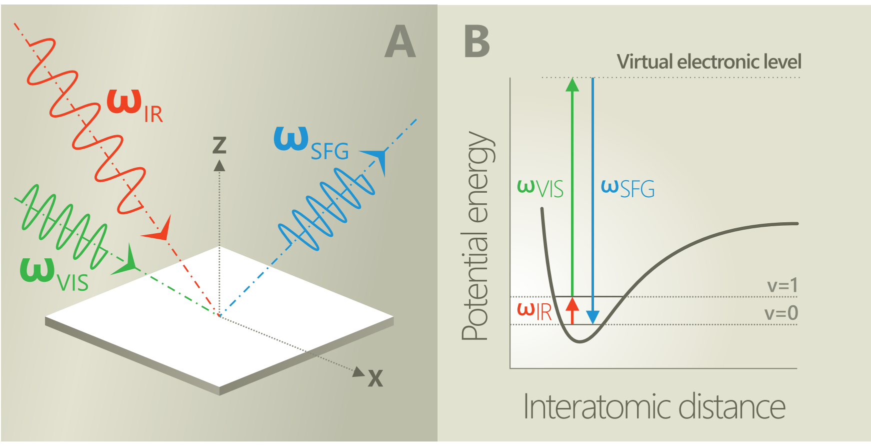
# Sum Frequency Generation Vibrational Spectroscopy

Sum Frequency Generation Vibrational Spectroscopy (SFG-VS) is powerful and versatile method for in-situ investigation of surfaces and interfaces. In SFG-VS experiment a pulsed tunable infrared IR ($\omega_{IR}$) laser beam is mixed with a visible VIS ($\omega_{VIS}$) beam to produce an output at the sum frequency ($\omega_{SFG} = \omega_{IR} + \omega_{VIS}$). SFG is second order nonlinear process, which is allowed only in media without inversion symmetry. At surfaces or interfaces inversion symmetry is necessarily broken, that makes SFG highly surface specific. As the IR wavelength is scanned, active vibrational modes of molecules at the interface give a resonant contribution to SF signal. The resonant enhancement provides spectral information on surface characteristic vibrational transitions.

Vibrational sum frequency generation (SFG) spectroscopy holds several important advantages over traditional spectroscopy methods for the molecular level analysis of interfaces, including (i) surface sensitivity, (ii) vibrational specificity, and (iii) the possibility to extract detailed information on the ordering and orientation of molecular groups at the interface by analysis of polarization-dependent SFG spectra.




SFG signal generation diagram (a) and the molecular energy level diagram for the SFG process (b)

## ADVANTAGES

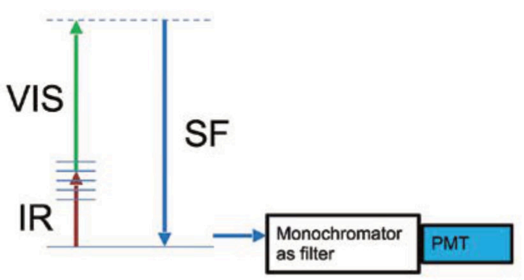
- *Sensitive and selective to the orientation of molecules in the surface layer*
- *Intrinsically surface specific*
- *Selective to adsorbed species*
- *Sensitive to submonolayer of molecules*
- *Applicable to all interfaces accessible to light*
- *Nondestructive*
- *Capable of high spectral and spatial resolution*

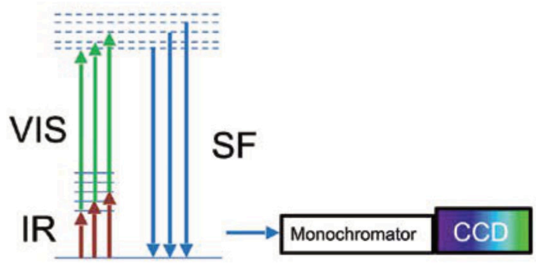
## APPLICATIONS

- *Investigation of surfaces and interfaces of solids, liquids, polymers, biological membranes and other systems*
- *Studies of surface structure, chemical composition and molecular orientation*
- *Remote sensing in hostile environment*
- *Investigation of surface reactions under real atmosphere, catalysis, surface dynamics*
- *Studies of epitaxial growth, electrochemistry, material and environmental problems*


Distributed by TOPAG Lasertechnik GmbH
+49 6151 42944 0 | info@topag.de | www.topag.de

# Narrowband picosecond scanning and broadband femtosecond SFG spectrometer




### Narrowband picosecond scanning SFG spectrometer

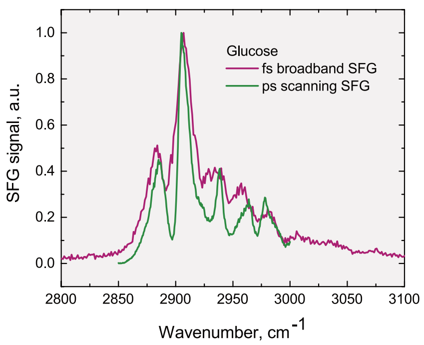
In order to get SFG spectrum during measurement wavelength of narrowband mid-IR pulse is changed point-by-point throughout the range of interest. Narrowband SFG signal is recorded by the time-gated photomultiplier. Energy of each mid-IR, VIS and SFG pulse is measured. After the measurement, the SFG spectrum can be normalised according to IR and VIS energy. Spectral resolution is determined by the bandwidth of the mid-IR light source. The narrower mid-IR pulse bandwidth, the better the SFG spectral resolution. Separate vibrational modes are excited during the measurement.

### Broadband femtosecond SFG spectrometer

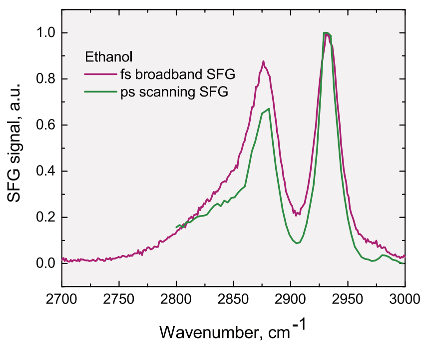
A broadband mid-IR pulse is mixed with a narrowband VIS pulse. The result is broadband SFG spectrum which is recorded using a monochromator and a sensitive CCD camera. The full spectrum is acquired simultaneously by integrating signal over time. Spectral resolution is determined by the bandwidth of the VIS pulse and on the monochromator-camera combination. The narrower the bandwidth of VIS pulse, the better the SFG spectral resolution.

## COMPARISON OF DIFFERENT SFG SPECTROMETRES

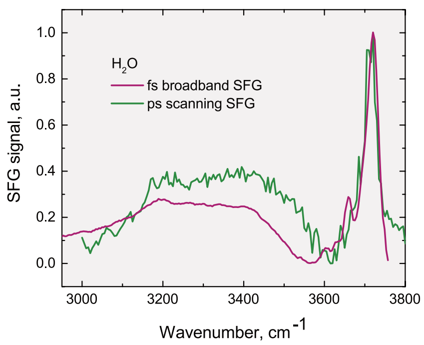
| Narrowband picosecond scanning spectrometer | Broadband femtosecond high resolution spectrometer |
|---|---|
| Narrowband mid-IR excitation, only one band is excited. Coupled states can be separated. | Simultaneous exsitation and recording of broad vibration spectrum with high resolution. |
| High mid-IR pulse energy. Less influence of IR absorbtion in the air. | High mid-IR intensity at low pulse energy – suitable for biological or other water containing samples. |
| No reference spectrum needed, IR energy measured at each spectral point. | Optically coupled IR and VIS channels. Reduced complexity and increased stability of the system. |
| System is more simple, lower ambient conditions requirements, easier to maintain. | Hight repetition rate up to 1 kHz. |




SFG spectra of glucose with 1 sec. acquisition time




SFG spectra of ethanol with 30 sec. acquisition time




SFG spectra of water-air interface

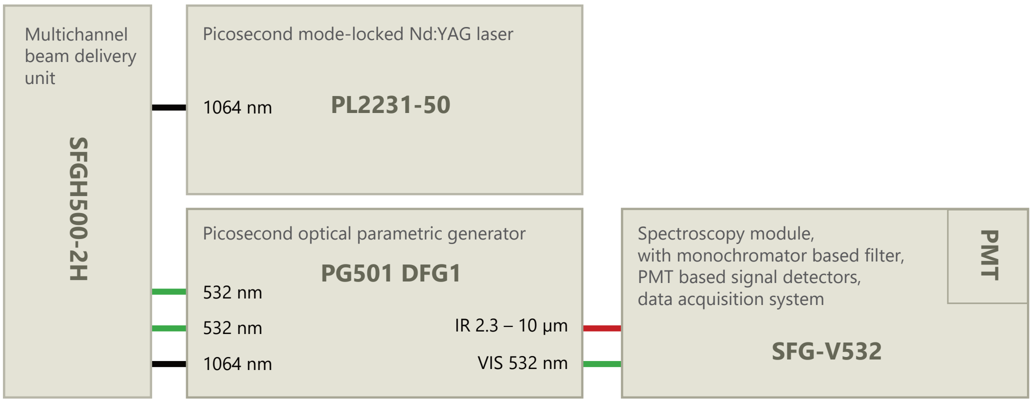
# Features and design of the picosecond scanning SFG spectrometer

The SFG spectrometer developed by Ekspla engineers is a nonlinear spectrometry instrument, convenient for everyday use. Ekspla manufactures SFG spectrometers, which are used by chemists, biologists, material scientists, and physicists. The spectrometer has many features that help to set up measurements and to make successful vibrational spectroscopy studies. For chemical and biochemical laboratories, this makes the Ekspla SFG spectrometer a reliable workhorse with a broad spectral region, automatically tuned from 1,000 to 4,300 $cm^{-1}$, a high spectral resolution (2 or 6 $cm^{-1}$), and easily controlled adjustment of polarisation optics.

The Ekspla SFG system is based on a mode-locked Nd:YAG laser with a 29 ps pulse duration, with 30 – 40 mJ pulse energy at 1,064 nm and a 50 Hz repetition rate. The VIS channel of the SFG spectrometer consists of part of a laser output beam, usually with doubled frequency (532 nm) up to 0.5 mJ. The main part of the laser radiation goes to an optical parametric generator (OPG) with a difference frequency generation (DFG) extension. The IR channel of the spectrometer is pumped by the DFG output beam with energy in the range of ~40 – 200 µJ. Infrared light can be tuned in a very broad spectral range from 2.3 up to 10 (optionaly up to 16) µm. The bandwidth is 2 or 6 $cm^{-1}$ (depending on the selected OPG model) and it is one of the main factors of SFG spectrometer spectral resolution. The second beam (VIS) is also narrowband at <2 $cm^{-1}$. The spectrometer detection system has a temporal gate. It reduces noise collection and ambient light influence, which allows the spectrometer to be used even in a brightly illuminated room. The spectrometer does not have any acoustic noise because the laser is pumped by diodes. The spot size of the IR beam is adjustable. In this way, the appropriate energy density is achieved to avoid damaging the sample. Spectrum scanning, polarisation control and VIS beam attenuation are controlled from a computer. The spectrometer has a motorized polarisation switch for the IR, optionaly for the VIS, and optionaly the generated SFG light beams . Special detectors continuously monitor the energy of the VIS and mid-IR laser pulses, so IR energy is checked at each measurement point. This makes it easy to normalize the resulting SFG vibrational spectrum.

## SYSTEM COMPONENTS

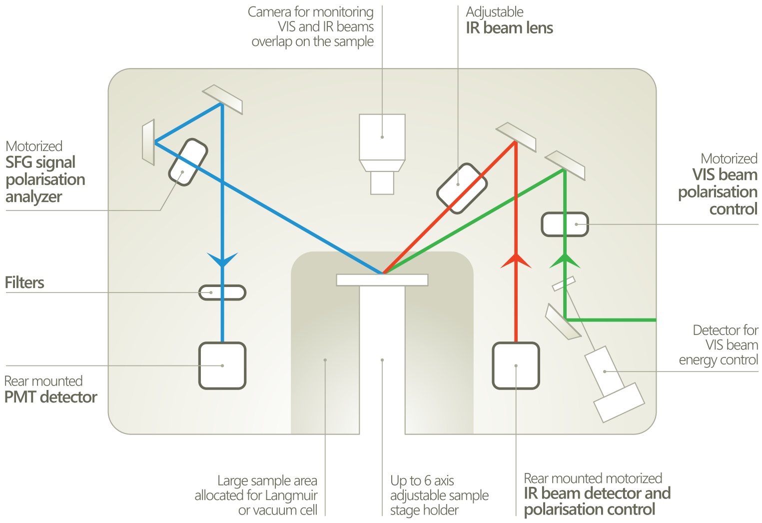
- *Picosecond mode-locked Nd:YAG laser*
- *Multichannel beam delivery unit*
- *Picosecond optical parametric generator*
- *Spectroscopy module*
- *Monochromator*
- *PMT based signal detectors*
- *Data acquisition system*
- *Dedicated LabView® software package for system control*




Schematic layout of **SFG Classic** spectrometer

## SPECTROSCOPY MODULE, SAMPLE COMPARTMENT

A large sample compartment can be customised and enables the use of various extensions and additional instruments for simultaneous control of the sample conditions, including a Langmuir-Blodgett trough for air/water and lipid/air interface studies, temperature and humidity-controlled cells, and other instruments.



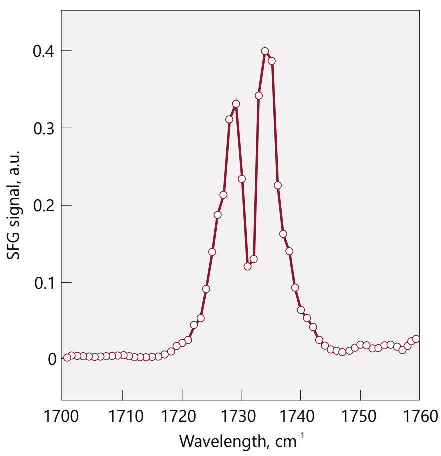

Standard layout of the vertically-arranged sample compartment of the SFG spectrometer

## SAFETY OF THE SFG SPECTROMETER

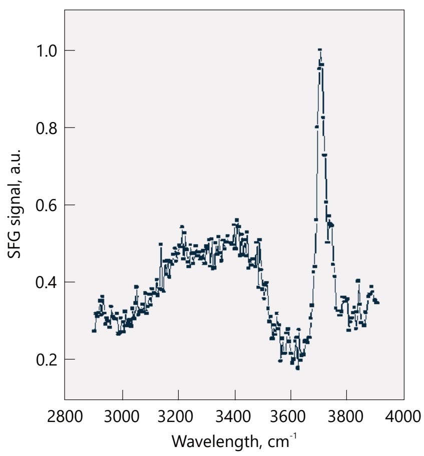
The spectrometer is safe to use: all high energy pulsed beams are enclosed. In addition, the sample area also has a special cover. During the measurements, it is possible to close the sample compartment so that radiation cannot penetrate outside.

The automatic change of polarisation and energy attenuation makes it possible to perform measurements without opening the spectrometer. Laser safety precautions are required only for the alignment of the laser beams on the studied surface.

## SPECTRA EXAMPLES




SFG spectra of monoolein surface, 1 $cm^{-1}$ scan step, 200 acquisitions per step




Water-air interface spectra, 200 acquisitions per step

*Courtesy of University of Michigan*

# Picosecond scanning SFG spectrometer Modifications and Options

## DOUBLE RESONANCE MODEL

**Both IR and VIS wavelengths are tunable in Double resonance SFG spectrometer model.**

This two-dimensional spectroscopy is more selective than single resonant SFG. Double resonant SFG allows investigation of vibrational mode coupling to electron states at a surface.

Double resonance enables the use of another wavelength for VIS beam if the sample has strong absorption at 532 nm and 1064 nm. A range 420 – 680 nm is typically used for VIS beam.

Two outputs PL2230 laser is used for this spectrometer.

## MODIFICATIONS

- *Double resonance SFG spectrometer – allows investigation of vibrational mode coupling to electron states at a surface*
- *Phase sensitive SFG spectrometer – allows measurement of the complex spectra of surface nonlinear response coefficients*

## SPECTRAL RANGE OF THE SFG SPECTROMETER

The spectral range of the infrared beam determines available vibrational spectra and the spectral range of the spectrometer.

**The main modification of the spectrometer enables a spectral range of 1,000 to 4,300 cm$^{-1}$.**

SFG Spectrometer available with a shorter spectral range **2,500 to 4,300 cm$^{-1}$**.

**SFG spectrometer with extended vibrational frequency range.**

Using an additional crystal in the laser light source, the range of the spectrometer expands by up to 625 cm$^{-1}$. This opens a fingerprint spectral region for the analysis of many inorganic compounds, the vibrations of ions and biomolecules.

## OPTIONS

- *Single or double wavelength VIS beam: 532 nm and/or 1064 nm*
- *One or two detection channels: main signal and reference*
- *Second harmonic generation surface spectroscopy option*
- *High resolution option – down to 2 cm$^{-1}$*
- *Motorized VIS and IR beams alignment system*
- *Motorized polarisation control for VIS and SFG beams*
- *Larger SFG box for Langmuir trough*

## SFG PHASE-SENSITIVE MODEL

**SFG spectrometer with additional phase sensitive measurements option.**

A phase sensitive spectrometer allows the measurement the phase of nonlinear susceptibility $\chi^{(2)}$. Reference and test samples are used and the SFG phase difference between them is scanned. The real and imaginary parts of second order susceptibility are calculated from the experimental results. Such an approach enables the unambiguous determination of the orientation of molecular groups at the interface.

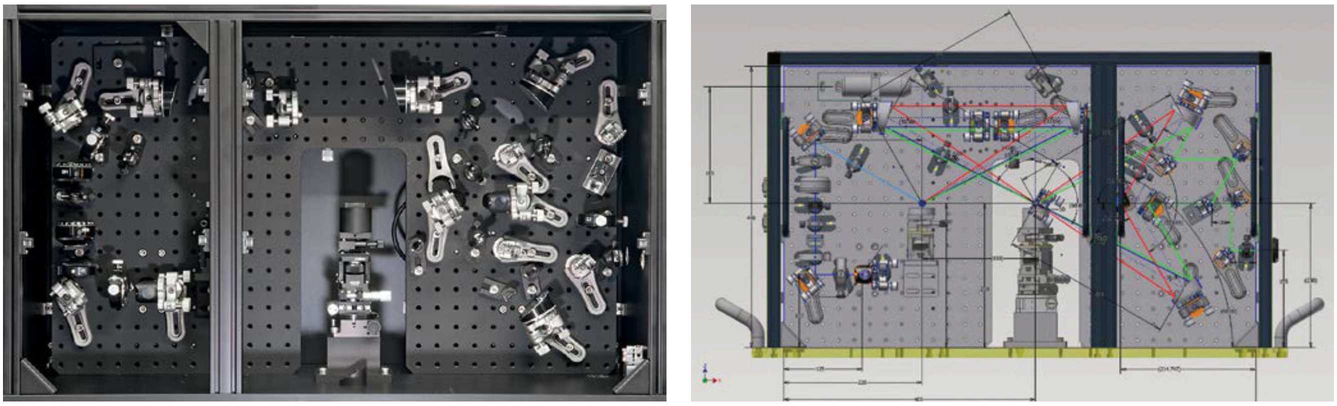
Availble PHASE SENSITIVE SFG + CLASSIC SFG SPECTROMETER IN ONE UNIT.

## PHASE-SENSITIVE SFG SPECTROMETER

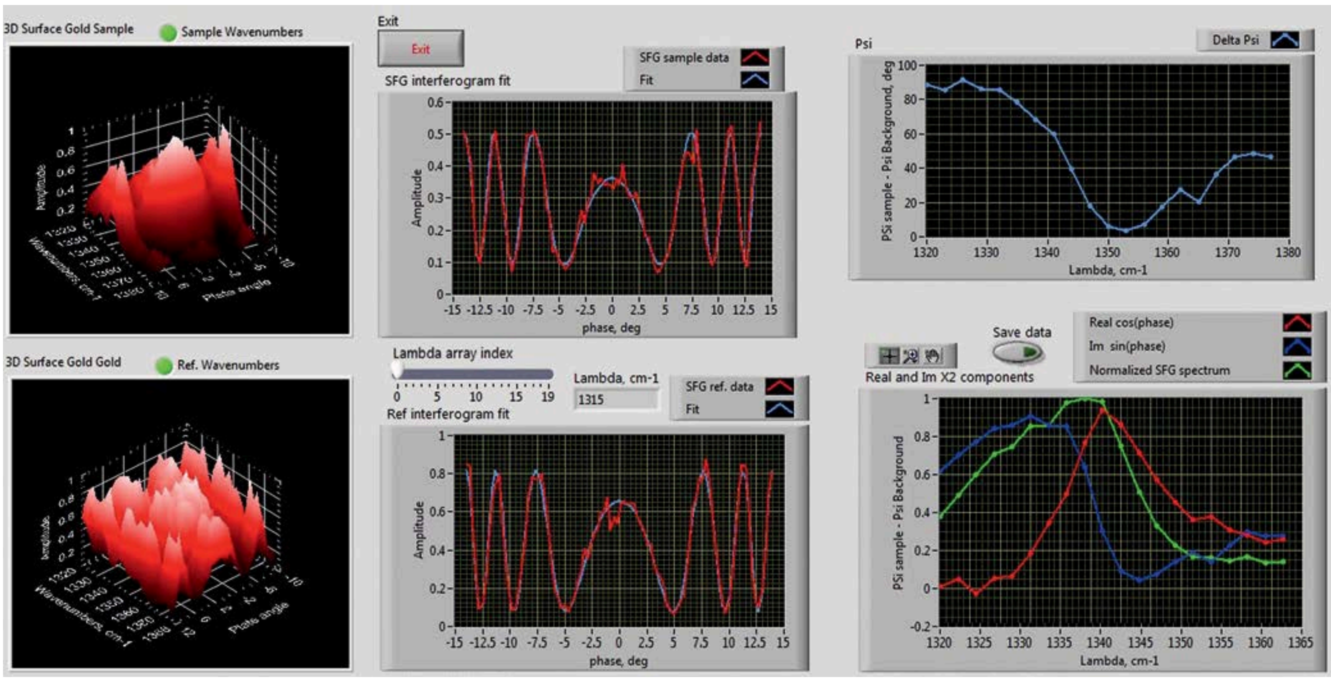
**Phase sensitive measurements with spectral resolution up to 6 cm$^{-1}$ (2 cm$^{-1}$).**

In conventional SFG-VS intensity of SF signal is measured. It is proportional to the square of second order nonlinear susceptibility $I_{SF} \sim |\chi^{(2)}|^2$. However, $\chi^{(2)}$ is complex, and for complete information, we need to know both the amplitude and the phase. This will allow us to determine the absolute direction in which the bonds are pointing and characterize their tilt angle with respect to the surface. Measurement of the phase of an optical wave requires an interference scheme. Mixing the wave of interest with a reference wave of known phase generates an interference pattern, from which the phase of the wave can be deduced.

In practice Phase-sensitive SFG experimental setup includes two samples generating SF signal simultaneously. One sample (usually called local oscillator) has well known and flat spectral response. Second one is investigated sample. The excitation beams are directed to first sample, where SFG beam is generated. Later all three beams are retranslated to the second sample, where another SFG beam is generated. Due to electromagnetic waves coherence both SFG beam are interfering. Setup contains the phase modular located on the SFG beam path between samples. We are able to change the phase of SFG beam by rotating it. This way we are recording two-dimensional intererogram with wavelength and phase shift on x and y axis. Using fitting algorithms we are able to calculate the amplitude and phase of SF signal.



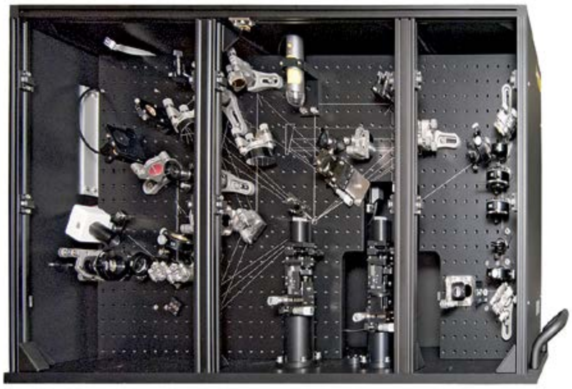
Spectroscopy module of **Phase-sensitive SFG** spectrometer: internal view (left) and 3D drawing (right)




**Phase-sensitive SFG** spectrometer software window showing interferograms of AZO (azophenylcarbazole) dyes on the Au surface and fitted SF spectra with amplitude and phase distinguished

## PHASE SENSITIVE SFG + CLASSIC SFG SPECTROMETER IN ONE UNIT

Interference measurements of SFG signals from reference sample and the investigated sample for Phase-sensitive configuration.



Classic + Phase sensitive versions in one unit

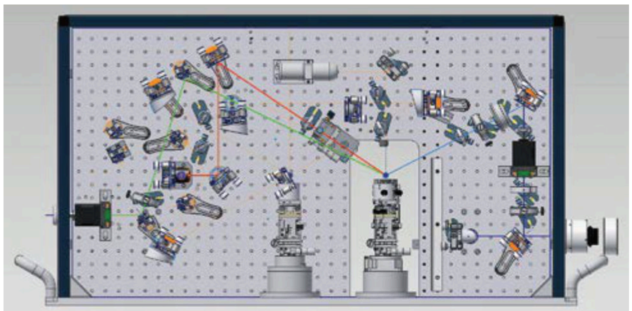
Switchable setup. Phase sensitiv / “Classic” (“Advanced”) ;
Top/ Bottom configuration.
Switch: VIS beam manual. IR mirrors motorised, $BaF_2$ lens manual.
Path length to the sample is same in all configuration
Motorised polarisation control.
VIS beam 532 nm. IR 2,3- up to 10 (16) µm.

### OPTIONS

*Spectrometer has "classic" and "Phase-sensitive" properties:*

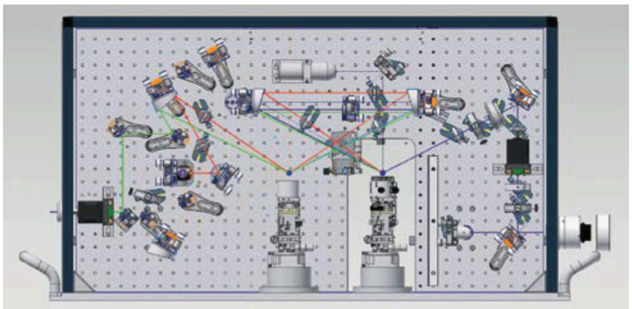
- *Easy switching between setups*
- *Adjustable spot size for classic configuration*

(“Classic”) configuration



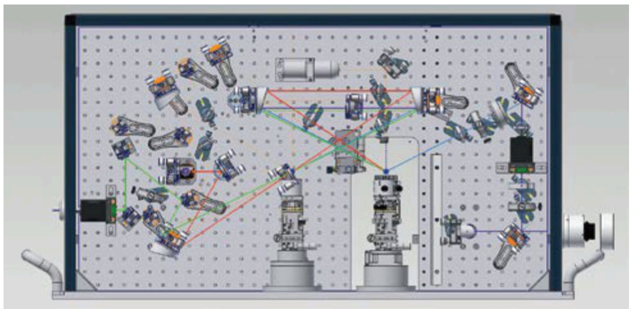
Tunable beam size for IR beam.
Beams are Focused with Lens. ($BaF_2$ lens for IR beam).
“Classic” configuration. IR 2.3-10 µm (up to 16 µm).

Phase sensitive, Top (Reflection- Reflection) configuration



Fixed beams sizes on the sample. VIS and IR beams.
Beams are Focused with Parabolic mirrors.
Interference configuration for Phase measurement.
IR 2.3-10 µm.

Phase sensitive, Transmission-reflection configuration



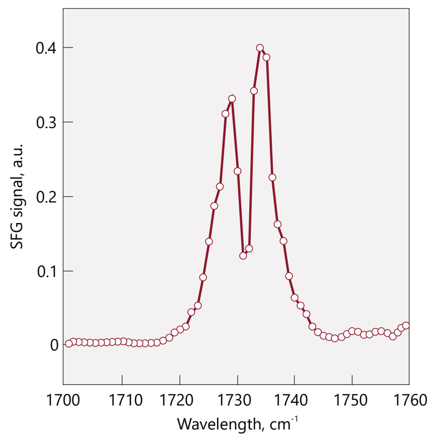
Fixed beams sizes on the sample. VIS and IR beams.
Beams are Focused with Parabolic mirrors.
Interference configuration for Phase measurement.
IR 2.3-3,5 µm .

## NARROWBAND SFG SYSTEM <2 $cm^{-1}$

Spectral resolution in of narrowband SFG is determined by light source – OPA. Monochromator is used only as filter.

**Light source for IR: PG511. Line width of mid-IR < 2 $cm^{-1}$.**

Synchronously pumped optical parametric generator with OPO with long focal length resonator.




SFG spectra of monoolein surface,
1 $cm^{-1}$ scan step, 200 acquisitions per step


EKSPLA
REV. 20230622
Distributed by TOPAG Lasertechnik GmbH
+49 6151 42944 0 | info@topag.de | www.topag.de
TOPAG

# Main Components of the picosecond scanning SFG Spectrometer

## PICOSECOND MODE-LOCKED Nd:YAG LASER


The heart of the spectrometer is solid-state picosecond laser. Its reliability is critical to perfect spectrometer operation and relevance of measured data. Two standard models of high energy lasers are dedicated for SFG spectrometers.

Model PL2230 is fully diode pumped, which means that master oscillator and all following amplification stages are diode pumped. It features great long term parameters stability and minimal maintenance requirements. This model provides up to 40 mJ per pulse output energy, which in most cases is enough for pumping OPG and VIS channel of SFG spectrometer.

Model PL2230 is available for double resonance SFG. This model usually is used for pumping of two independent OPG's. Such configuration is used in double resonance SFG version.

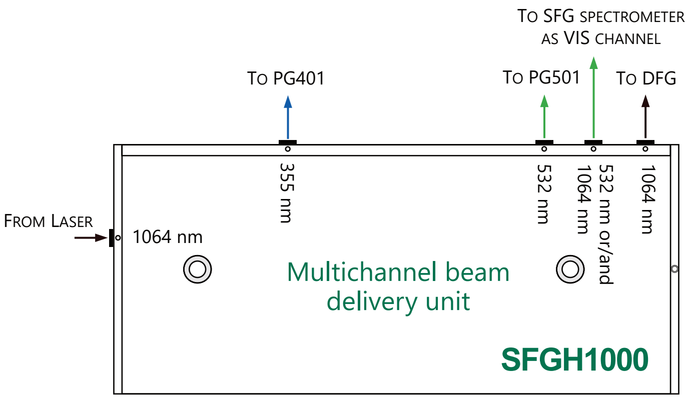
## MULTICHANNEL BEAMS DELIVERY UNIT

Fundamental laser radiation needs to be split into several channels and converted to different wavelenghts. Tunable IR radiation is generated in picosecond optical parametric generator (OPG). Large portion of laser output is converted into second or third harmonics and used for

OPG pumping. Residual beam is spatially filtered, delayed and directed into SFG spectrometer as VIS channel. Usually it is converted into second harmonic (532 nm), but in some cases can be used also at fundamental wavelength (1064 nm) or tunable in visible range, when second OPG is used.

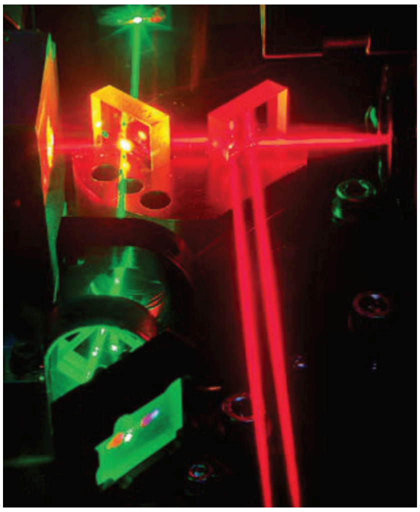
Multichannel beams delivery unit SFGHX00 series provides all these features. Additionally it contains automatized VIS channel input energy monitoring and control.

The VIS channel wavelength (if double wavelenght option is included) is changed manually. Setup also includes all needed separators and filters to block residual radiation and prevent it from reaching a sample.




An example of **Multichannel beams delivery unit** used for Double resonance SFG spectrometer

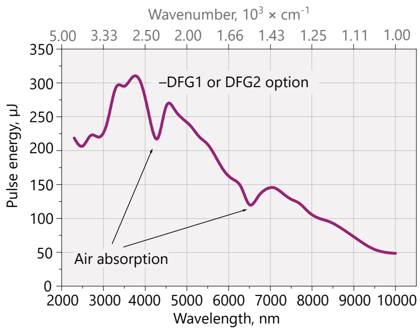
## PICOSECOND OPTICAL PARAMETRIC GENERATOR



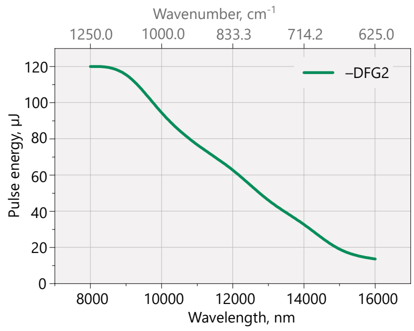
PG501 series picosecond optical parametric generator (OPG) feature high pulse energy and narrow linewidth. It is used for generation of tunable wavelength in broad spectral range. In SFG spectrometer it provides middle infrared radiation for IR channel.

DFG stage extends tuning range to mid IR, which corresponds to molecular vibrational fingerprints. Depending of OPG model, DFG output can cover spectral range 2.3 – 10 μm or 2.3 – 16 μm. All residual wavelengths are carefully filtered preventing residual radiation from reaching a sample. Visible laser pointer is installed inside each unit and aligned in-line with IR beam. It helps to manage invisible mid IR radiation and direct it through multiple optical elements into a sample.

Some SFG-VS studies require better than 6 cm$^{-1}$ spectral resolution. In such cases Ekspla offers unique design PG511 series OPG. In this system seed is generated in synchronously pumped optical parametric oscillator (SPOPO), which is temporally synchronized with laser regenerative amplifier. In this configuration radiation spectral width is narrowed down to 2 cm$^{-1}$ in mid IR range.

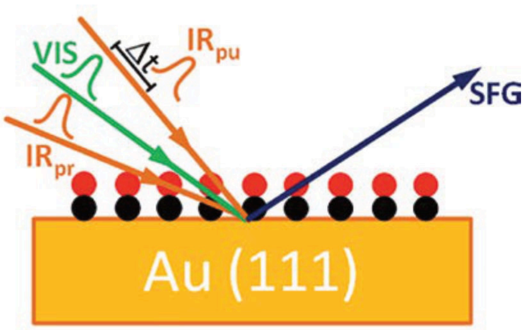



Typical PG501-DFG1 tuning curve in 2300 – 10000 nm range



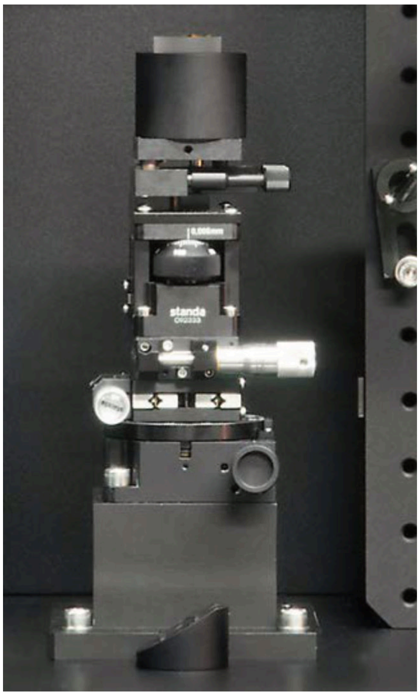

Typical PG501-DFG2 tuning curve in 8000 – 16000 nm range

## APPLICATION EXAMPLE: TWO PG511 FOR SFG PUMP PROBE

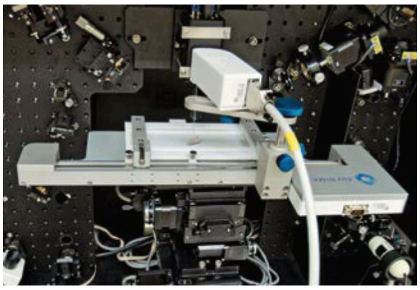



Source: Phys. Rev. Lett. 123, 156101

# SFG Spectrometer Accessories



Compact and stable six axis manipulator for precise sample positioning



SFG spectrometer with Langmuir trough used for studies of the unique properties of molecules in monolayers

Hermetically sealed sample cell with heater, specially designed for SFG spectrometer, allows experiments under controlled environmental conditions

## OPTIONAL ACCESSORIES

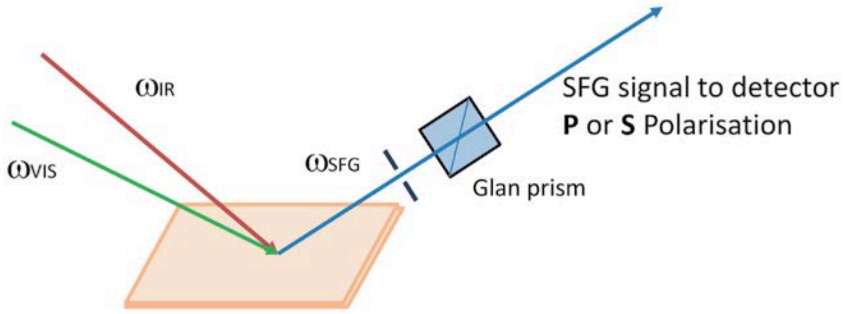
- *Six axis sample holder*
- *Sealed temperature controlled sample chamber*
- *Larger sample area – space for Langmuir trough*
- *Motorisation of polarisation control of VIS and IR beams, polarisation analyser for SFG signal*

# SFG Spectrometer polarisation control options

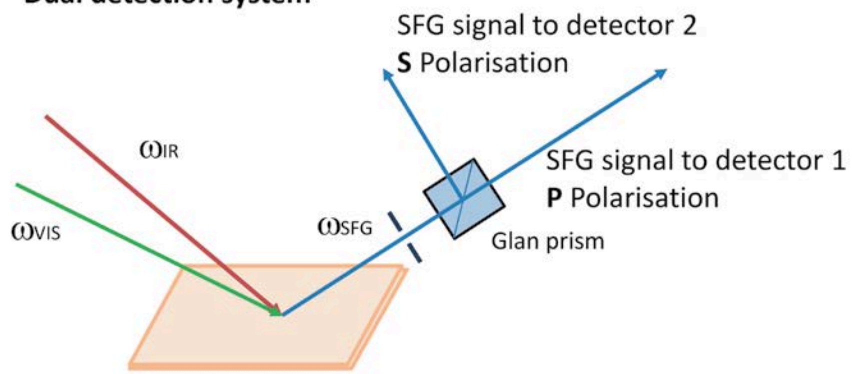
## SIMULTANEOUS MEASUREMENT OF S AND P POLARISATION

S and P polarisation of the SFG signal are detected during the same measurement in the dual polarisation detection system.

**Classic detection system**



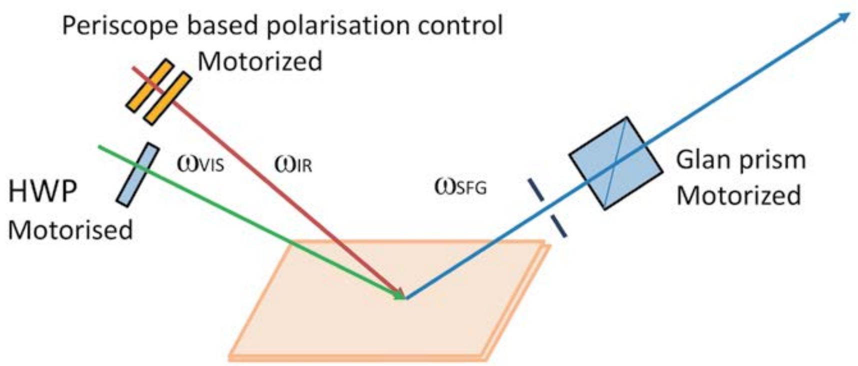

**Dual detection system**




## MOTORIZED POLARISATION CONTROL OF SFG, VIS, IR

The SFG spectrometer has a motorized polarisation switch for the IR, VIS, and the generated SFG light beams. The automatic change of polarisation and energy attenuation makes it possible to perform measurements without opening the spectrometer.

- Motorized switching of IR – standard
- Motorized control in small steps of SFG, VIS – optionally



# Technical specifications [1)] of picosecond scanning SFG spectrometer

<table>
<tr><th>Version</th><th>SFG Classic</th><th>SFG Advanced</th><th>SFG Double resonance</th><th>SFG Phase sensitive</th></tr>
<tr><td colspan="5">SYSTEM (GENERAL)</td></tr>
<tr><td>Spectral range</td><td>1000 – 4300 $cm^{-1}$</td><td>625 – 4300 $cm^{-1}$</td><td>1000 – 4300 $cm^{-1}$</td><td>1000 – 4300 $cm^{-1}$</td></tr>
<tr><td>Spectral resolution</td><td><6 $cm^{-1}$<br>(optional <2 $cm^{-1}$)</td><td><6 $cm^{-1}$<br>(optional <2 $cm^{-1}$)</td><td><10 $cm^{-1}$</td><td><6 $cm^{-1}$<br>(optional <2 $cm^{-1}$)</td></tr>
<tr><td>Spectra acquisition method</td><td colspan="4">Scanning</td></tr>
<tr><td>Sample illumination geometry</td><td colspan="4">Top side, reflection (optional: bottom side, top-bottom side )</td></tr>
<tr><td>Incidence beams geometry</td><td colspan="4">Co-propagating, non-colinear</td></tr>
<tr><td>Incidence angles</td><td colspan="3">Fixed, VIS ~60°, IR ~55° (optional: tunable)</td><td>Fixed, VIS ~60°, IR ~55°</td></tr>
<tr><td>VIS beam wavelength</td><td>532 nm<br>(optional: 1064 nm)</td><td>532 nm<br>(optional: 1064 nm)</td><td>532 nm and<br>tunable 420 – 680 nm</td><td>532 nm</td></tr>
<tr><td>Polarization (VIS, IR, SFG)</td><td colspan="4">Linear, selectable "s" or "p", purity > 1:100</td></tr>
<tr><td>IR Beam spot on the sample</td><td colspan="3">Selectable, ~150 – 600 µm</td><td>Fixed</td></tr>
<tr><td>Sensitivity</td><td colspan="3">Air-water spectra</td><td>Solid sample</td></tr>
<tr><td colspan="5">PUMP LASERS [2)]</td></tr>
<tr><td>Model</td><td>PL2231-50</td><td>PL2231-50</td><td>PL2231A</td><td>PL2231-50</td></tr>
<tr><td>Pulse energy</td><td colspan="4">Optimised to pump PG</td></tr>
<tr><td>Pulse duration</td><td colspan="4">29 ± 5 ps</td></tr>
<tr><td>Pulse repetition rate</td><td colspan="4">50 Hz</td></tr>
<tr><td colspan="5">OPTICAL PARAMETRIC GENERATORS</td></tr>
<tr><td>IR source with standard linewidth (<6 $cm^{-1}$)</td><td>PG501-DFG1</td><td>PG501-DFG2</td><td colspan="2">PG501-DFG1</td></tr>
<tr><td>IR source with narrow linewidth (<2 $cm^{-1}$)</td><td>PG511-DFG</td><td>PG511-DFG2</td><td>inquire</td><td>PG511-DFG</td></tr>
<tr><td>UV-VIS source for Double resonance SFG</td><td colspan="2">–</td><td>PG401</td><td>–</td></tr>
</table>

*For standard specifications please check the brochure of particular model.*

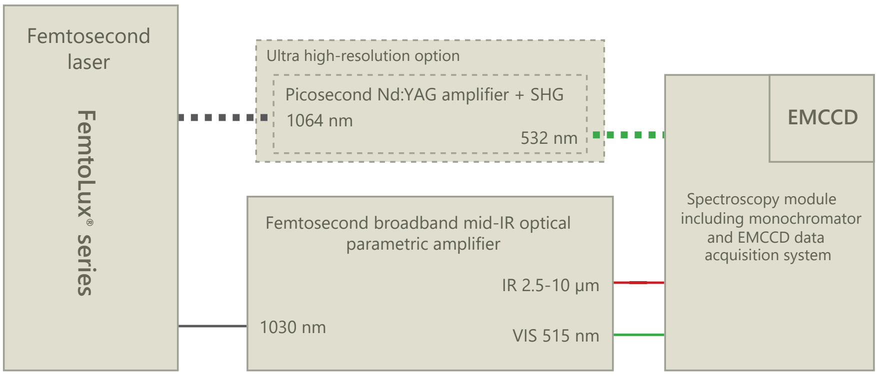
<table>
<tr><th colspan="5">PHYSICAL DIMENSIONS (FOOTPRINT)</th></tr>
<tr><td>Standard</td><td colspan="2">2700 × 1200 mm</td><td>3000 × 1500 mm</td><td>2700 × 1200 mm</td></tr>
<tr><td>Extended (with special options or large ccessories)</td><td colspan="2">2800 × 1200 mm</td><td>3000 × 1500 mm</td><td>2700 × 1200 mm</td></tr>
</table>

1) Due to continuous improvement, all specifications are subject to change without advance notice.
2) Laser is optimised for pumping parametrical generator, maximum output energy may be different than specified for stand alone application.

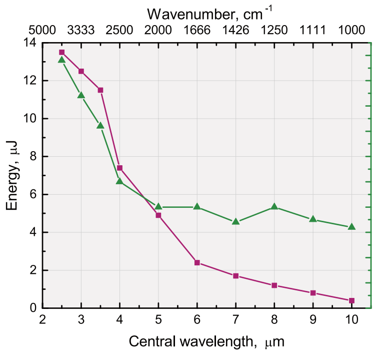
# Features and design of the broadband femtosecond SFG spectrometer

Femtosecond broadband SFG (BB SFG) spectrometer allows fast SFG spectra acquisition since most vibrational modes can be resolved without scanning. The advantage of the broadband SFG system is that intense femtosecond pulses allow efficient sum frequency generation at low pulse energies thus reducing the possibility of sample modification. It is especially important for aqueous and biological samples.

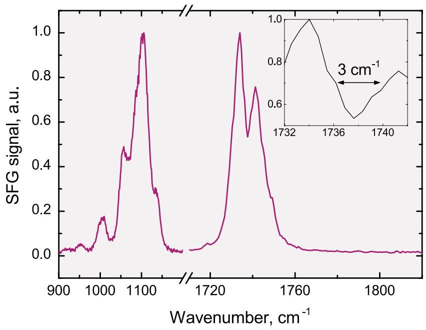
The system is based on a femtosecond industrial FemtoLux® series laser with 500 fs pulse duration, more than 1 mJ pulse energy at 1030 nm and a 1 kHz repetition rate. The main part of the laser radiation is directed to a broadband mid-IR OPA module. Broad bandwidth ( (150 – 450) $cm^{-1}$) mid-IR radiation can be continuously tuned in a spectral range from 2.5 up to 10 µm, providing from 0.5 to 12 µJ energy transform-limited pulses for the IR channel. The VIS channel realisation depends on the system configuration. In standard setup, a part of laser output radiation is frequency doubled (515 nm) ~20 µJ and then spectrally filtered to produce <8 $cm^{-1}$ bandwidth pulses. High resolution version consists of optically synchronised femtosecond and picosecond lasers. The combination of broadband mid-IR and narrowband VIS radiation allows to get the broadband sum frequency signal with exceptionally high spectral resolution close to 3 $cm^{-1}$.




Schematic layout of BB SFG spectrometer




Mid-IR parametrical amplifier characteristics. Energy and spectral bandwidth versus central wavelength




Monoolein SFG spectra demonstrated spectral bandwidth of 3 $cm^{-1}$



Distributed by TOPAG Lasertechnik GmbH
+49 6151 42944 0 | info@topag.de | www.topag.de