

Spectrometer for broadband vibrational sum-frequency generation at fluid interfaces



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Application Note

1. Principles of sum-frequency spectroscopy

Broadband vibrational sum-frequency generation (SFG) is a second-order optical process that involves frequency mixing of three photons. Specifically, a broadband infrared (IR) and a narrowband visible (VIS) beams are overlapped in time and space at the interface, where they generate a third beam with the sum-frequency ($\omega_{SF} = \omega_{IR} + \omega_{VIS}$) of the two impinging beams. The electric field of the induced sum-frequency (SF) polarization $P^{(2)}(\omega_{SF})$ is proportional to the effective second-order polarization of the interface: $P^{(2)}(\omega_{SF}) \propto \chi_{eff}^{(2)} E_{IR} E_{VIS}$. At interfaces of materials with inversion symmetry, the SF signal arises from both purely surface and contributions which are caused by the static electric field E_{DC} in the electric double layer and can originate from adsorbed molecules that carry a net charge (surfactants¹, proteins², polyelectrolytes³ etc.), while other signals from the bulk solution can be neglected due to symmetry reasons. The effective second-order electric susceptibility $\chi_{eff}^{(2)}$ of a charged interface can be expressed by:¹

$$\chi_{eff}^{(2)} = \chi_S^{(2)} + \chi_{S,EDL}^{(2)} \quad (1)$$

Here, the $\chi_{S,EDL}^{(2)}$ term accounts for the probing depth and the phase mismatch Δkz of the fundamental and SF waves at charged interfaces ($E_{DC} \neq 0$) that reflects possible interference effects at low ionic strengths.¹ The pure surface $\chi_S^{(2)}$ contribution can be written as a coherent overlap of vibrational bands that can contribute to the SFG spectrum. Here, we want to restrict the discussion only to homogeneously broadened bands with Lorentzian line shapes:

$$\chi_S^{(2)} = \chi_{NR}^{(2)} + \sum_k \frac{A_k}{\omega_k - \omega_{IR} + i\Gamma_k} \quad (2)$$

The oscillator strength $A_k = N \int f(\Omega) \beta_k(\Omega) d\Omega$, which represented by the amplitude of a vibrational mode k , depends on the number density N of interface-adsorbed molecules, their orientational distribution $f(\Omega)$ and on their hyperpolarizability β_k . $\chi_{NR}^{(2)}$ is a non-resonant contribution to the second-order electric susceptibility.

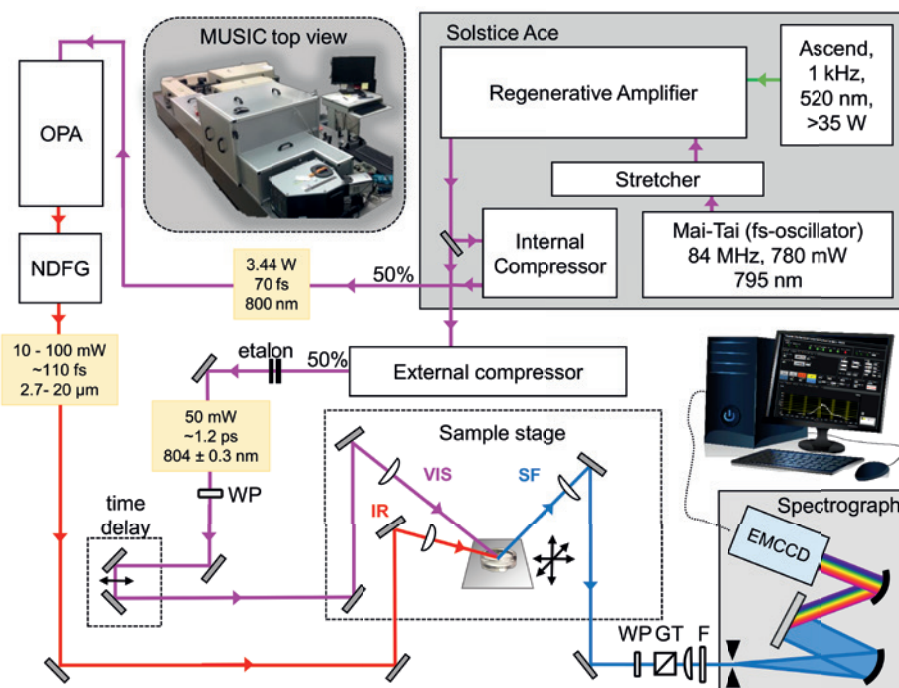


Figure 1 Schematic overview of MUSIC - Münster Ultra-fast Spectrometer for Interfacial Chemistry. Inset: Photograph of MUSIC showing a top view with the Andor Newton EMCCD detector and Kymera spectrograph in the front. Boxes are used to reduce stray light and to purge the IR beam path with dry air. Key: IR: broadband infrared pulse, VIS: narrowband visible pulse, SF: sum-frequency pulse generated, WP: retarders, GT: Glan-Taylor polarizer, F: short-pass filter, EMCCD: electron multiplying charge-coupled device.¹

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2. Description of broadband sum-frequency generation spectrometer

The Münster Ultra-fast Spectrometer for Interfacial Chemistry (MUSIC) is a user-friendly broadband sum-frequency spectrometer. MUSIC is composed of a 1 kHz Ti:Sapphire chirped pulse amplifier which is seeded by a Ti:Sapphire fs-oscillator. The amplifier delivers approximately 7 W (1 kHz, at 796 nm) average power. The uncompressed beam is divided by an internal (50:50) beam splitter. One beam is subsequently guided into an internal and the second beam to an external compressor. A total power of 3.2 W of the amplified and compressed fs beam (796 nm, 18 nm bandwidth) pumps an optical parametric amplifier with a subsequently unit for non-collinear difference frequency generation (NDFG) of the OPAs' idler and signal photons. The NDFG unit generates broadband femtosecond IR pulses which are tuneable from 2.5 to 20 μm . The broadband IR has $>300\text{ cm}^{-1}$ full width at half-maximum bandwidth. An air-spaced etalon (FSR 12.4 nm at 735 nm, $R=94.5\%$) was inserted into the external compressor to generate the VIS narrowband pulse centered at 804.1 nm and with a bandwidth of $\sim 4\text{ cm}^{-1}$ bandwidth. Etalon side bands are removed by beam blocks, which are also placed inside the external compressor.

For the generation of the SFG, the VIS and the IR pulses overlap in time and space at 55° and 60° incident angles, respectively. For SFG spectroscopy, the SF beam is guided into a spectrograph (Kymera-328i-D2-SIL, Andor) where it gets spectrally dispersed using either a 1200 l/mm or a 1800 l/mm grating and imaged onto an electron multiplying charge-coupled device (EMCCD) (Newton DU970P-BVF, Andor). Prior to the spectrograph, a short pass filter with cut-off at 763 nm was used to filter unwanted photons.

For the liquid-gas interfaces, all spectra (Figure 2) were recorded using s-polarized SF, s-polarized visible and p-polarized IR beams, that is in the ssp polarization configuration. The polarization optics used are a half-wave plate for the VIS and a combination of an achromatic half-wave plate with a Glan polarizing prism of calcite. The Glan polarizing prisms matches the polarization of the spectrograph-grating being then sensitivity-independent of the selected SFG polarization during the experiment.

3. Vibrational SFG spectra of air-water interfaces

In Figure 2, we show normalized SFG spectra of surfactant modified air-water interfaces that were obtained with the previously described spectrometer. For that the frequency of the tunable broadband IR beam was changed in 4 steps and SFG spectra were acquired, saved and stitched together afterwards. For that we have used a LabVIEW software that controlled both the OPA and with that the IR wavelength as well as the Andor spectrograph and EMCCD.

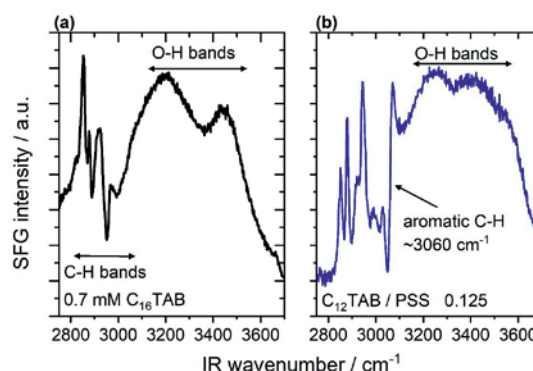


Figure 2 Vibrational SFG spectra of surfactant modified air-water interfaces from aqueous solutions with (a) 0.7 mM cetyltrimethyl ammonium bromide (C_{16}TAB) and (b) dodecyltrimethylammonium bromide (C_{12}TAB) mixtures with sodium polystyrene sulfonate (PSS) at a molar mixing ratio of 0.125 with respect to the monomer concentration of PSS:

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