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Light it up, twice the frequency!

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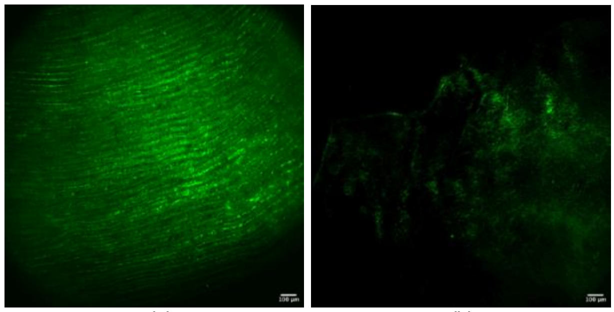
When light interacts with matter, it senses a gathering of electrons drawn by atomic nuclei. Its movement slows or hastens, depending on how dense and crowded the assembly is. It blazes through them, perturbing them to excitement! As these electrons transition from one energy state to another, and as they change speed and direction, they chirp! Trilling electromagnetic waves, that once again materialize into light! As if commanded, "Let there be light!", and from one wavelength forms another–a different light of a different wavenumber. A reminder it seems, that light begets light, and illumination begets enlightenment, even brilliance…

Absorption, refraction, and reflection–the many phenomena involving light are the result of these interactions. Sometimes, this gathering of electrons is ordered with specific symmetries, and sometimes the incoming light is powerful enough to cause frequency doubling of these chirps! This phenomenon is called second harmonic generation or SHG! Second harmonic generation involves two photons overlapping on the surface of matter to generate another photon twice the frequency of the incoming ones. These photons undergo spatial and temporal overlap in this so-called "electronic get-together", leading to the non-linear generation of light. This provides specific information that is not seen in linear events such as absorption and transmission. SHG can probe surface electronic transitions providing information on surface molecular orientation, aggregation, and dynamics, as well as chirality and molecular symmetry. Non-centrosymmetry (lack of inversion) in molecules lead to SHG. Surfaces, interfaces, crystals, proteins, DNA, semiconductors, and many more, that possess this quality, may generate this signal!



(a) (b)

Figure 1: SHG images (in false color) at 10X magnification of (a) milk fish scale and *(b) Stichopus horrens* dermis.

The development of the ruby maser in 1960 by Theodore Maiman is very much intertwined with the birth of SHG. (We need powerful and coherent light to generate second harmonic!) This was a result of the Townes-Schawlow proposal to extend maser wavelength to infrared and visible light, and a lot of prior work in the 50s mostly done in the Bell Labs. In fact, just a year after, Peter Franken and his co-workers observed the very first SHG signal coming from quartz crystal. Elucidation of the theory of non-linear optical generation and SHG itself, were also developing quickly with these technologies at that time. In 1962, Nicolaas Bloembergen and Peter Pershan developed the phenomenological scheme behind interfacial second harmonic generation, while David Kleinman in the same year published the theory behind SHG in crystals. It was not until 1981 that laser spectroscopy work was awarded the Nobel Prize in Physics. Recognition was given to Nicolaas Bloembergen and Arthur Leonard Schawlow for laser spectroscopy, and Kai Siegbahn for high resolution electron spectroscopy. We should also remember the guys behind the maser-laser principle, which kick-started the building of the actual instrument! These are Nikolay Basov, Aleksandr Prokhorov, and Charles Townes who did work on basic quantum electronics, and won the

Nobel in 1964. More recent Nobel prize winners relating to lasers are Arthur Ashkin, Donna Strickland, and Gérard Mourou in 2018, for their work on ultrashort laser pulses, and optical tweezers.

The SHG microscope currently housed in the Surface Science and Spectroscopy Laser Laboratory or S^3LLAB (fondly named after slabs of molecules on surfaces of matter), Institute of Chemistry, University of the Philippines-Diliman, is built 60 years after the development of the maser. As far as we know, this is the very first SHG microscope in the country. The home-built microscope is currently being used to probe sea cucumber stress and predatory response by imaging their mutable collagenous tissue (MCT) in their soft and hard state. Proteins called tensilin situated perpendicular to the length of the MCT act as scaffolds that stiffen the collagen fibers, while proteins such as softenin prevent the scaffolding process leading to extensive softening. These sea cucumbers called "Hanginan" are endemic to the Philippines. The presence of predators and other forms of stress from pressure, light, and sea water conditions cause these animals to instantaneously harden or soften, and sometimes even slough off their skin! Clearly, these can be indicators of environmental conditions in our beautiful blue waters. Moreover, sea cucumbers are high-grade sources of collagen–free from various diseases unlike those from mammalian sources, making them quite valuable. Their possible use for wound healing, as well as inspiration for biomaterials design, makes for interesting subject of study!

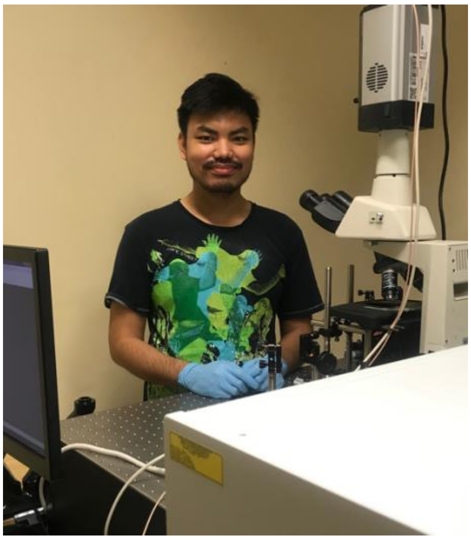


Figure 2: Allen Marbert Lee, MS Mat. Sci. Engg. Student–built the SHG set-up in the S^3LLAB group.

SHG may be used to look at extensive types of samples and surface events. In crystals, SHG is used to test the feasibility of newly synthesized material as harmonic generators. At present, the goal is to generate SHG at the lowest wavenumber of less than 200 nm. Adsorption kinetic studies may also be performed, such as gas adsorption on crystalline metal surfaces, and self-assembly of monolayers on both metals and semiconductors. Studies on 2D materials such a graphene and other metamaterials involve SH enhancement through doping and bilayer twisting. Chemisorption on electrolyte-metal electrode interfaces, including electrocatalysis and corrosion, can be observed in situ. pH-dependent surface charging and charge predominance on surfaces can also be studied using this technique. Modeling environmental events using liquid-solid interfaces such as antibiotic adsorption on mineral oxides are also interesting samples to observe. Membrane and liposome dynamics can be studied, which aids in drug delivery mechanism elucidation. SHG has also been used in nanomaterial characterization and metrology including both dielectric and plasmonic ones. In fact, the combination of nanomaterials and SHG imaging has exhibited very interesting phenomena! SHG coming from these nanostructures changed direction with nanoparticle orientation, and increased intensity with angular difference between incoming beam and nanoparticle symmetry axis. Biological sample studies, in addition to various collagen types, include tumor response to chemotherapy, hepatic steatosis distribution pattern, protein structure, and chromatin organization in live cells. High-resolution images of live neuronal membranes and a voltage map of local trans-membrane potential can also be seen. Chirality studies of aerosols, sugars, and others can also be done. Need we go on?

The list seems endless! There are a lot of possibilities and avenues for research that students and researchers can enjoy in the S^3LLAB group. It is just a matter of creativity and finding that perfect combination of beam geometry, polarization, and of course symmetry, to light things up at twice the frequency!

Acknowledgments

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