Sum frequency generation for studying plasma-wall interactions

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Abstract. Interaction of a plasma with a surface results in chemical and physical restructuring of the surface as well as the plasma in the vicinity of the surface. Studying such a reorganization of the atoms and molecules in the surface layer requires optical tools that can penetrate the plasma environment. At the same time, surface specificity is required. Sum Frequency Generation (SFG) is an optical method that fulfills these requirements. SFG has been developed into a surface specific probe during the eighties and nineties. Nowadays SFG is routinely applied in the research of complex interfaces. In such experiments, liquid/gas, solid/gas, solid/liquid, or liquid/liquid interfaces are probed, and the chemical surface composition, orientational distribution, order and chirality can be retrieved. An application to investigate plasma-wall interactions is feasible too.

1. Introduction
The operation of ITER strongly depends on the (absence of) interaction of the hydrogen plasma with the walls of the reactor [1, 2]. In order to design appropriate reactor walls composed of the most suitable material it is necessary to find out how a plasma interacts with the surface of the walls.

Plasma-surface interaction takes place on a highly confined location in a hostile environment. It typically involves processes such as atomic and molecular collision, surface charging, diffusion, neutralization, photon emission and electron emission. Due to these processes the surface will be restructured, many new chemical species can be formed as well as small dust particles [3].

In order to investigate such processes a multitude of plasma specific and surface specific techniques need to be combined. The Magnum-PSI project at the Institute for Plasma Physics Rijnhuizen aims to study plasma-wall interactions with surface specific methods. Most of the surface specific techniques (such as electron energy loss spectroscopy, X-ray photoelectron emission, Auger spectroscopy, or thermal desorption spectroscopy [4]) are operating either ex-situ (requiring transport through air), or in vacuo when the plasma source is turned off. In order to measure in-situ processes during plasma-wall interaction second-order nonlinear optical methods such as second harmonic and sum frequency generation are suitable. Since these are optical methods that can be applied in-situ during plasma-wall interaction they could be very valuable for controlling the plasma-wall interactions and the accompanied dust formation.

In this Article a description is given of the state of the art of sum frequency generation as well as an outline of how it might be used to measure plasma-wall interactions in-situ. The possible technological complications that might become important in such an implementation are discussed as well.
2. Sum Frequency Generation

Vibrationally resonant sum frequency generation (SFG) from a surface was first demonstrated by Hunt et al. [5] and Harris et al. [6] in 1987 who used SFG to study the structure of pentadecanoic acid on water surfaces and n-octadecylthiol on gold, cadmium stearate on silver, pentadecanoic acid on water surfaces and n-octadecylthiol on gold, cadmium stearate on silver, E. coli on silver, and stearic acid on germanium. In a sum frequency generation experiment, two electromagnetic fields, \( \mathbf{E}_1(\mathbf{r}, t) = \mathbf{E}_1(\omega_1) e^{i(\mathbf{k}_1 \cdot \mathbf{r} - \omega_1 t)} \) and \( \mathbf{E}_2(\mathbf{r}, t) = \mathbf{E}_2(\omega_2) e^{i(\mathbf{k}_2 \cdot \mathbf{r} - \omega_2 t)} \), with amplitudes \( \mathbf{E}_1 \) and \( \mathbf{E}_2 \), polarization states \( \mathbf{u}_1 \) and \( \mathbf{u}_2 \), and frequencies \( \omega_1 \) and \( \omega_2 \), are reflected from an interface. The frequency of the field \( \mathbf{E}_3 \) is tuned around the resonance of the vibrational modes of the interfacial molecules, so that the frequency will be in the infrared (IR) range of 3700 - 10000 cm\(^{-1}\) (which corresponds to wavelengths of 2700 nm - 10000 nm or energies of 0.45 - 0.12 eV). The other electromagnetic field is usually kept at a fixed visible (VIS) wavelength (usually 532 or 800 nm, but can in most setups be tuned in the visible wavelength region. Such pulses are readily available from ns, ps, or fs pulsed laser sources. At the interface the optical fields induce a second-order polarization that oscillates at the sum frequency (SF) of the incoming waves:

\[
\mathbf{P}^{(2)}_1(\omega_0 = \omega_1 + \omega_2) = \chi^{(2)}_{ijk}\mathbf{E}_{1,j}(\omega_1)\mathbf{E}_{2,k}(\omega_2). \tag{1}
\]

This polarization is the source of a sum frequency field that can be emitted from the interface. By solving Maxwell’s equations it can be found that the detected intensity is of the following form:

\[
I \propto \left| (\mathbf{u}_0 \cdot \mathbf{L}(\omega_0)) \cdot \mathbf{x}^{(2)} : (\mathbf{u}_1 \cdot \mathbf{L}(\omega_1))(\mathbf{u}_2 \cdot \mathbf{L}(\omega_2)) \right|^2 I_1(\omega_1)I_2(\omega_2). \tag{2}
\]

The magnitude and spectral shape of the intensity is determined by the Fresnel factors \( \mathbf{L}(\omega_i) \) that dictate the efficiency of the reflection of the optical beams [7, 8] and the second-order susceptibility tensor \( \chi^{(2)} \). \( \chi^{(2)} \) is a physical property of the material which must reflect the spatial symmetry properties of that material (Neumann’s principle). As a consequence (in the electric-dipole approximation) \( \chi^{(2)}_{ijk} \) vanishes in bulk media [8]. This means that SFG can often be applied as a surface specific technique, with which only the first few molecular layers situated at the interface are probed. The surface response, identified as \( \chi^{(2)}_s \), is usually split up in a frequency dependent resonant (res) and a frequency independent non-resonant (nr) response:

\[
\chi^{(2)}_{s,ijk} = \chi^{(2)}_{s,nr,ijk} + \chi^{(2)}_{s,res,ijk} \propto A_{nr} e^{i\Delta \phi} + \sum_n \frac{N_s \langle T_{ia} T_{jk} T_{kc} \rangle R_{n,a,b \mu n,c}}{\hbar(\omega_2 - \omega_{0,n} + i\gamma_n)}, \tag{3}
\]
where $n$ refers to a specific vibrational mode, with resonance frequency $\omega_{0n}$, and damping constant $\Upsilon_n$. This equation relates the resonant surface susceptibility $\chi_{s,\text{res}}^{(2)}$ to the hyperpolarizability tensor $\beta_{n}^{(2)}$, which is the product of the vibrational dipole moment $\mu_n$ with the Raman polarizability $R_n$ through a transformation matrix $T$ that transforms from the molecular coordinate frame $(a, b, c)$ to the surface coordinate frame $(i, j, k)$. $N_s$ is the density of surface molecules. $A_{nr}$ is the amplitude of the frequency independent non-resonant response that can be phase lagged with a factor $\Delta \phi$ with respect to the resonant response. The values of $\omega_{0n}$, $\Upsilon_n$, $\mu_n$, and $R_n$ depend on the type of molecules, their orientation, chirality and order (see e.g. [10, 11, 12]). This type of structural information is often exclusively interface specific and can be obtained non-invasively, label-free, and in-situ. Table 1 summarizes review papers that have been written about various types of interfaces. Fig. 2 shows example spectra of a polymer/air interface and a liquid/metal interface.

| General/historic/introductory | [13, 14, 15, 12] |
|-------------------------------|------------------|
| Chiral media                  | [16, 17, 18]     |
| Kinetics and dynamics         | [19, 20]         |
| Solid/solid interfaces        | [10, 21]         |
| Solid/liquid interfaces       | [10, 21]         |
| Solid/gas interfaces          | [22, 23, 24]     |
| Liquid/liquid interfaces      | [25, 26]         |
| Liquid/gas interfaces         | [27, 28, 29]     |
| Polymers                      | [22]             |
| Biologically relevant interfaces | [30, 31]      |
| Particle interfaces           | [32, 33]         |

2.1. Typical setup and experiment

In order to generate sufficient electric field amplitudes to generate detectable sum frequency photons, pulsed laser sources are needed. Nowadays, pulsed femtosecond and picosecond lasers can be fabricated routinely and a wide variety of options is available. Since femtosecond sources deliver pulses with a broad frequency bandwidth they allow for a simultaneous recording of multiple chemical species and are therefore the preferable choice for studying plasma-wall interactions during plasma operation. Typically a femtosecond system consists of an oscillator that delivers high repetition rate 800 nm pulses that are used as a seed in a chirped pulse amplifier. The amplified pulses can be converted into infrared pulses via optical parametric generation and amplification in combination with difference frequency generation.

The geometry for a surface SFG-experiment is given in Fig. 1. The chosen angles $\theta_i$ are determined by the optical properties of the substrate and have to be chosen such that there is an optimal geometry for SFG. This is dictated by the Fresnel factors of the substrate material (Eq. (2)) and the incident polarization of the light (i.e. parallel or perpendicular to the plane of incidence) [10, 7, 11, 12]. As an example, the optical properties of graphite dictate that the incoming visible beam should be incident under more than 75° with respect to the surface normal [37]. For s-polarized light there is no Brewster angle. These considerations would result in $\theta_1 = 80^\circ$ and $\theta_2 = 60^\circ$. For a metal such as platina both angles can be in the range $\theta_{1,2} = 80^\circ - 90^\circ$ for optimal sum frequency generation. In Fig. 3 an illustration of how an SFG setup might be combined with a vacuum machine placed inside a large magnet for generating the plasma is given.

1. Brewster angle for p-polarized 632 nm light
**Figure 2.** Sum frequency generation from two different interfaces, in different spectral regions. A: The polymer/air interface of the same polymer in a crystalline (red) and amorphous (blue) state. Although the chemical composition is identical, the crystalline polymer film is chiral while the amorphous one is racemic. The SFG spectra show that there is a big difference in the three dimensional surface structure of the two films [34]. B: An SFG spectrum of a liquid (acetonitrile) in contact with a metal (gold). It can be seen that there is interference between a metal originating non-resonant signal and a molecular symmetric resonance of the CN vibrational mode. The mode is red shifted with respect to the liquid value indication a strong interaction with the metal [35, 36]. The typical integration time to record these spectra is 100 s.

### 3. Probing in-situ surface-plasma interaction

#### 3.1. System and substrates
In a state-of-the-art setup (e.g. [38]), tunable infrared pulses with a duration of ~70 fs and an energy of >50 µJ/pulse can be generated in the 2.6-10 μm wavelength range. Using infrared transparent CaF$_2$ or MgF$_2$ optics for vacuum ports the accessible frequency range of interest will be 1200-3500 cm$^{-1}$, which is the region of interest for most chemical compounds. Table 2 summarizes vibrational frequencies of H and D on relevant substrates (S). It can be seen that H atoms on atop positions can be detected readily with SFG. H atoms in more complex bond conformations (like threefold and fourfold sites) exhibit lower resonance frequencies.

| species                  | calculated (cm$^{-1}$) | measured (cm$^{-1}$)  |
|--------------------------|------------------------|-----------------------|
| **Fusion materials**     |                        |                       |
| C-H (atop)               | 2733 [39]              | 2838 (H-C(111)$^2$ [40]) |
| C-D (atop)               | -                      | 2115 (D-C(111)$^3$ [40]) |
| W-H (atop)               | -                      | 1738 rare species [41]  |
| W(100)-H (twofold)       | -                      | 1070-1300 [42]         |
| B-H                     | 2282                   | -                     |
| Li-H                     | 1359                   | -                     |
| **Reference materials**  |                        |                       |
| Pt-H (atop)              | 2250                   | 2090 polycrystalline Pt electrode [42] |
| Pt(111)-H (threefold)    | -                      | 1230 (asym. stretch)/ 550 (sym. stretch) [42] |

Table 2. Relevant frequencies of typical plasma-wall compounds
3.2. Interference with the light emitted from the plasma

Sum frequency generation relies on the detection of photons and their frequency distribution. A light emitting plasma can therefore interfere with the exclusive detection of the generated sum frequency photons. To circumvent this issue a gated intensified CCD camera needs to be used in combination with fiber coupled optics that is positioned to collect the directionally emitted sum frequency photons. With the gated electronics it is possible to turn on the detection system for only 10 ns. If this electronic gate coincides with the time at which the laser pulses hit the substrate, the continuous incoherent background radiation will not interfere with the coherently generated signal. Furthermore, by using a visible laser source that is tunable from (e.g.) 600 to 800 nm it is possible to vary the frequency of the emitted SF photons while probing the same vibrational resonance. In this way gas emission lines should not interfere with the detection of SF photons.

3.3. Optical probes for dust analysis

The shape and size distribution of the particles in the plasma dust can be imaged and diagnosed with turbidity measurements and speckle pattern analysis. Also, if there are particles in the vicinity of the surface or if the surface is rough, it is possible to generate SF photons not only from the surface but also from the particles (see the right panel of Fig. 3 for an illustration). These photons will not be emitted in the same direction as the reflected phase matched SF beam but rather leave the sample under an angle that depends on the size and shape of the particles [33]. By spatially imaging the fiber output on the camera it is possible to distinguish between particle surfaces and the surface of the substrate. Particles larger than $\sim 1 \mu m$ will create backscattered SF photons [43, 44] than can be detected as well. The ratio between diffuse forward scattered light and backward scattered light can be used to make an estimate of the particle size distribution in the plasma.

![Figure 3](image-url)

**Figure 3.** Illustration of a possible sum frequency generation setup inside a vacuum machine surrounded by the coils of a large magnet. The sum frequency photons can be detected using a fiber bundle and a gated intensified CCD camera. The right panel illustrates the expected directions into which scattered SF photons can be emitted from the surface region.
4. Conclusions
We have described the possibility of using the second-order nonlinear optical method of sum frequency generation to study plasma-wall interactions in a setup such as the Magnum-PSI project. Sum frequency generation is an optical method that can be used during plasma operation. Thanks to the use of short pulses with a broad frequency content it should be possible to take snap-shot spectra of the surface during plasma-surface interaction. Further, by detecting as well diffuse (back)scattered light it should be possible to measure the surface structure of the dust particles in the vicinity of the surface as well as estimate their size range.

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6. References
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