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SERS on carbon chain segments: monitoring locally surface chemistry

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Abstract

Carbon films deposited (at elevated temperatures) on SERS active metal substrates show remarkable fluctuations in Raman spectra, if a Raman microscope is used. In subsequently recorded spectra distinct sets of intense, but rather narrow Raman lines appear, which are related to vibrations of corresponding carbonaceous groups. These spectral fluctuations evidence an enduring surface chemistry producing a variety of carbon chain configurations, which get temporarily in contact with metal sites, the so-called 'hot spots', that exhibit extremely large surface enhancements.

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1. Introduction

Surface-enhanced Raman spectroscopy (SERS) is commonly used to study interfacial processes at a molecular level [1,2]. Detailed vibrational information from a wide range of adsorbates can be achieved due to an average amplification of the Raman scattering up to 10^7 for adsorbates at metals such as silver, copper or gold [1,2]. It has been generally accepted that two co-operating processes contribute to the giant enhancement of Raman intensity: the so-called 'electromagnetic' and the 'chemical' one. The former is associated with (sub) microscopic surface geometries permitting surface plasmon resonances [3], the latter with mixing of the molecule and metal energy levels leading to a phenomenon similar to the resonance Raman effect [4]. In the case of a sufficiently large electromagnetic and chemical enhancement, Raman processes occur on a rate comparable to intramolecular relaxation processes. Then, the Raman process receives an additional gain from competition, i.e. the total enhancement factor is the product of the electromagnetic, the chemical and the competitional type of amplification [5,6].

In 1982 Moerl et al. reported that SERS originates from a fraction of adsorbed molecules that are bound to the so-called 'active sites' [7]. The enhancement factor for those molecules is, therefore, at least one or two orders of magnitude larger than earlier estimates taking all adsorbed molecules into account [7,8].

Using photon scanning tunneling microscopy Moskovits and co-workers [9,10] showed that there are highly localized, laser-excited optical modes at

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silver colloid fractal clusters, also called ‘hot spots’, which have an intensity enhancement at least two times larger than the lowest intensity of the sample. However, because of finite tip resolution, field measurements are convoluted by the tip collection function leading to a smoothing of sharp peaks and dips [9]. Bozhevolnyi et al. also reported a local intensity fluctuation of factor 7 of near-field optical images at a rough gold surface [11].

SERS investigations on colloidal systems revealed that a rather small fraction of nanoparticles have unusually high enhancement efficiencies compared to that of the total ensemble [12–16]. Consequently, only 0.01% of the molecules in the sample (crystal violet or rhodamine 6G) contributes to the observed SERS signal [16]. Obviously, SERS originates mainly from the so-called ‘hot spots’ although their numbers are limited.

Recently Shalaev et al. [17,18] presented calculations according to which the intensity of the localized electromagnetic waves can vary by more than 10^5 between the ‘hot spots’ and the cold zones. This implies local electromagnetic enhancements in excess of 10^{10} [18]. An enhancement of 10 orders of magnitudes is sufficient for ‘single molecule spectroscopy’ using SERS [12–16].

In SERS investigations one is often bothered with the presence of impurities. Due to a giant enhancement they can show up in the form of relatively intense amorphous carbon bands [19], but some times also in the form of (a group of) narrow Raman lines varying in intensity and frequency.

To investigate this phenomenon in a broader context, a carbon layer was deposited on SERS-active metal substrates such as Ag and Au by decomposition of CO at elevated temperatures. If a Raman microscope is used, such deposits show well discernible spectral fluctuations in the form of sudden appearance and disappearance of rather narrow Raman lines in a wide frequency regime. We will show that analogous fluctuations are observable also in experiments at silver and gold electrodes, where (carbon containing) impurities cannot be removed completely. We will discuss our observations in a generalized framework of ‘hot spots’, representing sites where both the electromagnetic and chemical enhancement is huge. In a sense, such ‘hot spots’ allows for monitoring spectroscopically an apparently rich surface chemistry on a local scale and low rate.

2. Experimental

Raman microscopic measurements were performed with a confocal microprobe Raman system (Dilor LabRAM 1000). A He–Ne laser (15 mW) provided excitation with radiation of 632.8 nm. The laser power was approximately 5 mW at the sample. The microscope attachment is based on an Olympus BX40 system and uses an objective (MPL10 × /NA 0.25) or 50 × or 100 × long distance objectives (LMPLFL50 × /NA 0.50 and LMPLFL100 × /NA 0.80, respectively).

The standard Raman system without microscopic optics was described previously [20].

The Au and Ag substrates were electrochemically roughened in a 0.1 M KCl solution according to the procedures described previously [21,22]. Carbon clusters were deposited on the rough metal substrates by decomposition of CO (the metal substrate was kept for 10 min at $T = 690$ K in pure CO, $p_{\mathrm{CO}} = 1$ atm) [23,24]. Because the rough substrates (which are still SERS active after this procedure) provide a variety of bonding sites for carbon chains, the carbon deposits can be composed of small crystalline carbon clusters or carbon nanotubes but also of a network of amorphous carbon. Thus, the overall nature of these carbon deposits can be best described as amorphous carbon, while its local elements can exhibit quite different character. In the following we refer to the deposited layer as amorphous carbon.

3. Results and discussion

The surface enhanced Raman cross-section of carbon deposits is exceptionally large allowing very short integration times. In Figs. 1 and 2, two series of SERS spectra are presented for rough Au and Ag surfaces covered with amorphous carbon. In these experiments, a Raman microscope equipped with a 50 × objective were used, and the samples were exposed to air.

Unexpectedly, these spectra exhibit huge fluctuations in number, intensity and frequency of narrow

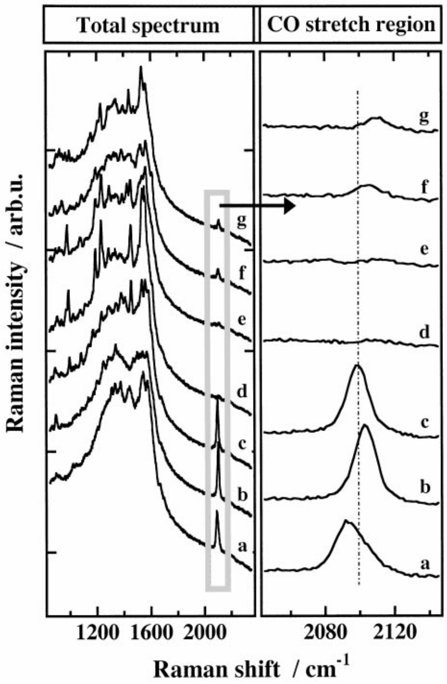

Fig. 1. SERS spectra of carbon clusters deposited on rough gold surface and measured in air at room temperature. Each spectrum was accumulated for 1 s. The waiting time between recording subsequent spectra was 2 s. (a) denotes the first spectrum, (g) the last one. All spectra have the same scaling, but are moved upwards in the figure to enhance the clarity of the presentation.

Raman lines appearing over a background composed by two broad bands around 1340 cm^{-1} and 1580 cm^{-1}. For the Au electrode there is a single band around 2095 cm^{-1}, which has about 20 cm^{-1} halfwidth. It appears at times, varies substantially in intensity and, to a minor extent, in frequency. Both effects are clearly seen in the frequency-expanded section of Fig. 1. Similar variations of CO bands are observed also for Ag electrodes (1800–2000 cm^{-1}), but not as spectacular as for Au (see Fig. 2). The adjacent frequency regimes from 2150 or 2000 to 3200 cm^{-1} are essentially featureless. In other words, there are no CH-stretches visible. Therefore, all observed spectral lines below 2150 cm^{-1} have to be assigned to vibrations within (segments of) carbon chains, carbonyls and adsorbed CO molecules.

The observed fluctuations evidence substantial variations of the local carbon chain configurations as well as of the local carbon metal bondings. Most surprisingly, the fluctuating bands display a rather narrow halfwidth (of < 20 cm^{-1}), but show up more or less randomly in a frequency range from 1000 to 1700 cm^{-1}. Average spectra are obtained by numerically adding several large series of spectra (containing usually 40 to 50 spectra showing particularly huge fluctuations). They still exhibit some reminiscence of the fluctuations, but are otherwise identical to those spectra that are measured either during periods without large fluctuations – compare spectra (a) and (b) in Fig. 3 – or with a standard Raman spectrograph. In these cases two broad bands are observed, denoted in literature as D- and G-bands. Curve fitting reveals integrated peak intensities of 1147 and 216, respectively. This indicates a sp^3/sp^2 ratio of about 0.84/0.16 and thus a substantial disorder in the carbon film; hence its denotation as amorphous carbon [25]. For comparison, curve (c) in Fig. 3 shows an average spectrum of an amorphous carbon layer deposited on a smooth Ag surface. Compared to the deposit on a rough silver surface, the intensity is by orders of magnitude

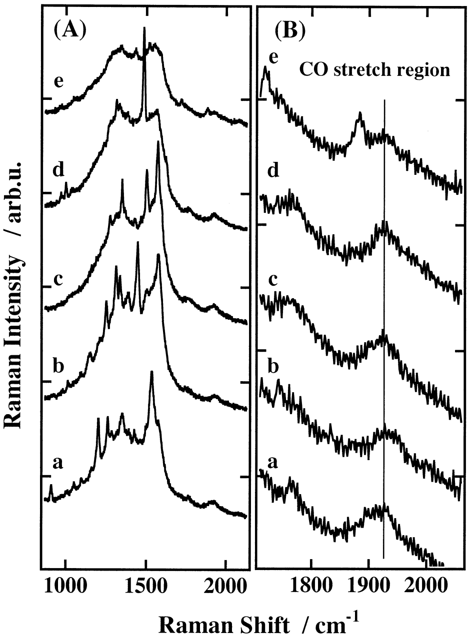

Fig. 2. (A) SERS spectra of carbon clusters deposited on rough silver surface and measured in air at room temperature. Each spectrum was accumulated for 0.3 s. Other parameters as in Fig. 1.

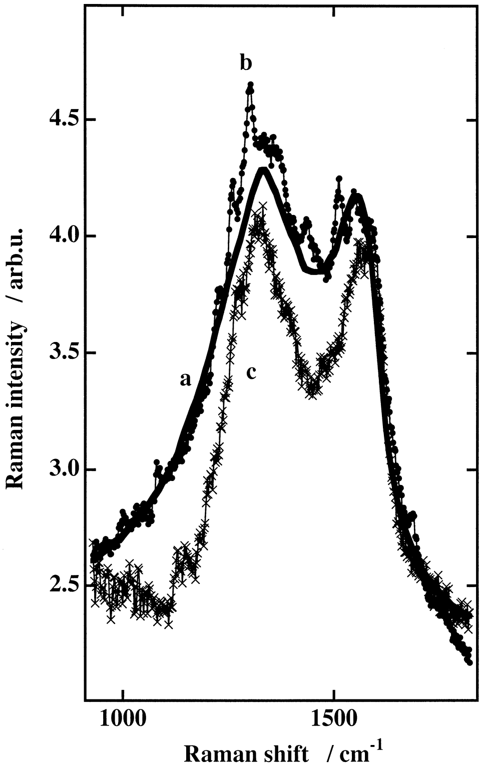

Fig. 3. Comparison of averaged SERS spectra: (a) Averaged SERS spectrum of carbon on Ag calculated from 40 recorded spectra shows minor or no fluctuations. (b) Averaged SERS spectrum of carbon on Ag calculated from 40 spectra with huge fluctuations. (c) Spectrum of amorphous carbon layer deposited on a smooth silver surface.

lower, the band frequencies are slightly shifted and the halfwidths of the amorphous carbon bands are significantly lower. From the sp^2/sp^3 ratio of about 0.62/0.38 we conclude a lower disorder within this deposit.

We noticed that intense fluctuations are only detectable in experiments where the Raman signal is collected from a very small focus area, achieved in experiments with 50 × and 100 × objectives. Using a 10 × objective we were also able to observe fluctuations, but the intensity of the fluctuating Raman bands dropped significantly and did not exceed 15–20% of the intensity of the maximum of the carbon background. Using a standard Raman spectrometer, which collects scattered light from a significantly larger area, we were not able to observe any fluctuation, despite identical sample preparation and measurement sequence.

Meixner and co-workers reported recently on SERS fluctuations for Ag nanocrystals [26]. Intensity fluctuations of broad Raman bands at 1380 and 1590 cm^{-1} were described together with more or less random appearance of shoulders and a band at 1275 cm^{-1} and ascribed to vibrations of small carbon clusters formed from impurities. These observations resemble our results. Because of limited spectral resolution, the authors were not able to observe narrow lines with a halfwidth < 20 cm^{-1} nor could the question be addressed whether or not the broad Raman bands they observed represent a superposition of a series of narrow lines.

A narrow halfwidth of Raman bands points to a low inhomogeneous spectral broadening. At a first glance, this is in contrast to what we expect for a carbon deposit on a rough surface prepared according to the procedure [23,24]. Let us describe this carbon deposit as an amorphous carbon network being in contact with the metal surface (we will arrive at the same conclusions if the deposit would be an ensemble of small crystalline carbon clusters, etc.). Such a network contains, even in the small focal area of a microscope (a few μm^2), a huge variety of carbon chain and carbon metal bonding configurations giving rise to large inhomogeneous broadening. Contrary to this expectation, the more or less accidental appearance and disappearance of a few narrow bands indicate that, in a corresponding time interval, only a few discrete interfacial configurations of the total ensemble participate in SERS. Such discrete interfacial configurations represent local surface areas where the electromagnetic surface enhancement is large and, at the same time, local carbon chain configuration(s) exist having a large resonance Raman enhancement. Note in this context that there is ample evidence that only a minority of adsorbed species contributes to SERS [7,8,16]. For dyes adsorbed at silver nanoparticles, for example, only 0.01% of the adsorbates contribute significantly to the observed SERS signal; consequently, the surface enhancement can be so huge that SER spectroscopy on single molecules is possible [16].

The fluctuations occur only if oxygen is present. When the sample is first exposed to O_2 for some time and then the ambient gas is switched to N_2, the number and height of fluctuations decrease continuously with a decay time of more than 45 min. Such an extended decay time is only explainable if there is an oxygen reservoir available for the surface chemistry, such as the oxygen incorporated in the metal surface or subsurface position. This oxygen dependence is a direct evidence for the fluctuations showing not only conformational changes within the carbon network but also changes in the chemical bonds and groups within this network. A further evidence for local surface chemistry is the random appearance of narrow bands centered around 2095 cm^{-1} and 1927 cm^{-1} for experiments on Au and Ag, respectively (see Fig. 1B and Fig. 2B). These bands, which display intensity fluctuations, but also some shifts in frequency (Au: maximal difference ca. 30 cm^{-1}), are characteristic for adsorbed CO molecules at the two metals [27,28]. Because these frequencies refer to triple bonded CO adsorbed at the metal, CO is produced by carbon oxidation and then disconnecting the CO group from the carbon chain. The fluctuations can be observed for samples kept in air for more than one month, hence the oxidation rate is very slow and – not surprisingly – intense CO bands appear rarely.

The shape of the average spectrum calculated from spectra displaying huge fluctuations is essentially identical to that of a spectrum recorded from samples showing no or negligible fluctuations. Since surface chemical processes are necessarily mapped into the SERS spectra, these findings indicate that the (locally different) chemistry occurring at ‘hot spots’ is essentially the same as the chemistry occurring at the average place of the substrate – when ‘averaged’ in time. Due to the giant local enhancement, individual events occurring at ‘hot spots’ become observable.

The observations described above show that the fluctuations represent a rather general phenomenon. They are spectroscopically evident for gold and silver surfaces, in the gas phase as well as in an electrochemical environment. For other surfaces such as ruthenium but also for very smooth Ag or Au surfaces there is (nearly) no surface enhancement; thus, we can only observe a weak spectrum representative of amorphous carbon.

The actual role of oxygen and its surface chemistry is unclear. The huge local increase in scattering efficiency could be caused by the oxygen-induced reconstruction of the metal surface leading to the production of unstable ‘active sites’ or by the chemical modification of local segments of the amorphous carbon network. The latter effect can lead to the huge increase of its Raman cross-section by a type of resonance Raman process. To answer this question we performed an experiment where pyridine and amorphous carbon are simultaneously adsorbed at a silver electrode: Pyridine is adsorbed from an electrolyte containing a 0.05 M pyridine + 0.1 M $\mathrm{Na_2SO_4}$ solution, while the amorphous carbon is continuously present in the form of (not removable) traces. Note in that context that whereas a reduction of the carbon coverage down to a few percent of a monolayer can be readily achieved, it is impossible to entirely remove carbon species from an electrode surface [29]. In this experiment there are no fluctuations of the pyridine spectrum (ν_1, ν_{12}, and ν_{8a} bands can be identified in these spectra) but large fluctuations in the spectral region of amorphous carbon (see Fig. 4). Evidently, the observed fluctuations cannot be ex-

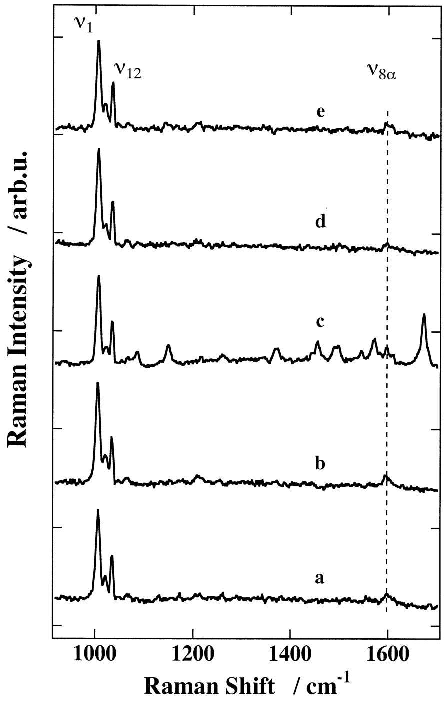

Fig. 4. SERS spectra at a silver electrode in contact with a 0.1 M $\mathrm{Na_2SO_4}$ + 0.05 M pyridine solution. Electrode potential $E = -0.2$ V vs. SCE. (a)–(d) subsequently recorded spectra.

plained by the creation of 'electromagnetic active sites' existing only for a short time. Such temporary electromagnetic 'hot spots', possibly created during reconstruction of silver or gold surfaces, should be similarly efficient for different molecules. Hence, there should also be fluctuations of the pyridine bands. The absence of spectral fluctuations for pyridine and large spectral fluctuations for carbon chain segments is striking and allows far-reaching conclusions: (i) the metallic structures are stable in the sense that they provide stable electromagnetic field enhancements varying locally along the surface. (ii) The pyridine molecules also form and break bonds to the metal surface. They may adsorb to different sites, but this has a minor effect on frequencies and intensities and, therefore, their SERS signal is constant. (iii) The carbon network can change its local chemical nature, for instance by incorporating oxygen atoms. This affects its local electronic configuration and the observable frequencies. Among the large manifold of interfacial configurations, some of them will tune into, others out of an optical resonance. Given a sufficient resonance, a local carbon chain segment behaves like an adsorbed dye. It will exhibit an extremely large cross-section for Raman scattering and show up in the SERS spectrum.

By decreasing the incident laser power by a factor of 100 only the general SERS intensity level is reduced, but not the rate of fluctuations for experiments carried with 50 × and 100 × objectives. This intensity reduction is higher than for a 10 × objective using 100% incident laser power. In the latter case, the fluctuations are substantially diminished, but the intensity at the sample drops only by a factor of 25. Obviously, the power density and a possibly correlated local increase in the surface temperature are not the key factors that determine the occurrence of fluctuations. In fact, our preliminary studies on the sample temperature influence on the rate of fluctuations reveal only a minor or negligible effect in the investigated region (297–490 K). However, because of the random character of this phenomenon a more advanced statistical analysis is required.

4. Conclusion

The appearance and variance of a small number of narrow Raman lines can only be explained by a superior surface enhancement for species adsorbed at so-called 'hot spots'. Due to their inhomogeneous structure, the number of carbonaceous groups associated with them must be limited to produce a low inhomogeneous spectral broadening. Most importantly, the spectral fluctuations indicate continuously progressing surface chemistry at rather small and discrete locations, which – when averaged in time – is still representative for the overall chemistry occurring at the sample.

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