

# Role of O<sub>2</sub> in Inducing Intensive Fluctuations of Surface-Enhanced Raman Scattering Spectra

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Confocal Raman microscopic measurements were performed on silver electrodes covered with hydrogenated amorphous carbon (a-C:H). When short accumulation time was used, the subsequently measured surface-enhanced Raman scattering (SERS) spectra exhibited fluctuations. As previously reported for other systems, the intensity of fluctuations of SERS spectra significantly decreases if O<sub>2</sub> was removed from the ambient medium. In this contribution we show that intensive SERS fluctuations can be also observed for a-C:H/Ag samples immersed in the deoxygenated electrolyte after applying a negative potential pulse to the silver electrode. It means that the O<sub>2</sub>-mediated Burstein mechanism of SERS fluctuations, which has been previously proposed to explain the SERS O<sub>2</sub> effect, is not adequate for these results. We suggest that oxygen chemisorbed on the silver surface decreases the average strength of the interaction between a-C:H clusters and the metal surface (and hence the speed of movement of a-C:H clusters across the metal surface) and that the SERS O<sub>2</sub> effect should be rather explained using the “classical” model of SERS fluctuations, in which fluctuations are interpreted as a result of the thermally activated diffusion of carbon segments in and out of the SERS “hot spots”. A numerical algorithm for modeling of the fluctuations of SERS intensity has been proposed, and some example simulations of SERS fluctuations have been carried out. For the first time, strongly fluctuating bands due to the stretching vibrations of significantly weakened C–H bonds have been identified.

## 1. Introduction

The Raman cross sections for molecules adsorbed on some rough metal substrates are substantially increased. This effect is known as surface-enhanced Raman scattering (SERS).<sup>1–6</sup> It has been generally accepted that two cooperating processes contribute to a very large enhancement of Raman intensity: the so-called “electromagnetic” and the “chemical” ones.<sup>2–6</sup> The first mechanism, the electromagnetic enhancement, is a consequence of the interaction of the electric field from the incident radiation with electrons in the metal surface. This causes excitation of surface plasmons (collective oscillations of metal electrons) and, as a result, enhancement of the electric field at the metal surface. The “chemical” enhancement (known also as “charge transfer” enhancement) is very similar to the resonance Raman process, which sometimes occurs in metal–ligand complexes. For formed surface complexes the metal electrons can be excited into unoccupied molecular orbitals of an adsorbed molecule and back to the metal state or the electrons at the occupied molecular orbital can be excited into the Fermi level of the metal and back to the adsorbed molecule. If the energy of just created electronic transitions for metal (or adsorbed molecule) electrons is similar to the energy of the excitation photons, the effectiveness of Raman scattering increases significantly.

The enhancement of the electromagnetic field in the proximity of highly SERS-active rough metal surfaces is very inhomogeneous. Theoretical simulations show that for self-affine fractal silver surfaces and for random silver–dielectric films, the intensity of the localized electromagnetic waves can vary by a factor of more than 10<sup>5</sup> between the “hot spots” and the “cold

zones”.<sup>7,8</sup> This implies local electromagnetic enhancements in excess of 10<sup>10</sup>.<sup>8</sup> Such very high local SERS enhancements make possible measurements of SERS spectra even of single molecules.<sup>9–17</sup> Highly SERS-active sites (“hot spots”) are not, however, only due to the very inhomogeneous enhancement of the electromagnetic field but also caused by the strong local differences in the “chemical” enhancement.<sup>18,19</sup> Therefore, in single molecule SERS measurements, the signals from solvents (water or methanol) or many other adsorbates (e.g., citrate ions) are not effectively enhanced.<sup>9–11</sup>

In a series of subsequently measured SERS spectra from a relatively small number of molecules, one can usually observe some fluctuations of every Raman band.<sup>6,20–29</sup> Since in measurements carried out on highly SERS active substrates, a significant part of measured SERS signal is scattered by a very small part of the molecules (by those molecules that reside in “hot spots”), strong spectral fluctuations can be observed even in measurements carried out with a standard Raman microscope that averages over a comparatively large number of molecules.

Etchegoin et al.<sup>25,26</sup> and our group<sup>20</sup> showed that the intensity of SERS spectral fluctuations decreases significantly when O<sub>2</sub> is removed from the ambient medium. On the basis of these findings, Etchegoin et al. proposed that SERS fluctuations are due to large O<sub>2</sub>-mediated fluctuations in the resonant charge-transfer interactions between the surface plasmons and adsorbed molecules (the so-called O<sub>2</sub>-mediated Burstein mechanism).<sup>25,26</sup> In this contribution we show that if a negative potential pulse is applied to the silver electrode just before Raman measurements, SERS spectral fluctuations can be also observed for a-C:H/Ag samples immersed in the deoxygenated electrolyte. It means that the O<sub>2</sub>-mediated Burstein mechanism of SERS fluctuations is not applicable in this case. We propose an

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alternative explanation of the influence of O<sub>2</sub> on the SERS fluctuations, which also explains inducing of the intensive SERS fluctuations by the negative potential pulse reported in this contribution. A simple algorithm for the modeling of the fluctuations of SERS intensity is presented, and some example simulations of the SERS fluctuations are described.

A model system used in this contribution to study SERS fluctuations is hydrogenated amorphous carbon (a-C:H) deposited on the electrochemically roughened silver. a-C:H is often formed on metal surfaces during decomposition of many carbonaceous compounds. Moreover, formation of a-C:H can be often carried out in the conditions (room temperature, not very negative potential) at which the SERS activity of the silver substrate does not significantly decrease. Therefore, Ag/a-C:H samples seem to be superior for observation of intensive SERS spectra and their fluctuations than amorphous carbon clusters deposited on Ag at the elevated temperatures previously used by our group.<sup>20</sup>

## 2. Experimental Section

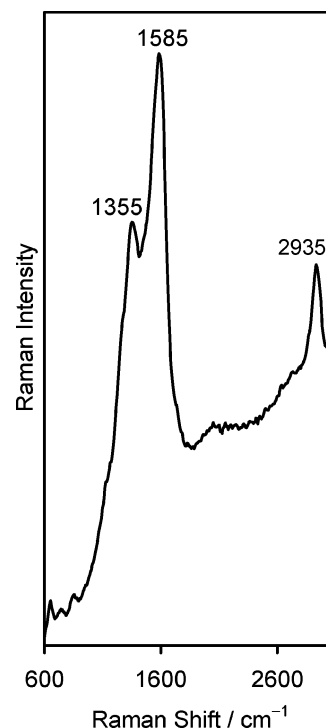
Laccase from the fungus *Trametes versicolor* and inorganic compounds (all of analytical reagent grade) were provided by commercial companies and were used as received. Water has been purified with a Millipore Milli-Q water system.

Silver substrates were roughened electrochemically by three successive positive–negative cycles in a 0.1 M KCl aqueous solution from –0.3 to 0.3 to –0.3 V (all potentials are referred to the potential of an 0.1 M KCl AgCl|Ag electrode) at a sweep rate of 5 mV s<sup>–1</sup>. The cycling was finished at –0.3 V, then the applied potential was changed to –0.4 V and the silver electrode was kept for 5 min at this potential. After that, the working electrode was removed at an open circuit potential and very carefully rinsed with water.

As mentioned in the Introduction, a-C:H clusters can be formed on the SERS-active silver surfaces by the decomposition of some organic compounds. In our previous work<sup>30</sup> we showed that a-C:H clusters are very effectively formed on the SERS-active silver substrates by the catalytic decomposition of laccase. Therefore, to deposit a-C:H clusters, electrochemically roughened silver substrates were immersed for 20 min in a 0.8 mg cm<sup>–3</sup> laccase aqueous solution and then very carefully rinsed with water.

Deoxygenation of solutions has been carried out using the method based on the oxidation of Mn(OH)<sub>2</sub> (suspension of Mn(OH)<sub>2</sub> has very large affinity to O<sub>2</sub> and very effectively removes oxygen from the surrounding liquid phase).<sup>31</sup> Before SERS experiments in the deoxygenated solutions, the spectro-electrochemical cell has been filled with the mixture of the supporting electrolyte and the freshly prepared Mn(OH)<sub>2</sub> sol. Mn(OH)<sub>2</sub> slowly precipitates, and the transparency of the solution increases gradually from the top of the cell. The working silver electrode has been mounted in the upper part of the spectroelectrochemical cell. About 30 min after the cell is filled with the Mn(OH)<sub>2</sub> sol, a sufficiently large part of the solution is transparent and optical measurements are possible. Construction of the cell prevents the working electrode from being covered with solid Mn(OH)<sub>2</sub>. Mn(OH)<sub>2</sub> sol was obtained by mixing of 25 cm<sup>3</sup> of 0.15 M MnSO<sub>4</sub> and 25 cm<sup>3</sup> of 0.4 M NaOH. Then, the pH of the Mn(OH)<sub>2</sub> sol was decrease by the addition of 50 cm<sup>3</sup> of 0.2 M NaH<sub>2</sub>PO<sub>4</sub> (pH of the final solution was ca. 7).

Raman spectra have been recorded with an ISA T64000 (Jobin Yvon) Raman spectrometer equipped with a Kaiser SuperNotch-Plus holographic filter, 600 grooves/mm holo-



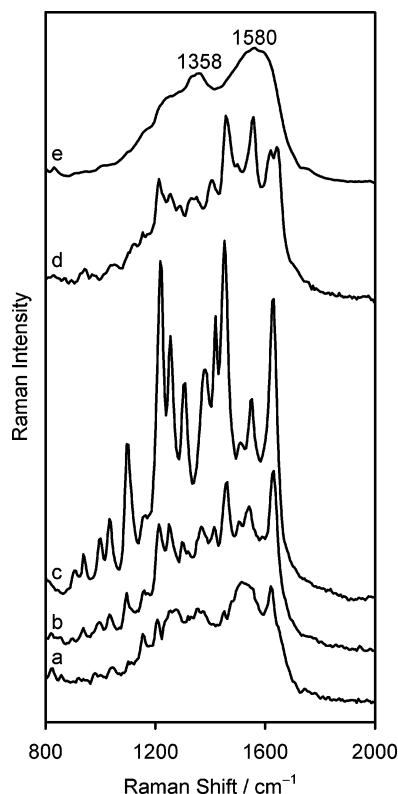
**Figure 1.** SERS spectrum of the products of the catalytic decomposition of laccase on silver. The Raman spectrum has been recorded for the modified metal substrate immersed in water saturated with O<sub>2</sub> at  $p_{\text{O}_2} = 0.2$  bar. Accumulation time  $10 \times 3$  s,  $10\times$  objective,  $\lambda_{\text{exc}} = 514.5$  nm.

graphic grating, an Olympus BX40 microscope with a  $10\times$  standard or a  $50\times$  long distance objective, and  $1024 \times 256$  pixel nitrogen-cooled CCD detector. A Laser-Tech model LJ-800 mixed argon/krypton laser provided excitation radiation of 488.0, 514.5, and 647.1 nm. The temporal instability of intensity of the laser radiation was less than 5%.

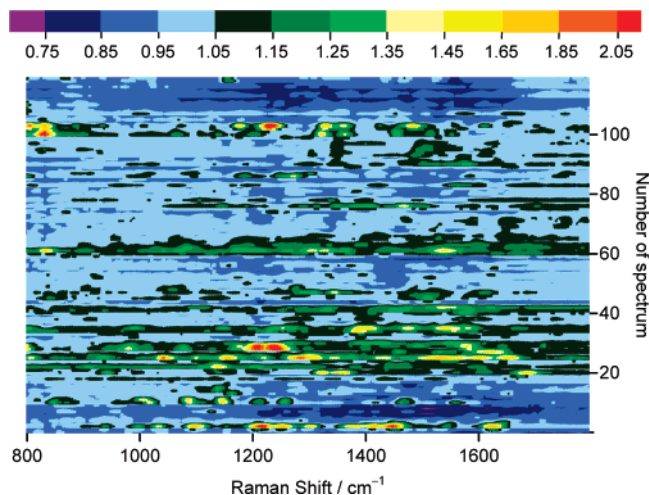
## 3. Experimental Results and Discussion

Figure 1 shows SERS spectrum of the products of the catalytic decomposition of laccase on silver. The measurement has been carried out for the modified silver substrate immersed in water saturated with O<sub>2</sub> at  $p_{\text{O}_2} = 0.2$  bar (the concentration of O<sub>2</sub> in the solution is ca. 8 mg dm<sup>–3</sup>). The Raman microscope was equipped with a  $10\times$  objective, accumulation time was  $10 \times 3$  s and  $\lambda_{\text{exc}} = 514.5$  nm. As can be seen in Figure 1, in the measured SERS spectrum one can identify three strong Raman bands around 1355, 1585, and 2935 cm<sup>–1</sup>. The spectrum presented in Figure 1 is characteristic for hydrogenated amorphous carbon (a-C:H).<sup>32,33</sup> The bands at 1355 and 1585 cm<sup>–1</sup> are due to the vibrations of the carbon network (these bands are called the “D peak” and “G peak”, respectively), whereas the band at 2935 cm<sup>–1</sup> is due to the C–H stretching vibrations.<sup>32,33</sup> Because the SERS spectrum of the products of the catalytic decomposition of laccase on silver is completely dominated by the contribution from a-C:H clusters (the Raman cross section of a-C:H is exceptionally large), in the next paragraphs of this contribution, the SERS spectra of such samples are referred to as the SERS spectra of a-C:H clusters. It is important to note that a-C:H clusters produced in different conditions can differ in size, in hydrogen content, and in the ratio of sp<sup>3</sup> and sp<sup>2</sup> hybridized carbon. Therefore, Raman spectra of various a-C:H films are slightly different.<sup>32,33</sup>

Figures 2 and 3 present many subsequently recorded SERS spectra of a-C:H clusters deposited on the silver surface. The

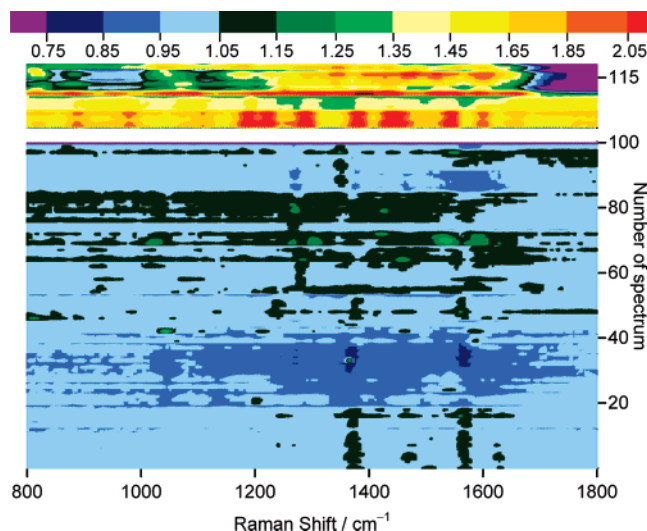


**Figure 2.** (a–d) Subsequently recorded SERS spectra of a-C:H deposited on silver. The Raman measurements have been carried out for the metal substrate immersed in water saturated with  $O_2$  at  $p_{O_2} = 0.2$  bar. Each spectrum was accumulated for 1 s. We used a  $50\times$  objective and  $\lambda_{exc} = 514.5$  nm. This figure presents the first 4 spectra from the series of 120 subsequently recorded spectra shown in Figure 3. (e) Average spectrum calculated from 120 SERS spectra presented in Figure 3. All spectra have the same scaling, but they are moved upward in the figure to enhance the clarity of the presentation.



**Figure 3.** 2D map constructed from the relative intensities of 120 subsequently recorded SERS spectra of a-C:H deposited on silver. Each row shows a single color-coded spectrum. The relative intensity has been calculated versus the intensity of the average spectrum calculated from all 120 spectra presented in this figure (the average spectrum is shown in Figure 2 as spectrum e). All experimental details are given in the caption to Figure 2.

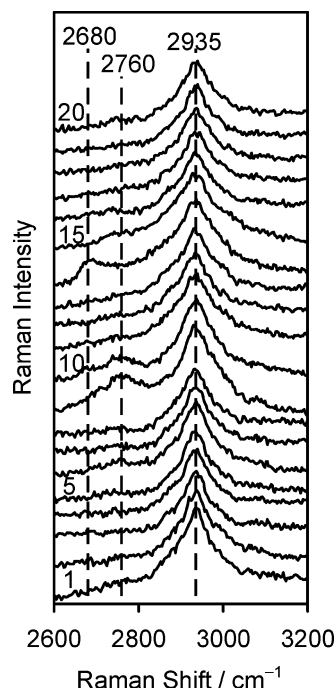
measurements have been carried out also for the a-C:H modified silver substrate immersed in water saturated with  $O_2$  at  $p_{O_2} = 0.2$  bar; however, in this case, the Raman microscope was equipped with a  $50\times$  objective and the accumulation time was 1 s. Figure 2 shows the first 4 SERS spectra from the series of



**Figure 4.** 2D maps constructed from the relative intensities of two series of subsequently recorded SERS spectra of a-C:H deposited on silver. The Raman measurements have been carried out for the a-C:H modified silver substrate immersed in the deoxygenated aqueous solution of  $0.075$  M  $Na_2SO_4 + 0.075$  M  $NaH_2PO_4 + 0.025$  M  $Na_2HPO_4$  ( $pH \approx 7$ ). We used  $50\times$  objective, accumulated time was 1 s, and  $\lambda_{exc} = 514.5$  nm. The spectra presented in the bottom panel (1–100) have been measured before the electrochemical treatment at the open circuit potential ( $+0.09$  V). The spectra presented in the top panel (101–120) have been measured also at  $+0.09$  V, however, after the negative potential pulse ( $+0.09$  V  $\rightarrow -0.8$  V  $\rightarrow +0.09$  V) applied to the silver electrode. The relative intensities of all spectra have been calculated versus the intensity of the average SERS spectrum calculated from 100 spectra recorded before the electrochemical treatment (spectra 1–100 presented in the bottom panel).

120 subsequently measured spectra shown in Figure 3 plotted in the traditional way (Raman intensity vs Raman shift). The whole series of 120 spectra is presented as a two-dimensional (2D) map in which each spectrum is color coded in a single row (a series of 120 spectra presented in the traditional way is very difficult to analyze). Fluctuating Raman bands appear over a strong background (see Figure 2); therefore to demonstrate more clearly spectral fluctuations in the wavenumbers regions, in which the background is weak, the 2D map shown in Figure 3 was constructed from the relative intensities of the measured SERS spectra. The relative intensity of each spectrum has been calculated versus the intensity of the average spectrum calculated from all spectra measured in the analyzed series. The average spectrum calculated from all 120 spectra presented in Figure 3 is shown in Figure 2 as spectrum e. As it was already shown for other systems,<sup>20</sup> if the number of averaged spectra is large, the average spectrum calculated from a series of spectra with intensive fluctuations becomes practically identical with the spectrum measured with a standard Raman spectrometer, which collects scattered light from a significantly larger area. Spectra presented in Figures 2 and 3 have been measured with 514.5 nm excitation radiation; however, we have also observed intensive SERS fluctuations in a series of spectra measured with 488.0 and 647.1 nm excitation radiation (two examples of series of SERS spectra measured with 647.1 nm excitation radiation are shown in Figures 4 and 5). The laser power density has only a minor effect on the spectral fluctuations (for details see ref 20). We found that strong spectral fluctuations can be also observed in SERS measurements carried out for Ag/a-C:H samples immersed in various electrolytes (KCl,  $Na_2SO_4$ , phosphorus buffer with  $pH = 7$ ) saturated with  $O_2$  at  $p_{O_2} = 0.2$  bar. Because of technical problems, we were unable to record SERS spectra simultaneously in the wavenumbers region





**Figure 5.** 20 subsequently recorded SERS spectra of a-C:H deposited on silver. The Raman measurements have been carried out for the metal substrate immersed in H<sub>2</sub>O saturated with O<sub>2</sub> at  $p_{O_2} = 0.2$  bar. Each spectrum was accumulated for 1 s. All spectra have the same scaling, but they are moved upward in the figure to enhance the clarity of the presentation (50 $\times$  objective;  $\lambda_{exc} = 647.1$  nm).

between 800 and 1800 cm<sup>-1</sup> and in the wavenumbers region characteristic for the  $\nu(C-H)$  stretching vibrations (around 2900 cm<sup>-1</sup>). Therefore, some series of SERS spectra in the region around 2900 cm<sup>-1</sup> have been measured in the separate experiments and obtained results are discussed in one of the next paragraphs.

As can be seen in Figures 2 and 3, subsequently recorded SERS spectra of a-C:H clusters show very large fluctuations, which seem to be significantly stronger than the fluctuations observed in the analogous experiments with amorphous carbon deposits (compare Figure 2 from this contribution with Figure 2 in ref 20). It is likely that for a-C:H deposited on activated Ag, higher intensity of SERS spectra and their more intensive fluctuations are mainly due to higher SERS activity of silver substrates. Previously studied amorphous carbon was deposited on silver surfaces at high temperature, which led to significant decrease of SERS activity of substrates.

Figure 4 shows two series of SERS spectra of the a-C:H modified silver electrode immersed in the deoxygenated solution of Na<sub>2</sub>SO<sub>4</sub> + NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub> (for details see the Experimental Section). First, we measured 100 spectra at the open circuit potential (ca. +0.09 V). The relative intensities of these spectra are presented as the 2D map in the bottom panel of Figure 4. As can be seen in Figure 4, at all wavenumbers the relative intensities of all spectra 1–100 are in the range between 0.75 and 1.35 (moreover, the relative intensity of about 99% “spectral points” is in the range between 0.85 and 1.25). It means that, similarly to other studied systems,<sup>20,25,26</sup> the intensity of the SERS spectral fluctuations significantly decreases if O<sub>2</sub> is removed from the ambient medium (in experiments carried out for silver substrates immersed in the solution saturated with O<sub>2</sub> at  $p_{O_2} = 0.2$  bar, the relative intensity of even more than 0.8% “spectral points” is higher than 1.45—see Figure 3).

After the first series of spectra were recorded (spectra 1–100), the potential equal to -0.8 V has been applied to the silver

electrode for 4 s. Then, the potential equal to the previously measured open circuit potential (+0.09 V) was applied, and the second series of SERS spectra has been recorded. From the ratios of the intensities of each SERS spectrum recorded after the potential pulse and the averaged SERS spectrum calculated from the 100 SERS spectra measured before the potential pulse, we constructed a 2D map, which is shown in the top panel of Figure 4. As can be seen from the comparison of both panels presented in Figure 4, after the negative potential pulse, the average intensity of the SERS spectrum in the region due to the vibrations of carbon network (1100–1600 cm<sup>-1</sup>) significantly increases and strong fluctuations of narrow Raman bands appear (on the top panel one can observe strong local maximums denoted as red regions). Undoubtedly, applied electrochemical treatment (+0.09 V  $\rightarrow$  -0.8 V  $\rightarrow$  +0.09 V) does not cause the appearance of O<sub>2</sub> molecules in the a-C:H film. It means that the O<sub>2</sub>-mediated Burstein mechanism of SERS spectral fluctuations, which have been previously proposed to explain “SERS oxygen effect”, cannot shed light on these results. In our opinion, the O<sub>2</sub> effect is better explained on the basis of the “classical” model of SERS fluctuations, in which the fluctuations are interpreted as a result of thermally activated diffusion of carbon segments which get temporarily in contact with the SERS “hot spots” (the appearance of the carbon segment in the “hot spot” causes sudden increase of the measured SERS signal). The number of SERS “hot spots” in the focal area of the Raman microscope is very small (probably only a few). If oxygen is present in the ambient medium, the silver surface is partially covered by the chemisorbed oxygen species.<sup>34,35</sup> We suggest that if the silver surface is covered by the oxygen species, the strength of the interaction between a-C:H clusters and the metal surface significantly decreases because adsorbed oxygen partially blocks the metal surface and disturbs the (a-C:H)–metal interactions. In the absence of O<sub>2</sub>, a-C:H clusters interact stronger with the silver surface and therefore move slower across the metal surface, and hence fewer carbon clusters get in contact with the SERS “hot spots” during the same time period. The density of energy of the electromagnetic field is significantly higher in the “hot spot” than outside. Therefore, when a carbon segment comes in contact with the SERS “hot spot”, it is likely that its further diffusion is strongly thermally activated in the case of experiments both with and without O<sub>2</sub>. It means that fluctuations observed for Ag/a-C:H samples kept in the deoxygenated solution cannot be treated in the same manner as the slower fluctuations observed in the O<sub>2</sub>-containing media. For more details see the section “Simulation of SERS Fluctuations”.

If after the contact with the SERS “hot spot” the diffusion of the carbon segments is strongly thermally activated, in experiments carried out in the deoxygenated media the average intensity of the measured SERS spectra should be smaller. We found that the deoxygenation of the ambient solution causes about a 1.5 times decrease of the average intensity of SERS spectra, which means that our experimental results are in agreement with this hypothesis. Unfortunately, due to some irreproducibility of the measurement of the intensity of SERS spectra, we should consider the above conclusion only as a suggestion.

We suppose that after the negative potential pulse one can again observe strong SERS fluctuations because the average strength of the interactions between a-C:H clusters and the silver surface decreases. Weaker bonding of the a-C:H clusters to the silver surface may be caused by the combination of two effects: (i) after the negative potential pulse the silver surface is covered with chemisorbed hydrogen,<sup>36,37</sup> which, similarly to

oxygen in the other conditions, disturbs the strong adsorption of a-C:H clusters on the metal surface and/or (ii) the structure of a-C:H clusters is modified in such a way that the adsorption energy of a-C:H decreases (it is likely that a-C:H clusters interact with the silver surface mainly via fragments rich in the  $\pi$ -electrons which can be partially reduced during the negative potential pulse).

As already mentioned, due to technical problems, we were unable to simultaneously record SERS spectrum in the whole wavenumber region, in which all three “D”, “G”, and  $\nu(\text{C-H})$  bands are located. Therefore, SERS spectra in the higher wavenumbers region have been recorded in separate experiments. Figure 5 shows a series of 20 subsequently recorded spectra between 2600 and 3200  $\text{cm}^{-1}$  of the a-C:H modified silver surface ( $\lambda_{\text{exc}} = 647.1 \text{ nm}$ , 1 s accumulation time,  $50\times$  objective). The Ag/a-C:H sample was immersed in water saturated with  $\text{O}_2$  at  $p_{\text{O}_2} = 0.2 \text{ bar}$ . As can be seen from Figure 5, in some cases, in addition to the band at 2935  $\text{cm}^{-1}$ , which is characteristic for the C-H stretching vibrations of a-C:H clusters, one can also observe bands at slightly lower wavenumbers (for example at 2680 and 2760  $\text{cm}^{-1}$ ). The bands at 2680 and 2760  $\text{cm}^{-1}$  can be due to the overtones of the vibrations of the carbon network or can be due to the stretching vibrations of the weakened C-H bonds. If the bands at 2680 and 2760  $\text{cm}^{-1}$  are the overtones, the basic wavenumbers of the respective vibrations are slightly higher than 1340 and 1380  $\text{cm}^{-1}$ , respectively. As can be seen in Figure 2, one can observe some strong fluctuating Raman bands at such wavenumbers; however, many strong fluctuating Raman bands due to the vibrations of the carbon network can be also observed at significantly higher wavenumbers (up to about 1600  $\text{cm}^{-1}$ ). Therefore, if the bands at 2680 and 2760  $\text{cm}^{-1}$  are overtones, one should also expect appearance of other overtones up to about 3200  $\text{cm}^{-1}$ . Because in the experimentally measured spectra we have not observed such bands, the bands at 2680 and 2760  $\text{cm}^{-1}$  should be assigned to the  $\nu(\text{C-H})$  stretching vibrations of the significantly weakened C-H bonds. It is likely that a-C:H clusters having some C-H bonds weakened are formed as the intermediates in surface reactions, during which a-C:H clusters strongly interact with the silver surface. Probably only a small portion of C-H bonds is significantly weakened even in very strongly bonded a-C:H clusters. Therefore, even though we expect that for Ag/a-C:H samples kept in the deoxygenated solution the ratio of the weakened C-H bonds is higher than that for samples kept in the  $\text{O}_2$ -containing solution, we sometimes observed the appearance of clearly noticeable bands due to the stretching vibration of the weakened C-H bonds only during strong spectral fluctuations (e.g., during measurements in  $\text{O}_2$ -saturated solution). If one observes strong SERS fluctuations, a significant part of the measured SERS signal appears from a very small part of the a-C:H cluster; therefore, one was able to observe a noticeable contribution from an intermediate, which, due to the averaging, could not be observed in the standard Raman experiment. According to our knowledge, the fluctuations of the bands due to the C-H stretching vibrations presented above are the first reported example of the SERS fluctuation of the  $\nu(\text{C-H})$  band.

#### 4. Simulation of SERS Fluctuations

To simplify the modeling of the movement of carbon clusters in and out of the “hot spot”, we assume that the surface density of a-C:H clusters is very large, and therefore, in the time period just after leaving of the “hot spot” by the a-C:H cluster, the probability of the diffusion of any a-C:H cluster into this “hot

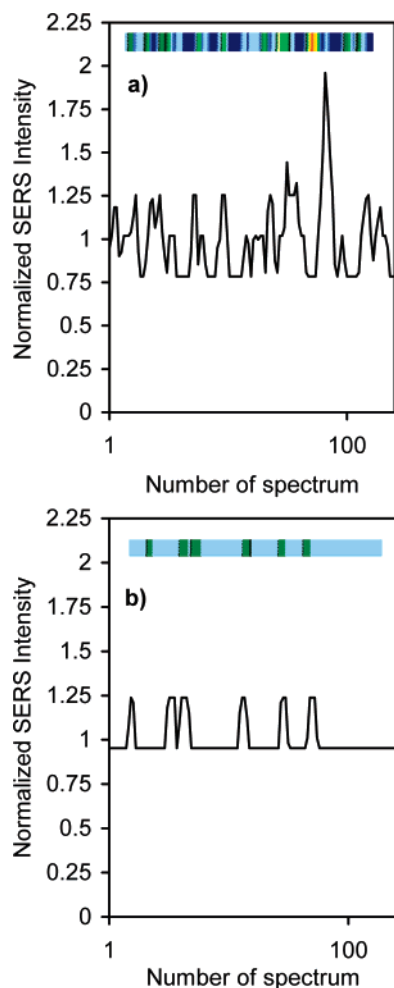
spot” is not significantly higher than the average value. We also assume that the time of the contact of a carbon segment with a SERS “hot spot” ( $\tau$ ) can be generated for the subsequent contacts semirandomly assuming that the probability of obtaining various values is described by the Gauss curve, the average value is  $\tau_{\text{av}}$ , and the standard deviation is  $\sigma\tau$ . To simplify calculations, we divided the time period, in which we simulate fluctuations, into  $k$  time periods  $t$ , which are significantly shorter than both  $\tau_{\text{av}}$  and the accumulation time of the single SERS spectrum ( $t_{\text{ac}}$ ). In the proposed model, the temporal behavior of each “hot spot” is described by the  $k$ -element binary string. If during the time period  $t_q$  any a-C:H cluster interacts with the analyzed SERS “hot spot”, the  $q$ th element of the string ( $x_q$ ) assigned to this “hot spot” is equal to 1; if there is not such interaction,  $x_q = 0$ . The numbers 0 or 1 have been generated by the computer’s semirandom generator. In our simulations we changed the probability of obtaining 1, which, from the definition, is equal to the probability ( $p_t$ ) of the diffusion of a-C:H cluster into the unoccupied “hot spot” during the time period  $t$ . The generation of the string ( $x_1, x_2, \dots, x_k$ ) was started from the generation of the element  $x_1$ . If  $x_q = 0$ , in the next step, the element  $x_{q+1}$  has been randomly generated. If  $x_q = 1$ , in the next step  $\tau$  has been generated as an integer multiple of  $t$  (for details see above), the elements from  $x_{q+1}$  to  $x_{q+\tau/t-1}$  were set to 1 and then, the element  $x_{q+\tau/t}$  has been generated.

In the pioneering SERS single molecule work, Kneipp et al. showed that the effective enhancement factor for molecules adsorbed at various “hot spots” is very similar, which means that every molecule in the “hot spot” contributes practically equally to the SERS signal.<sup>9</sup> If one assumes that also other properties ( $p_t$ ,  $\tau_{\text{av}}$ ,  $\sigma\tau$ ) of SERS “hot spots” are very similar, the temporal dependence of the intensity ( $I$ ) of measured SERS signal can be described by the following equation

$$I(t_j) = a \frac{t_{\text{ac}}}{t} + b \sum_{m=1}^n \sum_{l=(j-1)t_{\text{ac}}+1}^{l=jt_{\text{ac}}} x_{m,l}$$

where  $a$  is the intensity of SERS signal from a-C:H clusters adsorbed outside the “hot spots”,  $b$  is the intensity of SERS signal from the single a-C:H cluster being in contact with the “hot spot”,  $n$  is the number of “hot spots” in the focal area of the Raman microscope, and  $x_{m,l}$  is the  $l$ th element of the string (for details see above) corresponding to the  $m$ th SERS “hot spot”.

Figure 6a shows the modeled temporal dependence of the intensity of SERS spectrum. The calculations have been carried out for 1200 time intervals  $t$ . The other parameters were set to  $n = 5$ ,  $t_{\text{ac}} = 10t$ ,  $\tau_{\text{av}} = 30t$ ,  $\sigma\tau = 10t$ ,  $b/a = 0.3$ , and  $p_t = 1/150$ . Despite the fact that the proposed model is clearly a very rough approximation, as can be seen from the comparison of Figures 6a and 3, for some sets of parameters, the modeled dependence roughly reproduces the experimentally measured dependence. Figure 6b shows spectral fluctuations modeled for  $p_t = 1/750$ , which corresponds to a factor of 5 decrease of the average speed of movement of a-C:H clusters across the metal surface in comparison to the simulation presented in Figure 6a. The other parameters are the same as those used for the previous simulation. Significant decrease of the speed of movement of carbon clusters across the silver surface (such a decrease is a consequence of the increase of the strength of interaction between a-C:H clusters and the metal surface) causes the probability of the observation of the individual SERS spectrum of the intensity being significantly (e.g., 1.5 times) stronger than the intensity of the average spectrum to become very small. Therefore, it is likely that even in a very long series of



**Figure 6.** (a, b) Simulated intensities of the subsequently measured SERS spectra (for details see text). Spectra have been normalized in such a way that for both plots (a and b) the average intensity is equal to 1. The results presented in plot a have been obtained for  $p_t = 1/150$ , whereas the results shown on plot b are for  $p_t = 1/750$ . Intensities of the subsequent spectra are also presented as the color bars. The color coding is the same as those in Figures 3 and 4.

subsequently measured SERS spectra, one could not observe such a fluctuation. For example, if we assume that five “hot spots” are present in the focal area (of course this number could not be treated as the result of previous experiments) and  $p_t \ll 0.1$ , a factor of 5 decrease of the speed of movement of a-C:H clusters across the metal surface causes the probability of the observation of a SERS spectrum, in which four carbon clusters in the “hot spots” simultaneously contribute to the measured SERS spectrum (an example of such fluctuation is presented in Figure 6a) to become roughly  $5^4$  times smaller.

## 5. Conclusions

We showed that the O<sub>2</sub> effect on the SERS spectral fluctuations should be explained by the “classical” model of SERS fluctuations (as a result of thermally activated diffusion of carbon segments which get temporarily in contact with the SERS “hot spots”) rather than by the previously proposed O<sub>2</sub>-mediated Burstein mechanism. We suggest that if fewer O<sub>2</sub> are adsorbed on the silver surface, the average strength of the interaction between a-C:H clusters and the metal surface significantly increases. Stronger bonded a-C:H clusters move slower across the metal surface, and therefore, the average intensity of the spectral fluctuations significantly decreases if O<sub>2</sub> was removed from the ambient medium.

Our results may be helpful for a better understanding of SERS spectral fluctuations. We hope that they may be also useful in solving one of the major challenges of single-molecule SERS spectroscopy: how we can facilitate a molecule of the studied substance to go to the right position (SERS “hot spot”) in order to observe its SERS signal. Solving this problem will be necessary, for example, in the realization of SERS single-molecule DNA sequencing, which is one of the most exciting proposed applications of SERS.

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## References and Notes

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