

SFG Spectrometers

Sum Frequency Generation
Vibrational Spectroscopy

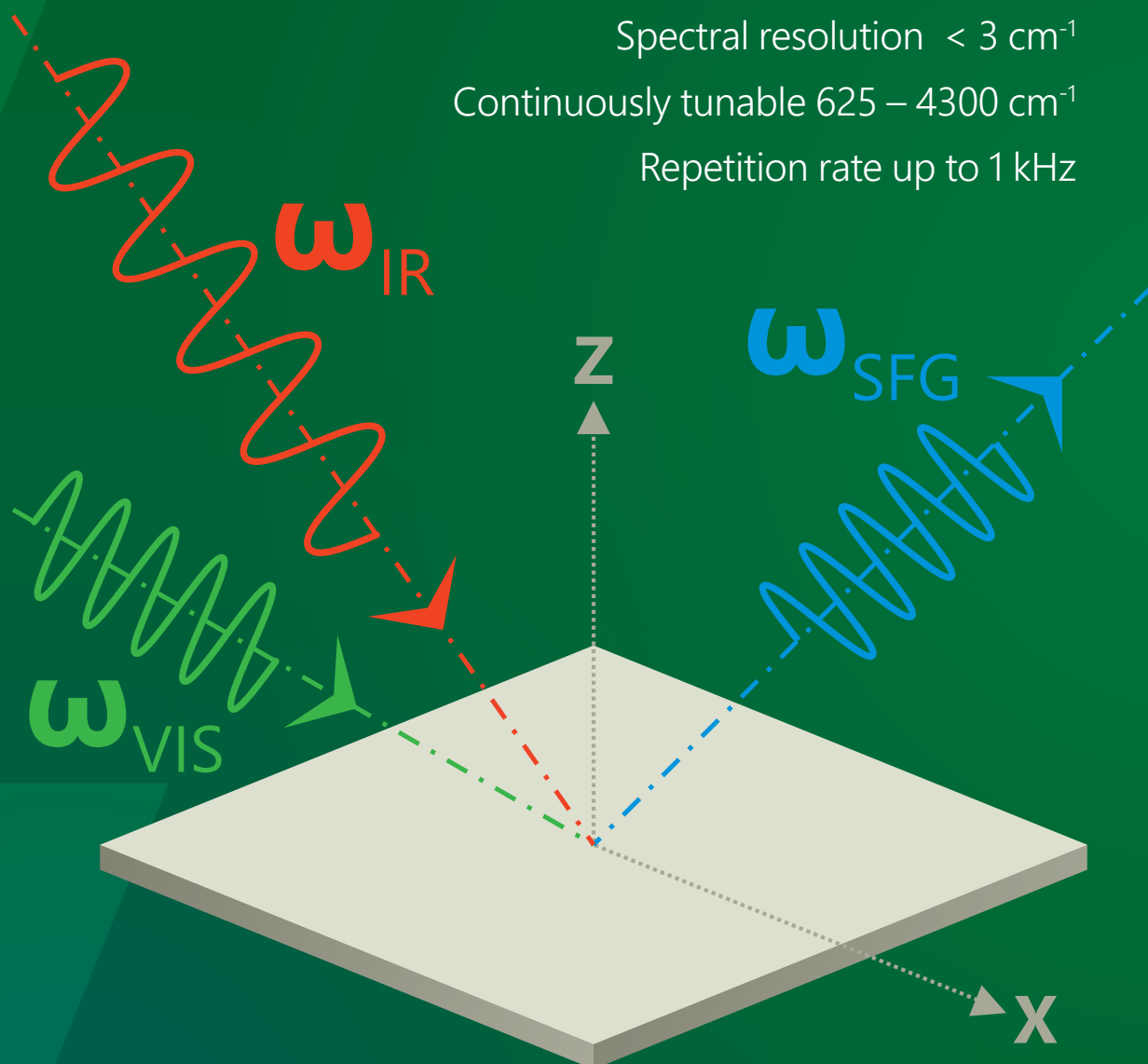
Picosecond scanning _____

Femtosecond broadband _____

Spectral resolution $< 3 \text{ cm}^{-1}$

Continuously tunable $625 - 4300 \text{ cm}^{-1}$

Repetition rate up to 1 kHz



Sum Frequency Generation Vibrational Spectroscopy

Sum Frequency Generation Vibrational Spectroscopy (SFG-VS) is a powerful and versatile method for in-situ investigation of surfaces and interfaces. In SFG-VS experiment a pulsed tunable infrared IR (ω_{IR}) laser beam is mixed with a visible VIS (ω_{VIS}) beam to produce an output at the sum frequency ($\omega_{SFG} = \omega_{IR} + \omega_{VIS}$). SFG is a 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.

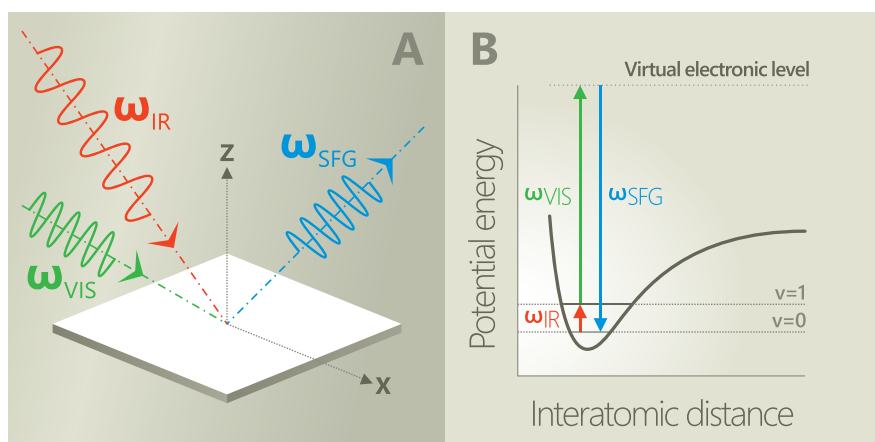
Vibrational sum frequency generation (SFG) spectroscopy holds several important advantages over traditional spectroscopy methods for the molecular level analysis of interfaces, including (i) surface sensitivity, (ii) vibrational specificity, and (iii) the possibility to extract detailed information on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

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

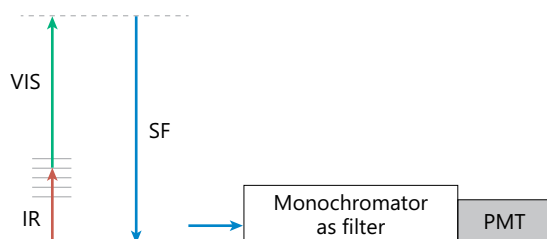
APPLICATIONS

- ▶ 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



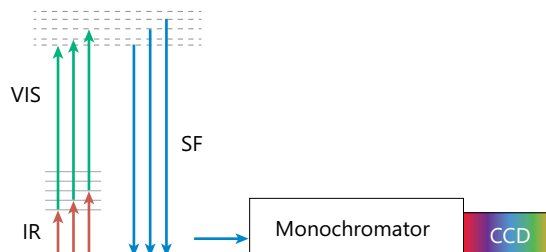
SFG signal generation diagram (a) and the molecular energy level diagram for the SFG process (b)

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.

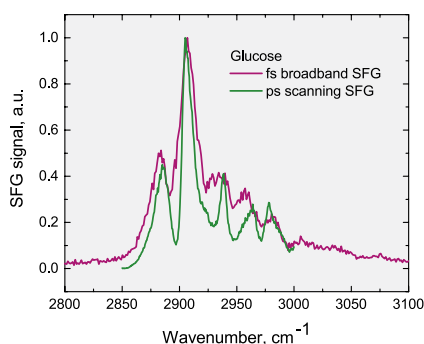


Broadband femtosecond SFG spectrometer

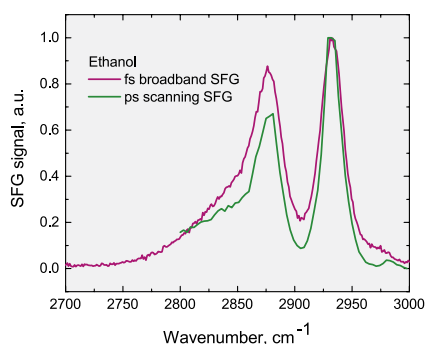
A broadband mid-IR pulse is mixed with a narrowband VIS pulse. The result is broadband SFG spectrum which is recorded using a monochromator and a sensitive CCD camera. The full spectrum is acquired simultaneously by integrating signal over time. Spectral resolution is determined by the bandwidth of the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

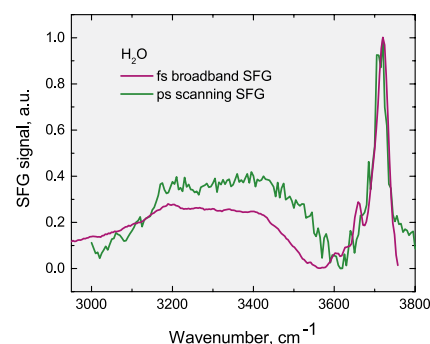
Narrowband picosecond scanning spectrometer	Broadband femtosecond high resolution spectrometer
Narrowband mid-IR excitation, only one band is excited. Coupled states can be separated.	Simultaneous excitation and recording of broad vibration spectrum with high resolution.
High mid-IR pulse energy. Less influence of IR absorption 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.



SFG spectra of glucose



SFG spectra of ethanol



SFG spectra of water

Spectra are different because of different water samples. Water spectrum strongly depends on purity of the water.

Features and design of the picosecond scanning SFG spectrometer

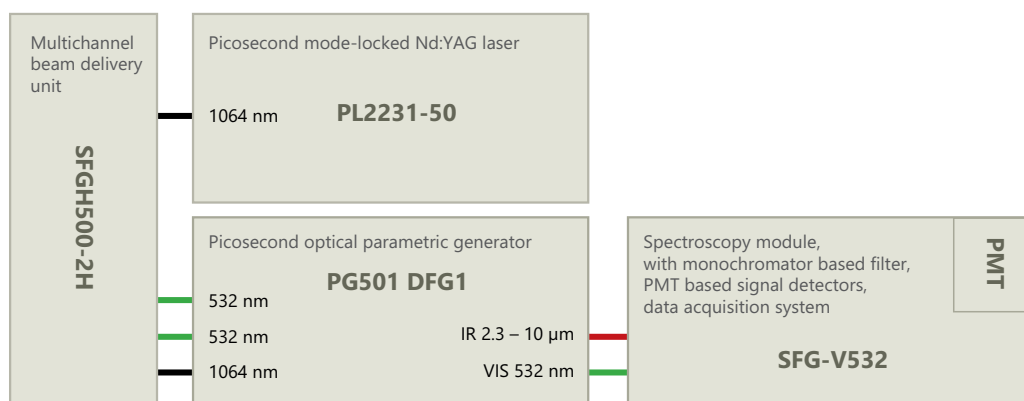
The SFG spectrometer developed by Ekspla engineers is a nonlinear spectrometry instrument, convenient for everyday use. Ekspla manufactures SFG spectrometers, which are used by chemists, biologists, material scientists, and physicists. The spectrometer has many features that help to set up measurements 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 (optionally 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, optionally for the VIS, and optionally 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

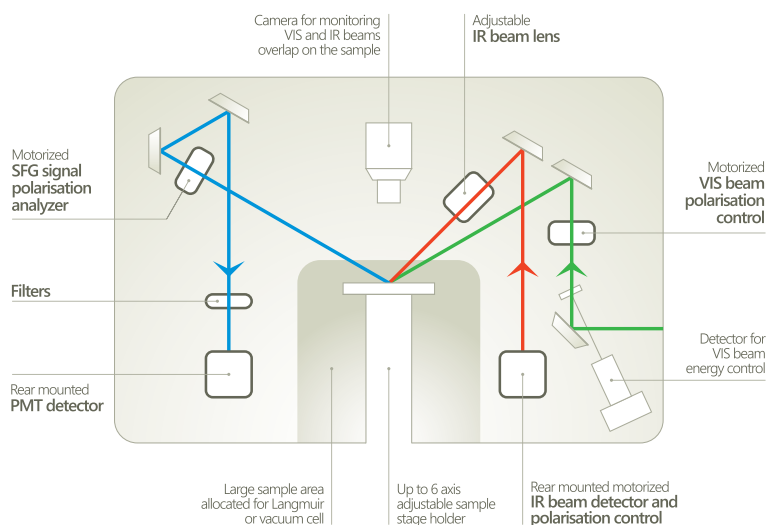
- ▶ Picosecond mode-locked Nd:YAG laser
- ▶ Multichannel beam delivery unit
- ▶ Picosecond optical parametric generator
- ▶ Spectroscopy module
- ▶ Monochromator
- ▶ PMT based signal detectors
- ▶ Data acquisition system
- ▶ Dedicated LabView® software package for system control



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.

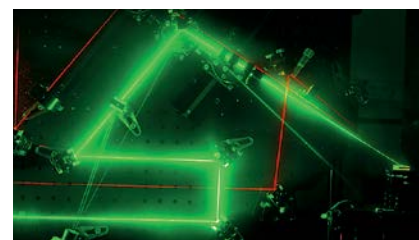


Standard layout of the vertically-arranged sample compartment of the SFG spectrometer

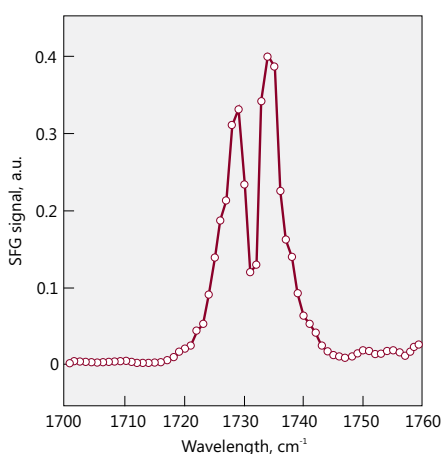
SAFETY OF THE SFG SPECTROMETER

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.

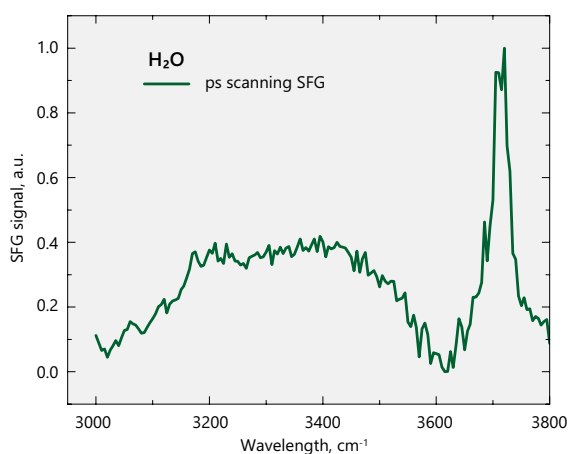
The automatic change of polarisation and energy attenuation makes it possible to perform measurements without opening the spectrometer. Laser safety precautions are required only for the alignment of the laser beams on the studied surface.



SPECTRA EXAMPLES



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



Water-air interface spectra, 200 acquisitions per step

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.

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

PHASE-SENSITIVE SFG SPECTROMETER

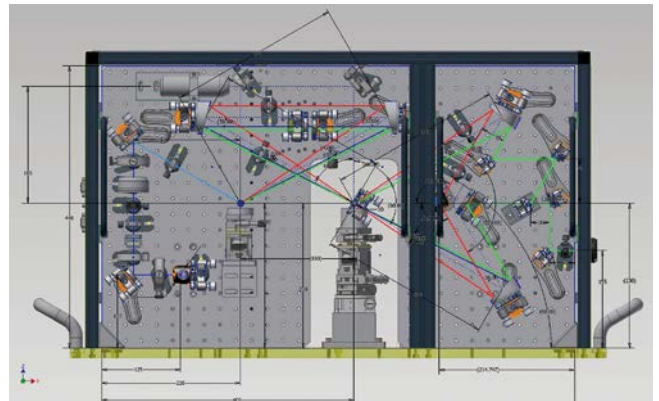
Phase sensitive measurements with spectral resolution up to 6 cm^{-1} (2 cm^{-1}).

In conventional SFG-VS intensity of SF signal is measured. It is proportional to the square of second order nonlinear susceptibility $I_{\text{SF}} \sim |\chi^{(2)}|^2$. 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

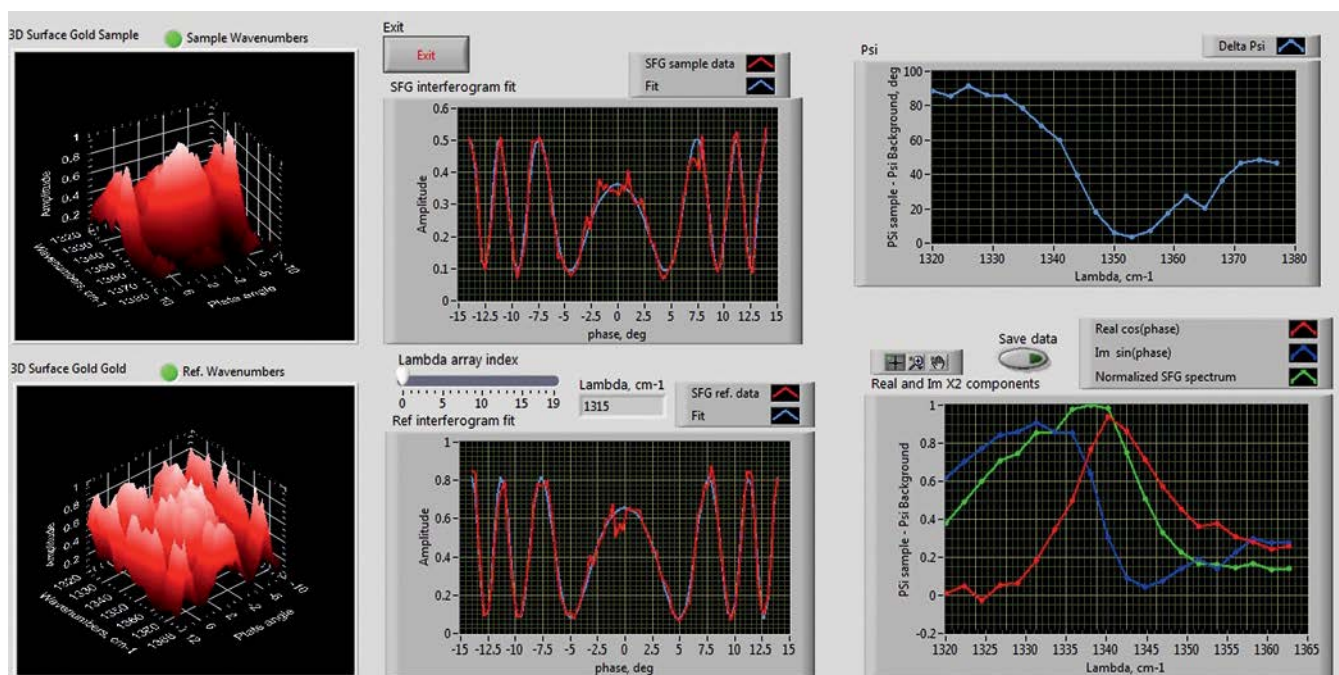
optical wave requires an interference scheme. Mixing the wave of interest with a reference wave of known phase generates an interference pattern, from which the phase of the wave can be deduced.

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 interfererogram 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.



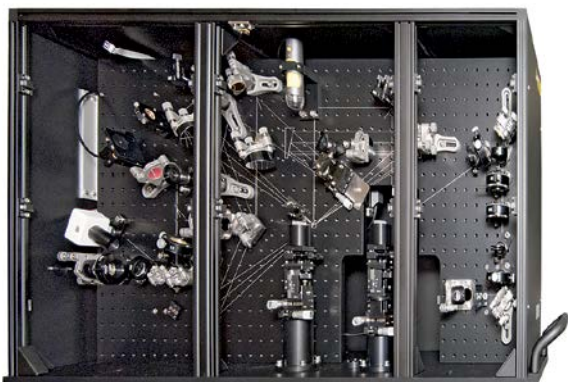
Spectroscopy module of Phase-sensitive SFG spectrometer: internal view (left) and 3D drawing (right)



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 sensitive / "Classic" ("Advanced") ; Top/ Bottom configuration.

Switch: VIS beam manual. IR mirrors motorised, BaF₂ lens manual.

Path length to the sample is same in all configuration
Motorised polarisation control.

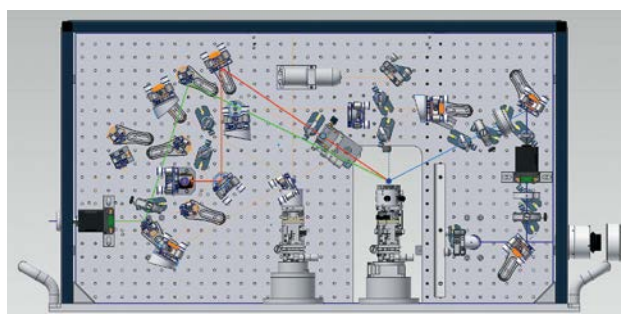
VIS beam 532 nm. IR 2,3- up to 10 (16) μm .

OPTIONS

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

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

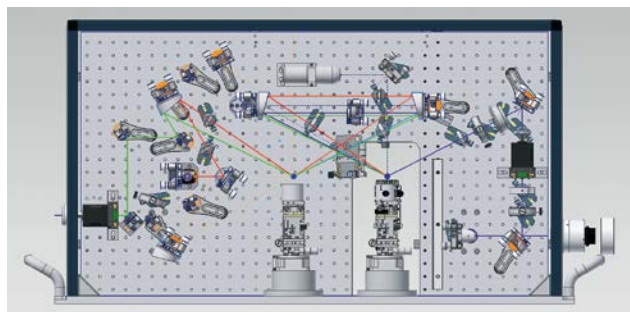
("Classic") configuration



Tunable beam size for IR beam.

Beams are Focused with Lens. (BaF₂ lens for IR beam).
"Classic" configuration. IR 2.3-10 μm (up to 16 μm).

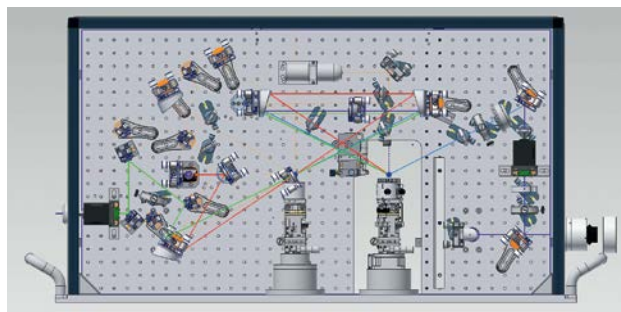
Phase sensitive, Top (Reflection- Reflection) configuration



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.

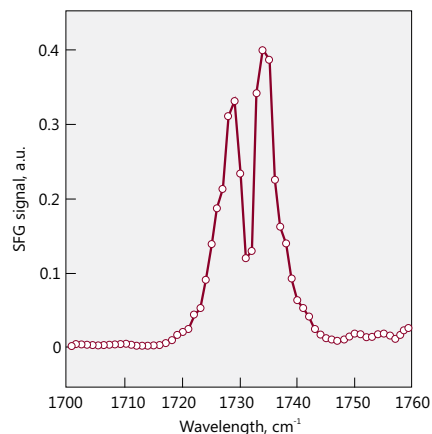
Interference configuration for Phase measurement.
IR 2.3-3,5 μm .

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

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 $< 2 \text{ cm}^{-1}$.

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

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

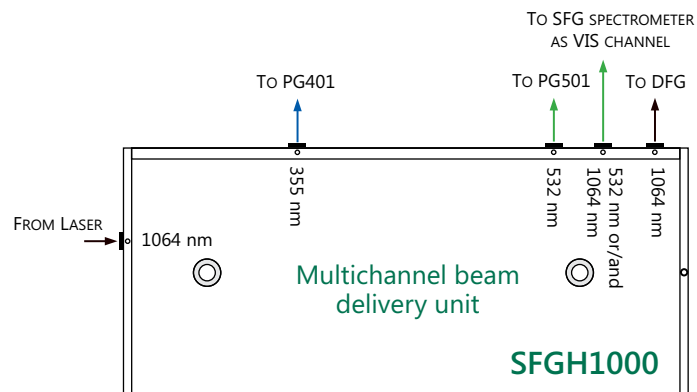
Fundamental laser radiation needs to be split into several channels and converted to different wavelengths. Tunable IR radiation is generated in picosecond optical parametric generator (OPG). Large portion of laser output is converted into second or third harmonics and used for

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.

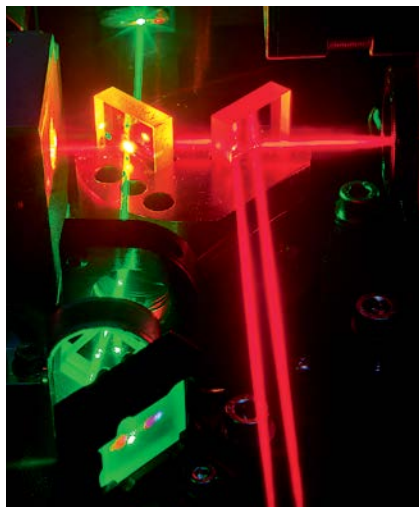
Multichannel beams delivery unit SFGHX00 series provides all these features. Additionally it contains automatized VIS channel input energy monitoring and control.

The VIS channel wavelength (if double wavelength 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

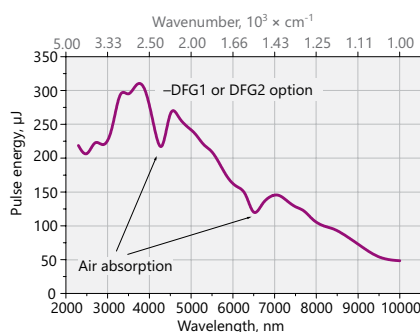


PG501 series picosecond optical parametric generator (OPG) feature high pulse energy and narrow linewidth. It is used for generation of tunable wavelength in broad spectral range. In SFG spectrometer it provides middle infrared radiation for IR channel.

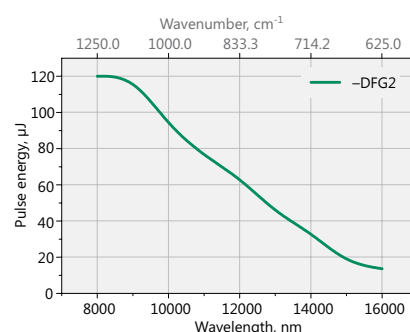
DFG stage extends tuning range to mid IR, which corresponds to molecular vibrational fingerprints. Depending of OPG model, DFG output can cover spectral range 2.3–10 μm or 2.3–16 μm . All residual wavelengths are carefully filtered preventing residual radiation from reaching a

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.

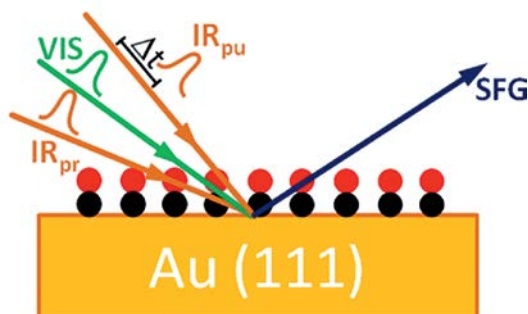


Typical PG501-DFG1 tuning curve in 2300–10000 nm range



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

APPLICATION EXAMPLE: TWO PG511 FOR SFG PUMP PROBE

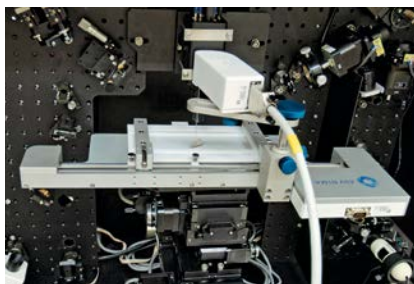


Source: Phys. Rev. Lett. 123, 156101

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

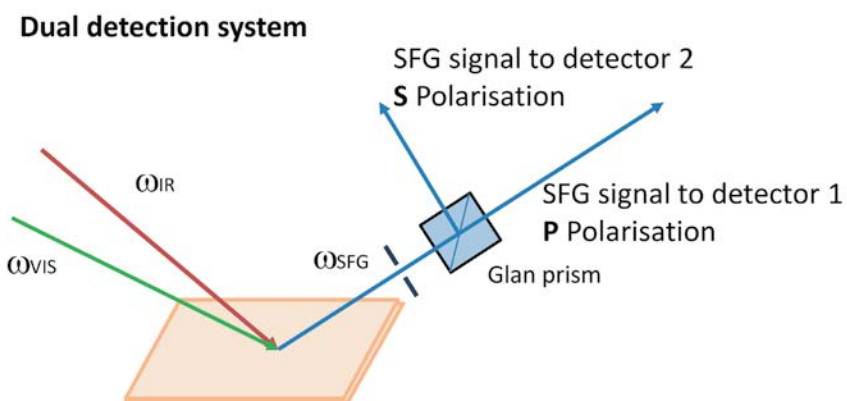
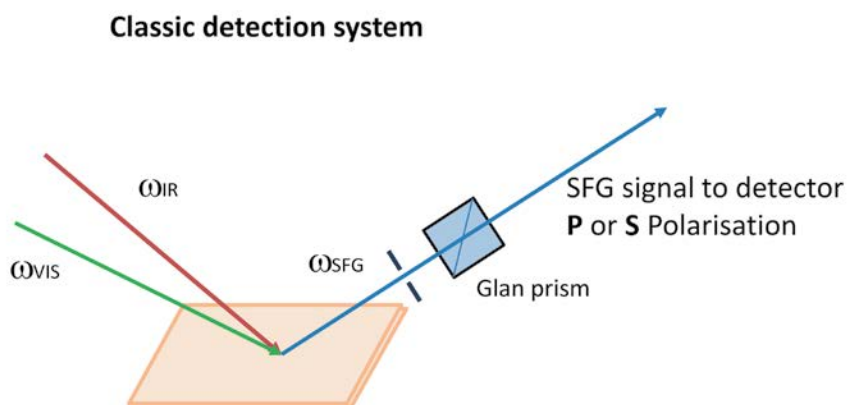
OPTIONAL ACCESSORIES

- ▶ 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

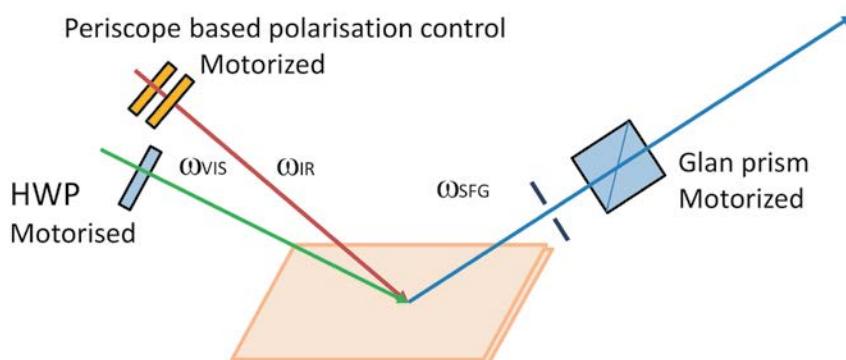
S and P polarisation of the SFG signal are detected during the same measurement in the dual polarisation detection system.



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 specifications¹⁾ of picosecond scanning SFG spectrometer

Version	SFG Classic	SFG Advanced	SFG Double resonance	SFG Phase sensitive
SYSTEM (GENERAL)				
Spectral range	1000 – 4300 cm ⁻¹	625 – 4300 cm ⁻¹	1000 – 4300 cm ⁻¹	1000 – 4300 cm ⁻¹
Spectral resolution	<6 cm ⁻¹ (optional <2 cm ⁻¹)	<6 cm ⁻¹ (optional <2 cm ⁻¹)	<10 cm ⁻¹	<6 cm ⁻¹ (optional <2 cm ⁻¹)
Spectra acquisition method	Scanning			
Sample illumination geometry	Top side, reflection (optional: bottom side, top-bottom side)			
Incidence beams geometry	Co-propagating, non-colinear			
Incidence angles	Fixed, VIS ~60°, IR ~55° (optional: tunable)			Fixed, VIS ~60°, IR ~55°
VIS beam wavelength	532 nm (optional: 1064 nm)	532 nm (optional: 1064 nm)	532 nm and tunable 420 – 680 nm	532 nm
Polarization (VIS, IR, SFG)	Linear, selectable “s” or “p”, purity > 1:100			
IR Beam spot on the sample	Selectable, ~150 – 600 μm			Fixed
Sensitivity	Air-water spectra			Solid sample
PUMP LASERS ²⁾				
Model	PL2231-50	PL2231-50	PL2231A	PL2231-50
Pulse energy	Optimised to pump PG			
Pulse duration	29 ± 5 ps			
Pulse repetition rate	50 Hz			
OPTICAL PARAMETRIC GENERATORS				
IR source with standard linewidth (<6 cm ⁻¹)	PG501-DFG1	PG501-DFG2	PG501-DFG1	
IR source with narrow linewidth (<2 cm ⁻¹)	PG511-DFG	PG511-DFG2	inquire	PG511-DFG
UV-VIS source for Double resonance SFG	–		PG401	–
For standard specifications please check the brochure of particular model.				
PHYSICAL DIMENSIONS (FOOTPRINT)				
Standard	2700 × 1200 mm		3000 × 1500 mm	2700 × 1200 mm
Extended (with special options or large ccessories)	2800 × 1200 mm		3000 × 1500 mm	2700 × 1200 mm

¹⁾ Due to continuous improvement, all specifications are subject to change without advance notice.

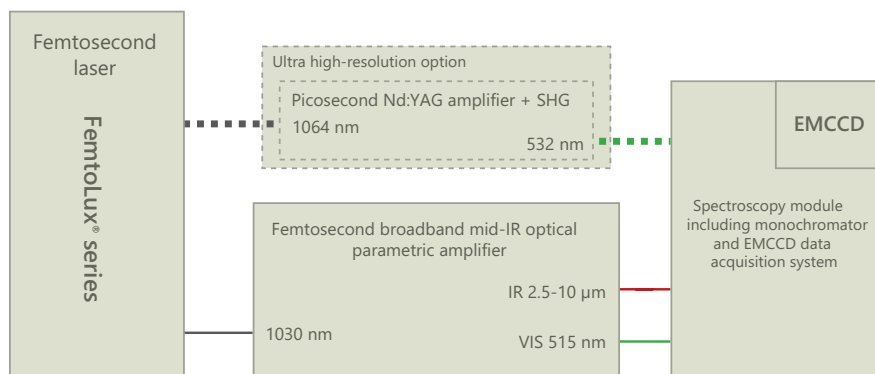
²⁾ Laser is optimised for pumping parametrical generator, maximum output energy may be different than specified for stand alone application.

Features and design of the broadband femtosecond SFG spectrometer

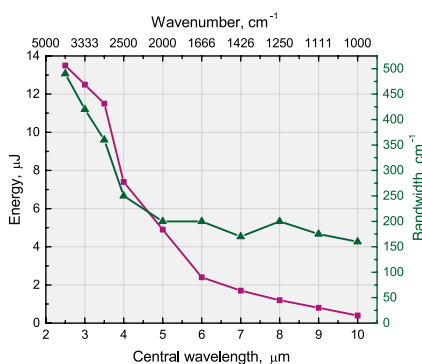
Femtosecond broadband SFG (BB SFG) spectrometer allows fast SFG spectra acquisition since most vibrational modes can be resolved without scanning. The advantage of the broadband SFG system is that intense femtosecond pulses allow efficient sum frequency generation at low pulse energies thus reducing 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

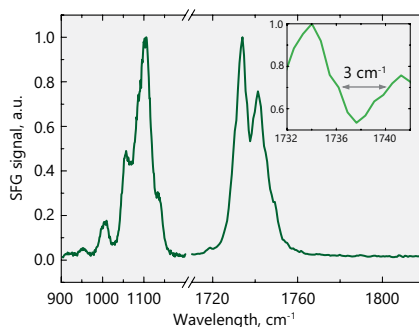
depends on the system configuration. In standard setup, a part of laser output radiation is frequency doubled (515 nm) $\sim 20 \mu\text{J}$ and then spectrally filtered to produce $< 8 \text{ cm}^{-1}$ bandwidth pulses. High resolution version consists of optically synchronised femtosecond and picosecond 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} .



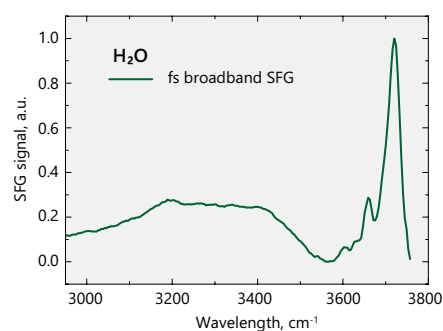
Schematic layout of BB SFG spectrometer



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



Spectral resolution of 3 cm^{-1} demonstrated by measuring monoolein SFG spectrum



Pure water spectrum.
Spectrum acquisition time 10 min

Technical specifications¹⁾ of broadband femtosecond SFG spectrometer

Version	SFG fs	SFG fs high resolution
SYSTEM (general)		
Spectral range	1000 – 4300 cm ⁻¹	1000 – 4300 cm ⁻¹
Spectral resolution	< 8 cm ⁻¹	< 3 cm ⁻¹
Spectral bandwidth	150 – 450 cm ⁻¹	
Spectra acquisition method	Broadband accumulative	
Sample illumination geometry	Top side, reflection (optional: bottom side, top-bottom side, total internal reflection)	
Incidence beams geometry	Co-propagating, non-colinear (optional: colinear)	
Incidence angles	Fixed, VIS ~60°, IR ~55° (optional: tunable)	
VIS beam wavelength	515 nm	532 nm
Polarization (VIS, IR, SFG)	Linear, selectable “s” or “p”, purity > 1:100	
Beam spot on the sample	Adjustable, ~150 – 600 μm	
Sensitivity	Air-water spectra	
PHYSICAL DIMENSIONS (footprint)		
Standard	2000 × 1500 mm	2200 × 1500 mm

¹⁾ Due to continuous improvement, all specifications are subject to change without advance notice.

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