

# ***frequency generation spectroscopy***

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# ***Sum frequency generation spectroscopy***

- Sum frequency generation spectroscopy (SFG) is a technique used to analyze surfaces and interfaces.
- SFG was first observed and described in the 1960s.
- It was developed into a surface specific vibrational spectroscopy in 1987 by the groups of Shen and Harris.
- This nonlinear laser spectroscopy method was developed and rapidly applied to deduce the composition, orientation distributions, and some structural information of molecules at gas–solid, gas–liquid and liquid–solid interfaces.
- SFG has advantages in its ability to be monolayer surface sensitive, ability to be performed in situ (for example aqueous surfaces and in gases), and not causing much damage to the sample surface.
- SFG is comparable to second harmonic generation (SFG is a more general form) and Infrared and Raman spectroscopy.

# Sum-frequency generation

➤ **Sum-frequency generation (SFG)** is a [non-linear optical](#) process. This phenomenon is based on the annihilation of two input photons at [angular frequencies](#) and while, simultaneously, one photon at frequency is generated. As with any phenomenon in [nonlinear optics](#), this can only occur under conditions where:

- The light is interacting with matter;
- The light has a very high intensity (typically from a [pulsed laser](#)).

➤ Sum-frequency generation is a "parametric process", meaning that the photons satisfy energy conservation, leaving the matter unchanged:

$$\hbar\omega_3 = \hbar\omega_1 + \hbar\omega_2$$

➤ A special case of sum-frequency generation is [second-harmonic generation](#), in which  $\omega_1 = \omega_2 = 1/2\omega_3$ . In fact, in experimental physics, this is the most common type of sum-frequency generation. This is because in second-harmonic generation, only one input light beam is required, but if  $\omega_1 \neq \omega_2$ , 2 simultaneous beams are required, which can be more difficult to arrange. In practice, the term "sum-frequency generation" usually refers to the less common case where  $\omega_1 \neq \omega_2$ .

➤ For sum-frequency generation to occur efficiently, a condition called [phase-matching](#) must be satisfied

$$\hbar k_3 = \hbar k_1 + \hbar k_2$$

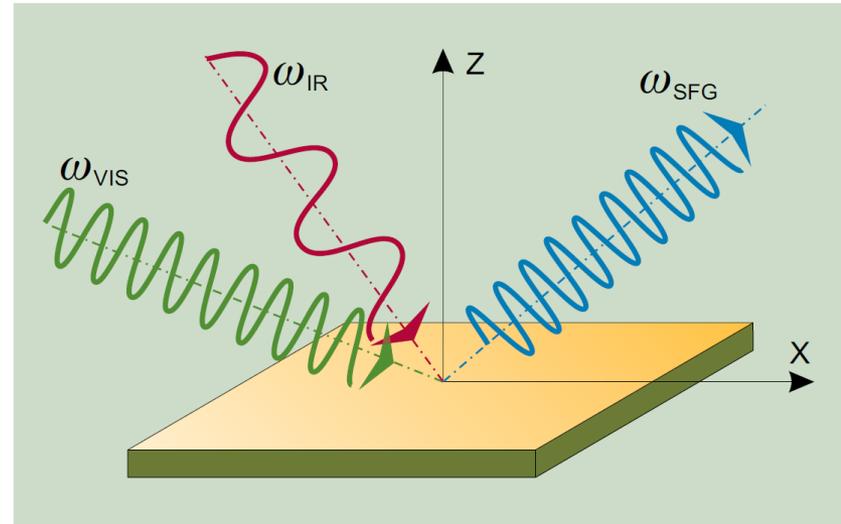
$k$  - **angular wavenumber**

➤ As this condition is satisfied more and more accurately, the sum-frequency generation becomes more and more efficient. Also, as sum-frequency generation occurs over a longer and longer length, the phase-matching must become more and more accurate

# Basic operation principles

➤ In SFG 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 ( $\omega_{SFG} = \omega_{IR} + \omega_{VIS}$ ).

➤ **Second harmonic generation** (also called **frequency doubling** or abbreviated **SHG**) is a nonlinear optical process, in which photons interacting with a nonlinear material are effectively "combined" to form new photons with twice the energy, and therefore twice the frequency and half the wavelength of the initial photons.

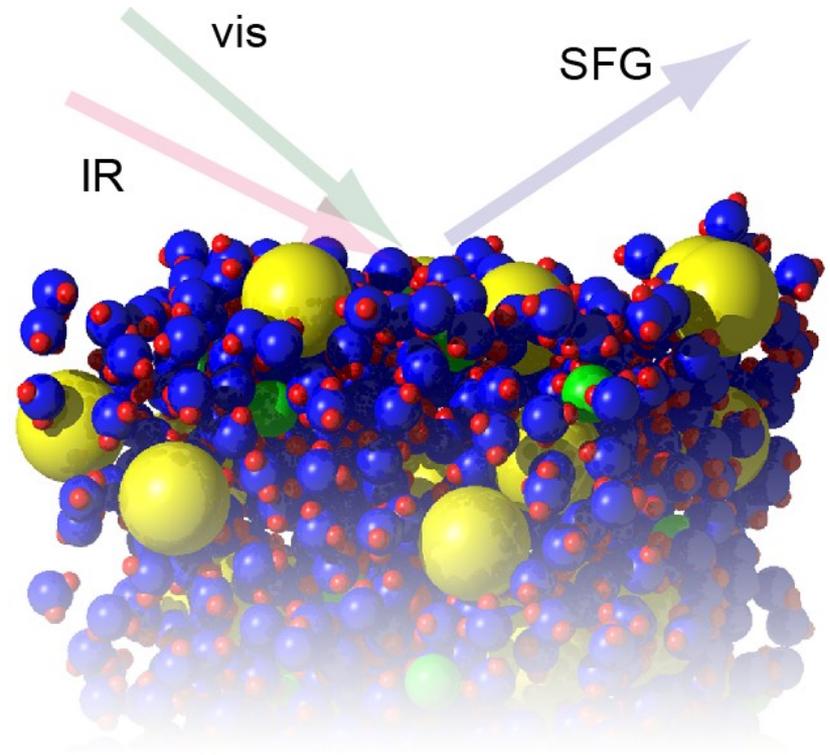


➤ SFG is second-order nonlinear process, which is allowed only in media without inversion symmetry. At surfaces or interfaces inversion symmetry is necessarily broken, that makes SFG highly surface specific.

➤ As the IR wavelength is scanned, active vibrational modes of molecules at the interface give a resonant contribution to SFG signal. The resonant enhancement provides spectral information on surface characteristic vibrational transitions.

Different combinations of input and output beam polarizations allow the determination of surface symmetry or molecular orientation.

- SFG detects vibrational modes, which are rather localized to specific groups of atoms within the molecules. Information about relative orientation of different groups within the same molecule maybe obtained, and, hence, the molecular structure can be deduced.
- Referring to the SFG signal phase measurements, information about the absolute orientation of molecule in respect to the surface can be obtained.



## ***Theory***

IR-visible sum frequency generation spectroscopy uses two laser beams that overlap at a surface of a material or the interface between two materials. An output beam is generated at a frequency of the sum of the two input beams. The two input beams have to be able to access the surface, and the output beam needs to be able to leave the surface to be picked up by a detector. One of the beams is a visible wavelength laser held at a constant frequency and the other is a tunable infrared laser. By tuning the IR laser, the system can scan over resonances and obtain the vibrational spectrum of the interfacial region.

➤ As a nonlinear optical process, the polarization which generates the output depends on the electric fields of the two input beams.

$$P = \epsilon_0 (\chi(1) : E + \chi(2) : EE + \chi(3) : EEE + \dots)$$

➤ As a second-order nonlinear process, SFG is dependent on the 2nd order susceptibility  $\chi$ . The fact that the 2nd order susceptibility, a third rank tensor, becomes zero in centrosymmetric media, limits what samples are accessible for SFG. Centrosymmetric media include the bulk of gases, liquids, and most solids under the assumption of the electric-dipole approximation, which neglects the signal generated by multipoles and magnetic moments. At an interface between two different materials or two centrosymmetric media, the inversion symmetry is broken and an SFG signal can be generated. This suggests that the resulting spectra represent a thin layer of molecules. A signal is found when there is a net polar orientation

## ***SFG intensity***

➤ The output beam is collected by a detector and its intensity is measured. The intensity of the beam is given by

$$I(\omega) \propto [\chi(2)]^2 I_1(\omega_1) I_2(\omega_2)$$

➤ The second order susceptibility has two contributions

$$\chi = \chi_r + \chi_{nr}$$

where  $\chi_{nr}$  is the non-resonating contribution and  $\chi_r$  is the resonating contribution.

Here, intensity is directly proportional to the susceptibility squared and the product of the intensities of the incoming beams. The IR frequency is given as  $\omega_2$  and the visible frequency is given as  $\omega_1$ .

The non-resonating contribution is assumed to be from electronic responses. Although this contribution has often been considered to be constant over the spectrum, because it is generated simultaneously with the resonant response, the two responses must compete for intensity. This competition shapes the nonresonant contribution in the presence of resonant features by resonant attenuation. Because it is not currently known how to adequately correct for nonresonant interferences, it is very important to experimentally isolate the resonant contributions from any nonresonant interference, often done using the technique of nonresonant suppression

The resonating contribution is from the vibrational modes and shows changes in resonance. It can be expressed as a sum of a series of Lorentz oscillators

$$\sum \frac{A_q}{\omega^2 - \omega_q^2 + i\Gamma_q \omega}$$

where A is the strength or amplitude,  $\omega$  is the frequency or energy,  $\Gamma$  is the damping or linewidth coefficient, and each q is a resonance mode. The amplitude is a product of  $\mu$ , the induced dipole moment, and  $\alpha$ , the polarizability. Together, this indicates that the transition must be both IR and Raman active.

The above equations can be combined to form

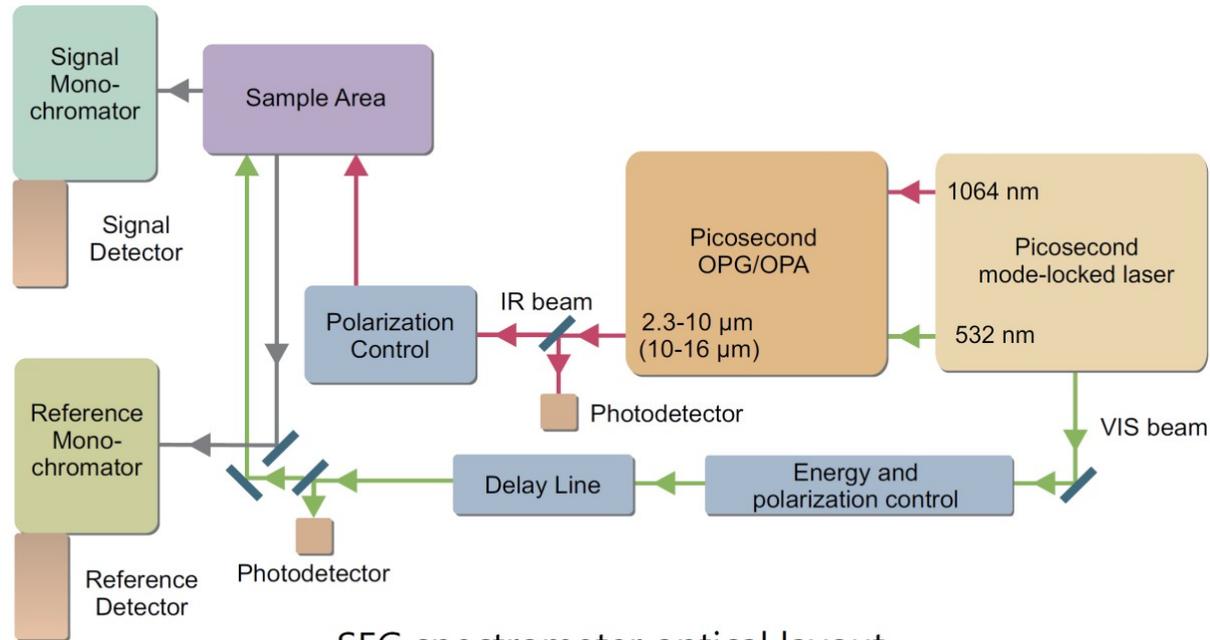
$$\chi = \chi_{nr} e^{i\phi} + \sum \frac{A_q}{\omega^2 - \omega_q^2 + i\Gamma_q \omega}$$

## ***Orientation information***

- From the second order susceptibility, it is possible to ascertain information about the orientation of molecules at the surface.  $\chi(2)$  describes how the molecules at the interface respond to the input beam. A change in the net orientation of the polar molecules results in a change of sign of  $\chi(2)$

# Design of the spectrometer

- Sum frequency excitation system is based on picosecond pump laser and optical parametric generator/amplifier/difference frequency generator (OPG/OPA/DFG).



SFG spectrometer optical layout

- Solid state mode-locked Nd:YAG laser featuring high pulse duration and energy stability is used to pump the system. Second harmonic (532 nm) of laser fundamental radiation is used as VIS pump beam for sum frequency generation.
- Tunable IR radiation is generated in three stage optical parametric generator / amplifier / difference frequency generator. Spectral and spatial filtration of OPG seed beam provides narrow bandwidth and low divergency of mid-IR radiation. Beam walk-off compensation design ensures overlapping pump beams over the full wavelength range

- VIS beam delivery optics includes: spatial filter for homogenous beam profile, energy and polarization control system for smooth adjustment of pulse energy and polarization direction, delay line for temporal overlap of VIS and IR pulses.
- IR beam delivery optics include mirror based polarization control and beam delivery systems.
- The energy of both the VIS and IR beams is monitored by photodetectors for SFG signal normalization.
- Optional 6 axis (three translational and three rotational) including PC controlled X ,Y and  $\theta$  axes stage enables sample mapping and investigation of molecules orientation.
- SF guiding optics includes steering mirrors, focusing lens, polarization analyser and holographic notch filter for scattered VIS light rejection.
- Detection system consists of monochromator and gated PMT based SF signal detector.
- Low power laser diode guiding beam is integrated for alignment convenience.
- Optional reference channel improves the signal/noise ratio for samples with high non-resonant background.

# ***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