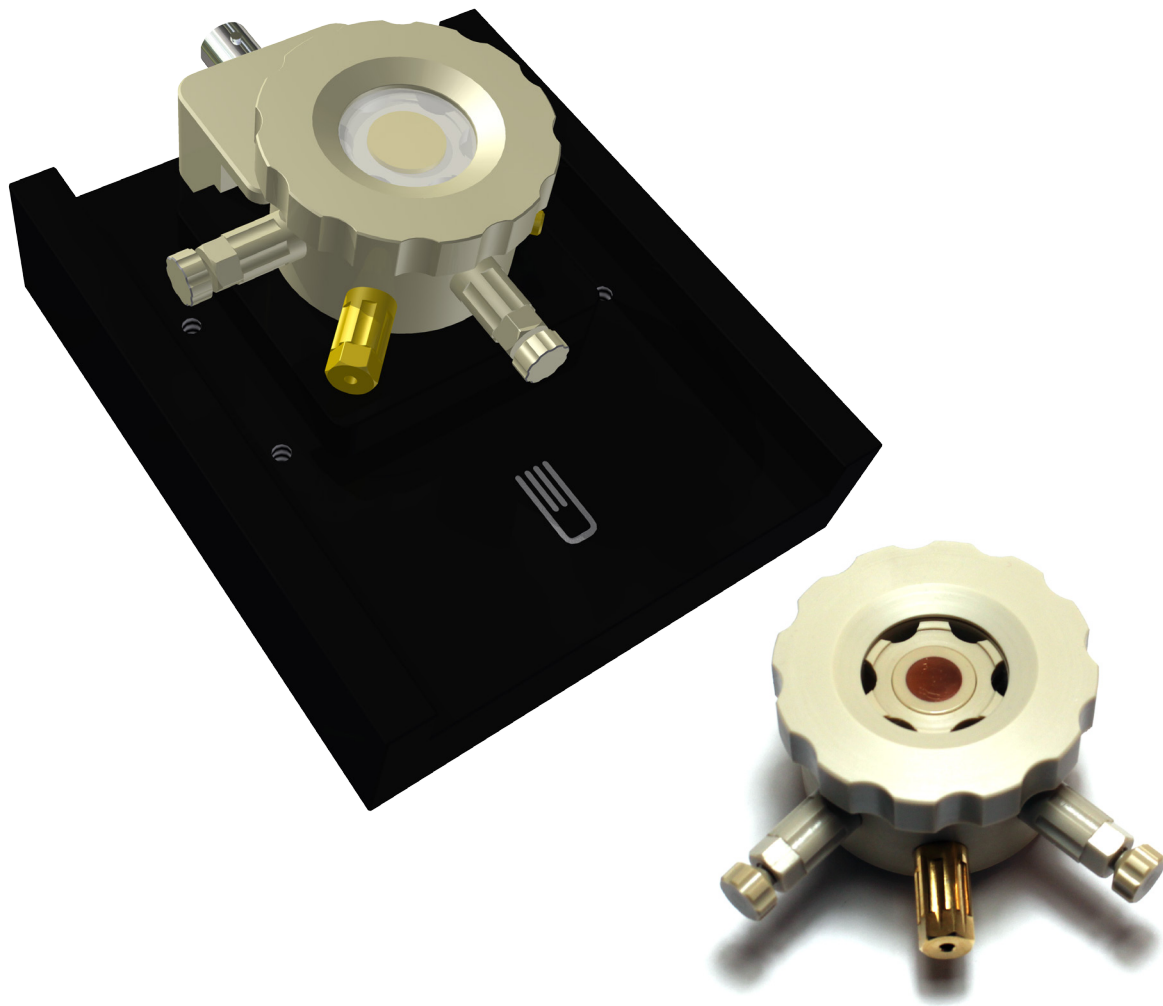# rhd instruments
flexible cell solutions

Application note

SERS study of EMImTFSI on gold surfaces

Introduction

Vibrational spectroscopy techniques like infrared or Raman spectroscopy are powerful investigation tools enabling in-situ studies about the electrode/electrolyte interface [1]. For example such as the identity of adsorbates and intermediates, the strength of intermolecular interactions and the nature of chemisorbate-surface bonding [1]. In the Raman experiment the substrate is irradiated by monochromatic light usually from a laser and the resultant scattering is analyzed [2]. Raman spectroscopy uses the inelastic scattering of photons by the vibrational chemical bonds of a molecule [3]. Due to different vibrational modes present within diverse molecules the Raman spectrum of each one is unique allowing for an unambiguous identification [3]. Its basic principle is schematically sketched in Figure 1. Not only liquid, but also solid samples can be investigated.
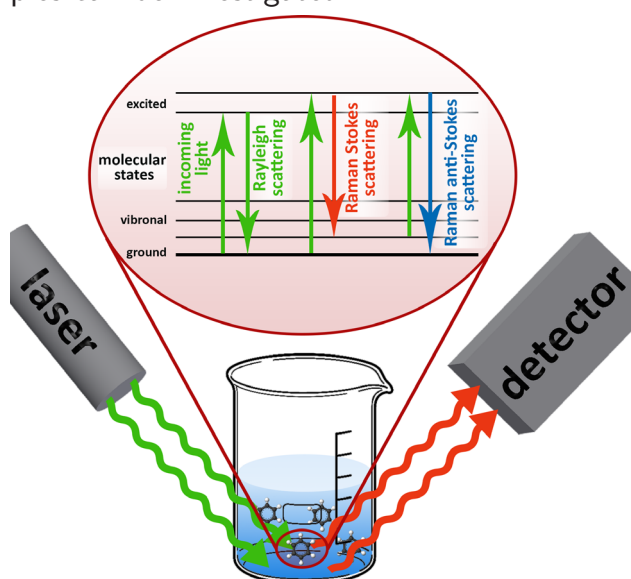

Figure 1: Basic principle of Raman spectroscopy.

[1] R.C. Alkire, D.M. Kolb, J. Lipowski, P.N. Ross (Eds.), *Advances in Electrochemical Science and Engineering, Volume 9: Diffraction and Spectroscopic Methods in Electrochemistry*, Wiley-VCH, Weinheim, 2006

[2] G. McNay et al., ***Applied Spectroscopy*** **65**, 8 (2011) 825-837

[3] H. Wei et al., ***Environ. Sci.: Nano*** **2** (2015) 120-135

[4] S. Schlücker, ***Angew. Chem. Int. Ed.*** **53** (2014) 4756–4795

[5] C. L. Haynes et al., ***Anal. Chem.*** (2005) 338A-346A

[6] C. Muehlethaler et al., ***Anal. Chem.*** **88** (2016) 152 – 169

Unfortunately, Raman scattering cross sections are rather small - typically 14 orders of magnitude smaller than those of fluorescence - resulting in low sensitivities for standard Raman spectroscopy making it challenging to use Raman to detect low concentration analytes [3], [5]. In contrast, surface-enhanced Raman spectroscopy (SERS) as a variant of Raman spectroscopy often provides high sensitivity due to a giant signal enhancement thus enabling the study of submonolayer quantity of adsorbates [1]. But which effect or difference causes this great increase in signal intensity? In comparison to normal Raman spectroscopy, SERS additionally requires the presence of (metal) nanostructures like colloides or nanoparticles [4]. When a molecule is adsorbed on gold or silver nanoparticles, its Raman cross section can be enhanced by several orders of magnitude [3]. While for initial work on SERS roughened silver electrodes were used, usage of silver colloids as substrates led to a sharp reduction of the detection limit in case of organic dye molecules down to the single-molecule regime [6].

Short introduction to basic SERS theory

For understanding the enhancement effect in SERS not only the interaction between light and molecules/matter, but also between light and (metal) nanostructures needs to be considered [4]. Two primary mechanisms are responsible for SERS: electromagnetic (EM) and chemical (CM) enhancement [3].

a) *EM mechanism*

The EM is a long-range mechanism referring to the enhanced local electromagnetic field near the nanoparticle surface and occurs also at larger distances away from the nanoparticle surface [3]. Although the long range coupling of the electromagnetic fields decays exponentially with particle distance, it can extend to a distance of 2.5 times the nanoparticle di-

ameter [3].

Laser light as an electromagnetic wave can resonantly excite the delocalized conduction electrons in a metal giving rise to so called plasma oscillations [4]. Among other parameters, the resonance frequency ω_{max} of the plasma oscillations (plasmons) in the metal nanostructure depends on the dielectric functions of the metal $\varepsilon_{metal}(\omega)$ and the surrounding medium $\varepsilon_m(\omega)$ [4]. In case of a resonant excitation, the oscillating electric field of the incoming laser radiation with angular frequency ω_{inc} and amplitude E_0 induces an oscillation of the conduction electrons, e.g. in a nanoparticle, resulting in a charge separation termed dipolar localized surface plasmon resonance (LSPR) [4]. Its magnitude $\mu_{ind(metal)}$ is determined by the polarizability of the metal sphere α_{metal} and the incident electric field strength $E(\omega_{inc})$:

$$\mu_{ind} = \alpha_{metal} E_0(\omega_{inc})$$

and its sign changes periodically with the angular frequency ω_{inc} of the electromagnetic wave as the external driving force [4]. This localized induced dipole can emit radiation at the same frequency ω_{inc} (right green arrow in Figure 2), i.e. resonant elastic light scattering of a metal sphere [4]. This leads to an increased local electric field $E_{loc}(\omega_{inc})$ in the vicinity of the metal particle relative to the incident electric field $E_0(\omega_{inc})$ responsible for the significantly increased signal strength observed in SERS relative to normal Raman scattering [4]. While plasmon energy on a smooth surface is bound to the surface, roughened ones give a perpendicular component to the plasmon, thus enabling scattering [2]. This explains the need of roughed or nanostructured surfaces for SERS. In case a molecule is located near the surface of the metal sphere, the local electric field $E_{loc}(\omega_{inc})$ interacts with it and similar to the dipole induction in the metal sphere, also dipoles in molecules can be induced [4]:

$$\mu_{ind} = \alpha_{molecule} E_{loc}(\omega_{inc})$$

In classical theory, inelastic light scattering can be explained by a modulation of the incident electric field $E_{loc}(\omega_{inc})$ by a vibrating molecule with angular eigenfrequency ω_{vib}, resulting in three dipole components: $\mu_{ind}(\omega_{inc})$, $\mu_{ind}(\omega_{inc}-\omega_{vib})$, and $\mu_{ind}(\omega_{inc}+\omega_{vib})$, corresponding to Rayleigh, Stokes Raman, and anti-Stokes Raman scattering, respectively [4]. While Rayleigh scattering is an elastic scattering mode, in which the initial and final states are the same, i.e. the scattered light has the same frequency like the incoming light (green down pointing arrow in Figure 1), Stokes Raman and anti-Stokes Raman are inelastic
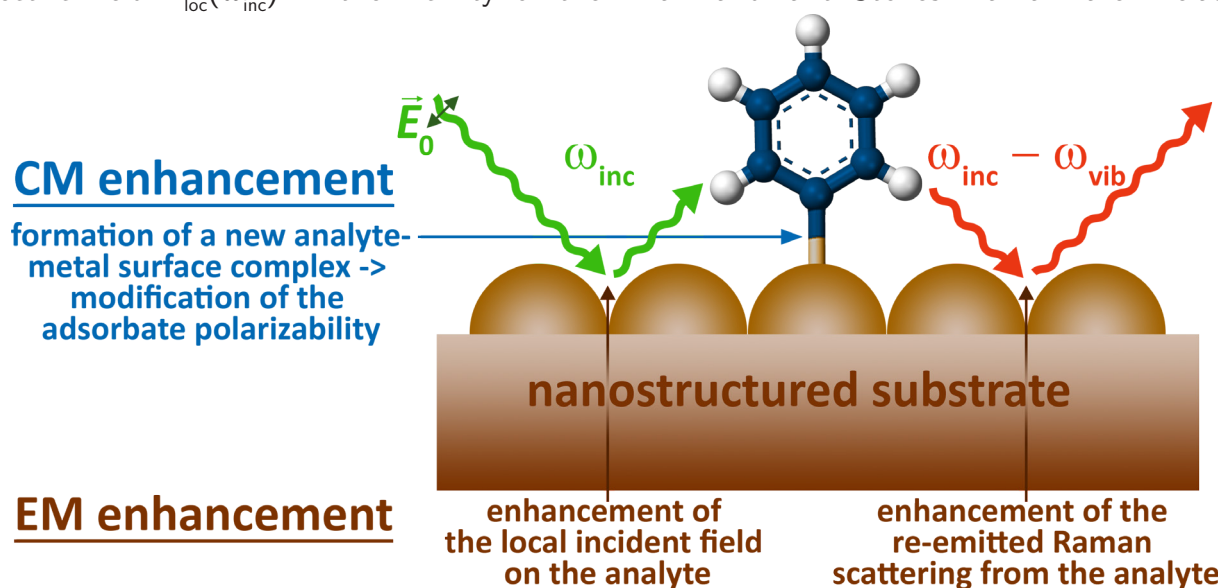

Figure 2: Basic principle of SERS showing the electromagnetic (EM) as well as the chemical (CM) enhancement effect.

scattering modes [7]. For Stokes Raman scattering some photon energy is consumed in the molecular vibrations of the sample causing a red-shift of the scattered light (red down pointing arrow in Figure 1) [7]. In contrast, for anti-Stokes scattering the vibrating molecules emit a photon carrying away some vibrational energy resulting in a blue-shift of the scattered light (blue down pointing arrow in Figure 1) [7]. This frequency-shifted radiation at ω_{inc}-ω_{vib} (left red arrow in Figure 2) itself can excite a LSPR of the metal colloid and again, elastic light scattering off the metal sphere can take place (right red arrow in Figure 2) emitting radiation being detected in the far field [4]. As the overall SERS intensity depends on both the "incoming" (ω_{inc}) and the "outgoing" (ω_{inc}-ω_{vib}) field, optimal SERS enhancements require that the incident radiation as well as the Stokes Raman shifted one are in resonance with the plasmon peak of the metal nanostructure [4]. In case the frequency of the incident laser light and that of the Stokes Raman scattering for one particular vibration/Raman band are close to each other the SERS intensity I_{SERS} approximately depends on the widely used $|E|^4$ approximation [4]. As the electric field strength of dipolar radiation scales with $E(r) \sim 1/r^3$, with r as radius, the distance dependence of $I_{SERS} \sim 1/r^{12} = r^{12}$ making SERS a truly surface-selective effect [4]. The enhancement factor (EF) is an important figure in SERS for quantifying the signal enhancement in comparison to "normal" Raman spectroscopy with I_{RS} as "normal" Raman intensity, N_{surf} as number of molecules bound to the enhancing metallic substrate and N_{vol} as number of molecules in the excitation volume [4], [8]:

$$EF = \frac{I_{SERS}\,/\,N_{surf}}{I_{RS}\,/\,N_{vol}}$$

[7] G. Wedler, Lehrbuch der Physikalischen Chemie, Fünfte, vollständig überarbeitete und aktualisierte Auflage, Wiley-VCH, Weinheim, 2004

[8] P.L. Stiles et al., *Annu. Rev. Anal. Chem.* **1** (2008) 601–626

b) *CM mechanism*

The local field enhancements caused by the excitation of LSPRs (EM effect) actually do not require the presence of molecules at all as they are only responsible for the "frequency conversion" from ω_{inc} to ω_{inc}-ω_{vib} due to inelastic light scattering [4]. Thus, the EM effect does not take a direct interaction between the molecule and the underlying metal surface into account, whereas the CE mechanism is related to the electronic properties of the adsorbate taking into account the increase in the electronic polarizability $\alpha_{molecule@metal}$ of the adsorbed molecule on the induced dipole μ_{ind} [4]. With one to three orders of magnitude, the CE enhancements are distinctly smaller than the EM contribution [4]. Several different effects contribute to the CM enhancement, but their experimental disentangling is very difficult to impossible [4]. The charge transfer (CT) between the molecule in its electronic ground state and the metal can change the polarizability of the molecule, resulting in an altered Raman scattering cross-section of the molecule as it is also known from coordination chemistry when ligand molecules are bound to a metal centre [4]. It is a short-range mechanism which can only occur when the analyte is absorbed to a nanoparticle surface [3]. In case the molecules are not only physisorbed, but chemisorbed on the metal surface, this "charge transfer" bonding between analyte and metal will affect the local structure of the metal thereby creating large polarizable orbitals in the metal cluster and significantly increase the intensity of scattering from the analyte [2]. Another aspect is that the energy levels of an adsorbate molecule usually differ from those of the same molecule in its unbound or "free" state, so that for instance, the laser excitation wavelength only coincides with an electronic absorption band of the adsorbed molecule, but not with one of the "free" one [4]. This resonant excitation of electronic transitions in molecules is known as resonance Raman scattering giving rise to sur-

face enhanced resonance Raman spectroscopy (SERRS) [4], [6]. At the same time, through a photoinduced CT mechanism, e.g. from the metal to the adsorbed molecule, new electronic excitation channels can arise with the transition energies depending on the energy separation between molecular and metallic energy levels [4].

In conclusion, current research attributes the experimentally observed signal enhancements in SERS to two contributions, namely the electromagnetic and the chemical enhancement effect [4]. The EM mechanism as pure physical effect describes the enhanced local electromagnetic fields caused by resonant excitation of plasma oscillations in the nanostructure and is the most dominant contribution to the SERS enhancement with EFs in the range of $10^3 - 10^{10}$ [4]. The CE mechanism showing enhancements of maximal three orders of magnitude takes the direct interaction between the molecule and the underlying metal surface into account.

c) *Additional aspects in SERS*

Analyte molecules positioned in the junction between two particles show a much stronger Raman signal than those located on a single nanoparticle surface [3]. This can be attributed to the coupling of the intense localized electromagnetic fields on each nanoparticle produced by incident light excitation of the appropriate wavelength and polarization [3]. Although still under debate, it is generally thought that significant Raman enhancements primarily occur within gaps smaller than 10 nm often referred to as "hot spots", i.e. highly spatially localized regions exhibiting extreme field enhancements [3], [4]. In Figure 3, a schematic sketch showing the occurrence of hot spots as well as the influence of different molecule positions on the nanoparticles on the resulting spectrum is depicted. Not only the gap between two adjacent nanoparticles, but also the sharp corners and tips of anisotropic plasmonic nanoparticles such as nanorods, nanoprisms and nanostars can serve as SERS "hot spots" [3]. The probability of accidentally finding a molecule in a hot spot, i.e., positioned exactly in the gap between two particles, is very small and it is much more likely to find a molecule somewhere on the surface of one of the two particles, where it experiences only moderate enhancements [4]. However, a single molecule in a hot spot with an enhancement factor of 10^{10} results in the same Raman signal like 10 million molecules experiencing only a moderate EF of 10^3 [4].

In addition to SERS hot spots, several factors like nanoparticle type, shape, size or pH of
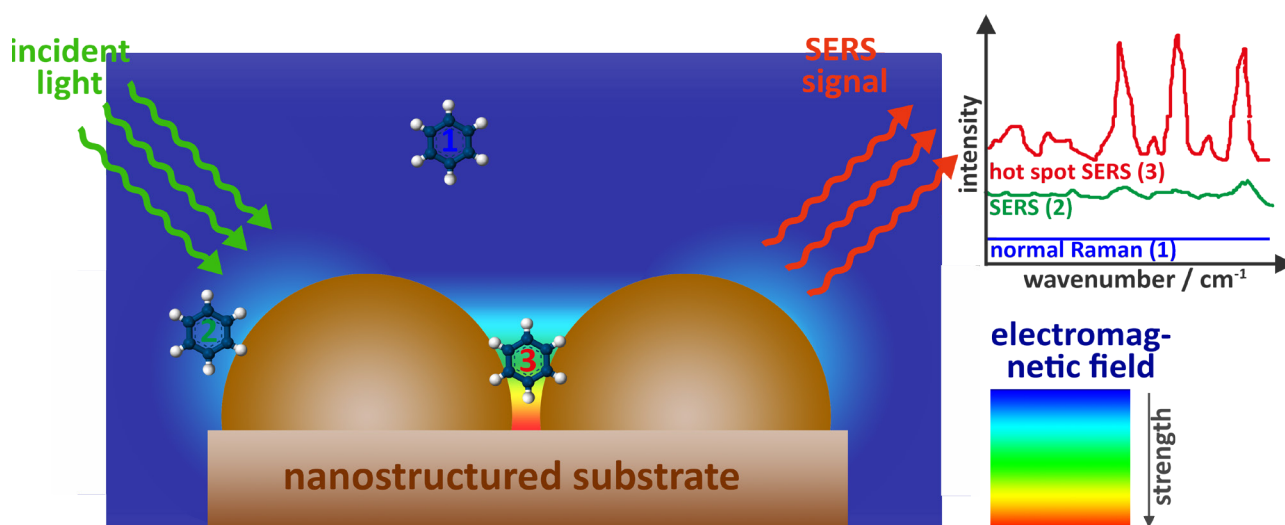

Figure 3: Schematic sketch showing the variation of the electromagnetic field around two nanoparticles emphasizing the occurrence of hot spots in SERS. The influence of different positions of the analyte molecules on the nanoparticle surface (2, 3) or further away from the surface (1) on the resulting spectrum is also shown.

the solution significantly influence SERS: due to a four-time higher extinction coefficient Ag nanoparticles can generate stronger SERS intensities than Au ones of the same size and shape and are thus commonly used for single-molecule and ultrasensitive SERS experiments [3], [4]. On the other hand, Au is chemically more inert and thus preferable in applications where maximum enhancement is less important than stability of the system [4]. Anisotropic plasmonic nanoparticles are suitable for usage under different laser lines as they show multiple LSPR modes [3]. The nanoparticle size also affects its LSPR; as the enhancement can be two orders of magnitude higher when the plasmon band of the nanoparticle overlaps with the excitation wavelength, the nanoparticle size should be chosen according to the excitation laser wavelength [3]. The Fermi level of the metal can be modified by a few eV e.g. by doping it with other metals or by applying an external potential so that charge-transfer occurs using a specific laser excitation [6]. Adjustment of these resonances is crucial for obtaining significant enhancements to be able to sensitively measure just a few molecules [6]. As the solution pH influences the analyte adsorption to the nanoparticle surface it subsequently can influence its SERS signal [3]. The orientation of the molecule relative to the surface normal (flat vs. tilted vs. perpendicular) is important and can be detected as the various vibrational bands of the adsorbed molecule are differently enhanced for the diverse orientations thus giving rise to distinct SERS signatures [4]. Besides metals, recently semiconductors have gained an increased interest for usage in SERS as semiconductor nanoparticles are easily produced and much more stable and reproducible than metal nanoparticle solutions [6].

Experimental

For the electrochemical studies a TSC raman measuring cell, see Figure 4, has been used.

This measuring cell enables the simultaneous spectroscopic and electrochemical investigation of liquid moisture- and/or airsensitive samples under temperature control. The PEEK casing guarantees hermetic sealing of the cell interior from the outside. The cell is optimized for SERS studies as its setup is configured in a way that only a very thin liquid film can form on the working electrode thus enabling true interface studies. As working electrode a cylindric copper electrode encased in PEEK and as counter electrode a gold-plated ring electrode were used. On the working electrode, thin, plane substrates can be placed to study the interface between the employed electrolyte and this substrate. After filling the cell with the electrolyte until a thin liquid film has formed on the substrate, a quartz glass plate is placed on top of the cell and is screwed using a ring shaped PEEK cap to hermetically seal the cell. The glass plate serves as optical window for the Raman experiment and confines the liquid film so that only a very thin film forms on the substrate. This measuring cell also enables the use of reference electrodes.
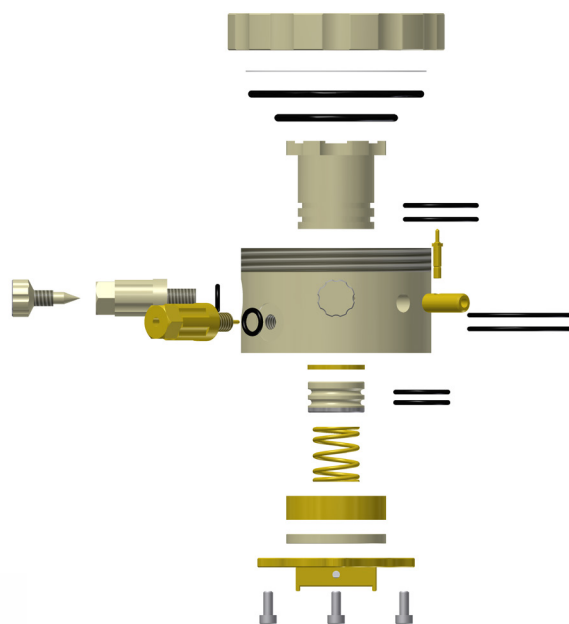

Figure 4: Exploded view of measuring cell TSC raman. On the working electrode, thin, plane substrates can be placed to study the interface between the employed electrolyte and this substrate.

The sample investigated was the ionic liq-

rhd ⦀ instruments
flexible cell solutions

uid (IL) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI) on two differently prepared gold surfaces serving as substrate: While one of them had a rather plane surface, the other one was prepared by electrochemical deposition of gold nanoparticles using a 0.25 mmol/l chloroauric acid solution with 1 mol/l $NaNO_3$ and application of a potential of -0.8 V vs. glassy carbon for 300 s.

For SERS measurements a Renishaw inVia Raman Microscope by Soliton equipped with a Nd:YAG laser was used. The laser wavelength and power were 532 nm and 100 mW, respectively. The results depicted below were recorded using a x20 objective, i.e. a 20 fold enhancement, at a laser power of 0.5 % and a measurement time of 60 s. For background correction the Wire Software by Renishaw was used. Measurements were performed at room temperature of about 18 °C at open circuit potential. Sample preparation as well as the measurements were performed and kindly provided by Roling group (Marburg University).
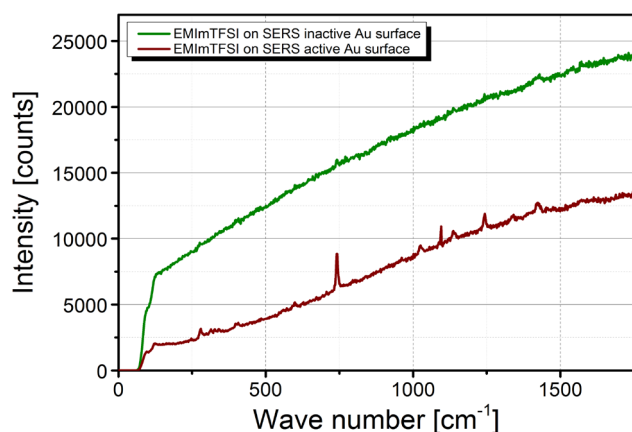
Results and discussion

Figure 5: Raw spectra of the SERS measurements of EMImTFSI on a rather smooth, SERS inactive gold surface (green curve) as well as on a SERS active one prepared by electrochemical deposition of gold nanoparticles (red curve).

In Figure 5 the measured raw spectra are depicted. The green curve shows the Raman spectrum of EMImTFSI on a rather smooth and therefore SERS inactive gold surface,

while for recording of the red curve the same ionic liquid, but a SERS active gold surface prepared by electrochemical deposition of gold nanoparticles was used. In contrast to the green curve hardly showing the Raman signal of the ionic liquid but a rather high background signal, for the red one a clear rise of the Raman signal of the IL together with a reduction of the background signal is visible.

In Figure 6 the background corrected graphs are depicted showing a distinct increase of the signal intensity for the SERS active substrate thus revealing the suitability of the measuring cell for SERS studies. As only a very thin liquid film of the IL is present on the substrate, without SERS activation hardy any signal of the liquid is detectable. For the SERS activated surface the assumption can be made that the recorded signal results nearly completely from the signal at the interface. Thus, this measuring cell enables a quantitative evaluation of the SERS signal as due to setup of the measuring cell the bulk signal is minimized. All peaks visible in the spectrum recorded on the SERS active gold surface can be assigned to the ionic liquid[9], [10], [11]. A summary of them and their tentative assignment is given in Table 1.
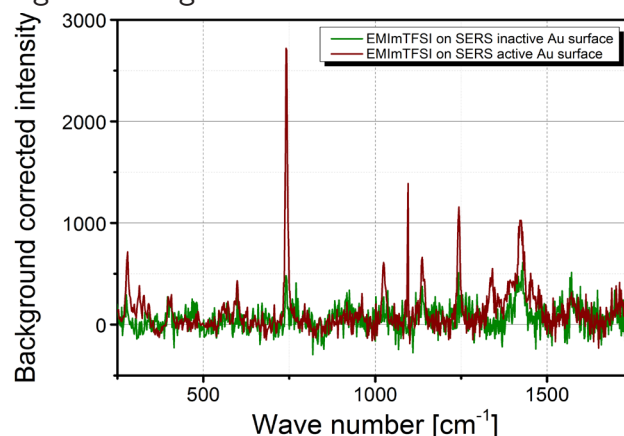

Figure 6: Background corrected spectra of the SERS measurements of EMImTFSI on a rather smooth, SERS inactive gold surface (green curve) as well as on a SERS

[9] B. Bozzini et al., *J. Electroanal.Chem.* **651** (2011) 1–11

[10] V. O. Santos et al., *J. Phys. Chem. B* **110** (2006) 20379-20385

[11] Y.-X. Yuan et al., *J. Raman Spectrosc.* **41** (2010) 516–523

active one prepared by electrochemical deposition of gold nanoparticles (red curve).

Table 1: Summary of the peaks present in the SERS spectrum of EMImTFSI on the SERS active gold surface prepared by electrochemical deposition of gold nanoparticles (red curve in Figure 6).

Wavelenght [cm^{-1}]	Tentative assignment according to [9], [10], [11]
280	Au-S vibration (?) [12]
599	$CH_3(N)$ stretching, $CH_2(N)$ stretching, ring out of plane bending
741	CF_3 symmetric deformation
1024	ring deformation
1095	symmetric in plane ring stretching
1137	SO_2 in-plane symmetric stretching
1244	CF_3 symmetric stretching
1341	ring stretching
1424	CH_3 umbrella deformation
1452	asymmetric CH_3 deformation

Acknowledgement

[12] T. Bürgi, *Nanoscale* **7** (2015) 15553-15567

rhd ||| instruments
flexible cell solutions