FUNDAMENTALS OF SUM-FREQUENCY SPECTROSCOPY

The first book on the topic, and written by the founder of the technique, this comprehensive resource provides a detailed overview of sum-frequency spectroscopy, its fundamental principles, and the wide range of applications for surfaces, interfaces, and bulk.

Beginning with an overview of the historical context, and introductions to the basic theory of nonlinear optics and surface sum-frequency generation, topics covered include discussion of different experimental arrangements adopted by researchers, notes on proper data analysis, an up-to-date survey commenting on the wide range of successful applications of the tool, and a valuable insight into current unsolved problems and potential areas to be explored in the future.

With the addition of chapter appendices that offer the opportunity for more in-depth theoretical discussion, this is an essential resource that integrates all aspects of the subject and is ideal for anyone using, or interested in using, sum-frequency spectroscopy.

Y.R. SHEN is responsible for the development of second harmonic and sum-frequency generation spectroscopy into viable tools for surface and interface studies. He has been on the faculty of the physics department of the University of California at Berkeley since 1964 and has received many awards, including the Charles Hard Townes Award from the OSA, the Arthur L. Schawlow Prize and the Frank Isakson Prize from the APS, and the Max Planck Research Award. He is also a distinguished professor at Fudan University in Shanghai and an elected member of the US National Academy of Sciences, the American Academy of Arts and Sciences, the Chinese Academy of Sciences, and Academia Sinica.

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As we move further into the twenty-first century, chemistry is positioning itself as the central science. Its subject matter, atoms and the bonds between them, is now central to so many of the life sciences on the one hand, as biological chemistry brings the subject to the atomic level, and to condensed matter and molecular physics on the other. Developments in quantum chemistry and in statistical mechanics have also created a fruitful overlap with mathematics and theoretical physics. Consequently, boundaries between chemistry and other traditional sciences are fading and the term *Molecular Science* now describes this vibrant area of research.

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Y. R. Shen
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FUNDAMENTALS OF SUM-FREQUENCY SPECTROSCOPY

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Preface

Surfaces and interfaces are omnipresent in nature as well as in the man-made world. They unavoidably control many important processes and play an essential role in many disciplines. Advancement of modern surface science and technology relies critically on the molecular-level understanding of surface properties and functionalities. Many techniques have been invented and developed in the past half century to probe surfaces and interfaces. Most notable among them are X-ray spectroscopy, particle scattering, scanning microscopy, and optical spectroscopy. Each has its own unique advantages and disadvantages. Optical spectroscopy is attractive because it allows in situ, remote, non-destructive, and non-perturbative probing of surfaces in real environments with sub-monolayer sensitivity. Vibrational spectroscopy, in particular, can provide detailed structural information about a surface. However, commonly available techniques, such as IR absorption/reflection spectroscopy, Raman scattering, and ellipsometry, are limited in their surface specificity and generally are not suitable for surface studies. Clear distinction of spectra and structural symmetry between surface and bulk is needed for optical techniques to be applicable.

Soon after the birth of nonlinear optics, it was recognized that second-harmonic generation (SHG) and sum-frequency generation (SFG) are electric-dipole forbidden in media with inversion symmetry. Because the inversion symmetry is necessarily broken at a surface or interface, one would expect that SHG/SFG be highly surface-specific in such media assuming that higher-order multipole contribution from the bulk is negligible. This happens to be true in many cases of practical interest. Since the first demonstration of SHG as a surface characterization tool in 1981 and SFG in 1987, the techniques have gained increasing popularity in the surface science community. Sum-frequency vibrational spectroscopy (SFVS), in particular, has grown into a most viable surface analytical tool because of the large amount of information it can provide through the dependence on input frequencies, beam geometry, and polarizations. As true for all material characterization techniques, raw data or spectra of SHG/SFG might reveal useful qualitative information about a surface, but quantitative reliable information only comes from proper data or spectral analysis based on a thorough understanding of the underlying theory of the processes. Most importantly, care must be taken to use the correct expression of the Fresnel coefficients, especially for absorbing media, and to make sure that bulk contribution is negligible or properly accounted for in the data analysis. Such a theoretical understanding has actually taken years to form. A review on the recent theoretical development is not yet available.

Over the years, SHG/SFG have found a wide range of applications in different fields and various disciplines, not only for surface and interface studies, but also for bulk characterization. Benefiting from advances in laser technology, new experimental schemes have surfaced, and experimental techniques in general have been greatly improved. Significant advances in SHG/SFG, however, have appeared scattered in many different journals, and review articles tend to focus on special topics. A researcher practicing the techniques in certain areas of surface science may not appreciate its possible applications in other areas. There also exist likely mistakes in measurement results and spectral analysis reported in the literature that many are not aware of. The situation calls for a treatise overviewing all general aspects of the techniques, including both theory and applications.

This book aims at beginners interested in adopting SHG/SFG as analytical tools as well as practitioners who are familiar with the techniques. The goal is to provide a resource volume as complete and comprehensible as possible on the subject, with comments on current limitation on the applicability of the techniques and challenges for further improvement. Of course, it is impossible to have thorough and complete discussions on all topics in a book of this nature. In most cases, the readers are necessarily referred to the original articles on a topic for details. Even so, many significant published works must have been inadvertently neglected, and for that, I apologize in advance.

The book is organized as follows. Chapter 1 provides a historical perspective on how SHG/SFG were invented and developed into viable surface probes, followed by a brief description of their current status and future prospect. The next three Chapters (2–4) present the basics of theory and experiment of SHG/SFG. Physical reasoning is emphasized in the presentation, but for the theory to be correctly stated, some mathematics is unavoidable. More rigorous theoretical derivations are given in appendices, which readers with no theoretical interest can ignore. The rest of the Chapters (5–12) are on applications of SHG/SFG in specific areas. Chapter 5 reviews characterization of bulk materials by SHG/SFG. Chapters 6 to 10 discuss, respectively, applications to interfacial molecular adsorption, neat solid surfaces, liquid interfaces, organic and polymer interfaces, and biological interfaces. Chapter 11 focuses on SHG/SFG as novel, potentially powerful, chiral spectroscopy for chiral materials. Finally, Chapter 12 describes a number of other applications of SHG/SFG: electrochemical interfaces, ultrafast surface dynamics, SHG/SFG microscopy, and interfaces of colloidal particles.

I am indebted to many past members of our group in Berkeley, from whom I have learned the essentials in the development of SHG/SFG spectroscopy. All of them have made significant contributions to the field. Specifically, Chenson Chen, Tony Heinz, Harry Tom, Rubens de Castro, and Daniel Ricard did the pioneering works on surface characterization by SHG, and Jeff Hunt, Philippe Guyot-Sionnest, X.D. Zhu, Wei Chen, Richard Superfine, Quan Du, and Hajo Suhr on surface SF vibrational spectroscopy. Many others, including Marla Feller, Theo Rasing, Gary Boyd, Hui Hsiung, Garry Berkovic, Chris Mullin, Xiaodong Xiao, Viola Vogel, Jung Y. Huanag, Rodney Chin, Rupin Pan, Thomas Stehlin, Eric Freysz, Peixuan Ye, Jing-yuan Zhang, Winfried Daum, Dieter Johannsmann, and Colin Stanners, also made most significant contributions to the advancement of the spectroscopy. More recently, Doseok Kim, Xiaowei Zhuang, George Selfer, Dieter Wilk, Xing Wei, Paulo Miranda, Mikhail Belkin, Seok-Cheol Hong, Na Ji, John McGuire, Weitao Liu, Luning Zhang, Lorenzo Marrucci, Herman Held, Alex Lvovsky, Masahito Oh-e, Song-Hee Han, Chun Zhang, V. Pflumio, Wolfgang Beck, Timofei Kulakov, Shen Ye, Toshiya Saito, T. Goto, Karl Heinz-Ernst, Yuh-Ling Yeh , Chrisian Raduge, Min-yao Mao, Francois Lagugne-Labarthet, Victor Ostroverkhov, Pasquale Pagliusi, Chao-yuan Chen, Markus Raschke, Jahoe Sung, Steven Byrnes, Chuanshan Tian, and Yu-Chieh Wen have further improved on the technique and theoretical understanding, and extended the range of applications of SF spectroscopy. I have had the good fortune to collaborate with a number of outstanding research groups over the years in developing SHG/SFG spectroscopy: Francesco DeMartini in Rome, Mahn-Won Kim at Exxon, Gerd Marowsky in Göttingen, Michitoshi Hayashi and Sheng Lin in Taiwan, Tung Chung at IBM, Doseok Kim in Korea, and Gabor Somorjai, Miguel Salmeron, Hao Yang, and Glenn Waychunas in Berkeley. Somorjai's students and postdocs, particularly Mathew Mate, John Crowell, Dana Zhang, Paul Cremer, Xingcai Su, Steve Baldelli, Zhen Chen, David Gracias, and Ken Chou have contributed enormously in our collaboration. Research support from the Department of Energy and the National Science Foundation throughout the development of SHG/SFG spectroscopy is greatly appreciated. My utmost sincere thanks go to my wife who helped proofread the manuscript and solve numerous problems I had encountered with the computer Word program during preparation of the manuscript.