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Review article

# Sum frequency generation vibrational spectroscopy (SFG-VS) for complex molecular surfaces and interfaces: Spectral lineshape measurement and analysis plus some controversial issues

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ABSTRACT

Sum-frequency generation vibrational spectroscopy (SFG-VS) was first developed in the 1980s and it has been proven a uniquely sensitive and surface/interface selective spectroscopic probe for characterization of the structure, conformation and dynamics of molecular surfaces and interfaces. In recent years, there have been many progresses in the development of methodology and instrumentation in the SFG-VS toolbox that have significantly broadened the application to complex molecular surfaces and interfaces. In this review, after presenting a unified view on the theory and methodology focusing on the SFG-VS spectral lineshape, as well as the new opportunities in SFG-VS applications with such developments, some of the controversial issues that have been puzzling the community are discussed. The aim of this review is to present to the researchers and students interested in molecular surfaces and interfacial sciences up-to-date perspectives complementary to the existing textbooks and reviews on SFG-VS.



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## 1. Introduction

Surfaces and interfaces are the entity in between the two different phases of matter. They are ubiquitous in nature and man-made world, and they control and influence all the heterogeneous chemical and biological processes. Even though characterization and understanding of the structural properties and interactions of molecular surfaces and interfaces are in need for many scientifically and technologically important fields, since the surfaces and interfaces are only molecularly thin, and the molecular structure and conformation are usually significantly different from those in the isotropic bulk due to the asymmetric forces the molecules experience on the surfaces or at the interfaces, surfaces and interfaces have been the most elusive subjects to be studied and understood at the molecular level [1]. Particularly, our understanding of the buried interfaces, such as the liquid/solid interface [2], has been even more limited. It is not an exaggeration to view surfaces and interfaces as among the last frontiers of our scientific endeavors towards the understanding of the physical and biological world. Venturing into such territories, unique tools, such as sum-frequency generation vibrational spectroscopy (SFG-VS), that can selectively make non-invasive and in-situ measurement on the surfaces and the interfaces, are required (Fig. 1).

Over the more than three decades since the inception of the surface SFG-VS in the early 1980s [3–5], there have been many review articles and a most recent monograph by the founder of the field [6] on the fundamentals theory [7–16], methods and technical developments [17–31], specific applications to various systems [32–55], and progresses reports [56–62] of SFG-VS on the studies of the structure and dynamics of various surfaces and interfaces. Instead of repeating what has been covered in the literature, this review aims to focus on the recent progresses and understandings that need to be summarized for the reference of the researchers and students, who are interested in the nonlinear vibrational spectroscopy of complex molecular surfaces and interfaces, by focusing on the new developments on the accurate measurement and analysis of SFG-VS spectral lineshape that is crucial for the applications to complex molecular surfaces and interfaces.

SFG-VS is the coherent second-order nonlinear optical process where a signal at the frequency of the sum ($\omega = \omega_1 + \omega_2$) of a visible photon ($\omega_1$) and an infrared (IR) photon ($\omega_2$) is generated from the simultaneous interaction of the two photons with a nonlinear optical medium (Fig. 2a) [63]. When the two photons are with the same frequency and come from the same light beam, the process is called second harmonic generation (SHG). SFG-VS, as well as SHG, is intrinsically surface/interface selective because the symmetry requirements for the second order nonlinear optical processes dictate that the SFG-VS signal from the surface of an isotropic medium or the interface between two isotropic media is dominated by the surface or interfacial dipolar contributions [12]. The SFG and SHG processes are intrinsically weak, and even with intense IR and visible laser beams the resulted SFG signal is small. Typically with $10^{12}$ IR and visible photons, respectively, the SFG signal is only around the 10 photon level. However, since the SFG frequency is different from the frequencies of the intense IR and visible light, the

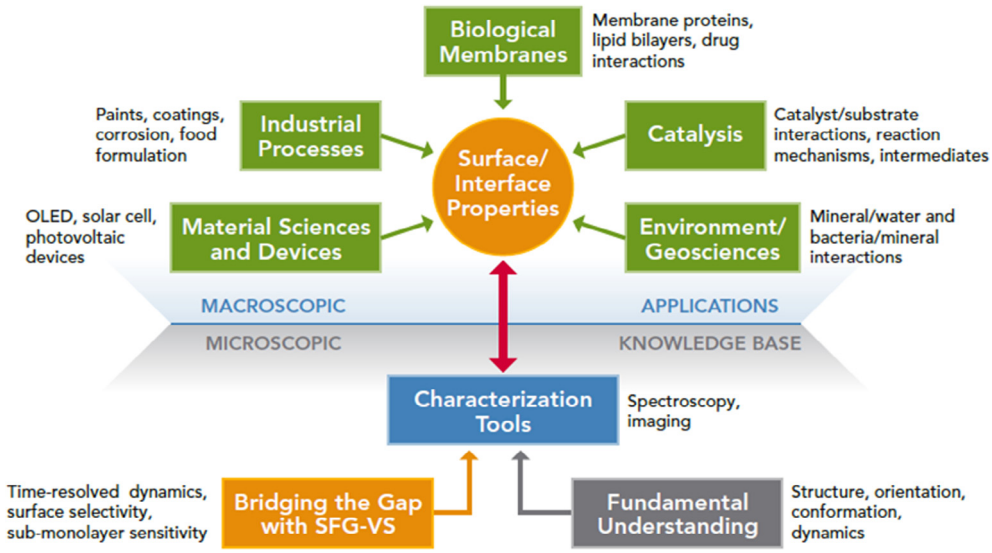


**Fig. 1.** Broad applications of SFG-VS as a characterization tool for molecular level structure and dynamics information of molecular surfaces and interfaces in various fields of fundamental and applied studies. Molecular level characterization and understanding are the foundation for understand and control of surface and interfacial structures and properties that have been crucial and useful for many field of studies and applications.