

## TIP-ENHANCED RAMAN SPECTROSCOPY ON ADSORBATES AT SMOOTH METAL FILM ELECTRODES

Bruno Pettinger, Gennaro Picardi, Rolf Schuster, and Gerhard Ertl

Fritz-Haber-Institut der Max-Planck-Gesellschaft  
Faradayweg 4-6, D-14195 Berlin, Germany

When a STM-tip made of Ag wire is brought into tunneling contact with an adsorbate covered metal substrate and is illuminated by a laser, Raman scattering by the adsorbate in the vicinity of the tip apex is enhanced considerably. An extension of this approach to electrochemistry will be presented.

Raman spectroscopy at interfaces such as the metal electrode – electrolyte interface is hampered by the very low Raman cross section of most molecules ( $\sim 10^{-29} \text{ cm}^2 \text{ sr}^{-1}$ ). Only the use of Resonance Raman or Surface-Enhanced Raman scattering (SERS) permits in-situ studies. Both approaches have their limitations, such as the restriction to particular frequency regimes, in order to take the advantage of electronic resonances of the adsorbate and/or on resonances of the metal substrate. In addition, SERS requires using non-planar surface geometries, i.e., roughened surfaces or metal-cluster configurations. This is related to the importance of (local) surface plasmon excitations for SERS, which can lead to a substantial enhancement of the interfacial electromagnetic field for surfaces having some fractal character.

A highly roughened metal surface not only has different optical properties, it can also show quite different electrochemical behaviors (1). One attempt to overcome these problems is to do Raman spectroscopy without SERS, relying on highly efficient Raman spectrometer systems. Although there are a few reports on “surface unenhanced Raman spectroscopy” (2), this approach failed to show a real breakthrough.

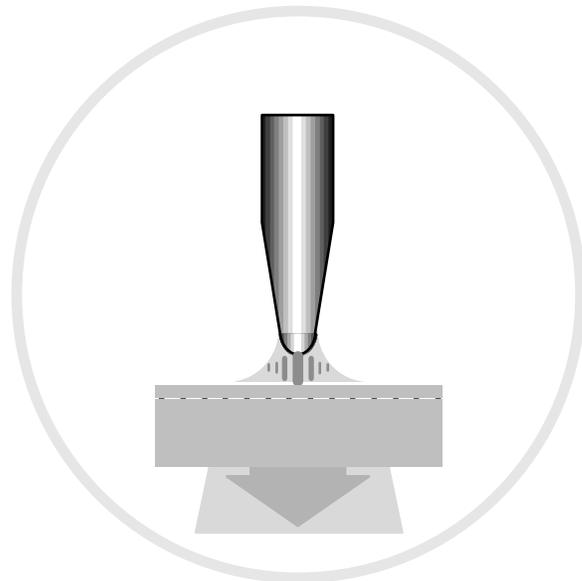
In recent years, a number of experimental and theoretical papers appeared claiming huge enhancements of the Raman process, in excess of  $10^{12}$  (3,4). Experimental and theoretical work showed that only a minority of sites, clusters or small fractions of a fractal surface show such extraordinary surface enhancements. They are associated with the concept of rather local, but very efficient “hot spots”.

This gave rise to a new concept, the use of an AFM- or STM-tip to enhance Raman scattering for molecules deposited at a substrate (5,6,7). Our approach uses an STM tip, which can be brought into tunneling contact with a thin metal film substrate, and controlled amounts of adsorbates (in monolayer or submonolayer amounts). The STM-tip operates as a “single hot spot”, but only for molecules in close vicinity to the tip apex (7). A sketch of the STM-tip enhanced Raman spectroscopy (TERS) is shown in Fig. 1. Depending on the tip radius (about 100 nm and 500 nm), the number of molecules exposed to the highest enhancement in the central zone varies between about 400 to about 10 000 molecules (7). Their contribution to the total Raman signal can be equal or even larger than the Raman scattering from the total ensemble

of molecules (about 1 600 000) present in the whole illu-

minated area in the absence of a tip enhancement. This approach can be easily extended to electrochemical cells, by employing the type of cells used for in-situ STM investigations. The difficulty is to discriminate between TERS for the adsorbate at the metal film electrode and the same species adsorbed at the STM tip. We will

Fig.1 Scheme of TERS. The laser light passes through



a thin metal film (6-12 nm) towards the STM tip, at which localized surface plasmons are excited. Their near field produces the enhanced Raman scattering by the adsorbates on the metal film, but only for those located in close vicinity to the STM-tip apex.

present several strategies for extraction of the desired spectral information such as the use of (i) species that exhibit different frequencies when adsorbed at the tip or metal film materials; (ii) species that show much more intensity when adsorbed on the metal film than on the tip; (iii) a potential modulation technique, similar to that of potential modulated FTIR experiments.

Finally, we will present TERS results, among them the adsorption of  $\text{CN}^-$  ions at Ag and Au film electrodes and discuss the experimental findings.

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