

The bock diagram in figure 4.3 illustrates the signal path of the two signals.

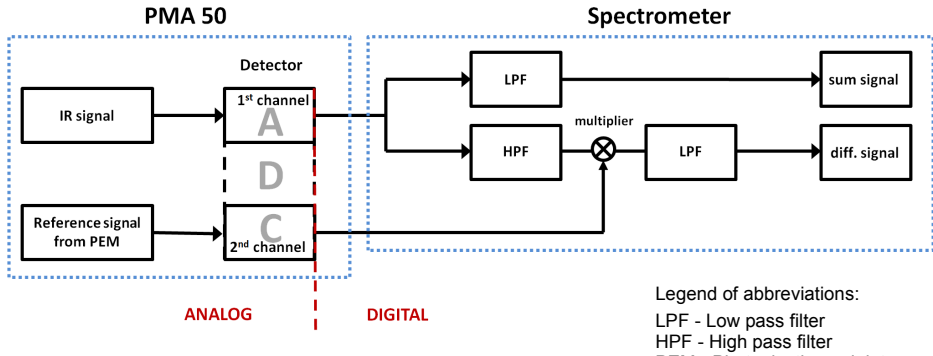


Figure 4.3: Signal path of the different types of signal

For VCD and PM-IRRAS measurements, the dual channel acquisition mode of the detector needs to be activated. With the activated dual channel acquisition mode, the detector detects the IR signal and the reference signal from the PEM simultaneously. The integrated ADC digitizes the two signals. Then, the two signals are transferred to the spectrometer electronics. Using these two signals, the spectrometer electronics generates the sum signal and the difference signal as follows:

The digitized IR signal passes parallel a digital low-pass filter and a digital high-pass filter. The low-pass filtered part of IR signal is the sum signal (i.e. the normal signal).

The high-pass filtered part of IR signal is mixed down with the reference signal from the PEM by a multiplier. The result signal is the difference signal. Afterwards, the difference signal passes an LPF.

5 Operation

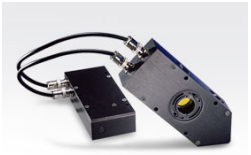
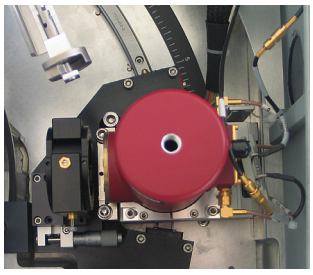
5.1 General information

The PMA50 module is designed for the following spectroscopic measurement techniques: PM-IRRAS and VCD. Depending on the measurement technique, the measurement procedure and the special equipment are different.

☞ For detailed information about these measurement techniques refer to the glossary in appendix D.

5.2 Standard equipment

For both measurement techniques - VCD and PM-IRRAS - the following standard equipment is required:

	PMA50 module coupled to a FT-IR spectrometer of the TENSOR or VERTEX series
 	Photoelastic modulator (PEM) and PEM controller
	Linear polarizer (rotatable) including holder Note: The polarizer at the left side of the PEM is meant.
	Detector with modified preamplifier
OPUS Spectroscopy Software	OPUS/IR package (Standard software program for spectroscopic measurements)

5.3 Switching on the analysis system

Switching on the complete analysis system (i.e. FT-IR spectrometer, PEM and PEM controller, PC and monitor) involves the following steps:

Switch on the spectrometer using the ON/OFF switch (1) at the spectrometer rear side.

➢ After having switched on the spectrometer, wait at least 15 minutes before starting the first measurement. This allows for the spectrometer to stabilize. For high-precision measurements, wait at least two hours to allow the laser to stabilize.

☞ For detailed information about the spectrometer, refer to the User Manual of the spectrometer in question.

Switch on the PEM controller using the POWER button (1).

☞ For detailed information about the PEM controller, refer to the User Manual of the PEM-100 Photoelastic Modulator.

➢ Switching on the PEM controller sets automatically the PEM into operation.

Switch on the PC and the monitor.

☞ See the user manual of the PC and the monitor.

5.4 Activating / deactivating the polarization modulation mode

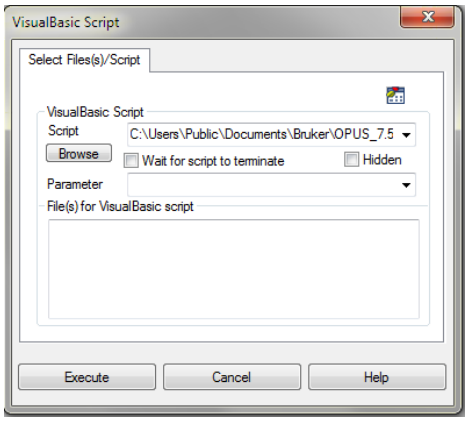
Before you start a VCD measurement or a PM-IRRAS measurement, you need to activate the corresponding polarization modulation mode for the optical bench of the analysis system. Otherwise, the measurement is performed without polarization modulation or with the wrong polarization modulation frequency.

In case you want to perform a non-polarization-modulated measurement with the FT-IR spectrometer to which the PMA50 module is coupled, you need to deactivate the polarization modulation mode. Otherwise an error message is displayed in OPUS. See section 7.3.6.

The polarization modulation mode can be activated / deactivated:

- by using a dedicated VBscript or
- by entering the corresponding direct command in OPUS and sending it to the optical bench.

5.4.1 Dedicated VBscript

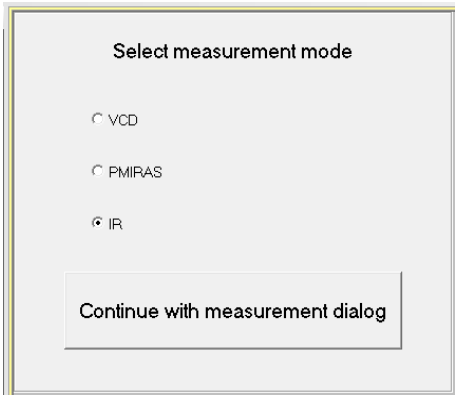


Proceed as follows:

1. Open the OPUS program.
2. In OPUS → *File* menu → *VisualBasic Script* function
3. Browse to *C:\Users\Public\Documents\Bruker\OPUS xxx [with xxx being the current OPUS version] \VBSample.*

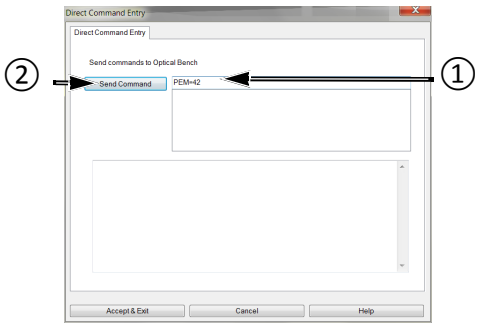
➢ Note: To browse to this directory, navigate in the file manager as follows: *Libraries\Documents\public documents \Bruker\OPUS xxx [with xxx being the current OPUS version] \VBSample.*

4. Select the VBscript file *Measurement_mode.obs*.
5. Click on the *Execute* button.



6. Activate the corresponding option button:
   - VCD: for activating the VCD polarization modulation mode (PEM frequency: 42 kHz)
   - PM-IRRAS: for activating the PM-IRRAS polarization modulation mode (PEM frequency: 84 kHz)
   - IR: for deactivating any polarization modulation mode
7. Click on the *Continue with measurement dialog* button.

5.4.2 Direct OPUS command



Proceed as follows:

1. Open the OPUS program.
2. In OPUS → *Measure* menu → *Command Entry* function
3. Enter the corresponding command ①.
   - For activating the VCD polarization modulation mode: PEM=42
   - For activating the PM-IRRAS polarization modulation mode: PEM=84
   - For deactivating any polarization modulation mode: PEM=0
4. Click on the *Send Command* button ②.

5.5 Switching off the analysis system

Switching off the complete analysis system (i.e. FT-IR spectrometer, PEM controller, PC and monitor) involves the following steps:

<table>
<tr>
<td> 
</td>
<td>➢ It is highly recommended to switch off the PEM controller when the PMA50 module is not in use. This measure prolongs the service life of the PEM. Note: Switching off the PEM controller puts the PEM automatically out of operation.

Switch off the PEM controller using the POWER button ①.

☞ For detailed information about the PEM controller, refer to the User Manual of the PEM-100 Photoelastic Modulator.</td>
</tr>
<tr>
<td> 
</td>
<td>Switch off the spectrometer using the ON/OFF switch ① at the spectrometer rear side.

☞ For detailed information about the spectrometer, refer to the User Manual of the spectrometer in question.</td>
</tr>
<tr>
<td colspan="2">Close the OPUS software program.
Switch off the PC and the monitor.

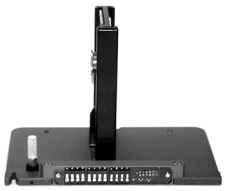
☞ See the user manual of the PC and the monitor.</td>
</tr>
</table>

5.6 VCD measurements

For background information about VCD spectroscopy, refer to the glossary in appendix D.

5.6.1 Special hardware and software

Besides the standard equipment listed in section 5.2, the following hardware components are required especially for VCD measurements:

	Standard sample holder
	Optical low-pass filter (either LWP < 1,828 cm^{-1} or LWP < 3860cm^{-1}) including supporting frame
	Multiple wavelength plate (calibration crystal CdS)
	Linear polarizer (rotatable) including holder Note: The second polarizer required for calibration measurements is meant.
	For VCD measurements of liquid samples, a liquid cell is required. ☞ For information about the available liquid cells, see section 4.3.1
	For VCD measurements of KBr pellets, a pellet holder is required.

The special software implies the VCD calculation function.

- In case of OPUS version 7 and lower: VisualBasic scripts
- In case of OPUS version 7.2 and higher: optional software package OPUS/VCD

5.6.2 Optics setup for VCD calibration and sample measurement

The schematic presentation in figure 5.1 illustrates the optics setup for the calibration measurement and for the sample measurement.

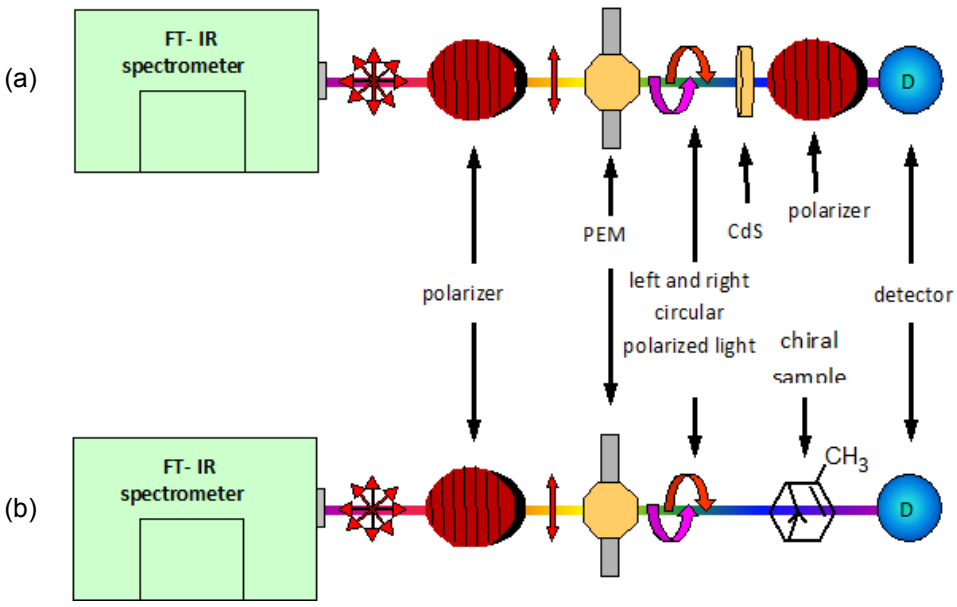
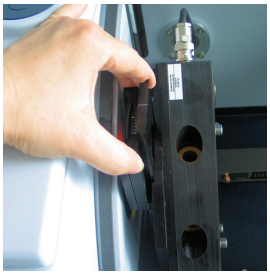
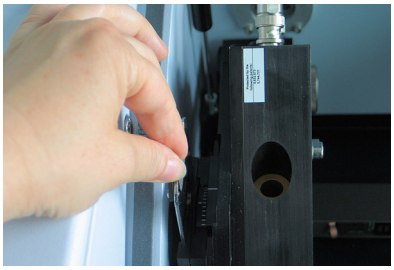


Figure 5.1: Optics setup for VCD calibration measurement (a) and sample measurement (b)

5.6.3 Installing the polarizer

1		If not already done, insert the polarizer ① in the right slide rail at the left side of the PEM.

5.6.4 Installing the optical low-pass filter

1		If not already done, insert the optical low pass filter in the left slide rail at the left side of the PEM. ➢ Note: Alternatively, the optical filter can be installed in the optical filter wheel of the FT-IR spectrometer.

i An optical filter (low-pass filter) being installed in the beam path before the polarizer and the PEM allows for the usage of a larger aperture. A larger aperture increases the amount of light which in turn improves the S/N ratio. For this purpose, the following optical filters are available: low-pass filter < 1,828 cm^{-1} (standard) and low-pass filter < 3860cm^{-1} (option).

Figure 5.2 shows the single channel spectrum acquired with each available optical low-pass filter.

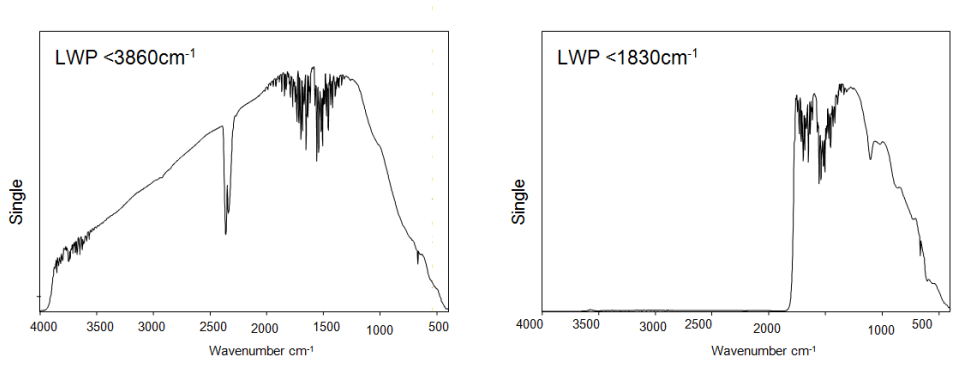


Figure 5.2: Single channel spectra using optical low-pass filters

➢ Use that low-pass filter which transmits the wavelengths of the spectral range in which the sample in question is IR active.

5.6.5 Setting the PEM parameters for VCD

At the PEM controller

➢ Make sure that the currently active display mode of the PEM controller is the ***Local Control Mode***.

Set the parameters as follows:

- Wavelength unit: 1/cm
- Wavelength: depends on the sample
  - For the fingerprint region (1500 - 1000 cm^{-1}): typically 1300 cm^{-1}
  - For carbonyl or amide I regions: typically 1600 cm^{-1}
  - For the CH-stretch region: typically 3000 cm^{-1}
- Retardation unit: λ
- Retardation: 0.25
- Frequency unit: kHz
- Frequency: 1f (i.e. 42 kHz)

☞ For detailed information about how to set the parameters, refer to the PEM-100 Photoelastic Modulator User Manual.

5.6.6 Calibration measurement

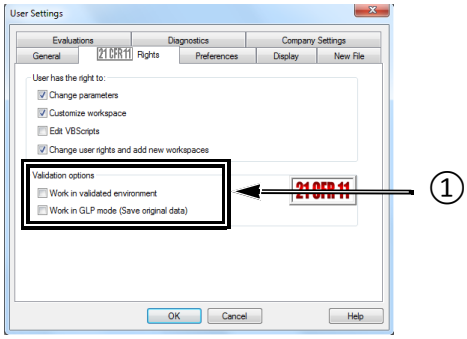
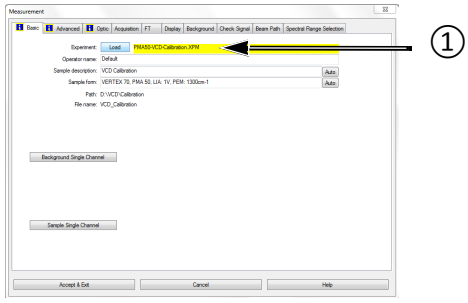
5.6.6.1 General information

In VCD spectroscopy, calibration measurements are necessary for the following reasons:

- The FT phase and ZPD[1] information are required for the calculation of the result sample spectra.
- The large signal in the calibration setup[2] is used for the adjustment of the (demodulation) phase angle at the internal demodulator.
- The calibration spectrum is used for the y-axis normalization of the sample spectra.
- The sign of the sample spectra is verified.

The result of a calibration measurement (i.e. two interferograms) can be used for the calculation of all those result VCD spectra of which the raw sample data have been acquired with the same OPUS parameter settings (except for scan time and aperture), the same PEM parameter settings and the same polarizer angle as the calibration measurement data. When you change a parameter setting in OPUS and/or set a different polarizer angle and/or change a PEM parameter setting, you have to perform a new calibration measurement.

5.6.6.2 Setting the parameters in OPUS for calibration measurement

1		For VCD measurements, make sure that OPUS is **NOT** operated in the GLP mode. OPUS →*Setup* menu → *User settings* function → *21CFR11 Rights* dialog page Make sure that the two *Validation Options* ① are **not** activated!
2		OPUS → *Measure* menu → *Advanced measurement* function Load the *PMA50-VCD-Calibration.XPM* experiment file ①. Note: The XPM-file is stored in the OPUS path → XPM directory.

1. ZPD - zero path difference (center burst of the interferogram)
2. Calibration setup means that there is a multiple wavelength plate (CdS) and an additional polarizer in the sample position. See figure 5.1.

The following table shows the recommended parameter settings and values for VCD measurements:

Parameter	Setting / Value
Sample scan time	10 scans ➢ The optimal scan time depends on the sample. The longer the measurement time, the better the obtained signal-to-noise-ratio.)
Resolution	4, 6 or 8 cm^{-1} (typical)
Data blocks to be saved*	Sample interferometer
Optical filter setting	Open
Aperture setting	Select the optimal aperture[a]. ☞ The selected aperture is optimal when the amplitude value of the sum signal is between 12,000 and 20,000 ADC count. For displaying the sum signal in OPUS, select the detector option *LN-MCT Narrow [PMA module].*
Measurement channel*	Right exit
Detector setting*	LN-MCT Narrow/Mid/xxx + DC_IN [PMA module]
Preamp gain*	A
Scanner velocity*	10 kHz
Sample signal gain*	1
Wanted high frequency limit*	8,000
Wanted low frequency limit*	0
High-pass filter*	On
Low-pass filter*	5 kHz
Acquisition mode*	double-sided, forward backward
Correlation mode*	Off

a. By default, the aperture wheel of a FT-IR spectrometer of the VERTEX series has 12 occupied positions which allow for the following aperture settings: 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6 and 8mm. By default, the aperture wheel of a FT-IR spectrometer of the TENSOR series has 11 occupied positions which allow for the following aperture settings: 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, and 6mm. For VCD measurement, the optimal aperture setting depends on the thickness and homogeneity of the sample in question.

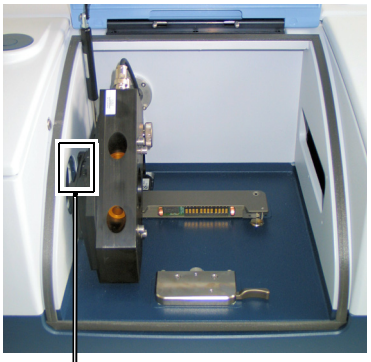
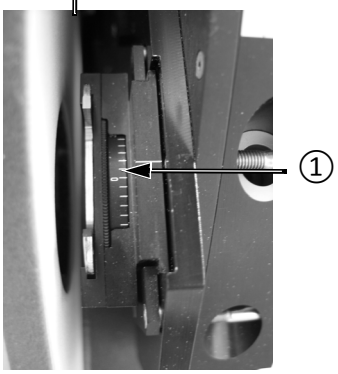
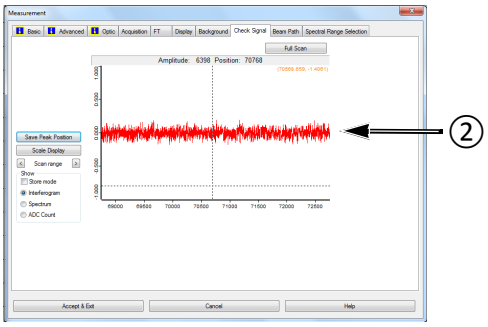
* For these parameters, use only the settings listed in the table above!

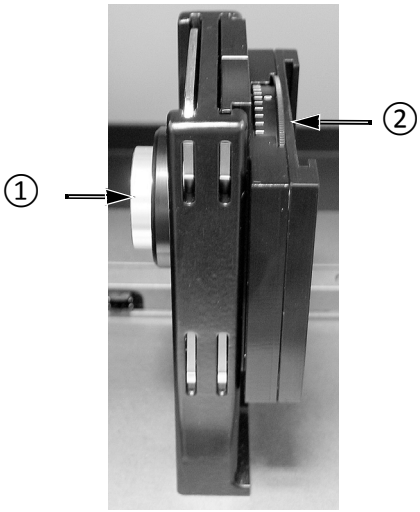
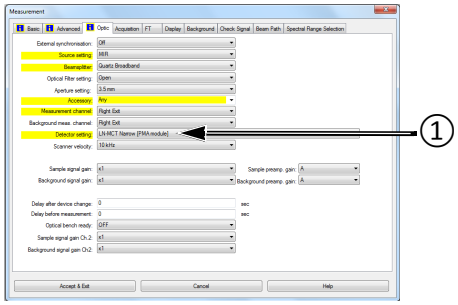
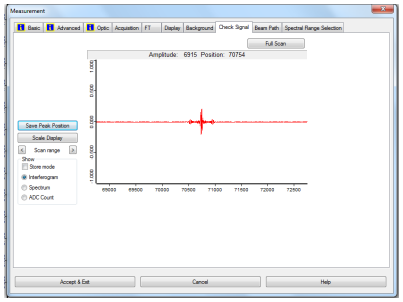
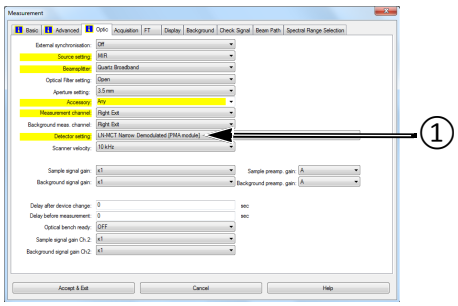
5.6.6.3 Preparing the PMA50 module for calibration measurement

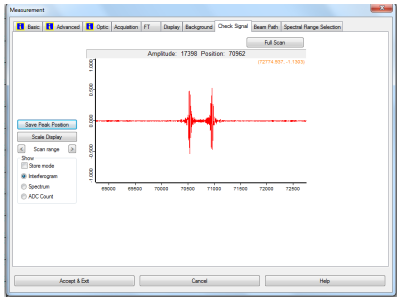
Before starting a VCD calibration measurement, make sure that ...:

- the MCT detector is cooled down to its operating temperature. (See section 5.11.)
- the FT-IR spectrometer is switched on. (See section 5.3.)
- the VCD polarization modulation mode is activated for the optical bench of the analysis system. (See section 5.4.)
- the cable connection between the PEM controller and the PMA50 module is meant for VCD measurements. (See section 3.7.)
- the PEM controller is switched on. (See section 5.3.)
- the PEM parameters are set for VCD measurement. (See section 5.6.5.)

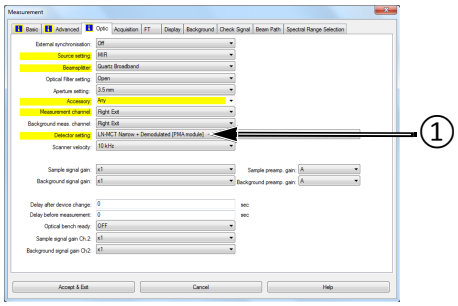
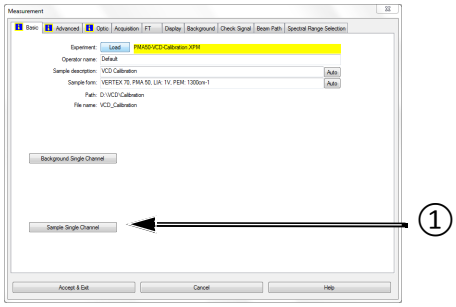
In addition to the general preparatory work listed above, you have to ...:

1	  	**Adjust the angle of polarizer ① which is located at the left side of the PEM.** (This means attuning the polarizer orientation to the orientation of the optical element of the PEM.) Proceed as follows: 1. Make sure that the sample holder is **not** in the PMA50 sample compartment. 2. OPUS → *Measure* menu→ *Advanced measurement* function 3. Load *PMA50-VCD-Calibration.XPM* experiment file. 4. *Optics* dialog page → Parameter detector setting: *DC_IN [PMA module]* 5. Open the *Check signal* dialog page. 6. By rotating the angle scale ①, position the polarizer in such a way that the E vector of the linearly polarized light, which passes through the polarizer, is parallel to the fast axis of the optical element of the PEM. Typically, this condition is achieved with a polarizer angle setting of 0° ± ca. 10°. While rotating the polarizer, check the signal in OPUS. The polarizer position is optimal when the displayed interferogram exhibits no center burst ②. ➢ **Important:** Adjust the angle of this polarizer before starting the calibration measurement. After the calibration measurement, do **NOT** change the angle setting for the subsequent sample measurement(s)!

2		**Calibrate the phase angle.** The purpose of the phase angle calibration is to eliminate the effect of the phase shift caused by the photoelastic modulation. To do this, proceed as follows: 1. Lock the sample holder in the PMA50 sample compartment. (See section 5.9.) 2. Insert the multiple wavelength plate ① into the left slide rail of the sample holder. 3. Insert a second linear polarizer ② in the right slide rail of the sample holder. 4. Make sure that the polarizer angle is set to 0° (With this polarizer orientation, the light is polarized horizontally).
3.1		**Check the signal.** In OPUS → *Measurement* dialog → *Optic* dialog page → Detector setting: *LN-MCT Narrow/Mid/xxx [PMA module]* ① ☞ With this detector setting, the low-pass-filtered sum signal is selected.
3.2		In OPUS → *Measurement* dialog → *Check signal* dialog page The interferogram will look like as follows:
3.3		In OPUS → *Measurement* dialog → *Optic* dialog page → Detector setting: *DC_IN [PMA module]* ① ☞ With this detector setting, the high-pass-filtered and demodulated difference signal is selected.

3.4		In OPUS → *Measurement* dialog → *Check signal* dialog page The interferogram will look like as follows:

5.6.6.4 Starting the calibration measurement

1		In OPUS → *Measurement* dialog → *Optic* dialog page → Detector setting: *LN-MCT Narrow/Mid/xxx + DC_IN [PMA module]* ① ☞ With this detector setting, the dual channel acquisition mode for both signals - sum signal and difference signal - is activated.
2		In OPUS → *Measurement* dialog → *Basic* dialog page → Click on the *Sample Single Channel* button ①.

5.6.6.5 Result of the calibration measurement

The result of the calibration measurement are two interferograms which are stored in one OPUS file. The OPUS file consists of the following data blocks:

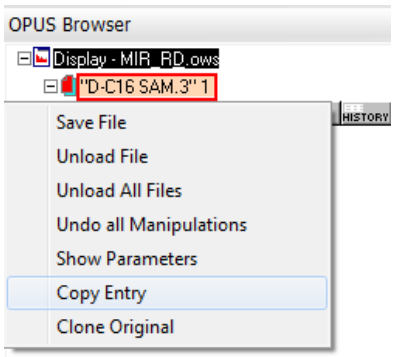
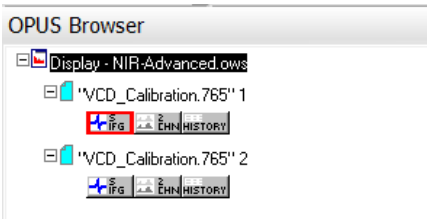
- **S IFG:** This data block contains the interferogram of the difference signal.
- **2 CHN:** This data block contains the interferogram of sum signal.

➢ Note: The two interferograms have been acquired in the dual channel acquisition mode, i.e. they have been acquired simultaneously.

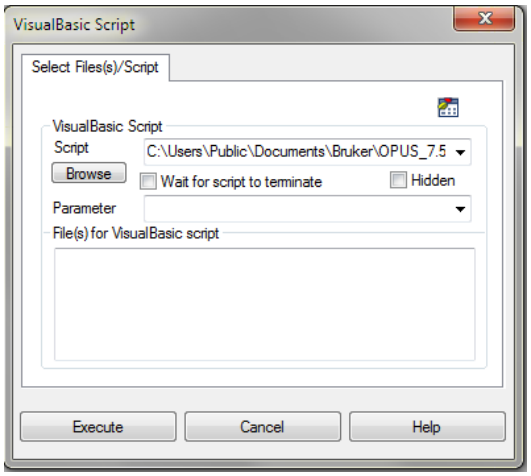
For more detailed information about the two types of signal, refer to section 4.9.

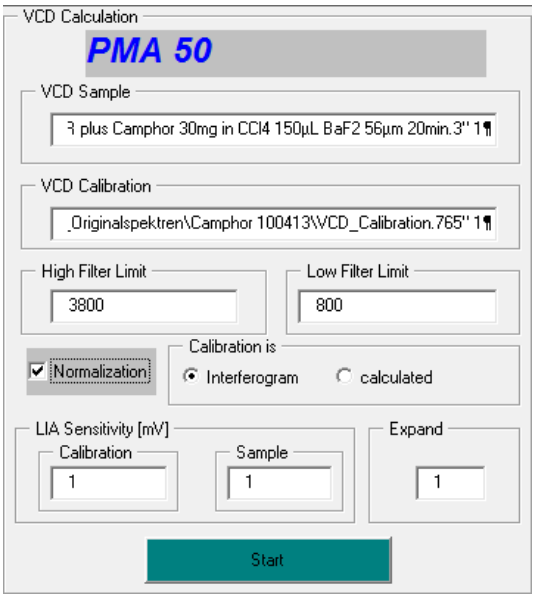
After the calibration measurement, the OPUS file is loaded automatically in the OPUS browser.

5.6.6.6 Calculation of the calibration curve and calibration spectrum

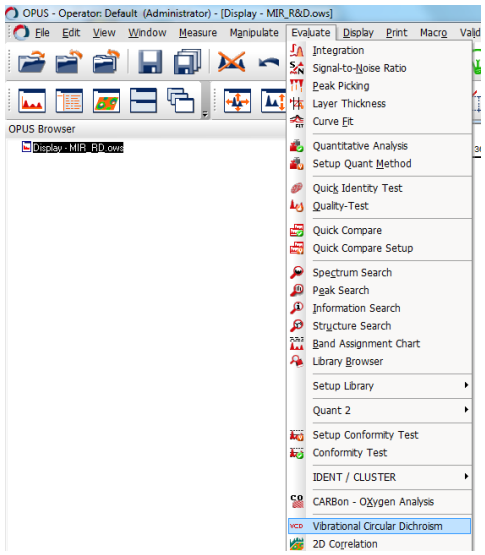
1		**Duplicate the OPUS file containing the original data of the calibration measurement.** To do this, proceed as follows: 1. In the OPUS browser, right-click on the file in question and select the *Copy Entry* function of the context menu.
2		As a result, the file is duplicated in the OPUS browser with the same file name but with incremented file extension.

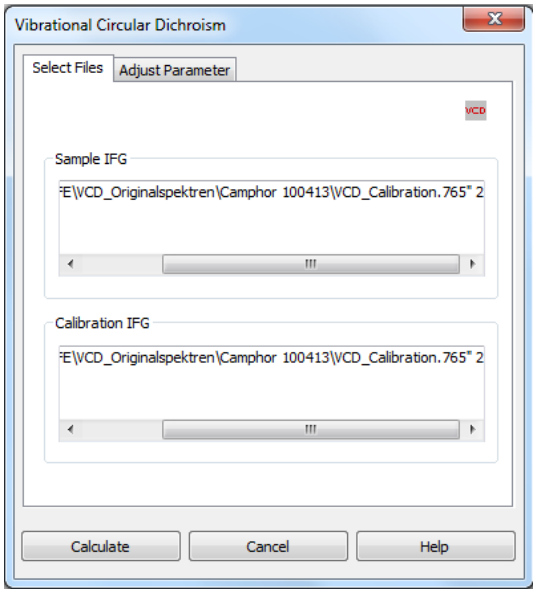
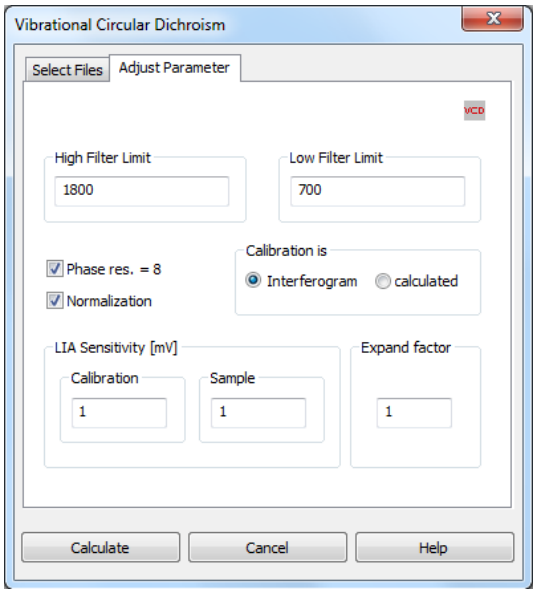
In case of OPUS version 7 and lower, proceed as follows:

1		**Open the VB script *PAM50-VCD.*** To do this, proceed as follows: 1. Open the OPUS program. 2. In OPUS → *File* menu → *VisualBasic Script* function 3. Browse to *C:\Users\Public\Documents\Bruker\OPUS xxx [with xxx being the current OPUS version] \VBSample.* ➢ Note: To browse to this directory, navigate in the file manager as follows: *Libraries\Documents\public documents \Bruker\OPUS xxx [with xxx being the current OPUS version] \VBSample.* 4. Select the VBscript file *PMA50-VCD-65-080602 phaseres8.obs*. 5. Click on the *Execute* button.

2		1. Drag the original file and drop it into the *VCD Sample* field. 2. Drag the copied file and drop it into the *VCD Calibration* field. 3. Enter the upper and the lower limit value of the spectral range [in cm^{-1}]. ➢ Note: The usable spectral range is determined by the optical components, for example: optical low pass filter, cutoff frequency of the detector, windows of the liquid cell etc. 4. If the VCD spectra intensity is to be normalized (it is the standard setting), activate the *Normalization* checkbox. 5. Select for the parameter *Calibration is* the option *Interferogram*. 6. Make sure that all two *LIA Sensitivity* parameters and the *Expand factor* have the same value (e.g. 1). 7. Click on the *Start* button.

In case of OPUS version 7.2 and higher, proceed as follows:

1		**Activate the VCD calculation function.** To do this, proceed as follows: 1. In OPUS → *Evaluate* menu → *Vibrational Circular Dichroism* function

2		1. Drag the original file and drop it into the *Sample IFG* field. 2. Drag the copied file and drop it into the *Calibration IFG* field.
3		3. Enter the upper and the lower limit value of the spectral range [in cm^{-1}]. ➢ Note: The usable spectral range is determined by the optical components, for example: optical low pass filter, cutoff frequency of the detector, windows of the liquid cell etc. 4. Activate the *Phase res.=8* check box. 5. If the VCD spectra intensity is to be normalized, activate the *Normalization* checkbox. (Note: The activated normalization is the standard setting.) 6. Select for the parameter *Calibration is* the option *Interferogram*. 7. Make sure that all two *LIA Sensitivity* parameters and the *Expand factor* have the same value (e.g. 1). 8. Click on the *Calculate* button.

The calculation generates two files. But only the file which consists of the following data blocks contains the calibration result:

Data block	The data block contains the following spectral information:
	VCD calibration spectrum ➢ The calibration spectrum (absorption spectrum) is calculated as follows: SSC divided by RSC
	Calibration curve ➢ The normalized band intensities calculated on the basis of the calibration spectrum are plotted in form of a calibration curve. (See fig. 5.3.) From the calibration curve, the normalization factor is derived so that the relative band intensities in the result spectrum are displayed correctly
	Interferogram of the difference signal (raw data)
	Single channel spectrum ➢ Fourier-transformed interferogram which is stored in the SIFG data block
	FT phase (backward) of interferogram which is stored in the SIFG data block
	FT phase (forward) of interferogram which is stored in the SIFG data block
	Interferogram of the sum signal (raw data)
	Single channel spectrum ➢ Fourier-transformed interferogram which is stored in the RIFG data block

To view the calibration spectrum and the calibration curve, drag and drop the *AB* data block and the *?* data block of the second file in the spectrum display window.

Figure 5.3 shows the calibration curve and the calibration spectrum how it should look like.

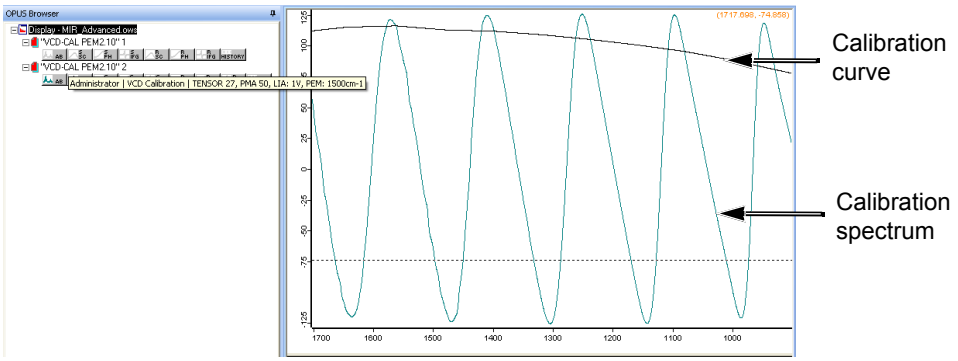


Figure 5.3: Calibration curve and calibration spectrum

5.6.7 Sample measurement

Important: The sample measurement(s) have to be performed with the same OPUS measurement parameter settings (except for scan time and aperture) and the same PEM parameter settings as well as with the same polarizer angle as the previous calibration measurement. (Note: The polarizer at the left side of the PEM is meant).

5.6.7.1 Sample preparation

For VCD spectroscopic measurements, solid samples can be analyzed as solutions filled in a liquid cell as well as a KBr pellet.

Preparing a sample solution

In case your sample is a soluble solid (e.g. soluble powder), prepare a solution of the sample using a suitable solvent.

☞ Regarding the sample concentration of the solution, keep in mind the following fact: To obtain best VCD measurement results, the absorbance of the sample solution should between 0.3 and 0.9 absorption units because a stronger absorbance produces very intense VCD signals which can lead to artifacts in the VCD sample spectra. For this reason, it is recommended to acquire at first a FT-IR spectroscopic absorption spectrum of the prepared sample solution (measured in transmission) to determine the absorptive power of the sample in the region of interest. If the absorbance peaks are too strong or too weak, adjust the sample concentration in the solution or the path length correspondingly.

☞ The major problem in preparing a sample solution is choosing a suitable solvent. Most solvents have a strong absorptivity and so their absorption bands will superimpose those of the solute. Therefore, you have to ensure that the used solvent is not strongly absorbing in the wavelength region of interest. Use only spectrophotometrically pure solvents and solvents which are not infrared active in the spectral region of interest. No solvent is perfect but if the spectral information about the sample is known, the solvent can be chosen accordingly. Consult the relevant reference books for the absorptivity of the various solvents.

Pressing a KBr pellet

This sample preparation technique is very suitable for solid samples in terms of the information yield from an IR spectrum because KBr is significantly more IR transparent than most solvents. KBr has no absorption in the region 4000cm^{-1} to 250cm^{-1} so that a good sample spectrum (i.e. a spectrum that does not contain spectral information about the dispersing agent) is obtained.

Proceed as follows:

- Put a small amount of the sample in an agate mortar and grind it up as fine as possible.

☞ The success of this technique strongly depends on the grain size of the ground sample. Grind the sample as fine as possible (particle size of at least 200 mesh, better 500 mesh) to minimize the infrared light scattering on the particle surface, also called Christiansen effect. This effect is caused by a refraction index mismatch between the salt (KBr) and the sample powder that leads to reflections at the salt-sample interface. Therefore, proper grinding is required to ensure a good contact between KBr and sample powder and to minimize the portion of the reflected light.

- Add a spatula full of oven-dry KBr material to the ground sample and mix it until a uniform mixture is obtained. Do not grind the mixture as this may increase the absorption of water by KBr.

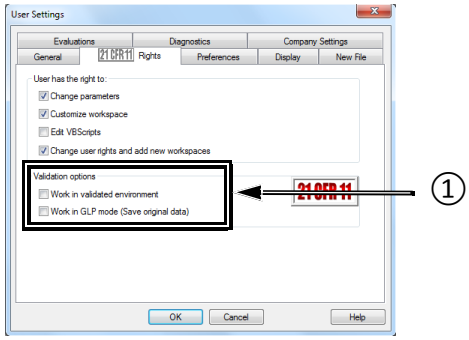
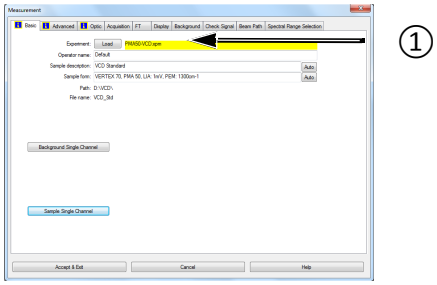
☞ A common mistake is to use to much sample. The concentration of the sample in KBr should be in the range of 0.2% to 1% (i.e. typically a 300:1 dilution by mass).

☞ Another important factor in this technique is to keep everything moisture free as the KBr material is hygroscopic. To prevent the KBr material from absorbing moisture, keep it in a drying oven at a temperature of 50 to 60°C. Failure to do so will result in opaque pellets that yield distorted spectra. A correctly prepared KBr pellet will be transparent to IR light.

- Put the mixture into the die of a hydraulic press or a hand press and subject it to very high pressure (ca. 20,000 psi) for a few minutes (2 to 5 minutes). The result should be a translucent pellet with an ideal thickness of 0.5 to 1mm.
- Carefully remove the pellet from the die, place it in the pellet holder and put it in the sample compartment of the PMA50 module.

☞ The KBr pellet is very hygroscopic and fragile. Handle it with care and use gloves to avoid contact with moisture from your hands. Measure the KBr pellet immediately after removing it from the press as the pellet will fairly rapidly begin to absorb moisture from the ambient air and becomes opaque.

5.6.7.2 Setting the parameters in OPUS for sample measurement

1		For VCD measurements, make sure that OPUS is **NOT** operated in the GLP mode. OPUS →*Setup* menu → *User settings* function → *21CFR11 Rights* dialog page Make sure that the two *Validation Options* ① are **not** activated!
2		OPUS → *Measure* menu → *Advanced measurement* function Load the *PMA50-VCD.XPM* experiment file ①. Note: The XPM-file is stored in the OPUS path → XPM directory.

The following table shows the recommended parameter settings and values for VCD measurements:

Parameter	Setting
Sample scan time	10 min ➢ The optimal scan time depends on the sample. The longer the measurement time, the better the obtained signal-to-noise-ratio.)
Resolution	4, 6 or 8 cm^{-1} (typical)
Data blocks to be saved*	Sample interferometer
Optical filter setting	Open
Aperture setting	Select the optimal aperture[a] for the sample in question. ☞ The selected aperture is optimal when the amplitude value of the sum signal is between 12,000 and 20,000 ADC count. For displaying the sum signal in OPUS, select the detector option *LN-MCT Narrow [PMA module].*
Measurement channel*	Right exit
Detector setting*	LN-MCT Narrow/Mid/xxx + DC_IN [PMA module]
Preamp gain*	A
Scanner velocity*	10 kHz
Sample signal gain*	1
Wanted high frequency limit*	8,000
Wanted low frequency limit*	0
High-pass filter*	On
Low-pass filter*	5 kHz
Acquisition mode*	double-sided, forward backward
Correlation mode*	Off

a. By default, the aperture wheel of a FT-IR spectrometer of the VERTEX series has 12 occupied positions which allow for the following aperture settings: 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6 and 8mm. By default, the aperture wheel of a FT-IR spectrometer of the TENSOR series has 11 occupied positions which allow for the following aperture settings: 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, and 6mm. For VCD measurement, the optimal aperture setting depends on the sample in question regarding sample thickness and homogeneity.

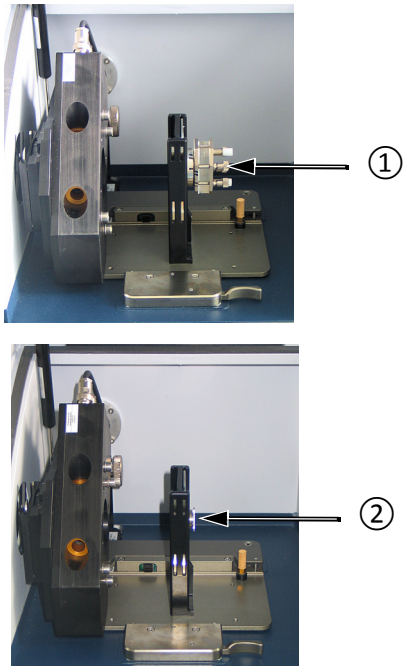
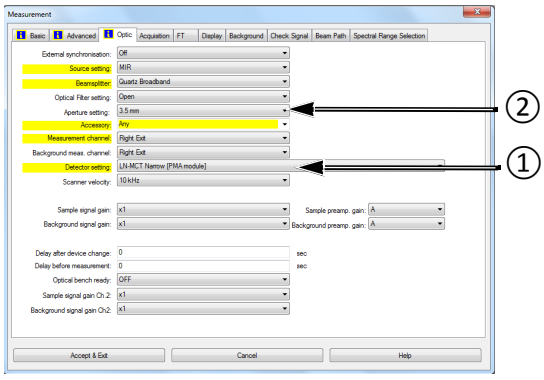
* For these parameters, use only the settings listed in the table above!

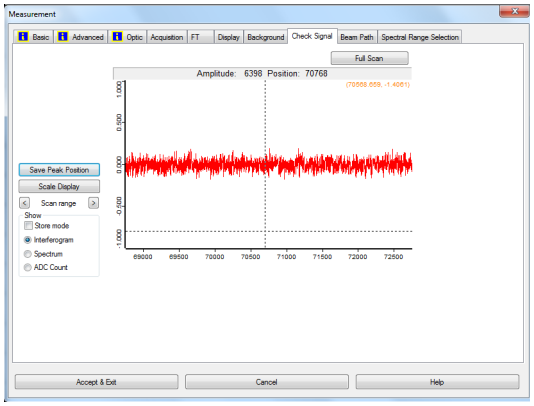
5.6.7.3 Preparing the PMA50 module sample measurement

Before starting a VCD sample measurement, make sure that ...:

- the MCT detector is cooled down to its operating temperature. (See section 5.11.)
- the FT-IR spectrometer is switched on. (See section 5.3.)
- the VCD polarization modulation mode is activated for the optical bench of the analysis system. (See section 5.4.)
- the cable connection between the PEM controller and the PMA50 module is meant for VCD measurements. (See section 3.7.)
- the PEM controller is switched on. (See section 5.3.)
- the PEM parameters are set for VCD measurement. (See section 5.6.5.)

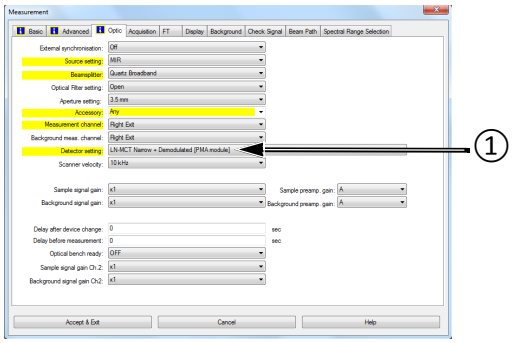
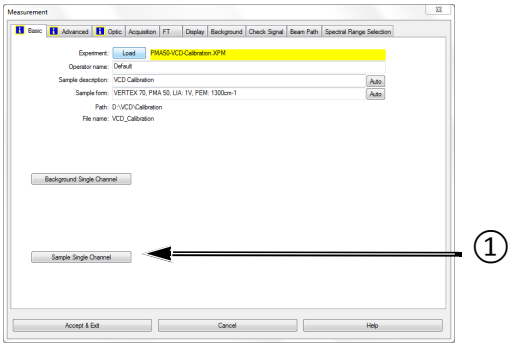
In addition to the general preparatory work listed above, you have to ...:

1		**Place the sample in the measurement position of the PMA50 sample compartment.** To do this, proceed as follows: 1. Lock the sample holder in the PMA50 sample compartment, if not already done. (See section 5.9.) 2. In case of a liquid sample, fill the sample in a liquid cell and insert the liquid cell ① in the right slide rail of the sample holder. In case of a KBr pellet, put the KBr pellet in the pellet holder and insert the pellet holder ② in the either of the two slide rail of the sample holder. ➢ For information about sample preparation, see section 5.6.7.1.
5		**Find the optimal aperture setting for the sample in question.** To do this, proceed as follows: 1. In OPUS → *Measurement* dialog → *Optic* dialog page → Detector setting: *LN-MCT Narrow/Mid/xxx [PMA module]* ① ☞ With this detector setting, the sum signal is selected. 2. Select an aperture setting[a] ②. 3. In OPUS → *Measurement* dialog → *Check signal* dialog page ☞ On the basis of the ADC count value, find the optimal aperture setting by trial and error. Ideally, the amplitude value of the sum signal should be between 12,000 and 20,000 ADC counts.

6		In OPUS → *Measurement* dialog →*Optic* dialog page → Detector setting: *DC_IN [PMA module]* ☞ With this detector setting, the difference signal is selected. In OPUS → *Measure* menu → *Advanced measurement* function → *Check signal* dialog page Check the interferogram. The interferogram should show no center burst. ➢ If there is a center burst, minimize it by rotating the liquid cell. The amplitude value should not exceed 30,000 ADC counts.

a. By default, the aperture wheel of a FT-IR spectrometer of the VERTEX series has 12 occupied positions which allow for the following aperture settings: 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6 and 8mm. By default, the aperture wheel of a FT-IR spectrometer of the TENSOR series has 11 occupied positions which allow for the following aperture settings: 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, and 6mm. For VCD measurement, the optimal aperture setting depends on the thickness and homogeneity of the sample in question.

5.6.7.4 Starting the sample measurement

1		In OPUS → *Measurement* dialog → *Optic* dialog page → Detector setting: *LN-MCT Narrow/Mid/xxx + DC_IN [PMA module]* ① ☞ With this detector setting, the dual channel acquisition mode for both signals - sum signal and difference signal - is activated.
2		In OPUS → *Measurement* dialog → *Basic* dialog page → Click on the *Sample Single Channel* button ①.

5.6.7.5 Result of the sample measurement

The result of the sample measurement (acquired raw data) are two interferograms stored in one OPUS file. The OPUS file consists of the following data blocks:

- **S IFG:** This data block contains the interferogram of the difference signal.
- **2 CHN:** This data block contains the interferogram of the sum signal.

➢ Note: The two interferograms have been acquired in the dual channel acquisition mode, i.e. they have been acquired simultaneously.

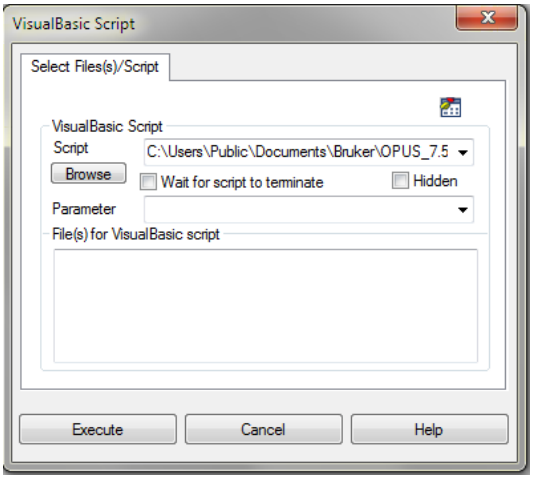
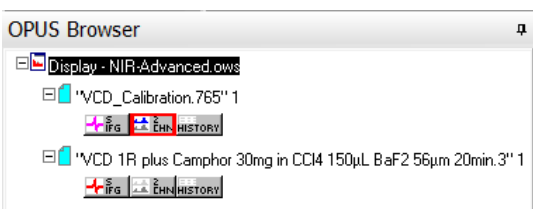
For more detailed information about the two types of signal, refer to section 4.9.

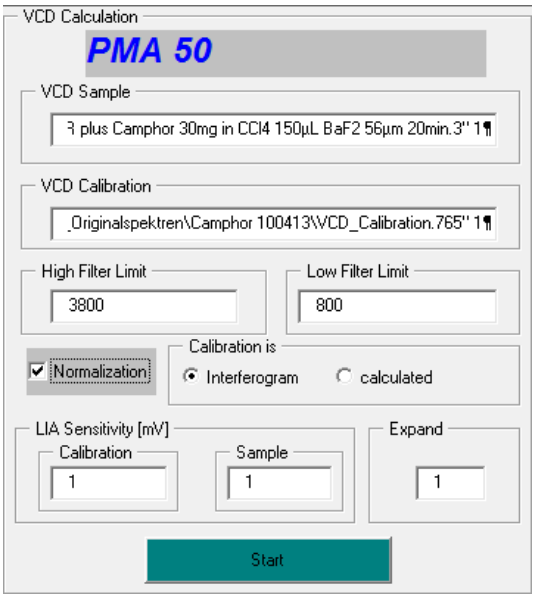
After the sample measurement, the OPUS file is loaded automatically in the OPUS browser.

5.6.8 Calculation of the VCD result

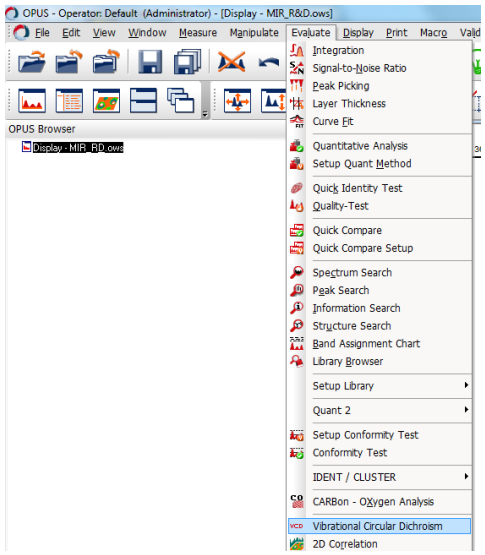
5.6.8.1 Defining the calculation parameters in OPUS

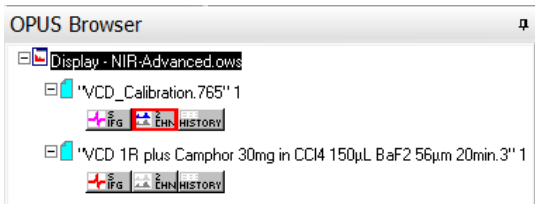
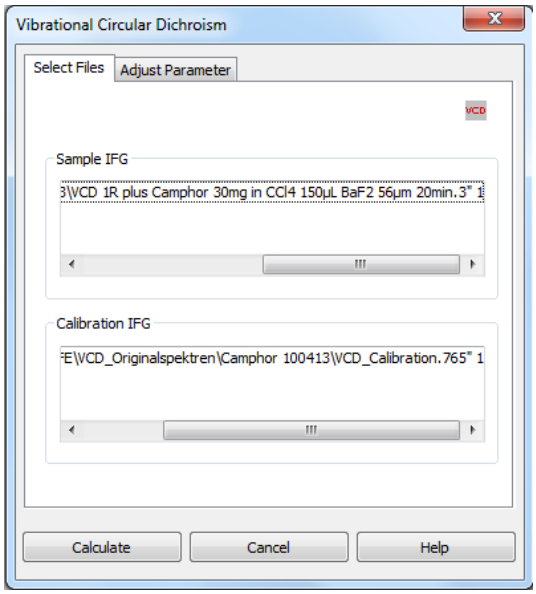
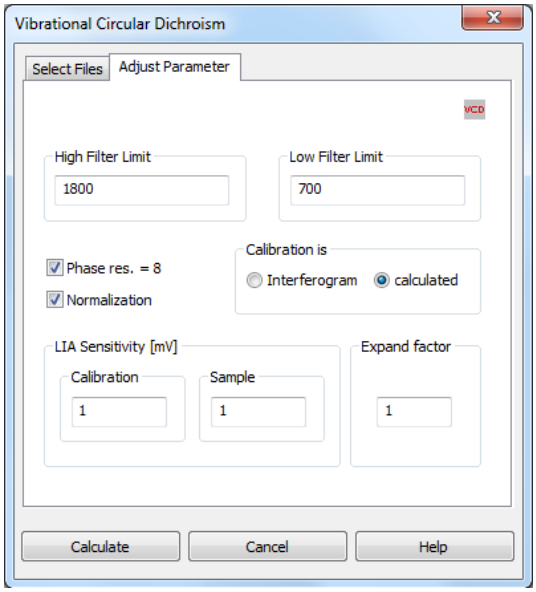
In case of OPUS version 7 and lower, proceed as follows:

1		**Open the VB script *PAM50-VCD.*** To do this, proceed as follows: 1. Open the OPUS program. 2. In OPUS → *File* menu → *VisualBasic Script* function 3. Browse to *C:\Users\Public\Documents\Bruker\OPUS xxx [with xxx being the current OPUS version] \VBSample.* ➢ Note: To browse to this directory, navigate in the file manager as follows: *Libraries\Documents\public documents \Bruker\OPUS xxx [with xxx being the current OPUS version] \VBSample.* 4. Select the VBscript file *PMA50-VCD-65-080602 phaseres8.obs*. 5. Click on the *Execute* button.
2		Make sure that the following OPUS files are loaded in the OPUS browser: • the file containing the calibration measurement result (the raw data i.e. the interferograms or the calculated data) • the file containing the sample measurement result

3		1. Drag the OPUS file containing the sample measurement result and drop it into the *VCD Sample* field. 2. Drag the OPUS file containing the calibration measurement result and drop it into the *VCD Calibration* field. 3. In case of the measured raw data (interferograms) are used, select for *Calibration is* the option *Interferogram*. In case the calibration interferograms are already converted by the Fourier Transformation, select for *Calibration is* the option *calculated*. 4. Enter the upper and the lower limit value of the spectral range [in cm^{-1}]. ➢ Note: The usable spectral range is determined by the optical components, for example: optical low pass filter, cutoff frequency of the detector, windows of the liquid cell etc. 5. If the VCD spectra intensity is to be normalized (it is the standard setting), activate the *Normalization* checkbox. 6. Make sure that all two *LIA Sensitivity* parameters and the *Expand factor* have the same value (e.g. 1). 7. Click on the *Start* button.

In case of OPUS version 7.2 and higher, proceed as follows:

1		**Activate the VCD calculation function.** To do this, proceed as follows: 1. In OPUS → *Evaluate* menu → *Vibrational Circular Dichroism* function

2		Make sure that the following OPUS files are loaded in the OPUS browser: • the file containing the calibration measurement result (the raw data i.e. the interferograms or the calculated data) • the file containing the sample measurement result
3		1. Drag the OPUS file containing the sample measurement result and drop it into the *Sample IFG* field. 2. Drag the OPUS file containing the calibration measurement result and drop it into the *Calibration IFG* field.
4		3. Enter the upper and the lower limit value of the spectral range [in cm^{-1}]. ➢ Note: The usable spectral range is determined by the optical components, for example: optical low pass filter, cutoff frequency of the detector, windows of the liquid cell etc. 4. In case of the measured raw data (interferograms) are used, select for *Calibration is* the option *Interferogram*. In case the calibration interferograms are already converted by the Fourier Transformation, select for *Calibration is* the option *calculated*. 5. Activate the *Phase res.=8* checkbox. 6. If the VCD spectra intensity is to be normalized (it is the standard setting), activate the *Normalization* checkbox. 7. Make sure that all two *LIA Sensitivity* parameters and the *Expand factor* have the same value (e.g. 1). 8. Click on the *Calculate* button.

5.6.8.2 General calculation process

1. At first, the interferograms (raw data) are converted into single channel spectra by applying the Fourier transformation.
2. Afterwards, a VCD result spectrum is calculated.

5.6.8.3 Fourier Transformation (FT)

The FT parameters which are used for the calibration measurement data are listed in the following table.

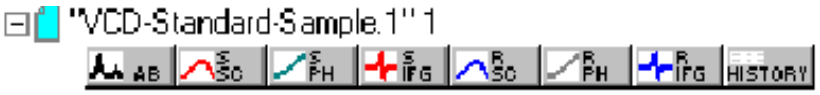
FT parameter	Value used for the FT of the DC interferogram	Value used for the FT of the "normal" interferogram
Start frequency limit	4000	4000
End frequency limit	600	600
Phase correction mode	Mertz stored phase	Mertz
Apodisation function	Blackman-Harris 4-Term	Blackman-Harris 4-Term
Zero filling factor	16	4
Peak search mode	Take from stored phase	Absolute largest value
Non linearity correction	No	Yes: Cut off: 580, eff.: 0.9

5.6.8.4 Check for the correct sign

The result of the VCD calibration measurement is used to check the VCD sample measurement for a correct sign.

5.6.9 Result of the calculation

For the sample measurement, an OPUS file is generated which consists of the following data blocks:



Data block	The data block contains the following spectral information:
	VCD sample spectrum ➢ The sample spectrum (absorption spectrum) is calculated as follows: SSC divided by RSC
	Interferogram of the difference signal (raw data)
	Single channel spectrum ➢ Fourier-transformed interferogram which is stored in the SIFG data block
	FT phase (backward) transferred from the calibration measurement
	FT phase (forward) transferred from the calibration measurement
	Interferogram of the sum signal (raw data)
	Single channel spectrum ➢ Fourier-transformed interferogram which is stored in the RIFG data block

➢ **Important note:** Store the files containing the calculation results with a different file name. Otherwise the files containing the original measurement data will be overwritten!

Figure 5.4 shows the VCD result spectrum of the Bruker VCD standard sample. The raw data have been acquired with a measurement time of 5 minutes.

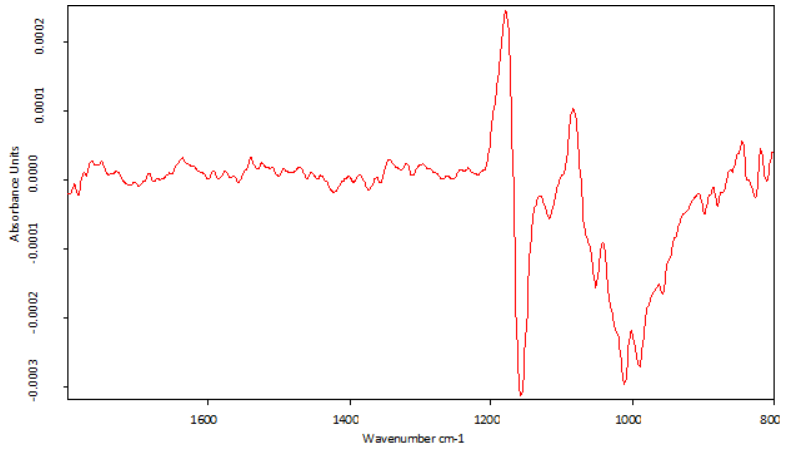


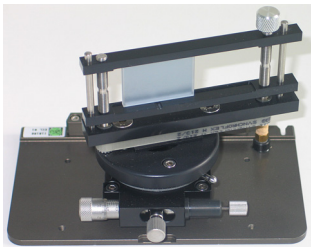
Figure 5.4: VCD result spectrum of the Bruker VCD standard sample (KBr pellet)

5.7 PM-IRRAS measurements

For background information about PM-IRRAS measurements, refer to the glossary in appendix D.

5.7.1 Special hardware and software

Besides the standard equipment listed in section 5.2, the following hardware components are especially required for PM-IRRAS measurements:

	Sample holder for PM-IRRAS
	For PM-IRRAS measurements, an optical filter (LWP) < 3,861cm^{-1} including supporting frame is recommended in addition.

The special software for PM-IRRAS implies the following:

- VisualBasic script for FT and calculation of the PM-IRRAS spectrum: *PMA50-PMIRRAS-030708.obs*
- Macro for converting the PM-IRRAS spectrum into a absorption spectrum: *PMA50-PMIRRAS-CALC-EN-030708.mxt*

5.7.2 Optics setup for PM-IRRAS measurement

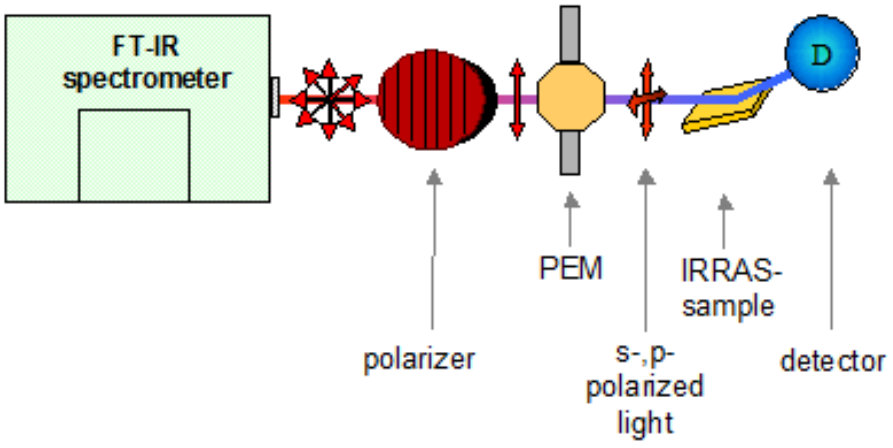


Figure 5.5: Optics setup for PM-IRRAS measurements

5.7.3 General considerations about reference measurement

For PM-IRRAS experiments, performing a reference measurement is not necessary. Instead, a mathematically fitted reference[1] can be used, which the user calculates on the basis of the measured sample data. (See section 5.7.9.3.)

If, however, you intend to perform a spectroscopic reference measurement, keep in mind that very high requirements are put on the reference sample (substrate) regarding an absolute clean surface. Obtaining such a reference sample might be difficult or very elaborate. Therefore, we recommend the calculation of a mathematically fitted reference. The procedure described in detail in this manual is restricted to the variant of the mathematically fitted reference.

In case of the spectroscopic reference measurement variant, perform the reference measurement and the sample measurement with the same PEM parameter settings, the same OPUS parameter settings, the same polarizer angle, same lens-detector-assembly position and the same rotational state of the sample holder.

After the reference measurement, use the VisualBasic script *PM50-PMIRRAS* for the conversion of the measured reference interferograms into single channel spectra and the calculation of the PM-IRRAS reference spectrum. (For detailed information, see section 5.7.9.2.) For the conversion of the PM-IRRAS sample spectrum into a reflectance spectrum, use the PM-IRRAS reference spectrum instead of the mathematically fitted reference. (For detailed information, see section 5.7.9.4.)

5.7.4 Setting the PEM parameters for PM-IRRAS

At the PEM controller

➢ Make sure that the currently active display mode of the PEM controller is the ***Local Control Mode***.

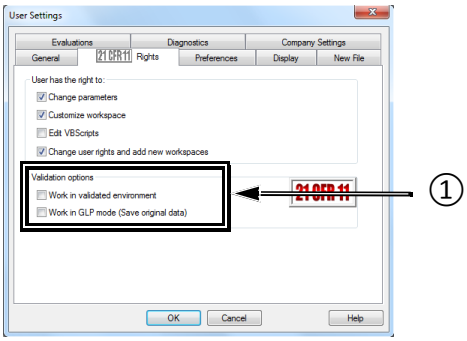
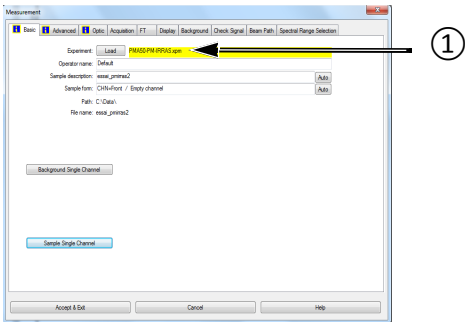
Set the parameters as follows:

- Wavelength unit: 1/cm
- Wavelength: depends on the spectral region of interest (for example: fingerprint region 1300 cm^{-1}, carbonyl compounds: 1600 cm^{-1}, CH-stretching vibration: 2000 cm^{-1})
- Retardation unit: λ
- Retardation: 0.5
- Frequency unit: kHz
- Frequency: 2f (i.e. 84 kHz)

☞ For detailed information about how to set the parameters, refer to the PEM-100 Photoelastic Modulator User Manual.

1. The mathematically fitted reference is a Bessel function which is used for the subsequent calculation of the PM-IRRAS spectrum using a dedicated macro. (See section 5.7.9.4.)

5.7.5 Setting the measurement parameters in OPUS

1		For PM-IRRAS measurements, make sure that OPUS is **NOT** operated in the GLP mode. OPUS → *Setup* menu → *User settings* function → *21CFR11 Rights* dialog page Make sure that the two *Validation Options* ① are **not** activated!
2		OPUS → *Measure* menu → *Advanced measurement* function Load the *PMA50-PMIRRAS. XPM* experiment file ①. Note: The XPM-file is stored in the OPUS path → XPM directory.

The following table shows the standard parameter settings and values for PM-IRRAS measurements.

Parameter	Setting
Sample scan time	5 min ➢ The optimal scan time depends on the sample. The longer the measurement time, the better the obtained signal-to-noise-ratio.)
Resolution	4, 6 or 8 cm^{-1} (typical)
Data blocks to be saved*	Sample interferogram
Optical filter setting	Open
Aperture setting	Select the optimal aperture[a] for the sample in question. ☞ The selected aperture is optimal when the amplitude value of the sum signal is between 12,000 and 20,000 ADC count. For displaying the sum signal in OPUS, select the detector option *LN-MCT Narrow [PMA module].* Hint: For VERTEX: $Aperture_{min}$ = sample length / 1.8 For TENSOR: $Aperture_{min}$ = sample length / 1.6

Parameter	Setting
Measurement channel*	Right exit
Detector setting*	LN-MCT Narrow/Mid/xxx + DC_IN [PMA module]
Scanner velocity*	10 kHz
Sample signal gain*	x1
Sample preamp gain*	A
Sample signal gain Ch. 2*	x1
Wanted high frequency limit*	8,000
Wanted low frequency limit*	0
High-pass filter*	On
Low-pass filter*	5 kHz
Acquisition mode*	double-sided, forward backward
Correlation mode*	Off

a. By default, the aperture wheel of a FT-IR spectrometer of the VERTEX series has 12 occupied positions which allow for the following aperture settings: 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6 and 8mm. By default, the aperture wheel of a FT-IR spectrometer of the TENSOR series has 11 occupied positions which allow for the following aperture settings: 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, and 6mm. For PM-IRRAS measurement, the aperture setting depends on the sample length.

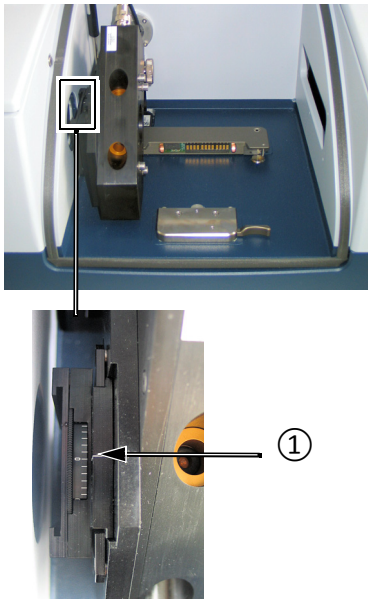
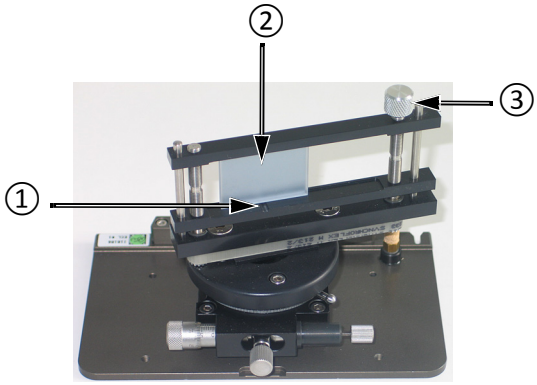
* For these parameters, use only the settings listed in the table above!

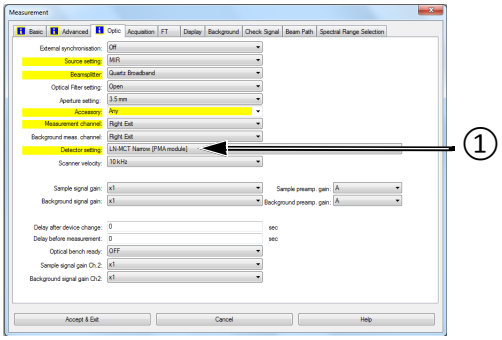
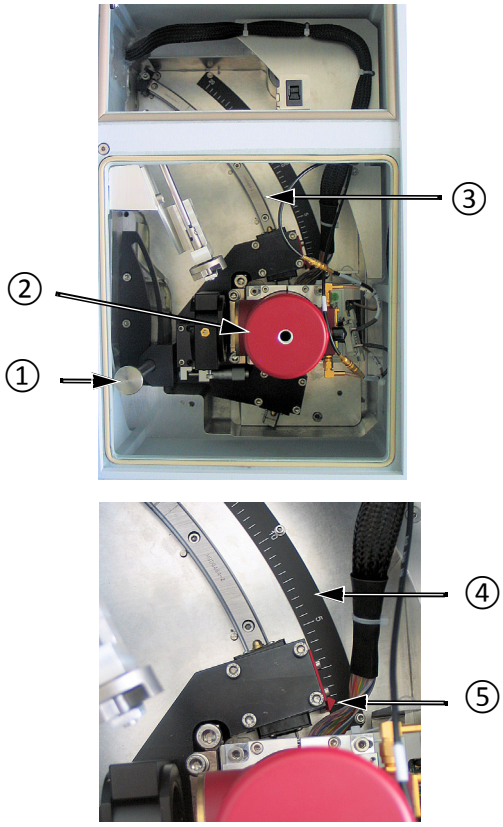
5.7.6 Preparing the PMA50 module for PM-IRRAS measurement

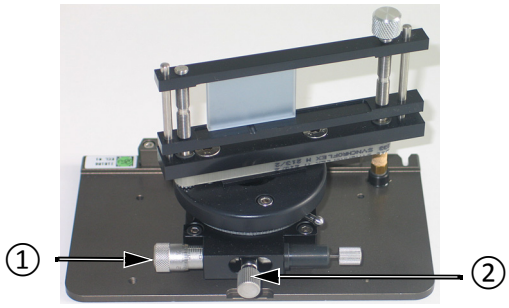
Before starting the PM-IIRRAS sample measurement, make sure that ...:

- the MCT detector is cooled down to its operating temperature. (See section 5.11.)
- the FT-IR spectrometer is switched on. (See section 5.3.)
- the PM-IRRAS polarization modulation mode is activated for the optical bench of the analysis system. (See section 5.4.)
- the cable connection between the PEM controller and the PMA50 module is meant for PM-IRRAS measurements. (See section 3.7.)
- the PEM controller is switched on. (See section 5.3.)
- the PEM parameters are set for PM-IRRAS measurement. (See section 5.7.4.)

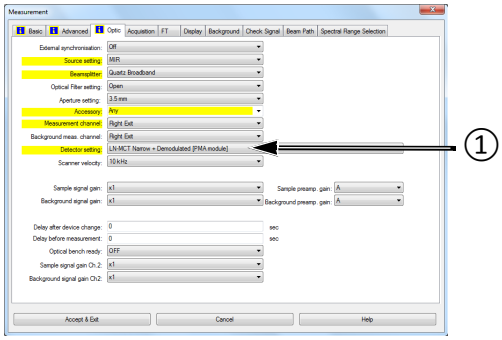
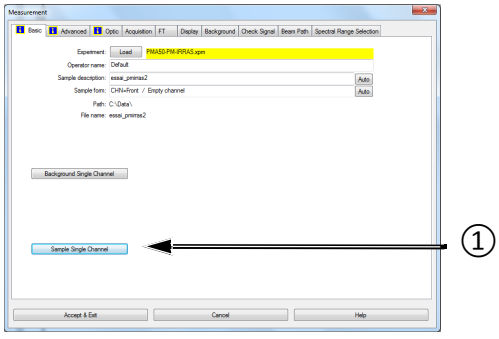
In addition to the general preparatory work listed above, you have to ...:

1		**Adjust the angle of polarizer ① which is located at the left side of the PEM.** Set the polarizer angle to 0° by rotating the angle scale. (Note: With a polarizer angle of 0° and a vertical sample surface, the light is p-polarized.)
2		**Fix the sample in the holder and place it in the PMA50 sample compartment.** To do this, proceed as follows: 1. Position the sample ② in the holder in such a way that the notch ① is in the center of the sample. (Note: The notch marks the focus position.) Clamp the sample in the holder by rotating the knurled screw ③. 2. Lock the sample holder in the PMA50 sample compartment. (See section 5.9.)

3		**Setting the optimal angle of incidence.** Note: The optimal angle of incidence is determined by the metallic substrate material. (Note For most metallic substrates, the optimal angle of incidence is 80°. The user sets the angle of incidence by positioning the detector correspondingly. (See step 3.1.) Afterwards, the user needs to change the sample position by rotating the sample holder in such a way that the IR beam impinges on the detector element. See step 3.2. Proceed as follows: 1. In OPUS → *Measurement* dialog → *Optic* dialog page → Detector setting: *LN-MCT Narrow/Mid/xxx [PMA module]* ① ☞ With this detector setting, the sum signal is selected. 2. In OPUS → *Measurement* dialog → *Check signal* dialog page
3.1	 	**How to position the detector:** 1. Loosen the locking screw ①. 2. Move the lens-detector-unit ② on the arc rail ③ to the desired angle position. ➢ Note: The angle of incidence is defined as 90° minus the angle position of the lens-detector-assembly. For taking the reading of the current angle position of the lens-detector-assembly, there is an angle scale ④. The current angle position is indicated by red arrow ⑤.) 3. When the desired angle of incidence is set, fix the lens-detector-assembly by retightening the locking screw ①.

3.2		**How to position the sample:** 1. Loosen the locking screw ②. 2. Rotate the sample while checking the signal in OPUS. Optimize the signal intensity (ADC counts) by rotating the sample fixture device. For a rough adjustment, rotate the sample fixture device by hand. Then fine-tune the rotational position of the sample using the micrometer screw ①. 3. When the sample is positioned in an optimal manner, retighten the locking screw ②.

5.7.7 Starting the sample measurement

1		In OPUS → *Measurement* dialog → *Optic* dialog page → Detector setting: *LN-MCT Narrow/Mid/xxx + DC_IN [PMA module]* ① ☞ With this detector setting, the dual channel acquisition mode for both signals - sum signal and difference signal - is activated.
2		In OPUS → *Measurement* dialog → *Basic* dialog page Click on the *Sample Single Channel* button ①.

5.7.8 Result of the sample measurement

The result of the sample measurement are two interferograms (i.e. the acquired raw data). Note: The two interferograms have been acquired in the dual channel acquisition mode, i.e. they have been acquired simultaneously.

The two interferograms are stored in one OPUS file. After the measurement, this OPUS file is displayed automatically in the OPUS browser.

This OPUS file consists of the following data blocks:

- S FIG: This data block contains the interferogram of the difference signal.
- 2 CHN: This data block contains the interferogram of the sum signal.

☞ For more detailed information about the two types of signal, refer to section 4.9.

Figure 5.6 shows the acquired raw data (i.e. interferograms) of the sample measurement.

Sample interferogram of the difference signal (stored in the data block SIFG)

Sample interferogram of the sum signal (stored in the data block 2CHN)

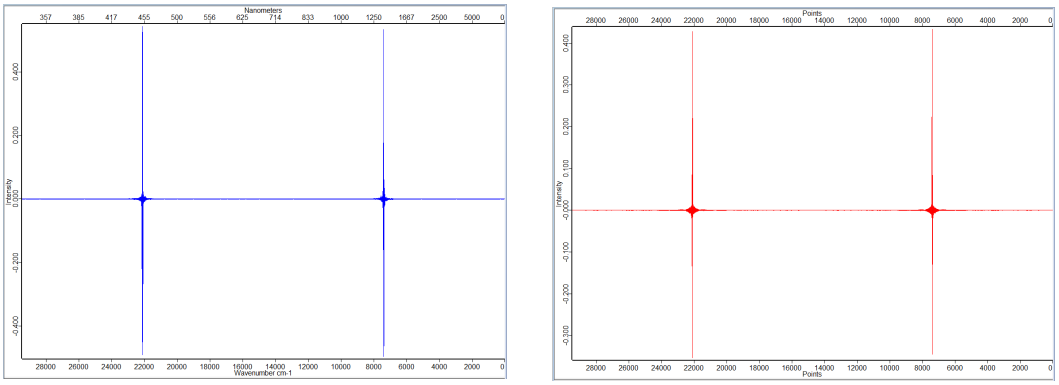


Figure 5.6: Sample interferograms (raw data before FT)

5.7.9 Calculation of the PM-IRRAS sample spectrum

5.7.9.1 General information

The calculation of the PM-IRRAS sample spectrum involves the following steps:

1. Conversion of the two acquired sample interferograms (raw data) into single channel spectra using the Fourier Transformation algorithm.

☞ This step of calculation is done by the OPUS VisualBasic script *PMA50-PMIRRAS*.

2. Calculation of the ratio spectrum by dividing the single channel spectrum resulting from the interferogram of the difference signal by the single channel spectrum resulting from the interferogram of the sum signal.

☞ This step of calculation is done by the OPUS VisualBasic script *PMA50-PMIRRAS*.

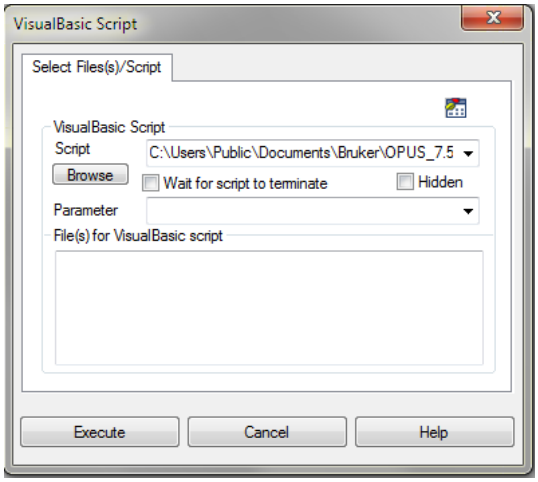
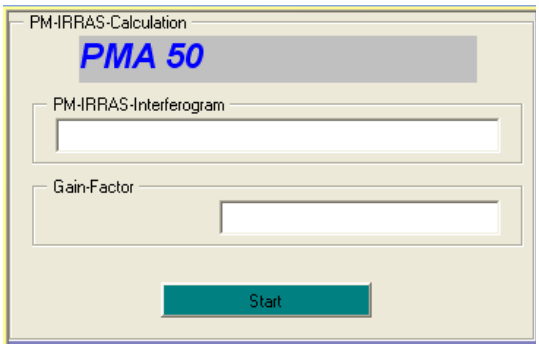
3. Calculation of a mathematically fitted reference background (Bessel function) on the basis of the sample measurement data.

☞ This step of calculation has to be done by the user. See section 5.7.9.3. (Note: In case there are reference measurement data, you can skip this step and use the reference measurement data instead for the calculation of the PM-IRRAS sample spectrum.)

4. Calculation of the PM-IRRAS sample spectrum in form of an absorption spectrum.

☞ This step of calculation is done by the OPUS macro *PMA50-PMIRRAS-CALC.MXT*.

5.7.9.2 Fourier Transformation and calculation of the ratio spectrum

1		Make sure that the OPUS file containing the raw data of the sample measurement is loaded in the OPUS browser.
2		**Open the VB script *PAM50-PMIRRAS.*.** To do this, proceed as follows: 1. Open the OPUS program. 2. In OPUS → *File* menu → *VisualBasic Script* function 3. Browse to *C:\Users\Public\Documents\Bruker\OPUS xxx [with xxx being the current OPUS version] \VBSample.* ➢ Note: To browse to this directory, navigate in the file manager as follows: *Libraries\Documents\public documents \Bruker\OPUS xxx [with xxx being the current OPUS version] \VBSample.* 4. Select the VBscript file *PMA50-PMIRRASxxx.obs*. 5. Click on the *Execute* button.
3		1. Drag the OPUS file as a whole and drop it into the *PM-IRRAS-Interferogram* field. 2. For the parameter *Gain Factor*, enter the value 50. 3. Click on the *Start* button.
	The VB script performs the following steps of calculation automatically: • Conversion of the interferograms into single channel spectra by using the FT algorithm • Calculation of the ratio spectrum by dividing the single channel spectrum resulting from the interferogram resulting from the difference signal by the single channel spectrum resulting from the interferogram of the sum signal.	

➢ For the Fourier Transformation, the VB scripts uses the following parameter values:

FT parameter	Value used for the FT of the DC interferogram	Value used for the FT of the "normal" interferogram
Start frequency limit	4000	4000
End frequency limit	600	600
Phase correction mode	Mertz stored phase	Mertz

FT parameter	Value used for the FT of the DC interferogram	Value used for the FT of the "normal" interferogram
Apodisation function	Blackman-Harris 4-Term	Blackman-Harris 4-Term
Zero filling factor	16	4
Peak search mode	Take from stored phase	Absolute largest value
Non linearity correction	No	Yes: Cut off: 580, eff.: 0.9

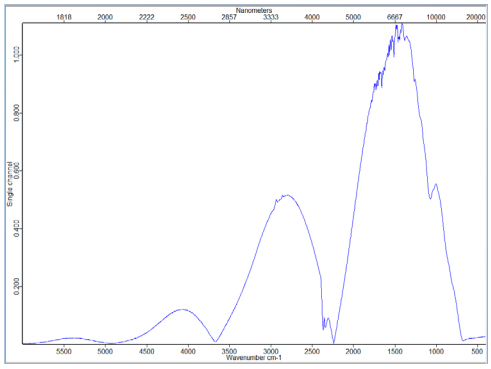
➢ Afterwards, the VB script calculates automatically the ratio spectrum by dividing the single channel spectrum resulting from interferogram of the difference signal by the single channel spectrum resulting from the interferogram of the sum signal.

The OPUS file resulting from the VBscript calculation consists of the following data blocks:

Data block	The data block contains the following spectral information:
	Ratio spectrum ➢ The ratio spectrum is calculated as follows: SSC (sample single channel spectrum resulting from the sum signal) divided by RSC (sample single channel spectrum resulting from the difference signal). ☞ See figure 5.8.
	Interferogram resulting from the difference signal ➢ Note: In case of the original OPUS file, it is the data block 2CHN. ☞ See figure 5.6.
	Single channel spectrum ➢ Result of the Fourier Transformation being performed with interferogram of the difference signal (Note: This interferogram is stored in the SIFG data block.) ☞ See figure 5.7.
	Interferogram resulting from the sum signal ☞ See figure 5.6
	Single channel spectrum ➢ Result of the Fourier Transformation being performed with interferogram of the sum signal (Note: This interferogram is stored in the RIFG data block.) ☞ See figure 5.7.

Figure 5.7 shows the single channel spectra resulting from the two signals. The single channel spectra are the result of the Fourier Transformation applied to the two interferograms.

Single channel spectrum resulting from the interferogram of the difference signal (stored in the data block SSC)



Single channel spectrum resulting from the interferogram of the sum signal (stored in the data block RSC)

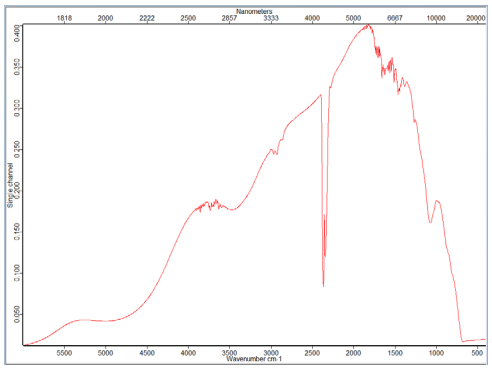


Figure 5.7: Sample single channel spectra (after FT)

Figure 5.8 shows the ratio spectrum calculated by the VB script. The ratio spectrum is calculated by dividing the sample single channel spectrum resulting from the difference signal (stored in the data block SSC) by the sample single channel spectrum resulting from the sum signal (stored in the data block RSC). The ratio spectrum is stored in the data block AB.

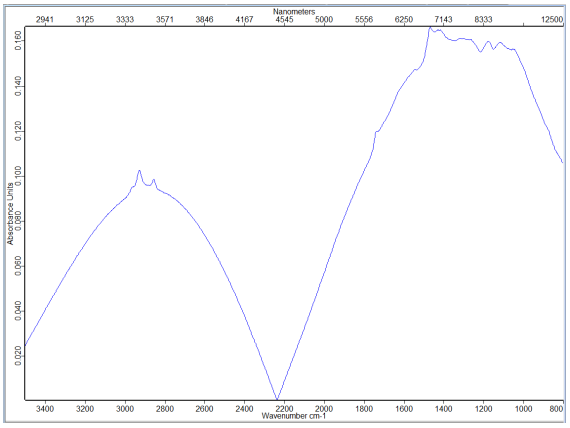
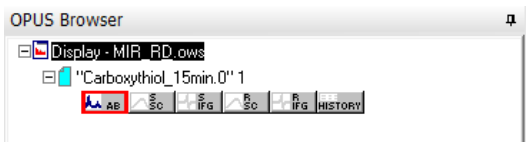
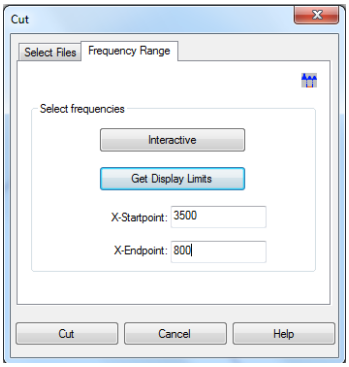
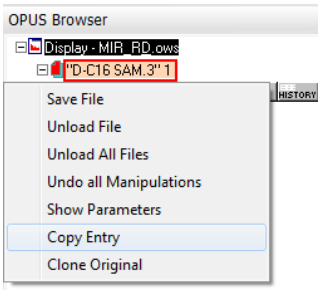
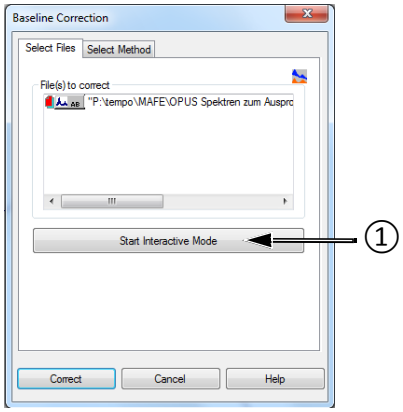


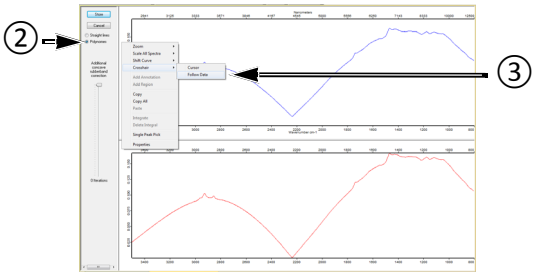
Figure 5.8: Ratio spectrum

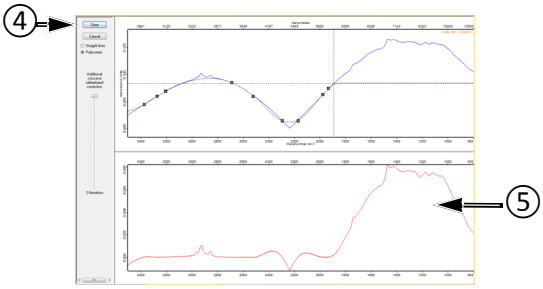
5.7.9.3 Calculation of the mathematically fitted reference

☞ **Important note:** If there is not a reference sample available, then you have to calculate a mathematically fitted reference (Bessel function) on the basis of the sample measurement data. Otherwise, you can skip this step. (See also section 5.7.3.)

1		Make sure that the OPUS file containing the calculated raw PM-IRRAS spectrum is loaded in the OPUS browser.
2		Limit the spectral range of the PM-IRRAS raw spectrum to the region of interest using the OPUS manipulation function *Cut*. (For detailed information about this function, refer to the OPUS Reference Manual.)
3		Store the OPUS file containing the cut result with a different file name and copy the file using the OPUS function *Copy entry*. (For detailed information about this function, refer to the OPUS Reference Manual.)

<table>
<tr>
<td>4</td>
<td>


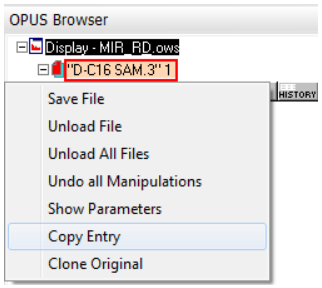




</td>
<td>
1. Open the dialog of the OPUS manipulation function Baseline correction.
2. Drag and drop the AB data block of the OPUS file containing the cut result into the field File(s) to correct.
3. Click on the Start Interactive Mode button ①.

4. Activate the Polynomes option button ②.
5. Right-click on the original spectrum (upper spectrum) and select the context menu function Crosshair - Follow data ③.

6. Add baseline points by double-clicking on the original spectrum (upper spectrum). The result is displayed in real time in the lower spectrum window ⑤.
7. When the baseline is corrected, click on the Store button ④.

☞ For detailed information about this function, refer to the OPUS Reference Manual.
</td>
</tr>
<tr>
<td>5</td>
<td>


</td>
<td>
Store the OPUS file containing the baseline correction result with a different file name and copy the file using the OPUS function Copy entry.
</td>
</tr>
</table>

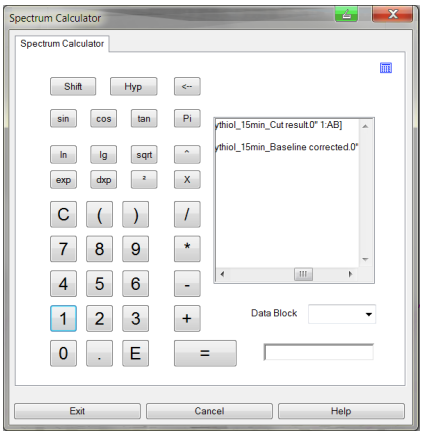
6		OPUS → *Manipulate* menu → *Spectrum Calculator* function Calculate: AB block of the file with the cut result minus the AB block of the file with the baseline correction result. ☞ For detailed information about spectrum calculator, refer to the OPUS Reference Manual. ☞ The calculation result is the Bessel function which is required for the calculation of the PM-IRAAS sample spectrum. See section 5.7.9.4.

Figure 5.9 shows the mathematically fitted reference (Bessel function) which is also a kind of ratio spectrum. It is stored in the AB data block of the OPUS file containing the mathematically fitted reference calculated by the user.

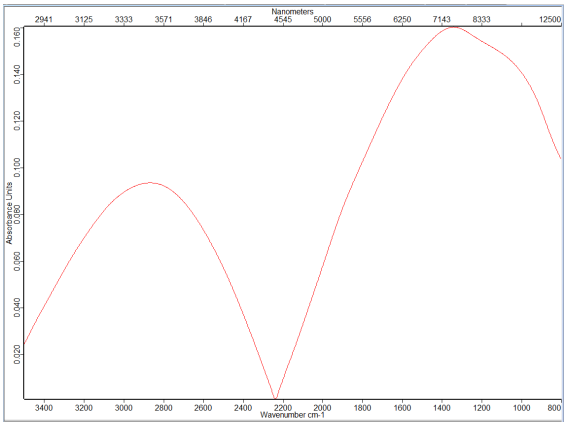
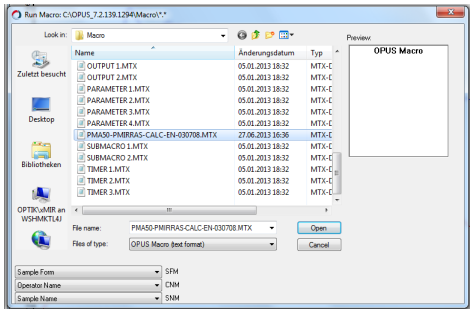
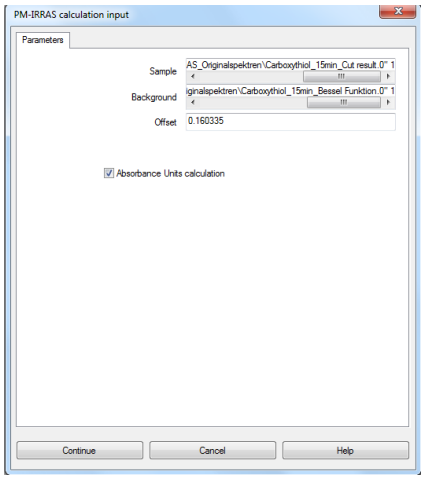
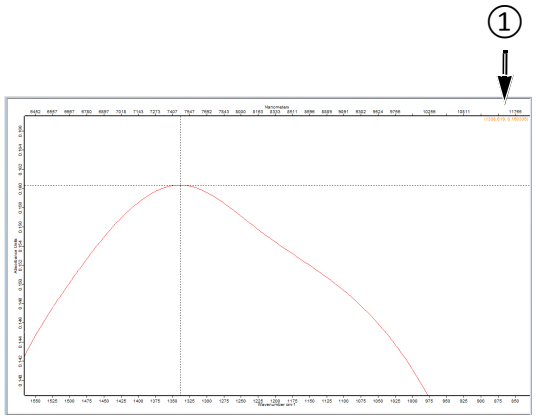
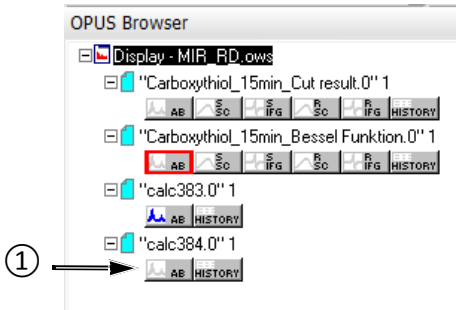


Figure 5.9: Bessel function (mathematically fitted reference)

5.7.9.4 Calculation of the PM-IRRAS sample spectrum

1		OPUS → *Macro* menu → *Run Macro* function Open the macro *PMA50-PMIRRAS-CALC-EN-030708.MXT*.

2	 	1. Drag and drop the AB block of the file containing the cut result into the *Sample* field. 2. Drag and drop the AB block of the file containing the Bessel function into the *Background* field. 3. Enter the offset, i.e. the maximum y-value of the mathematically fitted reference curve (Bessel function). To read this value, proceed as follows: With the Bessel function being displayed in the OPUS display window, zoom in the curve area of the max. y-value. Right-click on the display window and select the context menu function *Crosshair → Follow data*. Move the cursor along the spectrum curve while watching the x- and y-coordinate values ① displayed in the upper right corner of the display window. Make a note of the max. y-value of the curve. 4. When you activate the *Absorbance Units calculation* checkbox, two files (named by default *calcxxx)* are generated: The first file contains the PM-IRRAS spectrum in form of a reflectance spectrum [ΔR/R]; the second file contains the PM-IRRAS spectrum in form of an absorbance spectrum. When you do not activate the *Absorbance Units calculation* checkbox, only one file is generated which contains the PM-IRRAS spectrum in form of a reflectance spectrum [ΔR/R]. 5. Click on the *Continue* button.
3		➢ The result of the calculation are two files which are named *calcxxx* by default. ➢ After the calculation, the two files are loaded automatically in the OPUS browser. ➢ The AB data block of the second file ① contains the PM-IRRAS sample spectrum in form of an absorbance spectrum. See figure 5.10.

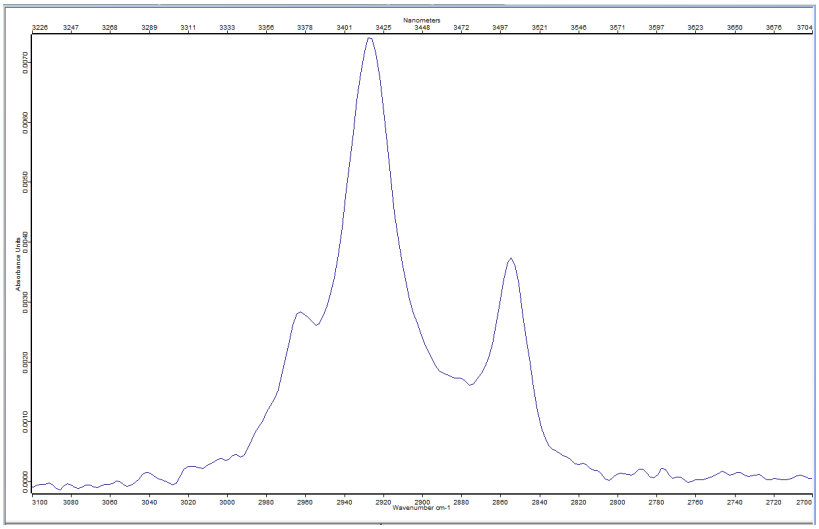


Figure 5.10: PM-IRRAS sample absorption spectrum

➢ Note: The information about the chosen wavenumber for the PEM is not stored in OPUS. It is recommended to write it manually in the data file.

5.8 Switching between VCD and PM-IRRAS

When you switch between the measurement techniques VCD and PM-IRRAS, do not forget to ..:

- set the PEM parameters for the measurement technique in question.

  ☞ For VCD, see section 5.6.5. For PM-IRRAS, see section 5.7.4. For detailed information about the PEM controller, refer to User manual of the PEM-100 Photoelastic Modulator.

- activate the polarization modulation mode for the measurement technique in question.

  ☞ See section 5.4.

- realize the cable connection between PMA50 module and PEM controller for the measurement technique in question.

  ☞ See section 3.7. For detailed information about the PEM controller, refer to User manual of the PEM-100 Photoelastic Modulator.

NOTE

To avoid damage to the electronic head of the PEM, observe the following instruction:

➢ Before you change the cable connection at the rear side of the PEM controller, switch off the PEM controller first. (Note: The POWER button is at the front side of the PEM controller.)

- For VCD, make sure that the optical low-pass filter is installed. For PM-IRRAS, make sure that this filter is removed.

  ☞ See section 5.6.4.

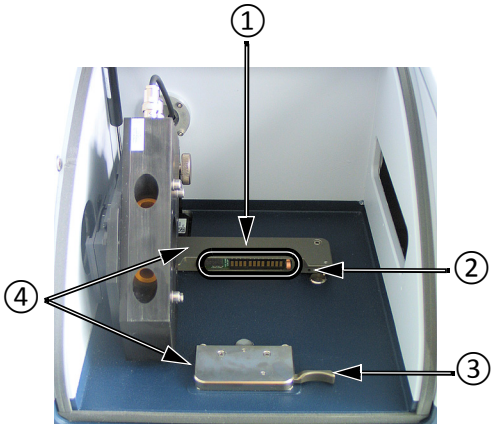
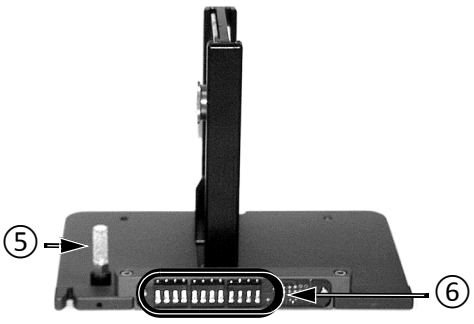
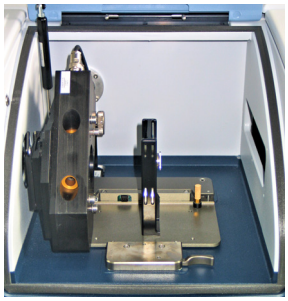
- For VCD, make sure that the detector is again in its home position (i.e. angle position of the lens-detector-assembly: 0°).

  ☞ See section 5.7.6.

5.9 Placing the sample holder in the sample compartment

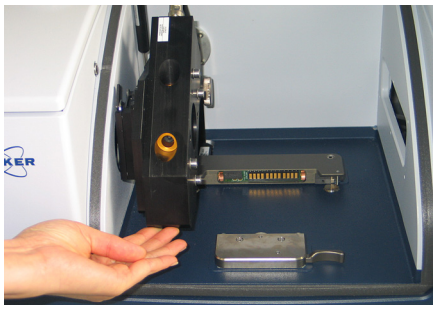
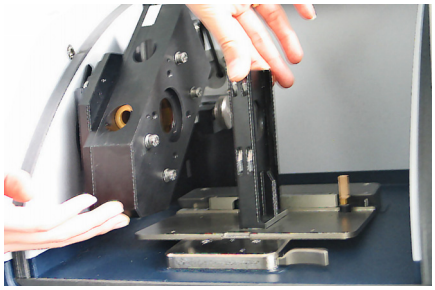
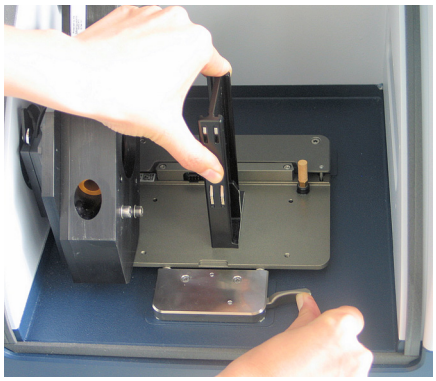
5.9.1 QuickLock mechanism

The sample compartment of the PMA50 module is equipped with an accessory locking mechanism called QuickLock. The QuickLock locking device allows for a solid lock and a quick, exact and reproducible positioning of the sample holders[1] in the sample compartment.

<table>
<tr>
<td> 
</td>
<td>PMA50 sample compartment (inside view)
① - Contract strip (electronic connectors for AAR and CAN bus; it is the counterpart to the contact strip at the QuickLock baseplate of the sample holder ⑥)
② - Purge gas inlet (Note: The purge gas inlet provides for purging the sample compartment with dry air or nitrogen gas. With installed sample holder, the purge gas enters the sample compartment via the purge gas diffuser ⑤ at the sample holder.)
③ - QuickLock release lever
④ - QuickLock mechanism for locking the sample holder</td>
</tr>
<tr>
<td> 
</td>
<td>Standard sample holder with QuickLock baseplate
⑤ - Purge gas diffuser for purging the sample compartment with dry air, if desired
⑥ - Contract strip (electronic connectors for AAR and CAN bus; it is the counterpart to the contact strip at the QuickLock mechanism in the sample compartment ①)</td>
</tr>
<tr>
<td>  </td>
<td>Sample compartment with installed QuickLock-type sample holder
Note: This sample holder is included in the standard delivery scope of the spectrometer.</td>
</tr>
</table>

1. For the PMA50 module, the following sample holders are typically used: the standard sample holder and the special PM-IRAAS sample holder. Both sample holders are mounted on a QuickLock baseplate. (See also section 4.3.)

5.9.2 Locking the sample holder in the sample compartment

1		Slightly lift up the PEM.
2		Put the sample holder into the sample compartment with the contact strip of the QuickLock baseplate facing to the contact strip of the QuickLock mechanism in the sample compartment. While inserting the sample holder in the QuickLock mechanism of the sample compartment, tilt the QuickLock baseplate front edge slightly upwards.
3		While pushing the QuickLock release lever, press the front edge of the QuickLock baseplate downwards until it snaps into the QuickLock mechanism.
3	➢ As soon as the QuickLock baseplate of the sample holder locks in place, the electronic connections for AAR are established. This is indicated by a beep.	

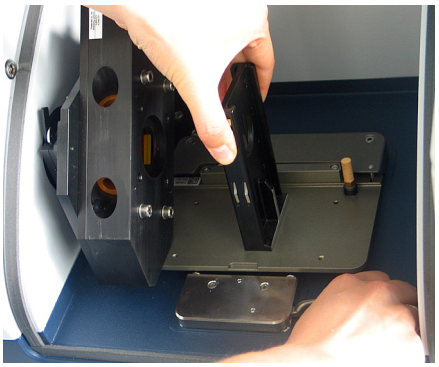
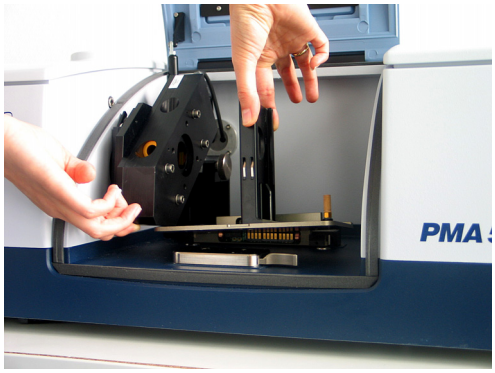
5.9.3 Automatic accessory recognition (AAR)

All QuickLock-type accessories are electronically coded. So, as soon as an accessory locks in place of the spectrometer QuickLock mechanism, it is automatically recognized by the OPUS software program. This software feature is called AAR (Automatic Accessory Recognition). In addition, the OPUS/AAR program performs several predefined OVP tests and loads automatically the corresponding experiment file including the adequate measurement parameter settings and values, provided the user has already defined and stored them for the accessory in question.

Note: When you put a certain accessory in the sample compartment for the very first time, the OPUS/AAR software cannot recognize it because it is not yet registered. In this case, the software prompts you to register the new accessory.

For detailed information about the OPUS software feature AAR, refer to the OPUS Reference Manual. For detailed information about how to define OVP test parameters for certain accessory types, see the Accessory Manager User Manual.

5.9.4 Unlocking the sample holder in the sample compartment

1		While pushing the QuickLock release lever, lift the front edge of the sample holder QuickLock baseplate until the baseplate snaps free.
2		While slightly lifting up the PEM, take the sample holder out of the QuickLock mechanism. Be careful not to damage the contact strips.

5.10 Purging the PMA50 module

5.10.1 General information

The PMA50 module provides for purging both the sample compartment and the optical bench (i.e. interferometer and the detector compartment).

Purging the PMA50 module with dry air or nitrogen gas reduces the content of unwanted atmospheric interferents like water vapor and carbon dioxide inside the PMA50 module significantly. Especially the water vapor in the ambient air absorbs IR radiation. These absorptions are unwanted because they manifest in the spectrum. In the worst case, H_2O bands mask the spectral bands resulting from the sample. Therefore, purging the PMA50 module is recommended, especially when you frequently open the compartment cover(s) or if the ambient air has a high water vapor concentration.

When you measure with a purged PMA50 module, bear in mind the following: After the measurement, OPUS calculates automatically the result sample spectrum by dividing the measured sample spectrum by the background spectrum (measurement without sample). In doing so, the H_2O and CO_2 bands, that result from the ambient air, are eliminated from the result sample spectrum. Consequently, to get a result sample spectrum that is (almost) free of H_2O and CO_2 bands that result from the air inside the PMA50 module, it is not necessary to purge the PMA50 module over a long period of time because not the absolute concentration of H_2O and CO_2 inside the PMA50 module is important but a constant concentration of these gases during both the background and the sample measurement, i.e. the H_2O and CO_2 concentration inside the PMA50 module should be (almost) identical during both measurements.

This can be achieved by proceeding as follows: Before starting the background measurement, simulate a sample exchange (with regard to the duration of the open sample compartment) and a PMA50 module purging (with regard to the purge duration before the measurement) as you will do it later for the real sample measurement.

➢ **Important:** Spectrometer and PMA50 module should be purged similarly.

For the above mentioned reason, it is not recommended trying to reduce the H_2O and CO_2 content as far as possible by purging the PMA50 module for a long period of time before starting the background measurement because the subsequent sample measurement would require the same long purge period before the sample measurement can be started.

5.11 Cooling the MCT detector

5.11.1 General information

The PMA50 module is equipped with a MCT detector.

The operating temperature of the MCT detector is significantly below room temperature. To achieve the required operating temperature, the MCT detector needs to be cooled with liquid nitrogen, i.e. liquid nitrogen is filled in the MCT detector.

The hold time indicates how long the cooling effect of the liquid nitrogen lasts. To ensure an optimum signal detection, the MCT detector needs to be filled with liquid nitrogen in regular intervals. The installed MCT detector has a nominal hold time of 8 hours.

Indications of a weakened or disappeared cooling effect are a low signal intensity or no signal detection. In case no signal is detected, the OPUS status lamp turns to red. This problem is also indicated by the following instrument status message in OPUS: *Detector not ready.* See also section 7.3.2.

If the actual hold time of the MCT detector is considerably shorter than the nominal hold time, the MCT detector dewar needs to be evacuated. See section 6.2.

5.11.2 Safety notes

The temperature of liquid nitrogen is minus 196°C (minus 320.8°F).

⚠ CAUTION

Injury due to improper handling of liquid nitrogen

Non-observance of the following safety instructions may result in an injury.

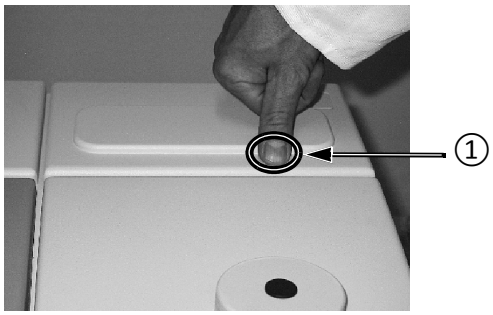
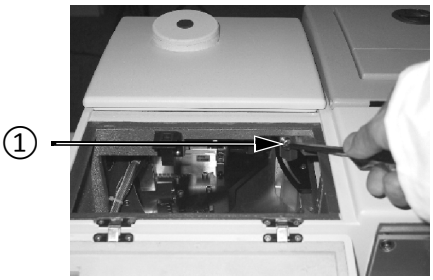
- ➢ Risk of frostbites. Avoid skin contact. Handle liquid nitrogen always with care.
- ➢ Also the gases escaping from the liquid nitrogen are extremely cold and can cause frostbite. The delicate eye tissue can be damaged if exposed to this cold gas even for a short time. Protect your eyes by wearing a face shield or safety goggles! Note that goggles without side shields do not provide adequate protection!
- ➢ High nitrogen gas concentrations in an enclosed area can cause asphyxiation! Nitrogen gas is colorless, odorless and tasteless. Therefore, it can not be detected by human senses and will be inhaled as if it were normal air. Use liquid nitrogen only in well-ventilated areas.

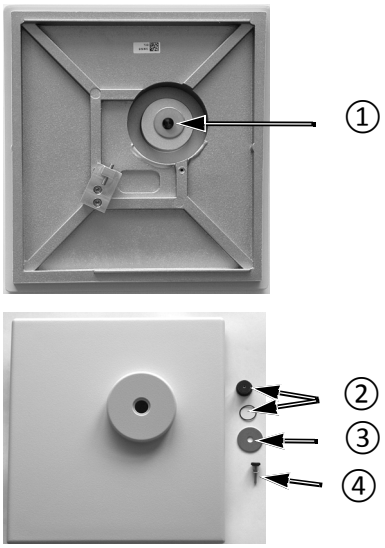
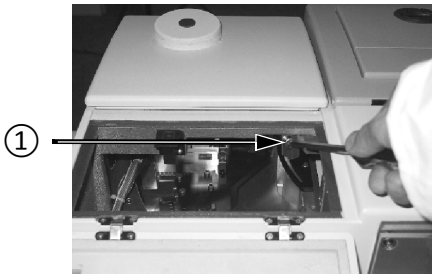
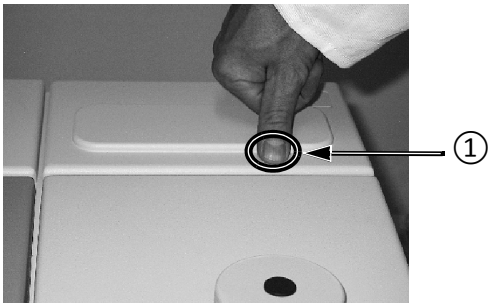
5.11.3 Preparing the detector compartment cover

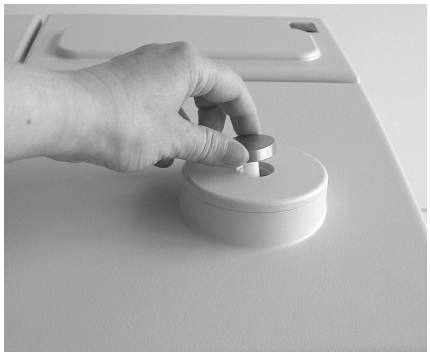
General information

To fill the detector with liquid nitrogen you need neither have to remove the detector nor even open the detector compartment. There is a filling hole in the detector compartment cover. This hole is intended to insert the funnel. Upon delivery, this hole is closed by a cap. The funnel facilitates the filling in of liquid nitrogen in the MCT detector. (Note: The funnel is included in the delivery scope of the MCT detector.)

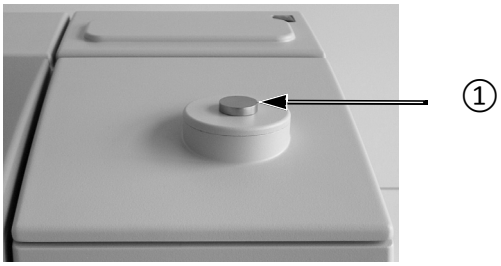
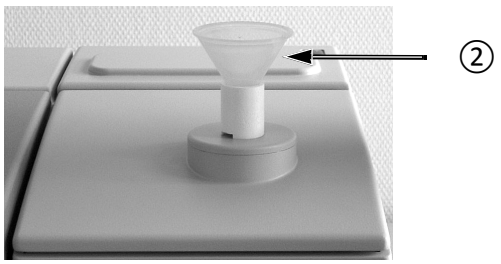
Procedure

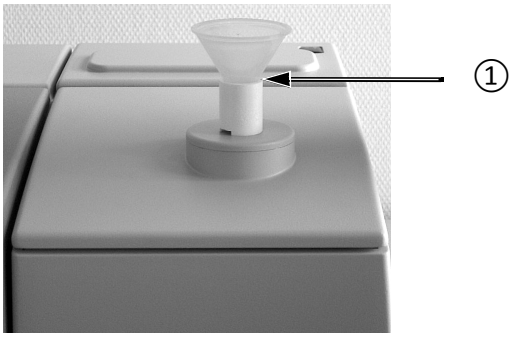
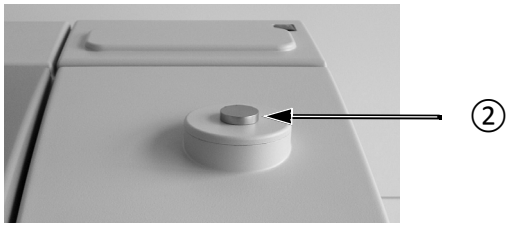
1		There are two detector compartment covers: a rear detector compartment cover ① and a front detector compartment cover ②.
2		First open the rear detector compartment by pressing down the front edge of the rear detector compartment cover (at the pressure point ①) and folding back the cover.
3		To remove the front detector compartment cover, loosen the screw ① by turing it approx. a half turn using an Allen key (size: 6mm). Then lift up the front detector compartment cover.

4		Turn the front detector compartment cover upside down and remove the cap from the filling hole. To do this, screw off the knurled screw ① and remove the complete closure assembly. The closure assembly consists of the following items: ② - cap and O-ring ③ - washer ④- knurled screw
5		**Attention:** Before closing the detector compartment, make sure that the bellows-type sealing adapter ① is screwed on the MCT detector that is installed in spectrometer. Otherwise, when you fill liquid nitrogen in the detector dewar using the funnel, it will flow into the detector compartment and cause serious damage! **Note:** The MCT detector is delivered with a bellows-type sealing adapter. By default, the sealing adapter is factory-mounted. If not, screw the sealing bellows on the filling piece of the MCT detector.
6		Put the front cover on the detector compartment again and fix it by fastening the Allen screw ① with an Allen key (size: 6mm).
7		Fold the rear detector compartment cover forward and close it by pressing down the front edge of the rear detector compartment cover (at the pressure point ①).

8		Then insert the supplied plug in the filling hole. ☞ Note: Always close the filling hole with the plug when you are not filling in liquid nitrogen. The purpose of the plug is to prevent particles and small objects from getting the detector dewar. Remove this plug only when the MCT detector needs to be cooled with liquid nitrogen. Afterwards remove the funnel and reinsert the plug.

5.11.4 Filling the MCT detector with liquid nitrogen

1	 	Open the filling hole by removing the plug ①. Insert the funnel ② instead. ❑ The funnel is included in the delivery scope of the MCT detector.

2		Pour slowly liquid nitrogen in the funnel. Avoid spilling the liquid on the spectrometer housing. At first the liquid nitrogen evaporates and streams out again. Liquid nitrogen boils and splashes when it is filled a warm container. Especially at the beginning, when the temperature difference between the detector dewar and the liquid nitrogen is still very large, the liquid nitrogen may squirt out forcefully due to the boiling delay. Therefore, fill in the liquid nitrogen slowly to minimize boiling and splashing. **Stand clear of boiling and splashing liquid nitrogen and its issuing gas!** Be aware that during the entire filling process, liquid nitrogen can squirt out of the detector dewar from time to time. Wait until the funnel is empty before refilling. When the liquid nitrogen stops streaming out the detector dewar has reached liquid nitrogen temperature. Then, pour again liquid nitrogen in the funnel. Repeat this procedure until the detector has been filled to maximum. (As a rough rule of thumb for the standard MCT detector: the maximum capacity is about the quantity of two to three funnel fillings. Note that the first two funnel filling will evaporate almost completely.) **Avoid overfilling!** In this case the liquid flows out of the filling port.
3	 	After having filled in sufficient liquid nitrogen, take the funnel ① out of the filling hole and insert the plug ② instead.
4	➢ Wait about 20 minutes before starting a measurement to allow the detector to stabilize thermally.	

6 Maintenance and Repair

6.1 General information

The spectrometer is a low-maintenance instrument.

Only a few spectrometer components have a limited service life (e.g. IR source). These components are easy to replace.

The following maintenance and repair works can be performed by the user:

- Evacuating the MCT detector dewar
- Cleaning the PMA50 module

Perform only those maintenance and repair works which are described in this manual. Adhere strictly to the described procedures and observe all relevant safety precautions. Otherwise, personal injury and/or spectrometer damage can be the result. In this case, Bruker does not assume any liability. Maintenance and repair works which are not described in this manual have to be performed by Bruker service personnel only. For the Bruker service contact data, see section 1.6.

NOTE

Damage to ESD-sensitive electronic spectrometer components because of accidental electrostatic discharges (ESD)

➢ Make sure that you are electrostatically discharged before you touch any electronic spectrometer component. Either use a grounded wrist strap or touch a grounded object (e.g. radiator). Note: The grounded wrist strap is the most effective (and the preferred) grounding method.

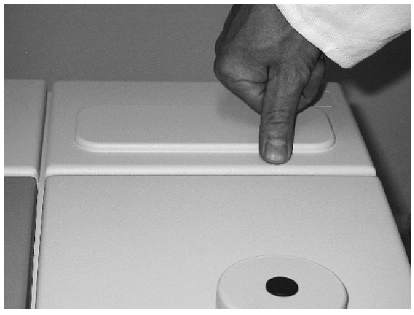
6.2 Evacuating the MCT detector dewar

6.2.1 General information

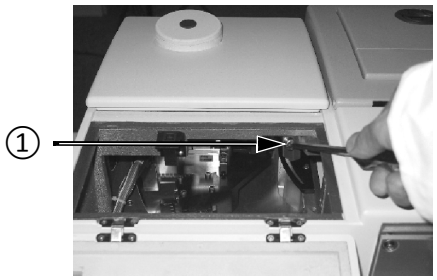
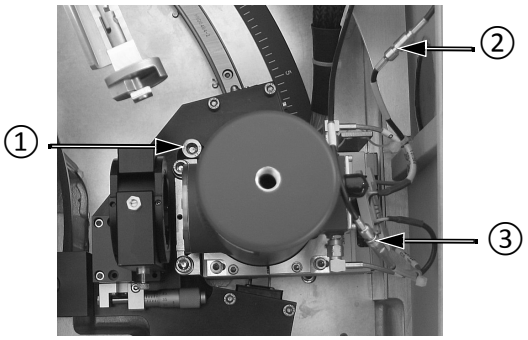
The operating temperature of the MCT detector is significantly below room temperature. To achieve the required operating temperature, the MCT detector is cooled down with liquid nitrogen. The available MCT detectors have different nominal hold time[1]: of 8 hours. To provide for the longest possible hold time, the MCT detector is integrated in a dewar. So, the actual hold time strongly depends on the quality of the vacuum in the detector dewar.

If the actual hold time decreases considerably with regard to the nominal hold time, the detector dewar needs to be evacuated. The existence of condensation water on the detector outside indicates that the vacuum must be evacuated soon. If the MCT detector outside is iced the detector dewar must be evacuated immediately.

6.2.2 Removing the MCT detector

1		The detector compartment is covered by two covers ① and ②.
2		To gain access to the MCT detector, first remove the rear detector compartment cover by pressing down the front side of the rear detector compartment cover and lifting up the cover.

1. The hold time indicates how long the cooling effect of the liquid nitrogen lasts.

3		To remove the front detector compartment cover, loosen the screw ① by turing it approx. a half turn using an Allen key (size: 6mm). Then lift up the front detector compartment cover.
4		Loosen the Allen screw ① using the long end of the Allen wrench (size: 6mm). Disconnect the two detector signal cables ② and ③. Pull the detector straight upwards out of the dovetail guide.

6.2.3 Required evacuating equipment

- Vacuum pump (turbo molecular pump or oil-free high-vacuum pump that is capable of generating a vacuum of at least < 10^{-5}mbar)
- Adapter for connecting the vacuum pump to the MCT detector dewar
- Shut-off valve
- 2x flexible metal hoses

i The above listed evacuating equipment is NOT included in the standard delivery scope of the MCT detector. If desired, Bruker offers suitable evacuating equipment (part number S105-V2, D126 and I10290). Alternatively, Bruker also offers the service of evacuating the MCT detector dewar (part number SD128). This option requires the removal of the MCT detector from the spectrometer and the sending of the complete MCT detector to Bruker for evacuation.

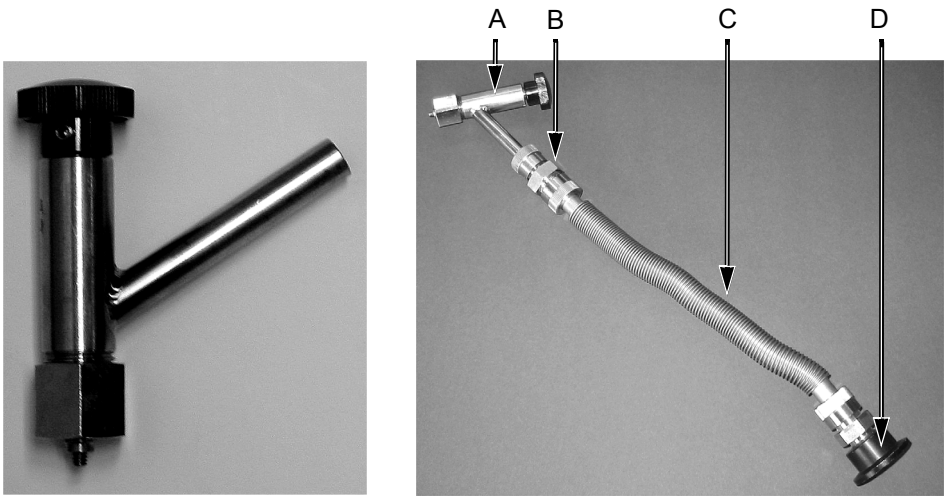


Figure 6.1: a) Adapter b) Adapter with flexible Metal Hose and Flange

Fig. 6.1	Component
A	Connecting adapter (for connecting the vacuum pump to the detector dewar)
B	Flange
C	Flexible metal hose
D	NW 25 flange (for connecting to the vacuum pump)

6.2.4 Evacuation procedure

☞ Before starting to evacuate the MCT detector dewar, make sure that the dewar does not contain any more liquid nitrogen and that the detector has warmed up to room temperature. Take into consideration that the detector warming-up from operating temperature to room temperature takes at least 3 hours after the residual liquid nitrogen has been emptied.

1. Remove the MCT detector from the PMA50 module. See section .6.2.2
2. Connect the adapter to the vacuum pump by flanging a flexible metal hose to the connecting piece of the adapter (E in fig. 6.3) and to the vacuum pump. See fig. 6.1b. (Note: The connecting piece of the adapter has an OD of 9.7mm.) In addition, install a shut-off valve between adapter and vacuum pump.
3. Make sure whether the shut-off valve is closed. Switch on the vacuum pump. Leave the pump running until it has reached its operating temperature.
4. Inspect the O-ring inside the adapter (C in fig. 6.3) for signs of wear.

☞ The O-ring inside the adapter is a wearing part that needs to be replaced after 4 or 5 evacuations at maximum.

5. Remove the cap from the connection nozzle of the detector. (See fig. 6.2a.)

6. Pull the adapter knob (G in fig. 6.3) to the open position and loosen the coupling nut (A in fig. 6.3).
7. Push the adapter carefully over the connection nozzle of detector dewar and fasten the coupling nut (A in fig. 6.3 hand-tight while holding the adapter and the detector as shown in fig. 6.2b. (A hand-tight tightening of the coupling nut is sufficient.)

☞ Hold the adapter and the detector always as shown in fig. 6.2b when you have to carry out the following tasks: opening and closing the evacuation valve by pushing or pulling the adapter knob (step 8, 12, 14 and 17), screwing the threaded adapter rod in or out of the connection thread of the dewar evacuation valve (step 11 and 15) and loosening the coupling nut (step 18).

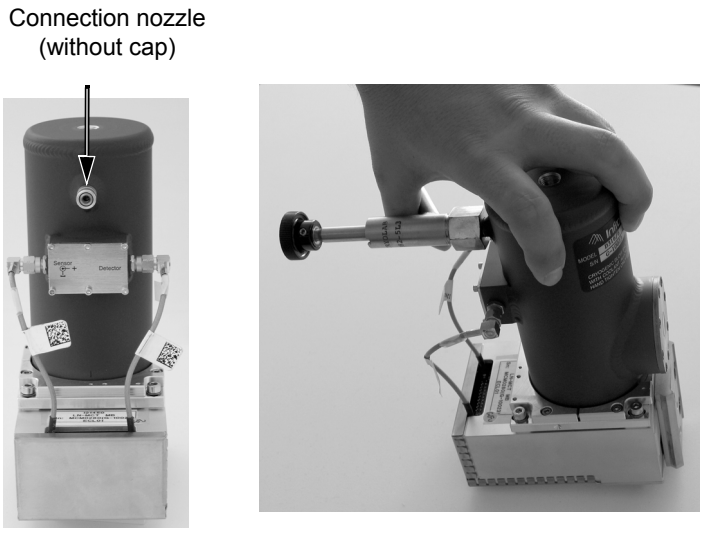


Figure 6.2: a) MCT detector b) How to hold the MCT detector when oping or closing the dewar evacuation valve

8. Push the adapter knob (G in fig. 6.3) in the closed position until the threaded rod (D in fig. 6.3) of the adapter is in contact with the sealing plug of the dewar evacuation valve.
9. Before you begin to evacuate the detector dewar, check the connections for leak tightness by evacuating the section between vacuum pump and detector at first. To do this, open the shut-off valve. If a vacuum of 10^{-4}mbar is generated within a few minutes it is an indication of the leak tightness of this section.
10. Close the shut-off valve again.
11. Screw the threaded rod of the adapter (D in fig. 6.3) in the connection thread of dewar evacuation valve by turning the adapter knob (G in fig. 6.3) clockwise; 2 to 3 rotations are sufficient. **Attention: In case of more than 2 or 3 knob rotations there is a risk that the threaded connection becomes inseparable! That means the threaded rod of the adapter cannot be screwed out of the connection thread of the dewar evacuation valve again.**
12. Pull the knob (G in fig. 6.3) to the open position in order to open the dewar evacuation valve.
13. Begin to evacuate the detector dewar by opening the shut-off valve.

☞ We recommend an evacuation time of at least 3 days to allow for generating an optimal vacuum inside the dewar. The final pressure in the detector dewar should be less than 10^{-5} mbar.

14. When the optimal vacuum is achieved, close the dewar evacuation valve by pushing the adapter knob (G in fig. 6.3) to the closed position. Press the adapter knob firmly to the stop position to ensure that the dewar evacuation valve is sealed airtightly.
15. Screw the threaded rod of the adapter (D in fig. 6.3) out of the connection thread of the dewar evacuation valve by rotating the adapter knob (G in fig. 6.3) several turns counterclockwise until you sense that the threaded adapter rod and the connection thread of the dewar evacuation valve are not joint any more. Be careful in order to prevent an unintentional opening of the evacuation valve and consequently to prevent the detector dewar from being vented again.
16. Vent the section between vacuum pump and adapter.
17. Pull the knob (G in fig. 6.3) to the open position. Attention: Make sure that the sealing plug of the evacuation valve is NOT pulled out! This may occur when you have screwed the threaded adapter rod too far in the connection thread of the dewar evacuation valve. (See step 10.) In this case repeat the dewar evacuation. If you do not succeed in closing the evacuation valve at all you have to send the detector in to Bruker.
18. Loosen the coupling nut (A in fig. 6.3) and remove the adapter from the connection nozzle of the detector dewar.
19. Reinstall the MCT detector in the PMA50 module. (See section 6.2.5.)

☞ If a tiny amount of air should unawares get into the detector dewar during the evacuation procedure (e.g. when you close the evacuation valve) you can perform measurements with this MCT detector for the moment but after a relatively short period of time you have to repeat the detector evacuation.

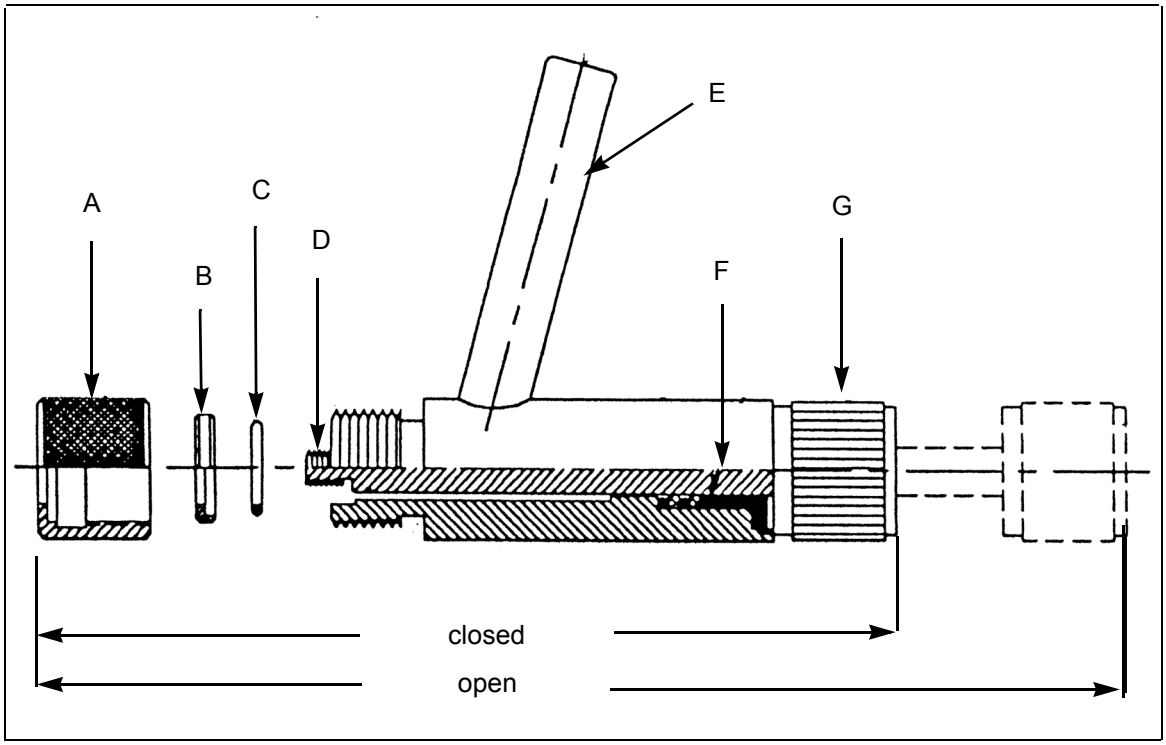
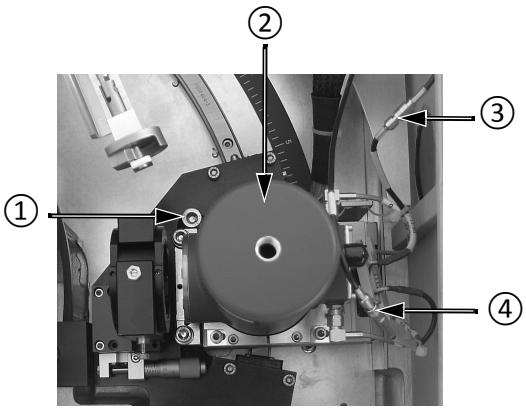
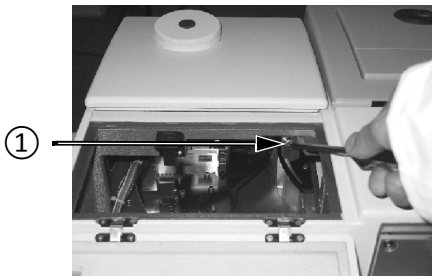
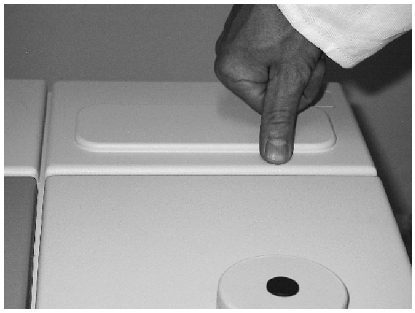


Figure 6.3: Connecting adapter - Cross section

Fig. 6.3	Components of the connecting adapter
A	Coupling nut
B	O-ring retainer
C	O-ring
D	Threaded rod (to remove the valve closure of the detector dewar)
E	Connecting piece for vacuum pump (OD = 9,7mm)
F	Washer and O-ring packing
G	Knob

6.2.5 Reinstalling the MCT detector

1		Insert the detector ② into the dovetail guide and press the detector right down. Fasten the Allen screw ① using the long end of the Allen wrench (size: 6mm). Connect the two detector signal cables ③ and ④.
2		Put the front cover on the detector compartment and fasten it by tightening the screw ①. Turn it approx. a half turn using an Allen key (size: 6mm).
2		Close the rear detector compartment and press on the front side of the rear detector compartment cover to lock the cover.

6.3 Cleaning the PMA50 module

If required, you can clean the outer housing of the PMA50 module with a dry or damp cloth.

NOTE

PMA50 module damage because of improper cleaning

- ➢ Do not use detergents with organic solvents, acid or base!
- ➢ Do not try to clean the optical material of the polarizer, the PEM or other components using a cleaning cloth or something similar. This may lead to an irreversible damage of the component in question. Instead, try to blow off dust particles using clean compressed air, for example. In case you do not succeed in blowing off the dirt, contact the Bruker service. (See section 1.6.)

7 Troubleshooting

7.1 General information

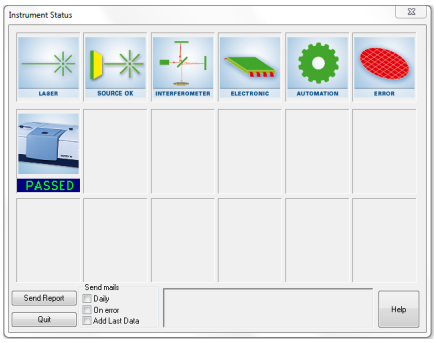
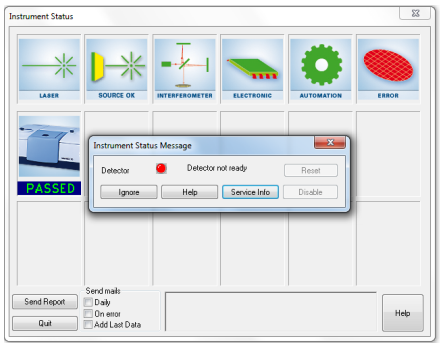
This chapter deals mainly with the most common PMA50 problems that may occur as experience has shown. It provides information about the possible causes of the problem and presents solutions for troubleshooting.

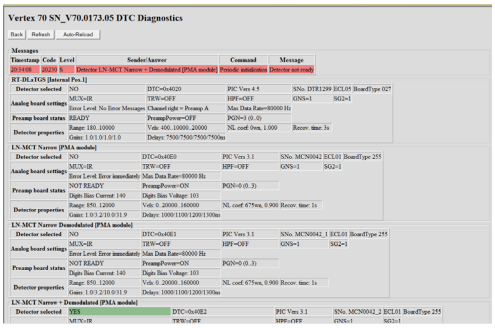
As the PMA50 module is an accessory which is integrated into a complex instrumental setup, proceed systematically to find out first of all which instrument has caused the problem. For problems regarding the spectrometer, consult the User Manual of the spectrometer. For problems regarding the PEM, consult the User manual of the PEM-100 Photoelastic Modulator.

If you do not succeed in solving the problem, contact the Bruker service. For the service contact data, see section 1.5.

7.2 Diagnostic means

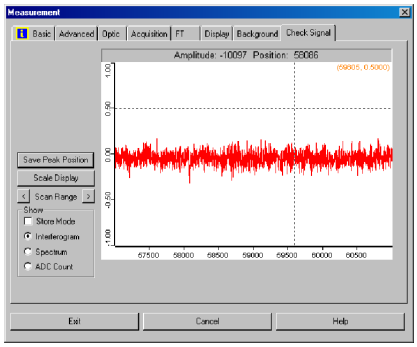
For a systematic fault diagnosis, the following diagnostic means are available:

	***Instrument Status* dialog in OPUS** ➢ To open this dialog, either click on the OPUS status light or select in the *Measure* menu the *Optics Diagnostics* function. ➢ Note: The first row of icons refers to the optical components. The only component being installed in the PMA50 module is the detector. The other components like source, laser etc. are installed in the spectrometer.
	***Instrument Status Message* in OPUS** ➢ If the detector has the status WARNING or ERROR click on the corresponding icon. The *Instrument Status Message* dialog opens. The message gives an indication of the cause of the problem.

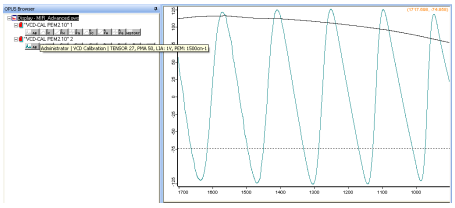


Diagnostics page of the spectrometer firmware

☞ For more detailed information about the component causing a problem, consult the corresponding diagnostic page. To open the diagnostics page of the component in question, click in the *Instrument Status Message* dialog on the *Service Info* button.



***Check Signal* page of the *Measurement* dialog in OPUS**



Especially for VCD, the VCD curve can provide an indication of possible operating errors.

☞ See section 5.6.6.6.

7.3 Problem - Possible cause - Solution

7.3.1 No signal detected or signal intensity is too low

Provided that all instruments and the PC are properly connected and switched on and the computer can access the spectrometer, this problem can have the following possible causes:

Possible Causes	Solutions
Beam path is blocked.	Check whether the IR beam is blocked by an object. Trace the beam path from the beginning in the spectrometer to the end at the detector in the PMA50 module. Remove the object and check the signal again.
The detector is not cooled down to its operating temperature. ➢ This problem is indicated by the instrument status message *Detector not ready*.	Cool down the detector by filling liquid nitrogen into the detector dewar. ☞ See section .5.11.
Detector is not or not properly installed and/or connected. ➢ This problem is indicated by the instrument status message *Device not connected. No analog board selected*.	Install the detector properly and/or examine the detector cable connections. ☞ See section 6.2.5 and section 3.6.
Detector oversaturation or A/D converter overflow	Either reduce the source intensity by using a smaller aperture or reduce the gain settings. ➢ Both parameters (aperture and gain) are set in the OPUS dialog *Measurement*. See the OPUS Reference Manual.
In case of PM-IRRAS only: The sample is not positioned properly so that the light beam does not impinge on the detector element and/or the set angle of incidence is not adequate.	Check whether the set angle of incidence is adequate for the sample in question. If required adapt the detector position. While checking the signal in OPUS, reposition the sample by rotating the sample fixture device. ☞ See section 5.7.6.
A temporary or permanent optics misalignment caused by strong shock.	Place the spectrometer on a vibration-free surface. In case of a temporary optics misalignment, this action can solve the problem. If this action does not solve the problem contact the Bruker service. ☞ See section 1.5

7.3.2 Detector problem

A detector problem is indicated by the following instrument status messages in OPUS:

Instrument status message	Possible causes	Solutions
Detector not ready.	The MCT detector is not cooled down to its operating temperature.	Cool down the MCT detector by filling liquid nitrogen into the detector dewar. ☞ See section .5.11.
Device not connected. No analog board selected. OR No analog board found.	Detector which you have selected in OPUS is not installed in the spectrometer.	Install the detector properly and/ or examine the detector cable connections. ☞ See section 6.2.5 and section 3.6.

7.3.3 Typical VCD-related problems

The interferogram displayed in OPUS has a centerburst and you do not succeed in eliminating the centerburst by rotating the polarizer.

Possible Causes	Solutions
The cable connection between PEM controller and PMA50 module is meant for PM-IRRAS instead for VCD.	Establish the cable connection for VCD. ☞ See section 3.7.
At the PEM controller, the PEM parameters are set for PM-IRRAS instead for VCD.	Set the PEM parameter for VCD. ☞ See section 5.6.5.
For the optical bench of the analysis system, no polarization modulation mode or the PM-IRRAS polarization modulation mode is activated.	Activate the VCD polarization modulation mode by entering the direct command *PEM=42* in OPUS. ☞ See section 5.4.

Your calibration curve does not look like as shown in figure 5.3.

Possible Causes	Solutions
The cable connection between PEM controller and PMA50 module is meant for PM-IRRAS instead for VCD.	Establish the cable connection for VCD. ☞ See section 3.7.
At the PEM controller, the PEM parameters are set for PM-IRRAS instead for VCD.	Set the PEM parameter for VCD. ☞ See section 5.6.5.

Possible Causes	Solutions
For the optical bench of the analysis system, no polarization modulation mode or the PM-IRRAS polarization modulation mode is activated.	Activate the VCD polarization modulation mode by entering the direct command *PEM=42* in OPUS. ☞ See section 5.4.
The PMA50 module is not properly prepared for the VCD calibration measurement For example: • The multiple calibration plate has not been inserted in the sample holder. • One or both polarizers have not been inserted or the orientation (angle setting) of one or both polarizers is not correct. • The detector is not in its home position. (This might be case when a PM-IRRAS measurement has been performed before.)	Correct the hardware setting and repeat the calibration measurement. ☞ See section 5.6.6.3. ☞ Regarding correcting the detector position, see section 5.7.6.
For the calculation of the calibration curve only the original file has been used instead of the original and the cloned file.	Repeat the calculation of the calibration curve using the original and the cloned file. ☞ See section 5.6.6.6.

Artefacts in the sample spectrum.

Possible Causes	Solutions
Sample concentration is too high (> 0.9 absorption units). Note: The absorbance of the sample should between 0.3 and 0.9 absorption units because a stronger absorbance produces very intense VCD signals which can lead to artifacts in the VCD sample spectra.	First check the absorptive power of the sample by acquiring a FT-IR spectroscopic absorption spectrum of the prepared sample solution (measured in transmission). If the absorbance peaks are too strong (> 0.9 absorption units), adjust the sample concentration in the solution or the path length correspondingly.

The sample spectrum exhibits no bands or only weak bands.

Possible Causes	Solutions
Sample concentration is too low (< 0.3 absorption units). Note: The absorbance of the sample should between 0.3 and 0.9 absorption units.	First check the absorptive power of the sample by acquiring a FT-IR spectroscopic absorption spectrum of the prepared sample solution (measured in transmission). If the absorbance peaks are too low (> 0.3 absorption units), increase the sample concentration in the solution.

The baseline of the spectrum is not as it should.

Possible Causes	Solutions
The liquid cell has been inserted in the left slide rail of the sample holder instead of the right slide rail.	Insert the liquid cell in the right slide rail of the sample holder and repeat the measurement.

7.3.4 Typical PM-IRRAS-related problems

No signal or extremely low signal

Possible Causes	Solutions
The substrate of the sample does not reflect.	Prepare a new sample using a metallic substrate which reflects.
With the current angle position of the detector and / or sample, light beam does not impinge on the detector element.	Check whether the set angle of incidence is adequate for the sample in question. If required adapt the detector position. While checking the signal in OPUS, reposition the sample by rotating the sample fixture device. ☞ See section 5.7.6.
Sample is not properly fixed in the sample holder.	Fix the sample properly in the sample holder. ☞ See section 5.7.6.

Signal-to-noise ratio is very low.

Possible Causes	Solutions
Sample is not properly fixed in the sample holder.	Fix the sample properly in the sample holder. ☞ See section 5.7.6.
In OPUS, the selected aperture is too small for the length of the sample in question. ➢ If this is the cause of the problem, the spectrum has only weak bands as well.	Select a larger aperture in OPUS. Hint: For VERTEX: $Aperture_{min}$ = sample length / 1.8 For TENSOR: $Aperture_{min}$ = sample length / 1.6

In the spectral range which is of interest, there are not any spectral information.

Possible Causes	Solutions
In case a VCD measurement has been performed before, the standard optical low pass filter is still installed.	Remove the optical low pass filter and repeat the PM-IRRAS measurement. ☞ See section 5.6.4.

The ratio sample spectrum does not come up to your expectations.

Possible Causes	Solutions
The cable connection between PEM controller and PMA50 module is meant for VCD instead for PM-IRRAS.	Establish the cable connection for PM-IRRAS. ☞ See section 3.7.
At the PEM controller, the PEM parameters are set for VCD instead for PM-IRRAS.	Set the PEM parameter for PM-IRRAS. ☞ See section 5.7.4.
For the optical bench of the analysis system, no polarization modulation mode or the VCD polarization modulation mode is activated.	Activate the PM-IRRAS polarization modulation mode by entering the direct command *PEM=84* in OPUS. ☞ See section 5.4.

7.3.5 PEM controller message "PEM Overload!"

The PEM controller displays the message *PEM Overload!* In addition, no frequency value is shown on the PEM controller displayed. (See figure 7.1.)

Figure 7.1: PEM controller display

Possible Causes	Solutions
No cable connection between PEM controller and PEM.	First of all, switch off the PEM controller. **Otherwise the PEM can be damaged!** ☞ See section 5.5 Then realize the cable connection for the measurement technique you intend to use. ☞ See section 3.7. Then, switch on the PEM controller. ☞ See section 5.3.

☞ For other problems regarding the PEM and/or the PEM controller, consult the User Manual of the PEM-100 Photoelastic Modulator.

7.3.6 Measurement with the FT-IR spectrometer is not possible

In case the you want to perform a non-polarization-modulated-measurement with the FT-IR spectrometer to which the PMA50 module is coupled, the following error message appears:

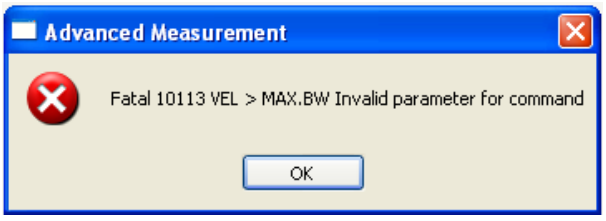


Figure 7.2: OPUS error message

Possible Causes	Solutions
For the optical bench of the analysis system, a polarization modulation mode is activated.	Deactivate any polarization modulation mode by entering the direct command *PEM=0* in OPUS and sending the command to the optical bench. ☞ See section 5.4.

A Specifications

A.1 PMA50 module

Parameter	PMA50
Dimensions	67cm (w) x 46cm (d) x 27cm (h)
Weight	ca. 35 kg
Angle of incidence for PM-IRRAS experiments	between 70° and 89°
Spectral range	Depends on the spectral range of the FT-IR spectrometer to which the PMA50 module is coupled. Note: The basic spectrometer configuration covers a spectral range of 8000 - 750 cm^{-1} which is limited by the PEM and/or the polarizer efficiency only
Spectral resolution	Depends on the spectral resolution of the FT-IR spectrometer to the PMA50 module is coupled.
Electronics	Especially adapted for double modulation Electronics is integrated into the PMA50 module.
Data acquisition	Parallel dual channel data acquisition technique (DigiTect™) with 24 bit dynamic range provides for the simultaneous acquisition of sum signal and difference signal
Demodulation technique	synchronous demodulator integrated in the electronics unit of the FT-IR spectrometer to which the PMA50 module is coupled.
Focusing optics	ZnSe lens for non-polarizing beam focusing on the detector element
Optical bench	purgeable Purge gas requirements: • dry air or nitrogen gas (dew point < -40°C corresponds to a degree of dryness of 128ppm humidity) • oil-free and dust-free • max. pressure: 2 bar (29 psi) • Controllable flow rate (Note: When the spectrometer is purged continuously the recommended flow rate is 200 liters/hour. Make sure that the flow rate does not exceed 500 liters/hour.)

A.2 PEM

Parameter	Specification
optical material	ZnSe
nominal frequency	42 kHz
Useful aperture diameter	16.7mm (Note: It is the aperture diameter of which any point in the aperture field has > 90% of the maximum retardation.)
Coating	anti-reflection coating (for enhanced throughput)
Ambient temperature	max. 50 °C (max. 122 °F) ➢ **Important note:** In case the PEM is operated at ambient temperatures higher than the normal room temperature, a stabilization period between 30 and 45 minutes is highly recommended before the user starts the first measurement.

☞ For more information about the specifications of the PEM and the PEM controller, refer to the PEM-100 Photoeleastic Modulator User Manual.

A.3 Polarizer

Parameter	Specification
Optical material	ZnSe
Outer diameter	35mm
Clear aperture	diameter: 25mm
Usable spectral range	5,000 - 250cm^{-1}
Extinction ratio (typical)	375 @ 1000cm^{-1}
T_{max}	75%

B Spare parts

9.1 Polarizer

Order number	Component
F350	MIR polarizer (KRS-5)

9.2 Optical filter

Order number	Component
F311	Long wave pass filter < 1,828 cm^{-1}
F321	long wave pass filter < 3860cm^{-1}

Spare parts B

C Technical drawings

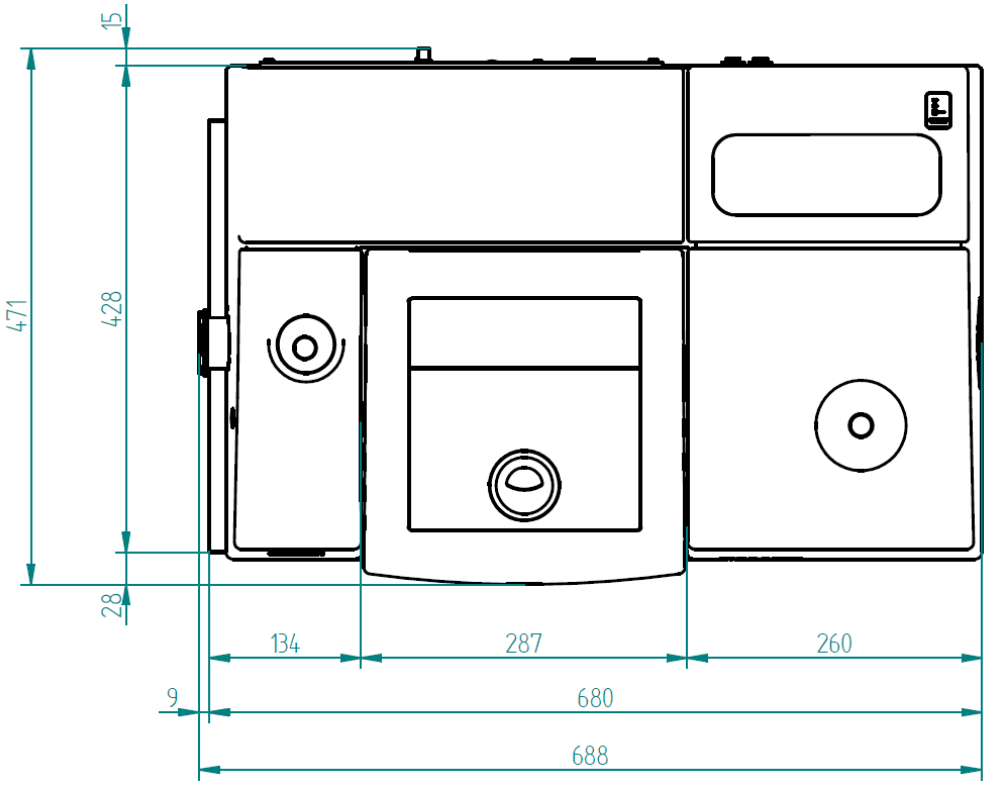


Figure B.1: PMA50 module - Top side view

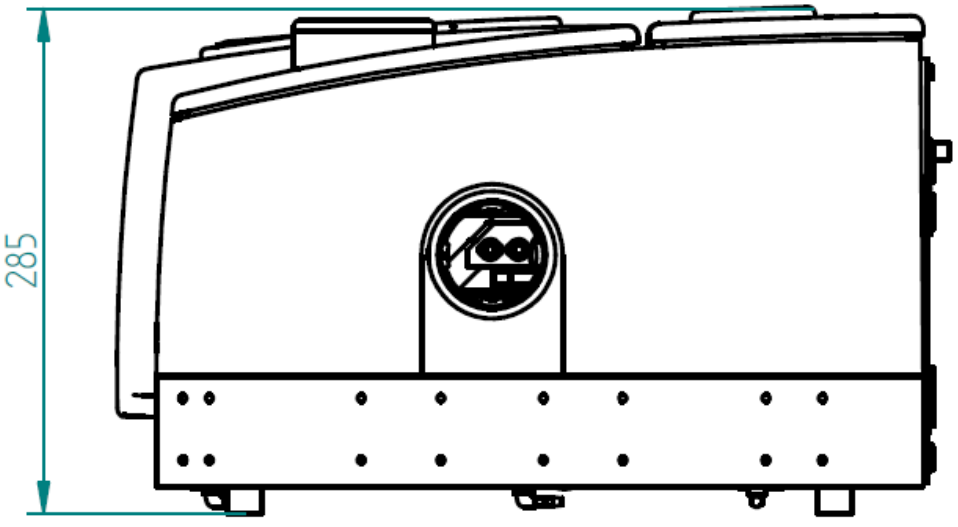


Figure B.2: PMA50 - Right side view

Technical drawings C

D Glossary

This glossary explains the most important key words and abbreviations related to the special spectroscopic measurement techniques for which the PMA50 module is designed.

Birefringence	Birefringence (double refraction) is the optical property of a material having a refractive index which depends on the polarization and the propagation direction of the incident light. When light of different polarizations is incident on a birefringent material, the material splits the light beam into two beams, each being refracted at a different angle and each being polarized perpendicular to the other. The physical effect of birefringence can be used to produce polarized light. See also *Photoelastic Modulator, Polarization* and *Polarizer*.
Circular dichroism	Circular dichroism refers to the phenomenon that an optically active sample absorbs left and right circularly light differently. When circularly light passes through the sample, the speeds of the right and left polarized light are different as well as their wavelengths and the extend to which they are absorbed. Circular dichroism is the difference of the amount of absorbed left circularly polarized light energy and right circularly polarized light energy. See also *Polarization* and *VCD*.
Electromagnetic wave	Electromagnetic waves have electric and magnetic fields which are perpendicular to the direction of propagation. The electric field and the magnetic field are orthogonal, i.e. perpendicular to each other. Both fields are at the same frequency, although their amplitudes may be different and they may be out of phase. See also *Light*.
High-pass filter (HPF)	A high-pass filter is an electronic filter which allows high-frequency signals to pass through but attenuates or reduces the amplitude of signals with frequencies lower than the cutoff frequency. See also *Low-pass filter.*

IRRAS **Infrared reflection absorption spectroscopy**	IRRAS is an spectroscopic measurement technique for the analysis of adsorbed matter or very thin layers on reflecting surfaces (mostly metal substrates). Principle: The IR light is reflected by the reflecting surface of the substrate and passes through the adsorbate or the thin layer twice. While passing through the adsorbate or the thin layer, the IR light is absorbed by it. So the IRRAS measurement technique is a combination of reflection and absorption. A major problem of IRRAS, however, is that of detection sensitivity. Because of the very small number of sample molecules (e.g. adsorbate), the detected signal is usually very weak. The sensitivity can be enhanced by a large incident angle of the IR light (typically 50° - 85°) near the grazing angle. In addition, the sensitivity of this measurement technique can be further enhanced significantly by using the polarization modulation (PM) technique. See also *Polarization modulation* and *PM-IRRAS*.
Light	Light can be considered as electromagnetic radiation. The electric field and the magnetic field of the light wave are perpendicular to the direction of the propagation and to each other. In free space, light mostly propagates as a transverse wave. "Transverse" means that the electric field vector is perpendicular to the direction of propagation of the light wave. Due to the wave-like character, light can be polarized. Polarizers can manipulate light waves in such a way that they oscillate consistently in a plane or along a circle, for example. See also *Electromagnetic wave, Polarization* and *Polarizer*.
Low-pass filter (LPF)	A low-pass filter is an electronic filter which allows low-frequency signals to pass through but attenuates or reduces the amplitude of signals with frequencies higher than the cutoff frequency. See also *High-pass filter.*

Photoelastic modulator (PEM)	A photoelastic modulator is an optical device used to modulate the polarization of a light beam by making use of the photoelastic effect. In its simplest design, the photoelastic modulator consists of an optical element and a piezoelectric transducer with the optical element being attached to the piezoelectric transducer. The transducer causes the optical element to vibrate by stretching and compressing the optical element. This varying mechanical stress changes the birefringence of the optical element in a time-varying manner. The mechanically stressed material of optical element vibrates at a certain frequency which is determined by its length and the speed of a longitudinal sound wave in the optical element material. Both the optical element and the transducer are tuned to the same frequency. The transducer is driven by an electronic circuit which controls the amplitude of the vibration. (Note: Because of the resonant character of the optical element, the birefringence can be modulated to large amplitudes, but for the same reason, the operation of the PEM is restricted to a single frequency only.) Because the optical element of the PEM acts as a wave plate, it modulates the polarization of the light which passes through the optical element. See also *Photoelasticity*, *Polarization*, *Polarization modulation, Wave plate.*
Photoelasticity	Principle of photoelasticity If a solid is stressed by compression or stretching, the material becomes birefringent. As a consequence of this, different polarizations of light have slightly different speeds of light when passing through the stressed material. The stress amplitude can be selected so that the photoelastic modulator acts like a half-wave plate or a quarter-wave plate. This means that the plane of the linear polarized light is rotated by 90° after passing through the PEM crystal. The stress applied to the PEM crystal is modulated in a sinusoidal manner. Thus, the state of polarization is modulated too. The effective polarization modulation frequency of the light is twice the mechanical oscillation frequency of the PEM. See also *Birefringence, Photoelatic modulator* and *Wave plate*.

PM-IRRAS

(Polarization Modulation Infrared Reflection Absorption Spectroscopy)

This analytical technique is a combination of PM (Polarization modulation) and IRRAS (Infrared reflection absorption spectroscopy).

Principle: As the IR light is reflected by the reflecting surface of the substrate, it passes through the adsorbate or the thin layer on the substrate twice. While passing through the adsorbate or the thin layer, the IR light is absorbed by it. So the IRRAS measurement technique is a combination of reflection and absorption.

A major problem of IRRAS, however, is that of detection sensitivity. Because of the very small number of sample molecules (e.g. adsorbate), the detected signal is usually extremely weak. The sensitivity can be enhanced by a large incident angle of the IR light. near the grazing angle. In addition, the sensitivity of this measurement technique can be further enhanced significantly by employing the polarization modulation (PM) technique.

PM-IRRAS takes advantage of the fact that the adsorbate or the thin layer on the reflecting substrate interacts mainly with p-polarized light at a large angle of incidence, but not with s-polarized light.

So, when the sample is exposed to p-polarized light, the spectral information of the sample (i.e. the spectral information of the adsorbate or thin film) is acquired, whereas when the sample is exposed to s-polarized light, the spectral information of the reference (i.e. data without the spectral information of the sample) is acquired.

For the spectroscopic measurement, the polarization of the IR light beam is modulated by a photoelastic modulator (PEM) in an oscillating manner. So the sample is exposed alternately to p-polarized light and s-polarized light.

Due to the nearly simultaneous acquisition of the spectral reference data and sample data, the disturbing absorption of atmospheric components like water vapor and CO_2 is eliminated.

PM-IRRAS delivers two signals: the sum signal and the difference signal.

In surface science, PM-IRRAS is a widely used measurement technique. Typical fields of application are the analysis of:

- coatings and ultra thin layers
- organic (sub-) monolayers on a reflective (metal) surface
- corrosion processes
- molecules adsorbed from the gas phase
- catalytic reactions
- adsorbate-modified electrode / electrolyte interfaces

See also *IRRAS, Photoelaticity, Photoelatic Modulator (PEM)* and *Polarization Modulation*.

Polarization

The polarization of a transverse light wave describes the direction of its oscillation. By convention, the polarization of light is described by specifying the orientation of the electric field vector at a certain point in space over one period of oscillation. The shape traced out by the electric field vector in a fixed plane when the wave passes over it, is a description of the polarization state.

Possible polarization states are: linear polarization and circular polarization.

Linear polarization: The amplitude of the electric and the magnetic field is constant and both fields in phase. In this case, the electric field is oriented in one direction.

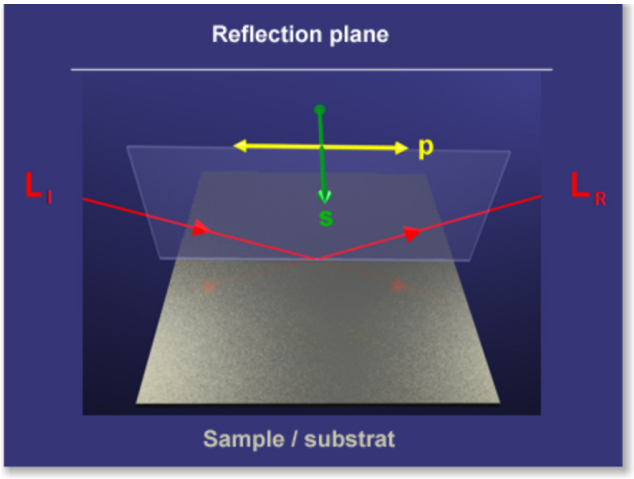
Because the tip of the electric field vector traces out a single line in the plane, this state of polarization is called linear polarization. The direction of this line depends on the relative amplitudes of the two components.

Circular polarization: The electric and the magnetic field vectors are of the same amplitude and exactly 90 degrees out of phase. In this case one field vector is zero when the other is at minimum or maximum amplitude. this case, the electric field vector traces out a circle in the plane.

The electric field may rotate in either direction. The rotational direction of the electric field vector depends on which of the two fields is ahead of the other. So, the circular polarization is either left-handed (counter-clockwise) or right-handed (clockwise).

S and P polarization

When light is incident on a reflective surface, those light waves are called p-polarized of which the electric field runs parallel to the reflection plane (i.e. the polarizing direction is parallel to the reflection plane). And those light waves of which the electric field is perpendicular to reflection plane (i.e. the polarizing direction is perpendicular to the reflection plane) are termed s-polarized.



Reflection plane:
The reflection plane is defined by incident and reflected beam

p-polarized light: polarization direction is parallel to the reflection plane

s-polarized light: polarization direction is perpendicular to the reflection plane

See also *Light*, *Electromagnetic wave* and *Polarizer*.

Polarization modulation (PM)

For modulating the polarization of a light wave, a photo-elastic modulator is used.

Basic principle of polarization modulation

When a linearly polarized light wave passes through the optical element of the PEM, it is split into a s-polarized light wave (i.e. perpendicular to the optical axis of the optical element) and a p-polarized light wave (i.e. parallel to the optical axis of the optical element). As the optical element of the PEM can act as a wave plate, the two types of polarized light waves pass through it with slightly different speeds.

Polarization modulation for VCD

VCD is a spectroscopic measurement technique which detects the difference in absorption of right and left circularly polarized IR light passing through the sample (i.e. optically active compounds). The PEM modulates the polarization of the IR beam in such a way that the sample is exposed alternately to left and right circularly polarized IR light.

Principle of operation

For VCD, the optical element of the PEM acts as a quarter-wave plate. This means that on the far side of the optical element, one type of the polarized light wave is exactly quarter of a wavelength delayed relative to the other type of the polarized light wave.

When the optical element of the PEM is compressed, the p-polarized light wave travels slightly faster than the s-polarized light wave making the light right circularly polarized. When the optical element is stretched, the p-polarized light wave travels slightly slower than the s-polarized light wave making the light left circularly polarized.

As the optical element of the PEM is alternately compressed and stretched with constant frequency, the PEM produces light which oscillates between left and right circular polarization.

Polarization modulation for PM-IRRAS

The spectroscopic measurement technique PM-IRRAS takes advantage of the fact that the sample (i.e. an adsorbate or a thin layer on a reflecting substrate) interacts mainly with p-polarized light, but not with s-polarized light. The PEM modulates the polarization of the IR beam in such a way that the sample is exposed alternately to p-polarized and s-polarized light.

Principle of operation

For PM-IRRAS, the optical element of the PEM acts as a half-wave plate. This means that on the far side of the optical element, one type of the polarized light wave is exactly half of a wavelength delayed relative to the other type of the polarized light wave.

When the optical element of the PEM is compressed, the p-polarized light wave travels slightly faster than the s-polarized light wave. When the optical element is stretched, the p-polarized light wave travels slightly slower than the s-polarized light wave.

As the optical element of the PEM is alternately compressed and stretched with constant frequency, the polarization of light beam passing the optical element is modulated correspondingly.

See also *PEM, Polarization* and *Wave plate*.

Polarization plane	The plane which is perpendicular to the electric field vector in case of linearly polarized light. See also *Polarization, Polarizer* and *Polarizing direction*.
Polarizer	A polarizer is an optical filter which allows light of a specific polarization to pass through and blocks light waves of other polarization. Most light sources emit light waves with no preference for a certain direction of oscillation. A polarizer helps to separate a certain oscillation plane from the mixture of different planes. It filters the incident light in such a way that only light of a specific polarization leaves the polarizer at the other side. This is achieved by absorbing light waves of unwanted polarization or by splitting an unpolarized beam into beams of particular polarization states, for example. An unpolarized light beam can be polarized by making use of one of the following physical effects: • Polarization by reflection • Polarization by birefringence • Polarization by dichroism Depending on the state of polarization they produce, there are linear polarizers and circular polarizers. See also *Polarization*.
Polarizing direction	The polarizing direction is the direction of the electric field vector of an electromagnetic wave. In case of linearly polarized light, the polarizing direction is identical with the electric field vector. Polarizing direction and polarization plane are perpendicular to one other. See also *Polarization, Polarization plane* and *Polarizer.*
RAIRS	RAIRS (reflection-absorption infrared spectroscopy) is a synonymous abbreviations of IRRAS. See also IRRAS.

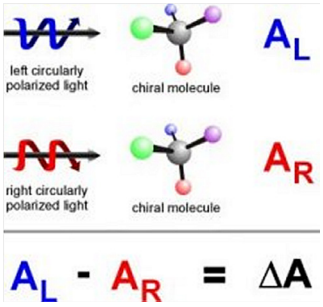
Vibrational circular dichroism (VCD)

VCD is a spectroscopic measurement technique which detects the difference in absorption of right and left circularly polarized IR radiation $\Delta A = A_L - A_R$ passing through optically active compounds.

All chiral molecules are optically active. (Note: Chiral molecules exist in two different mirror-inverted configurations which are not congruent by rotation. Two mirror-inverted configurations are called enantiomers.)

The interaction between chiral molecules and IR light shows different absorption for both enantiomers depending on the circular polarization of light.

The absorption of right circularly polarized light (A_R) and left circularly polarized light (A_L) for optically active compounds is of different intensity. The difference $\Delta A = A_L - A_R$ is unequal to zero for all chiral molecules. This effect is known as **circular dichroism**.



In a VCD experiment, the sample is measured in transmission. The spectral intensities range typically between 10^{-4} and 10^{-5} absorption units.

Typical fields of application are the determination of:
- secondary structure of proteins and peptides
- purity of enantiomers
- absolute structure of enantiomers

See also *Polarization*.

Wave plate	The wave plate is an optical device which changes the polarization state of a light wave which travels through it. Wave plates are made from a birefringent material for which the index of refraction is different from the orientation of light passing through it. A wave plate shifts the polarization direction of linearly polarized light, i.e. it splits the linearly polarized light wave into two waves: the s-polarized light wave (i.e. perpendicular to the optical axis of the wave plate) and p-polarized light wave (i.e. parallel to the optical axis of the wave plate). In the wave plate, the p-polarized light wave propagates slightly slower than the s-polarized one. Depending on the amount of retardation, there are mainly two types of wave plate: half-wave plate and quarter-wave plate. When linearly polarized light passes through a **half-wave plate**, the p-polarized light wave is exactly half of a wavelength delayed relative to the s-polarized light wave. Note: For PM-IRRAS measurements, the vibrating optical element of the PEM acts as a half-wave plate. When linearly polarized light passes through a **quarter-wave plate**, the p-polarized light wave is exactly quarter of a wavelength delayed relative to the s-polarized light wave. So, linear polarized light is converted into circularly polarized light. Note: For VCD measurements, the vibrating optical element of the PEM acts as a quarter-wave plate producing light which oscillates between left and right circular polarized light. See also *Photoelastic Modulator, PM-IRRAS, Polarization, Polarization modulation* and *VCD*.

Glossary D