

Tip-Enhanced Raman Spectroscopy (TERS)

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1 Introduction

The understanding and knowledge of interfaces is of vital importance for science and technology. Yet, their investigation represents a great challenge still today. It becomes more and more important to achieve information at the level of individual structural blocks of the interfacial region. For the full understanding of interfacial processes, one needs both structural and chemical information at the atomic level. One example for developments in this direction is the advent of the scanning probe microscopies (SPM) [1, 2, 3, 4]. They permit monitoring of surface structures and even their changes in time with atomic resolution. While initially the SPM techniques could not reveal the chemical nature of atoms seen in SPM images, recent development, leading to ISTS (inelastic scanning tunneling spectroscopy), opens the view to the chemical nature of surface atoms and molecules [5, 6]. A major limitation in these experiments is the need for UHV conditions and cryogenic temperatures for the necessary stability of the sample–probe arrangement [6].

IST spectroscopy belongs to the class of vibronic spectroscopies, as well as Raman or infrared spectroscopy. The latter two are optical spectroscopies and provide information on the chemical nature of the investigated species. However, the information (spectrum) is usually averaged over a large ensemble and can, therefore, contain only a certain amount of structural information. While initially Raman spectroscopy was not considered to be sensitive enough to become a suitable tool for interfacial studies (in contrast to infrared spectroscopy), detections and developments in the last decades and even more in the last several years has turned this picture upside down: Due to the availability of huge surface enhancement(s), Raman spectroscopy belongs to the most sensitive vibronic spectroscopies today¹ [7, 8, 9, 10, 11].

The field of surface-enhanced Raman spectroscopy (SERS) started in 1973 with the famous papers of *Fleischmann* et al. [12] and *Jeanmarie* and *Van Duyne* [13], giving rise to more than 4000 papers in the following decades. Most recent key words for intriguing approaches in the SERS field are “hot

¹ Certainly, this will hold also for the next several years. The sensitivity of STS is similar; however, its spectral resolution is comparatively poor.

spots” and “single-molecule SERS” (this book will contain a number of contributions for both of these hot fields).

It is not necessary to present the case of surface-enhanced Raman spectroscopy in detail in this Chapter. What we would like to address here is the general problem of SERS: (Large) enhancements for adsorbates are only found for the coinage metals (copper, silver and gold) and only if these metals have nonplanar surfaces². There is a commonly accepted explanation for these observations: One of the enhancement mechanisms (denoted as *electromagnetic enhancement*) is correlated with the excitation of surface plasmons within small metal structures [14]. Excited surface plasmons are associated with collective electron oscillations in the surface region; they create a localized electromagnetic field with a field strength often much higher than that of the incident wave. In a sense, the nonplanar surface structures act as an antenna for the amplification of the incident *and* radiated electromagnetic fields. The second enhancement mechanism is denoted as the *chemical enhancement* mechanism and is often considered as a kind of resonance Raman enhancement for adsorbate–substrate complexes that provide new or modified orbitals for (pre-)resonant excitation of the Raman processes [15].

The general obstacle for SERS is that adsorption or chemisorption, electromagnetic and chemical enhancement are strongly interconnected. Adsorption and chemisorption can change the (local) surface structure, with impacts on the chemical, but also on the electromagnetic enhancement (particularly if very small structures in the nanometer regime are responsible for huge enhancements). In recent years, a powerful concept was proposed: The concept of a few “hot spots” making up most of the SER signal while the rest of the surface is comparatively SERS inactive [16, 17, 18]. Consensus has been reached that nanostructures or nanoparticles approaching each other very closely provide the scenario for such hot spots: The interstitial region between the particles provide new, very localized modes of surface plasmons with extraordinary field strengths. Hence, these regions produce the strongest enhancements. The field of *single-molecule SERS* is based on this fact (see other Chapters in this book) [14]. In a sense, the lightning-rod effect [19] can be considered as a precursor of the concept of hot spots [20], as both concepts describe a sort of focusing of field energy into narrow spatial regions.

As a consequence of the hot-spot concept, one could have considered to create a single hot spot, for example, by moving a sharp protrusion or a tip made of silver or gold towards the sample under investigation. Illuminating the whole unit should also produce enhanced Raman scattering. In contrast, the development of SERS towards tip-enhanced Raman spectroscopy (TERS) went along a different route (see the next Chapter). In fact, the use of the hot spot in terms of an external device was developed in the SNOM field (scanning

² Periodic and nonperiodic structures support SERS; to the latter belong roughened surfaces and fractal structures. SERS is also observed for small single spheres as well as for aggregated nanoparticles.