

SFG vibrational spectroscopy for the investigation of interfaces

Sum frequency generation to understand the architecture of biomolecules and monolayers in perovskite solar cells

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Fig. 1 SFG spectrometer: classic and microscopy setup in one unit. Customized setup (Source: Ekspla)

Vibrational sum frequency generation (SFG) spectroscopy offers detailed molecular level information on the structure, ordering, and orientation of molecular groups, and the function of monolayers at various interfaces, including buried ones, without noticeable contribution from the bulk phases.

Vibrational spectroscopy provides detailed information about the structure, function, and interactions of molecules through the analysis of the vibrations of atoms. Traditional infrared and Raman spectroscopies are extensively used for the analysis of bulk materials but also for the study of molecules at interfaces by exploring surface-enhanced Raman spectroscopy (SERS) or reflection-absorption infrared spectroscopy (RAIRS) approaches. Subsequently discovered 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 [1–3].

This nonlinear spectroscopic technique is heavily dependent on the quality of the pulsed laser beams used to generate the SFG signal. In classical

picosecond SFG systems, one beam of higher frequency is fixed in frequency (called the ω_{VIS} beam), while the second beam is tunable in the mid-infrared spectral region (called the ω_{IR} beam). The tunability range is very important and determines the vibrational frequency region of the SFG spectrometer. Fig. 2 shows the SFG signal generation scheme. Both incoming ω_{VIS} and ω_{IR} beams must overlap at the studied interface to generate the emitted SFG beam, ω_{SFG} . The intensity of the SFG signal increases as ω_{IR} reaches the vibra-

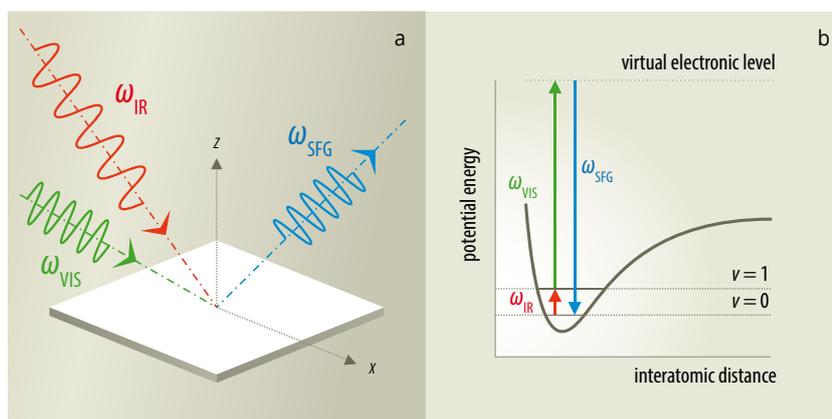


Fig. 2 SFG signal generation diagram (a) and the molecular energy level diagram for the SFG process (b).

tional transition in the molecule. Being a second order nonlinear optical spectroscopy, it obeys a strict selection rule: only a medium without inversion symmetry can generate SFG signal. In many cases, bulk compounds (for example water) retain inversion symmetry and consequently no contribution from this bulk phase is expected to be observed. However, SFG is by definition allowed at the interface where the inversion symmetry is broken. This interfacial specificity, combined with sub-monolayer sensitivity, has positioned SFG as an unrivaled tool for the in situ examination of liquid surfaces and various interfaces, including buried ones without the otherwise overwhelming bulk contributions. This is one of the most sensitive and selective ways to study the orientation of molecules in the surface layer.

Features of the SFG spectrometer

The SFG spectrometer developed by Ekspla scientists and engineers is a nonlinear spectrometry instrument, convenient for everyday use (Fig. 1). This spectrometer is not complicated, even for scientists who are not familiar with lasers. 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 polarization 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 – 250 μJ . Infrared light can be tuned in a very broad spectral range from 2.3 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 scan-

ning, polarization control and VIS beam attenuation are controlled from a computer. The spectrometer has a motorized polarization switch for the IR, VIS, and 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.

Sample compartment

A large sample compartment (Fig. 3) 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.

Safety of the SFG spectrometer

The spectrometer is safe to use: all high energy pulsed beams are enclosed (Fig. 1). 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

Companies

EKSPLA

The laser manufacturer from Vilnius, Lithuania, designs and manufactures advanced lasers and systems. Its main competence is the ability to effectively tailor products for specific applications and requirements. Many top universities and science institutions use Ekspla lasers. The main products are pulsed femtosecond, picosecond, nanosecond lasers and tunable wavelength systems for scientific and industrial application, spectroscopy systems, and high-intensity laser systems.

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TOPAG Lasertechnik

Incorporated in 1993 and located in Darmstadt, Germany, Topag supplies lasers, laser optics and optical metrology. Its main focus is the distribution and service of pulsed solid-state lasers for scientific and industrial applications. Further products include opto-mechanics, spectrometers, infrared viewers, crystals and ultrashort pulse spectroscopy. Topag Lasertechnik develops and manufactures innovative diffractive laser beam shaping optics.

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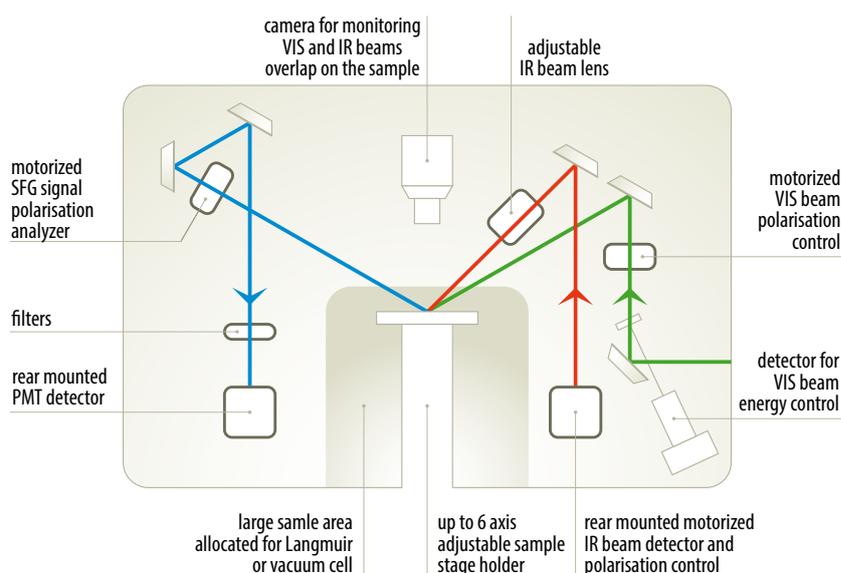


Fig. 3 Layout of the vertically-arranged sample compartment of the SFG spectrometer (Source: Ekspla)

penetrate outside. The automatic change of polarization 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.

Several modifications available
SFG spectrometer with extended vibrational frequency range (SFG Advanced). The main modification of the spectrometer enables a spectral range of $1,000$ to $4,300\text{ cm}^{-1}$. 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 anal-

ysis of many inorganic compounds, the vibrations of ions and biomolecules.

SFG spectrometer with additional phase sensitive measurements option.

A phase sensitive spectrometer allows the measurement of the phase of . 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.

Double resonance SFG spectrometer.

This modification enables to use a VIS beam from 420 up to 680 nm . It is helpful if the sample can absorb at 532 nm .

Structure determination of biomolecules at interfaces

Important biocatalytical reactions and biochemical processes take place at interfaces. To understand and control these processes, detailed molecular level information on the organization and structure of proteins, peptides, and lipids at the interface is required. Traditional spectroscopy methods lack the necessary molecular specificity (fluorescence and electronic spectroscopy) or required interfacial sensitivity (Raman and infrared spectroscopy). Amongst the experimental methods that are appropriate for interface studies of biomolecules, vibrational sum frequency generation spectroscopy seems particularly promising because of its combined molecular specificity and intrinsic surface sensitivity properties [1, 4]. For biomolecular studies, it is extremely important to access the vibrational frequency region from $1,000$ to $1,800\text{ cm}^{-1}$ where the particular amide group modes (Amide-I, Amide-II, and Amide-III) as well as the vibrations of side chains of amino acids take place. **Fig. 4** demonstrates pD-dependent SFG spectra of hen egg-white lysozyme oligomers adsorbed to a DOPG/ D_2O interface taken with SSP polarization combination in the frequency region of $1,560 - 1,800\text{ cm}^{-1}$ [5]. Vibrational resonances from the Amide-I group of adsorbed peptides and C=O stretching resonance from the DOPG monolayer are clearly resolved. Analysis of the Amide-I spectral region indicates the presence of adsorbed proteins in two different secondary structures at the interface: an unordered secondary structure associated with the $1,645\text{ cm}^{-1}$ band and a predominant β -sheet secondary structure as indicated by the resonance at $1,675\text{ cm}^{-1}$. Alteration in the solution pD induces dramatic changes in the Amide-I spectral region; the intensity of both resonances increases at higher pD values. The spectral changes were related with reorientation of an amide group dipole at the DOPG/ D_2O interface. The presented SFG study has revealed the importance of hydrophobic and electrostatic interactions for the adsorption of lysozyme aggregates to lipid/water and air/water interfaces. The aggregation of peptides and proteins and the adsorption behavior of such structures at interfaces is an important issue in the elucidation of pathogenesis of neurodegenerative illnesses such as Alzheimer's and Parkin-

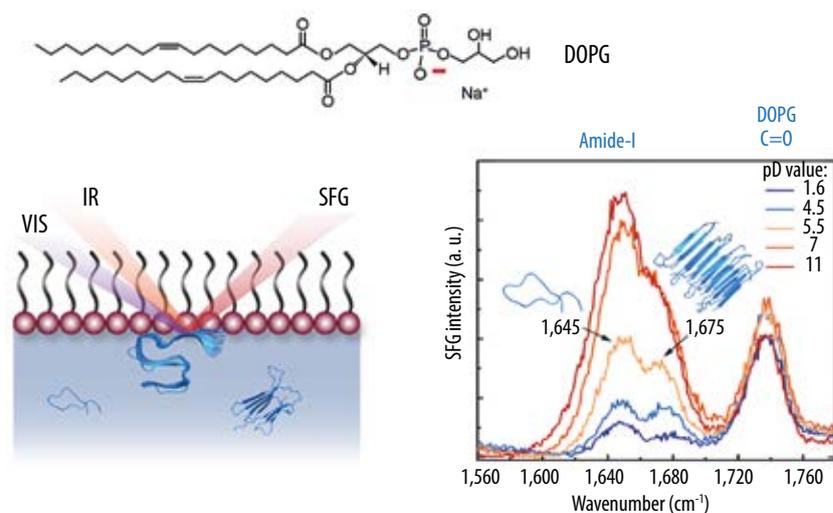


Fig. 4 The molecular structure of a lipid 1,2-dioleoyl-sn-glycerol-3-phospho-rac sodium salt (DOPG), which was used for monolayer formation (upper image). Schematic illustration of the SFG experiment (left image). The SFG spectra (right image) of hen egg-white lysozyme oligomers adsorbed to a DOPG/ D_2O interface taken with SSP (S-SFG, S-532 nm, and P-IR) polarization combination at different pD values (adapted from [5]).

son's disease [6]. SFG spectroscopy is able to provide detailed molecular level information of the interfacial aggregation of biomolecules and the adsorption of aggregated peptides and proteins at biological interfaces [1, 5].

Monolayers for perovskite solar cells

The current development of photovoltaic and optoelectronic science and technology is closely related with synthesis as well as understanding the structure and function of promising new materials based on halide perovskites. These are hybrid organic/inorganic structures containing several active layers. A recent study highlights the importance of interfaces for the performance of the photovoltaic devices [7]. These interfaces are very complex, and in many cases are buried and difficult to access by spectroscopic methods because of the contribution from the bulk phases to the signal [3]. Being surface sensitive and molecule specific, SFG spectroscopy is able to provide the required molecular level knowledge on the structure of these interfaces [3, 8]. Fig. 5 demonstrates what kind of unique information can be extracted from SFG measurements of monolayers formed on ITO substrates serving as hole transporting monolayers for highly efficient perovskite solar cells [8]. It was found that the function of devices depends on the composition of mixed monolayers deposited from

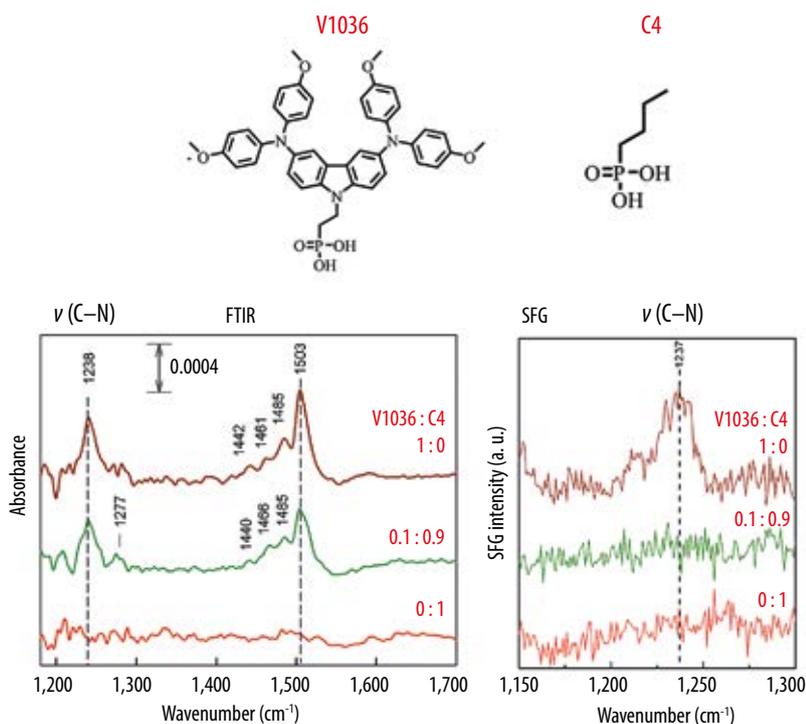


Fig. 5 The molecular formulas of compounds V1036 and C4 used to form the monolayers on the ITO surface (upper image). The FTIR absorbance spectra of monolayers on an ITO substrate prepared from a 1×10^{-3} M mixed solution of V1036:C4 (a). The SFG spectra collected from monolayers on ITO substrates prepared from a 1×10^{-3} M mixed solution of V1036:C4 in the spectral region of $1,150 - 1,300 \text{ cm}^{-1}$ (b). Spectra were taken with an SSP polarization combination (adapted from [8]).

the solution containing a different ratio of V1036:C4 compounds on an ITO substrate. FTIR spectra indicate only a slight decrease in intensity of the C–N stretching band, $\nu(\text{C–N})$, of compound V1036 near $1,238 \text{ cm}^{-1}$ comparing monolayers prepared from a solution containing only the V1036 compound and mixed solution V1036:C4

(0.1:0.9). Thus, adsorption of the larger molecular mass compound V1036 at the ITO surface through the phosphonic acid moiety is preferable compared with the C4 compound. In contrast, the SFG spectrum shows intense resonance due to $\nu(\text{C–N})$ vibration only for a monolayer prepared from the solution containing solely the V1036

compound; the SFG signal completely disappears in the case of a monolayer prepared from the solution containing a mixture of compounds V1036 and C4. This is related with specific selection rules for SFG spectroscopy. The intensity of SFG resonances depends not only on the number of molecules at the interface but also on the alignment of dipoles. An intense signal is expected for oriented dipoles at the interface, the intensity decreases for more disordered structures and no signal is expected to be observed for a completely disordered monolayer at the interface. So the presented SFG spectra reveal disordering of the V1036 molecules in the monolayer prepared from mixed V1036:C4 (0.1:0.9) solution. Such disordering correlates with the function of constructed perovskite-based solar cells; higher solar cell device efficiency was observed in the case of disordered monolayers. Unique information on the ordering of molecules in the monolayer was obtained by SFG spectroscopy – such information cannot be acquired by using other spectroscopic methods.

Conclusions

A modern picosecond SFG spectrometer developed by Ekspla offers the reliable vibrational spectroscopy analysis of biomolecules at interfaces as well as monolayers at buried interfaces of perovskite solar cell elements, polymers, and other molecular structures. An additional vibrational frequency region extension, phase-sensitive detection option and the possibility to conduct microscopy measurements are also available if required by users.

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